

**SYNTHESIS, CHARACTERIZATION, MODIFICATION
AND EVALUATION OF POLYMERS HAVING
STYRENE MOIETIES**

**A THESIS SUBMITTED TO THE
UNIVERSITY OF PUNE**

**FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY**

(IN CHEMISTRY)

BY

SARIKA BABASAHEB DEOKAR

**POLYMER SCIENCE AND ENGINEERING GROUP
CHEMICAL ENGINEERING & PROCESS DEVELOPMENT DIVISION
NATIONAL CHEMICAL LABORATORY
PUNE – 411008
INDIA**

September 2007

CERTIFICATE

Certified that the work incorporated in this thesis entitled “**Synthesis, Characterization, Modification and Evaluation of Polymers Having Styrene Moieties**” submitted by **Sarika B. Deokar** was carried out under my supervision. Such material as obtained from other sources has been duly acknowledged in this thesis.

September 2007

Pune

Dr. S. Ponrathnam

(Research Guide)

DECLARATION

I hereby declare that the thesis entitled “**Synthesis, Characterization, Modification and Evaluation of Polymers Having Styrene Moieties**” submitted for Ph. D. degree to the University of Pune has been carried out under the supervision of **Dr. S. Ponrathnam** at the Polymer Science and Engineering, Chemical Engineering & Process Development Division, National Chemical Laboratory, Pune, India. The work is original and has not been submitted in part or full by me for any degree or diploma to this or any other University.

September 2007

Pune

Sarika B. Deokar

*Dedicated to Anna, my parents, grandparents and the energy
that gave me patience and gratification*

ACKNOWLEDGEMENTS

I would like to express my deep sense of gratitude to my research guide Dr. Surendra Ponrathnam, Scientist, National Chemical Laboratory, Pune, for his invaluable guidance and help rendered throughout the course of this investigation, without which I could not have completed this thesis. He always tried to develop my thinking ability, to find a solution for a given problem that can be useful for my future career.

My sincere gratitude to Dr. C. R. Rajan, for all the advice and help he rendered in overcoming all hurdles, scientific and administrative, as well as personnel where he has the best solution for any problem that will rise. I have learned all kinds of management skills from him. He was always very kind and never said no to me. Dr. Rajan is the first scientist whom I met in NCL and his encouragement inspired me to join NCL. I am lucky to be in contact with such a good human being.

I am grateful to Dr. Ramesh Ghadge and Dr. Arika Kotha who mentored me to develop my laboratory skills.

I am obliged to Ganesh, Wasif, Abhijit, Harikrishna, Sunny, Timothy, Prachi, Sujata, Pragya, Surubhi, Dr. S. A. Mule and Dr. N. N. Chavan who have helped me during the tenure of my work. All of them and many other well wishers have left an indelible mark in the preparation of this dissertation.

Apart from laboratory, there is a list of friends who are well wishers who always encouraged and supported me. To mention few are: Shailesh, Mahesh, Girish, Rupali, Archana and Anagha, Mr. Sunil and Abhijeet. I am thankful to all of them.

I thank Mr. S. Sathe and L. Giri for their technical help.

How can I forget to mention the name of Dr. Jayant Gadgil who introduced me the route of National Chemical Laboratory to start my research career.

I am fortunate for having a great family support. Finally, mere words cannot express my gratitude to Anna, my parents, grandparents and brothers for their patience and tremendous support at all the times. I am grateful to all my relatives who have always encouraged me and I would like to mention few names Mrs. Mandakini S. Sutar Mr. Sadanand Satav and Mr. Maruti Dagade who have always boosted my energy.

I am thankful to Dr. B. D. Kulkarni, Head, Chemical Engineering Division, National Chemical Laboratory and Dr. S. Sivaram, Director, National Chemical Laboratory, Pune for the permission to submit this work in the form of thesis. Finally I thank Council of Scientific and Industrial Research (CSIR) for the award of fellowship during the period of this work.

Sarika B. Deokar

Table of Contents	i - v
List of Figures	vi - xv
List of Tables	xvi - xx
Abstract of thesis	xxi - xxiv

TABLE OF CONTENTS

CHAPTER I

INTRODUCTION

Section No.		Page No.
1.1	History of polystyrene	1
1.2	Properties of polystyrene	1
1.3	History of porous polymers and ion exchange resins	2
1.4	Synthesis strategies of porous polymers	3
1.5	Polymerisation techniques	5
	<i>1.5.1 Suspension polymerisation</i>	5
	<i>1.5.2 Emulsion polymerisation</i>	6
	<i>1.5.3 High internal phase emulsion</i>	11
1.6	Macroporous resin	14
	<i>1.6.1 Types of resins</i>	15
1.7	Functionalised polymers	18
1.8	Reactivity of functionalised polymers	20
1.9	Applications of modified polystyrenes	22
	<i>1.9.1 Ion-exchange resin catalysts</i>	22
	<i>1.9.2 Catalysis</i>	23
	<i>1.9.3 Imbibing polymers</i>	24
1.10	Photoresists	25
	<i>1.10.1 Classification of photoresists</i>	27
	<i>1.10.1.1 Positive resists</i>	27
	<i>1.10.1.2 Negative resists</i>	27
	<i>1.10.2 Composition and working of Photoresists</i>	28
1.10.3	Sensitisers for photoresist	29

1.10.4	Polymers used in photoresists	30
1.10.4.1	<i>Bisazide cross-linking</i>	30
1.10.4.2	<i>Poly(vinyl cinnamate)</i>	31
1.10.4.3	<i>Novolaks</i>	32
1.10.5	Chemically amplified resists (for 248 and 193 nm)	34
1.10.5.1	<i>Photoacid generators</i>	36
1.10.5.2	<i>Polymers for chemically amplified resists</i>	37
1.11	Present Work	39
1.12	References	40

CHAPTER II

MATERIALS AND CHARACTERIZATION

Section No.		Page No.
2.1	Materials	49
2.2	Characterisation	59
2.2.1	<i>Mercury porosimetry</i>	59
2.2.1.1	<i>Principle of mercury porosimetry</i>	60
2.2.2	<i>Surface area</i>	61
2.2.2.1	<i>Principle of surface area using nitrogen sorption method</i>	63
2.2.3	<i>Infra-red spectroscopy</i>	64
2.2.4	<i>HPLC analysis</i>	65
2.2.5	<i>UV analysis</i>	65
2.2.6	<i>Gel permeation chromatography (GPC)</i>	65
2.2.7	<i>Differential scanning calorimetry (DSC)</i>	66
2.2.8	<i>Scanning electron microscopy (SEM)</i>	66
2.3	References	66

CHAPTER III

SYNTHESIS OF BEADED POROUS POLYMERS USING SURFACTANTS

Section No.		Page No.
3	Synthesis of beaded cross-linked poly(styrene-co-divinyl benzene) in presence of surfactants	67
3.1	Synthesis of beaded cross-linked poly(styrene-co-divinyl benzene) using Brij 52	67
3.2	Synthesis of beaded cross-linked poly(styrene-co-divinyl benzene) polymers using Span 60	69
3.3	Beaded poly(styrene-co-divinyl benzene)	71
3.4	Results and discussion	72
3.5	Conclusion	92
3.6	References	93

CHAPTER IV

SYNTHESIS AND EVALUATION OF LOW CROSS-LINK DENSITY POROUS POLYMERS FOR IMBIBING

Section No.		Page No.
4	Synthesis and evaluation of low cross-link density porous poly(styrene-co-divinyl benzene) for imbibing	95
4.1	Synthesis of poly(styrene-co-divinyl benzene) with 1% cross-link density	95
4.2	Synthesis of poly(styrene-co-divinyl benzene) of 0.5% cross-link density	96
4.3	Synthesis of poly(styrene-co-divinyl benzene) of 0.25% cross-link density	98
4.4	Properties of imbibing polymers	99
4.4.1	<i>Bulk density</i>	100
4.4.2	<i>Toluene uptake capacity</i>	100
4.5	Results and Discussion	103
4.6	Conclusion	120
4.7	References	121

CHAPTER V

SYNTHESIS AND EVALUATION OF POLYMERIC MONOLITHS

Section No.		Page No.
5.0	Synthesis of poly(styrene-co-divinyl benzene) monoliths by HIPE methodology	122
5.1	Synthesis by HIPE methodology using thermal initiator	122
5.2	Postmodification of poly(styrene-co-divinyl benzene) monoliths	125
5.2.1	<i>Preparation of sulphonic acid derivatives</i>	125
5.3	Solvent uptake capacity of polymers synthesised using thermal initiators	128
5.4	Sulphonated polymers as solid phase catalysts	130
5.4.1	<i>Synthesis of methyl salicylate using heterogeneous acid catalyst</i>	130
5.4.2	<i>HPLC analysis of salicylic acid esterification to methyl salicylate</i>	131
5.5	Synthesis of poly(styrene-co-divinyl benzene) monoliths by HIPE using redox initiators	132
5.5.1	<i>Solvent absorption studies of monoliths</i>	135
5.6	Results and discussion	137
5.6.1	<i>Synthesis of poly(styrene-co-divinyl benzene) by HIPE technique</i>	137
5.6.2	<i>Postmodification of monoliths</i>	143
5.6.3	<i>Solvent uptake capacity of polymers</i>	147
5.6.4	<i>Sulphonated poly(styrene-co-divinyl benzene) as catalysts</i>	151
5.6.5	<i>Synthesis of poly(styrene-co-divinyl benzene) by HIPE technique using redox initiator</i>	153
5.7	Conclusion	165
5.8	References	165

CHAPTER VI

SYNTHESIS AND EVALUATION OF POLYMERS IN PHOTORESISTS FORMULATIONS

Section No.		Page No.
6.1	Introduction	167
6.2	Synthesis of polymers for photoresists	167
6.2.1	<i>Synthesis of low molecular weight polystyrene</i>	167
6.2.2	<i>Post modification of linear Polystyrene</i>	168
6.2.2.1	<i>Acetylation of polystyrene</i>	169
6.2.2.2	<i>Baeyer Villiger oxidation</i>	171
6.2.2.3	<i>Hydrolysis of acetoxy groups to hydroxyl groups</i>	173
6.3	Synthesis of sensitisers for photoresist	174
6.3.1	<i>Synthesis of 1,2-naphthoquinone diazide-5-sulphonyl chloride</i>	174
6.3.2	<i>Diester (DES) of 1,2,5-naphthoquinone diazide sulphonyl chloride (DNQ-SO₂Cl) and 2,3,4-trihydroxy benzophenone (THBP)</i>	174
6.3.3	<i>Triester (TES) of 1,2,5-naphthoquinone diazide sulphonyl chloride (DNQ-SO₂Cl) and 2,3,4-trihydroxy benzophenone (THBP)</i>	175
6.3.4	<i>Synthesis of random polymer (RP)</i>	176
6.3.4.1	<i>Synthesis of random Polymeric sensitiser based on random polymer (RP) and 2,1,5-naphthoquinone diazide sulphonyl chloride (DNQ-SO₂Cl) [RPS]</i>	176
6.3.5	<i>Synthesis of ordered phenolic resin (OP)</i>	177
6.3.5.1	<i>Synthesis of ordered polymeric sensitiser based on ordered polymer (OP) and 2,1,5-naphthoquinone diazide sulphonyl chloride (DNQ-SO₂Cl) [DMP]</i>	178
6.4	Lithographic studies	179
6.5	Results and discussion	180
6.5.1	<i>Sensitisers for photoresists</i>	198
6.5.2	<i>Process of photoresist development</i>	204
6.6	Conclusion	209
6.7	References	209

LIST OF FIGURES

CHAPTER I: INTRODUCTION

FIGURE NO.	CAPTION	PAGE NO
1.1	Schematic representation of micelle formation in emulsion polymerisation	9
1.2	Schematic representation of HIPE formation	13
1.3	Detailed structure of macroporous resins having pores of different pore sizes.	17
1.4	Modification of Polystyrene or crosslinked polystyrene with different functionalities	21
1.5	Pattern differences in positive and negative resist.	28
1.6	Photocrosslinking of Bisazide polymers	31
1.7	Poly (vinyl cinnamate)	31
1.8	Photocrosslinking of poly(vinyl cinnamate)	32
1.9	Polymer and sensitisers for G line photoresist	33
1.10	Acid catalysed deprotection for polarity change (t-BOC resist); cleavage of pendant group to convert lipophilic polymer to hydrophilic polymer	38

CHAPTER II: MATERIALS AND CHARACTERIZATION

FIGURE NO.	CAPTION	PAGE NO
2.1	A typical isotherm plot for measurement of surface area obtained from Nova 2000e instrument.	62
2.2	A typical isotherm plot obtained from Brunauer-Emmet-Teller (B.E.T) measurements.	62

CHAPTER III: SYNTHESIS OF BEADED POROUS POLYMERS USING SURFACTANTS

FIGURE NO.	CAPTION	PAGE NO
3.1a	Spherical beads obtained on polymerisation in presence of surfactants in the oil phase	74
3.1b	Interactions of oil phase and aqueous phase to form micelles in emulsion	74
3.2	Effect of cross-link density on pore volume and surface area of poly(styrene-co-divinyl benzene) synthesised using Brij-52 as surfactant	75
3.3	Effect of cross-link density on volume % pore size distribution of poly(styrene-co-divinyl benzene) synthesised using Brij-52	75

3.4	Effect of internal water on pore volume and surface area of 100% cross-linked poly(styrene-co-divinyl benzene) synthesised using Brij-52	77
3.5	Effect of internal water on differential volume pore size distribution of 100% cross-linked poly(styrene-co-divinyl benzene) synthesised using Brij-52	77
3.6	Effect of stirring time on pore volume and surface area of 100% cross-linked poly(styrene-co-divinyl benzene) synthesised by using Brij-52	78
3.7	Effect of stirring time on volume % pore size distribution of 100 % cross-linked poly(styrene-co-divinyl benzene) synthesised by using Brij-52	79
3.8	Effect of variation in cross-link density using Span 60 on surface area of poly(styrene-co-divinyl benzene)	81
3.9	Pore size distribution in poly(styrene-co-divinyl benzene) with variation in cross-link density synthesised using Span-60	81
3.10	Comparison of pore size distribution (vol %) for 25 % cross-linked poly(styrene-co-divinyl benzene) with variation in surfactant type	83
3.11	Comparison of pore size distribution in poly(styrene-co-divinyl benzene) with variation in surfactant type and cross-link density	83
3.12	Comparison of surface area of poly(styrene-co-divinyl benzene) synthesised by using Span 60 and Brij 52	84
3.13	Comparison of pore volume of poly(styrene-co-divinyl benzene) synthesised by suspension polymerisation with variation in porogen type	86
3.14	Pore size distribution of poly(styrene-co-divinyl benzene) of 100% CLD synthesised by suspension polymerisation	87
3.15	Surface area of the poly(styrene-co-divinyl benzene) of 100% CLD using different porogens	87
3.16	Comparison of surface area of the poly(styrene-co-divinyl benzene) of 100% CLD prepared by using different synthesis strategies	88
3.17	Comparison of pore volume of poly(styrene-co-divinyl benzene) of 100% CLD prepared by using different synthesis strategies	89
3.18	Comparison of pore size distribution (vol %) in poly(styrene-co-divinyl benzene) synthesised by variation in porogen type	90

3.19a	Optical micrographs of polymer synthesised using Brij-52	90
3.19b	Optical micrographs of polymer synthesised using Span 60	90
3.20a	SEM micrographs of polymers using Brij-52	91
3.20b	SEM micrographs of polymers using Span 60	91
3.21	Schematic representation of connecting pores of gigaporous material	92

CHAPTER IV: SYNTHESIS AND EVALUATION OF LOW CROSS-LINK DENSITY POROUS POLYMERS FOR IMBIBING

FIGURE NO.	CAPTION	PAGE NO
4.1	Effect of HIPE stirring time on pore volume of poly(styrene-co-divinyl benzene) having 0.25 %, 0.5 % and 1 % cross-link density	103
4.2	Effect of stirring time on pore size distribution (vol %) of IM series poly(styrene-co-divinyl benzene) synthesised using Span 60 having 1% cross-link density	104
4.3	Effect of stirring time on pore size distribution (vol %) of IAB series poly(styrene-co-divinyl benzene) synthesised using Span 60 having 0.5% cross-link density	105
4.4	Effect on pore volume of poly(styrene-co-divinyl benzene) synthesised with variation in surfactant concentration and cross-link density	105
4.5	Effect of surfactant concentration on pore volume and surface area of poly(styrene-co-divinyl benzene) having 1% cross-link density	106
4.6	Effect of surfactant concentration on pore volume and surface area of poly(styrene-co-divinyl benzene) having 0.5% cross-link density	107
4.7	Effect of surfactant concentration on pore volume and surface area of poly(styrene-co-divinyl benzene) having 0.25% cross-link density	107
4.8	Effect of surfactant concentration on pore size distribution (vol%) of poly(styrene-co-divinyl benzene) having 0.25 % cross-link density	108
4.9	Effect of surfactant concentration on pore size distribution (vol %) of poly(styrene-co-divinyl benzene) having 0.5 % cross-link density	109

4.10	Effect of surfactant concentration on pore size distribution (vol %) of poly(styrene-co-divinyl benzene) having 1% cross-link density	109
4.11	Comparison of effect of oil:surfactant ratio of 1:0.08 on pore size distribution (vol%) of poly(styrene-co-divinyl benzene) with variation in cross-link density	110
4.12	Comparison of effect of oil:surfactant ratio of 1:0.17 on pore size distribution (vol%) of poly(styrene-co-divinyl benzene) with variation in cross-link density	110
4.13	Comparison of effect of oil:surfactant ratio of 1:0.26 on pore size distribution (vol%) of poly(styrene-co-divinyl benzene) with variation in cross-link density	111
4.14	Comparison of effect of oil:surfactant ratio of 1:0.35 on pore size distribution (vol%) of poly(styrene-co-divinyl benzene) with variation in cross-link density	111
4.15	Comparison of effect of oil:surfactant ratio of 1:0.71 on pore size distribution (vol%) of poly(styrene-co-divinyl benzene) with variation in cross-link density	112
4.16	Comparison of effect of heptane concentration in HIPE formation on pore volume of poly(styrene-co-divinyl benzene)	113
4.17	Effect of heptane concentration in HIPE formation on pore size distribution (vol %) of poly(styrene-co-divinyl benzene) having 0.5% cross-link density	113
4.18	Effect of heptane concentration in HIPE formation on pore size distribution (vol %) of poly(styrene-co-divinyl benzene) having 1% cross-link density	114
4.19	Comparison of pore volume of 1% cross-linked poly(styrene-co-divinyl benzene) synthesised using HIPE suspension or suspension polymerisation (in presence or absence of porogen)	115
4.20	Comparison of pore volume of 0.5% cross-linked poly(styrene-co-divinyl benzene) synthesised using HIPE suspension or suspension polymerisation (in presence or absence of porogen)	115
4.21	Comparison of pore size distribution (vol%) of polymers having 1% cross-link density synthesised using HIPE suspension or suspension polymerisation (in presence or absence of porogen)	117
4.22	Comparison of pore size distribution (vol%) of polymers having 0.5% cross-link density synthesised using HIPE suspension or suspension polymerisation (in presence or absence of porogen)	117

4.23	Comparison of toluene uptake capacity of poly(styrene-co-divinyl benzene) having different cross-link density	118
4.24	Comparison of toluene uptake capacity of poly(styrene-co-divinyl benzene) having different cross-link density with variation in internal water in HIPE formation	119
4.25	Comparison of toluene uptake capacity of poly(styrene-co-divinyl benzene) having different cross-link density with variation in heptane concentration in HIPE formation	119
4.26	Comparison of toluene uptake capacity of poly(styrene-co-divinyl benzene) having different cross-link density with variation in surfactant concentration in HIPE formation	120
4.27	Comparison of toluene uptake capacity of poly(styrene-co-divinyl benzene) having different cross-link density with variation in emulsion stirring time in HIPE formation	120

CHAPTER V : SYNTHESIS AND EVALUATION OF POLYMERIC MONOLITHS

FIGURE NO.	CAPTION	PAGE NO
5.1	Schematic representation of sulphonation	125
5.2	Pictorial view of emulsion of styrene and divinyl benzene formed.	139
5.3	Pictorial appearance of synthesised poly(styrene-co-divinyl benzene) polymer	140
5.4	Pictorial representation of interconnecting cells in HIPE formation	140
5.5	Comparison of B.E.T surface area with variation in cross-link density of polymers synthesised using surfactant comprising of poly glycerol mono isostearate	141
5.6	Comparison of B.E.T surface area with variation in cross-link density of polymers synthesised using surfactant comprising of poly glycerol succinate	141
5.7	SEM photographs of MSD 250 at 10 K magnification	143
5.8	SEM photographs of GSD 250 at 10 K magnification	143
5.9	IR spectra of sulphonated and unmodified poly(styrene-co-divinyl benzene)	144

5.10	BET surface area before and after sulphonation	145
5.11	Acid capacity of sulphonated poly(styrene-co-divinyl benzene) synthesised using surfactant comprising of polyglycerol mono isostearate	146
5.12	Acid capacity of sulphonated poly(styrene-co-divinylbenzene) synthesised using surfactant comprising of poly glycerol succinate	146
5.13	Equilibrium solvent uptake for MSD 50 series polymers having 50% cross-linking and synthesised using surfactant comprising of poly glycerol mono isostearate	148
5.14	Equilibrium solvent uptake for MSD 100 series polymers having 100% cross-linking and synthesised using surfactant comprising of poly glycerol mono isostearate	149
5.15	Equilibrium solvent uptake for MSD 200 series polymers having 100% cross-linking and synthesised using surfactant comprising of polyglycerol mono isostearate	149
5.16	Equilibrium solvent uptake for GSD 50 series polymers having 50% CLD and synthesised using surfactant comprising of poly glycerol succinate	150
5.17	Equilibrium solvent uptake for GSD 200 series polymers having 200% CLD and synthesised using surfactant comprising of poly glycerol mono isostearate	150
5.18	HPLC separation of salicylic acid and methyl salicylate at different retention times	151
5.19	Comparison of % esterification and acid capacity of MSD-50 series sulphonated polymers	152
5.20	Comparison of % esterification and acid capacity of GSD-50 series sulphonated polymers	152
5.21	Comparison of B.E.T surface area of MRD (synthesised using surfactant comprising of polyglycerol mono isostearate) series polymers with variation in cross-link-density	155
5.22	Comparison of pore volume of MRD (synthesised using surfactant comprising of polyglycerol mono isostearate) series polymers with variation in cross-link-density	156

5.23	Comparison of B.E.T surface area of GRD (synthesised using surfactant comprising of polyglycerol succinate) series polymers with variation in cross-link-density	156
5.24	Comparison of B.E.T surface area and pore volume of MRD (synthesised using surfactant comprising of poly glycerol mono isostearate) series polymers having 100% cross-link-density	157
5.25	Effect of internal water on pore volume for 50% cross-linked MRD polymers (synthesised using surfactant comprising of poly glycerol mono isostearate) and its comparison for solvent uptake capacity for different solvents	158
5.26	Effect of internal water on pore volume for 100% cross-linked MRD polymers (synthesised using surfactant comprising of poly glycerol mono isostearate) and its comparison for solvent uptake capacity for different solvents	158
5.27	Effect of internal water on pore volume for 50% cross-linked GRD polymers (synthesised using surfactant comprising of poly glycerol succinate) and its comparison for solvent uptake capacity for different solvents	159
5.28	Effect of internal water in pore volume 100% cross-linked GRD polymers (synthesised using surfactant comprising of poly glycerol succinate) and its comparison for solvent uptake capacity for different solvents	159
5.29	Effect of internal water in pore volume for 200% cross-linked GRD polymers (synthesised using surfactant comprising of polyglycerol succinate) and its comparison for solvent uptake capacity for different solvents	160
5.30	Comparison of pore volume of polymers synthesised using surfactant comprising of poly glycerol mono isostearate with variation in discontinuous phase and initiation type	162
5.31	Comparison of surface area of polymers synthesised using surfactant comprising of poly glycerol mono isostearate with variation in discontinuous phase and initiation type	162
5.32	Comparison of surface area of polymers synthesised using surfactant comprising of poly glycerol succinate with variation in discontinuous phase and initiation type	163

5.33	Comparison of solvent uptake capacity for 50% cross-linked polymers synthesised using surfactant comprising of poly glycerol mono isostearate with variation in initiator system.	163
5.34	SEM photographs of MRD 250 at 10 K magnification	164
5.35	SEM photographs of GRD 250 at 10 K magnification	164

CHAPTER VI: SYNTHESIS AND EVALUATION OF POLYMERS IN PHOTORESISTS FORMULATIONS

FIGURE NO.	CAPTION	PAGE NO
6.1	Reaction Scheme of post modification reactions	169
6.2	Conversion of 1,2-DNQ sodium salt to DNQ-SO ₂ Cl	174
6.3	Coupling of DNQ-SO ₂ Cl with 2,3,4-trihydroxy benzophenone to form diester	175
6.4	Coupling of DNQ-SO ₂ Cl with 2,3,4-trihydroxy benzophenone to form triester	175
6.5	Coupling of DNQ-SO ₂ Cl with oligomer to form random polymeric sensitiser	177
6.6	Coupling of DNQ-SO ₂ Cl with ordered polymer to form ordered polymeric sensitiser	179
6.7	Effect of chain transfer agent on M _w , M _n and polydispersity index of polystyrene	181
6.8	Comparison of infra-red spectra of poly(4-acetyl styrene) with polystyrene: Effect of mole ratio of acetylating reagent	186
6.9	Comparison of infra-red spectra of poly(4-acetyl styrene) with polystyrene: Effect of reaction temperature	186
6.10	Comparison of infra-red spectra of poly(4-acetyl styrene) with polystyrene: Reduction in reaction time under reflux condition	187
6.11	Comparison of infra-red spectra of poly(4-acetyl styrene) with polystyrene: Effect of reaction medium	187
6.12	Comparison of infra-red spectra of poly(4-acetyl styrene) with polystyrene in aromatic substitution region: Effect of reaction medium	188
6.13	Oxidation using hydrogen peroxide : disodium hydrogen phosphate : acetic anhydride/trichloroacetic acid in chloroform	191

6.14	Comparison of infra-red spectra of poly(4-acetoxy styrene) synthesised using sodium perborate in acetic acid with poly(hydroxy styrene) and poly(acetyl styrene): Effect of oxidation time	191
6.15	Increase in peak absorbance at 3500 cm ⁻¹ due to hydroxyl groups on hydrolysis of acetoxy groups in poly(acetyl styrene-co-acetoxy styrene)	192
6.16	Increase in peak absorbance between 1410 cm ⁻¹ -1310 cm ⁻¹ due to phenolic hydroxyl groups on hydrolysis of acetoxy groups in poly(acetyl styrene-co-acetoxy styrene)	192
6.17	Presence of peak at 1680 cm ⁻¹ in hydroxyl modified polymer due to partial oxidation of acetyl to acetoxy groups of poly(acetyl styrene-co-styrene)	193
6.18	Increase in peak absorbance between 1050 cm ⁻¹ to 1400 cm ⁻¹ due to C-O stretching due to hydrolysis of acetoxy groups in poly(acetyl styrene-co-acetoxy styrene)	193
6.19	Increase in peak absorbance at 820 cm ⁻¹ due to para substitution of benzene ring in poly(acetyl styrene-co-acetoxy styrene)	194
6.20	Comparison of IR spectra of polystyrene, poly(acetyl styrene-co-styrene), poly(acetyl styrene-co-acetoxy styrene-co-styrene) and poly(hydroxy styrene-co-acetyl styrene-co-styrene)	194
6.21	Comparison of IR spectra of polystyrene, poly(acetyl styrene-co-styrene), poly(acetyl styrene-co-acetoxystyrene-co-styrene) and poly(hydroxy styrene-co-acetyl styrene-co-styrene)	195
6.22	Comparison of IR spectra of poly(hydroxy styrene) from Aldrich and poly(hydroxy styrene-co-acetylstyrene-co-styrene) synthesised	195
6.23	NMR of polystyrene	197
6.24	NMR of poly(acetyl styrene-co-styrene)	197
6.25	NMR of poly(acetoxy styrene-co-acetyl styrene-co-styrene)	198
6.26	Poly(hydroxy styrene-co-acetoxy styrene-co-styrene)	198
6.27	NMR of poly(4-hydroxy styrene) standard	198
6.28	UV study of DES at 365 nm : Absorbance vs exposure time	199
6.29	UV study of TES at 365 nm : Absorbance vs exposure time	200

6.30	UV study of RPS at 365 nm : Absorbance vs exposure time	200
6.31	UV study of photoresist formulations at 365 nm : Absorbance vs exposure time	200
6.32	Mechanism of sensitisation, as proposed by Suss	202
6.33	Mechanism proposed by Levine	202
6.34 a	Pattern observed after exposure and development of PHS-8 (500 times magnification)	208
6.34 b	Butterfly Pattern observed on exposure and development of PHS-8 (2500 times magnification)	208
6.35 a	Pattern observed after exposure and development of the formulation PHS-9 (500 times magnification)	208
6.35 b	Pattern observed after exposure and development of the formulation PHS-9 (2500 times magnification)	208

LIST OF TABLES

CHAPTER I: INTRODUCTION

TABLE NO.	CAPTION	PAGE NO
1.1	Techniques of porous polymer synthesis	4

CHAPTER III: SYNTHESIS OF BEADED POROUS POLYMERS USING SURFACTANTS

TABLE NO.	CAPTION	PAGE NO
3.1	Compositions of poly(styrene-co-divinyl benzene) synthesised with Brij-52: Effect of cross-link density	67
3.2	Effect of change in internal water volume on pore volume and surface area of 100% cross-linked poly(styrene-co-divinyl benzene)	68
3.3	Effect of change in stirring time on pore volume and surface area of 100% cross-linked poly(styrene-co-divinyl benzene)	68
3.4	Effect of Brij-52 (surfactant) concentration on pore volume and surface area of 100% cross-linked poly(styrene-co-divinyl benzene)	69
3.5	The effect of cross-link density on surface area of poly(styrene-co-divinyl benzene) synthesised using Span 60	69
3.6	The effect of inner water on surface area of 100% cross-linked poly(styrene-co-divinyl benzene) synthesised using Span 60	70

3.7	The effect of stirring time on surface area of 100% cross-linked poly(styrene-co-divinyl benzene) synthesised using Span 60	70
3.8	The effect of surfactant concentration on surface area of 100% cross-linked poly(styrene-co-divinyl benzene) synthesised using Span 60	71
3.9	Effect of variation in porogen type and volume on pore volume and surface area of poly(styrene-co-divinyl benzene) synthesised by suspension polymerisation method	71
3.10	Pore size distribution (volume %) of polymers having different cross-link density synthesised using Brij-52	76
3.11	Pore size distribution (volume %) of polymers of different cross-link density synthesised using Span 60	80
3.12	Designing synthesis strategy on pore volume and surface area of poly(styrene-co-divinyl benzene) in the 100% CLD range	88

CHAPTER IV: SYNTHESIS AND EVALUATION OF LOW CROSS-LINK DENSITY POROUS POLYMERS FOR IMBIBING

TABLE NO.	CAPTION	PAGE NO
4.1	Effect on pore volume and surface area of compositions of 1 % cross-linked poly(styrene-co-divinyl benzene) synthesised using Span-60 with variation in volume of (a) inner water (b) heptane volume (c) surfactant concentration and (d) stirring time	95
4.2	Styrene (ST)-co-divinyl benzene (DVB) copolymers of 1% cross-link density synthesised by suspension polymerisation. Effect of solvent (heptane) on pore volume and surface area	96
4.3	Effect on pore volume and surface area of compositions of 0.5% cross-linked poly(styrene-co-divinyl benzene) synthesised using Span-60 with variation in (a) inner water (b) heptane volume (c) surfactant concentration and (d) stirring time	97
4.4	Styrene (ST)-co-divinyl benzene (DVB) copolymers of 0.5 % cross-link density synthesised by suspension polymerisation and its effect on pore volume and surface area	98

4.5	Effect on pore volume and surface area of 0.25% cross-linked poly(styrene-co-divinyl benzene) synthesised using Span-60 with variation in (a) inner water (b) heptane volume (c) surfactant concentration and (d) stirring time	98
4.6	Styrene (ST)-co-divinyl benzene (DVB) copolymers of 0.25% cross-link density synthesised by suspension polymerisation and its effect on pore volume and surface area	99
4.7	Bulk density and toluene uptake capacity of 0.25% cross-linked poly(styrene-co-divinyl benzene)	100
4.8	Bulk density and toluene uptake capacity of 0.5% cross-linked poly(styrene-co-divinyl benzene)	101
4.9	Bulk density and toluene uptake capacity of 1% cross-linked poly(styrene-co-divinyl benzene)	102

CHAPTER V : SYNTHESIS AND EVALUATION OF POLYMERIC MONOLITHS

TABLE NO.	CAPTION	PAGE NO
5.1	Synthesis of 50% cross-linked poly(styrene-co-divinyl benzene) monoliths with first surfactant blend	122
5.2	Synthesis of 100% cross-linked poly(styrene-co-divinyl benzene) monoliths with first surfactant blend	123
5.3	Synthesis of 200% cross-linked poly(styrene-co-divinyl benzene) monoliths with first surfactant blend	123
5.4	Synthesis of 50% cross-linked poly(styrene-co-divinyl benzene) monoliths with second surfactant blend	123
5.5	Synthesis of 100% cross-linked poly(styrene-co-divinyl benzene) monoliths with second surfactant blend	124
5.6	Synthesis of 200% cross-linked poly(styrene-co-divinyl benzene) monoliths with second surfactant blend	124
5.7	Sulphonation of 50% cross-linked poly(styrene-co-divinyl benzene) synthesised using surfactant having polyglycerol mono isostearate as part surfactant	126

5.8	Sulphonation of 100% cross-linked poly(styrene-co-divinyl benzene) synthesised using polyglycerol mono isostearate as part surfactant	126
5.9	Sulphonation of 200% cross-linked poly(styrene-co-divinyl benzene) synthesised using polyglycerol mono isostearate as part surfactant	126
5.10	Sulphonation of 50% cross-linked poly(styrene-co-divinyl benzene) synthesised polyglycerol succinate as part surfactant	127
5.11	Sulphonation of 100% cross-linked poly(styrene-co-divinyl benzene) synthesised using polyglycerol succinate as part surfactant	127
5.12	Sulphonation of 200% cross-linked poly(styrene-co-divinyl benzene) synthesised using surfactant having polyglycerol succinate	127
5.13	Solvent uptake for 50% cross-linked polymers synthesised using polyglycerol mono isostearate as part surfactant	128
5.14	Solvent uptake for 100% cross-linked polymers synthesised using polyglycerol mono isostearate as part surfactant	128
5.15	Solvent uptake for 200% cross-linked polymers synthesised using polyglycerol mono isostearate as part surfactant	129
5.16	Solvent uptake for 50% cross-linked polymers synthesised using polyglycerol succinate as part surfactant	129
5.17	Solvent uptake for 100% cross-linked polymers synthesised using polyglycerol succinate as part surfactant	129
5.18	Solvent uptake for 200% cross-linked polymers synthesised using polyglycerol succinate as part surfactant	130
5.19	Esterification of salicylic acid -1	131
5.20	Esterification of salicylic acid-2	132
5.21	Synthesis of 50% cross-linked poly(styrene-co-divinyl benzene) monoliths by HIPE technique using redox initiator	133
5.22	Synthesis of 100% cross-linked poly(styrene-co-divinyl benzene) monoliths by HIPE technique using redox initiator	133

5.23	Synthesis of 200% cross-link density poly(styrene-co-divinyl benzene) monoliths by HIPE technique using redox initiator	133
5.24	Synthesis of 50% cross-linked poly(styrene-co-divinyl benzene) monoliths by HIPE technique using redox initiator-2	134
5.25	Synthesis of 100% cross-linked poly(styrene-co-divinyl benzene) monoliths by HIPE technique using redox initiator-2	134
5.26	Synthesis of 200% cross-linked poly(styrene-co-divinyl benzene) monoliths by HIPE technique using redox initiator-2	135
5.27	Solvent uptake for 50% cross-linked polymers synthesised using polyglycerol succinate as part surfactant	135
5.28	Solvent uptake for 100% cross-linked polymers synthesised using polyglycerol succinate as part surfactant	136
5.29	Solvent uptake for 200% cross-linked polymers synthesised using polyglycerol succinate as part surfactant	136
5.30	Solvent uptake for 50% cross-linked polymers synthesised using polyglycerol mono isostearate as part surfactant	136
5.31	Solvent uptake for 100% cross-linked polymers synthesised using polyglycerol mono isostearate as part surfactant	137
5.32	Solvent uptake for 200% cross-linked polymers synthesised using polyglycerol mono isostearate as part surfactant	137

CHAPTER VI: SYNTHESIS AND EVALUATION OF POLYMERS IN PHOTORESISTS FORMULATIONS

TABLE NO.	CAPTION	PAGE NO
6.1	Polystyrenes synthesised and their characteristics	168
6.2	Acylation of polystyrene varying the concentration of acylating agent	170
6.3	Acylation of polystyrene by variation in reaction time	170
6.4	Acylation of polystyrene by using cyclohexane as solvent	171
6.5	Oxidation of acetyl to acetoxy groups with acetic anhydride and hydrogen peroxide	172

6.6	Oxidation of acetyl groups to acetoxy groups with sodium perborate	172
6.7	Oxidation of acetyl groups to acetoxy groups using sodium perborate : Effect of reaction time	173
6.8	Modification of random phenolic resin with variation in percent modification of hydroxyl groups	177
6.9	Modification of ordered phenolic resin with variation in percent modification of hydroxyl groups	178
6.10	Lithographic studies of various compositions (formulations)	179

ABSTRACT

SYNTHESIS, CHARACTERIZATION, MODIFICATION AND EVALUATION OF POLYMERS HAVING STYRENE MOIETIES

Polymers having styrene moieties are used in variety of applications such as ion exchange resins, imbibing polymers and in photoresists. The aromatic ring of styrene moiety can be subjected to nucleophilic or electrophilic substitution reactions to introduce functional groups on the polymer backbone so as to alter the properties. New processes have generated macroporous poly(styrene-co-divinyl benzene) gels by the use of porogens, which may be structuring solvents, non-solvents or linear polymers. Phase separation during polymerisation is the basic strategy of synthesising macroporous networks. A modern approach towards porous polymers is the use of templates in supramolecular chemistry. Others have used surfactants and high internal phase emulsion (HIPE) technique to synthesise polymers with well defined porous structures.

Styrene based polymers are also used in the lithography industry. Synthesis of different types of sensitisers and polymers for I-line photoresists and chemically amplified resists are researches to meet new technology requirements. The research into the replacement of conventional novolak resins with new polymer systems have been targeted at the study of the effects of molecular weights, glass transition temperature and solubility behaviour during the development process in lithography.

This work aims to synthesise polymers having styrene moieties by different strategies, to study the effect of synthesis strategies on the properties and morphology of the polymers and to study its potential use as imbibing polymers, heterogeneous catalysts and photoresists.

Chapter 1 deals with the current state of knowledge in synthesis of porous polymers and post modification of polymers to introduce different functional groups on polymer backbone. A review of synthesis strategies and applications of styrene based polymers is presented.

Chapter 2 deals with the different characterisation techniques of porous polymers and modified polymers. Porosity is characterised by mercury intrusion and B.E.T surface area. The post modification reaction on polymer is monitored by infrared and NMR spectroscopy. The acid capacity of the polymers is determined by titrimetric method. The efficiency of heterogeneous catalyst is studied by HPLC. The polymers synthesised for photoresist applications are characterised by ultra-violet and infrared spectroscopy.

Chapter 3 deals with synthesis of beaded poly(styrene-co-divinyl benzene). Conventionally porous, beaded polymers are synthesised using solvent, nonsolvent or linear polymers as porogen. The chapter explores the concept to synthesise porous polymers using surfactants. Cross-linked polymers synthesised in absence of porogen generates beaded polymers having a glassy appearance. This chapter discusses the synthesis of beaded poly(styrene-co-divinyl benzene) in presence of surfactant in the oil phase that acts as pore generating medium. The surfactant plays an important role in designing the pore volume, pore size distribution and surface area of the polymers. It is observed that polymers synthesised using Brij-52 surfactant have a pore volume in the range of 0.8-1.1 cm³/g and surface area of 100-200 m²/g. Polymers synthesised using Span-60 surfactant have a pore volume in the range of 1.5-2.0 cm³/g and surface area of 3-50 m²/g. The volume percent pore size distribution shows that polymers synthesised using Brij-52 have microporous structures while polymers synthesised using Span-60 gives rise to macropores.

Chapter 4 deals with the synthesis of low cross-linked porous beaded polymers by water-in-oil-in-water emulsion consisting of surfactant, monomer and aqueous phase added to a protective colloid containing aqueous phase. This technique of generating porous beads is different from conventional suspension polymerisation. The polymers are evaluated for its toluene uptake capacity so as to be used in imbibing applications. The data shows that the polymers have an equilibrium swelling index between 1.5 and 9. Highly porous polymers are obtained if a porogen is added to the oil phase during the emulsion formation.

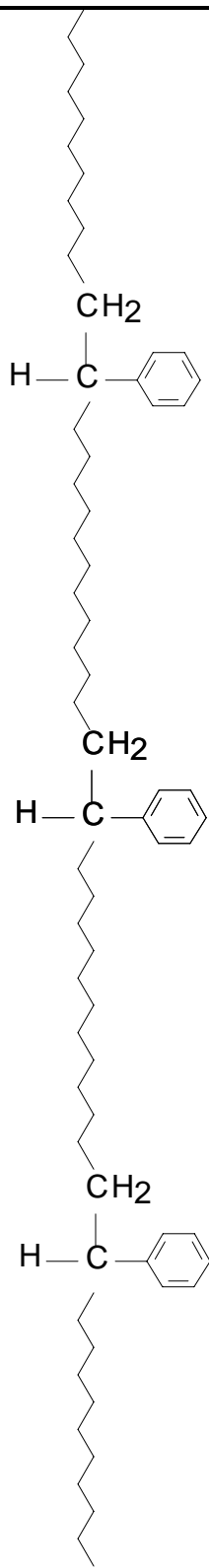
Chapter 5 deals with synthesis of porous poly(styrene-co-divinyl benzene) monoliths using high internal phase emulsion technique (HIPE). Water in oil emulsions are made prior to polymerisation and the emulsions are polymerised either by using a thermal initiator at elevated temperature or a redox pair of initiators at room temperature. The effect of synthesis parameters such as surfactant concentration, crosslinker, ratio of aqueous phase to monomer phase on the porous properties and morphology of the polymers is studied. The open celled polymers are post modified to introduce sulphonic acid groups on the polymer backbone and are tested for its efficiency as heterogeneous acid catalysts.

Chapter 6 deals with the synthesis and evaluation of polymeric materials and sensitisers as photoresists. Conventional phenolic resins have a high polydispersity index and high solubility in aqueous alkaline developer. Replacement of phenolic resins by a polymer having partial hydroxyl groups to decrease its solubility in developer is studied. Linear low molecular weight polystyrene were synthesised and subjected to post modification reactions to introduce hydroxyl group in the polymer backbone. The structure resembles phenolic resin except for the methylene bridges. Sensitiser based on naphthoquinone diazide were synthesised by esterification with

2,3,4-trihydroxy benzophenone or random low molecular weight phenolic resins. The modification reactions were monitored by infra-red and NMR spectroscopy. The polymers and sensitiser were formulated into photoresist and tested for development of lithographic images at 365 nm.

Student

Research Guide



INTRODUCTION

1 Introduction

1.1 History of polystyrene

Styrene was discovered by Newman prior to 1786, and was isolated by steam distillation from liquidambar, a solid resin obtained from a family of trees or shrubs native to the Far East and California. Liquidambar has a vanilla like odour and was used in medicine and perfumery. Cinnamic acid present in it could be easily decarboxylated to obtain styrene. Styrene is produced by passing ethylene into benzene in presence of aluminium trichloride as catalyst to produce ethyl benzene, which on passing over a catalyst such as iron oxide or magnesium oxide at high temperatures, usually 600°C, gets converted into styrene and hydrogen.¹ The first polymerisation of styrene is credited to E. Simmons in 1839. The solid product obtained after steam distillation from resinous gum was named as “Styrol”.

Styrene readily polymerises to polystyrene by conventional free radical, coordination, cationic and ionic methods. Typical initiators used in the suspension process include benzoyl peroxide and di-tert-butyl perbenzoate. Potassium peroxydisulphate is a typical initiator used in emulsion polymerisation.

1.2 Properties of polystyrene

The glass like solid behaviour of polystyrene below 100°C makes it unique, with a wide range of properties. Above this temperature the polymer chains at molecular level have rotational freedom that allows large chain segment mobility and the polymer is thus fluid enough to be easily shaped into useful forms. Styrene homo and copolymers are non-polar, chemically inert, resistant to water and easy to fabricate,² and these properties are product of choice for electronic, medical food packaging, optical appliances and automotive parts. The first styrene copolymer was styrene-butadiene synthetic rubber.

Other significant copolymers include tough solvent resistant copolymers with acrylonitrile, heat resistant polymers with maleic anhydride, and rubber modified transparent systems with methyl methacrylate.³

1.3 History of porous polymers and ion exchange resins

The use of polymer resins as an aid to synthesis is becoming an increasingly common feature in both academic and industrial laboratories.⁴⁻⁵ Industrial modification of styrene-divinylbenzene resins include mostly sulphonation, chloromethylation or amination leading to ion exchange resins.⁶ Suspension polymerisation is the technique that can be particularly suited to the production of large porous polymer beads, typically in the range 5–1000 μm .

Suspension polymerisation was first developed by Hoffman and Delbrück in 1909.⁷ The first suspension polymerisation based on acrylic monomers leading to the formation of beads was performed by Bauer and Lauth in 1931.⁸ In 1935, Hermann Staudinger published the first systematic examinations of the copolymerisation of styrene and divinyl benzene in organic solvents.⁹ The polymers were soft, gel-like at small divinyl benzene (DVB) contents, and had a three-dimensional network structure, with solvent-filled pores in the range 3 and 50 μm .

As early as 1963, Millar and coworkers described the preparation of the macroporous styrene-divinyl benzene (St-DVB) copolymer and the uptake of cyclohexane was greater than 0.1 mL/g and beads had opalescence.¹⁰ Porous St-DVB beads are converted to or used as adsorbents,¹¹ support for catalysts,¹²⁻¹³ anion exchangers,¹⁴⁻¹⁵ cation-exchangers¹⁶⁻¹⁷ etc. Cation-exchangers are among the most important commercial products derived from St-DVB for use in chromatographic

separations¹⁸ and as acid catalysts.¹⁹ The cation-exchangers are obtained by sulphonation, i.e., by the introduction of sulphonic acid ($-\text{SO}_3\text{H}$) groups with exchangeable protons onto benzene rings of monomer units in St-DVB.²⁰⁻²¹

To improve the exchange properties, new processes were explored to generate macroporous poly(styrene-co-divinyl benzene) gels, the so-called macroreticular polymers. These polymers usually have high cross-linking densities up to the point that they are made of pure cross-linker, they are mechanically more stable, and they provide larger pore structures which are also accessible for the polymer in non-solvents. The basis of these new approaches discovered in the late 1950's, was the presence of porogens in the polymerisation which are removed from the polymer gel after polymerisation.²²

1.4 Synthesis strategies of porous polymers

New processes were found to generate macroporous poly(styrene-co-divinyl benzene) gels by the addition of porogens. Porogens include structuring solvents, non-solvents or linear polymers. A modern approach towards porous polymers is the use of templates. Template synthesis concepts became increasingly important for supramolecular chemistry in the 1980's.²³ Phase separation during polymerisation is the basic strategy of synthesising macroporous networks.

Table 1.1 : Techniques of porous polymer synthesis⁸

Method	Porogen	Pore sizes ^a	Morphologies	Examples of matrix polymers
Foaming Gases	Gases Solvents Supercritical CO ₂	100 nm-1 mm	Isotropic Open-closed pores	Polystyrene, polylactide, polymethacrylate, poly(hydroxy ethyl methacrylate) polyurethane, polycarbonate etc.
Phase separation Thermally induced Chemically induced Immersion techniques	Solvents	1 µm- 1 mm	Typically isotropic and open porous	Polystyrene, polylactide Poly (ether ether ketone), polyamide, polyepoxide, poly (dicyclopentadiene) etc.
HIPE ^b -polymerisation	Emulsions	10 µm–100 µm	Isotropic, open porous	Poly(styrene-co-divinyl benzene), poly (vinyl benzyl chloride-co-divinyl benzene), poly (aryl ether sulfone) etc.
Template synthesis				
Molecular imprinting	Molecules	1 nm-10 nm	Isotropic,	Poly (methacrylic acid)
Micellar imprinting	Micelles	10 nm-50 nm	Open, closed pores	Poly (ethylene glycol dimethacrylate), polyurethane
Colloid crystal templating	Colloid crystals	50 nm-1 µm		
Polymerisation of bio microemulsions biocontinuous		5 nm-10 µm		polystyrene, poly (2-hydroxyethyl-methacrylate,
Polymerisation of liquid crystalline mesophases	Lyotropic mesophases PET,s ^c	5 nm-10 µm	Isotropic, anisotropic Open-closed pores	Poly(acrylic acid), Poly acrylamide, poly (methyl methacrylate), etc.
Polymerisation of liquid crystalline mesophases	Lyotropic mesophases PET,s ^c	5 nm-10 µm	Isotropic, anisotropic Open-closed pores	Poly(acrylic acid), Poly acrylamide, poly(methyl methacrylate), etc.
Other techniques				
Mechanical stretching	Mechanical deformation	10 nm-100 nm	Anisotropic, open pores	Polypropylene
Interparticular cross-linking	Solvent	1 µm -10 µm	Isotropic, open pores	Poly acrylic acid

a)Typical pore diameters; b) HIPE, high internal phase emulsion; c) PET, polyelectrolyte surfactant complexes.

1.5 Polymerisation techniques

Homopolymers and copolymers can be produced by bulk (or mass), solution (a modified bulk), suspension or emulsion polymerisation techniques.²⁴

1.5.1 Suspension polymerisation

The well-established route to synthesise beaded, porous polymer is by suspension polymerisation technique.²⁵⁻²⁶ Beaded polymer supports and gels, both organic and inorganic, are the widely used materials for various chromatographic techniques²⁷⁻²⁸ and a number of other applications such as solid phase peptide synthesis,²⁹ hydrometallurgy,³⁰ chemical catalysis³¹ etc. In suspension process, polymerisation occurs in a monomer containing phase that is dispersed in a continuous liquid phase. Controlled agitation and the presence of drop stabilisers are necessary to maintain the suspension.³²⁻³³ In most cases the continuous phase is aqueous and polymerisation occurs by free radical mechanism. For example, beaded polystyrene resins are produced by oil-in-water (o/w) suspension polymerisation.

The synthesised beads can be porous or non-porous depending on the synthesis strategies.³⁴⁻³⁸ An inert diluent solvent or nonsolvent for the polymer can be used as a chain transfer agent or pore generating diluent. A key problem is the formation of uniform suspension of monomer droplets in the aqueous phase and reduction of coalescence of the droplets during polymerisation.³⁹ Droplet formation in an oil-water mixture is achieved by mechanical stirring. A liquid-liquid dispersion exists in the initial stages of particle formation. The liquid monomer is dispersed in small droplets and stabilised by the combined action of the stirrer and the suspending agents. At intermediate (25 to 75%) conversions, when droplets comprise of polymer and monomer, the droplet surface is tacky and particles can agglomerate during collision. This stage of polymerisation is called sticky period. The droplets break up

by the impeller's shear stress and coalesce back after collision with each other. At the end of the sticky period, as the monomer is consumed further, particles become solid like and they do not stick any more. After this point, which is called particle identity point (PIP), the tendency of particle to agglomerate is reduced and their diameter remains constant.⁴⁰

1.5.2 Emulsion polymerisation

An emulsion is the product of the dispersion of two immiscible liquids, one liquid constitutes the continuous phase and second, which forms droplets within the continuous phase, is the discontinuous or dispersed phase. Luther first reported emulsion polymerisation and Heuck reported it in 1932.⁴¹ Emulsion polymerisation is a compartmentalised polymerisation reaction taking place in a large number of reaction loci dispersed in a continuous external phase. Polymerisation is carried out in heterogeneous systems, commonly with an aqueous and a non-aqueous phase. Depending upon the nature of the dispersed phase, emulsions can be either of oil-in-water type (o/w) or water-in-oil (w/o) type.⁴² The monomer and polymer usually belong to the non-aqueous phase. In inverse systems, water-soluble monomers are dispersed in a non-aqueous medium. A typical emulsion polymerisation system consists of water (or non-aqueous medium), monomer(s), emulsifier (surfactant) and initiator; typically, 30% monomer, 65% water and rest of it is surfactant, modifier and other additives. Generally, the monomer is sparingly soluble in water and generates a water-insoluble polymer which is swollen by monomer. Emulsification initially results in micelles (10^{19} - 10^{21} dm^{-3}) swollen with solubilised monomer and surfactant-stabilised monomer droplets (10^{12} - 10^{14} dm^{-3}). The micelles are usually 0.005-0.01 μm in size, whereas the monomer droplets are of the order of 1-10 μm . As initiator decomposition takes place, a new phase appears. The latex particles, which contain

macromolecules of fairly high degree of polymerisation, are swollen with monomer and stabilised by surfactant. The diameter of these latex particles is around $0.1 \mu\text{m}$ and the number density is usually in the range 10^{16} - 10^{18} dm^{-3} .⁴³⁻⁴⁴ The droplets act as reservoirs of monomer, that is fed to the growing polymer particles by diffusion through the aqueous phase.⁴⁵⁻⁴⁶

Emulsion polymerisation involves the propagation of relatively water-insoluble monomers (e.g. styrene in submicron latex particles dispersed in an aqueous phase with the aid of surfactant (e.g. sodium dodecyl sulphate [SDS]). The polymerisation process is generally divided into three distinct stages: nucleation of particle nuclei by capture of oligomeric radicals by the monomer-swollen micelles (Interval I), growth of latex particles by recruiting monomer and surfactant from the emulsified monomer droplets (Interval II), and depletion of residual monomer in the latex particles (Interval III).⁴⁷⁻⁵¹ The initiator is located in the aqueous phase and the monomer-polymer particles are quite small, of the order of $0.1 \mu\text{m}$ in diameter. The soap plays an important role in emulsion polymerisation. At the beginning of the reaction it exists in the form of micelles, aggregates of 50-100 soap molecules. Soon after (2-3% polymerisation) the polymer particles are much larger than the original micelles and absorb almost all the soap from the aqueous phase. Any micelles not already activated disappear and further polymerisation takes place within the already formed polymer particles. The monomer droplets are unstable at this stage and if agitation is stopped, they coalesce into a continuous oil phase containing no polymer. The polymer particles may contain about 50% monomer up to the point at which the monomer droplets disappear, at 60-80 % polymerisation. The rate of polymerisation is constant over most of the reaction up to this point, but then falls off as monomer is depleted in the polymer particles. Polymerisation can take place (at a very low rate) in

the homogeneous phase in the absence of soap, but this cannot account for the bulk of the polymer formed. At the beginning of the reaction, polymer is formed in the soap micelles. These represent a favourable environment for the free radicals generated in the aqueous phase, because of the relative abundance of monomer and the high surface to volume ratio of the micelles compared to the monomer droplets. As the polymer is formed, the micelles grow by the addition of monomer from the aqueous phase.

Emulsion polymerisation has some advantages over other polymerisation processes:

- (1) The heat generated by the exothermic free radical polymerisation can be readily dissipated into the aqueous phase, since the system remains perfectly fluid throughout the polymerisation.
- (2) The rate of polymerisation is usually much higher than equivalent bulk process.
- (3) The formed polymer often has a higher molecular weight than that formed in bulk or solution polymerisation.
- (4) The polymer is formed as a latex so that it can be more readily handled and it has an obvious advantage if the polymer is to be applied as a latex.
- (5) One can easily control the molecular weight by addition of chain transfer agents and thus control the properties of the final product.
- (6) The polymerisation process and the resulting polymer latex is water based, so environmental hazards are minimised.

Emulsion polymerisation process, along with the resulting polymer, also has certain inherent disadvantages. For example, latex formed contains surfactants and

initiator decomposition products, which are often difficult to remove. Therefore, emulsion polymers are usually excluded from applications requiring materials of high purity. In industrial process, the effective reactor volume available for polymerisation is reduced by the volume of the aqueous dispersion medium, compared with bulk polymerisation.

Emulsion polymerisation is one of the most widely used polymerisation techniques in industry, and emulsion polymers are utilised in various fields, including coatings, paints, inks, adhesives, and rubbers. More recently, emulsion polymers have been used as fine materials in paint industry, chromatography, drug delivery, and biochemical measurements.

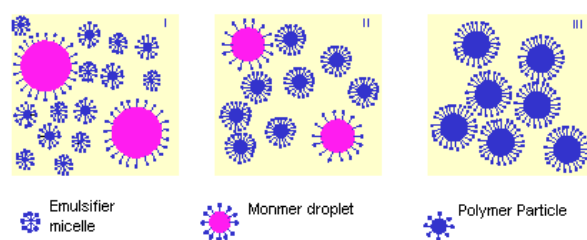


Figure 1.1: Schematic representation of micelle formation in emulsion polymerisation

The emulsion is stabilised with surface active agents, protective colloids and certain buffers along with the monomer being dispersed in the emulsion. The surfactants can be anionic (alkali salts of fatty acids and aryl and alkyl sulphonic acids), cationic (alkyl amine hydrochloride and alkyl ammonium halides) or non-ionic (alkyl glycosides and saccharose esters of fatty acids). Surfactants serve the purpose of lowering the surface tension at the monomer-water interface and facilitate emulsification of the monomer in water. Owing to their low solubility, surfactants are completely dissolved or molecularly dispersed only at low concentrations. Beyond a particular concentration, the excess quantity dopes and does not get molecularly

dispersed, but forms molecular aggregates known as “micelles”, and an equilibrium is set up between the dissolved surfactant molecules and aggregated ones. The highest concentration, wherein all the molecules are in dispersed state, or the concentration beyond which only micelle formation is possible, is known as critical micellar concentration.

The emulsifier is made of two parts a long non-polar hydrocarbon chain to which is attached a polar group such as $-\text{COONa}$, $-\text{SO}_3\text{Na}$, $-\text{NH}_2\text{Cl}$, or $-\text{NBr}$.⁵² In micelle formation, emulsifier molecules aggregate in such a way that the polar end of the molecules align themselves outward and hydrocarbon ends come close to each other at the interior. Due to close proximity of the hydrocarbon ends of all the emulsifier molecules, the interior of the micelle acts as hydrocarbon phase where the monomer is solubilised.⁵³ After addition of the monomer, the mixture is agitated and emulsification takes place. The resultant emulsion is a complex system, a molecular solution of emulsifier in water is continuous phase wherein the monomer droplets, micelles are uniformly dispersed. If the monomer is slightly soluble in water the aqueous emulsifier solution phase will also contain a part of the monomer dissolved in it.

1.5.3 High internal phase emulsion

Highly porous microcellular foams are well known structures. The more efficient way to obtain a fully interconnected morphology is by the polymerisation of continuous phase of a high internal phase emulsion (HIPE).⁵⁴⁻⁵⁶ These materials, known as poly HIPE's, have been widely used during the last two decades and belong to a class of emulsion derived foams.⁵⁷⁻⁵⁹ Their application in chemistry has always been made either in the form of monoliths having the shape of the mold in which they have been prepared or have irregular granular form. While small discs or other geometrical forms of macroporous polymers have been proposed as an alternative to classical beads, the spherical shape remains more desired for supports in solid phase synthesis. The only reported work on the macrocellular foams, synthesised via concentrated emulsion process, have been commercialised as Magnapore[®] beads are based on poly(styrene-co-divinyl benzene) without any functionalisation. Porous crosslinked polymeric microbeads have been reported in literature.⁶⁰ Highly porous organic materials, such as solid foams, (polyHIPE) materials, composites with high porosity, and very low density have been produced by so called concentrated emulsion polymerisation (different from conventional emulsion polymerisation).

After these initial studies, the area remained largely dormant until work on poly(styrene-co-divinyl benzene) (St-DVB) at Unilever in early 1980's.⁶¹ PolyHIPE materials have recently been successfully employed as supports in solid phase peptide synthesis,⁶² in which the porous structure acts as a scaffold for a soft polyamide gel.⁶³ Additionally, PolyHIPE monoliths have been used to immobilise flavin,⁶⁴ and granulated St-DVB PolyHIPE has been used as a catalyst support.⁶⁵⁻⁶⁶ These materials have also found applications in immobilisation of enzymes,⁶⁷ and selective

membranes, as templates for preparation of other materials⁶⁸ and drug delivery systems.⁶⁹

In this strategy the preformed domains of the liquid component are stabilised by surfactants in order to prevent macroscopic phase separation. Emulsion mainly comprises of three components a) continuous or outer phase, b) dispersed or inner phase c) and surfactant.

Lissant classed HIPE's as emulsions having greater than 70% internal phase volume.⁷⁰ The basic criterion for formation of HIPE is presence of two immiscible liquids one of which is water and other is hydrophobic monomer. The HIPE is generally formed by slow addition of external phase under constant agitation. Formation of stable HIPE is dependent on the nature of the surfactant. Functionality of non-ionic surfactant depends on the hydrophilic-lipophilic balance, that is an expression of relationship of size and strength of the polar (water soluble) and non polar (oil soluble) groups of the surfactant. Surfactants having a HLB value in the range 4-6 form water-in-oil emulsion and that having an HLB of 8-18 form oil in water emulsion.

Double emulsions exist when the droplets of the discontinuous phase contain finer droplets of the continuous phase liquid and are termed as emulsions of emulsions. Two type of double emulsions known are of the form : water-in-oil-in water ($W_1/O/W_2$) or oil-in-water-in-oil ($O_1/W/O_2$).⁷¹ $W_1/O/W_2$ contains a continuous aqueous phase, W_2 and oil globules within which are small aqueous droplets. $O_1/W/O_2$ double emulsion consists of continuous oil phase O_2 with aqueous globules entrapping oil droplets. The multiphase, compartmentalised structure of double emulsions makes them useful in systems requiring controlled release or uptake

capabilities. Of all potential applications for double emulsions, drug encapsulation and controlled release have received much attention.⁷²⁻⁷⁴

PolyHIPE materials have relatively low surface areas of the order of $\sim 5 \text{ m}^2/\text{g}$ due to the void sizes being in the range of single to tens of micrometers. However, by replacing some of the monomer in the organic phase with a hydrophobic solvent, it is possible to increase the surface areas.⁷⁵ The resulting monoliths have 'dual porosity' large voids characteristic of polyHIPE materials, and much smaller pores, which can be in the micro, meso, or macropore size range, resulting from phase separation of the polymer network from solution during polymerisation. PolyHIPE in which water droplets are used to generate the emulsion have a low surface area,⁷⁶ and if diluents are added in oil phase porous materials having specific surface area in the range of $350 \text{ m}^2/\text{g}$ can be obtained.⁷⁷

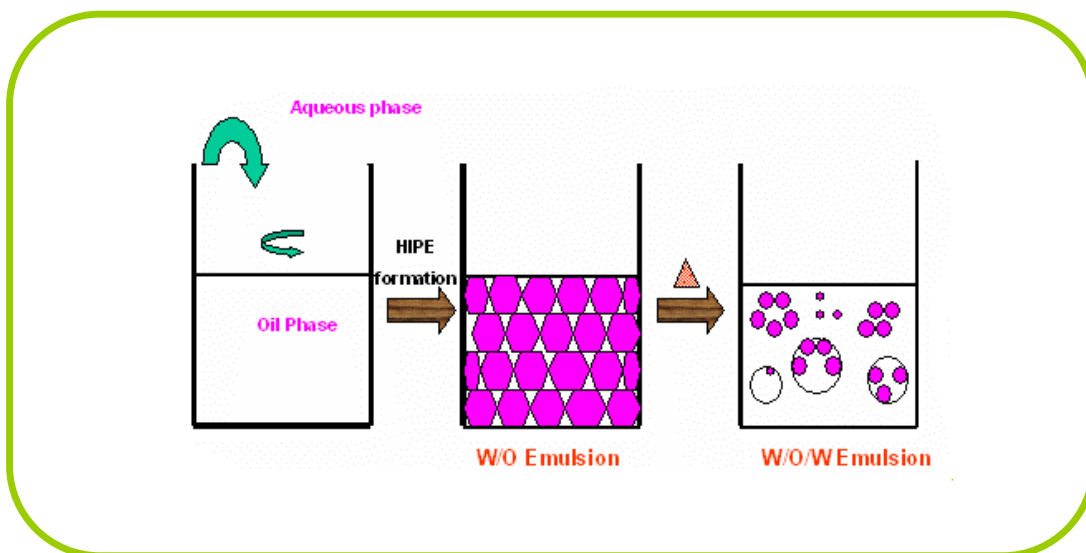


Figure 1.2: Schematic representation of HIPE formation

1.6 Macroporous resin

Matrix porosity is the basis of support characterisation in gel permeation chromatography. Porosity and surface area of porous matrices play important role in end applications such as ion exchange,⁷⁸ affinity chromatography,⁷⁹ polymer supported catalysis,⁸⁰ loading capacity⁸¹ and immobilisation efficiency of the enzymes.⁸² Extensive study of macroporous morphology and formation of porous texture have been conducted for beaded cross-linked polymers.⁸³⁻⁸⁴ This criteria determines the loading capacity of ion-exchange resin or enzyme immobilisation efficiency of the polymers. The imbibing capacity of a solvent is also dependent on the pore volume. Greater the surface area of the polymer, greater will be the extent of functional groups attached to the polymer. The important requisites for solid supports as catalysts for organic reactions and imbibing polymers is the specific pore size, pore size distribution, pore volume, surface area and optimum concentration of functional groups. The permeability limits according to the molecular size and accessibility of reactive and catalytic site depends on porous structure and swelling properties of the copolymers.⁸⁵⁻⁸⁷ These properties depend on synthesis conditions, nature of porogen, dilution degree of monomers, cross-linking degree and reaction temperature.⁸⁸⁻⁸⁹

Merrifield in 1963⁹⁰ introduced the “solid phase technique” for the synthesis of peptides in which an insoluble cross-linked macromolecule was used as a protecting group, simultaneously providing a facile method for isolating and purifying the product at each condensation step.⁹¹⁻⁹³ Haupke and Pientka⁹⁴ defined macroporous copolymers as opaque white materials with a measurable surface area. Such materials start to form in St-DVB copolymerisation at moderate or high cross-linker contents at intermediate concentrations of diluent. Jacobelli defined the macroporous copolymers as materials in which all sizes of intra-particle clusters (nuclei, microspheres and

agglomerates) are visible in electron microscope i.e materials having pores of a few angstroms to several thousand angstroms.⁹⁵ Sederal and De Jong defined micro and macroporosity with respect to the size of the pores inside the dry network.⁹⁶ The microporosity arises from the interstices between the nuclei where as macroporosity includes the pores between micropores and larger agglomerates. Rabelo and Coutinho defined porosity in copolymers in accordance with the kinetic data in heptane.⁹⁷

1.6.1 Types of resins

Gel and macroporous are the two well known types of resins. Kun and Kunin⁹⁸ suggested that mechanism of structure formation involves agglomeration of polymer chain to give nuclei (dimension of 5-20 nm) later on microsphere (60-500 nm) and finally beads (10000-100000 nm). These authors observed two successive steps in formation of porous texture during polymerisation i.e agglomeration of cross-linked microspheres and formation of macroreticular structure. In first step the porous volume is small and tends to decrease and in second step it increases. For commercial resins there is a third step: collapse of the pore structure during steam distillation to remove the residual monomer. Sederal and De Jong developed new methodologies for preparation of macroporous resin, using mixture of porogenic agents. They distinguished between microporosity, as the interstices between nuclei inside microspheres, and the macroporosity, including transitional pores (typically 25 nm in diameter) between microspheres and macropores.⁹⁹

When the comonomer mixture in a suspension polymerisation consists of monomer, cross-linker and initiator, the product obtained is in the form of hard glassy transparent resin beads. These resins are lightly cross-linked, having 0.05-2 mol% of cross-linker. In swollen state these resins are soft, compressible and relatively fragile

and are composed of an amorphous cross-linked infinite network of interpenetrating polymer chains without any fine structure. Surface area is less than 10 m²/g.

Macroporous resins are more highly cross-linked, having 15-80 mol % cross-linker and possess a complex system of permanent pores created by porogen.¹⁰⁰ Beads having a surface area of 50-1000 m²/g can be synthesised by this method. Macroporous resins are formed when the porogen present in the comonomer mixture causes phase separation of the polymer matrix. At full conversion each polymer bead is composed of cross-linked polymer phase and a discrete porogen phase. The porogen phase acts as a template for permanent porous structure of the resin. Opaque and permanently porous resins are obtained after removal of the porogen by drying. The point at which phase separation occurs depends on the nature of the porogen, its compatibility with incipient polymer matrix and its concentration.

Macroporous resins can be prepared with a wide range of porous structure. According to IUPAC nomenclature, pores with dimensions <20Å are micropores, 20-500 Å are mesopores and those >500 Å are macropores. When phase separation finally occurs the microgel particles are small and discrete. Separate porogen phase contains unreacted monomer and cross-linker. Polymerisation in porogen phase creates additional polymer that acts to fuse microgel particles together and relatively low levels of polymer are formed in the way since conversion of monomer to polymer at the point of phase separation is high. The microgel particles tend to retain their individual identity and network of micro and meso pores are generated between microgel particles.¹⁰¹ Such resins have high surface area and a pore size distribution with a maximum in the micropore and mesopore region.

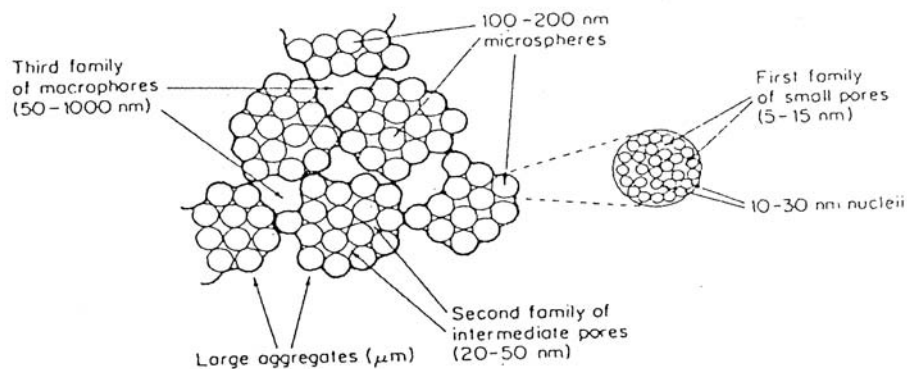


Figure 1.3: Detailed structure of macroporous resins having pores of different pore sizes

The internal structure of macroporous supports can be controlled by different parameters in the polymerisation process such as amount of cross-linking monomer used, type and volume of diluent / porogen / pore generating solvent (an inert organic solvent) added to the monomer phase. The main classes of porogens known are: a) solvents for the polymer b) non-solvents for the polymer and c) polymers soluble in monomers. The size of larger pores generated by polymers soluble in monomers depends on their molecular weight.

Copolymerisation by cross-linking reactions taking place in the monomer diluent droplets results in glassy, opaque or milky beads. Although the inert diluent must be soluble in monomer mixture and insoluble in continuous water phase, organised surfactant assemblies such as inverse micelles can be used to capture monomer insoluble diluents such as water inside the organic phase. The cross-linking copolymerisation in the continuous phase of water-in-oil microemulsion also yields macroporous networks. The nature of the porous structure is largely dependent on the microstructure of microemulsion.

1.7 Functionalised polymers

Functionalised polymers carry chemically bound functional groups that can be used as reagents, catalysts, protecting groups etc. It can be a linear species capable of forming molecular solution in a suitable solvent or alternatively a cross-linked resin that can be readily solvated by a suitable solvent but remains macroscopically insoluble. Active functional groups can be introduced into the polymer chains by:

- a) Direct polymerisation and copolymerisation of monomers containing the desired functional groups,
- b) Chemical modification of the preformed polymer, and
- c) Combination of both.

The preparation of functionalised polymers by chemical modification is an important technique used to modify the properties for various technological applications so as to prepare chemically reactive polymers. The chemical modification creates new polymers that cannot be prepared by direct polymerisation of monomers owing to their instability and unreactivity, as well as to modify the structure and physical properties of commercial polymers for specific applications.¹⁰² Functionalised polymers must possess structure that permits adequate diffusion of reagents into reactive sites. This depends on extent of swelling, compatibility, effective pore size, pore volume, chemical, thermal and mechanical stability of the resin. If the polymers are synthesised in presence of a cross-linking agent or cross-linked in post polymerisation process, the chains are effectively interconnected to form an infinite network. Such a system can no longer form true molecular solution and may be regarded as insoluble in thermodynamic sense.

Since the beads are insoluble in solvents, it offers great ease for processing. They can be prepared in form of spherical beads that do not coalesce when placed in

suspending solvent and can be separated from low molecular weight contaminants by filtration. Polymer beads with low degrees of cross-linking swell extensively, exposing their inner reactive groups to soluble reagents. More highly cross-linked resins may be prepared with highly porous structure that allows solvents and reagents to penetrate inside the beads to contact with the reactive groups.

Aliphatic and aromatic organic as well as inorganic polymers have been employed as carriers for functional group. Perhaps the most important insoluble support for organic synthesis is cross-linked polystyrene.¹⁰³ Derivatised polystyrene (PS) can be made either by copolymerisation of styrene, divinyl benzene¹⁰⁴ and functionalised styrene, or in a more divergent fashion by functionalising polystyrene.¹⁰⁵

The most recent work on chemical modification of various functionalities on polystyrene have limited success for lack of reactivity on polymer chain or other unsuitable properties of finished polymer. In principle, PS fulfills major requirements for a solid support because it offers many advantages.

Polystyrene and cross-linked polystyrene can be chemically modified by direct electrophilic and nucleophilic substitution of styrene moieties.¹⁰⁶

- 1) It undergoes functionalisation through aromatic ring by electrophilic substitution.
- 2) Compatibility: Styrenic polymers are compatible with most organic solvents and therefore functional groups are easily accessible to reagents and solvents.
- 3) Chemical stability: The aliphatic hydrocarbon backbone is resistant to attack by most reagents. Hence, polymer chains are not susceptible to degradative scission by most chemical reagents under ordinary conditions.

- 4) Mechanical stability: Styrenic polymers are mechanically stable to physical handling required in multistep sequential syntheses.
- 5) Cross-linking: Type and degree of cross-linking can be controlled by regulating the concentration of divinyl benzene. The degree of cross-linking in polymer influences swelling and pore dimension.

1.8 Reactivity of functionalised polymers

Functional groups attached to the polymer chain may have different reactivity from an analogous group on small molecules because of its macroreticular structure. Chemical behaviour of support depends on its physical form, cross-link density, flexibility of chain segments and degree of substitution.¹⁰⁷ Experimental problems are involved in the chemical modification of cross-linked polymer resins, since the reactive sites are located in the interior of polymer particles, the diffusion of the reactants to these sites is of paramount importance, if a high degree of modification has to be achieved.

Gel polymers are found to be slightly less reactive than linear polymers as the reactions will be limited by diffusion of the reagent within the resin pores. Resins with low crosslink density will be suitable as increased swelling will result in higher accessibility through enhanced diffusion properties. Swellable polymers are found to offer advantage of achieving higher loading capacity during functionalisation. Reactivity of the functional groups may be low when it is directly attached to the main chain, as that may result in steric hindrance by the polymer backbone and neighbouring side groups.

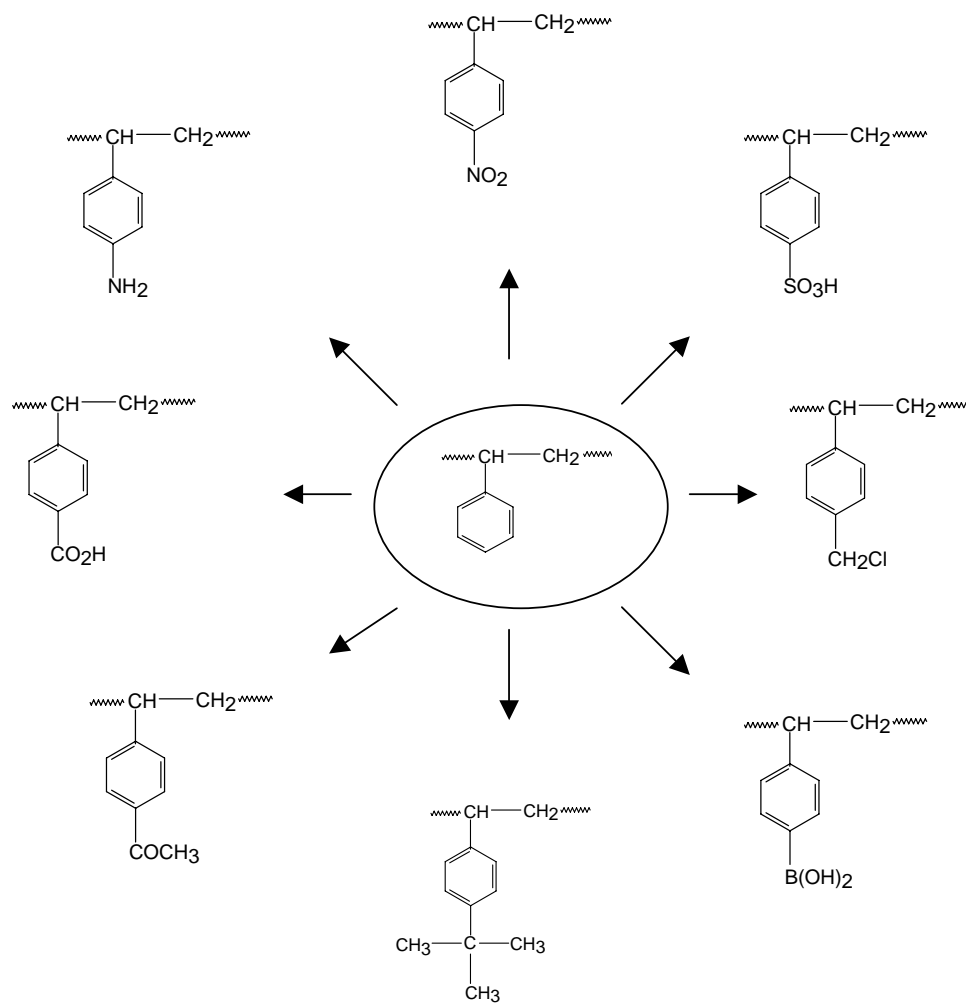


Figure 1.4: Modification of Polystyrene or cross-linked polystyrene with different functionalities

1.9 Applications of modified polystyrenes

1.9.1 Ion-exchange resin catalysts

Ion-exchange resins have electrically charged sites at which one ion may replace another. The acid and base forms of ion-exchange resins probably represent the earlier catalysts. Virtually all organic synthesis involving catalysts by homogeneous acid or base have been carried out by use of polymeric catalysts. The first commercial ion-exchange resin having bead structure was produced by Rohm and Haas in 1939. It is applied to the separation and purification of medical products and foods, the production of ultra pure water, purification of boiler water at power plants, and the production of chemical compounds with solid acid catalysts.

The capacity of an ion-exchange resin is defined as the total number of chemical equivalents available for exchange per some unit weight or unit volume of resin.¹⁰⁸ The capacity may be expressed in terms of milliequivalents per dry gram of resin or in terms of milliequivalents per dry or wet gram of resin. Polymers with very high capacity only react partially due to lack of accessibility of functional sites. The size of molecules attached to the polymer may increase during a synthesis and variation in polarity of the medium. The accessibility of the polymer substrate bond may become restricted and result in partial or difficult cleavage when synthesis is complete. Synthetic ion-exchange resins are usually cast as porous beads with considerable external and pore surface where ions can be attached. Adsorption plays a role in materials having high surface area. If a substance is adsorbed on to an ion-exchange resin, no ion is liberated. Testing for ions in the effluent will distinguish between removal by adsorption and removal by ion-exchange. Both mechanisms may be significant in certain cases, and mass balances comparing moles removed with moles of ions liberated will quantify the amounts of adsorption and ion-exchange.

1.9.2 Catalysis

The catalysis by solid support matrix is advantageous over homogeneous acid catalysts in many aspects. Solid-supported reagents also enable the use of excess reagents to drive the reaction to completion, without complicating the work-up procedure. Simple filtration, washing and solvent removal is all that is required to work-up the reactions, which is particularly beneficial to high through-put synthesis.¹⁰⁹ Attaching toxic or hazardous compounds to a solid support reduces the risks associated with the reagent. Simple filtration of solid supported catalysts also means that the catalyst can be recovered, regenerated and reused, reducing the cost associated with these reagents. The simple work up techniques associated with polymer-supported reagents and scavengers also make the use of automation a real possibility. The matrix effects allow reaction selectivity and reduce or eliminate undesirable side reactions. They also offer possibility of developing non-corrosive processes due to their ecofriendly nature. These catalysts can be used over a prolonged period. The accessibility of catalytic sites depend on the porous structures and swelling properties of the copolymers.¹¹⁰ In conventional industrial process involving homogeneous acids, utilisation of heterogeneous acid catalyst is gaining importance due as green alternatives.¹¹¹⁻¹¹⁴

Organic esters are most frequently used in perfumery and flavor chemicals. They fall in a wide category from aliphatic to aromatic substitution.¹¹⁵ Acylation and esterification reactions are commercially important with production of few hundreds to few thousand tones per year and are used to make ketones and esters which serve as precursors and additives for a wide variety of perfumes and flavors, pharmaceuticals, agrochemicals and polymers.¹¹⁶ To prepare the esters and ketones, homogeneous catalysts and Lewis acids such as AlCl_3 , BF_3 , ZnCl_2 , TiCl_4 , FeCl_3 , SbF_5 , ZrCl_4 and

Bronstead acids such as HF, H₂SO₄, HCl, H₃PO₄ and p-toluene sulphonic acid and finely divided materials such as tin, manganese, silver, copper, lead are used. Homogeneous catalysts leads to several problems such as corrosion of equipment, hazards of handling of corrosive acids which are not reused, neutralisation of resultant reactive mass, generation of large quantity of dissolved salts, including loss of conversion, yield, and selectivity. The biological oxygen demand (BOD), chemical oxygen demand (COD) and the total dissolved salts, loads on effluent treatment plants becomes enormous.

1.9.3 Imbibing polymers

Polymeric adsorbents are increasingly regarded as alternative to activated carbon due to their regeneration properties and mechanical stability. The functional groups on polymer matrix modify the surface chemistry of the adsorbent allowing specific adsorbent-adsorbate interactions and to improve adsorption behaviour of organic components.¹¹⁷

Imbibing polymers are organic fluid insoluble but swelling polymers.¹¹⁸ Poly(alkyl styrenes), with marginal cross-linking, are imbibing because they absorb fluids more rapidly than other polymers.¹¹⁹⁻¹²⁰ They are used to suck in organic fluids from surfaces like dirt, metals, wood and contaminated water. These are also used to make valves which close when the polymer particles absorb sufficient organic fluid to cause the particles to swell and restrict the flow of the fluid. Imbiber particles provide drift control for packaging, form combustible fuel slurries.

The utility of an imbibing polymer for absorbing a particular organic liquid is indicated by its swelling index. The term swelling index refers to the ratio of volume per unit length of a polymer swollen with organic fluid to its original volume per unit weight before contact of the organic liquid. An equilibrium swelling index can be

readily determined by immersing the polymer in organic liquid until equilibrium between absorption and release of the liquid is established and no further swelling takes place. The volume per unit weight of the polymer at equilibrium is determined and compared with polymer's original volume per unit weight. If the equilibrium swelling index of the polymer particles is greater than 1.2 the polymer particles are useful in imbibing fluid. Imbibing polymer particles should be cross-linked, to an extent sufficient to prevent dissolving in the fluid being imbibed but not enough to inhibit swelling necessary for imbibing.

Equilibrium swelling capacity of ideal polymer networks is determined by three parameters i.e. number of elastically active network chains, parameter of polymer-solvent interaction and so called memory term. All theories for equilibrium swelling consider only three dimensional structures with a low degree of cross-linking. Increase of cross-linking degree results in decrease of swelling ability of gel. The swelling of the polymeric material, which is determined by balance of interaction of polymeric chains and solvent, depends on chemical affinity.

1.10 Photoresists

The patterns of conductors on circuit boards and the tiny transistors on microchips are "printed" using photoresists. Technology of photoresists has been refined to the point where many millions of micron-sized devices can be fabricated simultaneously and reliably on silicon substrates. Micro fabrication the generation of small structures is essential to modern science and technology. Miniaturisation and integration of range of devices have resulted in the probability, reduction in time, cost and reagents. The most dynamical developments of microelectronics is based on utilisation of radiation cross-linked negative photoresists and radiation degradable positive photoresist polymers. Thick photoresist lithography is one of the most

important techniques for micro-electro-mechanical systems (MEMS). Photolithography is used in printing industry, photo machining of fine parts, and more recently to delineate the tiny features that make up LSI, VLSI, ULSI, the modern integrated circuits.¹²¹ The polymeric materials, used as radiation sensitive resist films, must be designed to exhibit specific requirements of lithographic technology and device process. The properties required for high resolution imaging systems are: (1) sensitivity (2) contrast (3) resolution (4) etching resistance (5) shelf life and (6) purity.

Resolution is defined as how fine a line the resist can reproduce from a real image and it is determined by contrast, thickness, proximity effects, swelling and contraction after development. Contrast is the ability of the resist to distinguish between light and dark regions and it is measured by exposing the resist of given thickness to varying radiation dose and measuring the dissolution rate. The steps involved in the photolithographic process are wafer cleaning, barrier layer formation, photoresist application, soft baking, mask alignment, exposure and development, and hard-baking.

All commercial photolithographic devices currently used are in the 193-436 nm (ultra-violet) region. Conventional G-line (436 nm) lithography employing 0.4 μm high numerical aperture reduction lenses is used in devices that feature 0.8 μm regime. I-line (365 nm) lenses are available that feature in 0.5 μm regime. Deep UV (230-260 nm) systems have become effectively competent with I-line technology for features of 0.4 μm level.¹²² The latest technology is to develop resist materials for far ultra-violet region, having higher integration and higher operation speed. Particularly, device generations will be produced with lithography systems employing shorter wavelengths using KrF excimer laser light (248 nm), ArF excimer laser light (193

nm) and F₂ excimer laser light (157nm) are employed to produce patterns of 0.3 μm size or less.

1.10.1 Classification of photoresists

Photoresists are classified in two types, 1) positive and 2) negative.

1.10.1.1 Positive resists

The exposed regions when removed by the developer (i.e., exposure makes the photoresist more soluble), the process is called *positive tone*. In these resists, exposure to the UV light changes the chemical structure of the resist so that it becomes more soluble in the developer, leaving behind an exact copy of the pattern that remains on the wafer. The major component is a base soluble resin that is rendered insoluble by the addition of a hydrophobic radiation sensitive material. Upon irradiation the hydrophobic entity may be either converted to an alkali soluble species or entirely removed, allowing removal of irradiated portions of the resist by an alkaline developer solution.

1.10.1.2 Negative resists

The process, in which the irradiated regions become insoluble in developer leaving it behind (i.e., irradiation makes the photoresist less soluble), is called *negative tone*. The image is developed by removal of the unirradiated, uncross-linked polymer chains which are swollen and dissolved on treatment by the solvent. Therefore, the negative resist remains on the surface wherever it is exposed, and the developer solution removes only the unexposed portions. Masks used for negative photoresists, therefore, carry the inverse (or photographic "negative") of the pattern to be transferred.

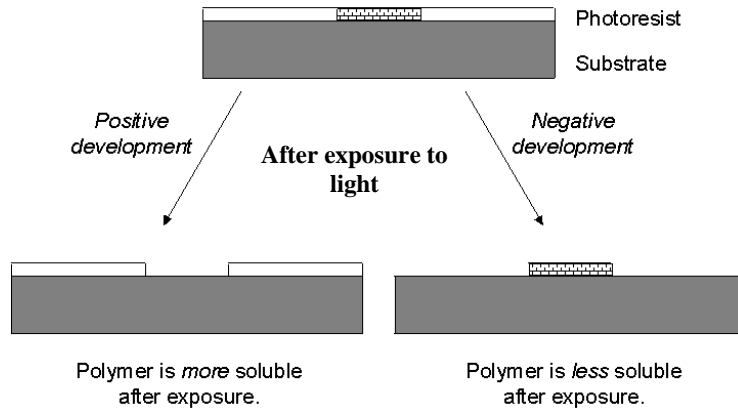


Figure 1.5: Pattern differences in positive and negative resists

Photoresist materials can also be classified as:

- a) One component system: Polymer that undergoes photochemical reaction eg. polystyrene systems, poly(methyl methacrylate).
- b) Two component system: Sensitiser molecule (monomeric) is dissolved in an inert polymeric matrix eg. cis-1,4-poly isoprene and bisazide, acid catalysed phenol-formaldehyde and diazoquinones.

1.10.2 Composition and working of Photoresists

A positive photoresist consists of a diazonaphthoquinone, known as photoactive compound (PAC), a resin that bonds with the unreacted photoacid generator to form a chemically and physically resistive coating and a solvent that keeps the formulation in liquid form until it is applied on to the resist.¹²³⁻¹²⁹ In a conventional positive resist, novolak resin is formulated with a sensitiser/photoactive compound, naphthoquinone diazide sulphonate ester (of trihydroxy benzophenone, novolak itself or a phenolic trimer), which inhibits dissolution.¹³⁰⁻¹³² A substrate is coated with the resist and solvent is driven off by a bake. A patterned glass photomask is aligned over the resist coated substrate and it is exposed to a 350-450 nm light. The PAC in the exposed regions forms indene carboxylic acid that is dissolved by a strong

base. Development is the final important stage of optical lithography. A subsequent bake at a controlled temperature and for a controlled length of time accelerates a chemical reaction that changes the rate at which the photoresist coating dissolves in developer, usually an aqueous solution of tetramethylammonium hydroxide. The exposed portion of the photoresist coating is removed by dissolution in the developer.¹³³ The wafer surface is then subjected to an etch (e.g. a fluorocarbon plasma) that removes silicon dioxide not protected by the photoresist coating. The coating must resist the etch long enough to enable complete removal of the unprotected silicon dioxide. The photoresist is then removed to yield a pattern of silicon dioxide on a silicon surface.

Transfer of an image from a mask to the photoresist coating depends ultimately on a difference in the dissolution rates of exposed and unexposed resist, which is controlled by the type of photoactive component and the novolak resin. The dissolution and molecular mechanism of a novolak resin coating by aqueous hydroxide has been described by physical models.¹³⁴⁻¹³⁵

1.10.3 Sensitisers for photoresist

Naphthoquinone diazide (DNQ) compounds, widely used in photoactive compounds (PAC) for photoresist in manufacturing process of semi-conductor devices and high density printed circuit boards for a period over last 25 years, are based on 1,2-naphthoquinone diazide-5-sulphonic esters and 1,2-naphthoquinone diazide-4 sulphonic esters.¹³⁶⁻¹³⁷ Upon exposure to the proper dose and type of radiation, the naphthoquinone diazide rearranges to form an indene carboxylic acid, which accelerates dissolution of the exposed portion of the coating. The difference in dissolution rates is maximised when the novolak resin alone dissolves very slowly in the developer, in the order of 10 Å/sec. DNQ compounds are known to be

photochemically or thermally converted to ketenes via Wolff rearrangement. Ketenes can readily react with water, alcohols and carboxylic acids to yield corresponding products. 1,2-Naphthoquinone diazide-5-sulphonic esters react with water in ambient condition under ultraviolet radiation and yield corresponding indene carboxylic acid derivatives. Therefore, the exposed esters increase their solubility to alkaline solutions. On the other hand esters inhibit their solubility of phenolic resins when they come in strong contact with strong alkaline solution like aqueous tetramethyl ammonium hydroxide.

1.10.4 Polymers used in photoresists

1.10.4.1 Bisazide cross-linking

The earliest photoresists were based on the photocross-linking of "cyclised rubber" using an additive that contained two azide groups. Cyclised rubber is obtained by acid treatment, a process which leads to some ring formation in the polymer, and stiffens it, thereby raising its T_g . When the bis-azide is photolysed, it extrudes nitrogen and produces two very reactive nitrene moieties. The nitrenes can form bonds with the cyclised rubber in a variety of ways, the most common of which is aziridine ring formation, as shown in Figure 1.6. Naturally, these reactions lead to cross-linking of the polymer, and it becomes less soluble, ready for negative development.

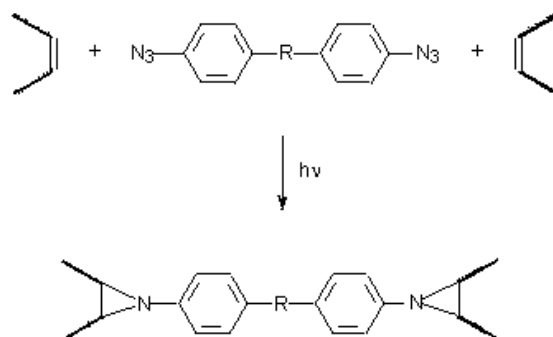


Figure 1.6: Photocross-linking of bisazide polymers

1.10.4.2 Poly(vinyl cinnamate)

Another interesting negative tone photoresist is poly(vinyl cinnamate). This polymer is synthesised by the partial esterification of poly(vinyl alcohol), which itself is made by a polymer modification reaction, hydrolysis of poly(vinyl acetate).

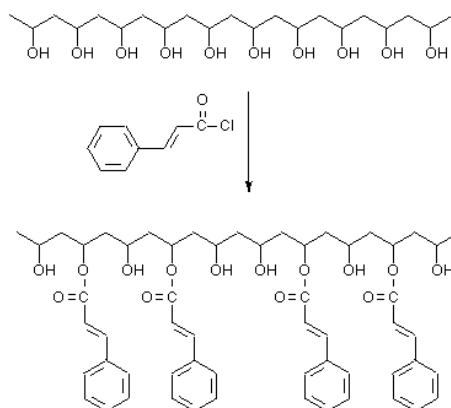


Figure 1.7: Poly(vinyl cinnamate)

The cinnamate groups undergo [2+2] cycloaddition when irradiated, leading to a cross-linked polymer suitable as a negative tone photoresist (Figure 1.8).

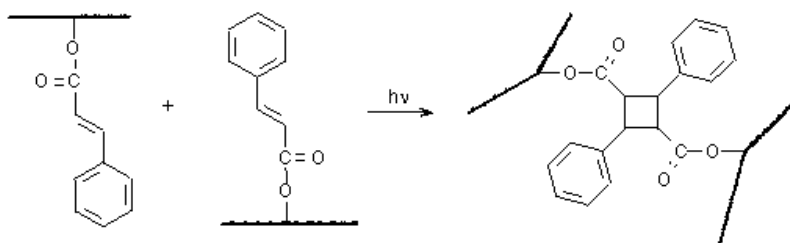


Figure 1.8: Photocross-linking of poly(vinyl cinnamate)

1.10.4.3 Novolaks

Novolak resins are the primary solid components of G and I line photoresists used in integrated circuits¹³⁸ and printing photoresists. Novolak resins are still used because they have the right blend of properties for this demanding task: they form defect-free films, they dissolve in high-pH aqueous solutions at controllable rates, they react or interact with other materials in ways that affect the dissolution rates of the novolak resins, they are resistant to etches commonly used in the fabrication of integrated circuits, and they perform reliably. Novolak resin structure and composition can be tailored so as to dissolve in an aqueous base at a suitable enough rate, to resolve dimensions of less than half a micron reproducibly on the basis of this differential solubility. Novolak resins are formed by acid or metal ion catalysed condensation of phenols with formaldehydes. Acid catalysts are the preferred choice for photoresist applications due to concern of metal contamination in semiconductor manufacturing. The aromatic phenol ring has three positions, two ortho and one para, that are activated toward electrophilic substitution by formaldehyde. The mixtures of meta and para cresol are used instead of phenol for the production of resist grade novolaks. The molecular weight of novolaks used for resist production are relatively small and the number average molecular weight (M_n) of the resist grade novolaks is generally between 1000 and 3000 that corresponds to between 8 to 20 repeat units

while the weight average molecular weight can be as large as 20,000. The polymer structure can have different types of polymer linkages during novolak synthesis that strongly affects the properties of the formulated resist. The four factors concerning the structure of the novolak resin, that influence the performance of DNQ-novolak resist are: 1) molecular weight of the resin, 2) polydispersity of the resin, 3) methylene linkage position, 4) ratio of m,p-cresol precursors.

Being phenols, these polymers are soluble in aqueous base, although the rate of dissolution is quite slow. In the presence of photosensitive additives, such as naphthoquinone diazide sulphonate esters, the dissolution process can be greatly decreased. Other additives, such as low molar mass phenolic dimers/trimers, are used to increase speed of dissolution (speed enhancers), especially after exposure to UV changes the naphthoquinone diazide sulphonates to indene carboxylic acids.

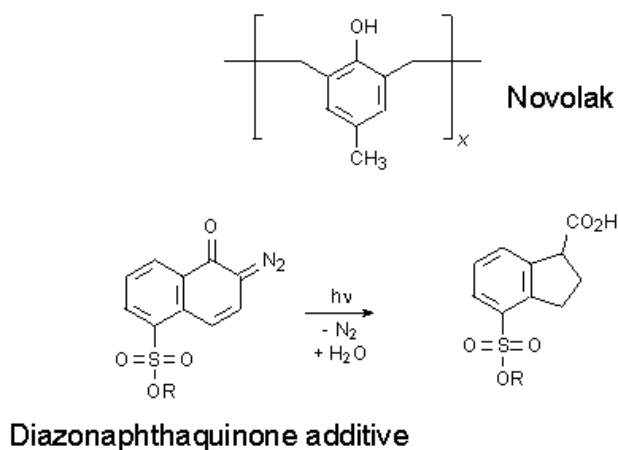


Figure 1.9: Polymer and sensitisers for G line photoresist

1.10.5 Chemically amplified resists (for 248 and 193 nm)

Devices with several million transistor cells are fabricated with minimum features of 0.5 μm or smaller, using conventional photolithography, employing 350-450 nm light. Incremental improvements in tool design and performance have allowed their continued use to produce small features, due to improvements in processing. The basic resist materials have remained largely unchanged for two decades as the same positive photoresist consisting of a photoactive compound that belongs to the diazonaphthoquinone chemical family and a novolak resin has been in use since the mid-1970's. The cost of new technology, the development and implementation of new hardware and resist materials, is the driving force pushing photolithography to its absolute resolution limit and extending its commercial viability. Conventional photoresists are not appropriate for use with the new lithographic technologies such as shorter wavelength (220-280 nm) photolithography, scanning or projection electron beam, 1:1 proximity X-ray or ion-beam lithography. As the exposure wavelength of modern microlithographic tools continues to decrease, chemically amplified photoresists have become important. Chemical amplification serves to increase the sensitivity of photoresists by creating a photogenerated catalyst, typically a strong acid.¹³⁹⁻¹⁴⁰

The amount of light or dosage required to produce sufficient enough chemical change for development could be reduced and the whole process could be carried out faster. This has resulted in the invention of the concept of *chemically amplified photoresists*. In this system, exposure to light creates an acid, *catalyst* for another chemical reaction. The second chemical reaction is responsible for the change in solubility needed for development. The essence of chemically amplified photoresists

is that one photon can lead to many secondary reactions; therefore the available light is used very efficiently (Quantum yield is much greater than 1).

The photo-generation of acidic species catalyses many subsequent chemical events such as deblocking of a protective group or cross-linking of a matrix resin. The overall quantum efficiency of such reactions is thus effectively much higher than that for initial acid generation. A chemically amplified resist is generally formulated with three or more elements; a matrix polymer, a photoacid generator, and a moiety capable of effecting differential solubility between the exposed and unexposed regions of the film in a developer, either through a cross-linking reaction or other molecular transformation.¹⁴¹ These elements may be either discrete molecular entities that are formulated into a multicomponent resist system or elements of a single polymer. The matrix polymer must: (i) exhibit solubility in solvents that allow the coating of uniform, defect free, thin films, (ii) be sufficiently thermally stable to withstand temperatures and conditions used with standard device processes, (iii) exhibit no flow during pattern transfer of the resist image into the device substrate, (iv) possess a reactive functionality that will allow a change in solubility after irradiation and PEB, and (v) have absorption characteristics that will permit uniform imaging through the thickness of a resist film. In general, materials that exhibit a thermal stability of $>140^{\circ}\text{C}$, and an absorption of less than 0.35 mm^{-1} at the wavelength of interest are desired.

The photoacid generator should have the following properties:

- (i) It should have sufficient radiation sensitivity to ensure adequate acid generation for good resist sensitivity (for photochemical reactions a quantum yield of >0.1 is desirable),

- (ii) Be free of metallic elements such as antimony or arsenic that are device contaminants,
- (iii) Be fully compatible with the matrix resin to eliminate the possibility of phase separation,
- (iv) Be stable to at least 175°C to avoid premature thermal generation of acid; be nonvolatile and possess functionalities that will allow a change in solubility after irradiation,
- (v) Be sufficiently acidic to effect the desired post-exposure reaction with high yield and
- (vi) Have absorbance characteristics that are commensurate with uniform absorption of light through the thickness of the resist film.

1.10.5.1 Photoacid generators

Photoacid generators are usually in the form of iodonium ($R_2I^+ X^-$) or sulphonium ($R_3S^+ X^-$) salts. These compounds decompose up on light exposure to provide a complicated mixture of products, chief among which is the acid, HX. On irradiation at wavelengths in the range of 200-300 nm, these onium salts undergo irreversible photolysis with rupture of a carbon-iodine or carbon-sulphur bond. Abstraction of a hydrogen atom from a surrounding “solvent” results in the formation of a protic acid. Onium salts are thermally stable (typically $>150^\circ\text{C}$), allow photogeneration of a wide variety of acids (including such strong inorganic acids as hexafluoroarsenic and hexafluoroantimonic acids and the strong organic acid, triflic acid), and may be structurally modified to alter their spectral absorption characteristics. Many systems described in the literature involve the generation of sulphonic acids that are strong organic acids with reasonably low nucleophilicity.¹⁴²

The use of inorganic onium salt as acid generator is not entirely desirable. There is possibility of contamination of device being processed by inorganic species as ionic acid generators have the tendency to phase separate from the acid sensitive resin. Organic acid generators have reasonable sensitivity to deep ultraviolet light; therefore their use in photoresists are desirable.¹⁴³ The ideal ones, based on 2-nitrobenzyl esters, photochemically generate acid with quantum efficiencies in a polymer matrix in the range of 0.05-0.25.¹⁴⁴ The mechanism involves an intramolecular o-nitrobenzyl rearrangement. Compounds based on nitro benzyl configuration employing an α substituent having high bulk, steric characteristics and electron drawing ability.¹⁴⁵ The nitrobenzyl sulphonates are readily designed to be thermally stable, with typical stabilities approaching 200°C. Additionally, the nonionic nature of these systems allows miscibility with a wide range of polymer materials.

1.10.5.2 Polymers for chemically amplified resists

Technology seems to have centered around the pioneering work of Ito et al. at IBM relating to the development of chemically amplified resists based on deprotection mechanisms of poly(4-tert-butoxycarbonyloxy styrene).¹⁴⁶ (PTBS) in which the thermally stable, acid-labile tert-butoxycarbonyl group is used to mask the hydroxyl functionality of poly(vinyl phenol). Irradiation of PTBS films containing small amounts of an onium salt, such as diphenyliodonium hexafluoroarsenate with UV light, liberates an acid species that up on subsequent baking catalyses cleavage of the protecting group to generate poly(p-hydroxy styrene). Substituted poly(hydroxy styrenes) are also used in chemically amplified systems.¹⁴⁷ Loss of the tert-butoxycarbonyloxy group results in a large polarity change in the exposed areas of the film. These resists are sensitive to deep UV and electron-beam irradiation and may be

sensitised to longer wavelengths through the addition of appropriate mid- and near-UV dyes. PTBS-onium salt resists have also been successfully used in the manufacture of integrated devices.

Although a number of other systems have been identified, the technology has centered around many synthetic strategies built around the polystyrene based system.¹⁴⁸ The most well known system of this kind is based on tert-butoxy carbonyloxy styrene polymer. Poly(tert-butoxy carbonyloxy styrene) (t-Boc) can also work as a positive tone photoresist by using another developing solvent. The unmodified, original polymer is soluble in nonpolar solvents, for example anisole, and can be selectively washed away to leave behind the more polar modified polymer, which is insoluble in anisole. However, the negative mode is more often used because of the low toxicity of the aqueous base developer. This acid then catalyses the deprotection reaction of many t-Boc groups. The protecting groups decompose to carbon dioxide and isobutylene, both gases that leave the coating. The deprotection reveals phenolic moieties, which are soluble in aqueous base. Therefore, this material can function as a *negative tone photoresist*.

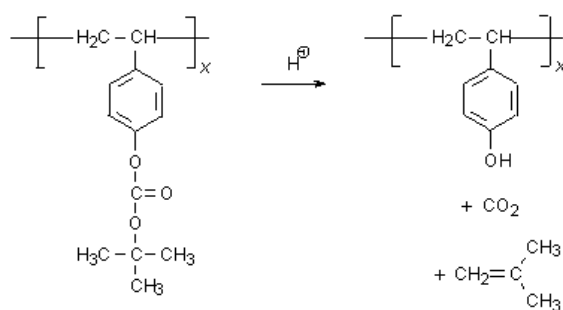


Figure 1.10: Acid catalysed deprotection for polarity change (t-BOC resist); cleavage of pendant group to convert lipophilic polymer to hydrophilic polymer

1.11 Present Work

The present work deals with synthesis of polymers having styrene moieties by different methods such as suspension polymerisation and high internal phase emulsion. The thesis comprises of 6 chapters. This is the first chapter. The second chapter deals with materials and characterisation details of the polymers synthesised.

The third chapter consists of details of synthesis of beaded highly cross-linked poly(styrene-divinyl benzene) by using different type of porogens different from conventional porogens. The effect of synthesis parameters on pore volume, pore size distribution and surface area of polymers were studied. A comparison between the properties of polymers synthesised using surfactants and conventional suspension polymerisation was also studied.

The fourth chapter comprises of synthesis strategies of beaded low cross-linked polymers to be investigated for imbibing. Beaded cross-linked poly(styrene-divinyl benzene) were synthesised by preparing an emulsion of monomer, surfactant and water before adding it to outer suspension. The effect of variation in synthesis strategy on the pore volume, pore size distribution and surface area of the polymers were studied. The polymers were then tested for its solvent uptake capacity.

The fifth chapter comprises of synthesis of highly cross-linked poly(styrene-divinyl benzene) monoliths using high internal phase emulsion technique. The reactions were conducted by variation in reaction parameters and their effect on the porous properties of the polymers were studied. The polymers obtained by this method have an interconnecting pore structure. The polymers were post modified to introduce sulphonic acid groups. The modified polymers were tested as heterogeneous acid catalysts in esterification reactions. The effect of different initiators, thermal and

redox, was investigated. The equilibrium solvent uptake of the polymers was determined.

The sixth chapter comprises of synthesis of linear polystyrenes for evaluation as photoresist. The polymers were synthesised having molecular weight of 5000-10000 and post modified to introduce acetyl, acetoxy and hydroxyl groups in the polymer. The modified polymers were characterised by infra-red spectroscopy. Different types of sensitisers were synthesised and the photoresist formulations were made and tested for pattern development. The hydroxy modified styrene systems were evaluated as materials that can be designed to display a strongly non-linear response in the dissolution rate versus exposure and provides good film forming characteristics, thermal stability and high etch resistance.

1.12 References

- 1 E. R. Moore, "*Encyclopedia of Polymer Science and Engineering*," **16**, John Wiley and Sons New York (1989).
- 2 F. W. Billmeyer, "*Text Book of Polymer Chemistry*," John Wiley and Sons, New York (1957).
- 3 J. R. Fried, "*Polymer Science and Technology*", Prentice-Hall of India, New Delhi (2000).
- 4 S. Jegasothy, N.K.H. Slater, C. Denecker, D.C. Sherrington, Z. Leic and A. J. Sutherland, *Chem. Eng. J.*, **105**,1, (2004).
- 5 P. Hodge, *Chem. Soc. Rev.*, **26**, 417 (1997).
- 6 A. Guyot and M. Bartholin, *Prog. Polym. Sci.*, **8**, 277 (1982).
- 7 F. Hoffman and K. Delbruch, Farbenfabriken, Patent (Ger.) No. 250690, Bayer, Germany (1909).
- 8 W. Bauer and H. Lauth, Darmstadt, Patent (Ger.) No. 656,134, Rohm and Haas (1931).

- 9 H-P. Hentze and M. Antonietti, *Reviews in Molecular Biotechnology*, **90**, 27 (2002).
- 10 J. R. Millar, D. G. Smith, W. E. Marr, and T. R. E. Kressman, *J. Chem. Soc.*, 218 (1963).
- 11 Y-D. Jo, K-S. Park, J-H. Ahn and S-K. Ihm, *Eur. Polym. J.*, **32**, 967 (1996).
- 12 R. Drake, D. C. Sherrington and S. J. Thomson, *J. Chem. Soc. Perkin. Trans.:***1**, 1523 (2002).
- 13 K. M. Dooley, J. A. Williams, B. C. Gates and R. L. Albright, *J. Catalysis*, **74**, 361 (1982).
- 14 K. W. Pepper, H. M. Paisley and M. A. Young, *J. Chem. Soc.*, 4097 (1953).
- 15 N. Jayaswal, S. Sinha and A. J. Kumar, *J. Appl. Polym. Sci.*, **79**, 1735 (2001).
- 16 M. Ahmed, M. A. Malik, S. Pervez, M. Raffiq, *Eur. Polym. J.*, **40**,1609, (2004).
- 17 J. R. Millar, *J. Chem. Soc.*, 1311 (1960).
- 18 J. S. Fritz and J. N. Story, *J. Chromatography*, **90**, 267 (1974).
- 19 M. Hart, G. Fuller, D. R. Brown, C. Park, M. A. Keane and J. A. Dale, *Catal. Lett.*, **72**, 135 (2001).
- 20 M. Struck and H. Widdecke, *Die Angew. Macromol. Chem.*, **235**, 131 (1996).
- 21 M. E. Leon-Gonzalez and L. V. Peres-Arribas, *J. Chromatography A*, **3**, 902 (2000).
- 22 J. Seidl, J. Malinsky, K. Dušek, and W. Heitz, *Adv. Polym. Sci*, **5**, 113, (1967).
- 23 M. Lehn in "Supramolecular Chemistry", Wiley-VCH, Weinheim, (1995).
- 24 V. R. Gowarikar, N. V. Viswanathan and J. Sreedhar, "Polymer Science", New Age International (P) Limited, Publishers, New Delhi, (1986).
- 25 E. Farber in "Encyclopedia of Polymer Science and Technology" (H. Mark, N. G. Gaylord and N. M. Bikales, eds.), Vol. **13**, Wiley Inter Science, London, pp. 552, (1970).
- 26 M. Munzer and E. Trommsdorff in "Polymerisation Processes", C. E Schildknecht and I. Skeist, ed.), High Polymers, **29**, Wiley Inter Science, London, pp. 106, (1977).
- 27 L. Jervis in "Synthesis and Separations using Functional Polymers", (D. C. Sherrington and P. Hodge, eds.), John Wiley and Sons, Chichester, pp. 265,

- (1988).
- 28 P. D. G. Dean, W. S. Johnson and F. A. Middle (eds.), "Affinity Chromatography: A Practical Approach", IRL Press, Oxford (1985).
 - 29 R. B. Merrifield, *Macromol. Chem. Macromol. Symp.*, **19**, 31 (1988).
 - 30 A. Warshawsky in "Ion-Exchange and Sorption Processes in Hydrometallurgy", (M. Streat and D. Naden, eds.), Wiley, New York, pp. 127 (1987).
 - 31 W. T. Ford (ed.), "Polymeric Reagents and Catalysis", American Chemical Society, Washington, DC (1986).
 - 32 P. J. Dowding and B. Vincent, *Colloids and Surfaces A: Physicochemical and Eng. Aspects*, **161**, 259 (2000).
 - 33 R. Arshady and A. Ledwith, *Reactive Polymer, Ion exchangers, Sorbents*, **1**, 159 (1983).
 - 34 I. C. Poinescu and C. D. Vlad, *Eur. Polym. J.* **33**, 1515, (1997).
 - 35 K. Dusek, *J. Polym. Sci. B*, **3**, 209 (1965).
 - 36 R. Kunin, E. F. Meitzner, N. J. Bortnick, *J. Am. Chem. Soc.*, **84**, 305 (1962).
 - 37 K. A. Kun, *J. Polym. Sci. A*, **3**, 1833 (1965).
 - 38 C. Luca, V. Neagu, B. C. Simionescu, I. Rabia, J. Zerouk and Z. Bencheikh, *Reactive & Functional Polymers*, **36**, 79, (1998).
 - 39 S. Hashim and B.W. Brooks, *Chem. Eng. Sci.*, **59**, 2321 (2004).
 - 40 J. Alvarez, J. Alvarez and M. Hernandez, *Chem. Eng. Sci.*, **49**, 99, (1994).
 - 41 M. Luther and C. Heuck, U.S. Patent 1,864,078 assigned to I.G. Farbenindustrie A.G., (1932).
 - 42 E. Ruckenstein and J. S. Park, *Polymer*, **33**, 2, 405 (1992).
 - 43 Q. Wang, S. Fu and T. Yu, *Prog. Polym. Sci.*, **19**, 703 (1994).
 - 44 A. E. Alexander and D. H. Napper, *Prog. Polym. Sci.*, **3**, 145 (1971).
 - 45 G. Odian in "Principles of Polymerisation", John Wiley and Sons, New York (1981).

- 46 S. R. Sandler and W. Karo, “*Polymer Synthesis*”, **1**, Academic Press, Inc., New York, 10003.
- 47 S.Y. Lin, C. S. Chern, T. J. Hsu, C. T. Hsu and I. Capek, *Polymer*, **42** 1481 (2001).
- 48 W. D. Harkins, *J. Am. Chem. Soc.*, **69**, 1428 (1947).
- 49 C.S. Chern, *Prog. Polym. Sci.* **31**, 443, (2006).
- 50 W. V. Smith, *J. Am. Chem. Soc.*, **70**, 3695 (1948).
- 51 W. V. Smith, *J. Am. Chem. Soc.*, **71**, 4077 (1949).
- 52 R. H. Ottewill, “Surfactants”, Edited by T. F. Tadros, Chapter 1, Academic Press Inc., London (1984).
- 53 A. R. M. Azad, J. Ugelstad, R. M. Fitch and F. K. Hansen in I. Piirma, J. L. Gardon, ACS Symposium Series **24**, American Chemical Society, Washington D. C., (1976).
- 54 N. R. Cameron and D. C. Sherrington, *Adv. Polym. Sci.*, **126**, 165 (1996).
- 55 J. Kiefer, J. G. Hilborn and J. L. Hedrick, *Polymer*, **37**, 5715 (1996).
- 56 N. R. Cameron and D. C. Sherrington, *Macromolecules*, **30**, 5860 (1997).
- 57 N. R. Cameron and D. C. Sherrington, *J. Mater. Chem.*, **7**, 2209 (1997).
- 58 H. Bartl and W. Bonin, *Makromol. Chem.*, **66**, 151 (1963).
- 59 H. Bartl and W. Bonin, *Makromol. Chem.*, **57**, 74 (1962).
- 60 L. Nai-Hong and J. R. Benson, US Patent No. 5,583,162, Assigned to Biopore Corporation, Los Gatos, California (1996).
- 61 D. Barby and Z. Haq, Eur. Pat. Appl. EP 60138 (1982).
- 62 M. Kempe, and G. Barany, *J. Am. Chem. Soc.*, **118**, 7083 (1996).
- 63 P.W. Small and D. C. Sherrington, *J. Chem. Soc., Chem. Commun.*, 1589 (1989).
- 64 H. F. M. Schoo, G. Challa, B. Rowatt and D. C. Sherrington, *React. Polym.*, **16**, 125 (1992).
- 65 E. Ruckenstein and L. Hong, *Chem. Mater.*, **4**, 122 (1992).
- 66 M. Ottens, G. Leene, A. A. C. M. Beenackers, N. Cameron, and D. C. Sherrington, *Ind. Eng. Chem. Res.*, **39**, 259 (2000).

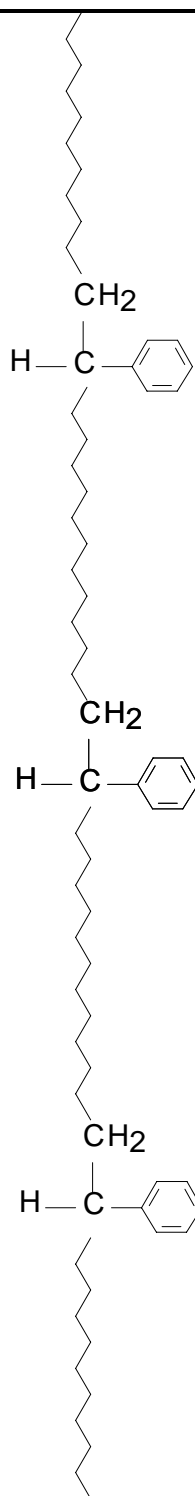
- 67 P. Krajnc, N. Leber, J. F. Brown and N. R. Cameron, *Reactive & Functional Polymers*, **66**, 81 (2006).
- 68 Y. Yin, Y. Lu, B. Gates, and Y. Xia, *J. Am. Chem. Soc.*, **123**, 8718 (2001).
- 69 Yi-Yan Yang, Tai-Shung Chung, Xin-Lai Bai and Woon-Khiong Chan, *Chem. Eng. Sci.*, **55**, 2223 (2000).
- 70 K. J. Lissant, M. J. Schick and F. M. Fowkes, “*Emulsions and Emulsion Technology*”, Part 2, Marcel Dekker, New York (1974).
- 71 C. H. Villa, L.B. Lawson, Yimin Li and K. D. Papadopoulos, *Langmuir*, **19**, 244 (2003).
- 72 K. Westesen, *Colloid Polym. Sci.*, **278**, 608 (2000).
- 73 A. Benichou, A. Aserin and N. Garti, *Advances in Colloid and Interface Science*, **108-109**, 29, (2004).
- 74 M. Lee, S. Oh, S. Moon, and S. Bae, *J. Colloid Interface Sci.*, **240**, 83 (2001).
- 75 P. Hainey, I. M. Huxham, B. Rowatt, D.C. Sherrington and L. Tetley, *Macromolecules* **24**, 117 (1991).
- 76 R. Butler, C. M. Davies and A. I. Cooper, *Adv. Mater*, **13**, 1459 (2001).
- 77 A. Barbetta and N. R. Cameron, *Macromolecules*, **37**, 3188, (2004).
- 78 M. Ahmed, M. A. Arif Malik, S. Pervez and M. Raffiq, *Eur. Polym. J.* **40**, 1609 (2004).
- 79 L. Trojer, G. Stecher, I. Feuerstein, S. Lubbad, and G. K. Bonn, *J. Chromatography A*, 1079, 197 (2005).
- 80 A. Liepold, K. Roos and W. Reschetilowski, *Chem. Eng. Sci.*, **51**, 3007 (1996).
- 81 E. Chin, M. Houlihan, and O. Nalamasu, U.S Patent 6,159,665, Assigned to Lucent Technologies, (2000).
- 82 M. Y. Arýca and G Bayramoglu, *J. Molecular Catalysis B: Enzymatic* **38** 131 (2006).
- 83 D. Horak, J. Labsky, J. Pilar, M. Bleha, Z. Pelzbauer and F. Svec, *Polymer*, **34**, (16), 3481 (1993).

- 84** D. C. Sherrington, *J. Association for Laboratory Automation*, **5**, 75 (2000).
- 85** J. C. Moore. *J. Polym. Sci., A*, 835 (1964).
- 86** A. Revillon, A. Guyot, Q. Yuan, and P. Da Prato. *React. Polym.*, **10**, 11 (1989).
- 87** B. Balakrishnan, S. Hari Babu, and T. K. Shabeer, *J. Polym. Sci., A* **31**, 317 (1993).
- 88** J. Seidl, J. Malinsky, K. Dusek and W. Heitz, *Adv. Polym. Sci.*, **5**, 113 (1967).
- 89** M. D. Price, J. L. Radosevich, M. J. Kurth and N. E. Schore, *Reactive & Functional Polymers*, **55**, 131, (2003).
- 90** R. B. Merrifield, *J. Am. Chem. Soc.*, **85**, 2149 (1963).
- 91** A. Akelah and D. C. Sherrington, *Chem. Rev.*, **81**, 557 (1981).
- 92** I.M. Krishnakumar and B. Mathew, *European Polymer Journal*, **38**, 1745, (2002).
- 93** A. Ajayaghosh and V. N. R. Pillai, *Tetrahedron*, **44**, 6661, (1988).
- 94** K. Haupke and J. Pientka, *J. Chromatography*, **102**, 117 (1974).
- 95** H. Jacobelli, M. Bartholin and A. Guyot, *Angew Makromol. Chem.*, **80**, 31 (1979).
- 96** W. L. Sederal and G. J. De Jong, *J. Appl. Polym. Sci.*, **17**, 2835 (1973).
- 97** D. Rabelo and F. M. B. Coutinho, *Macromol. Symp.*, **84**, 341 (1994).
- 98** K. A. Kun and R. Kunin, *J. Polym. Sci.*, **A1**, 2689 (1968).
- 99** O. Okay, *Prog. Polym. Sci.*, **25**, 711 (2000).
- 100** S. M. Howdle, K. Jerabek, V. Leocorbo, P. C. Marr and D. C. Sherrington, *Polymer*, **41**, 7273 (2000).
- 101** D. C. Sherrington, *Chem. Commun.*, **21**, 2275 (1998).
- 102** A. Akelah and A. Moet, “*Functionalised Polymers and their Applications*”, Chapman and Hall, London (1990).
- 103** G. L. Thomas, C. Bohner, M. Ladlow and D. R. Spring, *Tetrahedron*, **61**, 12153 (2005).
- 104** M. K. Choi, H. S. He and P. H. Toy, *J. Org. Chem.*, **68**, 9831 (2003).
- 105** A. Mercier, H. Deleuze, and O. Mondain-Monval , *Reactive & Functional Polymers*, **46**, 67 (2000).
- 106** J. A. Greig and D. C. Sherrington, *Eur. Polym. J.*, **15**, 867 (1979).
- 107** P. F. Siril, A. D. Davison, J. K. Randhawa and D. R. Brown, *Journal of Molecular Catalysis A: Chemical*, **267**, 72, (2007).

- 108** R. J. Wakeman and J. G. Bhungara, G. Akay, *Chem. Eng. J.*, **70**, 133 (1998).
- 109** S. V. Ley, I. R. Baxendale, R. N. Bream, P. S. Jackson, A. G. Leach, D. A. Longbottom, M. Nesi, J. S. Scott, R. I. Storer and S. J. Taylor, *Perkin Trans. 1*, 3815 (2000).
- 110** F. M. B. Coutinho, R. R. Souza, and A. S. Gomes, *Eur. Polym. J.*, **40**, 1525 (2004).
- 111** G. D. Yadav, N. J. Kirthivasan, *J. Chem. Soc., Chem. Commun.*, 203 (1995).
- 112** G. D. Yadav and V. V. Bokade, *Appl. Catal. A*, **147**, 299 (1996).
- 113** G. D. Yadav and T. S. Thorat, *Ind. Eng. Chem. Res.*, **35**, 721 (1996).
- 114** T. S. Thorat, V. M. Yadav and G. D. Yadav, *Appl. Catal. A*, **90**, 73, (1992).
- 115** G. D. Yadav, and M. S. Krishnan, *Organic Process Research & Development*, **2**, 86 (1998).
- 116** G. D. Yadav and P. Mehta. *Ind. Eng. Chem. Res.*, **33**, 2198 (1994).
- 117** G. C. Sypniewski, U.S Patent 4,895,909, Issued to The Dow Chemical Company, (1999).
- 118** J. Yan, X. Wang, and J. Chen, *J. Appl. Polym. Sci.*, **75**, 536 (2000).
- 119** M. Venhuis, S. Lesage, K. R. Millar and A. S. Crowe, *Water Qual. Res. J. Canada*, **34**, 455 (1992).
- 120** S. P. Roe and D. C. Sherrington, *Reactive Polymers*, **11**, 301 (1989).
- 121** H. Ito, S. Tagawa, and H. Kazayuki, “*Polymeric Materials for Microelectronic Applications Sci. and Technology*”, ACS Symposium Series **579**, American Chemical Society, Washington DC, (1994).
- 122** E. Reichmanis, S. A. MacDonald, and T. Iwayanagi, in “*Polymers in Microlithography Material and Process*”, E. Reichmanis, and L F. Thompson, ACS Symposium Series **412**, American Chemical Society, Washington DC, (1989).
- 123** D. V. Nicolau, T. Taguchi and S. Yoshikawa, *Langmuir*, **14**, 1927 (1998).
- 124** C. G. Willson, in “*Organic Resist Materials-Theory and Chemistry*”, ACS Symp. Ser. **219**, Washington, DC. (1983).
- 125** J. F. Tremblay, *Chemical and Engineering News*, **79** (47), 30 (2001).

- 126** M. McCoy, *Chemical and Engineering News*, **81** (25), 21 (2003).
- 127** L. F. Thomson and L. E. Kirwin, *Ann. Rev. Mat. Sci.*, **6**, 267 (1976).
- 128** O. Sus and J. Liebig, *Ann. Chem.*, **65**, 556 (1944).
- 129** O. Sus, *Ann. Chem.*, **557**, 237 (1944).
- 130** O. Sus, J. Munder and H. Stephan, *Angew. Chem.*, **74**, 985 (1962).
- 131** K. Ichikawa, H. Osaki and H. Inoue, U.S. Patent 5,866,724, Assigned to Sumitomo Chemical Company, Limited, Osaka Japan (1999).
- 132** A. T. Jeffries and D. J. Brzozowy, U.S. Patent 5,346,799, Assigned to OCG Microelectronic Materials, Inc., (1994).
- 133** M. Hagihara, K. Doi, H. Kohara, T. Nakayama, T. Nakajima, U.S. Patent 6,120,969, Assigned to Tokyo Ohka Kogyo Co. Ltd. (2000).
- 134** A. Reiser, J. P. Huang, X. He, T. F. Yeh, S. Jha, H. Y. Shih, M. S. Kim, Y. K. Han and K. Yan, *Eur. Polym. J.*, **38**, 619 (2002).
- 135** Y. K. Han, Z. Yan and A. Reiser, *Macromolecules*, **32**, 8421 (1999).
- 136** W. S. Deforest, “*Photoresist Materials and Process*”, McGraw-Hill Inc., New York (1975).
- 137** H. Shih and A. Reiser, *Macromolecules*, **29**, 2082, (1996).
- 138** G. Pawalowski, R. Dammel, C. R. Lindley, H-J. Merrem, H. Roschert and P. Wilkarm, *Microelectronic Eng.*, **11**, 491 (1990).
- 139** H. Ito, C. G. Willson, J. M. J. Frechet, U.S Patent 4,491,628 Assigned to International Business Machines Corporation (Armonk, NY) (1985).
- 140** J. B. Kim, J. H. Choi, Y. G. Kwon, M. H. Jung and K. H. Chang, *Polymer*, **40**, 1087 (1999).
- 141** J. W. Thackeray, W. James, P. R. Hagerty, R. Peter, J. F. Cameron, W. S. Huang, A. D. Katnani and W. E. Conley, U. S. Patent 6,300,035, Assigned to Shipley Company, L.L.C. (Marlborough, MA); International Business Machines Corporation (Armonk, NY) (2001).
- 142** F. M. Houlihan, E. Reichmanis and L. F. Thompson, U.S Patent 4,996,136 Assigned to AT&T Bell Laboratories (1991).
- 143** E. Chin, M. Houlihan and O. Nalamasu, U. S. Patent 6,159,665, Assigned to Lucent Technologies (2000).

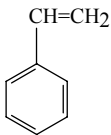
- 144** F. M. Houlihan, A. Shugard, R. Gooden and E. Reichmanis, *Macromolecules*, **21**, 2001 (1988).
- 145** E. Chin, F. M. Houlihan and O. Nalamasu, U. S. Patent 6,159,665, Assigned to Lucent Technologies Inc., Murray Hill, N. J., (2000).
- 146** T. Itani, S. Hashimoto, M. Yamana, N. Samoto, and K. Kasama, *Microelectronic Eng.*, **41/42**, 363 (1998).
- 147** G. Pawlowski, R. Dammel, C. Eckes, C. R. Lindley, W. Meier, K. J. Przybilla, Horst Ridschert, and W. Spiess, *Microelectronic Eng.*, **13**, 29 (1991).
- 148** B. Reck, R. D. Allen, R. J. Twieg, C. G. Willson, S. Matuszczak, H. D. H. Stover, N. H. Li, and J. M. J. Frechet, *Polym. Eng. Sci.*, **24**, 14 (1989).



MATERIALS AND CHARACTERISATION

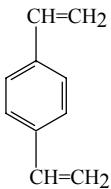
2.1 Materials

2.1.1 Styrene

Empirical formula	C_8H_8
Molecular weight	104.15
Density	0.909 g/cm^3
Chemical structure	

Styrene was obtained from Encore Chemicals Bombay. It was used as a monomer in homo and copolymerisation.

2.1.2 Divinyl benzene

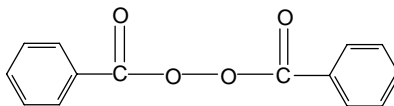
Empirical formula	$C_{10}H_{10}$
Molecular weight	130.19
Density	0.914 g/cm^3
Chemical structure	

Divinyl benzene was obtained as a mixture of the three isomers from Fluka A/G, Switzerland. 55% and 80% are the two technical grades of divinyl benzene available. The isomers present are 4-ethyl vinyl benzene and 3-ethyl vinyl benzene. It was used as cross-linking agent in the preparation of imbibing polymers and polymeric catalyst.

2.1.3 Benzoyl peroxide

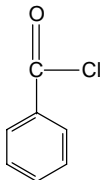
Empirical formula	$C_7H_5O_4$
Molecular weight	242.23

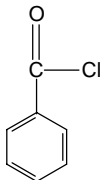
Chemical structure



Benzoyl peroxide was used obtained from Loba Chemie. It was used as an initiator in polymerisations.

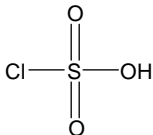
2.1.4 Acetyl chloride

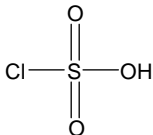
Empirical formula	C_7H_5OCl
Molecular weight	78.50
Density	1.104 g/cm^3
Chemical structure	



Acetyl chloride was purchased from Loba Chemicals and was used in Friedel-Craft's acylation.

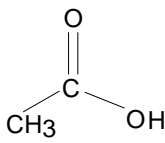
2.1.5 Chlorosulphonic acid

Empirical formula	$ClSO_3H$
Molecular weight	116.52
Density	1.753 g/cm^3
Chemical structure	



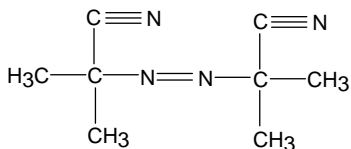
Chlorosulphonic acid was obtained from Spectrochem Chemicals, Mumbai. It was used as a reactant in sulphonation reactions and in conversion of sodium 1,2-naphthoquinone diazide-5-sulphonate.

2.1.6 Acetic acid

Empirical formula	$C_2H_4O_2$
Molecular weight	60.05
Density	1.049 g/cm^3
Chemical structure	

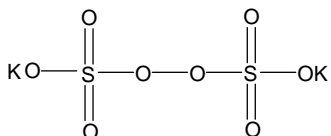
Acetyl chloride was purchased from Loba Chemicals and was used as a solvent in Friedel-Craft's Acylation.

2.1.7 Azo bis(isobutyronitrile)

Empirical formula	$C_8H_{12}N_4$
Molecular weight	164.21
m.p.	103°C
Chemical structure	

Azobis(isobutyronitrile) was obtained from Sisco, Mumbai, India. It was used as an initiator for suspension polymerisation.

2.1.8 Potassium peroxydisulphate

Empirical formula	$K_2S_2O_8$
Molecular weight	270.32
Chemical structure	

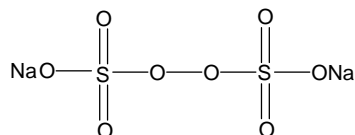
Potassium peroxydisulphate was obtained from Merck Chemicals Limited. It is used as an initiator in polymerisations.

2.1.9 Sodium peroxydisulphate

Empirical formula $\text{Na}_2\text{S}_2\text{O}_8$

Molecular weight 238.09

Chemical structure



Sodium peroxydisulphate was obtained from Merck Chemicals Limited. It is used as an initiator in polymerisations.

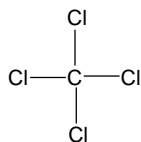
2.1.10 Carbon tetrachloride

Empirical formula CCl_4

Molecular weight 153.82

Density 1.594 g/cm^3

Chemical structure



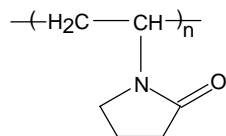
Carbon tetrachloride was obtained from Merck Chemicals. It was used as a chain transfer agent in polymerisations.

2.1.11 Poly(vinyl pyrrolidone)

Empirical formula $(\text{C}_6\text{H}_9\text{NO})_n$

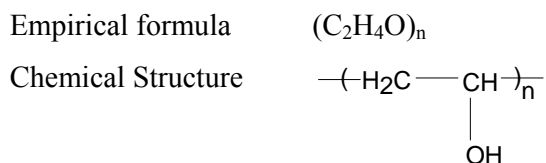
Molecular weight 3,60,000

Chemical Structure



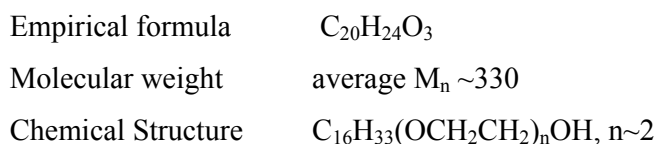
Poly(vinyl pyrrolidone) (PVP), K-90, was obtained from Fluka. It was used as protective colloid in the suspension polymerisation to generate porous polymers.

2.1.12 Poly(vinyl alcohol)



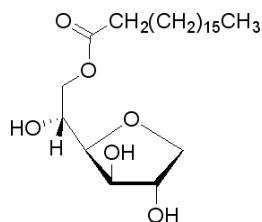
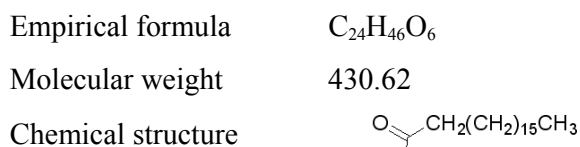
Poly(vinyl alcohol) was obtained from Baker and Baker Chemicals. It was used as protective colloid in the suspension polymerisation to generate porous polymers.

2.1.13 Polyoxyethylene-2-cetyl ether (Brij-52)



Polyoxyethylene-2-cetyl ether (Brij-52) was obtained from Aldrich Chemicals. It was used as a surfactant in emulsion polymerisation.

2.1.14 Sorbitan monostearate (Span 60)



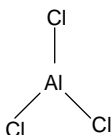
Span series of surfactants was obtained from Loba Chemicals. It was used as a surfactant in emulsion polymerisation.

2.1.15 Aluminium chloride

Empirical formula AlCl_3

Molecular weight 133.34

Chemical structure



Aluminium chloride was obtained from Loba Chemicals. It was used as a catalyst in Friedel-Craft's acylation to attach acetyl moiety to polystyrene backbone.

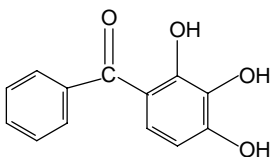
2.1.16 2,3,4-Trihydroxy benzophenone

Empirical formula $\text{C}_{13}\text{H}_{10}\text{O}_4$

Molecular weight 230.22

Melting point $139\text{-}141^\circ\text{C}$

Chemical structure



2,3,4-Trihydroxy benzophenone was obtained from Aldrich Chemicals (USA). It was used in the synthesis of sensitizer in photoresist formulation.

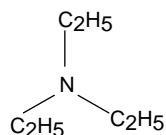
2.1.17 Triethylamine

Empirical formula $\text{C}_6\text{H}_{15}\text{N}$

Molecular weight 101.19

Density 0.726 g/cm^3

Chemical structure



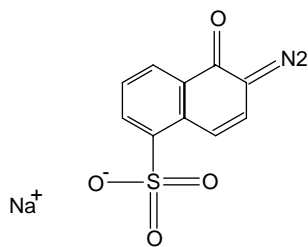
Triethylamine was obtained from Loba Chemicals. It used as a reagent in synthesis of sensitiser.

2.1.18 Sodium 1,2-naphthoquinone diazide-5-sulphonate

Empirical formula $C_{10}H_5O_5N_2$

Molecular weight 270

Chemical structure



Sodium 1,2-naphthoquinone diazide-5-sulphonate was obtained from Merck Chemicals. This was used in the synthesis of sensitiser by converting into sulfonyl chloride and coupling to 2,3,4-trihydroxy benzophenone.

2.1.19 Heptane

Empirical formula C_7H_{16}

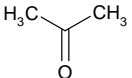
Molecular weight 100.20

Density 0.684 g/cm³

Chemical Structure

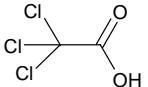
Heptane was obtained from Merck Chemicals. It was used as a porogen in polymerisations.

2.1.20 Acetone

Empirical formula	C_3H_6O
Molecular weight	58.08
Density	0.79 g/cm^3
Chemical Structure	

Acetone was obtained from Merck Chemicals. It was used as a solvent in various organic reactions.

2.1.21 Trichloro acetic acid

Empirical formula	$C_2HCl_3O_2$
Molecular weight	163.39
Density	1.63 g/cm^3
Chemical Structure	

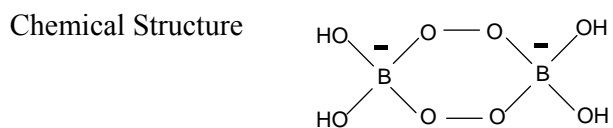
Trichloro acetic acid was obtained from Merck Chemicals. This was used as a reagent in Bayer-Villiger oxidation.

2.1.22 Sodium perborate

Empirical formula $\text{NaBO}_2 \cdot \text{H}_2\text{O}_2 \cdot 3\text{H}_2\text{O}$

Molecular weight 153.86

Density 1.73 g/cm^3



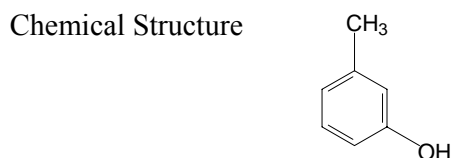
Sodium perborate was obtained from Merck Chemicals Limited. It was used as reagent in in Bayer-Villiger oxidation.

2.1.23 *m*-Cresol

Empirical formula $\text{CH}_3\text{C}_6\text{H}_4\text{OH}$

Molecular weight 108.14

Density 1.034 g/cm^3



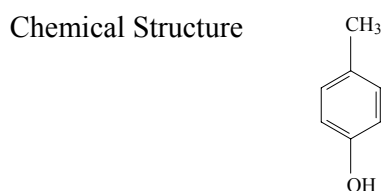
m-Cresol was obtained from Aldrich Chemicals Limited. It was used in synthesis of phenol-formaldehyde resins.

2.1.24 *p*-Cresol

Empirical formula $\text{CH}_3\text{C}_6\text{H}_4\text{OH}$

Molecular weight 108.14

Density 1.034 g/cm^3



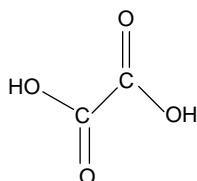
p-Cresol was obtained from Aldrich Chemicals Limited. It was used in synthesis of phenol-formaldehyde resins.

2.1.25 Oxalic acid

Empirical formula $\text{HO}_2\text{CCO}_2\text{H}$

Molecular weight 90.03

Chemical Structure



Oxalic acid was obtained from Merck Chemicals Limited. It was used as catalyst in synthesis of phenol-formaldehyde resins.

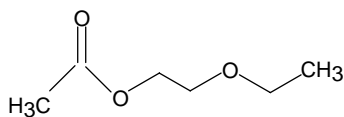
2.1.26 2-Ethoxy ethyl acetate

Empirical formula $\text{CH}_3\text{COOCH}_2\text{CH}_2\text{OC}_2\text{H}_5$

Molecular weight 132.16

Density 0.975 g/cm^3

Chemical Structure



2-Ethoxy ethyl acetate was obtained from Merck Chemicals Limited. It was used as solvent in photoresist formulations.

2.1.27 Formaldehyde

Empirical formula	HCHO
Molecular weight	30.03
Density	1.09 g/cm ³
Chemical Structure	$\begin{array}{c} \text{O} \\ \\ \text{H}-\text{C}-\text{H} \end{array}$

Formaldehyde 36 wt% solution was obtained from Merck Chemicals Limited. It was used in synthesis of phenol-formaldehyde resins.

Hydrogen peroxide, disodium hydrogen phosphate and thionyl chloride were obtained from Merck Chemicals Limited.

Ditallow dimethyl ammonium methyl sulphate, polyglycerol monoisostearate and polyglycerol succinate were procured from Witco Corporation and Lubrizol Corporation Limited.

2.2 Characterisation

The cross-linked polymers were characterised for surface area and pore volume. The acid content of the polymers was estimated by acid base titration so as to determine the number of acid groups bound. The cell morphology of the polymers was studied by scanning electron microscopy. The efficiency of the catalyst in esterification reactions was monitored by HPLC. The solvent uptake was determined by difference in weight before and after absorption.

2.2.1 Mercury porosimetry

The pore volume of the polymers was determined by mercury porosimetry technique. Two series of the samples were evaluated for mercury porosimetry.

Sampling: (0.2 g) sample was filled in sample cell for mercury porosimetry and filled with mercury. The sample cell was loaded in the instrument and subjected to a pressure of 60,000 psi. The plot of intruded volume vs pressure was obtained. The software was used to calculate the pore volume and the radii of the pores.

2.2.1.1 Principle of mercury porosimetry

Mercury porosimetry is the most extensively used tool for characterisation of various aspects of porous media and polymers. This is the simplest and most rapid technique to obtain a ‘fingerprint’ of porous medium. Washburn was the first to demonstrate in 1921 this methodology to obtain pore size distribution from pressure-volume data for mercury penetration into a porous body.¹ Ritter and Drake in 1945 were first to describe the construction and working of mercury porosimeter.²

Mercury behaves as a non-wetting liquid towards most substances. In experimentation porous solid is sealed into a vessel tapered in a capillary tube, evacuated, filled with mercury and subjected to increasing pressure. The mercury penetrates into the pores and its level in capillary decreases. This decrease is registered relative to the corresponding pressure. A porosimetric curve thus obtained indicates how large a volume of mercury has penetrated into the pores of sample at a given pressure. A plot of intruded (or extruded) volume of mercury versus pressure is called porogram.

The initial intrusion at very low pressure is due to penetration in large interparticle voids. Intrusion at high pressures are into the pores within the particles. All porosimetry curves exhibit hysteresis. The path followed by the extrusion curve is greater than that on intrusion curve. Thus, at a given volume pressure indicated on intrusion is greater than that on extrusion curve. The hysteresis loop is never closed. The intrusion extrusion hysteresis is due to two factors: (a) entrapment of mercury

after pressurisation-depressurisation cycle and (b) change in contact angle of mercury, between intrusion and extrusion processes.

The operating equation in mercury porosimetry is the Washburn equation as shown below:

$$P r = 2 \gamma \cos \theta \quad (2.1)$$

Pr is a constant assuming constancy of γ and θ . This implies pressure is inversely proportional to radius.

γ is 480 dynes/cm and θ is 140°C

Therefore Washburn equation is

$$r = \frac{0.736}{P}$$

where P is in Mpa and r in cm

2.2.2 Surface area

The surface area (S) of the particles was measured by nitrogen adsorption isotherms. Nitrogen adsorption at 77°K was determined volumetrically in a Nova 2000e System. The BET equation was used to analyse the nitrogen adsorption isotherms and to calculate the surface areas of the particles.

Sampling: 0.5 g sample was loaded in the cells for surface area measurement. The sample was vacuum degassed for 3 hours at 70°C to remove all the moisture trapped inside the pores. The sample was then loaded on the degas station. Nitrogen gas was purged in the sample cells loaded with sample. The surface area was calculated by software according to B.E.T equation. The data obtained from the instrument is as follows:

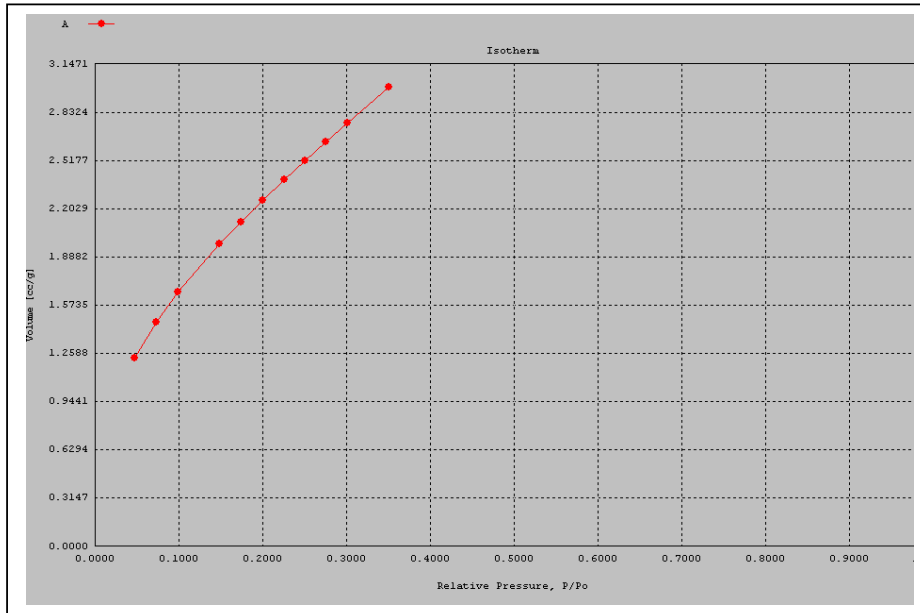


Figure 2.1: A typical isotherm plot for measurement of surface area obtained from Nova 2000e Instrument

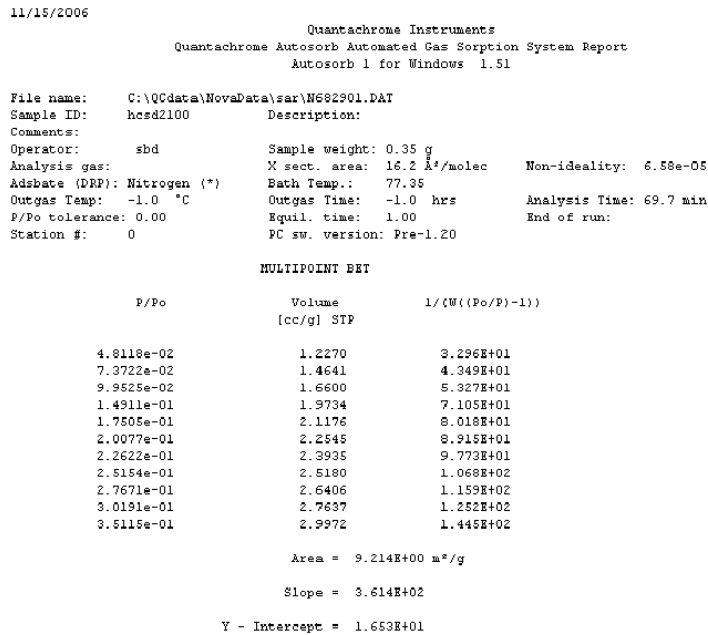


Figure 2.2: A typical isotherm plot obtained from Brunauer-Emmet-Teller (B.E.T) measurements

2.2.2.1 Principle of surface area using nitrogen sorption method

The Brunauer-Emmett-Teller (BET) method is the most widely used procedure for the determination of the surface area of solid materials and involves the use of BET equation. BET theory is a well-known rule for the physical adsorption of gas molecules on a solid surface.³ In 1938, Stephen Brunauer, Paul Hugh Emmett, and Edward Teller published an article about the BET theory; “BET” consists of the first initials of their family names.⁴ The concept of the theory is an extension of the Langmuir theory, theory for monolayer molecular adsorption, to multilayer adsorption with the following hypotheses: (a) gas molecules physically adsorb on a solid in layers infinitely; (b) there is no interaction between each adsorption layer; and (c) the Langmuir theory can be applied to each layer. The resulting BET equation is expressed by (2.2):

$$\frac{1}{v [(P_0/P)-1]} = \frac{1}{v_m c} \left(\frac{P}{P_0} \right) + \frac{1}{v_m} \quad (2.2)$$

P and P_0 are the equilibrium and the saturation pressure of adsorbates at the temperature of adsorption, v is the adsorbed gas quantity (for example, in volume units), and v_m is the monolayer adsorbed gas quantity. ‘ c ’ is the BET constant, which is expressed by (2.3):

$$c = \exp \left[\frac{E_1 - E_L}{RT} \right] \quad (2.3)$$

E_1 is the heat of adsorption for the first layer, and E_L is that for the second and higher layers and is equal to the heat of liquefaction.

Equation (2.2) is an adsorption isotherm and can be plotted as a straight line with $1 / v[(P_0 / P) - 1]$ on the y-axis and P / P_0 on the x-axis according to experimental

results. This plot is called a BET plot. The linear relationship of this equation is maintained only in the range of $0.05 < P / P_0 < 0.35$. The value of the slope and the y-intercept of the line are used to calculate the monolayer adsorbed gas quantity v_m and the BET constant c .

The BET method is widely used in surface science for the calculation of surface areas of solids by physical adsorption of gas molecules. A total surface area S_{total} and a specific surface area S are evaluated by the following equations (2.4):

$$S_{\text{total}} = \left(\frac{v_m Ns}{M} \right) \quad (2.4)$$

N : Avogadro's number, s : adsorption section, M : molecular weight of adsorbate, a : weight of sample solid.

For example, activated carbon, which is a strong adsorbate and usually has an adsorption cross section s of 0.16 nm^2 for nitrogen adsorption at liquid nitrogen temperature, is revealed from experimental data to have a large surface area around $3000 \text{ m}^2 \text{ g}^{-1}$. Moreover, in the field of solid catalysis, the surface area of catalysts is an important factor in catalytic activity. Porous inorganic materials such as mesoporous silica and layer clay minerals have high surface areas of several hundred m^2/g calculated by the BET method, indicating the possibility of application for efficient catalytic materials.

2.2.3 Infra-red spectroscopy

Polymer (2 mg) was mixed thoroughly in 100 mg potassium bromide (moisture free) in small mortar. Mixture was transferred to a pellet die, that contains smooth cylindrical pellet. It was fitted to a hydraulic press and pressure of 10 tons was applied on it. The die was removed from press after 2 minutes, the pellet was taken out and used to record the IR spectra. This pellet was fitted in specimen holder and

was exposed to IR radiation. Spectrum was recorded and prints were taken. The data was recorded as wavelength vs % transmittance.

2.2.4 HPLC analysis

The efficiency of the solid catalysts prepared in conversion of salicylic acid to methyl salicylate was analysed by high performance liquid chromatography. The conversion of esterification reaction was monitored by HPLC (LDC Analytical Autoinjector A1000) with CM 4000 pump and SM4000 UV detector at 254 nm, at ambient temperature, Nucleosil C18 column). The mobile phase used was methanol:water (80:20 v/v).

2.2.5 UV analysis

The behaviour of sensitizers and formulations used in photoresist applications on exposure was studied using ultra-violet spectroscopy. On exposure at 365 nm wavelength the 1,2-naphthoquinone diazide-5-sulphonate based sensitizers undergo Wolff rearrangement to form indenecarboxylic acid. The time required for disappearance of the sensitizer peaks is monitored by UV spectroscopy which is dependent on number of hydroxyl groups of the sensitizer modified.

2.2.6 Gel permeation chromatography (GPC)

The molecular weight of the polymers used in photoresist formulation was determined using gel permeation chromatography. In photoresist the coating and thickness of the formulation is dependent on the molecular weight of the resins used. Polymers to be used in formulations are preferred to have molecular weight between 5000-10000.

2.2.7 Differential scanning calorimetry (DSC)

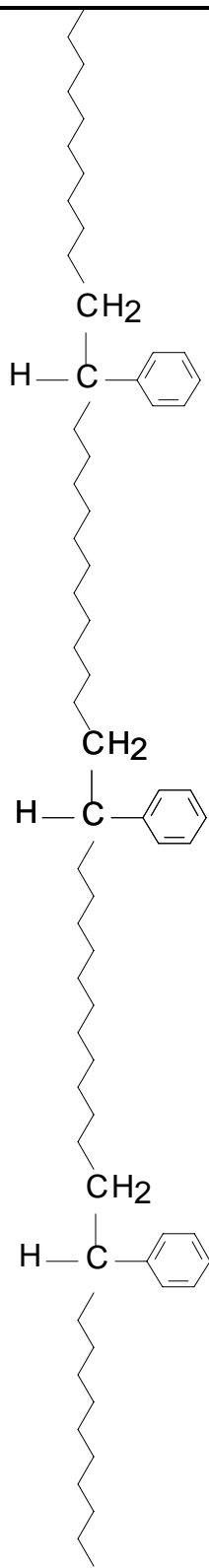
The glass transition temperature of the polymers was determined by differential scanning calorimeter. The uniform coating of formulation on a substrate is dependent on the glass transition temperature of the polymers.

2.2.8 Scanning electron microscopy (SEM)

The surface morphology of the polymers synthesised was studied using a scanning electron microscope. The types of pores formed i.e closed pores or interconnected pores is dependent on the synthesis strategy used. Effect of varying the synthesis parameters on the pore structure of the polymers is studied using SEM.

2.3 References

- 1 E. W. Washburn, *Proc. Natl. Acad. Sci.*, 7, 111, (1921).
- 2 H. L. Ritter and L. C. Drake, *Ind. Eng. Chem. Anal. Ed.*, 17, 782, (1945).
- 3 E. P. Barret, L. G. Joyner, P. P. Halenda, *J. Am. Chem. Soc.*, 73, 373 (1951).
- 4 S. Brunauer, P. H. Emmet, E. Teller, *J. Am. Chem. Soc.*, **60**, 309, (1938).



SYNTHESIS OF BEADED POROUS POLYMERS USING SURFACTANTS

3 Synthesis of beaded cross-linked poly(styrene-co-divinyl benzene) in presence of surfactants

3.1 Synthesis of beaded cross-linked poly(styrene-co-divinyl benzene) using Brij 52

Beaded cross-linked poly(styrene-co-divinyl benzene) were synthesised in presence of surfactants in oil phase, different from conventional suspension polymerisations. The monomer, cross-linker and surfactant (Brij-52) formed the oil phase. Water was added to the oil phase slowly with stirring at 1400 rotations per minute. The emulsion formed with Brij-52 was not a stable one. After stirring, the reactants were added to a stirred water phase at 250 rotations per minute, containing a protective colloid to disperse the above mixture in form of droplets. The temperature of the water phase was 70°C. The polymerisation was carried for 16 hours and product was obtained in the form of beads. The reaction parameters varied were cross-link density, internal water, stirring time and surfactant concentration. Tables 3.1-3.4 show the compositions of the polymers synthesised by variation in reaction parameters.

Table 3.1 Compositions of poly(styrene-co-divinyl benzene) synthesised with Brij-52: Effect of cross-link density

Polymer Code	Styrene		DVB		%	Pore volume cm ³ /g	Surface Area m ² /g
	Volume mL	mole	Volume mL	mole			
HSR-1	6.87	0.060	2.13	0.015	25	0.8990	143.9
HSR-2	5.55	0.048	3.45	0.024	50	0.8730	112.0
HSR-3	4.66	0.040	4.34	0.030	75	0.8810	113.9
HSR-4	4.01	0.035	4.99	0.035	100	0.8134	130.3
HSR-5	3.14	0.027	5.86	0.041	150	0.9302	229.7
HSR-6	2.75	0.024	6.25	0.043	200	0.9060	293.4

CLD = Cross-link density, polymerisation temperature = 70°C, polymerisation time = 16 hours, water outer phase = 200 mL, PVP = 1 g, RPM = 250, Agitator = Ruston turbine, 8 bladed, Oil phase: surfactant: Brij-52- 3.2 g, AIBN = 0.636 g, inner water = 9 mL pore volume- determined by mercury porosimetry, surface area- determined by B.E.T surface area method.

Table 3.2 Effect of change in internal water volume on pore volume and surface area of 100% cross-linked poly(styrene-co-divinyl benzene)

Polymer Code	Styrene		DVB		Inner Water mL	Pore volume cm ³ /g	Surface Area m ² /g
	Volume mL	mole	Volume mL	mole			
HSR-8	4.01	0.035	4.99	0.035	4.5	0.8622	190.4
HSR-4	4.01	0.035	4.99	0.035	9	0.8134	130.3
HSR-7	4.01	0.035	4.99	0.035	18	0.8475	166.3

Polymerisation temperature = 70°C, polymerisation time = 16 hours, water outer phase = 200 mL, PVP = 1 g, RPM = 250, Agitator = Ruston turbine, 8 bladed. Oil phase: surfactant: Brij-52- 3.2 g, AIBN = 0.636 g, pore volume- determined by mercury porosimetry, surface area- determined by B.E.T surface area method.

Table 3.3 Effect of change in stirring time on pore volume and surface area of 100% cross-linked poly(styrene-co-divinyl benzene)

Polymer Code	Styrene		DVB		Stirring Time (min)	Pore volume cm ³ /g	Surface Area m ² /g
	Volume mL	mole	Volume mL	mole			
HSR-4	4.01	0.035	4.99	0.035	5	0.8134	130.3
HSR-9	4.01	0.035	4.99	0.035	10	0.9223	149.1
HSR-10	4.01	0.035	4.99	0.035	15	1.1228	161.9

Polymerisation temperature = 70°C, polymerisation time = 16 hours, water outer phase = 200 mL, PVP = 1 g, RPM = 250, Agitator = Ruston turbine, 8 bladed. Oil phase: surfactant: Brij-52- 3.2 g, AIBN = 0.636 g, inner water = 9 mL, pore volume- determined by mercury porosimetry, surface area- determined by B.E.T surface area method.

Table 3.4 Effect of Brij-52 (surfactant) concentration on pore volume and surface area of 100% cross-linked poly(styrene-co-divinyl benzene)

Polymer Code	Styrene		DVB		Surfactant (g)	Pore volume cm ³ /g	Surface Area m ² /g
	Volume mL	mole	Volume mL	mole			
HSR-12	4.01	0.035	4.99	0.035	0.8	0.1699	-
HSR-11	4.01	0.035	4.99	0.035	1.6	0.4125	233.9
HSR-4	4.01	0.035	4.99	0.035	3.2	0.8134	130.3

Polymerisation temperature = 70°C, polymerisation time = 16 hours, water outer phase = 200 mL, PVP = 1 g, RPM = 250, Agitator = Ruston turbine, 8 bladed, Oil phase: surfactant: Brij-52- 3.2 g, AIBN = 0.636 g, inner water = 9 mL, pore volume- determined by mercury porosimetry, surface area- determined by B.E.T surface area method.

3.2 Synthesis of beaded cross-linked poly(styrene-co-divinyl benzene) polymers using Span 60

The procedure adopted in section 3.1 was used. Span 60 was used instead of Brij-52. The emulsion was a stable one with Span 60. After drying polymers with pores dependent on the synthesis strategies were obtained. The details of variation in reaction parameters and its effect on the pore volume and surface area are given in Tables 3.5-3.8.

Table 3.5 The effect of cross-link density on surface area of poly(styrene-co-divinyl benzene) synthesised using Span 60

Polymer Code	Styrene		DVB		% CLD	Surface Area m ² /g
	Volume mL	mole	Volume mL	mole		
SDH-1	6.87	0.060	2.13	0.015	25	15.43
SDH-2	5.55	0.048	3.45	0.024	50	42.76
SDH-3	4.66	0.040	4.34	0.030	75	12.23
SDH-4	4.01	0.035	4.99	0.035	100	11.79
SDH-5	3.14	0.027	5.86	0.041	150	7.75

SDH-6	2.75	0.024	6.25	0.043	200	3.96
-------	------	-------	------	-------	-----	------

Polymerisation temperature = 70°C, polymerisation time = 16 hours, water outer phase = 200 mL, PVP = 1 g, RPM = 250, Agitator = Ruston turbine, 8 bladed. Oil phase: surfactant: Span 60- 3.2 g, AIBN = 0.636 g, inner water = 9 mL, pore volume- determined by mercury porosimetry, surface area- determined by B.E.T surface area method, CLD = cross-link density

Table 3.6 The effect of inner water on surface area of 100% cross-linked poly(styrene-co-divinyl benzene) synthesised using Span 60

Polymer Code	Styrene		DVB		Inner Water mL	Surface Area m ² /g
	Volume mL	mole	Volume mL	mole		
SDH-14	4.01	0.035	4.99	0.035	4.5	30.73
SDH-4	4.01	0.035	4.99	0.035	9	11.79
SDH-13	4.01	0.035	4.99	0.035	18	21.88

Polymerisation temperature = 70°C, polymerisation time = 16 hours, water outer phase= 200 mL, PVP = 1 g, RPM = 250, Agitator = Ruston turbine, 8 bladed, Oil phase: surfactant: Span 60- 3.2 g, AIBN = 0.636 g, pore volume- determined by mercury porosimetry , surface area- determined by B.E.T surface area method.

Table 3.7 The effect of stirring time on surface area of 100% cross-linked poly(styrene-co-divinyl benzene) synthesised using Span 60

Polymer Code	Styrene		DVB		Stirring time (min)	Surface Area m ² /g
	Volume mL	mole	Volume mL	mole		
SDH-4	4.01	0.035	4.99	0.035	5	11.79
SDH-15	4.01	0.035	4.99	0.035	10	24.37
SDH-16	4.01	0.035	4.99	0.035	15	9.454

Polymerisation temperature = 70°C, polymerisation time = 16 hours, water outer phase= 200 mL, PVP = 1 g, RPM = 250, Agitator = Ruston turbine, 8 bladed, Oil phase: surfactant: Span 60- 3.2 g, AIBN = 0.636 g, inner water = 9 mL, pore volume- determined by mercury porosimetry, surface area- determined by B.E.T surface area method.

Table 3.8 The effect of surfactant concentration on surface area of 100% cross-linked poly(styrene-co-divinyl benzene) synthesised using Span 60

Polymer Code	Styrene		DVB		Surfactant (g)	Pore volume cm ³ /g	Surface Area m ² /g
	Volume mL	mole	Volume mL	mole			
SDH-18	4.01	0.035	4.99	0.035	0.8	0.6760	46.15
SDH-17	4.01	0.035	4.99	0.035	1.6	1.8183	98.96
SDH-4	4.01	0.035	4.99	0.035	3.2	1.7904	11.79

Polymerisation temperature = 70°C, polymerisation time = 16 hours, water outer phase= 200 mL, PVP = 1 g, RPM = 250, Agitator = Ruston turbine, 8 bladed. Oil phase: surfactant:, AIBN = 0.636 g, inner water = 9 mL pore volume- determined by mercury porosimetry, surface area- determined by B.E.T surface area method.

3.3 Beaded poly(styrene-co-divinyl benzene)

Poly(styrene-co-divinyl benzene) beads having 100% cross-link density were synthesised by suspension polymerisation, varying the porogen, type and its concentration.

Table 3.9 Effect of variation in porogen type and volume on pore volume and surface area of poly(styrene-co-divinyl benzene) synthesised by suspension polymerisation method

Polymer Code	Porogen	Volume mL	Pore volume m ² /g	Surface area m ² /g
SP-1	toluene	9	0.3495	223.3
SP-2	toluene	18	0.4000	399.7
SP-3	o-xylene	9	0.4759	458.7
SP-4	o-xylene	18	0.4480	403.0
SP-5	benzyl chloride	9	0.2732	300.0
SP-6	benzyl chloride	18	0.3395	557.1

SP-7	chlorobenzene	9	0.2917	470.7
SP-8	chlorobenzene	18	-	455.1
SP-9	n-dodecane	18	1.6070	7.028
SP-10	n-dodecane	9	1.6862	-
SP-13	chlorobenzene	27	0.3981	445.3
SP-14	m-xylene	9	0.3665	-
SP-15	m-xylene	18	-	459.2
SP-16	lauryl alcohol	9	1.3193	2.074
SP-17	lauryl alcohol	27	1.3924	-
SP-18	cyclohexanol	9	-	153.6
SP-19	cyclohexanol	27	-	112.5

Styrene- 4.01mL (0.035 mole), DVB- 4.99mL (0.035 mole), AIBN-0.636 g, PVP-1 g in 200 mL reaction time-12 h. polymerisation temperature: 70°C.

3.4 Results and discussion

Formation of porous structures in dried state is mainly due to phase separation during network formation. Depending on the synthesis strategy, the pores generated can be macro, micro or mesopores.¹ The synthesis of porous polymers was effected by different strategies and its effect on pore volume, pore size and surface area were studied. Porous polymers were synthesised by suspension polymerisation using porogen that can be a solvent, non-solvent or a low molecular weight linear polymer.²⁻¹²

Styrene and divinyl benzene co-polymerised in absence of porogen gives glassy transparent beads. These materials are amorphous and cross-linked, having interpenetrating polymer chains without any fine structure. The polymer chains are in molecular contact with each other and resins have in dry state surface area less than 10

m²/g. These materials swell in good solvents which create temporary porosity in polymers.¹³ Tables 3.1-3.4 show polymers synthesised using surfactant Brij-52, polyoxyethylene (2) cetyl ether (C₁₆H₃₃(OCH₂(CH₂)_nOH), with a HLB value of 5.3.

The polymers were synthesised by varying the surfactant concentration, internal water, stirring time and cross-link density of monomer. The required amount of surfactant, monomer and initiator were mixed and water was added with stirring at 1400 rpm for 5 minutes. The emulsions were transparent and unstable on standing. So immediately after stirring at 1400 rpm the mixture was added to 200 mL stirred aqueous phase having 0.5 wt% poly(vinyl pyrrolidone). The oil phase was added to this mixture with stirring. Emulsion formed was unstable but there was interaction between the oil and aqueous phases to form aggregates which may not be uniform through out the system. This system can be compared to formation of middle phase microemulsion, where the hydrophilic- lipophilic functional groups of the surfactant are more balanced that it results in a Winsor type III middle phase microemulsion, as shown in Figure 3.1b. The term middle phase refers to the actual location of the phase in static layered solutions where clear top and bottom layers exist, separated by the middle phase. This mixture containing monomer, surfactant and water after stirring is immediately added to a stirred aqueous phase containing protective colloid to polymerise the dispersed droplets to form a suspension polymerisation.

This process can be compared with synthesis of porous polymers by suspension polymerisation using a non-solvent as porogen. As shown in Figure 1a, the beads obtained are opaque, as the water droplets along with the surfactant in oil phase act as diluent to generate porous polymers. In this technique surfactant is used to form reverse

micelles. Depending on water solubilised in micelles, the size of droplets inside St-DVB is different. Adjusting the water content in reverse micelles, the size of the pores can be controlled. Non-ionic surfactants and twin tail surfactant can individually generate microemulsions.¹⁴ These systems form a middle phase microemulsion where organic and aqueous phases consist of interconnecting domains and surfactant molecules are locked at the interface.¹⁵⁻¹⁷ After polymerisation on removal of the surfactant by soxhlet extraction and on drying, polymers with permanent pores are obtained, characterised by pore volume and surface area.

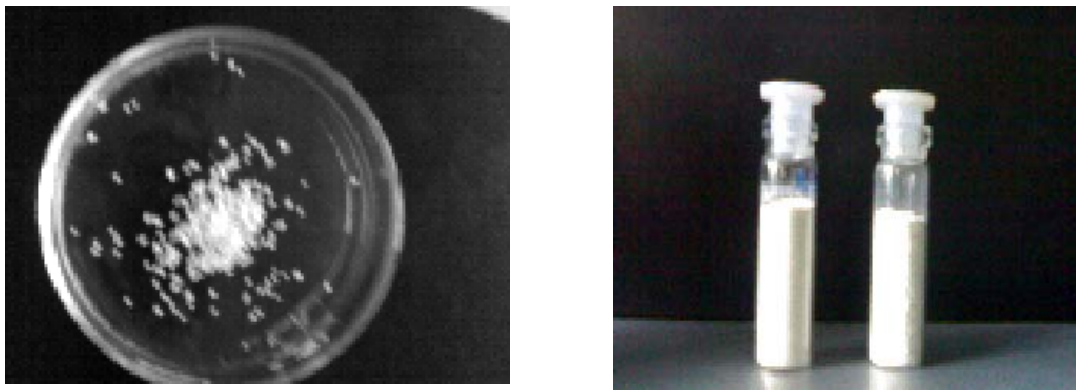


Figure 3.1a: Spherical beads obtained on polymerisation in presence of surfactants in the oil phase

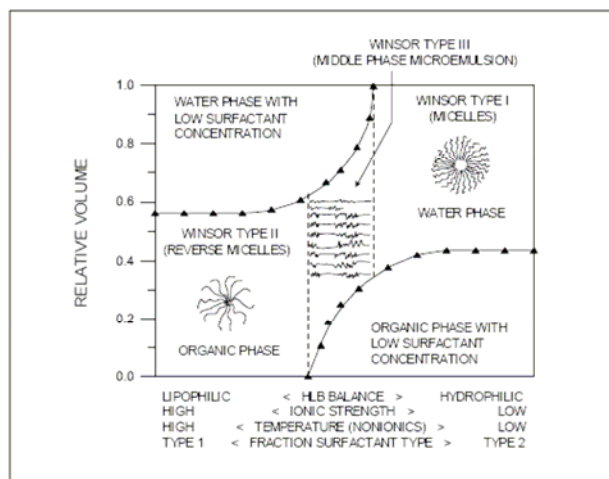


Figure 3.1b: Interactions of oil phase and aqueous phase to form micelles in emulsion

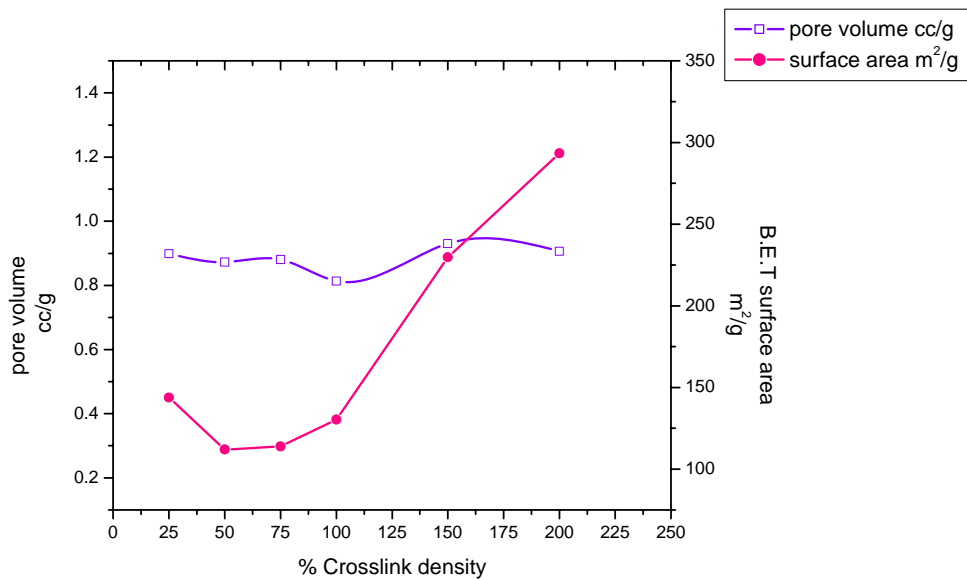


Figure 3.2 : Effect of cross-link density on pore volume and surface area of poly(styrene-co-divinyl benzene) synthesised using Brij-52 as surfactant

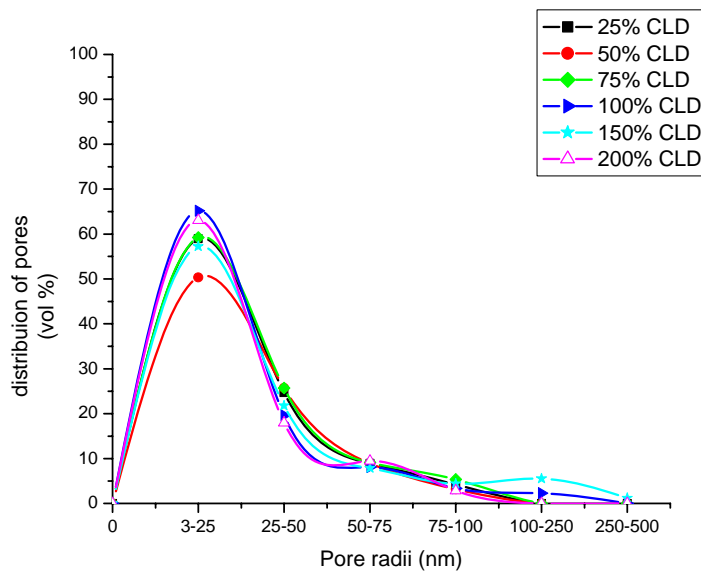


Figure 3.3 : Effect of cross-link density on volume % pore size distribution of poly(styrene-co-divinyl benzene) synthesised using Brij-52

The effect of cross-link density using Brij-52 on pore volume and surface area is depicted in Figure 3.2 and volume % pore size distribution is shown in Figure 3.3. As the cross-link density increases, the surface area of the polymers too increases but no considerable change in pore volume is observed. The pore volume remains nearly invariant but the pore radii shifts to lower values and its number increases appreciably. As micropores contribute more to the overall surface area of the polymers, an increase in surface area is observed. For 100 and 150 percent cross-linked polymers, 2-5 % pore radii in 100-500 nm region are observed. The total pore volume in polymer increases with increasing average pore size.

Table 3.10 Pore size distribution (volume %) of polymers having different cross-link density synthesised using Brij-52

Polymer Code	% CLD	3-25 nm	25-50 nm	50-75 nm	75-100 nm	100-250 nm	250-500 nm
HSR-1	25	58.93	24.70	8.92	4.21	-	-
HSR-2	50	58.33	25.71	8.94	3.18	-	-
HSR-3	75	59.24	25.74	9.13	5.36	-	-
HSR-4	100	65.14	19.64	8.11	3.36	2.28	-
HSR-5	150	57.23	21.77	7.85	4.39	5.55	1.22
HSR-6	250	63.07	17.98	9.46	2.84	-	-

Figure 3.4 shows effect of internal water in formation of micelles. Maximum surface area of 190.4 m²/g was obtained when ratio of monomer to water was 1:0.5. At 1:1 ratio of monomer:water a decrease in pore volume and surface area was observed. As micelle formation is dependent on the amount of water, it plays an important role in designing the pore radii. Figure 3.5 shows that in case of 1:0.5 and 1:1 oil : water ratio

pores having radii up to 250 nm are formed. For 1:2 oil : water ratio pore radii in the range of 250-500 nm are also formed.

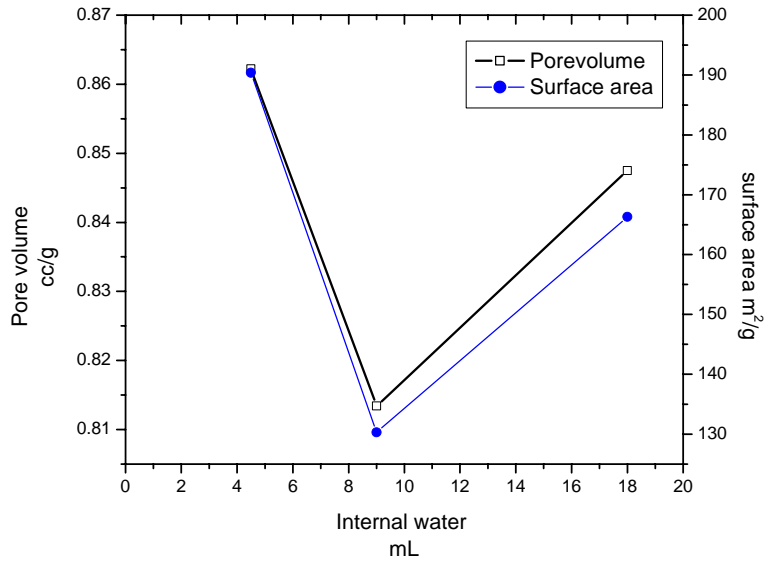


Figure 3.4 : Effect of internal water on pore volume and surface area of 100% cross-linked poly(styrene-co-divinyl benzene) synthesised using Brij-52

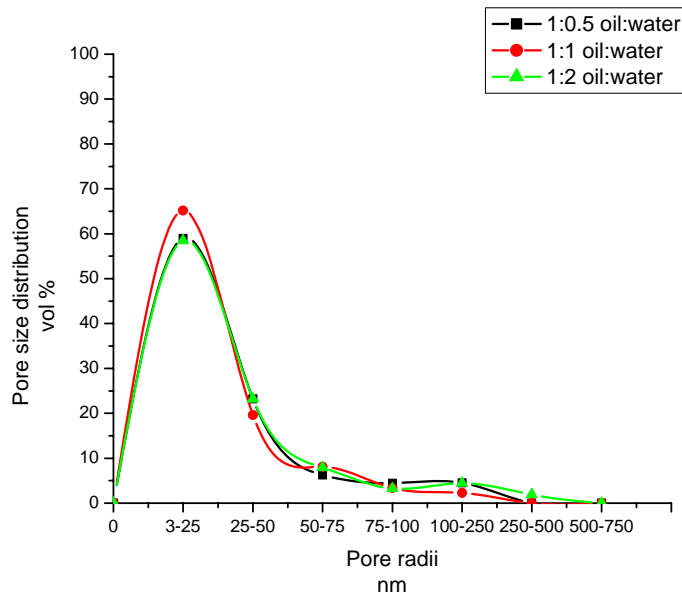


Figure 3.5 : Effect of internal water on differential volume pore size distribution of 100% cross-linked poly(styrene-co-divinyl benzene) synthesised using Brij-52

The effect of mixing time of oil phase and aqueous phase prior to suspension on formation of pores is depicted in Figure 3.6. Increasing stirring time increases pore volume as well as surface area in the poly(styrene-co-divinyl benzene) formed. This indicates that the emulsion takes time to stabilise. Stirring time ensures proper mixing of all the constituents and well distribution of micelles. Thus increase in stirring time leads to formation of a more homogeneous emulsion. Figure 3.7 indicates that increase in stirring time leads the volume % of pore radii in 3-25 nm region to be reduced and to increase the pore radii in the 100-500 nm range. On stirring for 15 minutes, pore radii in 500-750 nm range are also generated.

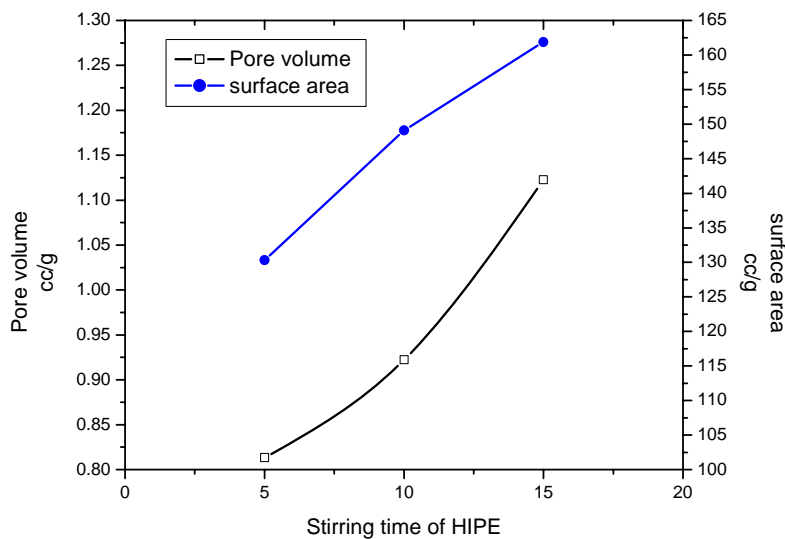


Figure 3.6 : Effect of stirring time on pore volume and surface area of 100% cross-linked poly(styrene-co-divinyl benzene) synthesised by using Brij-52

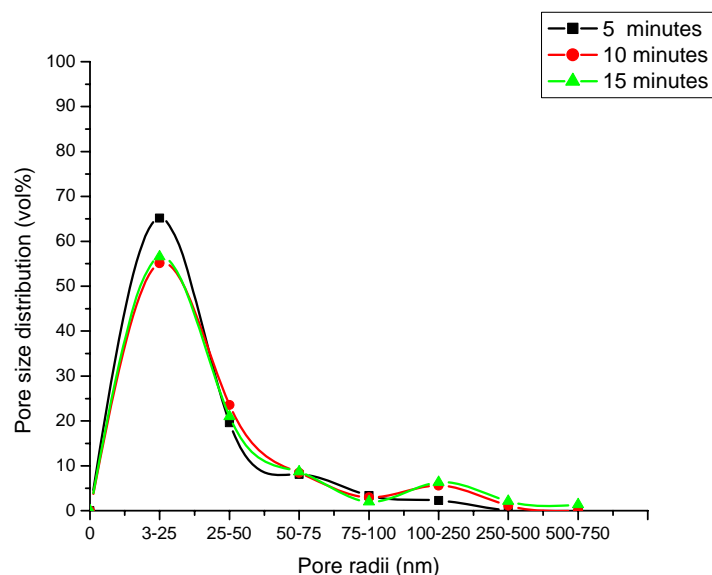


Figure 3.7 : Effect of stirring time on volume % pore size distribution of 100 % cross-linked poly(styrene-co-divinyl benzene) synthesised by using Brij-52

Tables 3.5-3.8 show synthesis of polymers using Span 60 as surfactant. Span 60, known as sorbitan monostearate, has a HLB value of 4.2. Span 60 is a saturated type sorbitan monoester with 15 $-CH_2-$ groups. The monomer, surfactant and initiator were mixed together and water was added slowly to the oil phase. Unlike Brij-52 a thick cream like emulsion is formed with Span 60. The emulsion was dispersed in aqueous phase in the form of beads. The beads were polymerised at $65^{\circ}C$ to obtain the beaded polymer. Sorbitan fatty acid esters are effective reducers of interfacial tension. Molecules of sorbitan monostearate, with small molecular area, are able to pack more tightly at all the interfaces and lower the interfacial tension more dramatically than other surfactants.¹⁸ Nitrogen adsorption shows that the surface area of the polymers is in the range $3-45 \text{ m}^2/\text{g}$.

The volume percent pore volume distribution of the polymers with 25%, 50% and 100% CLD synthesised using Span 60 surfactant is presented in Table 3.11. As the percent CLD increases, an increase in pore radii is observed. In case of 100% CLD

polymers having pore radii up to 2500 nm are formed. For 25 % CLD, maximum pores are observed in the 3-25 nm region. For 50 % CLD, pores having pore radii up to 1000 nm are being formed. The pore size distribution is as follows:

Table 3.11 Pore size distribution (volume %) of polymers of different cross-link density synthesised using Span 60

Pore radii (nm)	CLD 25 %	CLD 50 %	CLD 100 %
3-25	54.65	10.02	6.33
25-50	10.12	1.63	3.11
50-75	7.28	17.46	5.76
75-100	8.50	9.07	5.16
100-250	16.59	30.25	19.60
250-500	3.64	13.36	13.15
500-750	-	8.35	10.38
750-1000	-	10.26	18.08
1000-1500	-	-	6.93

Figure 3.8 shows that as the cross-link density increases, the surface area decreases. Figure 3.9 shows the volume % pore size distribution with variation in cross-link density using Span-60.

It is observed that as the cross-link density increases, pore radii as high as 2000 nm are formed. The graph reveals median pore radii increases with increase in cross-link density. The surfactant in this case must play the role of porogen, like the nonsolvent in conventional suspension polymerisation causing an earlier phase separation leading to pores in macroporous region.¹⁹

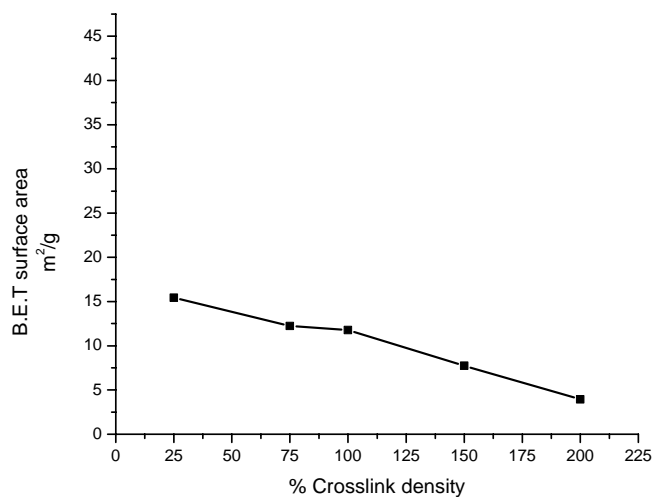


Figure 3.8 : Effect of variation in cross-link density using Span 60 on surface area of poly(styrene-co-divinyl benzene)

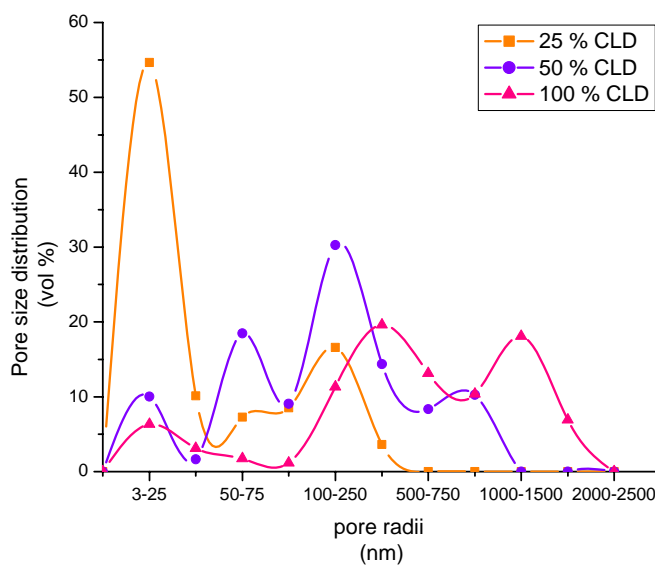


Figure 3.9 : Pore size distribution in poly(styrene-co-divinyl benzene) with variation in cross-link density synthesised using Span-60

In case of polymers synthesised using Span 60 a viscous curd like emulsion is formed which is then added to outer stirred water phase to obtain the polymer in the form

of beads. The surface area of the polymers is between 3-50 m²/g. The average diameter of each water droplet used in formation of HIPE is 10 μm and therefore surface area of these materials is low. The above results show that the pore volume and surface area of the polymers is dependent on surfactant type, surfactant concentration, stirring time, and amount of water.

There is a significant difference in the surface area of the polymers synthesised with the two surfactants. With Span 60 a thick viscous emulsion was obtained while with Brij-52 no such emulsion is formed after addition of water to the oil phase. Therefore, instead of conventional porogens (solvent, nonsolvent or linear polymer) the surfactant along with water acts as pore forming component. The pore volume for polymers in case of Span 60 is up to 1.8 cm³/g and surface area of 3-50 m²/g while polymers synthesised using Brij-52 had pore volume in the range 0.87-0.93 cm³/g and B.E.T surface area in the range 100-300 m²/g. The volume % of pore size distribution of the pores using Span 60 showed a wide distribution of pore radii from 3-2500 nm, while polymers using Brij-52 had pore radii in between 3-250 nm and at higher cross-link density pores between 250-500 nm, thus micropores contributed significantly to surface area. Therefore, the surface area was high for polymers synthesised using Brij-52. With Span 60 pores having pore radii of 2500 nm are formed and therefore surface area was low.

Figure 3.10 shows volume % distribution of pores with surfactant type, for 25 % cross-linked polymers. It is observed that with Span 60 pores with radii in 100-500 nm region and with Brij-52 pores between 3-100 nm are formed.

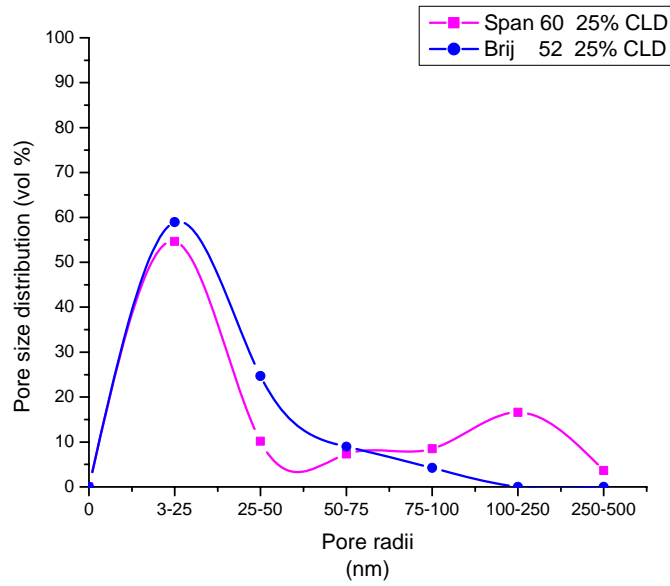


Figure 3.10 : Comparison of pore size distribution (vol %) for 25 % cross-linked poly(styrene-co-divinyl benzene) with variation in surfactant type

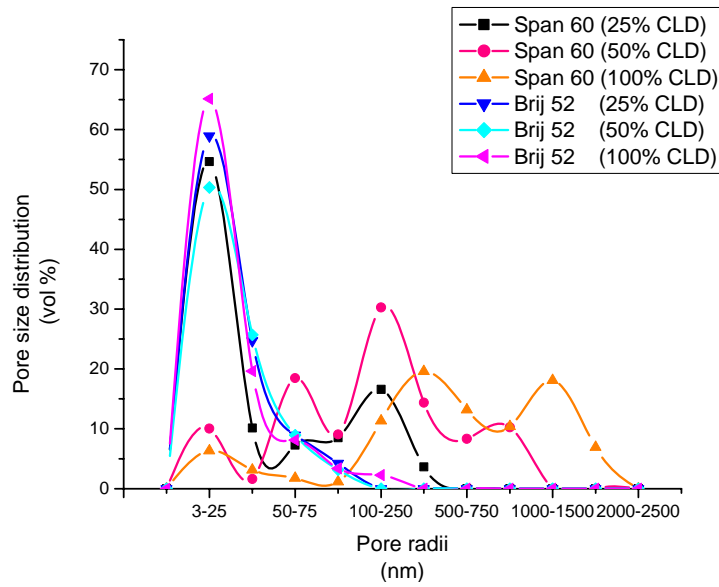


Figure 3.11 : Comparison of pore size distribution in poly(styrene-co-divinyl benzene) with variation in surfactant type and cross-link density

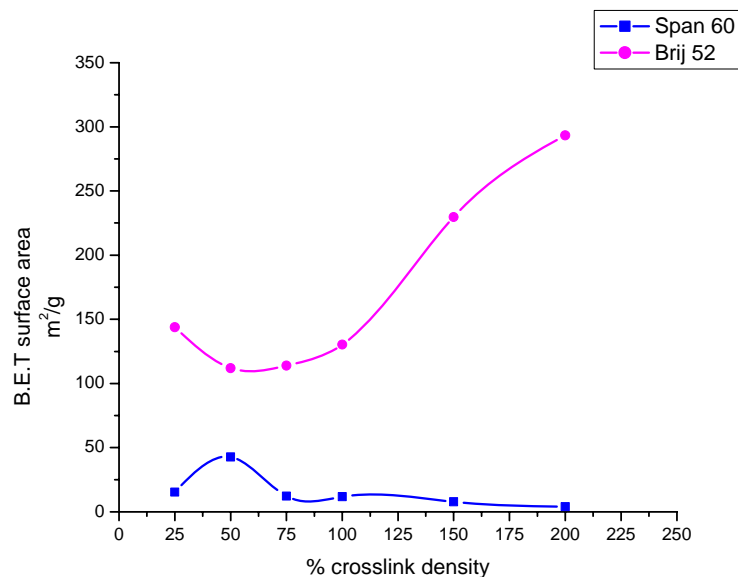


Figure 3.12 : Comparison of surface area of poly(styrene-co-divinyl benzene) synthesised by using Span 60 and Brij 52

Figures 3.10-3.12 being out the already stated fact that the surfactant type plays an important role in designing the pore volume and surface area of the polymers. The surface areas of the polymers obtained using Brij 52 is between 100-300 m²/g while using Span 60 the surface area obtained is 3-45 m²/g. Brij-52 dissolved in monomer phase acts as a template to form micelles along with water. This method of generating pores is different from conventional methods of using solvent or nonsolvent as porogen.

It is also observed that with Brij-52, as the cross-link density increases an increase in surface area is observed, while in case of Span 60 increase in cross-link density leads to a decrease in surface area. As observed, there is variation in pore radii distribution in both type of surfactants. In case of Brij-52 micropores are formed while in case of Span 60 pore radii in macroporous region are formed.

100% CLD polymers were synthesised by suspension polymerisation using porogens, to study their effects on pore volume and surface area. Figures 3.13-3.15 show

the pore volume, pore size distribution and surface area of the polymers synthesised using different porogens. Polymers synthesised using solvent for linear polymer as porogen have pore volume of 0.3-0.5 cm³/g and surface area of 225-550 m²/g. Polymers synthesised using non-solvent as porogen have pore volume of 1.3-1.6 cm³/g and surface area of 2-10 m²/g.

When a good solvent is used as porogen, the network remains fully solvated up to high conversion of monomers into polymer. When phase separation finally occurs the microgel particles are small and discrete, and are swollen with residual monomer and cross-linker. The separate porogen phase contains unreacted monomer and cross-linker. Further polymerisation in the porogen phase creates additional polymer that fuses the microgel particles together. However, relatively low levels of polymer are formed in this way, since the conversion of monomer to polymer at the point of phase separation is already rather high. The microgel particles, therefore, tend to retain their individual identity and the network of micro- and meso-pores, generated between the microgel particles when first formed, is essentially retained. Therefore, the polymers have high surface area and a pore size distribution, with a maximum in the micropore/mesopore region.

In case of non-solvent used as porogen, the phase separation occurs at much lower conversion, then again microgel particles are formed, now swollen with a high level of monomer and cross-linker, and the separate porogen phase comprises of significant levels of monomer and cross-linker. A great deal more copolymer is therefore formed in the porogen phase after the phase separation process, and this has the effect not only of fusing the microgel particles together, but also causing significant in-filling of small

pores between the microgel particles. In an extreme case, the individual microgel particles can lose their identity. Phase separation of styrene-based networks with formation of stable microgel particles occurs readily and polymers having high pore volume, less surface area and pores in macropore region are obtained. Thus, the total pore volume is controlled largely by the type of porogen used.

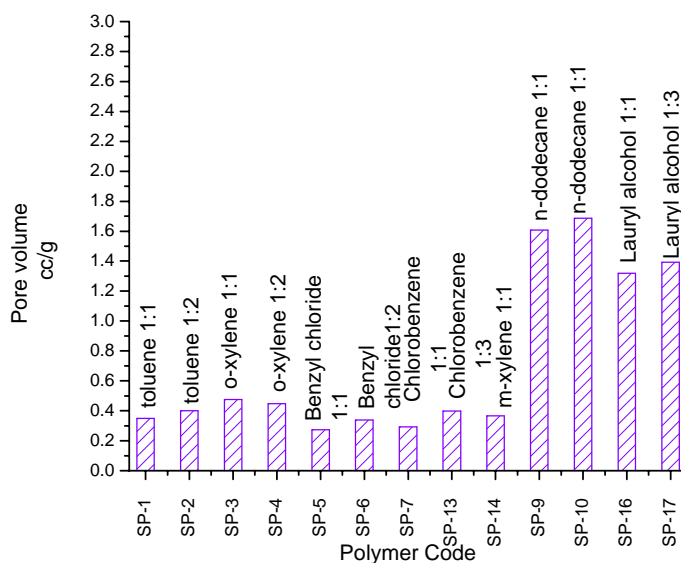


Figure 3.13 : Comparison of pore volume of poly(styrene-co-divinyl benzene) synthesised by suspension polymerisation with variation in porogen type

Figure 3.14 shows that 80-95 % of pores formed are in the 3-25 nm range for polymers synthesised by suspension polymerisation in presence of porogens.

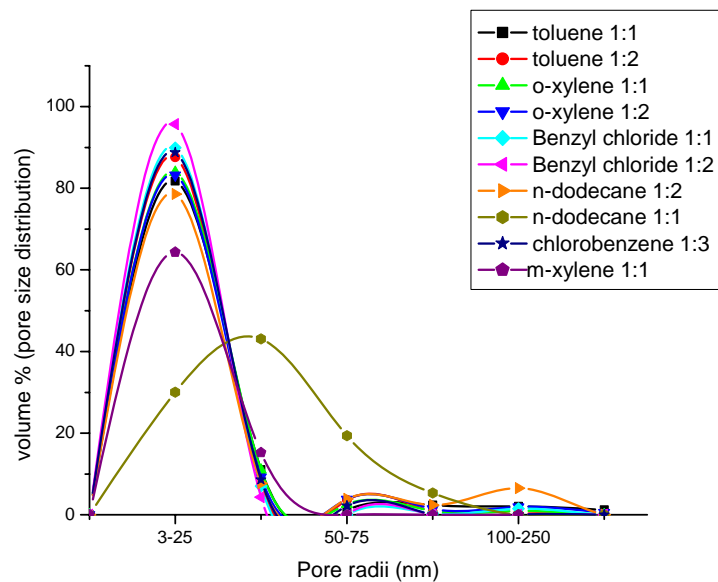


Figure 3.14 : Pore size distribution of poly(styrene-co-divinyl benzene) of 100% CLD synthesised by suspension polymerisation

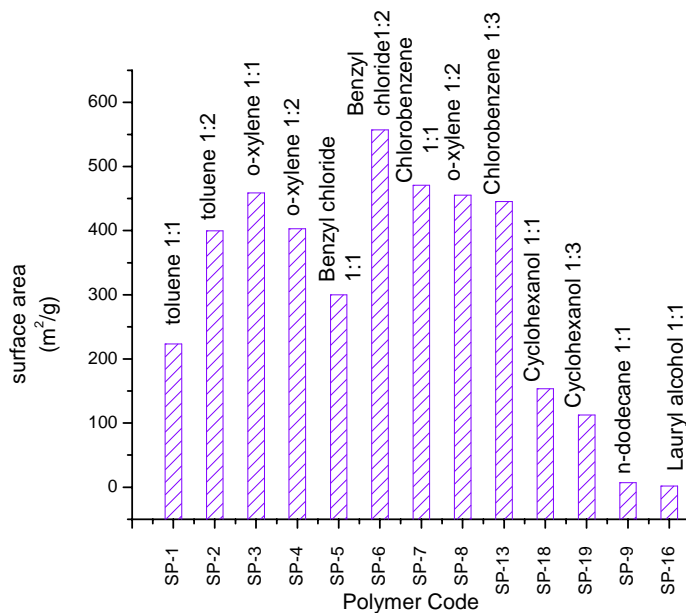


Figure 3.15 : Surface area of the poly(styrene-co-divinyl benzene) of 100% CLD using different porogens

The difference between pore volume and surface area of the polymers synthesised using surfactants and conventional porous polymers synthesised using porogen are shown in Figures 3.16 and 3.17, respectively. The general results are tabulated below.

Table 3.12 Designing synthesis strategy on pore volume and surface area of poly(styrene-co-divinyl benzene) in the 100% CLD range

Synthesis strategy	Pore volume cm ³ /g	Surface area m ² /g
Conventional Suspension polymerisation Porogen-solvent	0.3-0.5	225-550
Conventional Suspension polymerisation Porogen-non-solvent	1.3-1.6	2-10
Using Brij-52 as surfactant	0.8-1.1	100-200
Using Span-60 as surfactant	1.5-2.0	3-50

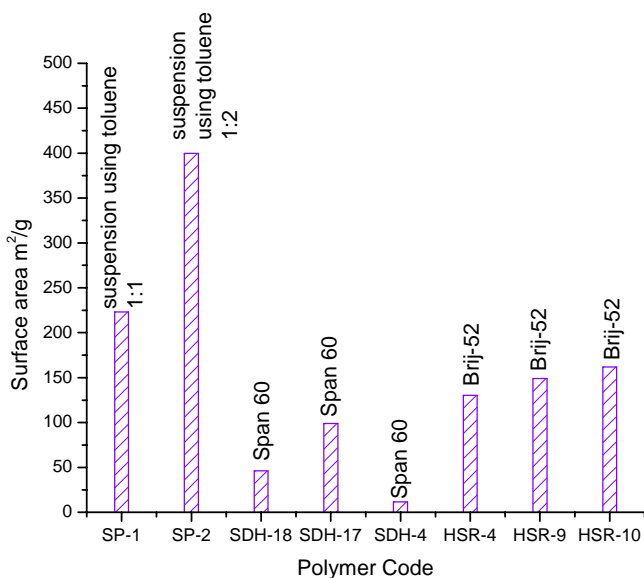


Figure 3.16 : Comparison of surface area of poly(styrene-co-divinyl benzene) of 100% CLD prepared

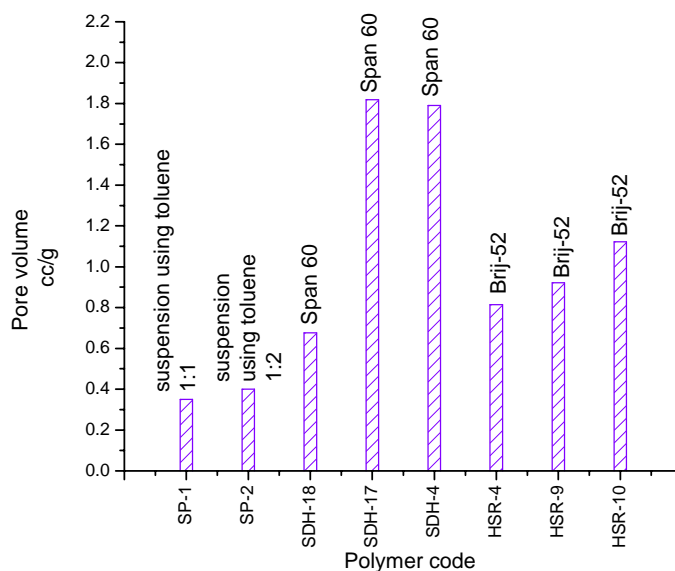


Figure 3.17 : Comparison of pore volume of poly(styrene-co-divinyl benzene) of 100% CLD prepared by using different synthesis strategies

The pore volume and surface area of the polymers synthesised by different methods show that the polymers synthesised using Span-60 have a high pore volume compared to conventional methods but the surface area of these materials is very low. These can be used in imbibing applications. In case of polymers synthesised using Brij-52 as surfactant the pore volume of the materials is high in comparison to polymers synthesised by suspension polymerisation using a solvent as porogen. The samples synthesised using non-solvent as porogen have high pore volume but the surface area is quite low. Brij-52 generates polymers having considerable high pore volume as well as surface area that could find application in enzyme immobilisation.

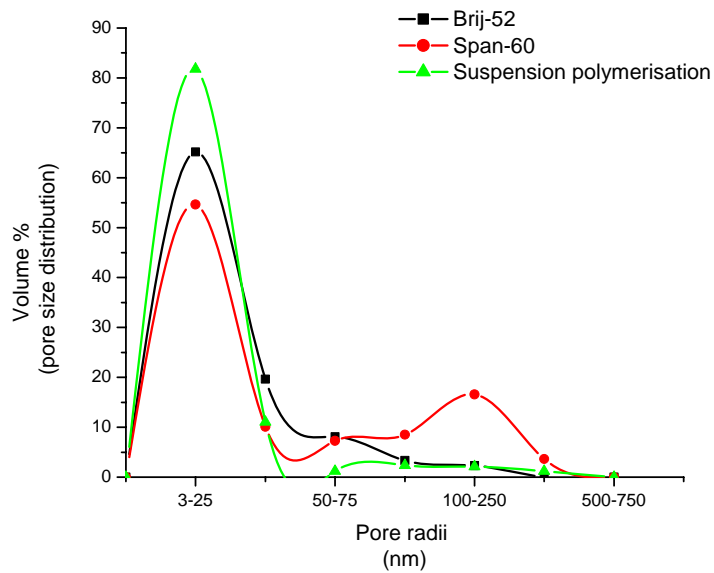
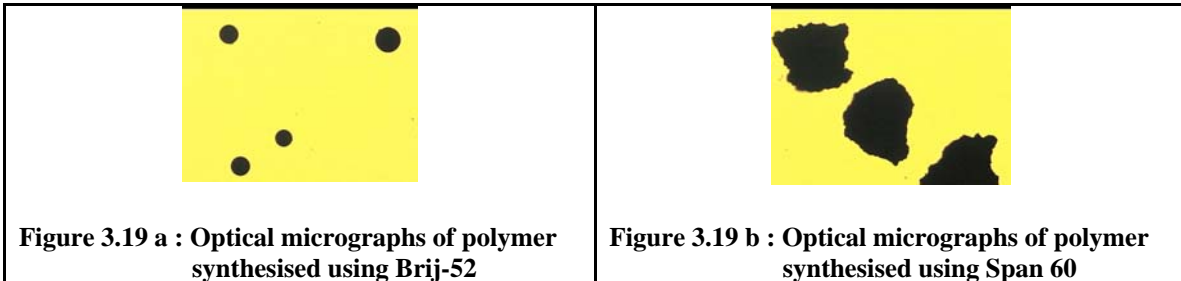


Figure 3.18 : Comparison of pore size distribution (vol %) in poly(styrene-co-divinyl benzene) synthesised by variation in porogen type

Figure 3.18 shows that microporous polymers are obtained on using Brij-52 while pores in macroporous region are obtained with Span 60.



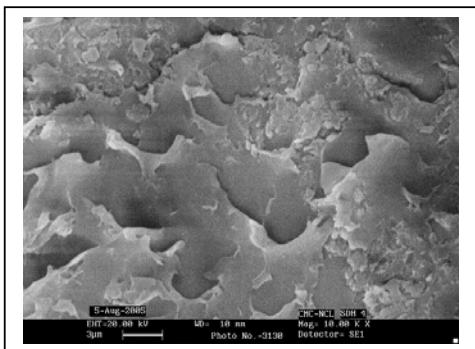


Figure 3.20 a : SEM micrographs of polymers using Brij-52

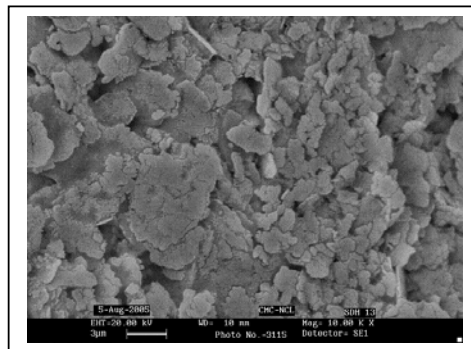


Figure 3.20 b : SEM micrographs of polymers using Span 60

The optical micrographs (40 x magnification) of the polymeric beads synthesised using Brij-52 and Span 60 as surfactants is shown in Figures 3.19a and 3.19b. Beads synthesised using Brij-52 were spherical while beads synthesised using Span 60 were irregular. Figures 3.20a and 3.20b show SEM micrographs of microtomed samples synthesised using Brij-52 and Span 60, respectively. The polymeric beads obtained in case of Brij-52 were smooth and had good mechanical strength. The SEM micrograph of polymer Figure 3.19a shows platelets with irregular pore structure. This may be due to polymerisation of middle phase emulsion due to interaction between monomer, surfactant and internal water that might lead to formation of crystalline phases that on polymerisation lead to generation of pores due to phase separation having a swiss cheese type structure. In case of polymers synthesised using Span 60 the polymers were soft and had poor mechanical strength. Polymers synthesised using Span 60 were gigaporous showing through pores.²⁰



Figure 3.21: Schematic representation of connecting pores of gigaporous material

3.5 Conclusion

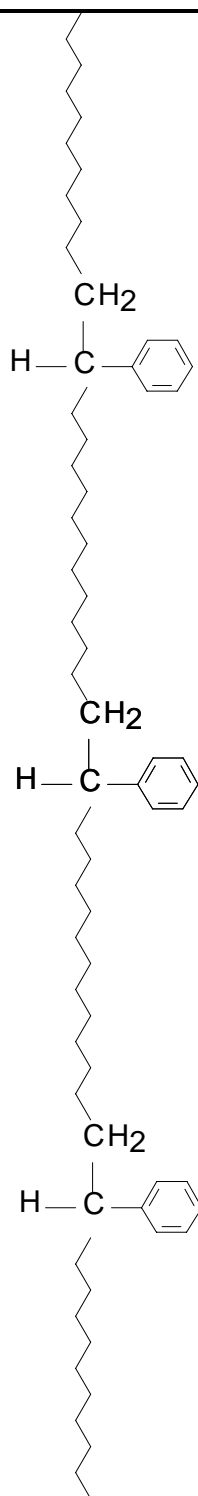
All the above synthesis details and characterisation reveal that the synthesis parameters have a strong influence on the porous properties of the polymer like pore volume, pore size distribution and surface area. Permanent porosity is introduced in cross-linked poly(styrene-co-divinyl benzene) using solvents, nonsolvents or linear polymers as porogen. It is observed that the use of surfactants like Brij-52 can introduce permanent porosity in the polymers, having a pore volume of 0.8-1 cm³/g and surface area of 100-200 m²/g. In cases where Span 60 is used the monomer mixture forms a thick curd like emulsion and the polymers synthesised have very low bulk density (0.1-0.4 g/cm³). The pore volume and surface area of these methods is compared with conventional suspension polymerisation. The results show that polymers synthesised using Brij-52 have high pore volume as well as surface area. Therefore, these polymers can be used as supports in enzyme immobilisation. Polymers synthesised using Span 60 have very high pore volume but low surface area. Therefore these polymers can be used to imbibe or remove contaminants from water. Polymers synthesised using suspension polymerisation and solvent as porogen have

low pore volume but very high surface area and in case of nonsolvent as porogen have high pore volume and low surface area. Therefore, poly(styrene-co-divinyl benzene) can be synthesised by different strategies to obtain polymers of particular pore volume and surface area and pore size distribution, as required for specific applications.

3.6 References

- 1 P. J. Dowding and B. Vincent, *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, **161**, 259 (2000).
- 2 D. Horak, F. Lednicky and M. Bleha, *Polymer*, **37**, 4243 (1996).
- 3 K. Haupke and H. Hoffmann, *J. Chem.* **8**, 463 (1968).
- 4 D. Rabelo and F. M. B. Coutinho, *Eur. Polym. J.*, **30**, 675 (1994).
- 5 F. M. B. Coutinho, C. C. R. Barbosa and S. M. Rezende, *Eur. Polym. J.*, **31**, 1243 (1995).
- 6 F. M. B. Coutinho, V. G. Teixeira and C. C. R. Barbosa, *J. Appl. Polym. Sci.*, **67**, 781 (1998).
- 7 F. M. B. Coutinho, M. L. LaTorre and D. Rabelo, *Eur. Polym. J.*, **34**, 805 (1998).
- 8 H. Guettaf, F. Iayadene, Z. Bencheikh, A. Saggou and I. Rabia., *Eur. Polym. J.*, **34**, 241 (1998).
- 9 K. Hosoya, S. Maroya, K. Kimata, H. Kinoshita, T. Araki and N. Tanaka, *J. Chromatogr.*, **625**, 121 (1992).
- 10 B. N. Kolarz, M. Wojaczynska and A. W. Trochimczuk, *Makromol. Chem. Macromol. Chem. Phys.*, **194**, 1299 (1993).
- 11 I. Kucuk, A. Kuyulu and O. Okay, *Polym. Bul.*, **35**, 511 (1995).
- 12 I. C. Poinescu and C. D. Vlad, *Eur. Polym. J.*, **33**, 1515 (1997).
- 13 D. C. Sherrington, *Chem. Commun.*, 2275 (1998).
- 14 L. M. Gan, J. Liu, L. P. Poon, C. H. Chew and L. H. Gan, *Polymer*, **38**, 5339 (1997).
- 15 M. Sasthav and H. M. Cheung, *Langmuir*, **7**, 1378 (1991).

- 16** X. X. Zhu, K. Banana and R. Yen, *Macromolecules*, **30**, 3031 (1997).
- 17** W. R. P. Raj, M. Sasthav and H. M. Cheung, *Langmuir*, **7**, 2586 (1991).
- 18** M. Korhonen, J. Hirvonen, L. Peltonen, O. Antikainen, L. Yrjanainen and J. Yliruusi, *International Journal of Pharmaceutics*, **269**, 227 (2004).
- 19** A. Kotha, R. C. Raman, S. Ponrathnam, J. G. Shewale, *Reactive & Functional Polymers*, **28**, 227, (1996).
- 20** T. Gu, W. Zhou, G. Ma and Z. Su, *China Particology*, **3**, 349,(2005).



**SYNTHESIS AND EVALUATION
OF LOW CROSS-LINK DENSITY
POROUS POLYMERS FOR
IMBIBING**

4 Synthesis and evaluation of low cross-link density porous poly(styrene-co-divinyl benzene) for imbibing

Poly(styrene-co-divinyl benzene) having a very low cross-link density of 1%, 0.5% and 0.25% were synthesised using Span 60 as surfactant. Internal water in HIPE formation, stirring speed, surfactant concentration and nonsolvent, were varied to study their effect on porosity, surface area and its solvent uptake capacity.

4.1 Synthesis of poly(styrene-co-divinyl benzene) with 1% cross-link density

Poly(styrene-co-divinyl benzene) having 1% cross-link density were synthesised using Span 60 by varying the reaction parameters shown in Table 4.1. The effect of variation in reaction parameters on pore volume, pore size distribution and surface area of the polymers were studied.

Table 4.1 Effect on pore volume and surface area of compositions of 1% cross-linked poly(styrene-co-divinyl benzene) synthesised using Span-60 with variation in (a) inner water (b) heptane volume (c) surfactant concentration and (d) stirring time

Polymer Code	Inner water mL	Heptane mL	Surfactant (g)	Stirring Time (min)	Pore volume cm ³ /g	Surface area m ² /g
IM-1	9	-	3.2	5	1.38	5.50
IM-2	4.5	-	3.2	5	0.90	16.41
IM-3	18	-	3.2	5	2.18	8.11
IM-4	9	-	3.2	5	1.38	5.50
IM-5	9	4.5	3.2	5	3.78	13.03
IM-6	9	18	3.2	5	1.87	15.25
IM-8	9	-	0.8	5	1.69	7.88
IM-7	9	-	1.6	5	1.55	23.60
IM-9	9	-	2.4	5	1.56	12.41
IM-10	9	-	6.4	5	1.14	5.43
IM-1	9	-	3.2	5	1.37	5.50

IM-11	9	-	3.2	10	2.06	8.86
IM-12	9	-	3.2	15	2.22	-
IM-13	9	-	3.2	20	1.72	8.86
IM-14	9	-	3.2	25	1.68	20.90

Styrene (8.889 mL, 0.0775 mole), divinyl benzene (0.110 mL, 7.72×10^{-4} mole), polymerisation temperature = 70°C, polymerisation time = 16 hours, water outer phase= 200 mL, AIBN = 0.636 g, PVP = 1 g, RPM = 250, Agitator = Ruston turbine, 8 bladed. Oil phase: surfactant: Span 60- 3.2 g, AIBN = 0.636 g, pore volume- determined by mercury porosimetry, surface area- determined by B.E.T surface area method.

Table 4.2 Styrene (ST)-co-divinyl benzene (DVB) copolymers of 1% cross-link density synthesised by suspension polymerisation. Effect of solvent (heptane) on pore volume and surface area

Polymer Code	Styrene		DVB		Inner Water mL	Pore volume cm ³ /g	Surface Area m ² /g
	Volume mL	mole	Volume mL	mole			
IM-15	8.889	0.0775	0.110	7.72×10^{-4}	9	0.6463	3.06
IM-16	8.889	0.0775	0.110	7.72×10^{-4}	-	0.4269	0.71

polymerisation temperature = 70°C, polymerisation time = 16 hours, water outer phase= 200 mL, AIBN = 0.636 g, PVP = 1 g, RPM = 250, Agitator = Ruston turbine, 8 bladed.

4.2 Synthesis of poly(styrene-co-divinyl benzene) of 0.5% cross-link density

Poly(styrene-co-divinyl benzene) having 0.5% cross-link density were synthesised using Span 60 by varying the reaction parameters shown in Table 4.3. The effect of these on pore volume, pore size distribution and surface area were studied.

Table 4.3 Effect on pore volume and surface area of compositions of 0.5% cross-linked poly(styrene-co-divinyl benzene) synthesised using Span-60 with variation in (a) inner water (b) heptane volume (c) surfactant concentration and (d) stirring time

Polymer Code	Inner water mL	Heptane mL	Surfactant (g)	Stirring Time (min)	Pore volume cm ³ /g	Surface area m ² /g
IAB-1	9	-	3.2	5	0.63	8.19
IAB -2	4.5	-	3.2	5	-	5.50
IAB -3	18	-	3.2	5	0.93	5.68
IAB -4	9	-	3.2	5	0.78	8.21
IAB -5	9	4.5	3.2	5	1.79	3.72
IAB -6	9	18	3.2	5	1.47	-
IAB -8	9	-	0.8	5	1.45	10.95
IAB -7	9	-	1.6	5	2.36	18.02
IAB -9	9	-	2.4	5	2.36	18.02
IAB -10	9	-	6.4	5	1.38	1.16
IAB -11	9	-	3.2	10	1.24	11.42
IAB -12	9	-	3.2	15	1.78	8.02
IAB -13	9	-	3.2	20	1.57	10.13
IAB -14	9	-	3.2	25	1.81	8.96

Styrene (8.944 mL, 0.0780 mole), divinyl benzene (0.055 mL, 3.89x10⁻⁴ mole), CLD = Cross-link density, polymerisation temperature = 70°C, polymerisation time = 16 hours, water outer phase= 200 mL, AIBN = 0.636 g, PVP = 1 g, RPM = 250, Agitator = Ruston turbine, 8 bladed, Oil phase: surfactant: Span 60- 3.2 g, AIBN = 0.636 g, pore volume- determined by mercury porosimetry, surface area- determined by B.E.T surface area method.

Table 4.4 Styrene (ST)-co-divinyl benzene (DVB) copolymers of 0.5 % cross-link density synthesised by suspension polymerisation and its effect on pore volume and surface area

Polymer Code	Styrene		DVB		Inner Water mL	Pore volume cm ³ /g	Surface Area m ² /g
	Volume mL	mole	Volume mL	mole			
IAB-15	8.944	0.0781	0.055	3.89x10 ⁻⁴	9	1.04	2.62
IAB-16	8.944	0.0781	0.055	3.89x10 ⁻⁴	-	0.14	-

Polymerisation temperature = 70°C, polymerisation time = 16 hours, water outer phase= 200 mL, AIBN = 0.636 g, PVP = 1 g, RPM = 250, Agitator = Ruston turbine, 8 bladed.

4.3 Synthesis of poly(styrene-co-divinyl benzene) of 0.25% cross-link density

Poly(styrene-co-divinyl benzene) having 0.25% cross-link density were synthesised using Span 60 by varying the reaction parameters as shown in Table 4.5. The effect of variation in reaction parameters on pore volume, pore size distribution and surface area of the polymers were investigated.

Table 4.5 Effect on pore volume and surface area of 0.25% cross-linked poly(styrene-co-divinyl benzene) synthesised using Span-60 with variation in (a) inner water (b) heptane volume (c) surfactant concentration and (d) stirring time

Polymer Code	Inner water mL	Heptane mL	Surfactant (g)	Stirring Time (min)	Pore volume cm ³ /g	Surface area m ² /g
IA-1	9	-	3.2	5	2.21	0.94
IA-2	4.5	-	3.2	5	0.99	16.41
IA-3	18	-	3.2	5	1.24	1.38
IA-4	9	9	3.2	5	2.04	16.91
IA-5	9	4.5	3.2	5	4.36	14.61
IA-6	9	18	3.2	5	-	1.050
IA-8	9	-	0.8	5	1.09	12.74

IA-7	9	-	1.6	5	1.31	13.37
IA-9	9	-	2.4	5	1.89	2.70
IA-10	9	-	6.4	5	1.68	3.88
IA-1	9	-	3.2	5	2.21	0.94
IA-11	9	-	3.2	10	1.20	0.69
IA-12	9	-	3.2	15	1.54	1.20
IA-13	9	-	3.2	20	2.00	4.60
IA-14	9	-	3.2	25	1.01	0.58

Styrene (8.971 mL, 0.0782 mole), divinyl benzene (0.0278 mL, 1.951×10^{-4} mole), CLD = Cross-link density, polymerisation temperature = 70°C, polymerisation time = 16 hours, water outer phase= 200 mL, AIBN = 0.636 g, PVP = 1 g, RPM = 250, Agitator = Ruston turbine, 8 bladed, Oil phase: surfactant: Span 60- 3.2 g, AIBN = 0.636 g, pore volume- determined by mercury porosimetry, surface area- determined by B.E.T surface area method.

Table 4.6 Styrene (ST)-co-divinyl benzene (DVB) copolymers of 0.25% cross-link density synthesised by suspension polymerisation and its effect on pore volume and surface area

Polymer Code	Styrene		DVB		Inner Water mL	Pore volume cm^3/g	Surface Area m^2/g
	Volume mL	mole	Volume mL	mole			
IA-15	8.971	0.0782	0.03	1.95×10^{-4}	9	1.6514	6.57
IA-16	8.971	0.0782	0.03	1.95×10^{-4}	-	-	-

Polymerisation temperature = 70°C, polymerisation time = 16 hours, water outer phase= 200 mL, AIBN = 0.636 g, PVP = 1 g, RPM = 250, Agitator = Ruston turbine, 8 bladed.

4.4 Properties of imbibing polymers

The bulk density and toluene uptake capacity of the low cross-link density polymers synthesised by making emulsions prior to suspension polymerisation were measured.

4.4.1 Bulk density

Polymer (1 g) was weighed and the volume occupied was measured using a measuring cylinder. The results shown in Tables 4.7-4.9 indicate that the polymers synthesised by the method of emulsion formation comprising of monomer, surfactant and water prior to suspension have a bulk density in the range 0.04-0.35 g/cm³.

4.4.2 Toluene uptake capacity

The toluene uptake capacity of the polymers was measured gravimetrically. Polymer (0.1 g) was weighed and immersed in toluene. After 24 hours the beads were filtered and weighed. The toluene uptake capacity was determined by:

$$\text{Toluene uptake capacity} = \frac{W_{\text{wet}} - W_{\text{dry}}}{W_{\text{dry}}}$$

Table 4.7 Bulk density and toluene uptake capacity of 0.25% cross-linked poly(styrene-co-divinyl benzene)

Polymer Code	Bulk density g /cm ³	Toluene uptake cm ³ /g
IA-1	0.04	1.83
IA-2	0.33	2.98
IA-3	0.25	2.61
IA-4	0.20	1.97
IA-5	0.09	3.96
IA-6	0.08	2.80
IA-7	0.20	2.75
IA-8	0.26	2.71
IA-9	0.14	1.32
IA-10	0.21	1.89

IA-11	0.20	1.91
IA-12	0.21	1.63
IA-13	0.14	2.35
IA-14	0.24	2.24
IA-15	0.18	1.14
IA-16	0.37	0.98

Table 4.8 Bulk density and toluene uptake capacity of 0.5% cross-linked poly(styrene-co-divinyl benzene)

Polymer Code	Bulk density g /cm ³	Toluene uptake cm ³ /g
IAB-1	0.15	3.82
IAB-2	0.23	5.04
IAB-3	0.20	5.13
IAB-4	0.29	3.60
IAB-5	0.11	7.97
IAB-6	0.13	4.20
IAB-7	0.21	4.52
IAB-8	0.19	4.96
IAB-9	0.15	3.87
IAB-10	0.17	4.27
IAB-11	0.23	4.80
IAB-12	0.26	3.94
IAB-13	0.21	5.58
IAB-14	0.22	6.56
IAB-15	0.17	6.97
IAB-16	0.35	3.97

Table 4.9 Bulk density and toluene uptake capacity of 1% cross-linked poly(styrene-co-divinyl benzene)

Polymer Code	Bulk density g /cm³	Toluene uptake cm³/g
IM-1	0.26	4.29
IM-2	0.25	4.43
IM-3	0.14	6.52
IM-4	0.23	4.40
IM-5	0.09	9.16
IM-6	0.16	5.67
IM-7	0.22	4.95
IM-8	0.17	5.69
IM-9	0.17	4.97
IM-10	0.19	5.20
IM-11	0.16	5.80
IM-12	0.15	4.92
IM-13	0.17	4.81
IM-14	0.19	4.67
IM-15	0.16	4.03
IM-16	0.31	4.59

4.5 Results and Discussion

Classical absorbents such as activated charcoal exhibit good absorbent properties but cannot be regenerated. The present study is to synthesise polymeric adsorbents. Sections 4.1-4.3 show details of 0.25%, 0.5% and 1% cross-linked poly(styrene-co-divinyl benzene) synthesised by HIPE methodology varying the internal water, heptane, surfactant concentration and stirring time. Polymers of similar composition were also synthesised by conventional suspension polymerisation with or without porogen. Polymers used in imbibing applications should be very marginally cross-linked to prevent from dissolving in fluid being imbibed, but not enough to inhibit swelling necessary for imbibing.¹

Tables 4.7-4.9 show the bulk density and toluene uptake capacity of the polymers. The polymers have extremely low density of about 0.1-0.35 g/cm³.

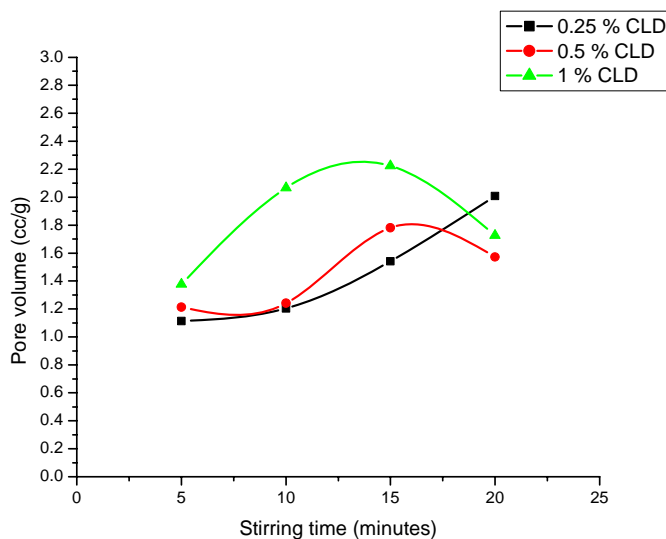


Figure 4.1 : Effect of HIPE stirring time on pore volume of poly(styrene-co-divinyl benzene) having 0.25 %, 0.5 % and 1 % cross-link density

The effect of HIPE stirring time on the pore volume of the polymers with 0.25 %, 0.5 % and 1 % cross-link is shown in Figure 4.1. An increase in pore volume is

observed with increase in stirring time. This shows that it takes a specific time to form a relatively stable HIPE emulsion even at low cross-link density studied here. Increase in cross-link density leads to increase in pore volume. The pore size distribution shows that as the HIPE stirring time increases an increase in pore radii is observed. As the stirring time increases, the % of pore radii in 3-25 nm decreases and maximum pores having pore radii of 250-500 nm are obtained. For 20 min, stirring time pore radii in the range up to 1000-1250 nm are obtained. Stirring time of HIPE plays an important role in the pore size distribution of porous materials. The detailed pore size distribution (volume %) with effect of stirring time, is shown in Figures 4.2 and 4.3.

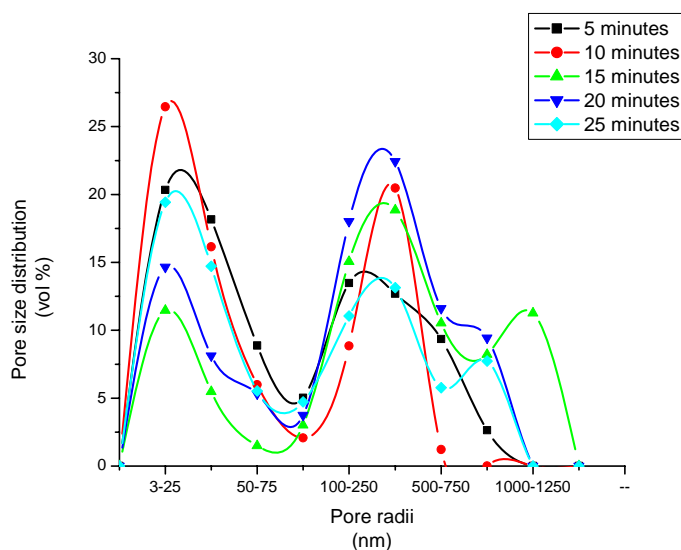


Figure 4.2 : Effect of stirring time on pore size distribution (vol %) of IM series poly(styrene-co-divinyl benzene) synthesised using Span 60 having 1% cross-link density

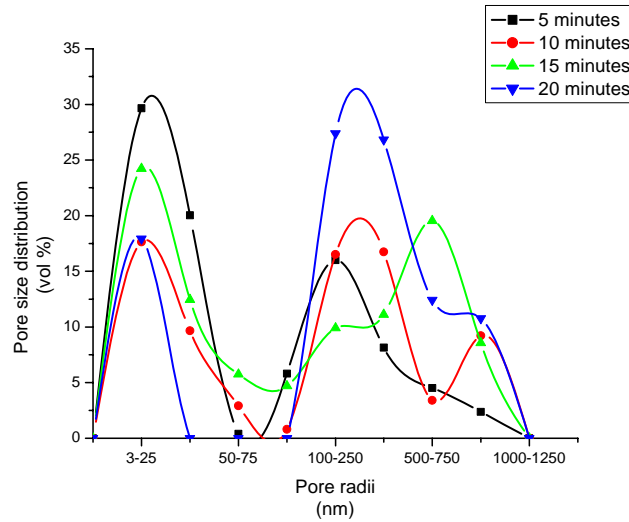


Figure 4.3 : Effect of stirring time on pore size distribution (vol %) of IAB series poly(styrene-co-divinyl benzene) synthesised using Span 60 having 0.5% cross-link density

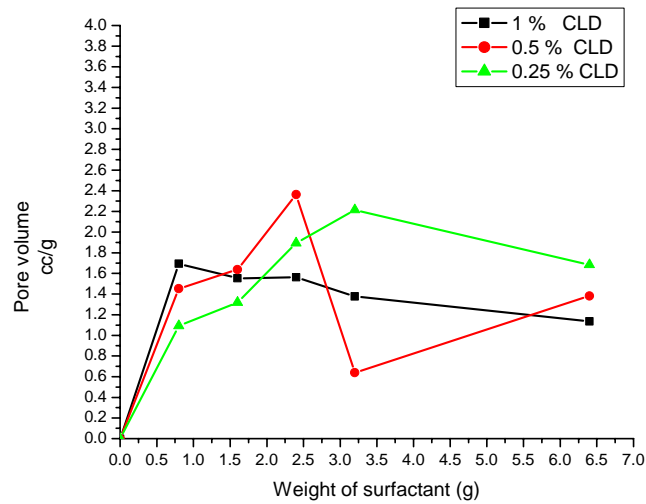


Figure 4.4 : Effect on pore volume of poly(styrene-co-divinyl benzene) synthesised with variation in surfactant concentration and cross-link density

Surfactant plays an important role in formation of emulsion as the interfacial tension is dependent on it. Low interfacial tension will favour the dispersion of

internal phase.² An increase in pore volume is observed in Figure 4.4 for monomer:surfactant ratio of 1:0.08, 1:0.17 and 1:0.28. As the cross-link density increases from 0.25 % to 0.5 % an increase in pore volume is observed. At 1% CLD increase in surfactant concentration leads to a decrease in pore volume. This shows that surfactant is one of the main constituents in emulsion formation and the nature and concentration of emulsion is important in formation of pore structure and size. Increase in DVB content gives rise to a greater number of networks. As a result, the number of micropores is increased, thereby decreasing the pore volume.

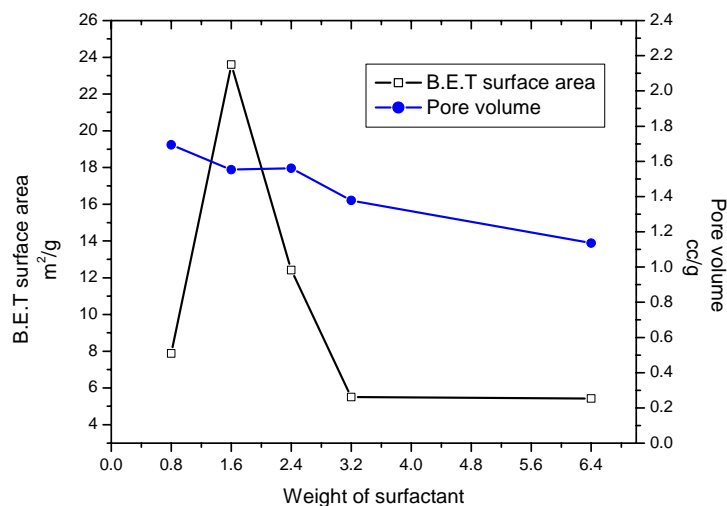


Figure 4.5 : Effect of surfactant concentration on pore volume and surface area of poly(styrene-co-divinyl benzene) having 1% cross-link density

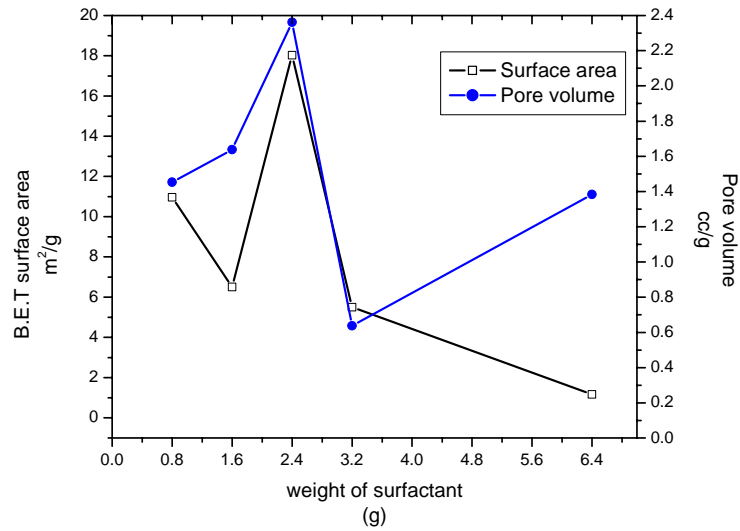


Figure 4.6 : Effect of surfactant concentration on pore volume and surface area of poly(styrene-co-divinyl benzene) having 0.5% cross-link density

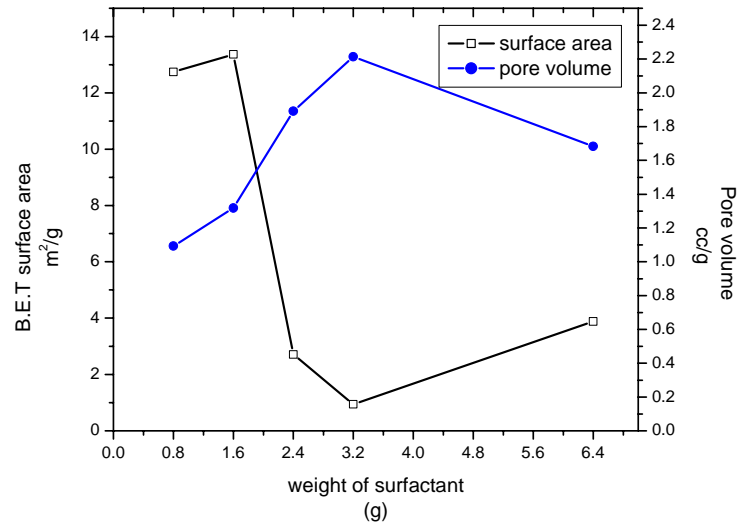


Figure 4.7 : Effect of surfactant concentration on pore volume and surface area of poly(styrene-co-divinyl benzene) having 0.25% cross-link density

Figures 4.5-4.7 show the effect of surfactant concentration on pore volume and surface area at three different cross-link densities. For 0.25 % CLD increase in amount of surfactant leads to increase in pore volume and decrease in surface area. For 0.5 % CLD an increase in surface area as well as pore volume is observed. At

higher concentration decrease in surface area while increase in pore volume is observed. At 1% CLD a decrease in pore volume as well as surface area of the polymers is observed. Thus, cross-linking is also an important parameter in generation of morphology of porous resins, contributing to controlling the point of phase separation of the growing polymer matrix.⁴

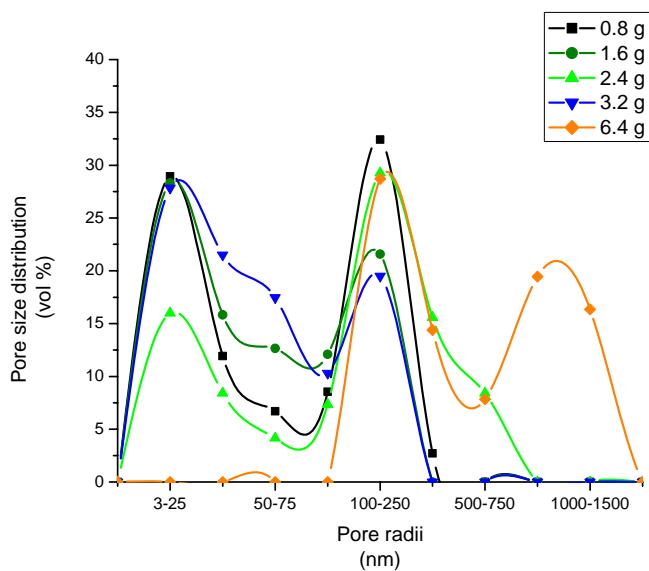


Figure 4.8 : Effect of surfactant concentration on pore size distribution (vol%) of poly(styrene-co-divinyl benzene) having 0.25 % cross-link density

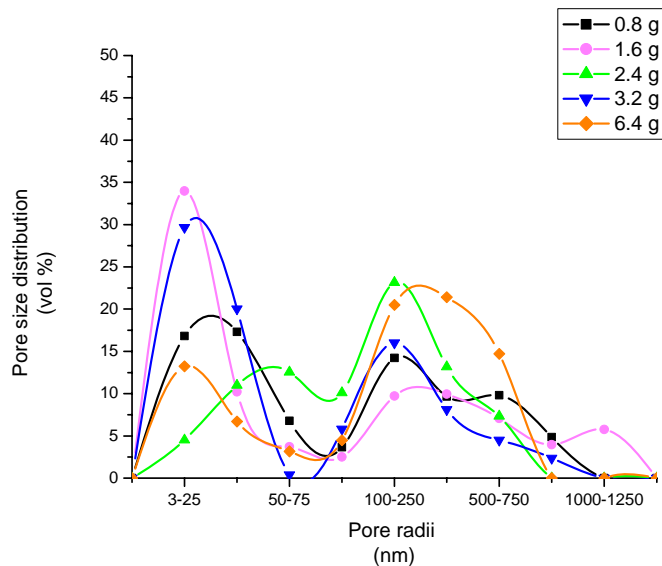


Figure 4.9 : Effect of surfactant concentration on pore size distribution (vol %) of poly(styrene-co-divinyl benzene) having 0.5 % cross-link density

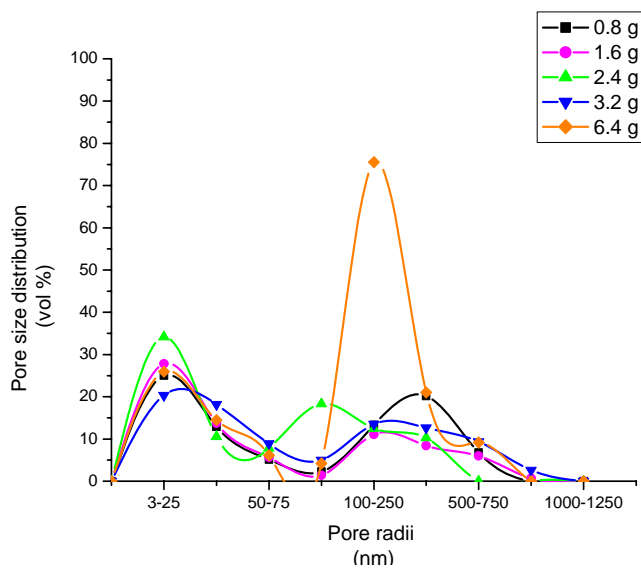


Figure 4.10 : Effect of surfactant concentration on pore size distribution (vol %) of poly(styrene-co-divinyl benzene) having 1% cross-link density

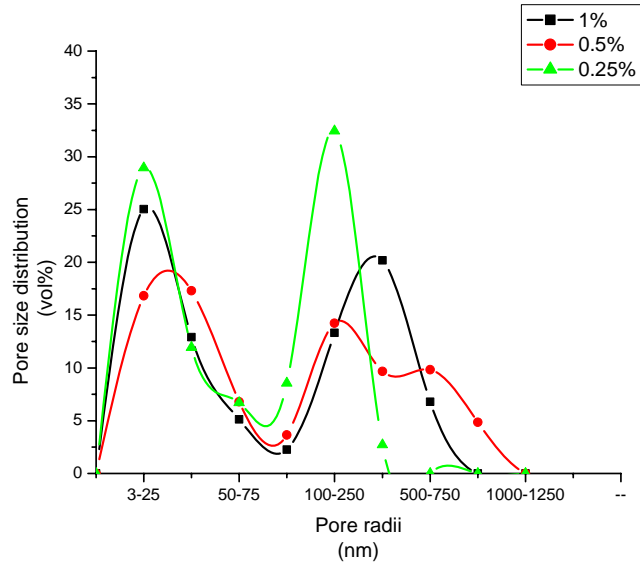


Figure 4.11 : Comparison of effect of oil:surfactant ratio of 1:0.08 on pore size distribution (vol%) of poly(styrene-co-divinyl benzene) with variation in cross-link density

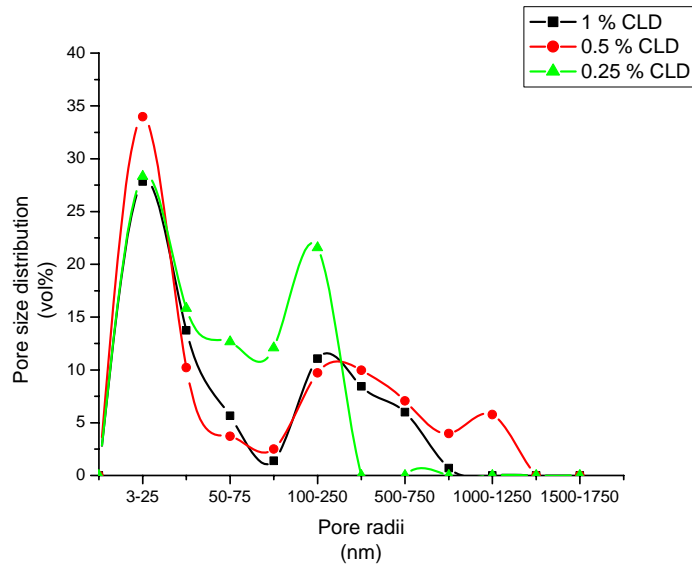


Figure 4.12 : Comparison of effect of oil:surfactant ratio of 1:0.17 on pore size distribution (vol%) of poly(styrene-co-divinyl benzene) with variation in cross-link density

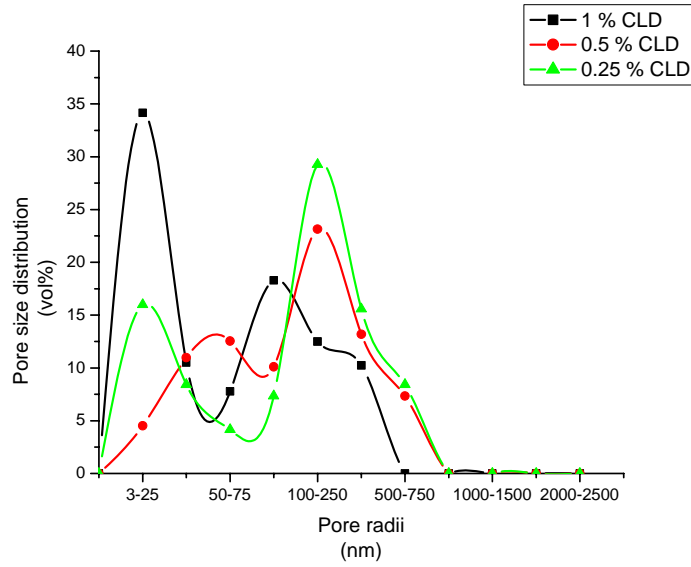


Figure 4.13 : Comparison of effect of oil:surfactant ratio of 1:0.26 on pore size distribution (vol%) of poly(styrene-co-divinyl benzene) with variation in cross-link density

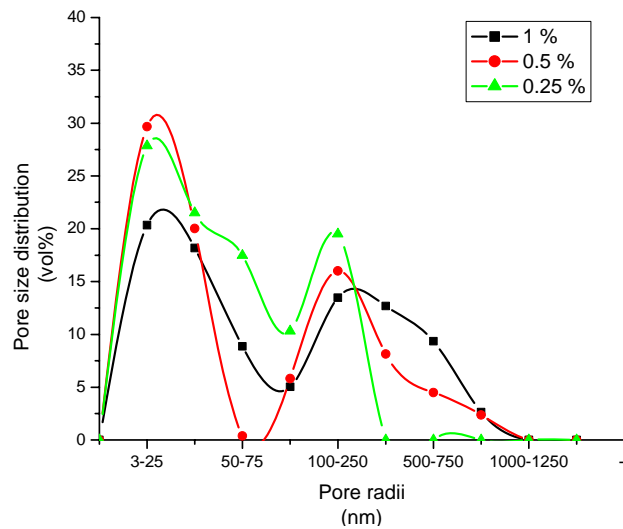


Figure 4.14 : Comparison of effect of oil:surfactant ratio of 1:0.35 on pore size distribution (vol%) of poly(styrene-co-divinyl benzene) with variation in cross-link density

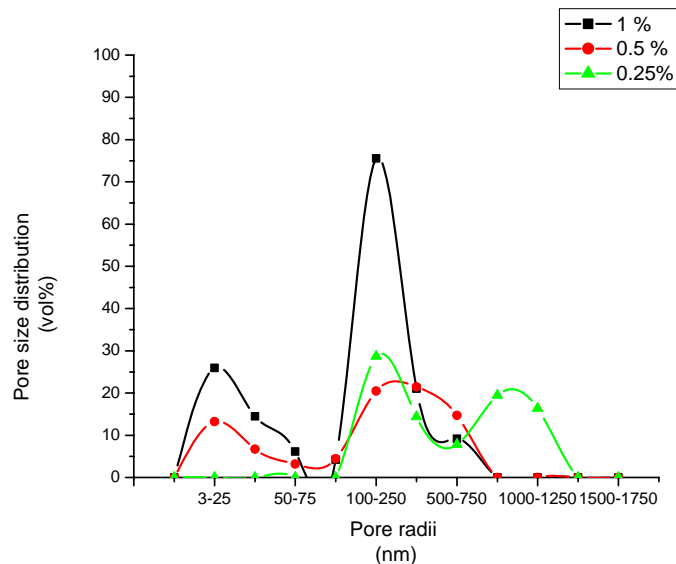


Figure 4.15 : Comparison of effect of oil:surfactant ratio of 1:0.71 on pore size distribution (vol%) of poly(styrene-co-divinyl benzene) with variation in cross-link density

The volume percent pore size distribution for different surfactant concentrations with variation in cross-link density is depicted in Figures 4.8-4.10. It is observed that polymers having 0.25% and 0.5% cross-link density, pore radii up to 1000-1500 nm are obtained. An increase in pore radii of polymer is observed with increase in surfactant concentration. Surfactant decreases the interfacial tension and as a result the cell size increases.³ A series of polymers were synthesised varying the ratio of monomer:surfactants as 1:0.08, 1: 0.17, 1:0.26, 1: 0.35, and 1:0.71. Figures 4.11-4.15 show the volume percent pore size distribution for different cross-link density at a particular surfactant concentration. In all cases it is observed that the divinyl comonomer concentration along with surfactant is important in defining the pore size of the polymers. At a particular point the surfactant acts as precipitant causing an earlier phase separation giving rise to pores having pore radii in macroporous region. At lower surfactant concentrations pores having pore radii upto 1500 nm are obtained. At extremely high surfactant concentration, for 1% cross-linked polymer, the pore radii is reduced, with narrow pore size distribution.

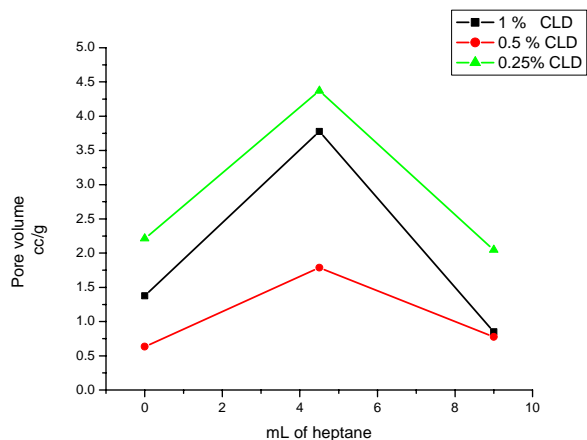


Figure 4.16 : Comparison of effect of heptane concentration in HIPE formation on pore volume of poly(styrene-co-divinyl benzene)

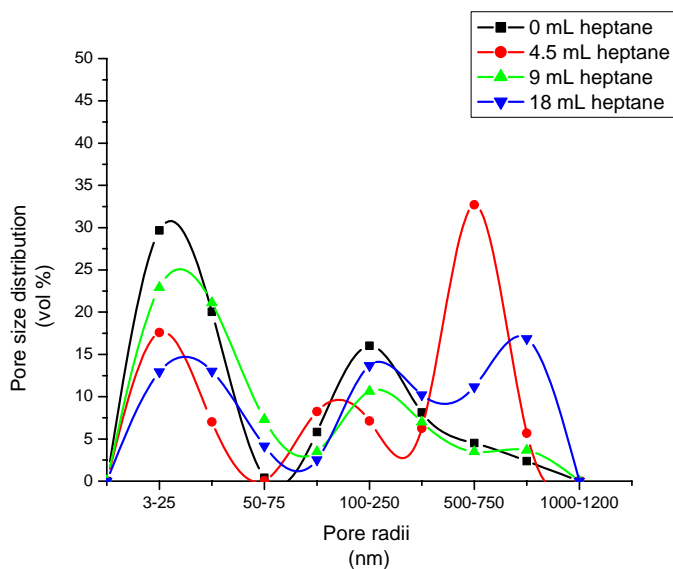


Figure 4.17 : Effect of heptane concentration in HIPE formation on pore size distribution (vol %) of poly(styrene-co-divinyl benzene) having 0.5% cross-link density

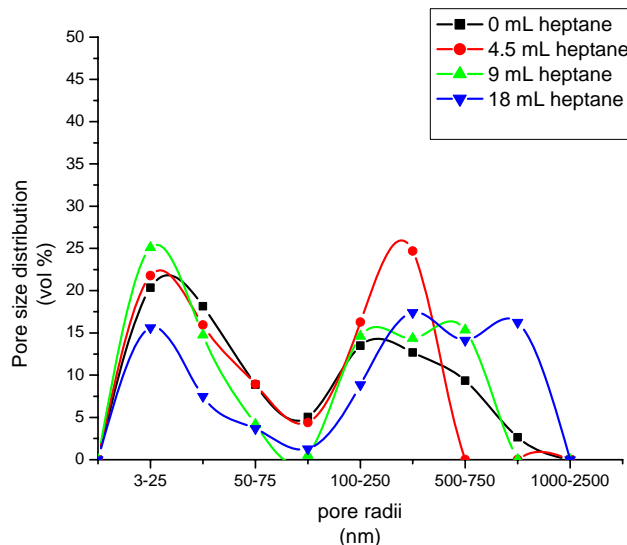


Figure 4.18 : Effect of heptane concentration in HIPE formation on pore size distribution (vol %) of poly(styrene-co-divinyl benzene) having 1% cross-link density

The effect of addition of a diluent (non-solvent for polymer) in oil phase is depicted in Figure 4.16. It is observed that at all cross-link densities the pore volume is maximum in case of monomer : heptane : water ratio 1: 0.5: 1. Figures 4.17 and 4.18 show pore size distribution (vol %) for polymers synthesised using heptane as diluent for polymer in oil phase along with surfactant and monomer. Similar to conventional suspension polymerisation, the non-solvent acts as a porogen. This is the first study of this kind with HIPE polymerisation methodology. It is observed that it gives rise to early phase separation during polymerisation leading to pores in macroporous region.⁵ It is observed that polymers synthesised using 1:0.5:1 (monomer : heptane : water) yielded highly porous polymers having a pore volume of 2.0-4.0 cm³/g and maximum pores having a pore radii in the range of 500-1500 nm.

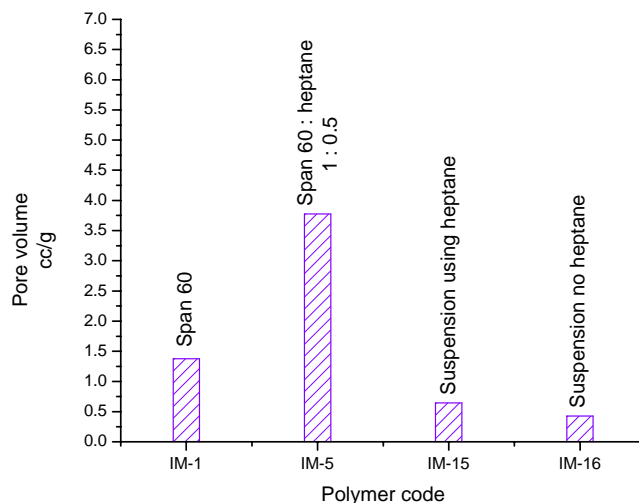


Figure 4.19 : Comparison of pore volume of 1% cross-linked poly(styrene-co-divinyl benzene) synthesised using HIPE suspension or suspension polymerisation (in presence or absence of porogen)

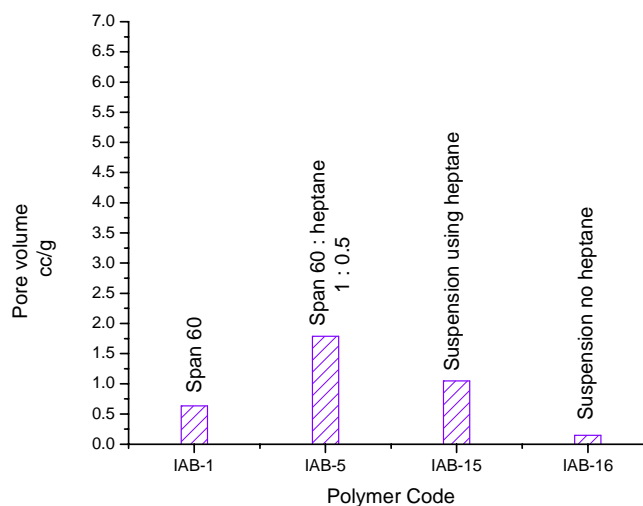


Figure 4.20 : Comparison of pore volume of 0.5% cross-linked poly(styrene-co-divinyl benzene) synthesised using HIPE suspension or suspension polymerisation (in presence or absence of porogen)

A comparison of porosity for polymers synthesised by suspension polymerisation but variation in oil phase is made in Figures 4.19 and 4.20. In cases

when Span 60 was used as surfactant an emulsion is formed prior to addition of oil phase in outer aqueous phase. The emulsion was prepared by adding either a non-solvent to the oil phase or without adding it. Others are conventional suspension polymers synthesised with and without porogen. It is observed that polymers synthesised in case of emulsions in presence of non-solvent and then polymerised in the form of beads have maximum porosity followed by synthesis using just a surfactant. Polymers synthesised by suspension polymerisation have less pore volume compared to that synthesised by emulsion method.

Pore size distribution (vol %) of the polymers synthesised by above mentioned 4 different strategies are presented in Figures 4.21 and 4.22. Polymers synthesised without porogen and by suspension polymerisation have maximum pore radii in 3-25 nm range. Polymers synthesised using a porogen have wide distribution of pore radii in range of 100-250 nm and few pores having radii of 750 nm. In polymers synthesised in presence of surfactants about 20 % of pores have radii in 3-25 nm range. In case of 1 % CLD, 60% of pores are in radii range of 100-750 nm. If porogen is added to the oil phase in emulsion formation, as in the case of 1% CLD polymers, 25 % of pores have pore radii in the range 250-500 nm. On increasing CLD up to 0.5 %, 30% of the pores are in the range 500-750 nm. Increase in divinyl co-monomer gives rise to greater number of cross-links in polymers. Therefore, the pore radii in the polymers decrease.

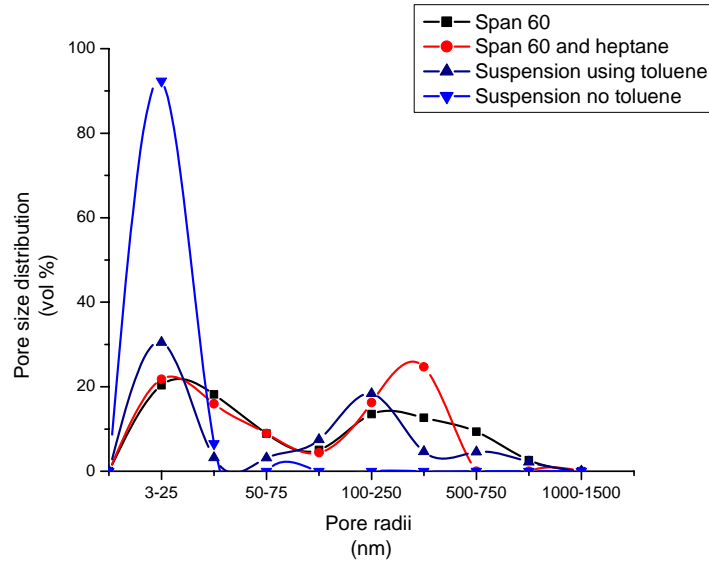


Figure 4.21 : Comparison of pore size distribution (vol%) of polymers having 1% cross-link density synthesised using HIPE suspension or suspension polymerisation (in presence or absence of porogen)

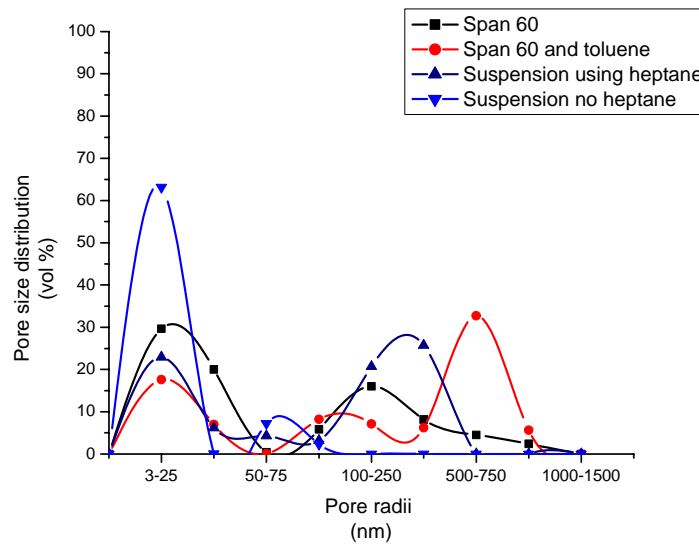


Table 4.22 : Comparison of pore size distribution (vol%) of polymers having 0.5% cross-link density synthesised using HIPE suspension or suspension polymerisation (in presence or absence of porogen)

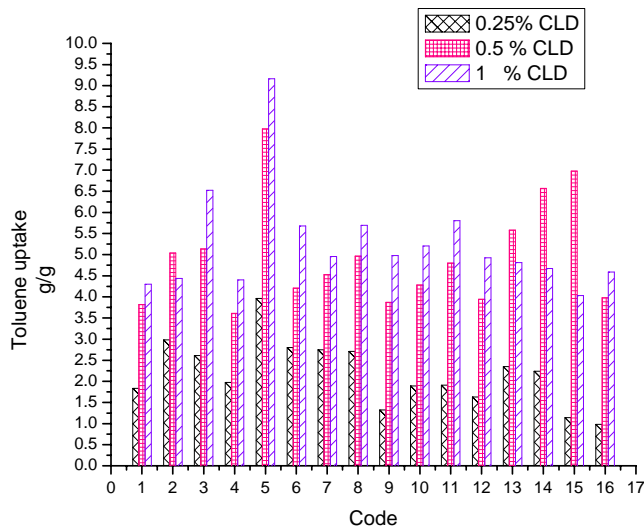


Figure 4.23 : Comparison of toluene uptake capacity of poly(styrene-co-divinyl benzene) having different cross-link density

All the polymers synthesised were tested for uptake of toluene. Figure 4.23 shows the toluene uptake capacity. Maximum uptake is obtained for polymers synthesised by preparing emulsion prior to suspension, having the concentration ratio of 1: 0.5: 1 of monomer : heptane : water for 0.25 %, 0.5 % and 1 % CLD. The swelling index of the polymer for imbibing applications must be at least 1.5, while 3 is desirable. Figure 4.23 shows that for all the polymers synthesised here the swelling index are between 1.5 and 9.

Figures 4.24-4.27 show the effect of variation in reaction parameter such as internal water, heptane, surfactant and stirring time effect on the toluene uptake capacity of the polymers. These parameters affect the imbibing capacity of the polymers. The figures reveal that variation in reaction parameter leads to difference in pore volume and surface area, and hence difference in solvent uptake capacity is observed. In all cases as the cross-link density increases, the solvent uptake of polymer also increases.

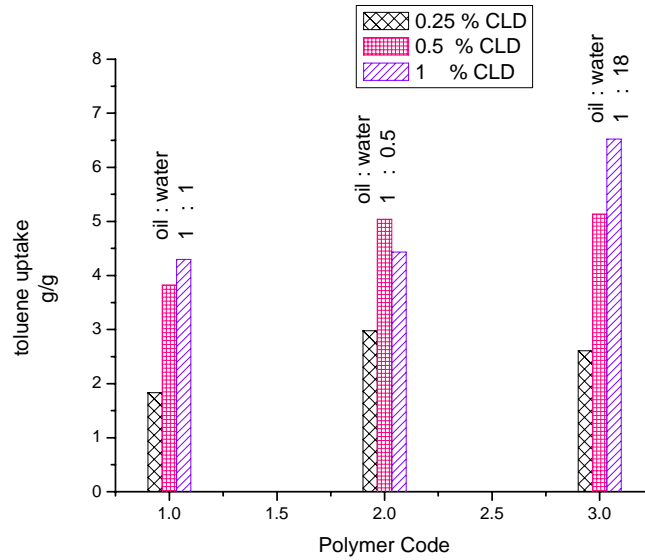


Figure 4.24 : Comparison of toluene uptake capacity of poly(styrene-co-divinyl benzene) having different cross-link density with variation in internal water in HIPE formation

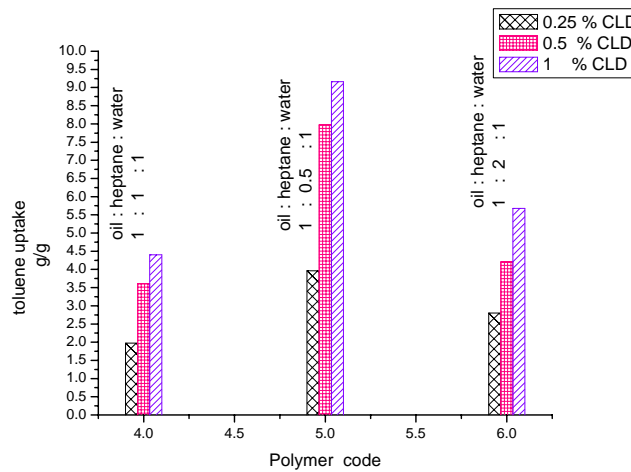


Figure 4.25 : Comparison of toluene uptake capacity of poly(styrene-co-divinyl benzene) having different cross-link density with variation in heptane concentration in HIPE formation

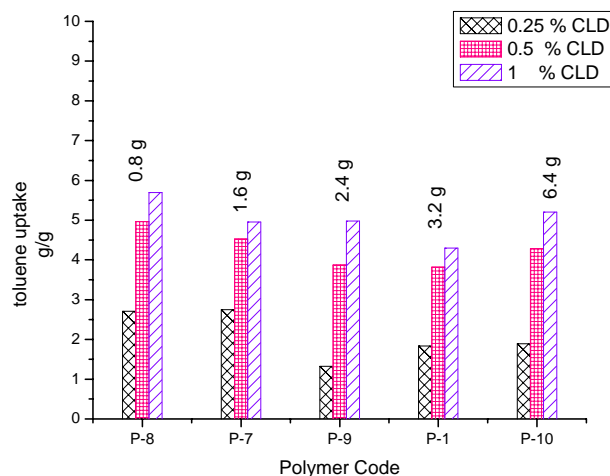


Figure 4.26 : Comparison of toluene uptake capacity of poly(styrene-co-divinyl benzene) having different cross-link density with variation in surfactant concentration in HIPE formation

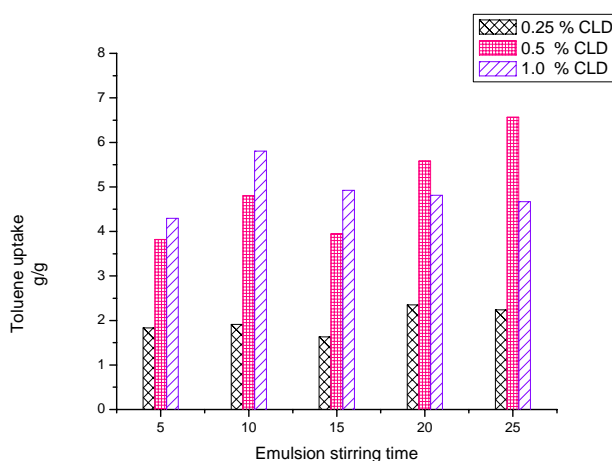


Figure 4.27 : Comparison of toluene uptake capacity of poly(styrene-co-divinyl benzene) having different cross-link density with variation in emulsion stirring time in HIPE formation

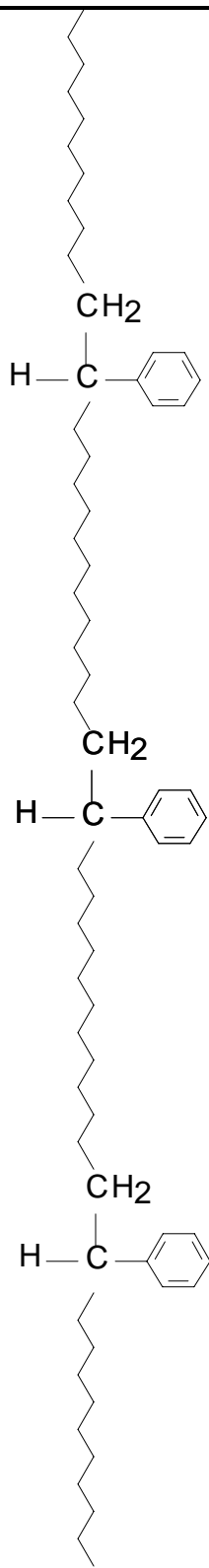
4.6 Conclusion

All the above synthesis details and characterisation reveal that the synthesis parameters have a strong influence on the porous properties of the polymer like pore volume, pore size distribution and surface area. Polymers having low cross-link density of 0.25%, 0.5% and 1% were synthesised by suspension method, but in this

case an emulsion using Span 60 as surfactant, monomer and water is made prior to addition to the outer water phase. The physicochemical character of the oil phase determines how the oil will be surrounded by the water droplet in the emulsion and not the quantity which is studied by varying the surfactant concentration i.e the ratio of surfactant to oil is important than the total amount of monomer or surfactant present. The polymers synthesised had a high pore volume in the range of 0.6-3.77 cm³/g and the surface area of these materials is very low 2-20 m²/g. The low surface area is an anomaly which arises from the evaluation technique due to collapse of the pores. The polymers synthesised by conventional suspension polymerisation had maximum pore radii in 3-25 nm region while polymers synthesised using heptane as porogen had maximum pores having pore radii in 250-500 nm region. In case of polymers synthesised by HIPE using Span 60 maximum pores were in the 250-500 nm range. The maximum solvent uptake obtained is 9.16 in case of 1 % CLD polymer having the composition monomer : heptane : water 1: 0.5:1.

4.7 References

- 1 G. C. Sypniewski, U.S. Patent No. 4,895,909, Issued to The Dow Chemical Company (1990).
- 2 A. Barbetta and N. R. Cameron, *Macromolecules*, **37**, 3188 (2004).
- 3 N. R. Cameron and A. Barbetta, *J. Mater. Chem.*, **10**, 2466 (2000).
- 4 C. Viklund, F. Svec and J. M. J. Frechet, *Chem. Mater.*, **8**, 744 (1996).
- 5 E. Erbay and O Okay, *J. App. Polym. Sci.*, **71**, 1055 (1999).



SYNTHESIS AND EVALUATION OF POLYMERIC MONOLITHS

5.0 Synthesis of poly(styrene-co-divinyl benzene) monoliths by HIPE methodology

5.1 Synthesis by HIPE methodology using thermal initiator

The monomers and the surfactants in requisite amount were first mixed together to constitute the continuous oil phase. The mixture was stirred at 1400 rotations per minute and while stirring requisite amount of water was added as discontinuous phase. After the entire amount of water was added dropwise the mixture was stirred for five minutes, to form a stable white emulsion. The emulsion formed was cured at 65°C to obtain cross-linked polymers in the monolithic form.

Poly(styrene-co-divinyl benzene) monoliths were synthesised by variation in reaction parameters such as cross-link density and amount of internal water in HIPE formation. Polymers having code MSD were synthesised by using mixture of surfactants comprising of ditallow dimethyl ammonium methyl sulphate and polyglycerol mono isostearate. Polymers coded GSD were synthesised using a mixture of ditallow dimethyl ammonium methyl sulphate and polyglycerol succinate.

Table 5.1 Synthesis of 50% cross-linked poly(styrene-co-divinyl benzene) monoliths with first surfactant blend

Polymer code	Water mL	Na ₂ S ₂ O ₈		CaCl ₂ (g)	Surface Area m ² /g
		g	mole		
MSD-150	45	0.09	3.78x10 ⁻⁴	0.5	5.66
MSD-250	90	0.18	7.56x10 ⁻⁴	1	8.22
MSD-350	180	0.36	1.51x10 ⁻⁴	2	6.58
MSD-450	360	0.72	3.02x10 ⁻³	4	15.97

Styrene-5.55 mL (0.0485 mole), DVB-3.45 mL (0.0242 mole), Styrene: DVB 2:1 mole/mole, surfactant- 7 wt% ditallow dimethyl ammonium methyl sulphate and polyglycerol mono isostearate, CaCl₂- 1.1 wt% of water, Na₂S₂O₈ – 0.2 wt% of water

Table 5.2 Synthesis of 100% cross-linked poly(styrene-co-divinyl benzene) monoliths with first surfactant blend

Polymer code	Water mL	Na ₂ S ₂ O ₈		CaCl ₂ (g)	Surface Area m ² /g
		g	mole		
MSD-1100	45	0.09	3.78x10 ⁻⁴	0.5	10.32
MSD-2100	90	0.18	7.56x10 ⁻⁴	1	8.52
MSD-3100	180	0.36	1.51x10 ⁻⁴	2	10.31
MSD-4100	360	0.72	3.02x10 ⁻³	4	15.13

Styrene-4.01 mL (0.0350 mole), DVB-4.99 mL (0.0350 mole), Na₂S₂O₈ – 0.2 wt% of water, Styrene: DVB 1:1 mole/mole, surfactant- 7 wt% ditallow dimethyl ammonium methyl sulphate and polyglycerol mono isostearate, CaCl₂- 1.1 wt% of water.

Table 5.3 Synthesis of 200% cross-linked poly(styrene-co-divinyl benzene) monoliths with first surfactant blend

Polymer code	Water mL	Na ₂ S ₂ O ₈		CaCl ₂ (g)	Surface Area m ² /g
		g	mole		
MSD-1200	45	0.09	3.78x10 ⁻⁴	0.5	8.16
MSD-2200	90	0.18	7.56x10 ⁻⁴	1	8.62
MSD-3200	180	0.36	1.51x10 ⁻⁴	2	10.79
MSD-4200	360	0.72	3.02x10 ⁻³	4	17.30

Styrene-2.75 mL (0.0240 mole), DVB-6.25 mL (0.0439 mole), Na₂S₂O₈ – 0.2 wt% of water, Styrene: DVB 1:2 mole/mole, surfactant- 7 wt% ditallow dimethyl ammonium methyl sulphate and polyglycerol mono isostearate, CaCl₂- 1.1 wt% of water

Table 5.4 Synthesis of 50% cross-linked poly(styrene-co-divinyl benzene) monoliths with second surfactant blend

Polymer code	Water mL	Na ₂ S ₂ O ₈		CaCl ₂ (g)	Surface Area m ² /g	Mercury porosimetry cm ³ /g
		g	mole			
GSD150	45	0.09	3.78x10 ⁻⁴	0.5	3.29	3.17
GSD250	90	0.18	7.56x10 ⁻⁴	1	4.01	7.40

GSD350	180	0.36	1.51×10^{-4}	2	10.21	10.91
GSD450	360	0.72	3.02×10^{-3}	4	18.94	Powdered form

Styrene-5.55 mL (0.0485 mole), DVB-3.45 mL (0.0242 mole), Styrene: DVB 2: 1 mole/mole, $\text{Na}_2\text{S}_2\text{O}_8$ – 0.2 wt% of water, Styrene: DVB 2:1 mole/mole, surfactant- 7 wt% ditallow dimethyl ammonium methyl sulphate and poly glycerol succinate, CaCl_2 - 1.1 wt% of water

Table 5.5 Synthesis of 100% cross-linked poly(styrene-co-divinyl benzene) monoliths with second surfactant blend

Polymer code	Water mL	$\text{Na}_2\text{S}_2\text{O}_8$		CaCl_2 (g)	Surface Area m^2/g	Mercury porosimetry cm^3/g
		g	mole			
GSD1100	45	0.09	3.78×10^{-4}	0.5	3.35	3.89
GSD2100	90	0.18	7.56×10^{-4}	1	9.21	7.16
GSD3100	180	0.36	1.51×10^{-4}	2	2.53	7.54
GSD4100	360	0.72	3.02×10^{-3}	4	11.91	12.02

Styrene-4.01 mL (0.0350 mole), DVB-4.99 mL (0.0350 mole), $\text{Na}_2\text{S}_2\text{O}_8$ – 0.2 wt% of water, Styrene: DVB 1:1 mole/mole, surfactant- 7 wt% ditallow dimethyl ammonium methyl sulphate and polyglycerol succinate, CaCl_2 - 1.1 wt% of water

Table 5.6 Synthesis of 200% cross-linked poly(styrene-co-divinyl benzene) monoliths with second surfactant blend

Polymer code	Water mL	$\text{Na}_2\text{S}_2\text{O}_8$		CaCl_2 (g)	Surface Area m^2/g
		g	mole		
GSD1200	45	0.09	3.78×10^{-4}	0.5	3.18
GSD2200	90	0.18	7.56×10^{-4}	1	9.07
GSD3200	180	0.36	1.51×10^{-4}	2	5.75
GSD4200	360	0.72	3.02×10^{-3}	4	10.64

Styrene-2.75 mL (0.0240 mole), DVB-6.25 mL (0.0439 mole), $\text{Na}_2\text{S}_2\text{O}_8$ – 0.2 wt% of water, Styrene: DVB 1:2 mole/mole, surfactant- 7 wt% ditallow dimethyl ammonium methyl sulphate and polyglycerol succinate, CaCl_2 - 1.1 wt% of water

5.2 Postmodification of poly(styrene-co-divinyl benzene) monoliths

5.2.1 Preparation of sulphonic acid derivatives

The monoliths synthesised were cut into pieces of approximately 1 cm size. 2 g of polymer was wetted with 30 mL 1,2-dichloromethane for half an hour and 10 mL (0.150 mole) of chlorosulphonic acid was added to the above mixture. The reaction was carried out for 48 h, filtered and solid polymer was chilled in ice cold water. The polymers were washed several times with water to remove the excess acid until the filtrate was neutral to pH.

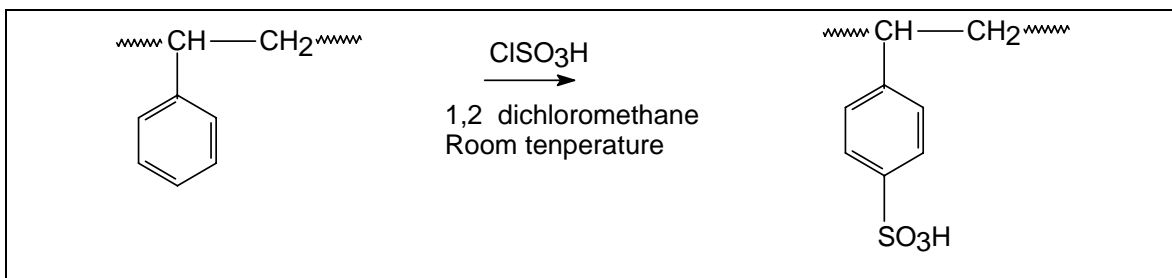


Figure 5.1: Schematic representation of sulphonation

The acid capacity of the sulphonated resins was estimated by acid base titration. Sulphonated polymer (0.1g) was converted into SO₃Na form by equilibrating with 25 mL 0.1 N sodium hydroxide. After 16 hours the mixture was titrated against 0.1 N HCl solution using phenolphthalein indicator. The consumed moles of sodium hydroxide were determined by back titration with hydrochloric acid. The synthesis details and acid capacity of polymers are tabulated in Tables 5.7-5.12.

Table 5.7 Sulphonation of 50% cross-linked poly(styrene-co-divinyl benzene) synthesised using surfactant having polyglycerol mono isostearate as part surfactant

Polymer Code	Dichloromethane (mL)	Chlorosulphonic acid (mL)	Acid capacity (meq/g)
MSD-150	30	10	3.20
MSD-250	30	10	3.00
MSD-350	30	10	2.61
MSD-450	30	10	3.00

Table 5.8 Sulphonation of 100% cross-linked poly(styrene-co-divinyl benzene) synthesised using polyglycerol mono isostearate as part surfactant

Polymer Code	Dichloromethane (mL)	Chlorosulphonic acid (mL)	Acid capacity (meq/g)
MSD-1100	30	10	2.81
MSD-2100	30	10	2.91
MSD-3100	30	10	1.94

Table 5.9 Sulphonation of 200% cross-linked poly(styrene-co-divinyl benzene) synthesised using polyglycerol mono isostearate as part surfactant

Polymer Code	Dichloromethane (mL)	Chlorosulphonic acid (mL)	Acid capacity (meq/g)
MSD-1200	30	10	3.68
MSD-2200	30	10	2.52
MSD-3200	30	10	2.52
MSD-4200	30	10	2.71

Table 5.10 Sulphonation of 50% cross-linked poly(styrene-co-divinyl benzene) synthesised polyglycerol succinate as part surfactant

Polymer Code	Dichloromethane (mL)	Chlorosulphonic acid (mL)	Acid capacity (meq/g)
GSD-150	30	10	3.78
GSD-250	30	10	3.00
GSD-350	30	10	2.42
GSD-450	30	10	2.32

Table 5.11 Sulphonation of 100% cross-linked poly(styrene-co-divinyl benzene) synthesised using polyglycerol succinate as part surfactant

Polymer Code	Dichloromethane (mL)	Chlorosulphonic acid (mL)	Acid capacity (meq/g)
GSD-1100	30	10	3.10
GSD-2100	30	10	2.42
GSD-3100	30	10	2.61
GSD-4100	30	10	2.42

Table 5.12 Sulphonation of 200% cross-linked poly(styrene-co-divinyl benzene) synthesised using surfactant having polyglycerol succinate

Polymer Code	Dichloromethane (mL)	Chlorosulphonic acid (mL)	Acid capacity (meq/g)
GSD-1200	30	10	3.58
GSD-2200	30	10	3.68
GSD-3200	30	10	2.23
GSD-4200	30	10	2.32

5.3 Solvent uptake capacity of polymers synthesised using thermal initiators

The solvent uptake capacity of the polymers prepared using thermal initiators was tested gravimetrically. The imbibing capacity of water, methanol (non-solvent for polystyrene) and toluene (solvent for polystyrene) for poly(styrene-co-divinyl benzene) were measured.

Table 5.13 Solvent uptake for 50% cross-linked polymers synthesised using polyglycerol mono isostearate as part surfactant

Polymer Code	Equilibrium water content (g/g)	Equilibrium methanol content (g/g)	Equilibrium toluene content (g/g)
MSD-150	3.48	3.31	4.45
MSD-250	3.69	7.68	9.71
MSD-350	2.13	10.25	13.56
MSD-450	6.31	22.56	29.87

Table 5.14 Solvent uptake for 100% cross-linked polymers synthesised using polyglycerol mono isostearate as part surfactant

Polymer Code	Equilibrium water content (g/g)	Equilibrium methanol content (g/g)	Equilibrium toluene content (g/g)
MSD-1100	0.68	4.28	5.46
MSD-2100	1.33	5.51	6.62
MSD-3100	2.08	9.62	13.70
MSD-4100	2.37	29.60	20.95

Table 5.15 Solvent uptake for 200% cross-linked polymers synthesised using polyglycerol mono isostearate as part surfactant

Polymer Code	Equilibrium water content (g/g)	Equilibrium methanol content (g/g)	Equilibrium toluene content (g/g)
MSD-1200	0.41	4.44	5.23
MSD-2200	7.27	6.84	7.39
MSD-3200	1.30	5.31	7.39
MSD-4200	4.80	20.76	20.76

Table 5.16 Solvent uptake for 50% cross-linked polymers synthesised using polyglycerol succinate as part surfactant

Polymer Code	Equilibrium water content (g/g)	Equilibrium methanol content (g/g)	Equilibrium toluene content (g/g)
GSD-150	2.72	3.89	4.89
GSD-250	4.76	6.60	7.72
GSD-350	6.20	9.31	12.61
GSD-450	26.91	36.61	22.22

Table 5.17 Solvent uptake for 100% cross-linked polymers synthesised using polyglycerol succinate as part surfactant

Polymer Code	Equilibrium water content (g/g)	Equilibrium methanol content (g/g)	Equilibrium toluene content (g/g)
GSD-1100	3.45	3.30	4.73
GSD-2100	1.17	7.01	9.11
GSD-3100	7.84	4.72	5.89
GSD-4100	1.99	10.39	9.98

Table 5.18 Solvent uptake for 200% cross-linked polymers synthesised using polyglycerol succinate as part surfactant

Polymer Code	Equilibrium water content (g/g)	Equilibrium methanol content (g/g)	Equilibrium toluene content (g/g)
GSD-1200	3.89	3.87	3.94
GSD-2200	5.24	6.067	7.12
GSD-3200	1.30	11.22	11.78
GSD-4200	7.50	17.03	10.06

5.4 Sulphonated polymers as solid phase catalysts

The sulphonated polymers were evaluated for their efficiency as heterogeneous solid phase catalysts in esterification reactions of salicylic acid to methyl salicylate.

5.4.1 Synthesis of methyl salicylate using heterogeneous acid catalyst

The methyl ester of salicylic acid was prepared by refluxing salicylic acid (SA) with methanol at 80°C to obtain methyl salicylate. The reactions were carried out using heterogeneous acid (catalyst) prepared by above methodology. The details of reaction are given in Tables 5.19 and 5.20.

The catalyst was added in the ratio 1:1 (SA:catalyst). For polymers above 20 times water the bulk density was very high so the catalyst was added in less proportion.

MSD350 (1:0.498)

MSD 450 (1:0.2029)

GSD 350 (1:0.5)

GSD 450 (1:0.058)

5.4.2 HPLC analysis of salicylic acid esterification to methyl salicylate

Esterification reactions are well known with homogeneous acid catalysts. Present work deals with esterification using sulphonated polymers as solid phase catalysts. Salicylic acid was converted to methyl salicylate in presence of methanol at 80°C and the reaction was monitored by HPLC technique (LDC Analytical with CM 4000 pump and SM4000 UV detector at 254 nm, at ambient temperature, Nucleosil C18 column). The experiments were conducted to optimise the composition of mobile phase to achieve complete base line resolution of the starting compounds and the product. Complete resolution was achieved with eluent 80:20 (v/v) ratio methanol – water mixture with flow rate of 0.7 mL/min. Individual salicylic acid and ester peaks were identified and separated from each other having retention times of 2.28 and 6.15 minutes, respectively. To obtain maximum conversion of the acid the reaction parameters such as reaction time and temperature were varied. The efficiency of different catalysts synthesised was then tested in these esterification reactions and monitored by HPLC. 50 µL of the reaction mixture was diluted with 5 mL of mobile phase and 20 µL sample was injected.

Table 5.19 Esterification of salicylic acid -1

Polymer Code	MeOH mL	Acid capacity of Catalyst meq/g	Actual added catalyst		% conversion
			(g)	(mole)	
MSD-150	10	3.201	1.310	4.199×10^{-3}	77:22
MSD-250	10	3.007	1.396	4.199×10^{-3}	41:58
MSD-350	10	2.619	0.8015	2.095×10^{-3}	33:66
MSD-450 20	10	3.007	0.396	8.520×10^{-4}	50:46

Salicylic acid- 0.58 g (4.19×10^{-3} mole), % conversion monitored by HPLC

Table 5.20 Esterification of salicylic acid-2

Polymer Code	MeOH mL	Acid capacity of Catalyst meq/g	Actual added catalyst		% conversion
			(g)	(mole)	
GSD-150	10	3.783	1.109	4.199×10^{-3}	70 : 22
GSD-250	10	3.007	1.396	4.199×10^{-3}	8 : 91
GSD-350 20	10	2.425	2.425	2.099×10^{-3}	9 : 89
GSD-450 20	10	2.328	0.1015	2.462×10^{-4}	51 : 48

Salicylic acid- 0.58 g (4.19×10^{-3} mole), % conversion monitored by HPLC

5.5 Synthesis of poly(styrene-co-divinyl benzene) monoliths by HIPE using redox initiators

Synthesis of styrene-divinyl benzene cross-linked polymers in high internal phase emulsions using the redox pair of initiator sodium peroxydisulphate-sodium bisulphite was investigated.

A range of different polymers were formed by using 7 wt% of surfactant, monomer, cross-linker along with reductant as oil phase. To the oil phase requisite amount of water with sodium peroxydisulphate was added dropwise with stirring at 1400 rpm to form a stable emulsion. The emulsions are kept for 48 hours at room temperature to allow polymerisation to proceed. The monoliths obtained were washed with water and dried. The polymers were synthesised by varying the surfactant and internal water in HIPE formation. All recorded HIPE synthesis in open literature have been by high temperature thermal initiation. HIPE polymerisation was studied using redox initiation system, sodium peroxydisulphate and sodium bisulphite at room temperature to form open celled, low density monoliths so as to compare with monoliths formed at high temperature.

Table 5.21 Synthesis of 50% cross-linked poly(styrene-co-divinyl benzene) monoliths by HIPE technique using redox initiator

Polymer code	Water mL	Na ₂ S ₂ O ₈ (g)	NaHSO ₃ (g)	Pore volume cm ³ /g	Surface Area m ² /g
GRD 150	45	0.090	0.039	1.79	1.54
GRD 250	90	0.090	0.039	4.48	4.67
GRD 350	180	0.090	0.039	3.76	3.21
GRD 450	270	0.090	0.039	2.22	2.70

Styrene-5.55 mL (0.0485 mole), DVB-3.45 mL (0.0242 mole), Styrene:DVB 2:1 mole/mole, Na₂S₂O₈- (3.780x10⁻⁴), NaHSO₃- (3.780x10⁻⁴), surfactant- 7 wt% ditallow dimethyl ammonium methyl sulphate and polyglycerol succinate; CaCl₂ – 4 wt% of water

Table 5.22 Synthesis of 100% cross-linked poly(styrene-co-divinyl benzene) monoliths by HIPE technique using redox initiator

Polymer code	Water mL	Na ₂ S ₂ O ₈ (g)	NaHSO ₃ (g)	Pore volume cm ³ /g	Surface Area m ² /g
GRD1100	45	0.090	0.039	1.92	2.31
GRD2100	90	0.090	0.039	1.27	2.91
GRD3100	180	0.090	0.039	3.54	1.95
GRD4100	270	0.090	0.039	5.26	3.37

Styrene-4.01 mL (0.0350 mole), DVB-4.99 mL (0.0350 mole), Styrene:DVB 1:1 mole/mole, surfactant- 7 wt% ditallow dimethyl ammonium methyl sulphate and polyglycerol succinate; CaCl₂ – 4 wt% of water

Table 5.23 Synthesis of 200% cross-link density poly(styrene-co-divinyl benzene) monoliths by HIPE technique using redox initiator

Polymer code	Water mL	Na ₂ S ₂ O ₈ (g)	NaHSO ₃ (g)	Pore volume cm ³ /g	Surface Area m ² /g
GRD1200	45	0.090	0.039	1.72	3.22
GRD2200	90	0.090	0.039	4.77	2.14
GRD3200	180	0.090	0.039	3.73	2.38
GRD4200	270	0.090	0.039	5.40	7.45

Styrene-2.75 mL (0.0240 mole), DVB-6.25 mL (0.0439 mole) Styrene:DVB 1:2 mole/mole, Na₂S₂O₈- (3.780x10⁻⁴), NaHSO₃- (3.780x10⁻⁴), surfactant- 7 wt% ditallow dimethyl ammonium methyl sulphate and polyglycerol succinate; CaCl₂ – 4 wt% of water

Table 5.24 Synthesis of 50% cross-linked poly(styrene-co-divinyl benzene) monoliths by HIPE technique using redox initiator-2

Polymer code	Water mL	Na ₂ S ₂ O ₈ (g)	NaHSO ₃ (g)	Pore volume cm ³ /g	Surface Area m ² /g
MRD 150	45	0.090	0.039	2.75	8.38
MRD 250	90	0.090	0.039	4.42	4.99
MRD 350	180	0.090	0.039	4.74	5.77
MRD 450	270	0.090	0.039	6.38	4.35

Styrene-5.55 mL (0.0485 mole), DVB-3.45 mL (0.0242 mole), Styrene: DVB 2:1 mole/mole, Na₂S₂O₈- (3.780x10⁻⁴), NaHSO₃- (3.780x10⁻⁴), surfactant- 7 wt% ditallow dimethyl ammonium methyl sulphate and polyglycerol mono isostearate, CaCl₂ – 4 wt% of water.

Table 5.25 Synthesis of 100% cross-linked poly(styrene-co-divinyl benzene) monoliths by HIPE technique using redox initiator-2

Polymer code	Water mL	Na ₂ S ₂ O ₈ (g)	NaHSO ₃ (g)	Pore volume cm ³ /g	Surface Area m ² /g
MRD1100	45	0.090	0.039	2.41	4.42
MRD2100	90	0.090	0.039	3.35	4.00
MRD3100	180	0.090	0.039	4.53	2.02
MRD4100	270	0.090	0.039	3.90	1.81

Styrene-4.01 mL (0.0350 mole), DVB-4.99 mL (0.0350 mole), Styrene: DVB 1:1 mole/mole, Na₂S₂O₈- (3.780x10⁻⁴), NaHSO₃- (3.780x10⁻⁴), surfactant- 7 wt% ditallow dimethyl ammonium methyl sulphate and polyglycerol mono isostearate, CaCl₂ – 4 wt% of water

Table 5.26 Synthesis of 200% cross-linked poly(styrene-co-divinyl benzene) monoliths by HIPE technique using redox initiator-2

Polymer code	Water mL	Na ₂ S ₂ O ₈ (g)	NaHSO ₃ (g)	Pore volume cm ³ /g	Surface Area m ² /g
MRD1200	45	0.09	0.039	2.28	5.65
MRD2200	90	0.09	0.039	3.23	5.68
MRD3200	180	0.09	0.039	5.62	2.61
MRD4200	270	0.09	0.039	4.61	4.29

Styrene-2.75 mL (0.0240 mole), DVB-6.25 mL (0.0439 mole), Styrene: DVB 1:2 mole/mole, Na₂S₂O₈- (3.780x10⁻⁴ mole), NaHSO₃- (3.780x10⁻⁴), surfactant- 7 wt% ditallow dimethyl ammonium methyl sulphate and polyglycerol mono isostearate, CaCl₂ – 4 wt% of water

5.5.1 Solvent absorption studies of monoliths

Water, methanol and toluene uptake capacity of the polymers polymerised using redox initiators was tested gravimetrically.

Table 5.27 Solvent uptake for 50% cross-linked polymers synthesised using polyglycerol succinate as part surfactant

Polymer Code	Equilibrium water content (g/g)	Equilibrium methanol content (g/g)	Equilibrium toluene Content (g/g)
GRD150	1.85	2.01	3.25
GRD250	1.92	3.86	3.97
GRD350	2.77	3.19	3.58
GRD450	1.16	4.13	6.36

Table 5.28 Solvent uptake for 100% cross-linked polymers synthesised using polyglycerol succinate as part surfactant

Polymer Code	Equilibrium water content (g/g)	Equilibrium methanol content (g/g)	Equilibrium toluene content (g/g)
GRD1100	1.10	2.07	2.60
GRD2100	0.41	2.91	3.56
GRD3100	0.11	5.09	5.42
GRD4100	1.30	4.39	5.34

Table 5.29 Solvent uptake for 200% cross-linked polymers synthesised using polyglycerol succinate as part surfactant

Polymer Code	Equilibrium water content (g/g)	Equilibrium methanol content (g/g)	Equilibrium toluene content (g/g)
GRD1200	1.80	2.21	2.48
GRD2200	0.21	3.10	3.88
GRD3200	0.32	4.35	5.12
GRD4200	1.59	4.56	6.33

Table 5.30 Solvent uptake for 50% cross-linked polymers synthesised using polyglycerol mono isostearate as part surfactant

Polymer Code	Equilibrium water content (g/g)	Equilibrium methanol content (g/g)	Equilibrium toluene content (g/g)
MRD-150	0.60	2.57	3.46
MRD-250	0.42	3.35	4.47
MRD-350	0.60	3.73	5.38
MRD-450	1.93	5.55	5.76

Table 5.31 Solvent uptake for 100% cross-linked polymers synthesised using polyglycerol mono isostearate as part surfactant

Polymer Code	Equilibrium water content (g/g)	Equilibrium methanol content (g/g)	Equilibrium toluene content (g/g)
MRD-1100	0.12	2.25	2.86
MRD-2100	0.26	3.98	4.99
MRD-3100	0.24	4.78	5.73
MRD-4100	0.32	4.08	5.28

Table 5.32 Solvent uptake for 200% cross-linked polymers synthesised using polyglycerol mono isostearate as part surfactant

Polymer Code	Equilibrium water content (g/g)	Equilibrium methanol content (g/g)	Equilibrium toluene content (g/g)
MRD-1200	0.20	1.92	2.47
MRD-2200	0.15	3.29	3.89
MRD-3200	0.40	4.03	7.53
MRD-4200	0.08	5.01	5.30

5.6 Results and discussion

5.6.1 Synthesis of poly(styrene-co-divinyl benzene) by HIPE technique

Styrene-divinylbenzene copolymers were synthesised by polymerising water in oil emulsions using high internal phase emulsion technique. Synthesis details are shown in Tables 5.1-5.6. The polymers were prepared with 3 different cross-link density, namely 50%, 100% and 200%. In each case the internal water was varied in the ratio of 5, 10, 20, 30 and 40 with respect to monomer. The photographs of emulsion formed and polymerised monolith is shown in Figures 5.2 and 5.3, respectively. It was observed that at 5, 10 and 20 times amount of water stable thick emulsions were formed but for 30 and 40 times amount of water the emulsion broke

down as some separation of water took place. This is because as more and more water is added to the oil phase a point is reached where the emulsifier system no longer accepts the water. At this point droplets begin to recombine resulting in polymodal distribution of large recombined droplets and smaller, as yet uncombined droplets. This process proceeds until virtually total breaking of emulsion occurs.¹

It was also observed that the viscosity of the emulsions increases with the increase in amount of water used in HIPE formation. The factors (other than the shear rate) that affect the viscosity of the emulsions are dispersed phase concentration, viscosity of the dispersed phase, temperature and the age of emulsion. Similar and almost exponential increase in viscosity has been observed earlier with an increase in concentration of dispersed phase.² The cell size in the concentrated emulsion is probably small initially, because the amount of surfactant available in the continuous phase can generate a large surface area and the amount of dispersed phase is relatively small. The size of the cells is expected to grow with increasing amount of dispersed phase because only in this way can the surfactant molecules accommodate a larger amount of dispersed phase.³ Increase in viscosity prevents efficient mixing of the system and lowers the amount of dispersed phase that can be incorporated in the emulsion. After polymerisation for 48 hours, materials with low bulk density (less than 0.1 g/cm³) and highly porous interconnecting structures are obtained. After drying the surface area of the polymers were analysed by B.E.T method.

Figure 5.4 shows a pictorial view of formation of open celled continuous pores to produce a highly porous polymer. HIPE is formed by dropwise addition of internal phase to a solution of surfactant in external phase, under constant agitation. When a centrifugal field is applied to an emulsion, the droplets can be forced into contact with each other and deformation into polyhedra occurs. The excess continuous phase is

forced out of the emulsion forming a separate phase, known as creaming phase.⁴ The void diameter of these materials is in the range of 20 μm , and the void size is inversely proportional to the emulsion stability.⁵

The polymers synthesised have a surface area of 5-20 m^2/g , as analysed by nitrogen adsorption method. The average diameter of water droplets in HIPE formation is about 10 μm , therefore the surface area of these materials is low.⁶



Figure 5.2 : Pictorial view of emulsion of styrene and divinyl benzene formed

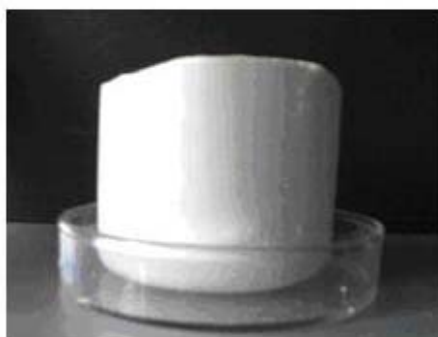


Figure 5.3: Pictorial appearance of synthesised poly(styrene-co-divinyl benzene) polymer

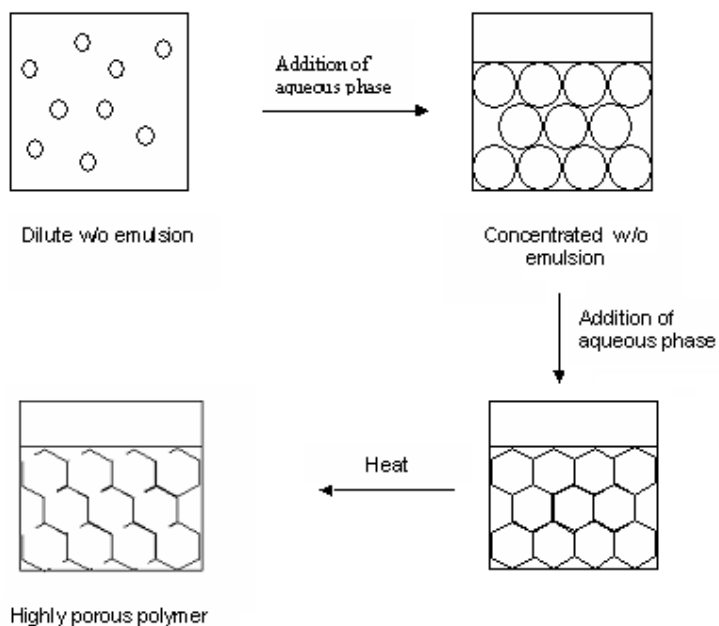


Figure 5.4: Pictorial representation of interconnecting cells in HIPE formation

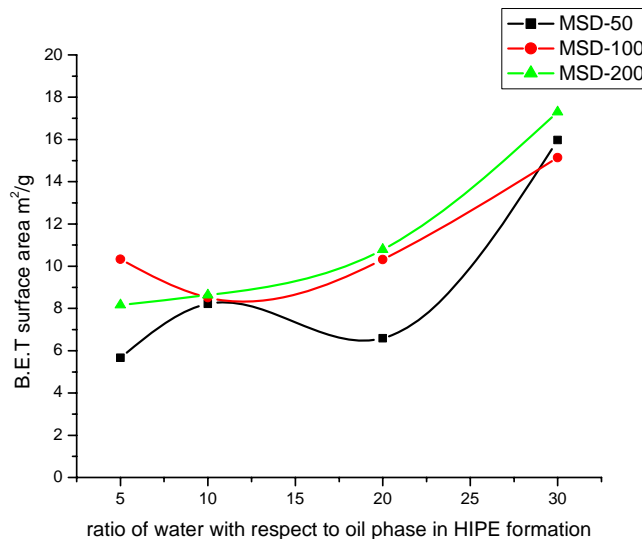


Figure 5.5 : Comparison of B.E.T surface area with variation in cross-link density of polymers synthesised using surfactant comprising of poly glycerol mono isostearate

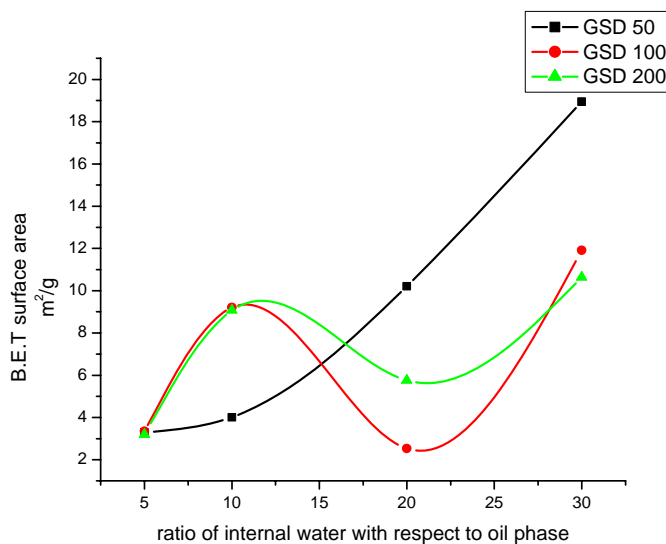


Figure 5.6 : Comparison of B.E.T surface area with variation in cross-link density of polymers synthesised using surfactant comprising of poly glycerol succinate

Figures 5.5 and 5.6 show the effect on surface area with variation in discontinuous phase for 50%, 100% and 200% cross-linked polymers, synthesised using two different surfactant blends. Similarly, an increase in surface area is

observed with increase in the ratio of internal water in HIPE formation. As the cross-link density increases an increase in surface area is observed. As the amount of water increases, the emulsion is formed comprises of smaller droplets, giving rise to micropores that leads to an increase in surface area. The increase in hydrophobicity of DVB compared to styrene results in formation of a more stable emulsion, giving a slower rate of droplet coalescence and smaller average cell size. The presence of increasing levels of DVB (increased emulsion stability) results in a smaller average droplet size, due to the (presumed) lower interfacial tension which permits a larger interfacial area.⁷ Therefore, a decrease in void diameter is caused by a decrease in HIPE droplet diameter that leads to an increase in surface area as the cross-link density increases. The porous structures can be clearly be seen from scanning electron microscope (SEM).

Open celled inter-connected macrocellular pores are obtained, as shown in Figures 5.7 and 5.8. The pore size is dependent on the type of surfactant, as seen in scanning electron micrographs.

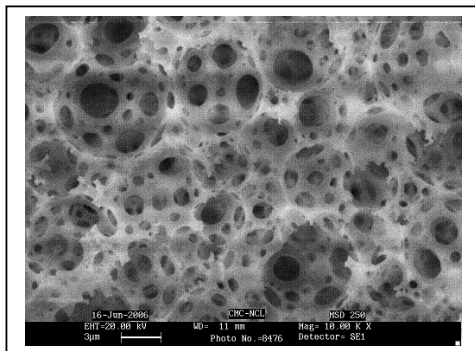


Figure 5.7 : SEM photographs of MSD 250 at 10 K magnification

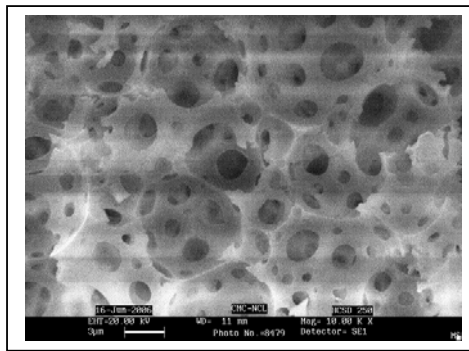


Figure 5.8 : SEM photographs of GSD 250 at 10 magnification

5.6.2 Postmodification of monoliths

Sulphonic acid moieties were introduced in the polymers using chlorosulphonic acid⁸ and were characterised by IR spectroscopy and the acid capacity of the modified polymers was estimated using titration method. The maximum capacity obtained is 3.783 meq/g. Tables 5.7-5.12 give the details of modification of the polymers. Reactions carried out in presence of chlorosulphonic acid proceeds in two steps. The first step leads to formation of sulphonated groups, while the second step is equilibrium between sulphonated and chlorosulphonic groups.⁹



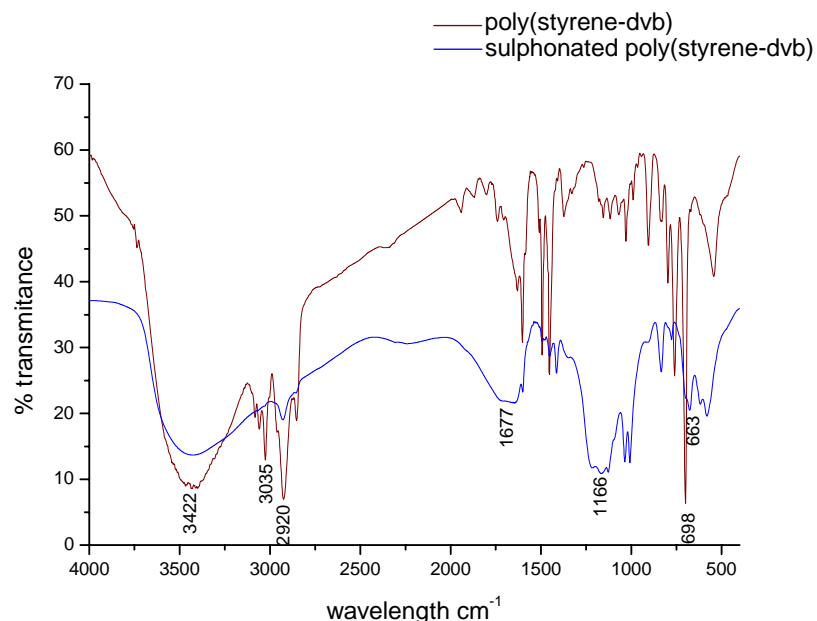


Figure 5.9 : IR spectra of sulphonated and unmodified poly(styrene-co-divinyl benzene)

The I.R peaks for modified and unmodified polymers are as follows:

Poly(styrene-DVB): 3425 cm⁻¹(OH), 3038 cm⁻¹ (Ar C-H), 2863 cm⁻¹ (CH), 2925 cm⁻¹ (CH₃), 1950-1700 cm⁻¹ (combinations and overtones), 1600 cm⁻¹, 1500 cm⁻¹, (ArC = C), 1450 cm⁻¹ (CH₂) 1050 cm⁻¹, 900 cm⁻¹ (Ar -C-H) , 775 cm⁻¹ (CH₂)

Sulphonated poly(styrene-DVB): 3422 cm⁻¹ (OH), 2929 cm⁻¹ (CH₂) 2863 cm⁻¹ (CH₂), 1677 cm⁻¹ (combinations and overtones) 1166 cm⁻¹ (S=O), 663 (C-S) cm⁻¹

Figure 5.9 shows IR spectra of modified and unmodified polymers. Modified polymer shows strong vibrations at 1166 cm⁻¹ and 663 cm⁻¹, which are characteristic peaks of S=O and C-S, respectively. At 1351 cm⁻¹ there is a weak peak characteristic of SO₂Cl group. The intensity of SO₂Cl group is very low and shows absence of characteristic peak of sulphone bridge at 1145 cm⁻¹. The surface area of the monoliths, determined by B.E.T technique, before and after modification, shows a decrease. As observed in Figure 5.10, the decrease in surface area on sulphonation is probably due

to agglomeration of some isolated copolymer nuclei during polymerisation.¹⁰ The significance of these sulphonation reactions is that sulphonic acid groups are introduced into polymers having open cell structure.¹¹

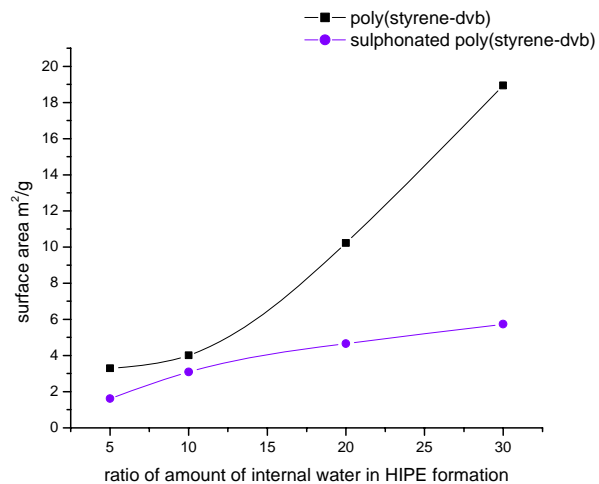


Figure 5.10 : BET surface area before and after sulphonation

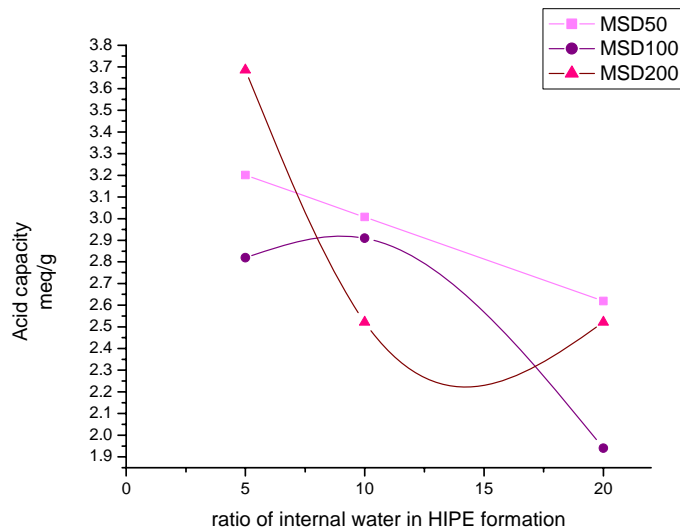


Figure 5.11 : Acid capacity of sulphonated poly(styrene-co-divinyl benzene) synthesised using surfactant comprising of polyglycerol mono isostearate

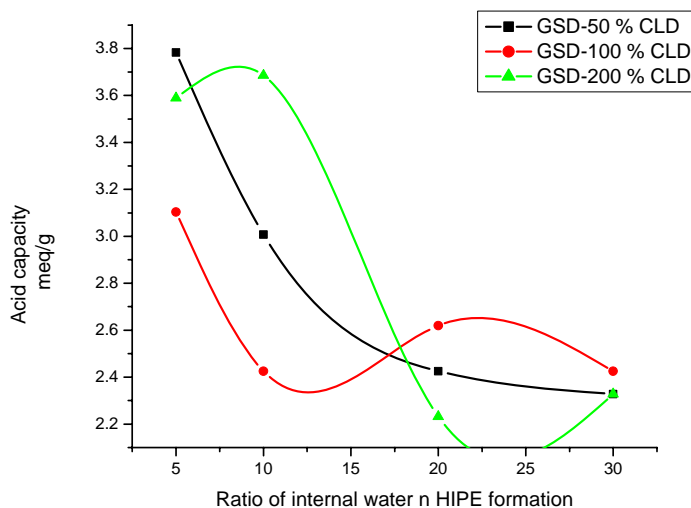


Figure 5.12 : Acid capacity of sulphonated poly(styrene-co-divinylbenzene) synthesised using surfactant comprising of poly glycerol succinate

Figures 5.11 and 5.12 show a decrease in acid capacity of the polymers as the amount of internal water in HIPE increases. It is also observed that acid capacity is greater for 50% CLD than 100% CLD. For 200% CLD no trend is observed. Increase

in water content leads to a decrease in pore size of the polymers. As a result, the area available for attachment of bulky SO₃H groups, as well as the easy accessibility of polystyrene backbone, decreases. An increase in divinyl benzene content in the oil phase decreases the pore diameter. An increase in number of cross-links leads to decrease in acid capacity of the polymers. The maximum acid capacity obtained was 3.783 meq/g.

5.6.3 Solvent uptake capacity of polymers

PolyHIPE materials have the unique property of forming open-cell structure that can be used for absorbing large quantities of solvent by capillary action. When a piece of material is immersed in liquid it causes absorption with displacement of air inside the matrix. This occurs until the voids are filled.¹² Polymer (0.1 g) was weighed and immersed in the solvent to be evaluated for adsorption. The polymers were kept for 24 hours to attain equilibrium. The equilibrium solvent content was estimated as follows.¹³

$$\text{ESC} = \frac{W_{\text{sol}} - W_{\text{dry}}}{W_{\text{dry}}}$$

Tables 5.13-5.18 show the equilibrium solvent content data for 3 different solvents water, methanol and toluene. Figures 5.13-5.17 show solvent uptake capacity for the polymers synthesised by varying the surfactant type and cross-link density. The nature of the liquid affects the volume that can be uptaken. The graphs show uptake of same polymer in three different solvents water, methanol and toluene. Maximum uptake was observed in case of toluene than methanol. Methanol, being a nonsolvent for the cross-linked polymer, was absorbed to a lesser extent than toluene, which caused walls of the polymer to swell. Water being polar was absorbed to a

lesser extent than other solvents because poly(styrene-co-divinyl benzene) is incompatible.¹⁴

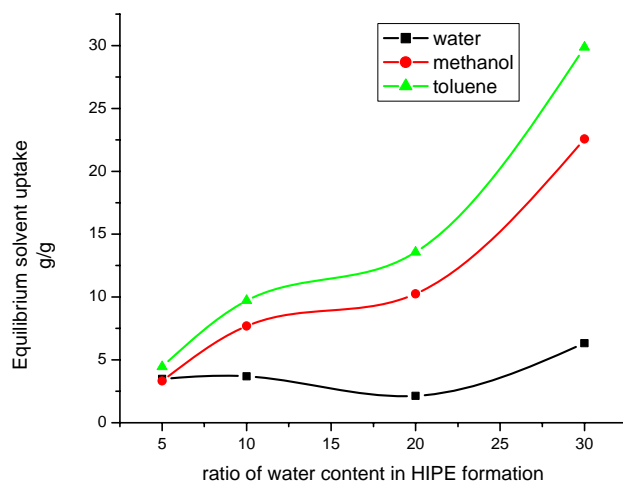


Figure 5.13 : Equilibrium solvent uptake for MSD 50 series polymers having 50% cross-linking and synthesised using surfactant comprising of poly glycerol mono isostearate

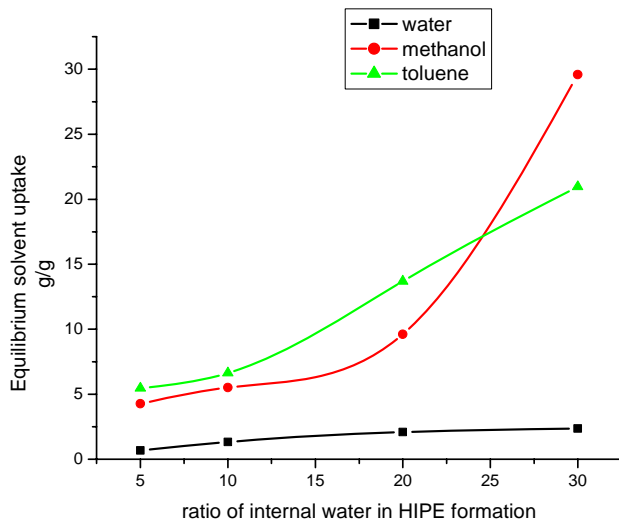


Figure 5.14 : Equilibrium solvent uptake for MSD 100 series polymers having 100% cross-linking and synthesised using surfactant comprising of poly glycerol mono isostearate

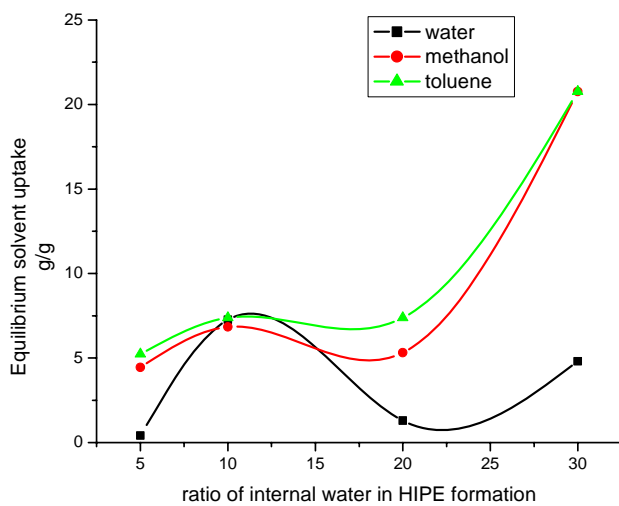


Figure 5.15 : Equilibrium solvent uptake for MSD 200 series polymers having 100% cross-linking and synthesised using surfactant comprising of polyglycerol mono isostearate

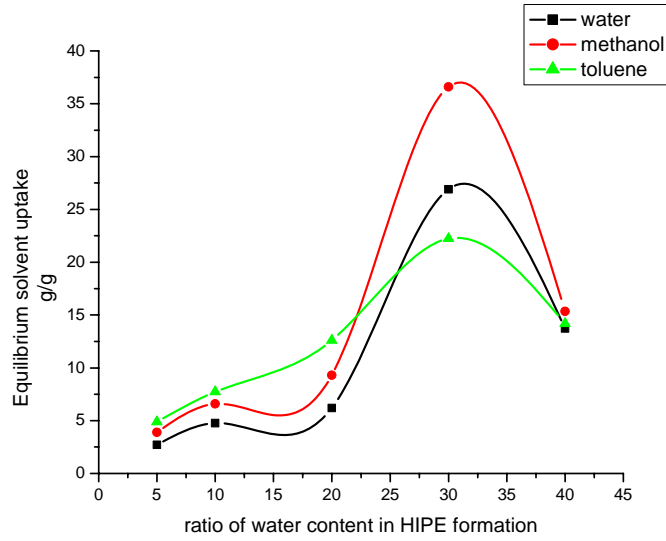


Figure 5.16 : Equilibrium solvent uptake for GSD 50 series polymers having 50% CLD and synthesised using surfactant comprising of poly glycerol succinate

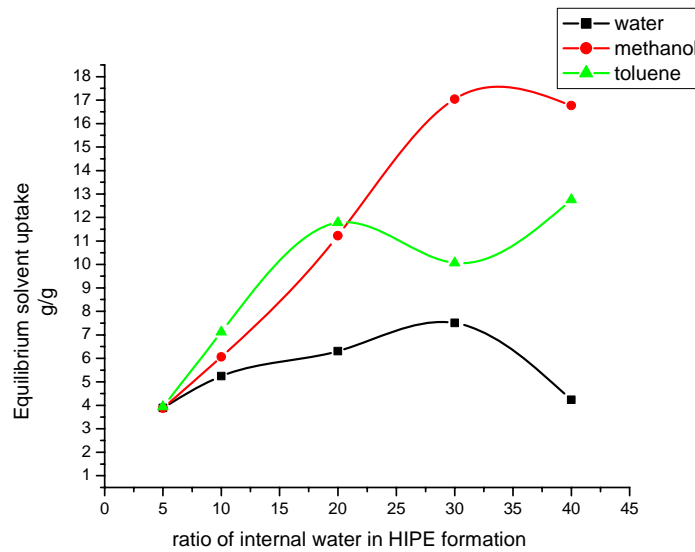


Figure 5.17 : Equilibrium solvent uptake for GSD 200 series polymers having 200% CLD and synthesised using surfactant comprising of poly glycerol mono isostearate

5.6.4 Sulphonated poly(styrene-co-divinyl benzene) as catalysts

The sulphonated monoliths can be used as heterogeneous acid catalysts in esterification reactions. Esterification of salicylic acid to methyl salicylate was studied at 80°C. The reaction was monitored by HPLC. The experiments were conducted to optimise the composition of mobile phase required to achieve a complete base line resolution of the reactants and the product. Complete resolution was achieved with eluent 80:20 (v/v) ratio methanol–water mixture at a flow rate of 0.7 mL/min. Individual salicylic acid and ester peaks were identified and separated from each other having retention times of 2.28 and 6.15, minutes respectively, as shown in Figure 5.18. To obtain maximum conversion of the acid the reaction parameters such as reaction time and temperature were varied. The efficiency of different polyHIPE catalysts synthesised was then tested in the esterification reaction and monitored by HPLC. PolyHIPE synthesised at water:monomer ratio of 10:1 showed maximum efficiency as esterification catalyst (91 % yield).

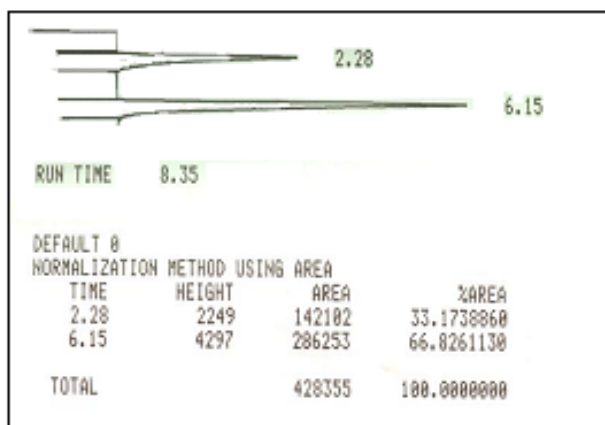


Figure 5.18 : HPLC separation of salicylic acid and methyl salicylate at different retention times

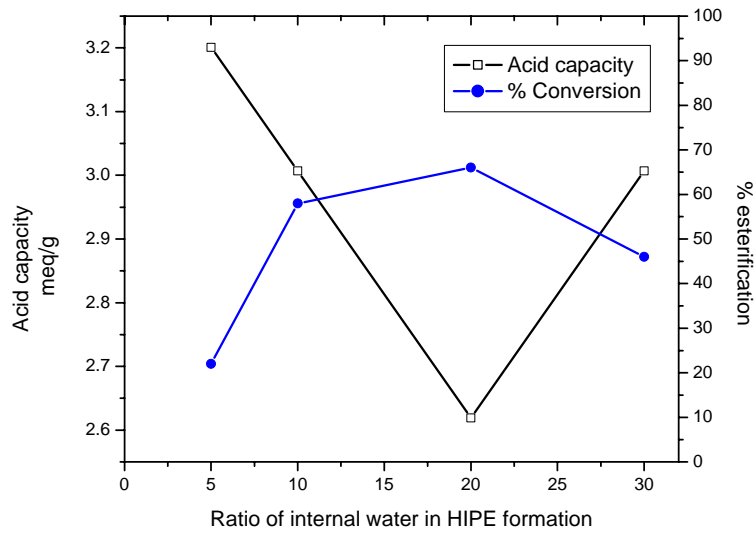


Figure 5.19 : Comparison of % esterification and acid capacity of MSD-50 series sulphonated polymers

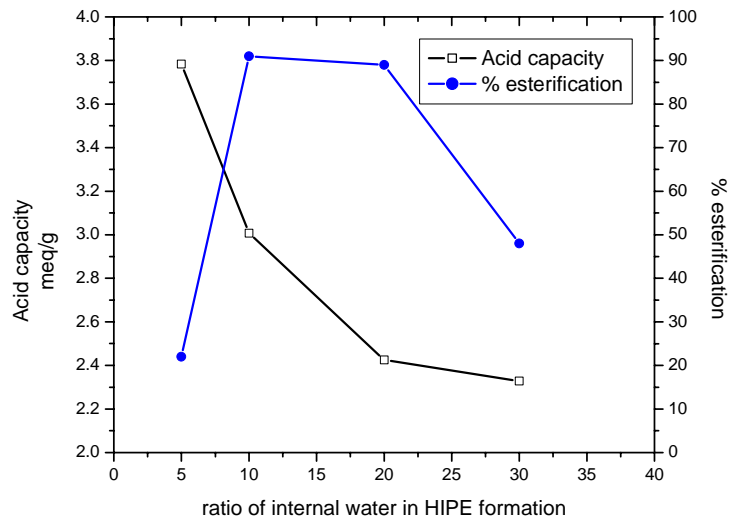


Figure 5.20 : Comparison of % esterification and acid capacity of GSD-50 series sulphonated polymers

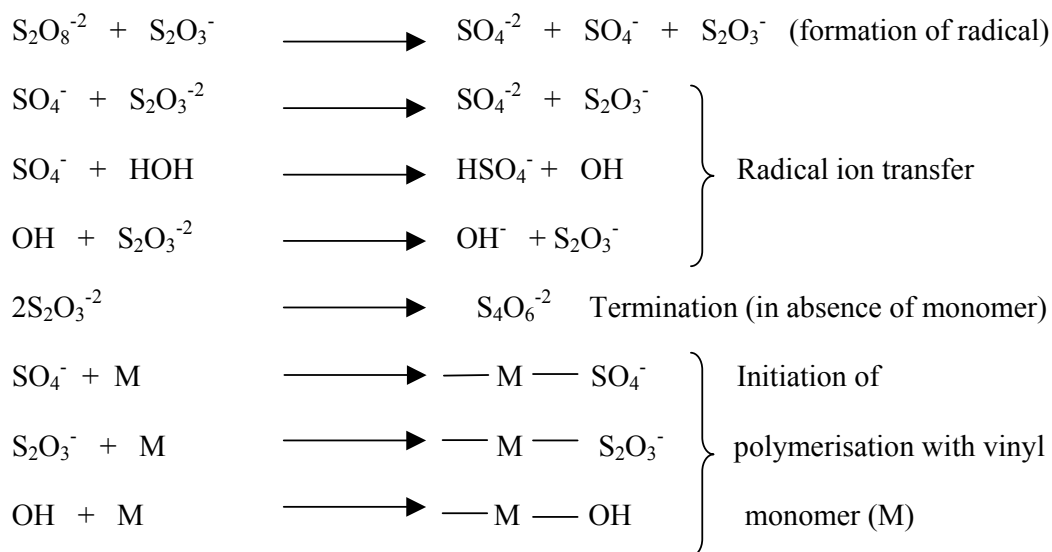
In Tables 5.10-5.12 the acid capacity of GSD polymers is tabulated. For 50% CLD the acid capacity was 3.78, 3.00, 2.42 and 2.32 meq/g for o/w ratio 5, 10, 20 and 30, respectively. In case of 100% CLD polymers, the acid capacity obtained was 3.10, 2.42, 2.61, and 2.42 meq/g for o/w ratio 5, 10, 20 and 30, respectively. In case of 200 % CLD polymers the acid capacity obtained was 3.58, 3.68, 2.23 and 2.32 meq/g for o/w ratio 5, 10, 20 and 30, respectively. Figures 5.19 and 5.20 show that the acid capacity decreases as the amount of internal water in HIPE formation increases. This is valid up to 20 times increase in water with respect to the monomer. On further addition the emulsion breaks down and hence no trend was observed in acid capacity. From surface area studies it is seen that as amount of water increases the surface area increases, indicating an increase in micropores. The easy accessibility of the aromatic ring backbone to attach a bulky $-\text{SO}_3\text{H}$ group is minimised. Therefore, a decrease in acid capacity was observed.

5.6.5 Synthesis of poly(styrene-co-divinyl benzene) by HIPE technique using redox initiator

All the above studies were done using thermal initiators. Reactions were also done using redox pair of initiators at room temperature. The synthesis details of poly(styrene-DVB) monoliths by HIPE methodology using redox initiators at ambient temperature are tabulated in Tables 5.21-5.26. When water is slowly added to stirred solution of surfactant of low HLB value, dissolved in oil phase, an internal phase volume of water upto 74% is achievable, and at this state water droplets in oil phase strongly interact. Continuous oil phase is composed of monomer and cross-linker, the cross-linking monomer in the continuous phase results in a solid cross-linked polymer which contains water droplets. On removal of water by vacuum drying highly porous monoliths having low bulk density can be obtained. The average diameter of water

droplets to form HIPE is 10 μm and therefore the surface area of the resulting materials have low surface area (about 10 m^2/g).

Sodium peroxydisulphate and sodium bisulphate redox pair initiator was used to polymerise the emulsions. The radical generation mechanism is as follows: ¹⁵⁻¹⁶



Peroxydisulphate ion is one of the strongest oxidising agent in aqueous solution. The polymers are polymerised at room temperature.

The polymers were synthesised by varying the reaction parameters such as cross-link density and amount of internal water in HIPE formation. Water was added in the ratio 5, 10, 20, 30 and 40 times that of the oil phase. It was observed that in the case where emulsions were added 5, 10 and 20 times water that of oil phase thick cream like emulsions were obtained whereas in case of 30 and 40 times water no uniform cream like emulsions were obtained as some water separation was observed in the emulsion. Since initiator system comprising of oxidant and reductant was added the polymerisation was observed in all cases.

Figure 5.21 shows the B.E.T surface area of MRD series polymers prepared with variation in cross-link density using redox pair initiator system and polyglycerol mono isostearate surfactant. As the water content in HIPE formation increased the

surface area of the polymers decreased. This was valid up to 20 times increase in water as for further increase in water no stable emulsion was formed. Graph shows that the pore volume of monoliths increased and B.E.T surface area decreased as the ratio of internal water in the HIPE formation increased. This was valid up to 1:20 (oil:water) ratio. The void size correlated inversely with emulsion stability. Therefore, the void volume increased as water content increased, as it destabilised the emulsion in a controlled manner. At larger water concentration this trend was not observed as emulsion stability was affected.

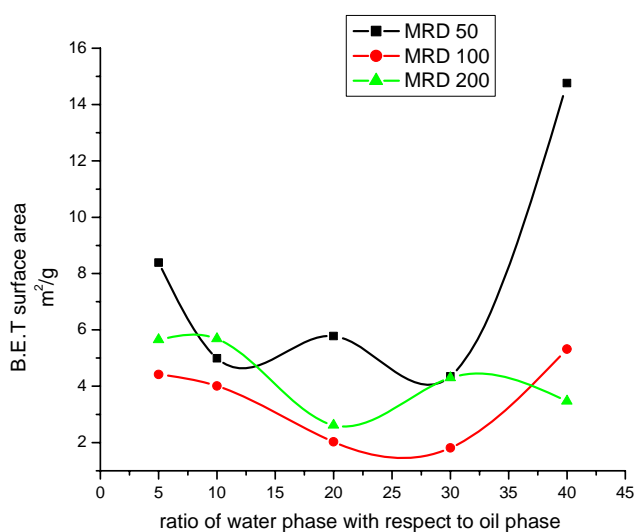


Figure 5.21 : Comparison of B.E.T surface area of MRD (synthesised using surfactant comprising of polyglycerol mono isostearate) series polymers with variation in cross-link-density

Figure 5.22 shows that the pore volume of the polymers increased as the water in HIPE formation increased. The surface area and pore volume decreased as cross-link density increased from 50% to 100%. But, no trend was observed for 200% CLD

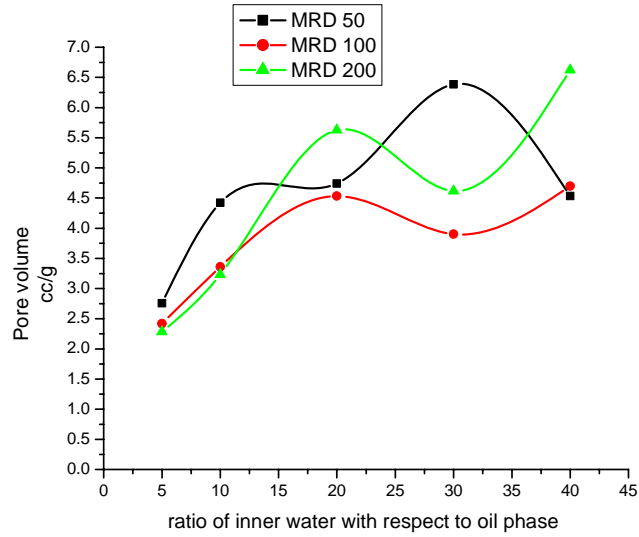


Figure 5.22 : Comparison of pore volume of MRD (synthesised using surfactant comprising of polyglycerol mono isostearate) series polymers with variation in cross-link-density

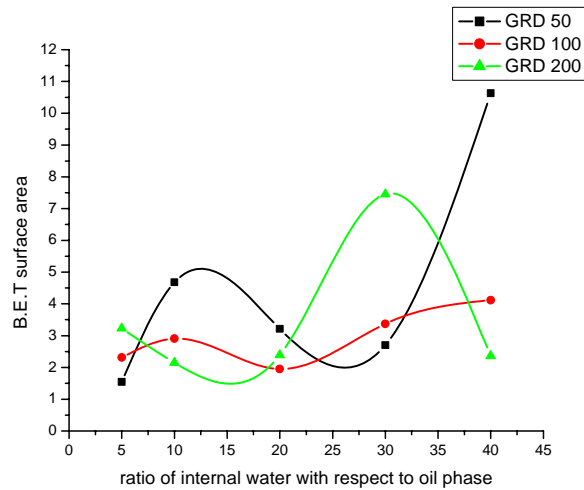


Figure 5.23 : Comparison of B.E.T surface area of GRD (synthesised using surfactant comprising of polyglycerol succinate) series polymers with variation in cross-link-density

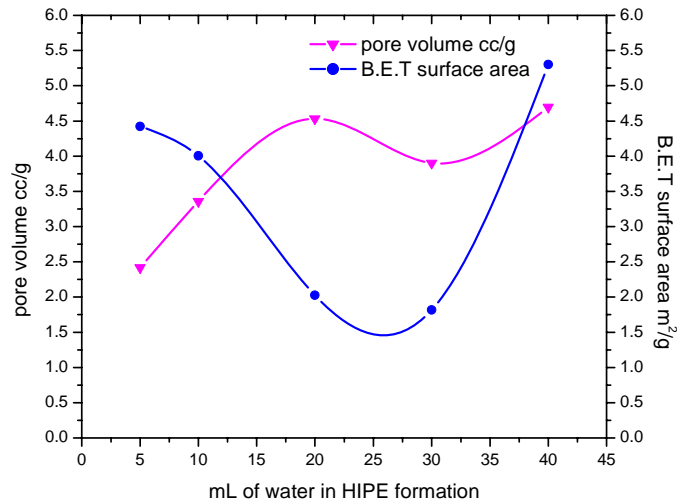


Figure 5.24 : Comparison of B.E.T surface area and pore volume of MRD (synthesised using surfactant comprising of poly glycerol mono isostearate) series polymers having 100% cross-link-density

As seen in Figure 5.23, no trend is observed in the surface area of polymers. Figure 5.24 shows the effect of discontinuous phase on pore volume and surface area for the 100 % cross-link density polymer. Till 20 times water discontinuous phase leads to an increase in pore volume and decrease in surface area. Beyond this stable emulsion is not formed and no trend is observed in surface area and pore volume.

Figures 5.26-5.29 show the solvent uptake capacity. There is change in pore volume with change in discontinuous phase. As a result the amount of solvent absorbed is also dependent on it.

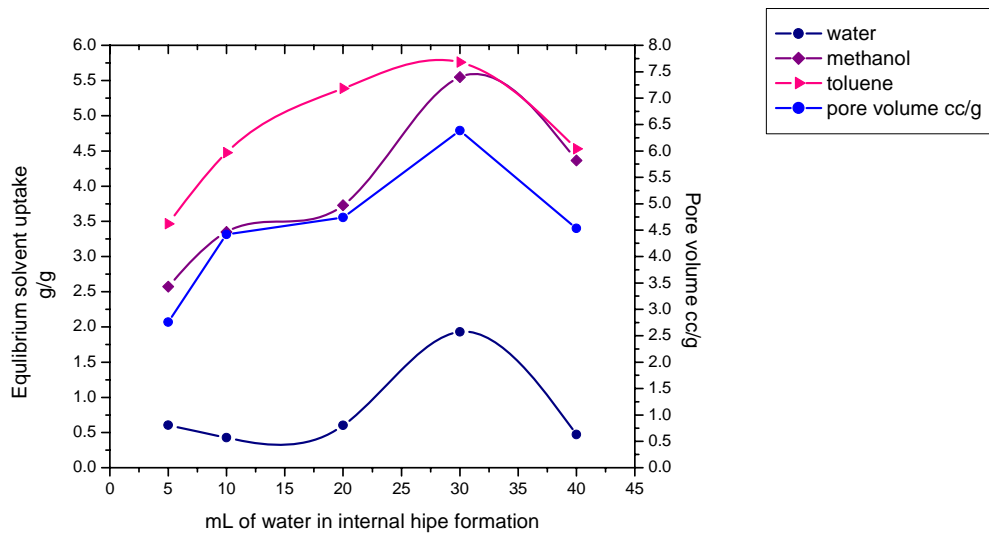


Figure 5.25 : Effect of internal water on pore volume for 50% cross-linked MRD polymers (synthesised using surfactant comprising of poly glycerol mono isostearate) and its comparison for solvent uptake capacity for different solvents

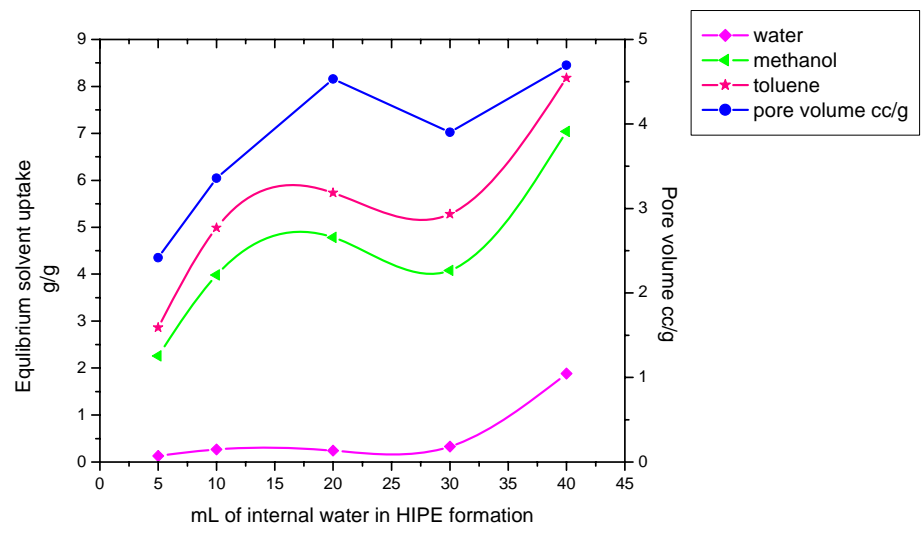


Figure 5.26 : Effect of internal water on pore volume for 100% cross-linked MRD polymers (synthesised using surfactant comprising of poly glycerol mono isostearate) and its comparison for solvent uptake capacity for different solvents

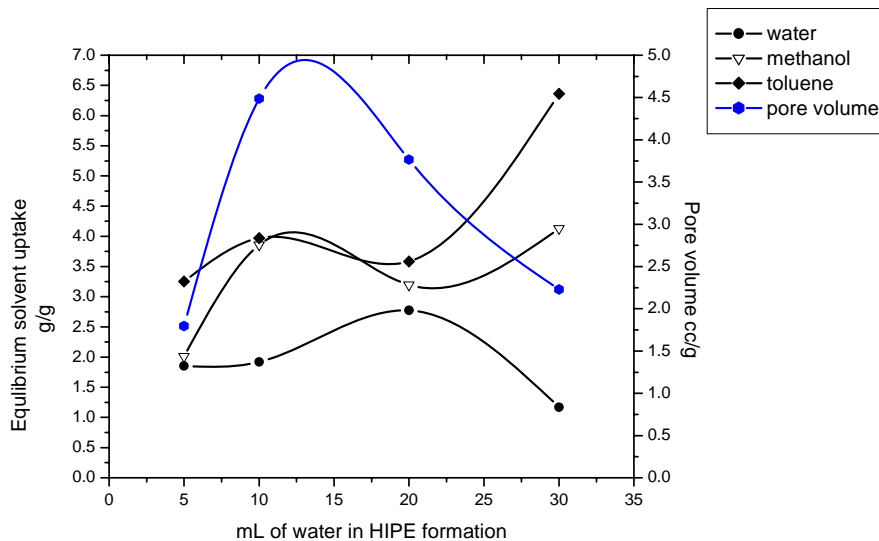


Figure 5.27 : Effect of internal water on pore volume for 50% cross-linked GRD polymers (synthesised using surfactant comprising of poly glycerol succinate) and its comparison for solvent uptake capacity for different solvents

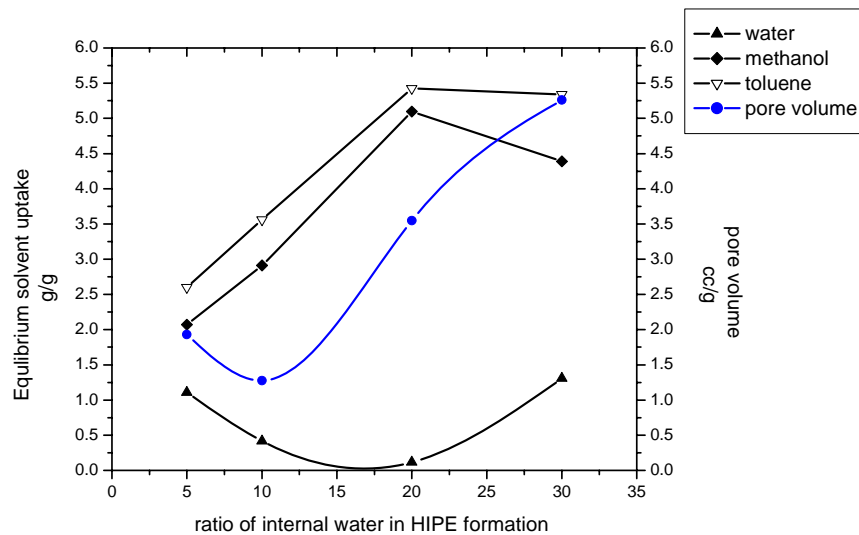


Figure 5.28 : Effect of internal water in pore volume 100% cross-linked GRD polymers (synthesised using surfactant comprising of poly glycerol succinate) and its comparison for solvent uptake capacity for different solvents

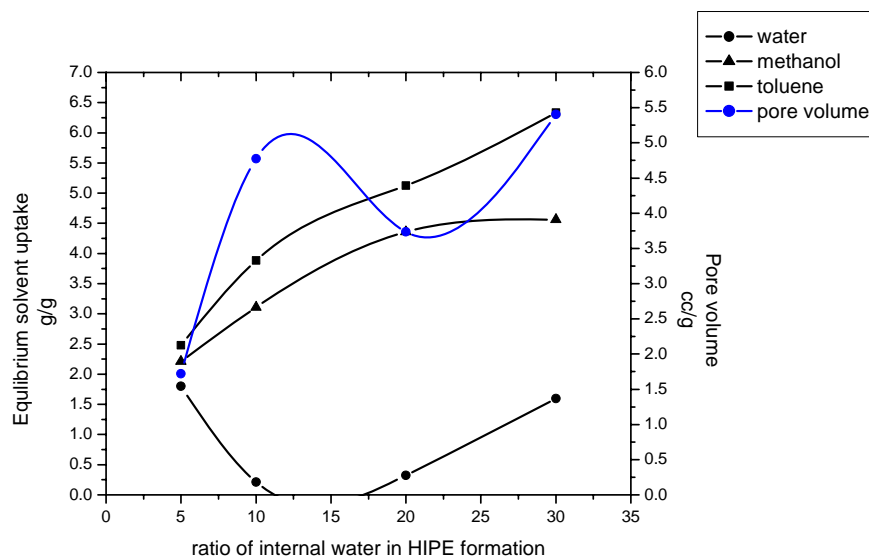


Figure 5.29 : Effect of internal water in pore volume for 200% cross-linked GRD polymers (synthesised using surfactant comprising of polyglycerol succinate) and its comparison for solvent uptake capacity for different solvents

Figures 5.30–5.32 show a comparison of polymers synthesised using thermal initiator and redox initiator. In all cases the surface area of the polymers synthesised using redox initiators is less compared to surface area of polymers synthesised using thermal initiators. In case of MRD polymers, as the discontinuous phase increases (in case of polymers synthesised using thermal initiators) an increase in surface area is observed while in case of polymers synthesised using redox initiators a decrease in surface area is observed. As reported by F. Svec and J. M. J. Frechet, higher the polymerisation temperature, smaller will be the pores due to nucleation in presence of precipitant.¹⁷ Higher the reaction temperature, larger will be the number of free radicals generated and as a result large number of nuclei will be formed. Phase separation of polymers from solution is a function of temperature. B.E.T technique is related to determination of small pores. Therefore, the surface area increases in case of polymers synthesised using thermal initiators. In case of redox initiators, the reaction is at room temperature and the polymerisation is initiated by SO_4^- ions. The

first order decomposition rate constant for $S_2O_8^{2-}$ at 60°C it is 10^{-5} sec^{-1} while for redox at 30°C is 10^{-3} sec^{-1} . Therefore in the case of redox the radical efficiency may be much lower.

Figure 5.30 shows that as the ratio of discontinuous phase increases, an increase in pore volume is observed in both cases (i.e polymers synthesised using thermal and redox initiators). As the cross-link density increases, an increase in pore volume is observed. In all cases the pore volume of polymers synthesised by redox polymerisation are lower than that of polymers synthesised using thermal initiators.

Figures 5.31 and 5.32 show a comparison of surface area of polymers prepared varying the discontinuous phase, cross-link density and initiation type. As the discontinuous phase increases, the surface area in polymers synthesised by thermal initiation increases while in case of polymers synthesised using redox initiator a decrease in surface area is observed. Though the surface area of these materials are very low, still polymers synthesised using thermal initiator have lower surface area as compared to thermally initiated polymers.

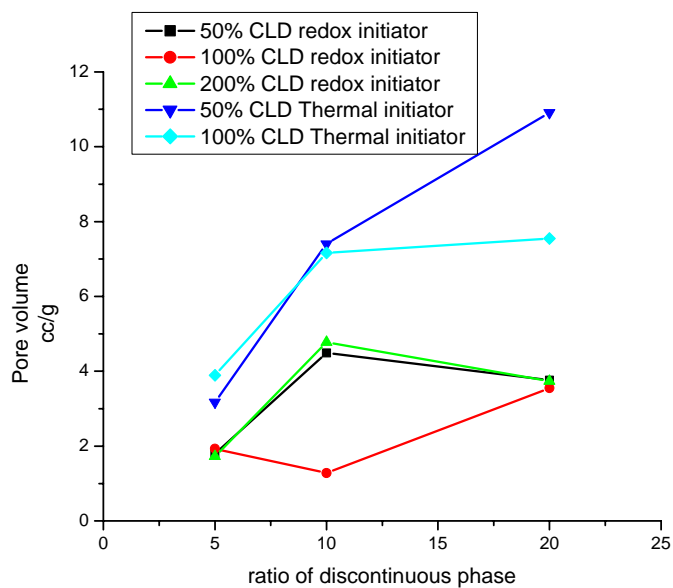


Figure 5.30 : Comparison of pore volume of polymers synthesised using surfactant comprising of poly glycerol mono isostearate with variation in discontinuous phase and initiation type

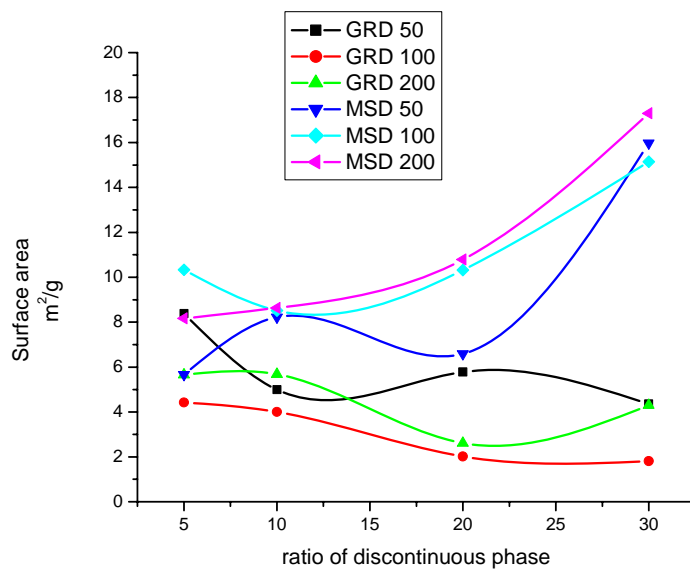


Figure 5.31: Comparison of surface area of polymers synthesised using surfactant comprising of poly glycerol mono isostearate with variation in discontinuous phase and initiation type

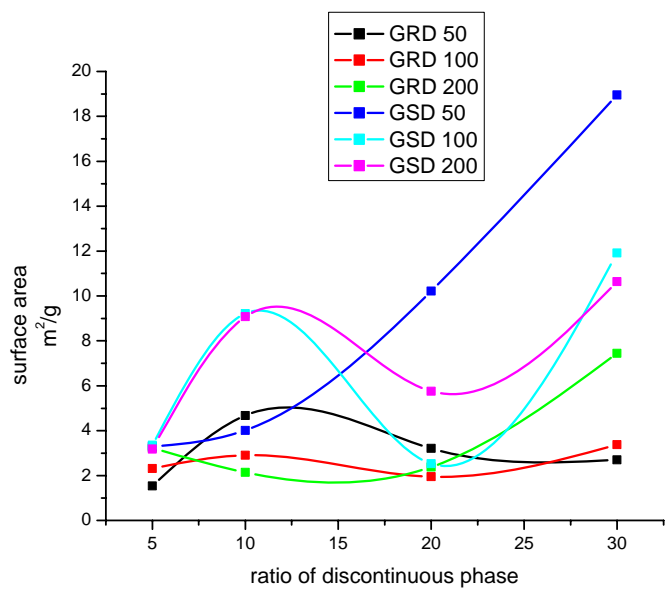


Figure 5.32 : Comparison of surface area of polymers synthesised using surfactant comprising of poly glycerol succinate with variation in discontinuous phase and initiation type

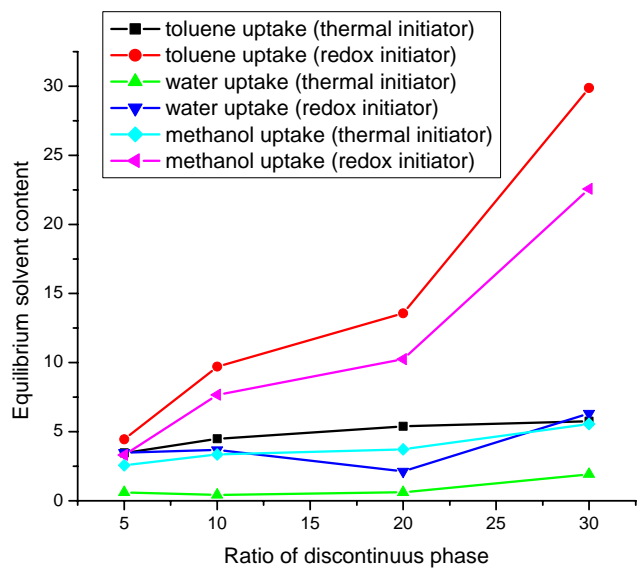


Figure 5.33 : Comparison of solvent uptake capacity for 50% cross-linked polymers synthesised using surfactant comprising of poly glycerol mono isostearate with variation in initiator system

Figure 5.33 shows that the solvent uptake in case of polymers synthesised using redox initiators is less than that in thermal ones and this is dependent on pore volume.

The details of equilibrium solvent uptake are given in Tables 5.13-5.18 and 5.27-5.32 for thermally initiated and redox initiated. The results show that in polymers synthesised using redox initiators have a maximum solvent uptake of 2, 5 and 6 g/g for water, methanol and toluene, approximately. Polymers synthesised using thermal initiator have a maximum solvent uptake of 4, 9 and 12 for water, methanol and toluene, respectively. Polymers synthesised by redox initiators have a short induction time, a lower energy of activation ($40\text{-}80\text{ kJ mole}^{-1}$) and therefore polymerisation can be carried out under mild conditions than thermal polymerisation. The above studies show that temperature also affects properties of the polymer.

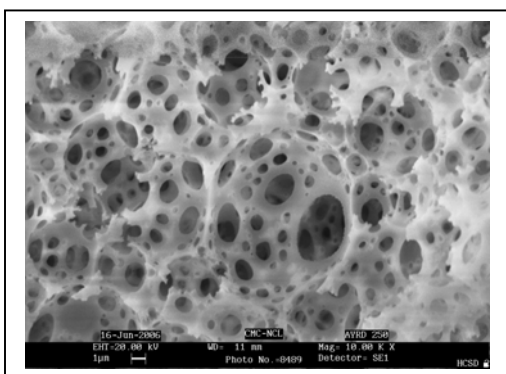


Figure 5.34: SEM photographs of MRD 250 at 10 K magnification

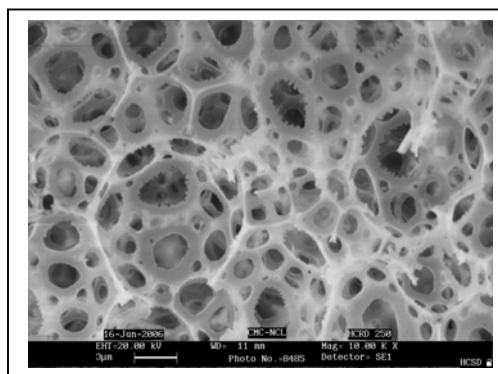


Figure 5.35: SEM photographs of GRD 250 at 10 K magnification

Figures 5.34 and 5.35 show the SEM micrographs of polymers synthesised using redox initiator. In both cases, well defined interconnecting pores are observed.

5.7 Conclusion

The HIPE emulsion was stable till a water : oil (monomer) ratio of 20:1, allowing the synthesis of porous polymers with open cell structure. In this composition range surface area was 3-20 m²/g and a maximum pore volume of 7 cm³/g was obtained.

Sulphonic acid groups were introduced quantitatively on the surface of pores of open-celled monolith structure. These resins can be used as heterogeneous acid catalysts. Esterification of salicylic acid to methyl salicylate was demonstrated as a test case. These polymers can also be used to imbibe in spilled solvents. They have a maximum uptake of 7 times for toluene and 4 times for methanol. Materials having such highly open celled pore structure are suited to a wide variety of applications such as enzyme immobilisation, chromatographic columns, solid acid catalyst and imbibing.

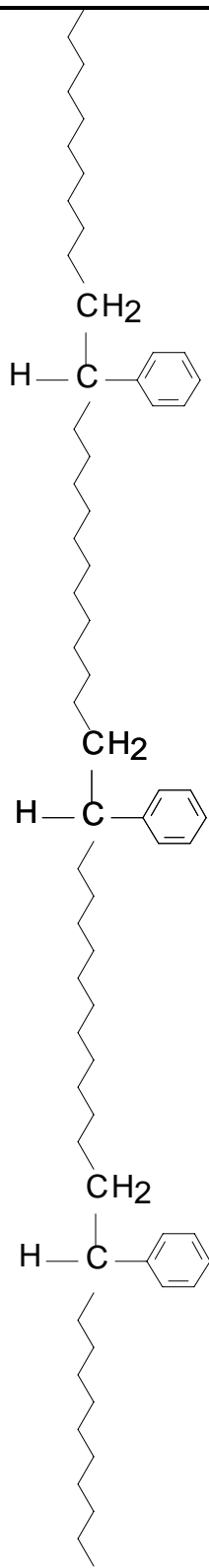
Redox polymerisation technique was used to polymerise high internal phase emulsions and to generate open celled interconnecting pores. The pore volume obtained was up to 5 cm³/g. The initiation type has a strong influence on the pore volume and surface area of the polymers. Therefore, polymers synthesised using redox initiators have low surface area and pore volume as compared to those with similar composition and synthesised using thermal initiators.

5.8 References

- 1 K. J. Lissant, *Journal of Colloid and Interface Science*, **22**, 462 (1966)
- 2 R. Pal and E. Rhodes, *Journal of Colloid and Interface Science*, **107**, 2, 301 (1985).
- 3 H. H. Chen and E. Ruckenstein, *Journal of Colloid and Interface Science*, **145**, 1, 260 (1991).
- 4 N. R. Cameron and D. C. Sherrington, *Advances in Polymer Science*, **126**, 165

(1996).

- 5 A. Barbetta, R. J. Carnachan, K. H. Smith, C. Zhao, N. R. Cameron, R. Katakya, M. Hayman, and S. A. Przyborski, *Macromol. Symp.*, **226**, 203 (2005).
- 6 O. Okay, *Prog. Polym. Sci.*, **25**, 711 (2000).
- 7 N. R. Cameron, *Polymer*, **46**, 5, 1439 (2005).
- 8 F. P. Regas, *Polymer*, **25**, 249 (1984).
- 9 M. Bacquet, M. Salunkhe and C. Caze, *Reactive Polymers*, **16**, 61 (1991/1992).
- 10 I. Rabia, J. Zerouk ,M. Kerkouche and M. Belkhodja, *Reactive & Functional Polymers*, **28**, 279 (1996).
- 11 R. J. Wakeman, J. G. Bhumgara and G. Akay, *Chemical Engineering*, **70**, 133 (1998).
- 12 D. Barby and Z. Haq, European patent 0,060138, Unilever (1982).
- 13 A. M. Atta and K-F Arndt, *Poly. Int.*, **53**, 11 1870 (2004).
- 14 P. Hainey, I. M. Huxham, B. Rowatt, D. C. Sherrington and L. Tetley, *Macromolecules*, **24**, 117 (1991).
- 15 A. S. Sarac, *Prog. Polym. Sci.*, **24**, 1149 (1999)
- 16 G. S. Mishra and U. D. N. Bajpai, *Prog. Polym. Sci.*, **8**, 61 (1982).
- 17 A. Svec and J. M. J. Frechet, *Macromolecules*, **28**, 7580 (1995).



**SYNTHESIS AND EVALUATION OF
POLYMERS IN PHOTORESIST
FORMULATIONS**

6.1 Introduction

Polystyrene based polymers are used in lithography. Synthesis of different type of sensitisers and polymers for I-line photoresists and chemically amplified resist is a vast area of research to meet the new technology requirements. Substitution of conventional novolak resins used in microlithography with new polymer systems and to study the effects of molecular weights, glass transition temperature and solubility behaviour during developing stage, to be able to work as positive photoresists are the objectives of the present study.

The type of functional group attached to the polymer makes the polymer either hydrophilic or hydrophobic, and alters its properties. Copolymers having partial hydroxyl groups are being tested out in photoresists applications for I-line photoresist i.e 365 nm technology. The present chapter deals with synthesis of polymers and sensitisers for photoresist applications. The photoresist formulations comprises of copolymer of styrene and sensitisers based on diazonaphthoquinones.

6.2 Synthesis of polymers for photoresists

6.2.1 Synthesis of low molecular weight polystyrene

Linear polystyrene was synthesised by suspension polymerisation and the molecular weight of the polymers was controlled by addition of chain transfer agents. The synthesis was conducted in a double walled cylindrical polymerisation reactor of 11 cm diameter and 15 cm height connected to a thermostatic water bath, nitrogen gas inlet, condenser and overhead stirrer. Nitrogen gas was purged into the reactor continuously. The reactor was charged with 25 mL (0.218 mole) of styrene, 0.6 g (2.4769×10^{-3} mole) benzoyl peroxide, 2 mL 1 wt % poly(vinyl alcohol) solution [protective colloid], diluted to 150 mL with distilled water. Varying amount of carbon tetrachloride was added to the

reaction mixture, as shown in the Table 6.1 as chain transfer agent. The reactants were stirred at 260 rotations per minute and the suspension polymerisation was allowed to proceed for 16 hours. The product was filtered, washed and dried. (Yield : 85%).

Table 6.1 Polystyrenes synthesised and their characteristics

Code No	CCl ₄		M _n	M _w	Poly dispersity
	mL	mole			
PS-1	-	-	31,520	63,300	2.01
PS-2	4.8	0.049	16,560	35,380	2.14
PS-3	10.4	0.107	10,320	20,870	2.02
PS-4	30.0	0.310	5,830	8,700	1.60
PS-5	40.0	0.414	5,590	8,700	1.55
PS-6	60.0	0.621	5,190	7,680	1.50

Styrene-25 mL (0.218 mole), Benzoyl peroxide- 0.6 g (2.476×10^{-3} mole), M_n= number average molecular weight, M_w= weight average molecular weight, M_n and M_w were determined by gel permeation chromatography (GPC).

6.2.2 Post modification of linear Polystyrene

Functional groups present in the polymer play an important role in modifying the polymer properties that can be used in a variety of applications. Post modification is used to attach different functional groups to the polymer backbone.

The post modification reactions performed here introduces hydroxyl pendent groups to make it alkali soluble so as to be aqueous developable. The post modification is done in three steps and the procedure is shown in Figure 6.1.

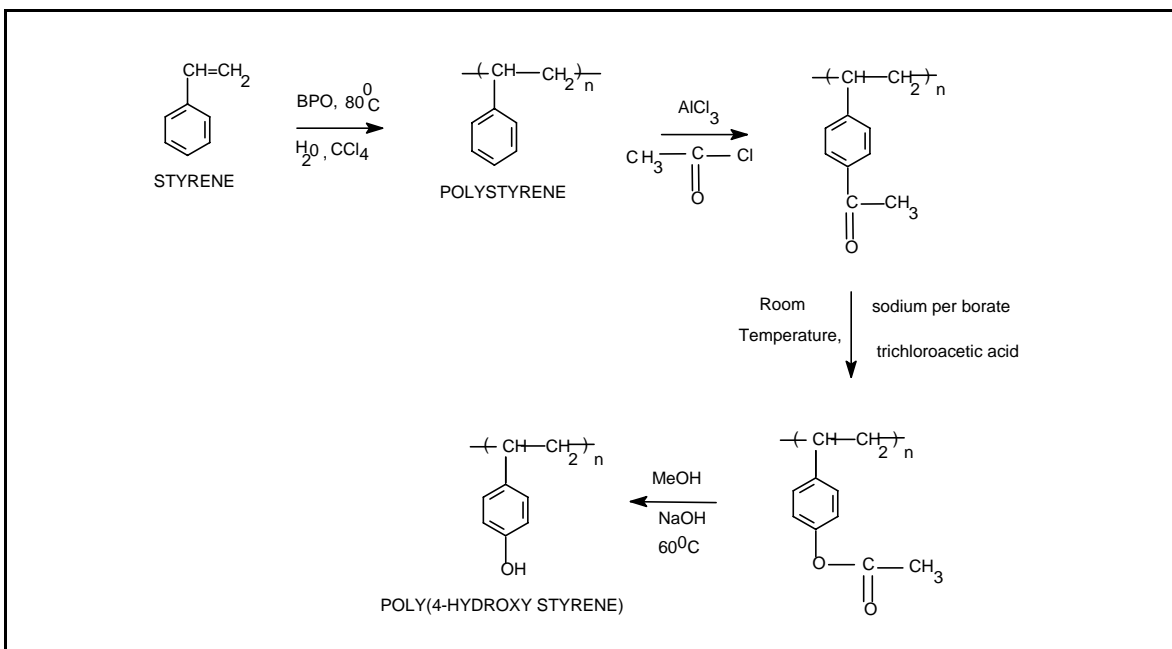


Figure 6.1: Reaction Scheme of post modification reactions

The three distinct steps in the modification of polystyrene are: Friedel-Craft's acylation to introduce acetyl groups; conversion of acetyl groups to acetoxy groups by Baeyer-Villiger oxidation; hydrolysis of acetoxy groups to hydroxy groups.

6.2.2.1 Acetylation of polystyrene

Friedel-Craft Acylation was done on polystyrene to introduce pendent acetyl groups.

Polystyrene (PS) (2.6 g; 0.025 mole) was dissolved in 25 mL carbon disulphide. A three-necked round bottom flask equipped with a condenser, dropping funnel, a magnetic needle was placed in ice water bath. Anhydrous aluminium chloride (AlCl_3) (6.7 g; 0.05 mole) and 25 mL carbon disulphide were added and the reactants were stirred vigorously. To this solution, 2.6 mL (0.0365 mole) acetyl chloride (CH_3COCl) was added dropwise. The reaction mixture turned red, with the evolution of hydrogen chloride (HCl) gas during the addition. The reaction was continued (6 h) till the evolution of hydrogen

chloride ceased. The reaction was stopped, carbon disulphide was distilled off using rotavapor. The residue obtained was air dried, transferred into a beaker containing 100 g crushed ice and 5 mL hydrochloric acid. Aluminium chloride decomposed and polymer was obtained as a yellow precipitate. It was filtered, dried, dissolved in acetone and precipitated in water. The pure polymer was filtered and dried.¹ Acetylation was evaluated using infrared (IR) spectroscopy. The parameters varied were: (1) reaction time; (2) mole ratio of polystyrene : acetyl chloride : aluminium chloride (PS : RX : AlX₃); (3) molar concentration; and (4) solvent. In the optimised reaction, the yield was 55%. The changes at IR spectra peaks followed were: 3024 cm⁻¹ (m, Ar C-H), 2192 cm⁻¹, 1680 cm⁻¹ (C=O) and 1600 cm⁻¹ (Ar-C=C).

Table 6.2 Acylation of polystyrene varying the concentration of acylating agent

Code	Acetyl chloride			% Acetylation
	mL	mole	Mole ratio Polymer:acetyl chloride	
APS-1	2.66	0.0375	1 : 1.5	25
APS-11	3.11	0.0437	1 : 1.75	75
APS-12	3.55	0.0500	1 : 2	80
APS-13	4.44	0.0625	1 :2.5	87

Polystyrene- 2.6 g (0.025 mole), aluminium chloride- 6.7 g (0.05 mole), ratio of polymer: catalyst-1:2, solvent-carbon disulphide, reaction time- 20 hours, reaction temperature- room temperature

Table 6.3 Acylation of polystyrene by variation in reaction time

Code	Time h	% Acetylation
AM-14	6	46
AM-15	17	66

AM-16	20	71
-------	----	----

Polystyrene-13 g (0.125 mole), aluminium chloride- 33.5 g (0.25 mole), Acetyl chloride-13.35 mL (0.1877 mole), solvent -carbon disulphide, reaction temperature- room temperature

Table 6.4 Acylation of polystyrene by using cyclohexane as solvent

Code	Acetyl chloride		Reaction Temperature	Reaction Time h	Solvent	% acetylation
	mL	mole				
AM-17	3.55	0.05	RT	20	CH	62
AM-18	3.55	0.05	RT	42	CH	72
AM-19	3.55	0.05	45	20	CH	87
AM-20	2.13	0.03	RT	42	CH	64
AM-21	3.55	0.05	55	5	CH	79
AM-22	3.55	0.05	55	7	CH	88
AM-23	3.55	0.05	RT	20	CH:CS ₂ 4:1 v/v	92

Polystyrene-2.6 g (0.025 mole), aluminium chloride- 6.7 g (0.05 mole), CH-cyclohexane, CS₂-carbon disulphide

6.2.2.2 Baeyer Villiger oxidation

Oxidation of poly(4-acetyl styrene-co-styrene): The acetyl groups of poly(4-acetyl styrene) were converted to acetoxy groups to form poly(4-acetoxy styrene) by Baeyer-Villiger oxidation. Hydrogen peroxide (H₂O₂) and peracetic acid have hitherto been used to oxidise acetyl to acetoxy groups.² We evaluated sodium perborate and trichloroacetic acid as oxidising agents. The modification of polymers was done by using two different types of reagents: acetic anhydride and hydrogen peroxide or sodium perborate and trichloroacetic acid.

Poly(4-acetyl styrene) (1 g) was dissolved in 10 mL glacial acetic acid. The polymeric solution was stirred in a round bottom flask. To the stirring solution 3 mole sodium perborate and 4 mole trichloroacetic acid were added in small lots at regular time intervals. The reaction mixture was stirred at room temperature for periods up to 120 h. The reaction mixture was filtered, the filtrate was precipitated with 250 mL distilled water, washed with water, filtered and dried.³ Yield - 70%. The product is a terpolymer of styrene, 4-acetyl styrene and 4-acetoxy styrene. 4-Acetoxy styrene has IR peaks at ν (cm^{-1}): 3024 (m, Ar-C-H), 2912 (s) 1753 (s, O-C=O), 1680 (C=O) 1600 (s, Ar-C=C), 1500, 1414 and 1200.

Table 6.5 Oxidation of acetyl to acetoxy groups with acetic anhydride and hydrogen peroxide

Code	H_2O_2 6 wt%		Trix		Reaction Temperature	Time (h)
	mL	mole	g	mole		
AC-1	5.8	0.0100	-	-	RT	72
AC-2	5.8	0.0100	-	-	RT	129
AC-3	5.8	0.0100	2.22	0.0135	RT	24
AC-4	5.8	0.0100	2.22	0.0135	80°C	10
AC-5	11.6	0.0201	2.22	0.0135	RT	90

Polymer PACS- 1g (6.84×10^{-3} mole), acetic anhydride- 1.3 mL (0.0137 mole), disodium hydrogen phosphate 3.635 (0.0256 mole) Trix- trichloroacetic acid

Table 6.6 Oxidation of acetyl groups to acetoxy groups with sodium perborate

Code	Trix acid		Reaction Time (h)	%
	g	mole		
EA-2	2.22	0.0135	48	36

EA-3	4.44	0.0271	24	50
EA-4	6.66	0.0407	24	66
EA-5	8.88	0.0543	24	65

Polymer PACS- 1g (6.84×10^{-3} mole), Na perborate- 3.16 g (0.0205 mole), acetic acid –30 mL

Table 6.7 Oxidation of acetyl groups to acetoxy groups using sodium perborate : Effect of reaction time

Code	Triox acid		Reaction Time (h)	%
	g	mole		
EM-6	4.44	0.0271	72	55
EM-7	4.44	0.0271	96	65
EM-8	4.44	0.0271	120	75

Polymer PACS- 1g (6.84×10^{-3} mole), Na perborate- 3.16 g (0.0205 mole), acetic acid –30 mL

6.2.2.3 Hydrolysis of acetoxy groups to hydroxyl groups

Sodium hydroxide (0.2 g) was dissolved in 10 mL methanol, taken in a round-bottom flask equipped with a magnetic pellet for stirring and a reflux condenser. Poly(4-acetylstyrene-co-4-acetoxystyrene-co-styrene) (1 g; 0.0068 mole) was taken in round-bottom flask and heated in an oil bath at 60°C for 5 h, cooled, and filtered. The filtrate was added to 250 mL distilled water and acidified with 5 mL of concentrated hydrochloric acid. The product, obtained as a cream-coloured precipitate, is poly(4-hydroxystyrene-co-acetylstyrene-co-styrene). The precipitate was filtered and washed with water and dried under vacuum. Yield was approximately 80%. IR spectra shows peaks at 3500-3200 cm^{-1} (br-OH), 3024 cm^{-1} (Ar-C-H) 2912 cm^{-1} , 1680 cm^{-1} (C=O), 1600 cm^{-1} (Ar-C=C), 1510, 1440 and 1219 cm^{-1} .

6.3 Synthesis of sensitisers for photoresist

6.3.1 Synthesis of 1,2-naphthoquinone diazide-5-sulphonyl chloride

A mixture of chloro sulphonic acid 90 mL and thionyl chloride 20 mL (0.1980 mole), was taken and 9.9 g (0.036 mole) sodium 1,2-naphthoquinone diazide-5-sulphonate was added slowly. The optimal time/temperature was 60 min at 45–50°C. The reaction product was isolated by pouring the mixture over ice water. The product was filtered and dried. It was dissolved in acetone and reprecipitated by pouring slowly into a 2 % solution of hydrochloric acid. The yield was 70 %.

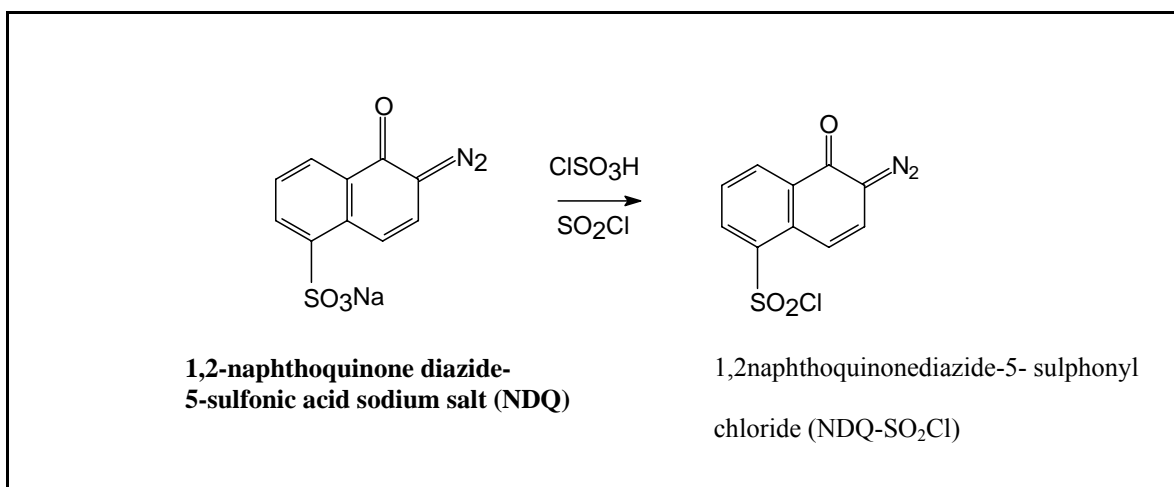


Figure 6.2: Conversion of 1,2-DNQ sodium salt to DNQ-SO₂Cl

IR spectra peaks observed were: 1634 cm⁻¹ (C=O), 1365 cm⁻¹ (S=O), 1360, 1389 cm⁻¹ (SO₂Cl), 1199, 1169 cm⁻¹ (SO₂Cl), 1630 cm⁻¹ (broad) (N=N).

6.3.2 Diester (DES) of 1,2,5-naphthoquinone diazide sulphonyl chloride (DNQ-SO₂Cl) and 2,3,4-trihydroxy benzophenone (THBP)

In a round bottom flask 5.4 g (0.020 mole) DNQ-SO₂Cl and 2.302 g (0.01 mole) THBP (2:1) were dissolved in 20 mL acetone and stirred for 10 minutes. 2.78 mL (0.02 mole) of triethylamine (Et₃N) was added dropwise over 15-20 minutes.⁴ After the addition, stirring was continued for 1 h. The reaction mixture was filtered and filtrate

poured into 100 mL of 1N hydrochloric acid solution. The precipitate obtained was filtered and dried.

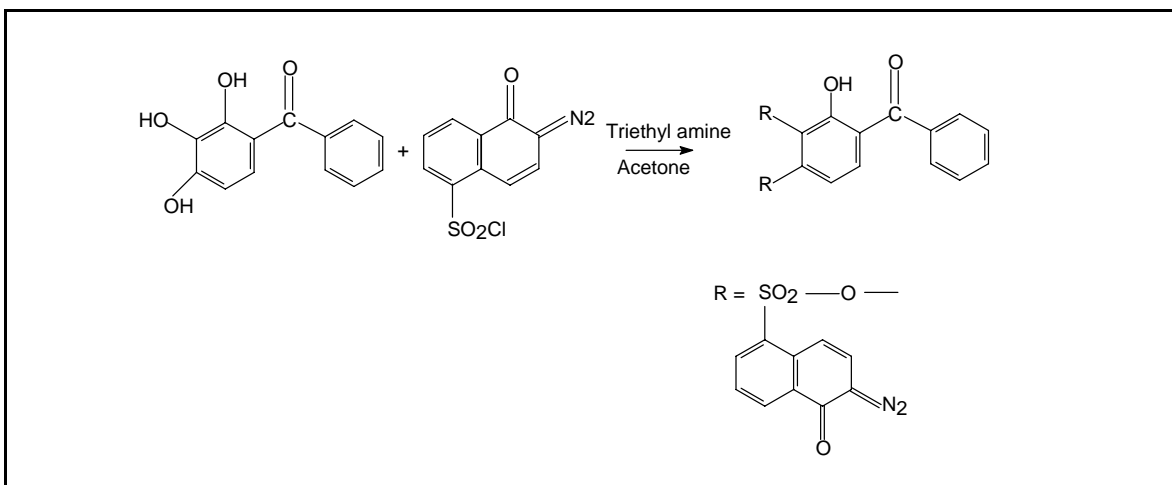


Figure 6.3 : Coupling of DNQ-SO₂Cl with 2,3,4-trihydroxy benzophenone to form diester

6.3.3 Triester (TES) of 1,2,5-naphthoquinone diazide sulphonyl chloride (DNQ-SO₂Cl) and 2,3,4-trihydroxy benzophenone (THBP)

The procedure followed was the same except that DNQ-SO₂Cl used was 8.07 g (0.03) mole), THBP was 2.3 g (0.01) and triethylamine was 4.65 mL (0.0334 mole). The mole ratio of DNQ-SO₂Cl to THBP was 3:1.

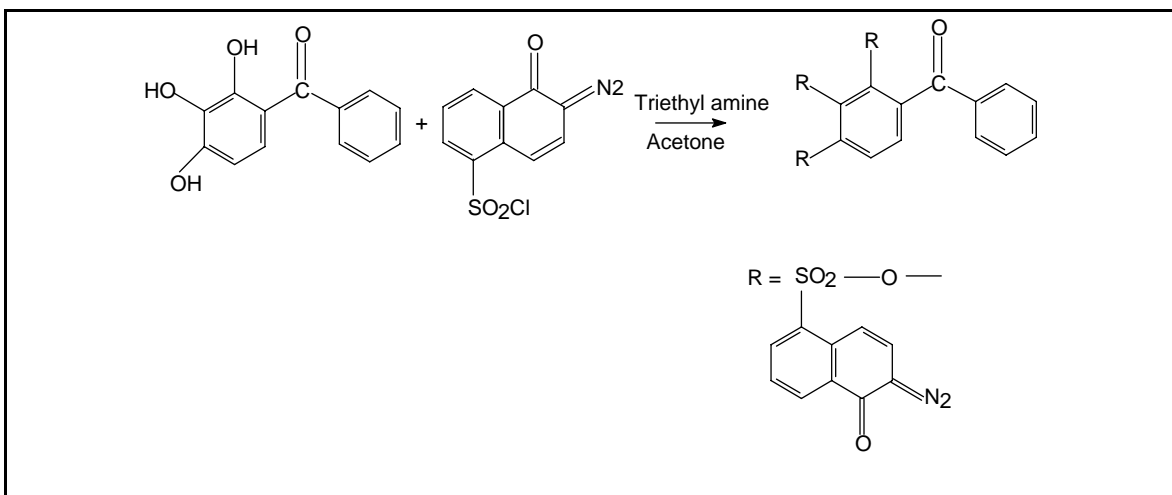


Figure 6.4 : Coupling of DNQ-SO₂Cl with 2,3,4-trihydroxy benzophenone to form triester

6.3.4 Synthesis of random polymer (RP)

A 500 mL three necked flask equipped with a stirrer was charged with 54.07 g of m-cresol (0.5 mole), 54.07 g of p-cresol (0.5 mole), 66.44 g of 36.155% formaldehyde (0.8 mole) and 1.4 g of oxalic acid (0.625 mole %). Water (20 mL) was added as solvent and reaction mixture was heated at 100°C for 18 h at 300 rpm. Autoclave was allowed to cool and water was decanted off. Novolak resin formed was dissolved in 100 mL acetone and precipitated in water methanol mixture (4:1 v/v). After several washings it was dried in vacuum oven at 45°C for 30 h.

6.3.4.1 Synthesis of random Polymeric sensitiser based on random polymer (RP) and 2,1,5-naphthoquinone diazide sulphonyl chloride (DNQ-SO₂Cl) [RPS]

Hydroxyl groups of random polymer were esterified with 2,1,5-naphthoquinone diazide sulphonyl chloride to obtain the random polymeric sensitiser. The required amount of polymer (random) and sensitiser in acid chloride form were taken in required proportions in acetone and stirred for 5-10 minutes. Triethyl amine was added slowly. The reaction flask was kept in ice water (20-25°C). After the addition was over stirring was continued for 2 hours at the end of which the reaction mixture was poured into 50 mL 1N hydrochloric acid solution. The precipitate formed was filtered. A series of polymeric sensitisers were synthesised by varying the ratio of polymer to sensitiser as 1:0.1, 1:0.2, 1:0.3, and 1:0.5. The details of the modified polymers are shown in Table 6.8.

Table 6.8 Modification of random phenolic resin with variation in percent modification of hydroxyl groups

Polymer code	Modification %	Sensitiser		Et ₃ N	
		g	mole	g	mole
Cmxo-4h-10	10	0.6	7.46 x 10 ⁻⁴	0.309	7.46x 10 ⁻⁴
Cmxo-4h-20	20	1.2	4.70 x 10 ⁻³	0.621	4.70x 10 ⁻³
Cmxo-4h-30	30	1.8	6.71x 10 ⁻³	0.935	6.71x 10 ⁻³
Cmxo-4h-50	50	2.9	1.11x 10 ⁻³	1.560	1.11x 10 ⁻³

Polymer-3.0 g (0.02238 mole)

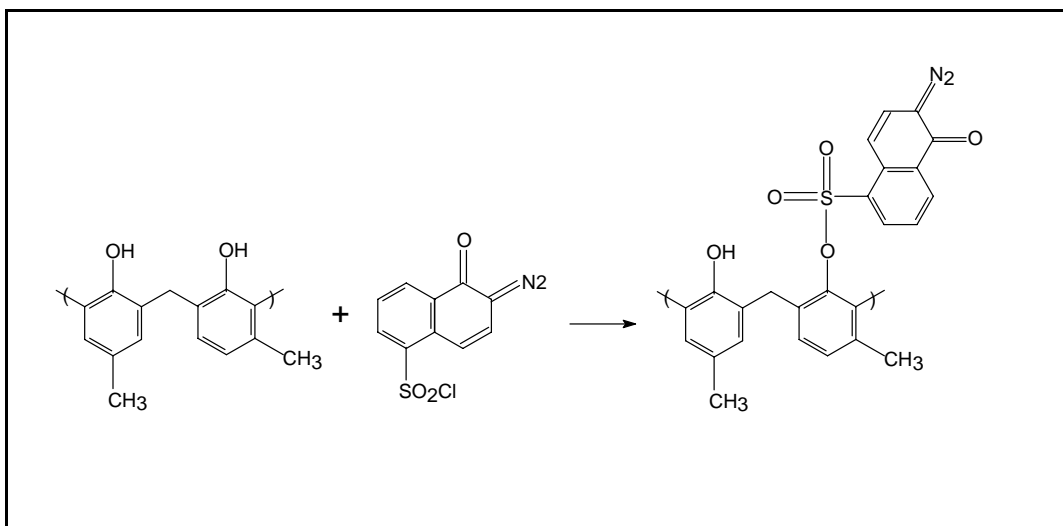


Figure 6.5 : Coupling of DNQ-SO₂Cl with oligomer to form random polymeric sensitizer

6.3.5 Synthesis of ordered phenolic resin (OP)

A 250 mL three necked flask equipped with a stirrer was charged with m-cresol (10.27 g; 0.095 mole), 2,6-dimethylol-4-methyl phenol (BMPC) (16.81 g; 0.105 mole), oxalic acid (0.153 g; 0.625 mole %) in water (30 mL) and 2-ethoxy ethyl acetate (20 mL). Reaction mixture was heated in an oil bath at 100°C for 18 h. The reaction was cooled and supernatant was decanted off. 2-Ethoxy ethyl acetate (40 mL)

was added to the reaction mixture. The product was kept for 24 h to dissolve completely in 2-ethoxy ethyl acetate. After the complete dissolution, the product was precipitated in water (200 mL). It was purified by washing and dried in vacuum oven at 45°C for 24 h.

6.3.5.1 Synthesis of ordered polymeric sensitiser based on ordered polymer (OP) and 2,1,5-naphthoquinone diazide sulphonyl chloride (DNQ-SO₂Cl) [DMP]

The procedure adopted in section 6.3.4.1 was used. Ordered polymer was used instead of random polymer. The procedure used is same as in section 6.3.4.1. A series of polymeric sensitisers were synthesised by varying the ratio of polymer to sensitiser as 1:0.1, 1:0.2, 1:0.3, and 1:0.5. The details of the modified polymers are shown in Table 6.9.

Table 6.9 Modification of ordered phenolic resin with variation in percent modification of hydroxyl groups

Polymer code	Modification %	Sensitiser		Et ₃ N	
		g	mole	g	mole
DMP-1	10	0.352	1.31 x 10 ⁻³	0.18	1.77 x 10 ⁻³
DMP-2	20	0.726	2.70 x 10 ⁻³	0.36	3.55 x 10 ⁻³
DMP-3	30	1.090	4.06 x 10 ⁻³	0.54	5.33 x 10 ⁻³
DMP-5	50	1.775	6.62 x 10 ⁻³	0.90	8.89 x 10 ⁻³

Polymer-2.0 g (0.0149 mole)

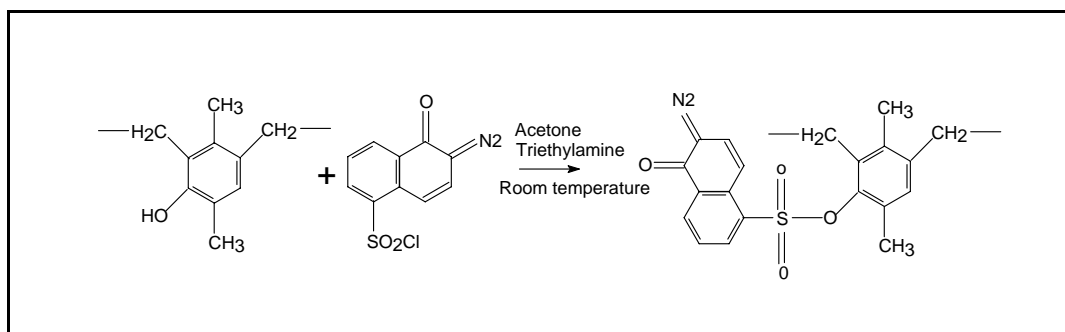


Figure 6.6 : Coupling of DNQ-SO₂Cl with ordered polymer to form ordered polymeric sensitiser

6.4 Lithographic studies

Photoresist formulations were prepared by varying the type and proportion of polymer, sensitiser and solvent. These were then coated on silicone wafer and then exposed at 365 nm and developed in aqueous alkaline developer. The following recipe were used for lithographic evaluation.

Base polymer	12.5%
Diazo naphthoquinone photosensitiser (DES or TES)	4.6%-6%
Polymeric sensitiser (RPS / DMP)	4.6%-12.5%

Table 6.10 Lithographic studies of various compositions (formulations)

Code	Solvent	Organic Sensitiser	Sensitiser	Exp. (s)	Develop (s)	Observation
PHS-1	EEA	DES ^a	-	70	75	Pattern developed in 60 s but the walls merged in next 15s
PHS-2	EEA	TES ^a	-	50	35	Pattern developed spacing between pattern is maintained thickness-1.396m
PHS-3	EL	TES ^a	RPS 10% ^b	50	120	Pattern developed

PHS-4	EEA	TES ^a	RPS 10% ^b	90	60	Pattern developed
PHS-5	EEA	TES ^a	RPS 50% ^b	120	70	Pattern developed but some patches of the resist not developed
PHS-6	EEA	TES ^c	RPS 20% ^c	60	90	Pattern developed but lots of particles
PHS-7	EEA	TES ^c	RPS 50% ^c	60	90	Film thickness of 0.499m
PHS-8	EEA	TES ^c	RPS 10% ^c	85	65	Film thickness of 1.45m
PHS-9	EEA	TES ^a	DMP 10% ^b	60	60	Pattern developed
PHS-10	EEA	TES ^c	DMP 20% ^c	90	60	Pattern developed but very thin film
PHS-11	EEA	TES ^c	DMP 50% ^c	60	90	Pattern developed having a thickness of the film 1.381

a-150 mg organic sensitizer ; b-250 mg polymeric sensitizer ; c-92 mg of respective components EEA-ethoxy ethylacetate, EL-Ethyl lactate, Exp.-Exposure time, Develop – Development time in seconds

6.5 Results and discussion

Lithographic images develop because of difference in dissolution kinetics between exposed and unexposed areas of the resist. The present work deals with the study of the behaviour of the terpolymer poly(acetylstyrene-co-hydroxystyrene-co-styrene) where in the aromatic ring of benzene rings contain hydroxyl groups, instead of conventionally used novolac resins, in I-line photoresist formulations along with di or trisubstituted naphthoquinone diazide sensitizers with or without polymeric sensitizer. The photoresist solutions, for lithographic evaluation, were formulated in ethyl lactate (EL) or ethoxy ethyl acetate (EEA). These comprised of terpolymer based on polystyrene where in the para position of benzene ring is partially substituted with acetyl, acetoxy and hydroxy groups along with the photoactive components.

Compositions of the polymer and sensitiser were varied and its effect on the exposure and development time were investigated.

According to literature, polymers suitable for photoresist application should have molecular weight in the range 5000-8000.⁵ Therefore, a series of polystyrene were synthesised by suspension polymerisation, using carbon tetrachloride as chain transfer agent. The details of the variations in chain transfer agent added, and the changes in molecular weight of the polymer obtained are tabulated in Table 6.1. As expected, in Figure 6.7, the molecular weight decreased with increase in concentration of the chain transfer agent. The gel permeation chromatography (GPC) data reveals a decrease in polydispersity index with increase in the relative mole ratio of the chain transfer agent, to give polymers with narrow molecular weight distribution.

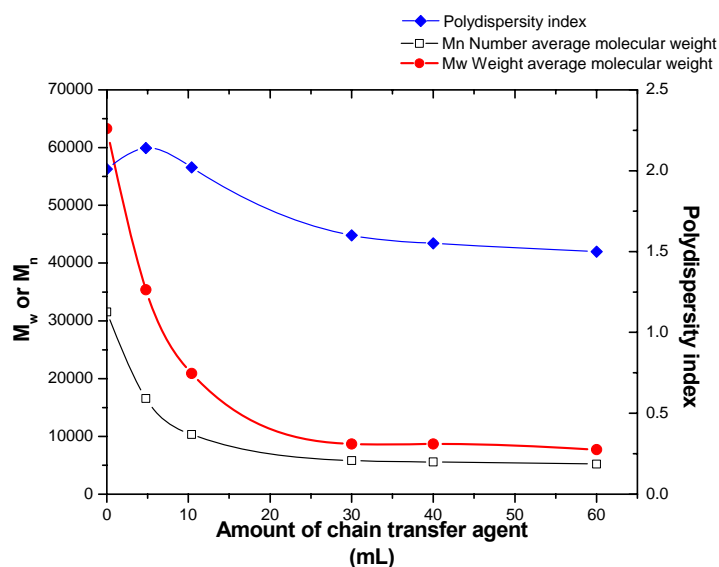


Figure 6.7 : Effect of chain transfer agent on M_w , M_n and polydispersity index of polystyrene

Chain transfer agent has the ability to stop the growth of molecular chain by yielding an atom to the active radical at the end of the growing chain. It in turn is left as a radical that can initiate growth of new chain. Carbon tetrachloride has a chain transfer constant of 9.3×10^{-4} at 60°C for styrene.⁶ Figure 6.7 shows that as the amount of chain transfer increases in the reaction medium there is a decrease in weight average molecular weight (M_w) and number average molecular weight (M_n) of the polymers. The polydispersity index of the polymers is between 1.5 to 2.1. Polymers conventionally used in I-line photoresists are phenolic resins. Phenolic resins have very high dissolution rate in aqueous alkaline developers but their polydispersity are high.

The modification were carried in three different steps as stated earlier: Friedel-Craft's Acylation (to introduce acetyl groups in the polymer); Baeyer-Villager oxidation (to convert acetyl groups to hydroxy groups) and hydrolysis (to convert acetoxy groups to hydroxyl groups). The factors affecting acylation are the catalyst, the acyl component and reaction time. These parameters were varied and the conditions were optimised to obtain maximum conversion.

The acetylation of polystyrene was conducted either exclusively in carbon disulphide (CS_2) or by a partial substitution of carbon disulphide with cyclohexane. Tables 6.2, 6.3 and 6.4 show synthesis strategies by variation in molar concentration of reactants, reaction time, temperature and solvent. The catalyst and its complex are insoluble in the solvent so the reaction is heterogeneous throughout.

The dependance of the extent of acetylation of polystyrene with variance in solvent, reaction time, temperature and mole ratio of acetylating agent was monitored by the reduction in IR peak at 700 cm^{-1} , which is characteristic of monosubstituted benzene⁷ (eg. polystyrene). This strong peak is due to C-H out of plane deformation

of 5 adjacent free hydrogen atoms. Similarly, the peak at 750 cm^{-1} is due to C-H out of plane deformation of 4 adjacent free hydrogen atoms. These peaks are absent in para disubstituted aromatic ring. The peak at 829 cm^{-1} is due to para disubstituted benzene ring. C-H out of plane deformations of two adjacent free hydrogen atoms in disubstituted aromatic compounds is observed in the $860\text{-}800\text{ cm}^{-1}$ region.

For quantitative estimation, the IR spectrum obtained was converted to base line corrected normalised spectrum. In normalised spectrum of polystyrene, the absorbance at 700 cm^{-1} is taken as 1, since this is the major peak. In other words, the spectrum is normalised with the major absorbance peak. IR spectra of poly(acetyl styrene-co-styrene) and poly(acetoxy styrene-co- 4-acetyl styrene-co-styrene) were normalised with respect to the peak at 1680 cm^{-1} , due to C=O stretching. The continued presence of peak at 700 cm^{-1} clearly indicates that acetylation is never quantitative. The absorbance at this peak directly depends on fraction of monosubstituted aromatic ring in the normalised IR spectra of polymers containing para disubstituted aromatic nucleus. The progress of acetylation in lower mass analogs such as benzene, toluene and so on depends on catalyst, acyl component, addition sequence, solvent and ratio of catalyst to acyl component.⁸ The percent yield of the product increases as the reaction time, mole ratio of acylating agent and temperature of reaction mixture is increased. The extent of the acylation of long chain molecules, such as in present investigation, presents difficulty in the accessibility of particular reaction site due to conformational complexity.

The effect of reaction time, temperature and mole ratio of catalyst to acyl component is discussed with respect to two different solvents. Polymers APS-1-13 and AM-14-16 were synthesised using carbon disulphide as solvent. Optimally 80 percent acylation can be achieved at ambient temperature in 20 h with the molar

composition of the reactants polystyrene (PS), aluminium chloride (AlCl_3), acetyl chloride (CH_3COCl) as 0.025 mole (repeat unit), 0.05 mole and 0.05 mole, respectively. It was observed that acetylation reaction conducted in non-polar solvents such as cyclohexane, n-hexane, CS_2 , was faster than acetylation reactions conducted in halogenated solvents.⁹ Monosubstituted benzene (eg styrene) is acylated at the para position because of the large steric requirement of the attacking reagent.

Polymers AM-17 to AM-22 were products of acetylation in cyclohexane. IR spectra of two acylated polystyrene samples (AM-18 and AM-20) prepared using two different mole ratios of polystyrene to acetyl chloride are compared with polystyrene in Figure 6.8. The substitution reactions were conducted at the ambient (25°C) for 42 h. In Figures 6.8-6.12 the Y-axis has arbitrary units since each spectrum is shifted upwards to avoid crowding. It is evident from Figure 6.8 that the peak at 700 cm^{-1} is reduced drastically in the reaction where the mole ratio of reactants used is 1:2 (polystyrene : acetylating agent) [72%] as compared to the reaction where mole ratio of reactants used is 1:1.5 (polystyrene : acetylating agent) [64%]. Simultaneously, the C = O stretching peak of ketone appears at 1680 cm^{-1} . Higher extent of acetylation can be achieved by increasing the reaction temperature from ambient to 45°C (AM-17 and AM-19). These two polymers were prepared by reacting PS, AlCl_3 , CH_3COCl having molar concentration of 0.025 mole (ru), 0.05 mole and 0.05 mole, for a period of 20 h at 25°C and 45°C , respectively. IR spectra of these two polymers are compared with that of polystyrene in Figure 6.9. The extent of acetylation in AM-17 and AM-19 are 62 and 87 %, respectively. Reaction time can drastically be reduced to 5-7 hours instead of 20 hours to achieve around 85 % acetylation (AM-21 and AM-22) by refluxing the reaction mixture at 55°C . IR spectra of these polymers are presented in Figure 6.10.

The above results indicate that acetylation reactions can be conducted in cyclohexane instead of toxic and flammable carbon disulphide by increasing reaction temperatures to achieve similar extent of acetylation. Acetylation levels (AM-23) identical to that in carbon disulphide can be achieved at room temperature by a partial substitution of cyclohexane with carbon disulphide (CH : CS₂ 4:1 v/v) solvent mixture. The IR analysis for acetylated polymers (AM-13, AM-18 and AM-23) synthesised using 3 different solvent systems is depicted in Figure 6.11. The IR spectra in aromatic substitution region 900-600 cm⁻¹ of acetylated polystyrene prepared in carbon disulphide, cyclohexane and mixed solvent system, along with polystyrene, are presented in Figure 6.12. This figure shows that the extent of acetylation obtained in the reaction where carbon disulphide is used is similar to the extent of acetylation obtained in mixed solvent system (with 20% v/v of carbon disulphide in cyclohexane). This points to a possible catalytic effect of carbon disulphide in the reaction in addition to its role in solvation.

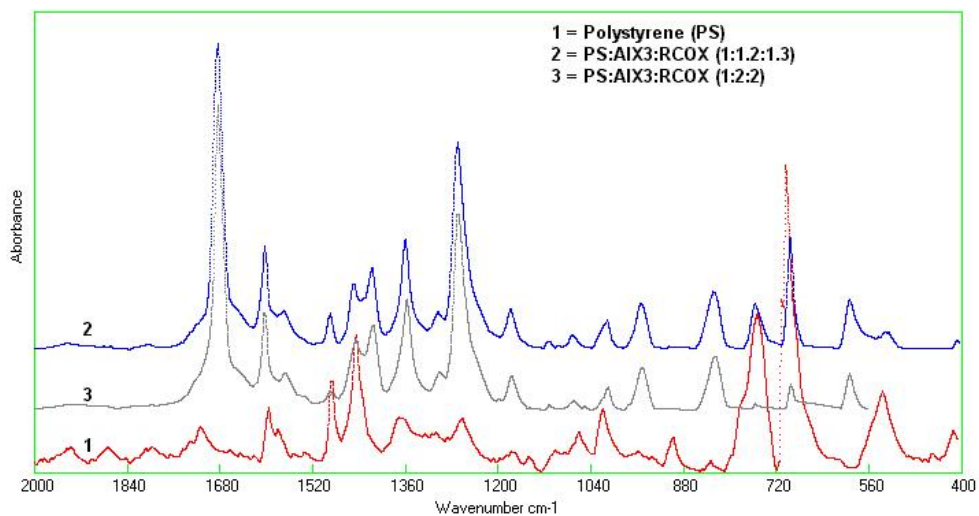


Figure 6.8 : Comparison of infra-red spectra of poly(4-acetyl styrene) with polystyrene: Effect of mole ratio of acetylating reagent

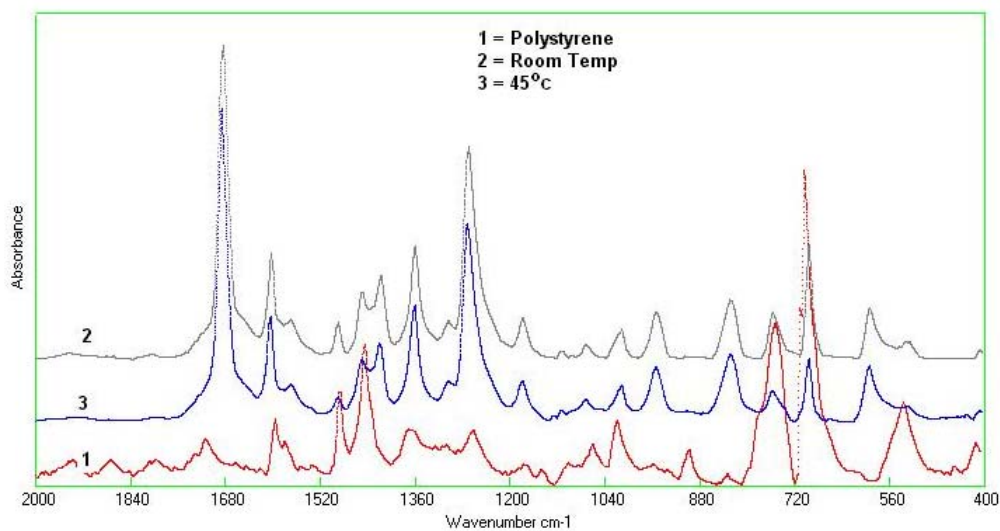


Figure 6.9 : Comparison of infra-red spectra of poly(4-acetyl styrene) with polystyrene: Effect of reaction temperature

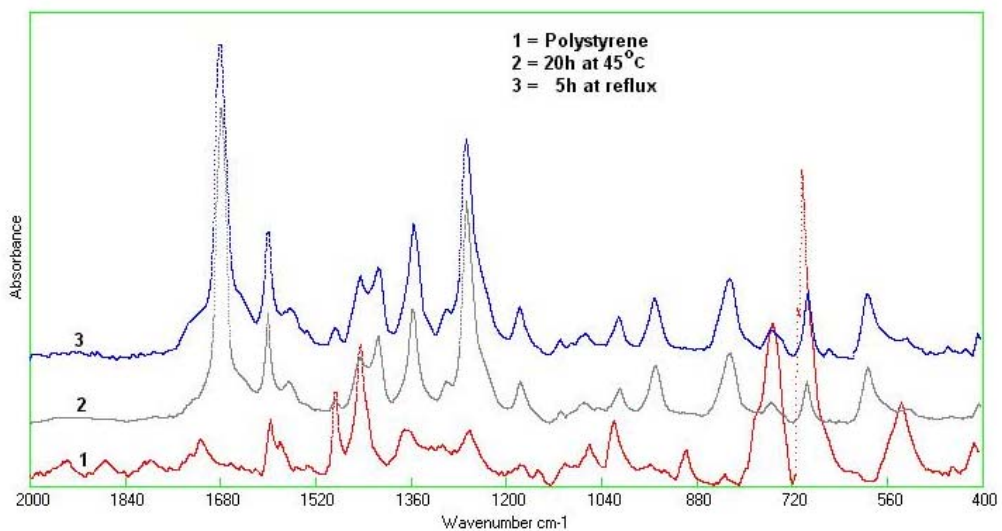


Figure 6.10 : Comparison of infra-red spectra of poly(4-acetyl styrene) with polystyrene: Reduction in reaction time under reflux condition

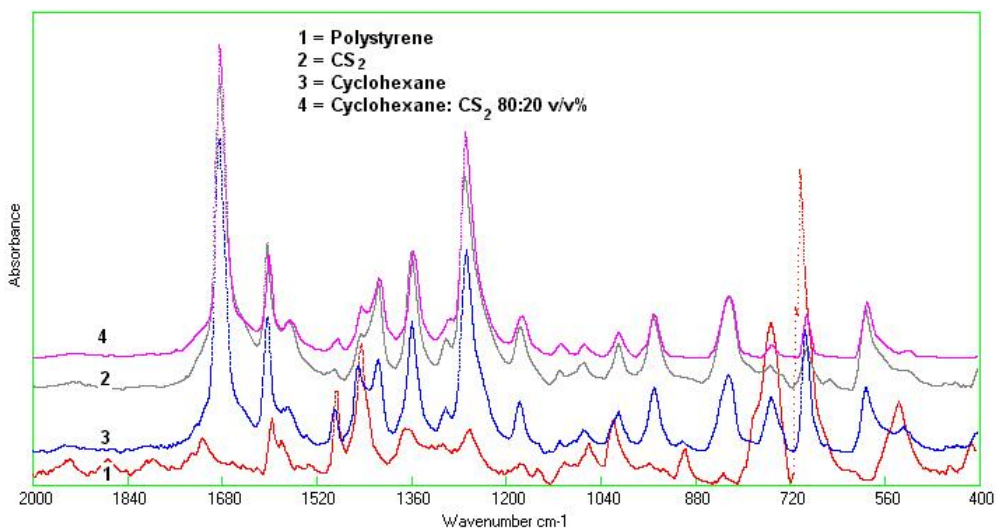


Figure 6.11 : Comparison of infra-red spectra of poly(4-acetyl styrene) with polystyrene: Effect of reaction medium

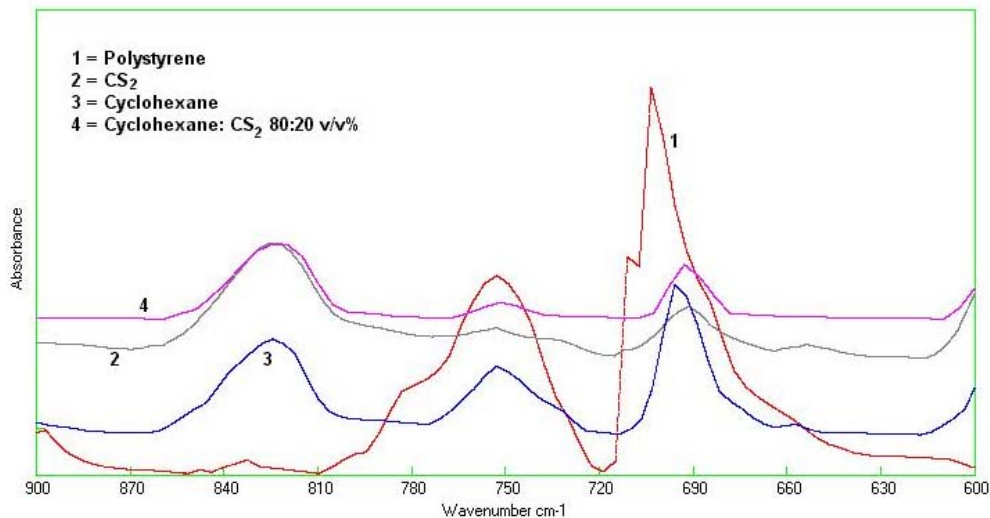


Figure 6.12 : Comparison of infra-red spectra of poly(4-acetyl styrene) with polystyrene in aromatic substitution region: Effect of reaction medium

Acetoxy polystyrene is typically prepared by Baeyer-Villiger oxidation of poly(acetyl styrene). Several oxidising agents have been reported to facilitate Baeyer-Villiger oxidation of low molar mass aromatic ketones to esters. These include permaleic acid,¹⁰ peracetic acid,¹¹ trifluoroacetic acid,¹² potassium peroxydisulphate.¹³ These oxidising agents were evaluated for oxidation of acetyl polystyrene by Dhamodharan et. al.¹⁴ We have evaluated sodium perborate in acetic acid or acetic acid/trichloroacetic acid as oxidising agents to effect the Baeyer-Villiger oxidation. Sodium perborate is an industrially used source of active oxygen to cleave α diketone and oxidation of aniline to azo compound. Oxidation of low molar mass sulphides to sulphoxides or sulphones and ketones to esters was studied by Mokillop et al.¹⁵ We have evaluated the oxidising agent for Baeyer-Villiger oxidation of the polymeric aromatic ketone containing at least one group of relatively high migratory aptitude, a fundamental requirement for oxidative procedure.

The results of the oxidation of acetyl polystyrene to acetoxy polystyrene under various reaction conditions are summarised in Tables 6.5-6.7. Oxidations were studied

under three different sets of reactions. These are: (1) reactions using acetic anhydride and hydrogen peroxide as reagent (AC-1-5) (2) variation in trihaloacetic acid concentration at fixed reaction time (EA-2 to EA-5) using sodium perborate and (3) variation in reaction time for sodium perborate in acetic acid / trihaloacetic acid mixture (samples EM-8 to EM-10).

The Baeyer-Villiger oxidation can be used in oxidation of ketones to esters using wide variety of reagents. The first set of reactions were done using acetic anhydride and hydrogen peroxide. All reactions were conducted at the ambient (25°C). The oxidation yield increased from 28 to 50% with increase in reaction time from 5 to 48 hours, as observed in the first set of reactions. In Tables 6.5-6.7 percent yield is given because it is difficult to quantitatively estimate percent acetoxylation spectroscopically, since C=O of ketone absorb strongly in the region 1600-1840 cm^{-1} . The detailed estimation of these groups requires advanced IR peak convolution software to determine concentration of these peaks on the basis of area under the peak by using molar extinction coefficient.¹⁶ Figure 6.13 shows comparison of IR spectra of conversion of acetyl groups to acetoxy groups using acetic anhydride and hydrogen peroxide as reagent by variation in reaction time. It is observed that as the reaction time increases the conversion is also increased, as an increase in intensity of the peak at 1753 cm^{-1} (s, O-C=O) is observed. It is also observed that in reactions where trichloroacetic acid is also used, the hydrolysis takes place in the reaction mixture. Therefore, increase in peak intensity at 3500 cm^{-1} is observed.

Hydrogen peroxide and acetic anhydride are sharp oxidising agents. Reactions were also carried out using mild oxidising agent such as sodium perborate and trichloroacetic acid. IR spectra of three different acetoxy polystyrene samples with variance in oxidation time are compared in Figure 6.14 with poly(4-hydroxy styrene)

(Aldrich standard) and parent poly(4-acetyl styrene). It is obvious from the figure that the peak at 1753 cm^{-1} due to O-C=O stretching emerges and increases with time. Partial hydrolysis is observed *in situ* when oxidation is conducted in presence of strong trichloroacetic acid / acetic acid mixture. In the second set of experiments, yield levels off at 1:2 (sodium perborate : trichloroacetic acid) mole ratio. In other words, the effect of trichloroacetic acid concentration levels off above 1:2 mole ratio (sodium perborate : trichloroacetic acid). The final experimental set indicates an increase in yield from 55 to 75% as the reaction time was increased from 72 to 120 hours, at room temperature. In this set, mole ratio of sodium perborate to trichloroacetic acid was kept constant (i.e 1:1).

The hydrolysis of acetoxy groups to alcoholic groups was done refluxing with alcoholic alkaline reagent like sodium hydroxide and methanol. Figures 6.15-6.19 show comparison of peaks of standard Aldrich poly(hydroxy styrene) peaks with the hydrolysed products. Peaks at $3500\text{-}3200\text{ cm}^{-1}$ (br-OH), 3024 cm^{-1} (Ar-C-H) 2912 cm^{-1} , 1680 cm^{-1} (C=O), 1600 cm^{-1} (Ar-C=C), 1510, 1440 and 1219 cm^{-1} are observed.

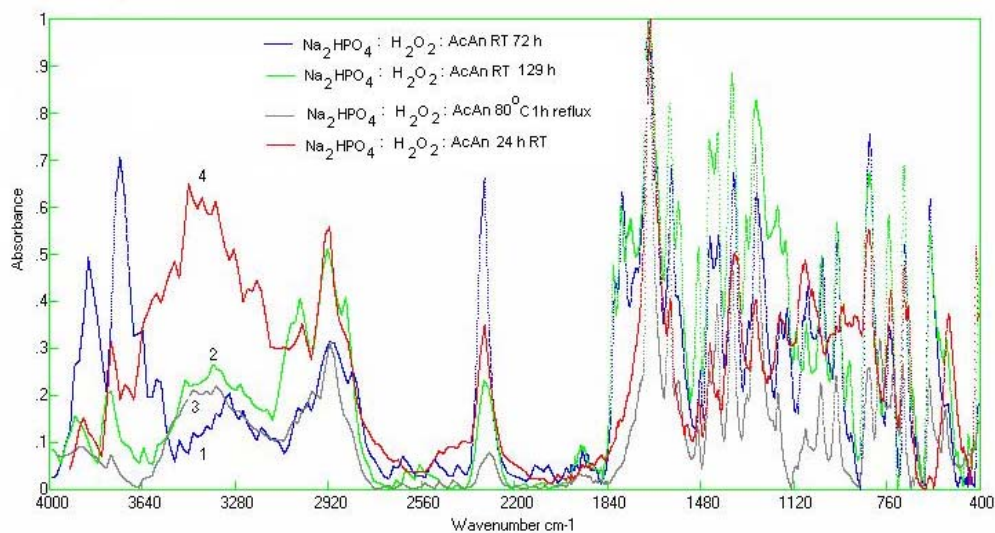


Figure 6.13 : Oxidation using hydrogen peroxide : disodium hydrogen phosphate : acetic anhydride/trichloroacetic acid in chloroform

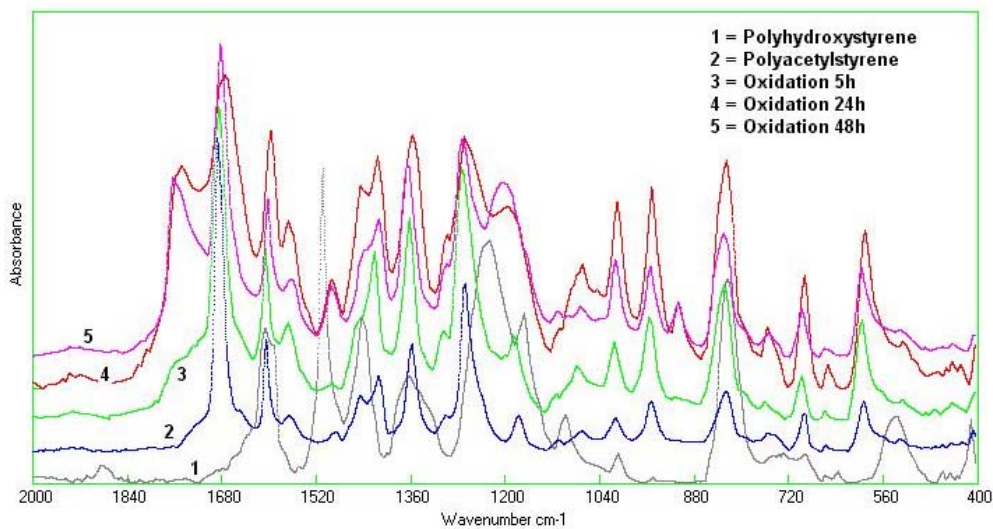


Figure 6.14 : Comparison of infra-red spectra of poly(4-acetoxy styrene) synthesised using sodium perborate in acetic acid with poly(hydroxy styrene) and poly(acetyl styrene): Effect of oxidation time

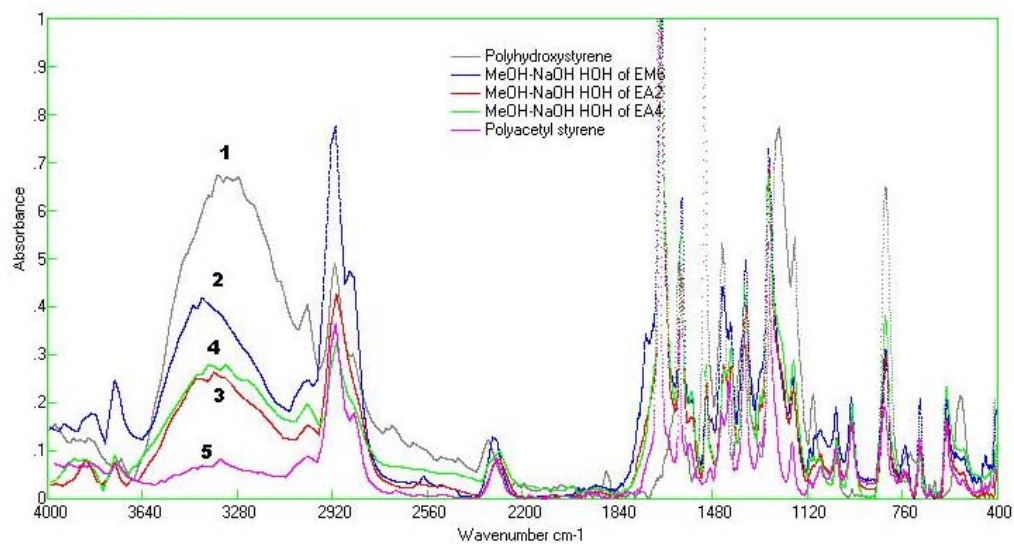


Figure 6.15 : Increase in peak absorbance at 3500 cm⁻¹ due to hydroxyl groups on hydrolysis of acetoxy groups in poly(acetyl styrene-co-acetoxy styrene)

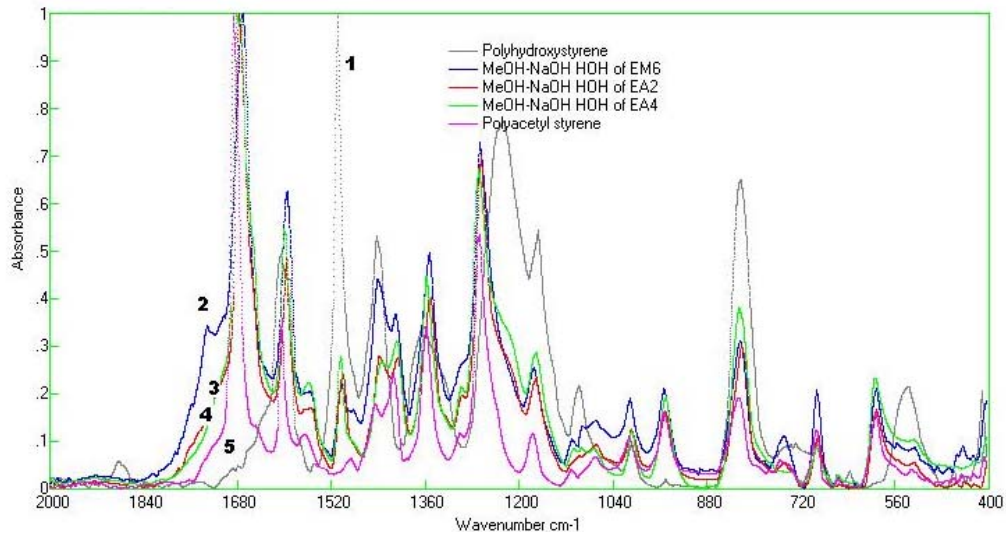


Figure 6.16 : Increase in peak absorbance between 1410 cm⁻¹-1310 cm⁻¹ due to phenolic hydroxyl groups on hydrolysis of acetoxy groups in poly(acetyl styrene-co-acetoxy styrene)

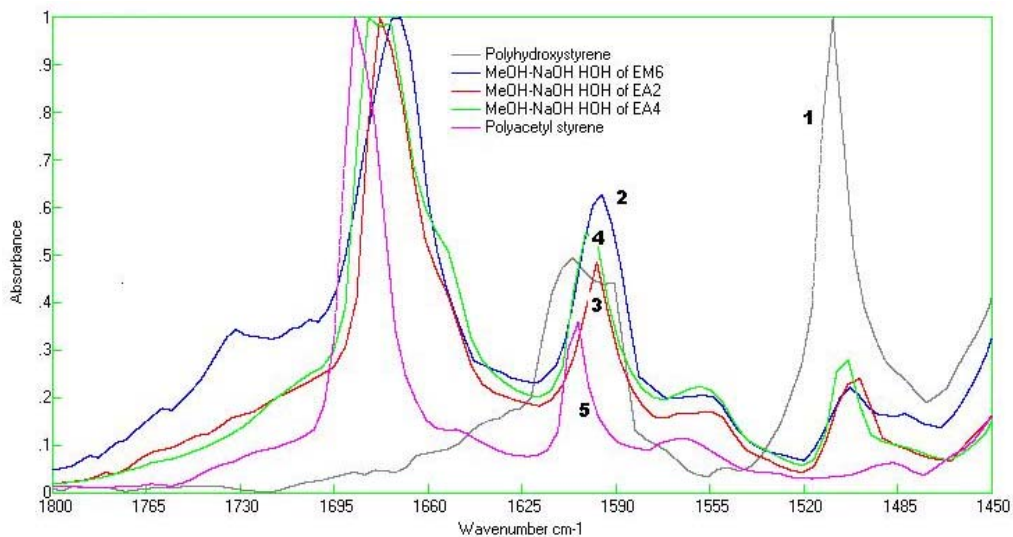


Figure 6.17 : Presence of peak at 1680 cm^{-1} in hydroxyl modified polymer due to partial oxidation of acetyl to acetoxy groups of poly(acetyl styrene-co-styrene)

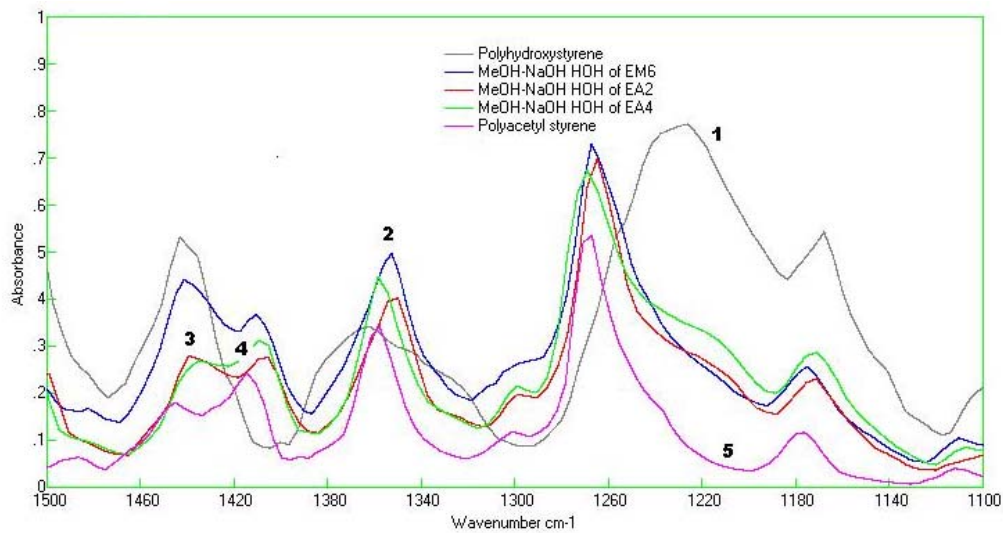


Figure 6.18 : Increase in peak absorbance between 1050 cm^{-1} to 1400 cm^{-1} due to C-O Stretching due to hydrolysis of acetoxy groups in poly(acetyl styrene-co-acetoxy styrene)

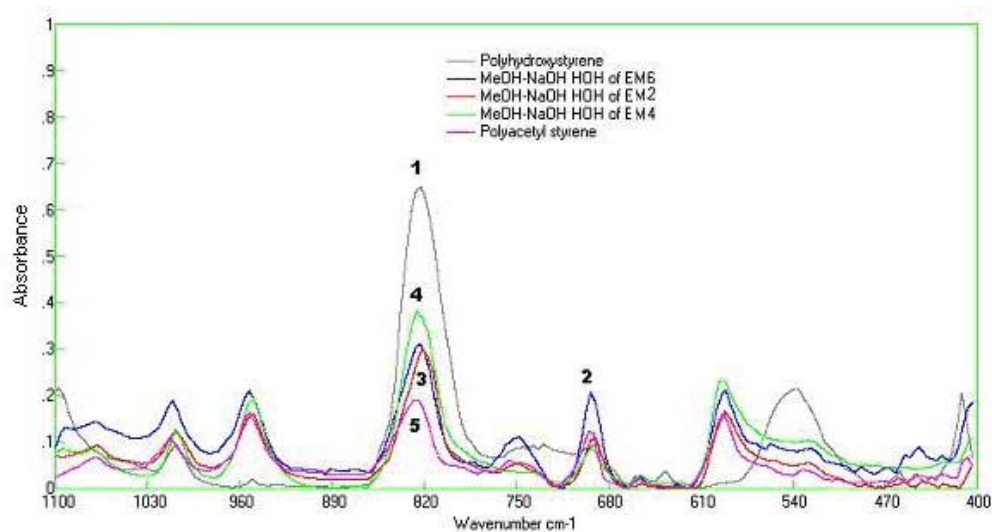


Figure 6.19 : Increase in peak absorbance at 820 cm⁻¹ due to para substitution of benzene ring in poly(acetyl styrene-co-acetoxy styrene)

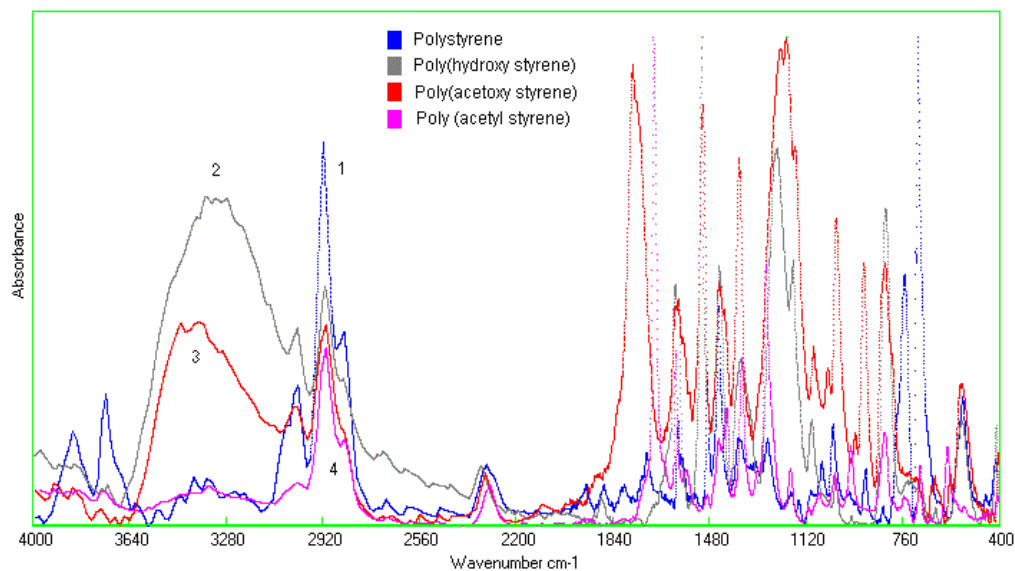


Figure 6.20 : Comparison of IR spectra of polystyrene, poly(acetyl styrene-co-styrene), poly(acetyl styrene-co-acetoxy styrene-co-styrene) and poly(hydroxy styrene-co-acetyl styrene-co-styrene)

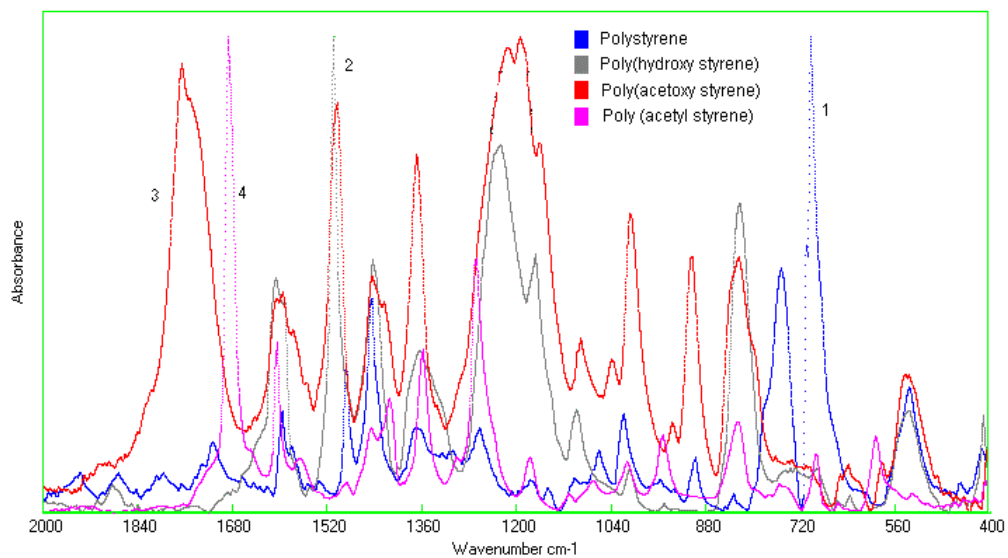


Figure 6.21 : Comparison of IR spectra of polystyrene, poly(acetyl styrene-co-styrene), poly(acetyl styrene-co-acetoxystyrene-co-styrene) and poly(hydroxy styrene-co-acetyl styrene-co-styrene)

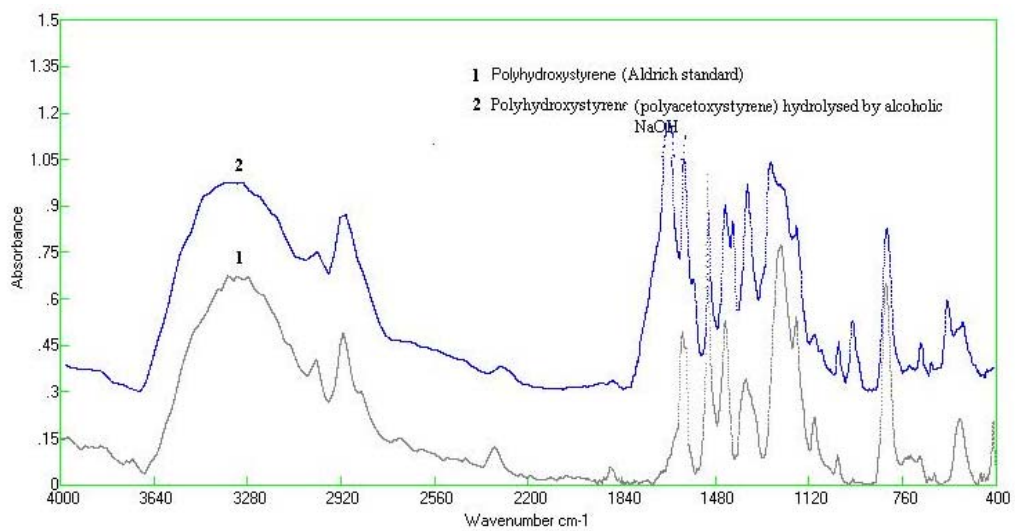


Figure 6.22 : Comparison of IR spectra of poly(hydroxy styrene) from Aldrich and poly(hydroxy styrene-co-acetylstyrene-co-styrene) synthesised

Figures 6.20 and 6.21 present a comparison of IR spectra of polystyrene, poly(acetyl styrene-co-styrene), poly(acetyl styrene-co-acetoxy styrene-co-styrene) and poly(hydroxy styrene-co-acetyl styrene-co-styrene). In Figure 6.22 the IR spectra of polystyrene comprising of partial hydroxyl and acetyl groups is compared with poly(4-hydroxy styrene) obtained from Aldrich Chemicals. All peaks except that at 1680 cm^{-1} are found to match, which is due to unconverted acetyl groups. The conversions in each step was studied by NMR spectroscopy. Figures 6.23-6.27 show the NMR spectra of polystyrene, poly(acetyl styrene-co-styrene), poly(acetoxy styrene-co-acetyl styrene-co-styrene) (CDCl_3 as solvent), poly(hydroxy styrene-co-acetoxy styrene-co-styrene) and standard poly(4-hydroxy styrene) from Aldrich (acetone d_6 as solvent), respectively. Figure 6.23 shows the NMR spectrum of polystyrene in CDCl_3 . Figure 6.24 shows the NMR spectrum of poly(acetyl styrene-co-styrene) in CDCl_3 . In this spectrum, the broad peak at $7.14\ \delta$ present in Figure 6.23 is lowered whereas a new peak at 7.58 appears, which is due to protons ortho to acetyl groups. Appearance of broad peak at $2.54\ \delta$ is due to $-\text{CH}_3$ of acetyl moiety. Figure 6.25 shows the NMR spectrum of poly(acetoxy styrene-co-acetyl styrene-co-styrene) in CDCl_3 . The broad peak at 2.54 is shifted to 2.19 which is due to acetoxy ($\text{CH}_3\text{-COO}$) moiety. The small peak at $2.56\ \delta$ is still present which is due to incomplete oxidation of acetyl groups. Figures 6.26 and 6.27 show the NMR spectrum of poly(hydroxy styrene-co-acetoxy styrene-co-styrene) and standard poly(4-hydroxy styrene) from Aldrich in deuterated acetone as solvent. Signals are observed at 7.68 , 6.64 , 2.07 , $2.9\ \delta$. The peaks match except that at $2.55\ \delta$ which is due to incomplete oxidation of acetyl groups. The signals in the final product are not as sharp as seen in standard homopolymer because it is a terpolymer and hence resolution of NMR signals is difficult. The GPC analysis of polystyrene used in the study was $M_n=5,190$;

$M_w=7,680$ and polydispersity=1.5. The glass transition temperature of poly(4-acetyl styrene), poly(4-acetoxy styrene), poly(4-hydroxy styrene) observed were 107, 134, 142°C, respectively. The glass transition temperature of standard poly(4-hydroxy styrene), having weight average molecular weight of 20,000, is 151°C. The T_g of poly(4-hydroxy styrene) obtained by modification of this polystyrene was 142°C. The IR spectra of the final product showed that the polymer chain comprises of styrene, acetyl styrene, acetoxy styrene and hydroxy styrene and therefore the T_g of the final product is low because it is a tetrapolymer.

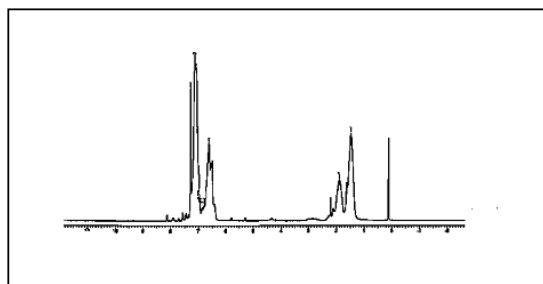


Figure 6.23 : NMR of polystyrene

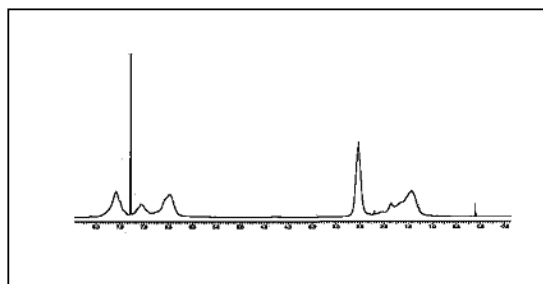


Figure 6.24 : NMR of poly(acetyl styrene-co-styrene)

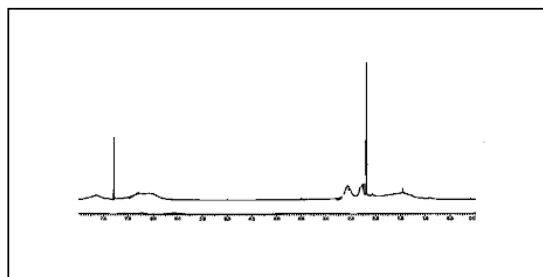


Figure 6.25 : NMR of poly(acetoxy styrene-co-acetyl styrene-co-styrene)

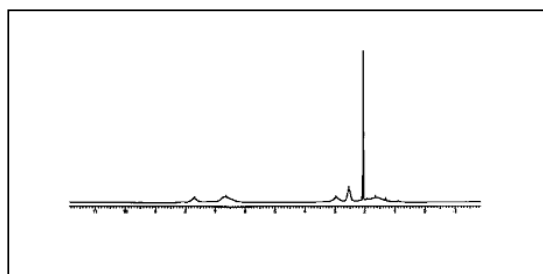


Figure 6.26 : NMR of poly(hydroxy styrene-co-acetoxy styrene-co-styrene)

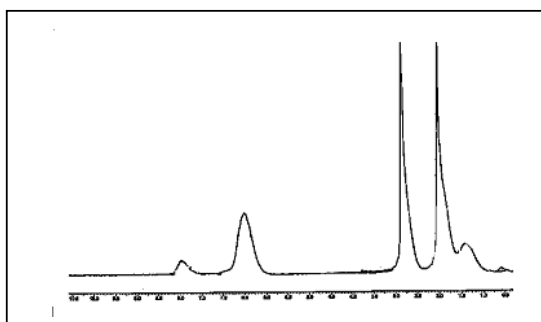


Figure 6.27 : NMR of poly(4-hydroxy styrene) standard

6.5.1 Sensitisers for photoresists

The sensitisers for photoresist applications were based on 2,1,5-diazonaphthoquinones (DNQ) attached to multifunctional hydroxyl groups as these compounds exhibit strong absorption bands in ultra-violet wavelength range 300-450 nm and better suited for exposure with G-line radiation.¹⁷ The sensitisers were synthesised and characterised by ultra-violet spectroscopy and infra-red spectroscopy.

The synthesis details are presented in Section 6.3. The sodium salt of 2,1,5-DNQ was converted to 2,1,5-DNQ acid chloride and then reacted with 2,3,4-trihydroxy benzophenone or oligomers to form organic sensitisers or polymeric sensitisers. The photosensitive behaviour of sensitisers were investigated, prior to their incorporation into the photoresist formulations, by exposure at 365 nm for varied times. The results, presented in Figures 6.28-6.31, depict that the UV absorption of the samples are altered by exposure to 365 nm. The UV spectra of DNQ-5 sulphonate shows characteristic absorption bands at 346 nm and 398 nm. Therefore, DNQ-5 sulphonates work better in the exposure range of Hg G-line radiation. The first two UV absorption bands of the DNQs is due to $n-\pi^*$ and $\pi-\pi^*$ transitions. The intensity of the peak at 398 nm, ascribed to 1,2-naphthoquinone diazide unit, decreased and vanished on exposure at 365 nm. This is because DNQ undergoes chemical change to form indene carboxylic acid on exposure to UV. This is known as bleaching effect as indene carboxylic acid is much less absorbing at wavelengths than DNQ and is important for lithographic performance of the resist material.¹⁸

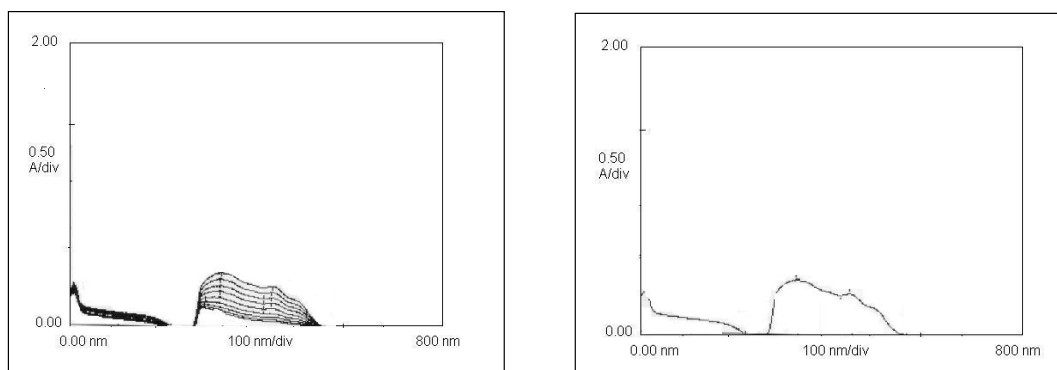


Figure 6.28 : UV study of DES at 365 nm : Absorbance vs exposure time

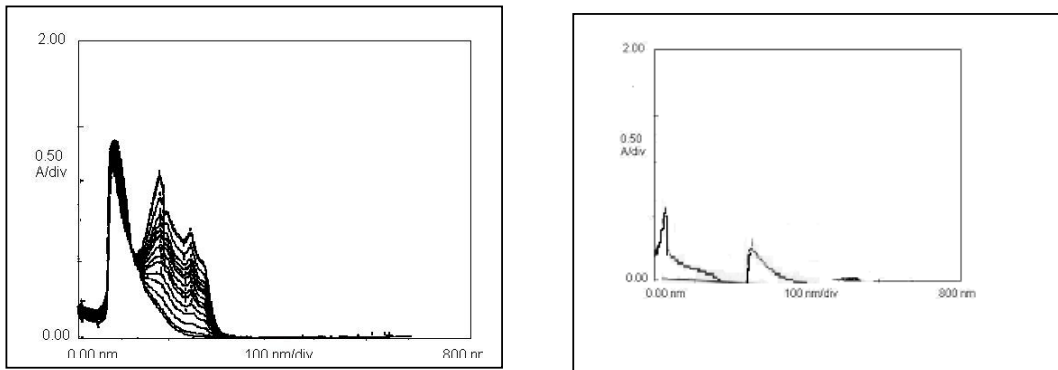


Figure 6.29 : UV study of TES at 365 nm : Absorbance vs exposure time

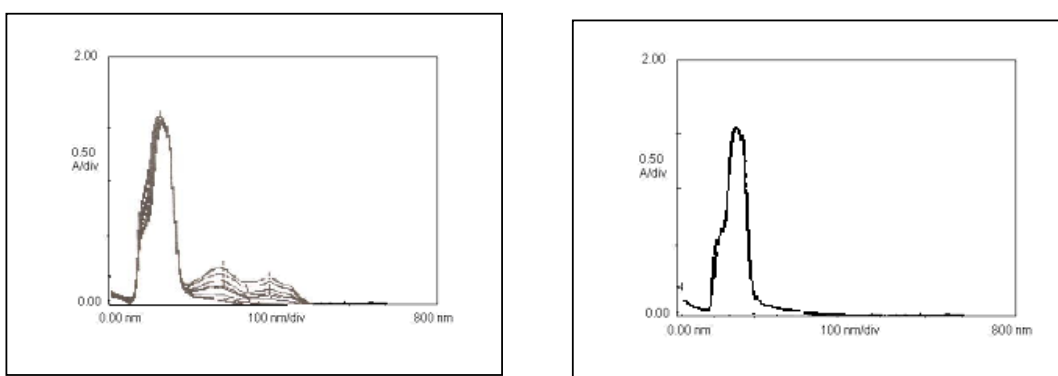


Figure 6.30 : UV study of RPS at 365 nm : Absorbance vs exposure time

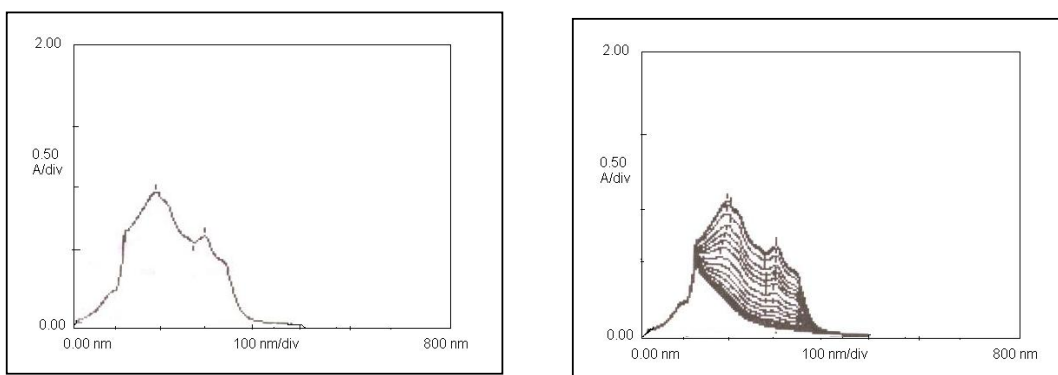


Figure 6.31 : UV study of photoresist formulations at 365 nm : Absorbance vs exposure time

Diester (DES) and triester (TES) synthesised by esterification of 2,3,4-trihydroxy benzophenone with diazonaphthoquinone chloride (DNQ) required 9 and 11 minutes, respectively, for disappearance of peak due to DNQ. TES required more

exposure time than DES because in TES all three hydroxy groups of 2,3,4-trihydroxy benzophenone are converted into DNQ ester while in DES only two hydroxy groups are reacted with photoactive component. Figure 6.30 shows that the polymeric sensitiser RPS required 20 minutes. The photoresist formulation comprising of TES and RPS along with the terpolymer required 20 minutes for the sensitiser peak to disappear after undergoing rearrangement. Sensitisers with one sulphonate group bonded to benzene ring show much lower sensitivity than those with two or three sulphonate groups bonded to 2,3,4-trihydroxy benzophenone.¹⁹ Thus, TES will yield a more photosensitive resist film than DES, at similar sensitiser loading. Higher the sensitivity of sulphonate groups, higher will be quantum yield of acid generation to the resist film. The quantum yield of DNQ photolysis is 0.15 to 0.3.²⁰ This indicates 1 in 6 and 1 in 3 absorbed photons lead to photochemical reaction. There are two proposed mechanisms given by Levine and Suss of photochemical reactions. The mechanism by Sus proposed the formation of indene carboxylic acid on exposure, as shown in Figure 6.32, while Levine suggested the formation of a lactone rather than carboxylic acid, as shown in Figure 6.33.²¹ An internal ester is formed by heating and evolution of water. Both concepts start with formation of highly reactive compound called ketene up on exposure. Ketenes react rapidly to form carboxylic acid group. The acid is then neutralised by developer solution. According to Levine, the ketene formed reacts with unreacted DNQ as the reaction proceeds downward from the surface. The compound is more resistant to dissolution in the alkaline developer as acid salt formation is easier than breaking of a lactone ring.²²⁻²³

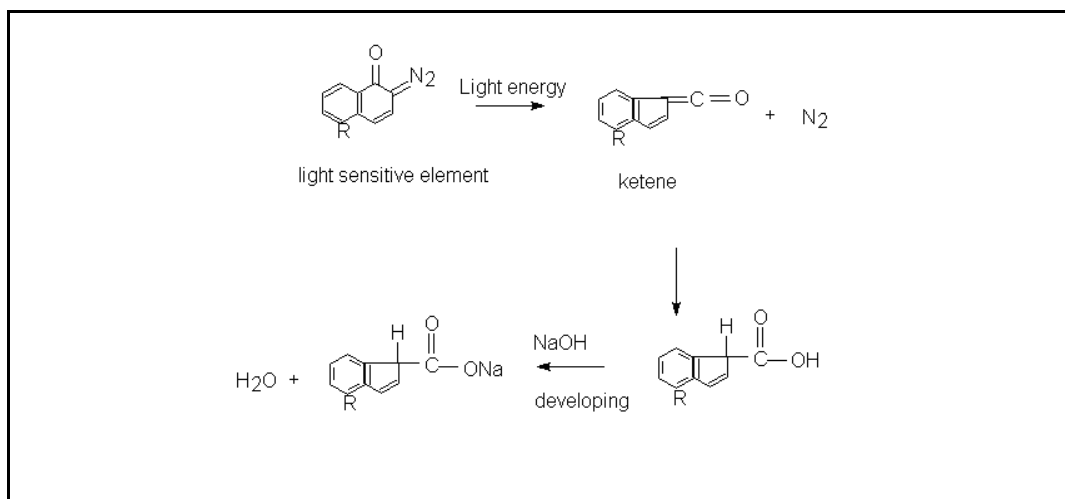


Figure 6.32 : Mechanism of sensitisation, as proposed by Suss²¹

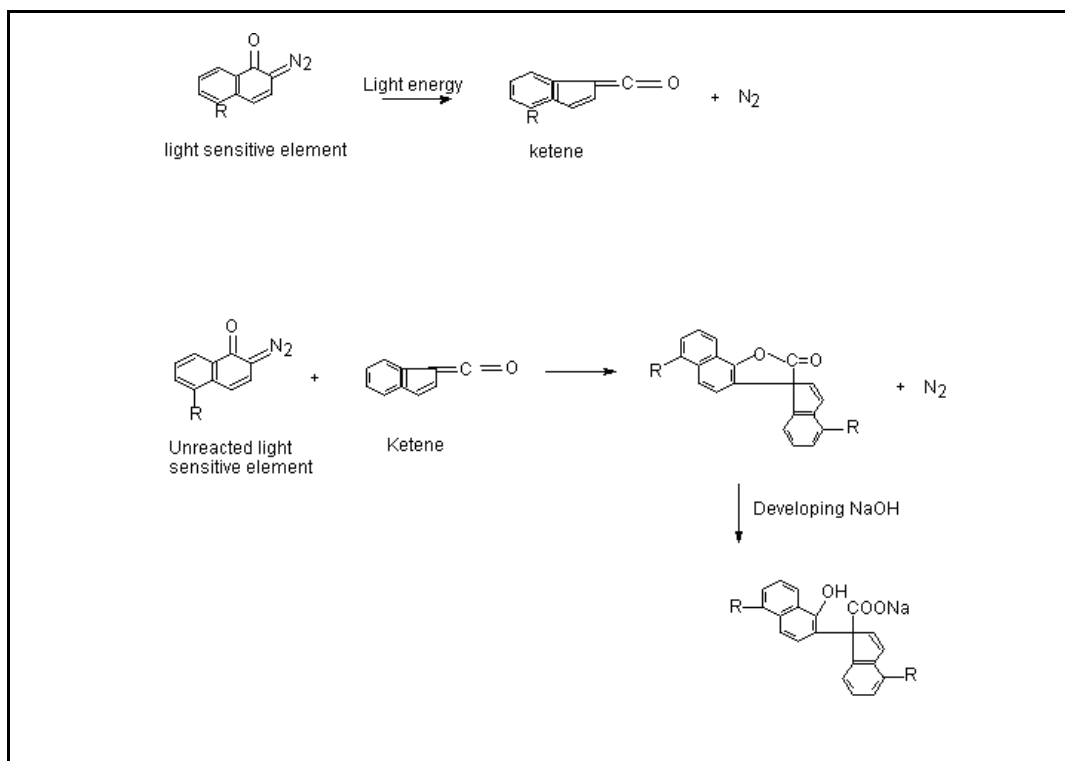


Figure 6.33 : Mechanism proposed by Levine²¹

The photoresist formulation is coated on a silicon wafer at 3000 rpm and the mask having the pattern to be develop is kept on the wafer and exposed at 365 nm. After the required dosage of radiation is given the wafer is the developed in 2.8 wt % of tetramethyl ammonium hydroxide. On developing the exposed regions are soluble

in the developer while the unexposed regions remain insoluble so as to develop a pattern.

The details of the composition of formulations as well as exposure and development times is tabulated in Table 6.10. In all the cases development of pattern was observed. Instead of conventional resins polymers based on modified styrene are used as resins along with diazoquinone compounds. Novolaks are well suited to the demand of photolithography i.e exhibit good imaging, high resistance to dry etch process, but have drawbacks such as high polydispersity, low glass transition temperature and prohibitive opacity at shorter wavelength. Therefore, these drawbacks have led to search of alternative resins.²⁴⁻²⁶ The terpolymer of polystyrene has a backbone structure of aromatic ring with a hydroxy group similar to that of phenolic resins except the $-CH_2-$ linkages in between the aromatics. Poly(hydroxy styrene) has a very high dissolution rate compared to conventional novolac. The dissolution rate can be minimised by using a polymer that has hydroxyl groups along with acetyl and acetoxy groups.

Sample PHS-1 was formulated using DES while TES was used in PHS-2. PHS-1 was exposed at 365 nm wavelength for 70 sec while PHS-2 was exposed for 50 sec. Pattern was developed by washing in aqueous alkaline developer. PHS-1 required 75 sec for development but the walls of the pattern merged in next 15 sec while in the case of PHS-2 pattern developed in 35 sec, with a thickness of 1.396 μ and the spacing between the pattern was maintained. Higher radiation dosage decreased the thickness of the film after development. It is well known that sensitivity of the film increases as the dose required to produce lithographic image decreases. The final dissolution rate of the films is dependent on the photoactive component. In TES the dissolution rate decreases. This produces most of the image in a shorter

exposure interval, and hence the image has high contrast. Sensitivity of positive resist is the dose required to effect complete solubility of exposed region while under same conditions the unexposed region remains completely insoluble. Therefore, formulation comprising of TES has high sensitivity where all three hydroxy groups of 2,3,4-trihydroxy benzophenone were modified as compared to DES, where only two hydroxy groups were modified to form the sulphonate ester.

6.5.2 Process of photoresist development

The development of photoresists is explained by percolation theory. The dual nature of the hydroxyl groups that act as hydrogen donors and acceptors are responsible for development of images.²⁷ The polymeric film is regarded as a hydrophobic solid in which the hydrophilic sites, the hydroxyl groups, are embedded. When the film is immersed in the aqueous base, the ions of the base are attracted towards the hydrophilic sites and repelled by the hydrophobic regions, and they diffuse into the film by jumping from one hydrophobic site to other and the mode of propagation is known as percolation process. The dissolution of novolak in alkaline developers is dependent on rate of diffusion of base and that depends on density of hydrophilic percolation sites.²⁸ When diazonaphthoquinone derivatives are added to the formulations the rate of dissolution is decreased. DNQ moiety is associated with the photoreactive function while the SO₂ group acts as inhibitor.²⁹ Therefore, as observed in Table 6.10, variation in sensitiser concentration and type leads to variation in exposure and development times as the DNQ moiety is attached with different ballast groups. Dissolution inhibition by DNQ and dissolution enhancement by indene carboxylic acid photoproducts are observed as a change in development times of the photoresist films. Poly(4-hydroxystyrene) (PHS) can be considered isomeric to cresol novolaks. But PHS has a very high dissolution rate and therefore it

is impossible to reduce tolerable levels by large amounts of DNQ, partially esterified with trihydroxy benzophenone.³⁰ To reduce the dissolution rate the use of partially modified hydroxy polymers is studied.

The high dissolution rate of PHS is explained by secondary structure model that relates the ratio of intramolecular and intermolecular hydrogen bonding to the dissolution rate of phenolic resin. PHS cannot form intramolecular hydrogen bonds. Therefore it interacts weakly with dissolution inhibitors resulting in image properties inferior to novolak based resins.³¹ Figures 6.34-6.35 show development of photoresist image on exposure of formulation PHS 8 and PHS 9. The formulations PHS 8 and PHS 9 were made varying the 10% modified polymeric sensitiser based on random (RP) and 2,6-dimethylol-4-methyl phenol (OP), respectively. In both cases patterns developed showing 0.1 μm geometry. In case of random polymeric sensitiser the walls of the butterfly pattern were distinctly separated while in case of DMP based polymeric sensitiser the walls were diffused.

The patterns are developed because when a photoactive component is introduced into a phenolic solution its hydrogen acceptors, the S=O units of sulphonic acid moieties and carbonyls of DNQs interact by hydrogen bonding with a nearby hydroxyl group of phenolic and in so doing polarise it. On exposure the DNQ group of photoactive component absorbs quantum of radiation, it releases a molecule of nitrogen and undergoes intramolecular rearrangement. The rearrangement is highly exothermic and causes a heat pulse to be emitted from location of photolysing DNQ. The dissolution of phenolic polymers occur through percolative mechanisms resulting from diffusion of the base along nascent channels formed by spatial proximity of hydroxyl groups. The hydrophilic sites constituting the diffusion channel are not the

hydroxy groups themselves but the phenolate ions created when the base reacts with the resins hydroxy group.

The secondary structure model has identification of the chemical nature of potential hydrophilic sites. Due to intermolecular and intramolecular interaction of –OH groups the novolaks form cyclic structure. Therefore, the number of hydroxy groups to form an unbroken chain of hydrophilic sites that can be ionised is less. In PHS there is no cyclic structure at all and the hydroxyl group forms a continuous spiral around the PHS backbone. All the OH groups are available for hydrophilic site creation it can form channels and have fastest dissolution rate. Therefore, the available hydroxy groups are minimised by using polymer having partial hydroxy and acetyl groups. According to Reiser, after immersion in the developer a thin gel layer, the penetration zone, forms on the surface of the polymer film.³² During development, this film moves the polymer bulk into the steady state, moving membrane type. The speed of dissolution depends on the rate of cation diffusion through the penetration zone, as the rate determining step. Since PHS based systems cannot form any intramolecular bonds it interacts weakly with dissolution inhibitors. The imaging properties are inferior to that of novolak based systems. When the resist film is immersed in the developer the base penetrates the resin matrix and a thin layer of phenolate is formed at the interface between the resin film and developer solution. As soon as sufficient number of OH groups are ionised, the polymer chains at back of penetration zone become soluble in water, disentangle and float on aqueous developer. PHS and novolak are amphiphilic materials having a hydrophilic as well as hydrophobic moieties. Base ions are attracted to the hydrophilic sites, are repelled by hydrophobic regions. As a result, they migrate into solid by transferring from one

hydrophilic side to next. This mode of progression is typical percolation process, the diffusion of base into amphiphilic solids will be governed by percolation theory.

PHS-3 and 4 were exposed to UV for 50 and 90 sec while the developing time required were 120 and 60 sec, respectively. Lithographic images develop because of difference in dissolution kinetics between the exposed and unexposed areas of resist. The long chains of the polymer i.e the molecular weight and glassy nature of the resist material makes dissolution dynamics complicated. The large pervaded volume and high degree of chain interpenetration of polymeric materials require considerable swelling on glassy material for dissolution to proceed. The solvent mobility in polymeric matrices is strongly affected by its local environment. The diazosensitiser is temperature sensitive and decomposes completely on heating at 110°C for 30 minutes.³³

The dissolution rate of the resist and thickness of the film also depends on the solvent used and the prebaked temperature. If the film is baked at higher temperature there is decrease in dissolution rate due to continued loss of the solvent in the polymer as well as photoresists. The baking time is so adjusted that the film is dried and annealed to reduce extra film volume created by rapid loss of solvent so that it allows transport of solvent in the glassy matrix. Ethyl lactate has a boiling point of 154°C and density of 1.042 g/cc while ethoxy ethyl acetate has a boiling point of 156°C and density of 0.975 g/cc. The residual solvent affects the interaction between DNQ and the polymer as result the dissolution rate is increased.

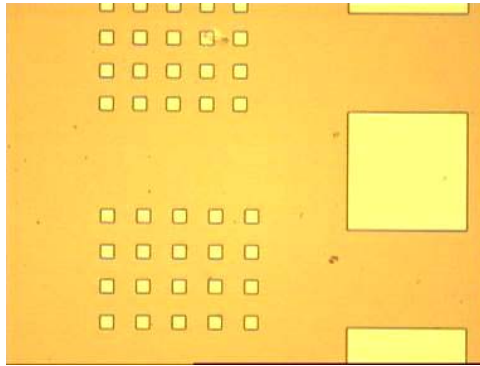


Figure 6.34a : Pattern observed after exposure and development of PHS-8 (500 times magnification)

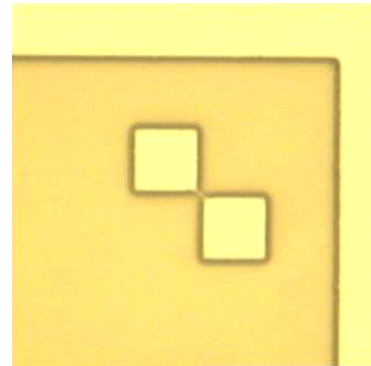


Figure 6.34b : Butterfly exposure and development magnification)

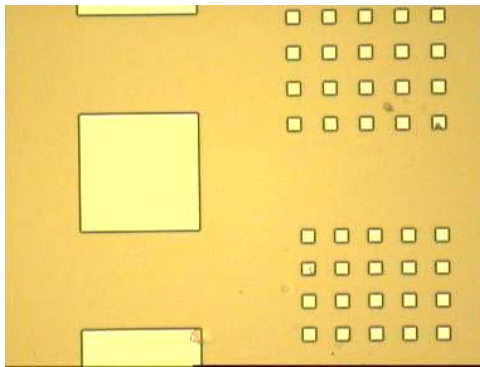


Figure 6.35 a : Pattern observed after exposure and development of the formulation PHS-9 (500 times magnification)

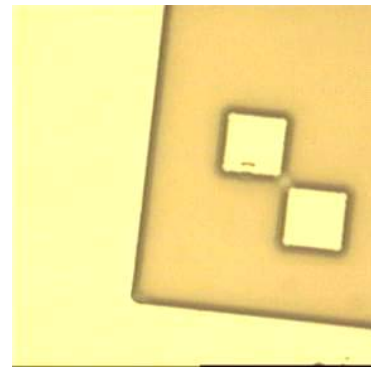


Figure 6.35 b : Pattern observed and development of the formulation PHS-9 (500 times magnification)

6.6 Conclusion

Polystyrene was synthesised and modified to introduce different functional groups, to be used in I- line photoresist applications instead of conventional novolak resins. Polystyrene having a narrow molecular weight distribution can be synthesised using a chain transfer agent. Subjecting polystyrene to different organic reactions it can successively be post modified to introduce acetyl, acetoxy or hydroxy groups in the backbone. These polymers are similar to novolak resins having a hydroxyl moiety except the variation in $-\text{CH}_2$ linkage. The modified polymer is a terpolymer comprising of partial acetyl, acetoxy and hydroxy groups. This partial substitution is essential to reduce the solubility of the polymer in aqueous alkaline developer, as development of a photoresist image is dependent on difference in solubilities in exposed and unexposed regions. Sensitisers of 2,1,5-diazonaphthoquinone family were used in photoresist formulations. On exposure of the photoresist film at 365 nm the lithographic images were developed, showing opening of $0.1\mu\text{m}$ geometry. The glass transition temperature of these polymers is higher than the conventional novolak resins therefore stability of the film can be achieved during processing.

6.7 References

- 1 C. C. Unruh, and C. F. H. Allen, U. S. Patent 2,706,725, Issued to Eastman Kodak Company, Rochester, N.Y. (1955).
- 2 March, J.; “*Advanced Organic Chemistry. Reaction, Mechanism and Structure*”, 3rd edition, Wiley Eastern Limited, New Delhi (1988).
- 3 M. A. Toukhy, and A. T. Jeffries, T. Alfred, U. S. Patent 5,019,478, Issued to Olin Hunt Speciality Products, Inc. Cheshire. (1991)
- 4 D. N. Khanna, U. S. Patent 5,395,871, Issued to Hoechst Celanese Corporation, Somerville, N. J. (1995).
- 5 C. G. Willson, Organic Resist Material in L. F. Thompson, C. G. Willson and M. I. Bowden in “*Introduction to Microlithography*”, ACS Symposium

Series 219, American Chemical Society Washington D.C. (1983).

- 6 S. L. Kapur, *J. Polym. Sci.* **11**, 399 (1953).
- 7 G. Elena, R. Lopez, and M. Albores-Velasco, *J. Chem. Educ.*, **74**, 551 (1997).
- 8 G. A. Olah, in “*Friedel–Craft and Related Reaction The Friedel–Crafts acylation reaction and its application to polycyclic aromatic hydrocarbons*”, P. H. Gore, **3**, Part 1, Chap. 31.
- 9 H. F. Bassilios, S. M. Makar, and Salem, *Bull. Soc. Chim. France*, **21**, 72 (1954).
- 10 I. Bidd, D. J. Kelly, P. M. Ottely, O. I. Paynter, D. J. Simmonds, and M. C. Whitting, *J. Chem. Soc. Perkin. Trans. 1*, **7**, 1369 (1983).
- 11 W. D. Emmons, *J. Am. Chem. Soc.*, **79**, 5528 (1957).
- 12 N. C. Deno, W. E. Billups, K. E. Kramer, and R. R. Lastomirsky, *J. Org. Chem.*, **35**, 3080 (1970).
- 13 W. D. Emmons, and A. F. Ferris, *J. Am. Chem. Soc.*, **75**, 4623 (1953).
- 14 J. M. Nasrullah, S. Raja, K. Vijayakumaran, and R. Dhamodharan, *J. Poly. Sci. Part A. Polym. Chem.*, **38**, 453 (2000).
- 15 A. McKillop, and J. A. Tarbin, *Tetrahedron*, **43**, 1753 (1987).
- 16 V. M. Parikh, “*Absorption Spectroscopy of Organic molecules*”; Addison-Wisley publishing Co. Inc, London (1974).
- 17 R. Dammel, “*Diazonaphthoquinone based resists*”, Washington (1993).
- 18 G. Degiorgis, P. Pateri, A. Pilenga, R. J. Hurditch, B. T. Beauchemin, Jr. and E. A. Fitzgerald, *Proc. SPIE* **1262**, 368 (1990).
- 19 E. Reichmanis, C. K. Ober, S. A. MacDonald, T. Iwayanagi, and T. Mishikuto, in “*Microelectronics Technology: Polymers for Advanced Imaging and Packaging*” ACS Symposium Series **614**, American Chemical Society Washington D.C. (1995).
- 20 H. Meier and K-P Zeller *Angew. Chem. Edit. J.*, **14** I (1975).
- 21 W. S. Deforest, “*Photoresist Materials : and Processess*”, McGraw Hill Book Company, New York (1975).
- 22 J. Bendig, E. Saur, K. Polz, G. Schopf and A. Koch, *Tetrahedron*, **48**, 9207 (1992).

- 23** R. W. Blevins, R. C. Daly and S. R. Turner “Lithographic Resists”, **9**, in Encyclopedia of Polymer Science and Technology, John Wiley & Sons (1987).
- 24** K. Przybilla, H. Rschert, W. Spieb, Ch. Eckes, S. Chatterjee, D. Khanna, G. Pawlowski and R. Dammel, *Proc. SPIE*, **1466**, 174 (1991).
- 25** G. Pawlowski, T. Sauer, R. Dammel, D. J. Jordon, W. Hinsberg, D. McKean, C. R. Lindley, H. J. Merrem, H. Roschert, R. Vicari and C. G. Willson, *Proc. SPIE*, **1262**, 391 (1990).
- 26** L. E. Bogan, Jr and K. A. Graziano, *Proc. SPIE*, **1262**, 180 (1990).
- 27** T-F. Yeh, H-Y. Shih, A. Reiser, *Macromolecules*, **25**, 5345 (1992).
- 28** H-Y Shih, A. Reiser, *Macromolecules*, **30**, 3859 (1997).
- 29** S. Jha, A. Reiser, L. Sroubkova and R. Zahradnik, *Macromolecules*, **31**, 6549 (1998).
- 30** J. P. Huang, T. K. Kwei, A. Reiser, *Macromolecules*, **22**, 4106 (1989).
- 31** R. Dammel, M. D. Rahman, P. H. Lu, and V. Elango, *Polymers for Advanced Technologies*, **5**, 28 (1993).
- 32** A. Reiser, H-Y Shih, T-F Yeh and J-P Huang, *Angew. Chem. Int. Ed. Engl.*, **35**, 2428 (1996).
- 33** T. Davidson and M. J. Comstock, “*Polymers in Electronics*” ACS Symposium Series 242, Chapter 7, American Chemical Society Washington D.C. (1983).

List of Publications

- Facile Synthesis of Poly (4-hydroxystyrene)

S. Deokar, R. S. Ghadge, C. R. Rajan, S. Ponrathnam, Journal of Applied Polymer Science, Vol. 91, 3192-3201 (2004)

- An improved process for preparation of functionalized polystyrene

S. B. Deokar, R. S. Ghadge, A. Kotha, C. R. Rajan, S. Ponrathnam, Indian Patent filed CSIR no-529/2003

Posters Presentations

- Characterization of modified polystyrenes for microlithography at Polymer Science & Engineering Division, 2006 NCL for Science Day

S. B. Deokar, R. S. Ghadge, C. R. Rajan and S. Ponrathnam

- Synthesis And Characterization Of Beaded Porous Polymers Using High Internal Phase Emulsion Technique in National Conference on Polymers, MACRO- 2006 held in February 2006 at, Kolkata, India.

S. B. Deokar and S. Ponrathnam.

- Modified High Internal Phase Emulsion in catalysis application in National Conference on Polymers, MACRO- 2006 held in December 2006 at, Pune, India.

S. B. Deokar, S. Chaudhari, S. A. Mule, S. Palimkar, C. R. Rajan and S. Ponrathnam

- Studies of Redox initiator in High Internal Phase Emulsion, in National Conference on Polymers, MACRO- 2006 held in December 2006 at, Pune, India.

S. B. Deokar, P. A. Apte, S. V. Pawar, P. G. Prasad, C. R. Rajan and S. Ponrathnam