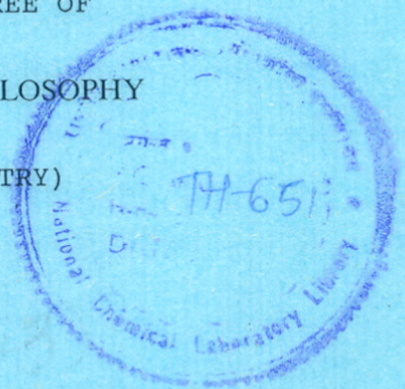


UNCLASSIFIED

SYNTHESIS AND CHARACTERISATION
OF
FUNCTIONAL POLYELECTROLYTES

A THESIS
SUBMITTED TO THE
UNIVERSITY OF POONA
FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY

(IN CHEMISTRY)



678.01:511.8
GAD

BY


JAYANT M. GADGIL

CHEMICAL ENGINEERING DIVISION
NATIONAL CHEMICAL LABORATORY
PUNE-411 008 (INDIA)

COMPUTERISED

CERTIFICATE

Certified that the work incorporated in the thesis entitled "**Synthesis and Characterisation of Functional Polyelectrolytes.**" submitted by **Mr. Jayant M. Gadgil** was carried out by the candidate under my supervision. Such material as has been obtained from other sources has been duly acknowledged in the thesis.


(**Dr. S. Ponrathnam**)

Research Guide

ACKNOWLEDGMENT

I consider it to be a proud privilege to have carried out my doctoral work under Dr.S.Ponrathnam. Working in the area of polymer synthesis and characterisation under the able guidance of Dr.S.Ponrathnam has been a stimulating and rewarding experience for me. I shall have long lasting gratitude and respect for him.

My sincere thanks are due to Dr.C.R.Rajan for his constant professional help and keen interest during entire work. I wish to acknowledge Dr.R.S.Ghadage, Dr.S.R.Inamdar and Mr.M.S.Joshi for assistance in computation work.

I take this opportunity to thank Mr.G.D.Shahapure for assistance in flame photometry, Dr.S.Ganapathy and Mr.P.R.Rajamohanan for their co-operation in NMR spectroscopy.

I wish to acknowledge Dr.R.V.Bahulekar, Mr.S.B.Pandit and Mr.M.M.Sonpatki for stimulating discussions and co-operation. The fruitful completion of a doctoral dissertation is indeed due to the efforts of a number of individuals. I would be failing in duties if I do not recall the encouragement and co-operation extended to me by colleagues in Synthesis section of the Polymer Science and Engineering Group.

My sincere thanks are due to Dr.V.M.Nadkarni, for allowing me to work in the Chemical Engineering Division and Dr. R.A.Mashelkar, Director, National Chemical Laboratory, for permission to submit the work in the form of a thesis.

Finally I thank Council of Scientific and Industrial Research (CSIR) for the award of fellowship during the tenure of this work.



[J.M.Gadgil]

ABSTRACT

In the present thesis entitled "Synthesis and characterisation of functional polyelectrolytes," investigations of functional polyelectrolytes are presented. Functional polyelectrolytes are water-soluble polymers bearing labile functional groups together with ionic moieties. The present work covers some aspects of copolymers of acrolein with acrylic acid and methacrylic acid.

The thesis is divided into three chapters. (I) Introduction (II) Experimental work and (III) Results and Discussions.

The first chapter consists of brief introduction of functional polymers. Functional polymers are the macromolecules bearing labile functional groups which can be easily modified to impart desired property profile to the polymers. These are obtained by one of the three routes, (i) chemical modification of polymers, (ii) modification of functional groups already present on the polymer molecule by incorporating spacer arm and (iii) copolymerisation of monomers having desired functional groups. The relative merits and demerits of the three routes are discussed.

The functional polymers have wide field of applications. They can be used in chemical reagents, catalysis and separation processes. They also find use in speciality applications such as enzyme immobilisation and control release of active ingredients such as drugs, agrochemicals etc. Some of these applications are discussed citing examples from the literature.

Polyelectrolytes, which form a class in itself, is useful as functional polymer. The applications of functional polyelectrolytes are surveyed. Due to the wide scope of the field, large amount of literature is being published as books, reviews and research papers. However, a limited applications having relevance to the present study are presented.

Functional polyelectrolytes in the present study are formed by copolymerisation of functional monomers. Hence relative rate expression (reactivity ratio), its significance is explained. Different methods for estimating reactivity ratios are evolved. Some of the important methods are reviewed. Parameters affecting the reactivity parameters are discussed.

In the second chapter, experimental work is presented. In the beginning, materials used in the work are listed. Aqueous solution copolymerisation of acrolein with acrylic acid initiated using redox pair is described. The reaction was carried out at 4 molar combined concentration of the monomers. The reactions were carried out at differing constant pH such as 1, 3, 5 and 7. At a constant pH, monomer composition was varied. In another set of copolymerisation, the reaction was carried out without controlling the pH of the reaction media. Phase separation was observed during copolymerisations of certain composition of monomers.

Copolymerisation of acrolein with methacrylic acid was carried out in similar manner. Phase separation was not observed during the copolymerisations. Copolymerisations carried out for estimation of reactivity ratios were stopped at low conversions. The reaction was taken to high conversions for selected compositions.

Acrolein-acrylic acid copolymers were investigated for the amount of free aldehyde present in the copolymer. ^{13}C NMR CP/MAS spectra were recorded in the solid state. Calcium sequestering capacity of acrolein-methacrylic acid copolymers and their derivatives like oxime and bisulphite were studied. Acrolein-methacrylic acid copolymers were reacted with phenol and m-cresol to form ortho novolak type polymers. Similar polymer was synthesised from acrolein-styrene copolymers.

The copolymers were characterised using infra-red spectrophotometer, differential scanning calorimeter. Potentiometric titrations were carried out for some of the acrolein-methacrylic acid polymers for conformational studies.

Results and discussion is presented in the third chapter. Anomalous behaviour was found in the copolymerisation. The deviation from ideal copolymerisation was due to molecular association, unequal interaction of solvent with the two monomers which violated assumptions made while deriving expression for reactivity ratios.

Aldehyde group being highly reactive, inter/intramolecular cyclisations took place. These cyclisations reduced the amount of free aldehyde present in the copolymer. Continuous blocks of acrolein were prone to cyclisations. This observation was made during ^{13}C NMR CP/MAS in solid state.

Calcium sequestering capacity of acrolein-methacrylic acid copolymers was dependant on pH of the medium, composition of the copolymer and sequence length of ionisable groups. The derivatisation of the copolymer was useful for the study of contribution of ionisable and non ionisable groups.

Differential scanning calorimeter was used for the study of the transition in the copolymers with rise in temperature. These transitions were found to vary with the composition of the copolymers. Curing behaviour of the novolak type copolymers is also discussed.

CONTENTS

Page No.

* ABSTRACT

* ACKNOWLEDGMENT

* LIST OF TABLES

* LIST OF FIGURES

CHAPTER I

INTRODUCTION

1.1	FUNCTIONAL POLYMERS	1
1.1.1	POLYMERISATION OF FUNCTIONAL MONOMER	3
1.1.2	FUNCTIONALISATION BY CHEMICAL MODIFICATION	3
1.1.3	SPACER ARM WITH FUNCTIONAL GROUP	4
1.2	APPLICATIONS OF FUNCTIONAL POLYMERS	4
1.2.1	POLYMERIC REAGENTS	4
1.2.1.1	OXIDISING AGENT	5
1.2.1.2	REDUCING AGENT	5
1.2.1.3	WITTING REAGENT	5
1.2.1.4	SULPHUR CONTAINING AGENT	5
1.2.1.5	HALOGENATING AGENT	6
1.2.1.6	PROTECTING GROUPS	6
1.2.2	POLYMERIC CATALYSIS	6
1.2.2.1	ION EXCHANGE RESINS	6

1.2.2.2	LEWIS ACIDS AND SUPER ACIDS	7
1.2.2.3	HYDROLYSIS AND DECARBOXYLATION	7
1.2.2.4	PHASE TRANSFER CATALYSTS	8
1.2.2.5	TRANSITION METAL CATALYSTS	8
1.2.2.6	IMMOBILISED ENZYMES	9
1.2.2.7	POLYMERIC INITIATORS	9
1.2.3	POLYMER AIDED SEPARATIONS	9
1.2.3.1	METAL ION SEPARATIONS	10
1.2.3.2	SEPARATION OF CHIRAL MOLECULES	10
1.2.3.3	GAS SEPARATION	11
1.2.3.4	SOLVENT PURIFICATION	11
1.2.3.5	AFFINITY CHROMATOGRAPHY	11
1.2.4	CONTROLLED RELEASE	12
1.2.5	POLYMERIC FOOD ADDITIVES	12
1.3	FUNCTIONAL POLYELECTROLYTES	13
1.3.1	SCALE INHIBITORS	13
1.3.2	SEQUESTERING AGENTS	14
1.4	COPOLYMERS OF ACROLEIN, ACRYLIC ACID AND METHACRYLIC ACID	15
1.4.1	BIOLOGICAL ACTIVITY	16
1.4.2	ENZYME IMMOBILISATION	16
1.4.3	SCALE PREVENTION	18
1.4.4	ANTICORROSIVE PROPERTY	18
1.4.5	POLYMERISATION AND ITS CHARACTERISTICS	19
1.5	COPOLYMERISATION AND MONOMER REACTIVITY	20

1.5.1	COPOLYMER COMPOSITION EQUATION	21
1.5.2	SIGNIFICANCE OF REACTIVITY RATIOS	24
1.5.3	METHODS OF ESTIMATING REACTIVITY RATIOS	25
1.5.3.1	MAYO-LEWIS METHOD	25
1.5.3.2	FINEMAN-ROSS METHOD	26
1.5.3.3	MAYER-LOWRY METHOD	28
1.5.3.4	TIDWELL-MORTIMER METHOD	30
1.5.3.5	YEZRIELEV -BROKHINA-ROSKIN METHOD	30
1.5.3.6	JOSHI-JOSHI METHOD	36
1.5.3.7	BRAUN-BRENDLEIN-MOTT METHOD	37
1.5.3.8	KELEN-TUDOS METHOD	38
1.5.3.9	SHAWKI-HAMIELEC METHOD	40
1.5.3.10	KUO-CHEN METHOD	41
1.5.4	PARAMETERS AFFECTING REACTIVITY RATIOS	45
1.5.4.1	MECHANISM OF POLYMERISATION	45
1.5.4.2	HYDROGEN ION CONCENTRATION	46
1.5.4.3	SOLVENT	48
1.5.4.4	CONCENTRATION	48
1.5.4.5	TEMPERATURE	52
1.5.4.6	INITIATOR SYSTEM	52
1.6	SCOPE OF WORK	55
1.6.1	COPOLYMERISATION	55
1.6.2	SYNTHESIS	57
1.6.3	CHARACTERISATION	57
1.6.4	SEQUESTRATION	57

1.6.5	MODIFICATION WITH PHENOLS	58
-------	---------------------------	----

CHAPTER II

EXPERIMENTAL

2.1	MATERIALS	60
2.2.1	STOCK SOLUTIONS	69
2.2.2	COPOLYMERISATION ACROLEIN -ACRYLICACID	70
2.2.3	COPOLYMREISATION OF ACROLEIN METHA - CRYLIC ACID	73
2.2.4	HIGH CONVERSION COPOLYMERISATION OF ACROLEIN METHACRYLIC ACID (MAC SERIES)	74
2.2.5	ACROLEIN-STYRENE COPOLYMERISATION	74
2.3	COPOLYMER ANALYSIS	76
2.4	COPOLYMER DERIVATISATION	97
2.4.1	OXIME DERIVATIVE	97
2.4.2	BISULPHITE DERIVATIVE	97
2.4.3	NOVOLAK TYPE DERIVATIVE	98
2.5	CHARACTERISATION	98
2.5.1	FREE AKDEHYDE ESTIMATIN	99
2.5.2	SOLID STATE C ¹³ NMR	99
2.5.3	ULTRA-VIOLET SPECTRA	100
2.5.4	INFRA-RED SPECTRA	100
2.5.5	POTENTIOMETRIC TITRATION	101
2.5.6	ESTIMATION OF CALCIUM SEQUESTRATION CAPACITY	101
2.5.7	DIFFERENTIAL SCANNING CALORIMETER	108

CHAPTER III

RESULTS AND DISCUSSION

3.1	COPOLYMER OF ACROLEIN-ACRYLIC ACID	110
3.1.1	EFFECT OF pH	111
3.1.2	PHASE SEPARATION	115
3.1.3	COPOLYMERISATION IN PRESENCE OF NON - SOLVENT	116
3.1.4	ABSORPTION OF MONOMER	117
3.1.5	MOLECULAR INTERACTION	117
3.1.6	EFFECT OF COUNTERION	126
3.1.7	NONLINEARITY IN THE SYSTEM	126
3.1.8	CONCLUSIONS	130
3.2	SOLID STATE C¹³ NMR	131
3.2.1	PEAK ASSIGNMENT	131
3.2.2	EFFECT OF MEAN SEQUENCE LENGTH	133
3.2.3	EFFECT OF ACROLEIN IN FEED AND POLYMER	137
3.3	CHARACTERISATION USING INFRA-RED SPECTRO- PHOTOMETER	137
3.3.1	CHARACTERISATION OF BISULPHITE OF POLY - ACROLEIN	137
3.3.2	CHARACTERISATION OF OXIME OF POLYACRO- LEIN	140
3.3.3	COPOLYMER OF ACROLEIN-METHACRYLIC ACID	145
3.4	COPOLYMER OF ACROLEIN-METHACRYLIC ACID	145
3.4.1	EFFECT OF pH	147

3.4.2	EFFECT OF COUNTER-ION	149
3.4.3	NONLINEARITY	151
3.5	POTENTIOMETRIC TITRATIONS	154
3.6	CALCIUM SEQUESTRATION	158
3.6.1	EFFECT OF POLYMER COMPOSITION	168
3.6.1.1	MAC-5	164
3.6.1.2	MAC-10	169
3.6.1.3	MAC-20	169
3.6.1.4	MAC-30	169
3.6.1.5	MAC-40	175
3.6.2	EFFECT OF pH	178
3.6.3	EFFECT OF MEAN SEQUENCE LENGTH	178
3.6.4	EFFECT OF DERIVATISATION	180
3.6.4.1	BISULPHITE DERIVATIVE	187
3.6.4.2	OXIME DERIVATIVE	187
3.6.5	PRESENCE OF ELECTROLYTE	188
3.6.6	CONCLUSION	188
3.7	CHARACTERISATION USING DIFFERENTIAL SCANNING CALORIMETRY	190
3.7.1	KINETIC PARAMETERS	190
3.7.2	ACROLEIN-ACRYLIC ACID COPOLYMER	196
3.7.3	ACROLEIN-METHACRYLIC ACID COPOLYMER	196
3.7.4	NOVOLAKS PREPARED FROM ACROLEIN COPOLYMERS	196

LIST OF TABLES

Table No.	Caption	Page No
1	REACTIVITY RATIOS FOR DIFFERENT MECHANISM ACRYLONITRILE-METHYL ACRYLATE	47
2	EFFECT OF pH AND ADDITION OF STRONG ELEC- TROLYTE	49
3	EFFECT OF SOLVENTS AND MIXTURE OF THE SOLVENTS	50
4	COPOLYMERIZATION OF STYRENE (r_1) AND MEH- TYL METHACRYLATE (r_2)	53
5	EFFECT OF INITIATOR SYSTEM	54
6	COPOLYMERISATION OF ACROLEIN-ACRYLIC ACID NO pH CONTROL, HOMOGENEOUS PHASE, 4 MOLAR CONC.	77
7	COPOLYMERISATION OF ACROLEIN-ACRYLIC ACID NO pH CONTROL, HETEROGENEOUS PHASE, 4 MOLAR CONC.	78
8	COPOLYMERISATION OF ACROLEIN-ACRYLIC ACID NO pH CONTROL, HOMOGENEOUS PHASE, 1 MOLAR CONC.	79
9	COPOLYMERISATION OF ACROLEIN-ACRYLIC ACID NO pH CONTROL, HETEROGENEOUS PHASE, 1 MOLAR CONC.	80

- 10 COPOLYMERISATION OF ACROLEIN-ACRYLIC 81
ACID, HOMOGENEOUS PHASE, pH 1
- 11 COPOLYMERISATION OF ACROLEIN-ACRYLIC 82
ACID, HETEROGENEOUS PHASE, pH 1
- 12 COPOLYMERISATION OF ACROLEIN-ACRYLIC 83
ACID, HOMOGENEOUS PHASE, pH 3
- 13 COPOLYMERISATION OF ACROLEIN-ACRYLIC 84
ACID, HETROGENEOUS PHASE, pH 3
- 14 COPOLYMERISATION OF ACROLEIN-ACRYLIC 85
ACID, HOMOGENEOUS PHASE, pH 5
- 15 COPOLYMERISATION OF ACROLEIN-ACRYLIC 86
ACID, HETEROGENEOUS PHASE, pH 5
- 16 COPOLYMERISATION OF ACROLEIN-ACRYLIC 87
ACID, HOMOGENEOUS PHASE, pH 7
- 17 COPOLYMERISATION OF ACROLEIN-ACRYLIC 88
ACID, HETEROGENEOUS PHASE, pH 7
- 18 COPOLYMERISATION OF ACROLEIN METHA- 90
CRYLIC ACID, NO pH CONTROL
- 19 COPOLYMERISATION OF ACROLEIN METHA- 92
CRYLIC ACID, pH 1
- 20 COPOLYMERISATION OF ACROLEIN METHA- 94
CRYLIC ACID, pH 3
- 21 COPOLYMERISATION OF ACROLEIN METHA- 95
CRYLIC ACID, pH 5

22	COPOLYMERISATION OF ACROLEIN METHA- CRYLIC ACID, pH 7	96
23	POTENTIOMETRIC TITRATION OF MAC-40	102
24	POTENTIOMETRIC TITRATION OF MAC-30	104
25	POTENTIOMETRIC TITRATION OF MAC-20	106
26	REACTIVITY RATIOS OF ACROLEIN-ACRYLIC ACID SYSTEM AT VARIOUS pH	112
27	U.V. INVESTIGATION FOR THE STUDY OF MOLEC- ULAR ASSOCIATION AQUEOUS SOLUTION; ABSORPTION AT 333 nm	119
28	U.V. INVESTIGATION FOR THE STUDY OF MOLEC- ULAR ASSOCIATION ACETONE SOLUTION; ABSORPTION AT 337-341 nm	120
29	EFFECT OF COUNTER ION ON REACTIVITY RATIO OF ACRYLIC ACID	127
30	PEAK AREAS OF SOLID STATE C ¹³ CP/MAS NMR SIGNALS OF ACRYLIC ACID COPOLYMER	134
31	MEAN SEQUENCE LENGTH OF ACROLEIN IN COPOLYMERS	135
32	REACTIVITY RATIOS OF METHACRYLIC ACID AND ACROLEIN AT DIFFERENT pH	146
33	EFFECT OF COUNTERION ON REACTIVITY RATIO OF METHACRYLIC ACID.	150
34	pK ₀ AND FREE ENERGIES OF TRANSITION FOR ACROLEIN-METHACRYLIC ACID COPOLYMERS	162

35	CSC OF POLY(ACRYLIC ACID) AND POLY(METHA- CRYLIC ACID)	166
36	CSC OF MAC-5 AND MAC-10	168
37	CSC OF MAC-20	172
38	CSC OF MAC-30	174
39	CSC OF MAC-40	177
40	MEAN SEQUENCE LENGTH OF METHACRYLIC ACID AND MAXIMUM CSC	179
41	CSC OF HYDROXYL AMINE AND BISULPHITE DERIVATIVES OF POLYACROLEIN	181
42	CSC OF DERIVATIVES OF MAC-5	182
43	CSC OF DERIVATIVES OF MAC-10	183
44	CSC OF DERIVATIVES OF MAC-20	184
45	CSC OF DERIVATIVES OF MAC-30	185
46	CSC OF DERIVATIVES OF MAC-40	186
47	CSC OF COPOLYMER DERIVATIVES IN PRESENCE OF NaCl	189
48	CURING OF AC-40ST WITH 2 WEIGHT PERCENT HEXA	198
49	CURING OF AC-40ST WITH 4 WEIGHT PERCENT HEXA	199
50	CURING OF AC-40ST WITH 6 WEIGHT PERCENT HEXA	200
51	CURING OF AC-40ST WITH 8 WEIGHT PERCENT HEXA	201

LIST OF FIGURES

Figure No.	Caption	Page No.
1	EFFECT OF MONOMER CONCENTRATION	51
2	COPOLYMERISATIONS, DERIVATISATIONS	56
3	DERIVATISATION WITH PHENOL TO FORM NOVOLAK TYPE POLYMERS	59
4	REACTION VESSEL USED FOR CONDUCTING COPOLYMERISATION AT LOW CONVERSION	71
5	REACTION VESSEL FOR COPOLYMERISATION AT HIGH CONVERSION	75
6	MOLECULAR ASSOCIATION OF ACRYLIC ACID AND ACROLEIN	122
7	INTER/INTRAMOLECULAR CYCLISATIONS IN POLYACROLEIN	124
8	FINEMAN-ROSS PLOT FOR ACROLEIN-ACRYLIC ACID, NO pH CONTROL	128
9	FINEMAN-ROSS PLOT FOR ACROLEIN-ACRYLIC ACID AT pH 1	129
10	SOLID STATE ^{13}C NMR OF POLYMERS	132
11	MEAN SEQUENCE LENGTH Vs MOLE FRAC- TION OF ACROLEIN IN FEED AND MEAN SEQUENCE LENGTH Vs FREE ALDEHYDE	136

12	MOLE FRACTION(S) Vs AMOUNT OF FREE ALDEHYDE GROUPS	138
13	IR SPECTRA OF POLY(ACROLEIN BISULPHITE)	139
14	IR SPECTRA OF POLY(ACROLEIN OXIME)	141
15	IR SPECTRA OF ACROLEIN-ACRYLIC ACID COPOLYMERS IN HOMOGENEOUS PHASE	142
16	IR SPECTRA OF ACROLEIN-ACRYLIC ACID COPOLYMERS IN HETEROGENEOUS PHASE	143
17	REACTIVITY RATIOS AT DIFFERENT pH	148
18	FINEMAN-ROSS PLOT FOR ACROLEIN-METHACRYLIC ACID, NO pH CONTROL	152
19	FINEMAN-ROSS PLOT FOR ACROLEIN-METHACRYLIC ACID AT pH 1	153
20	POTENTIOMETRIC TITRATION OF MAC-40	155
21	POTENTIOMETRIC TITRATION OF MAC-30	156
22	POTENTIOMETRIC TITRATION OF MAC-20	157
23	POTENTIOMETRIC TITRATION OF MAC-40	159
24	POTENTIOMETRIC TITRATION OF MAC-30	160
25	POTENTIOMETRIC TITRATION OF MAC-20	161
26	CSC OF POLY(CARBOXYLIC ACID)	165
27	CSC OF MAC-5	167
28	CSC OF MAC-10	170
29	CSC OF MAC-20	171
30	CSC OF MAC-30	173
31	CSC OF MAC-40	176

32	THERMOGRAMS OF ACROLEIN-ACRYLIC ACID COPOLYMERS IN HOMOGENEOUS RANGE	192
33	THERMOGRAMS OF ACROLEIN-ACRYLIC ACID COPOLYMERS IN HETEROGENEOUS RANGE	193
34	THERMOGRAMS OF ACROLEIN-METHACRYLIC ACID COPOLYMERS	194
35	THERMOGRAMS OF ACROLEIN-METHACRYLIC ACID COPOLYMERS	195
36	THERMOGRAMS OF ACROLEIN-METHACRYLIC ACID COPOLYMERS	202
37	THERMOGRAMS OF POLYMERS	203

CHAPTER I

INTRODUCTION

1.1 FUNCTIONAL POLYMERS

Polymers having reactive functional groups are called functional polymers. These macromolecules with functional groups have the potential advantage over similar model compounds. Their utility is related to the combination of polymeric character and the functional groups which induces co-operative interactions untenable in small molecules.

Merrifield introduced in 1963 the use of crosslinked polymers in organic synthesis¹. Peptides were synthesised through a sequence of reactions by solid phase technique. Since then functionalised polymers have been widely used as stoichiometric reagents, catalysts and as substrate carriers in multi-phase synthesis.

The advantages of crosslinked functionalised polymers may be summarised as:

1. Simpler separation and isolation from reaction side products. Linear polymers and low molecular weight homologues require precipitation, sedimentation or ultrafiltration whereas filtration and washing is sufficient with crosslinked polymers.
2. Ease of scale-up to commercial levels.(ion-exchange resins). Repetitive stepwise syntheses are possible.
3. Reaction rates can be enhanced by using reagents in excess. In reversible reactions equilibrium can be shifted towards product to force the reaction to completion.
4. The reagent can be loaded and recycled many times. It is also possible to quantitatively regenerate expensive reagent.

5. Reactivity of highly reactive, unstable reagent/enzyme is decreased by loading on to a polymer. Stability of such reagents is increased and potential hazards of reactive substances are reduced, thereby enabling safer handling and prolonged storage.
6. Polymers being less degradable decrease pollution problems in air and water.
7. Many polymers acquire stereo or regio specificity by intrinsic arrangement of functional group and can be designed to impart substrate specificity.
8. Situation akin to infinite dilution could be generated by controlling cross-link density, reagent loading and flow rate to induce selectivity.
9. High reagents loading to induce reaction with another polymer bound species.
10. Flexibility of design allowing fabrication of highly specific chemical reactor systems such as hollow fibre, membrane, plug flow and column packing. Number of unit processes are reduced and energetics are improved.

Studies on functional polymers are production/application oriented rather than directed at the physico-chemical characterisation. Applications have evolved in health, nutrition, environmental and pollution control.

The functional groups may be an integral part of polymer backbone or linked as a side chain (pendant). The active group can be introduced during polymerisation by incorporation of another molecule. Polymerisation of monomer with desired functional groups and chemical modification of a nonfunctional polymer are other methodologies used. The specific route of choice is dictated by the desired physico-chemical properties.

1.1.1 POLYMERISATION OF FUNCTIONAL MONOMER

This methodology of synthesising a functional polymer using a functional monomer has a number of advantages.

1. The distribution of active group is uniform. This is not possible with chemical modification of polymer, due to miscibility restrictions.
2. Functional group structure can be ascertained in monomer, enabling designing suitable monomer. Such a prediction and control of active group is difficult by the chemical modification route.
3. Degree of functionalisation can be controlled. In some cases presence of functional group in fullest extent is desirable while separation of functional groups, distant to each other, are desirable for other specific applications. The control of loading and distribution of functional group is achievable through copolymerisation with nonreactive comonomer.
4. Support is not contaminated by traces of other reagents used during chemical modification. Side reactions on support are also avoided.

1.1.2 FUNCTIONALISATION BY CHEMICAL MODIFICATION

Chemical modification procedure is used extensively with crosslinked polymers. Such modification would be restricted to the surface due to difficulty in penetration. Ideal modification reactions without any side reactions are limited in number. Thus, multistep modifications are ruled out. It is difficult to control the distribution of reactive group. Chemical modification generally occurs at easily accessible sites. Hence, most functional groups are available for later reactions.

1.1.3 SPACER ARM WITH FUNCTIONAL GROUP

Functional group mobility is lowered by direct attachment to a polymer backbone^{2,3}. This restricted mobility which affects accessibility and reactivity, is overcome through the use of spacer groups⁴ in monomers. In chemical modification of polymer, the spacer is attached to the active reagent and the latter is attached to the polymer, through the second reactive end of the spacer^{5,6} to avoid coupling of the spacer from both ends to the polymer. The difunctional spacer molecules vary in chain lengths⁷.

Amongst different routes to the functional polymer, copolymerisation of functional monomer has a definite edge over polymer modification. The polymer can be structurally varied over a wide range in copolymerisation to subtly alter the properties. The type and relative amounts of two or more monomer units could be varied to make innumerable combinations within a copolymer system with desired property profile.

1.2 APPLICATIONS OF FUNCTIONAL POLYMERS

Functional polymers are used in a variety of applications. Some are summarised below.

1.2.1 POLYMERIC REAGENTS

These consist of reactive group attached to polymer. Chemical reactions can be conducted with the reactive group. The functional group is consumed during the reaction and should be used stoichiometrically to achieve the desired reaction.

1.2.1.1 Oxidising agent

Chromium trioxide bound to poly(vinyl pyridine) is used for oxidation of alcohols to aldehyde and ketones⁸. The chromium containing by-products are retained on the support. Overoxidation is avoided over a long reaction time. It could be reused for five cycles without loss of activity⁹.

1.2.1.2 Reducing agent

Macroreticular polystyrene bound tin dihydride reduces primary and secondary alcohols¹⁰. It selectively reduces one aldehyde group of terephthalaldehyde. Borohydride bound to poly(vinyl pyridine)^{11, 12} is used for carbonyl reduction.

1.2.1.3 Wittig reagent

Phosphine containing polystyrene beads are used in Wittig reaction¹³ for olefin synthesis. The by-product remains unattached and polymeric phosphine oxide can be recycled¹⁴. Trans olefin is formed in conventional Wittig reaction. In polymeric reagent cis olefins are formed in high yields¹⁵ if the inorganic lithium salt is filtered off prior to the addition of carbonyl compound. Polymeric phosphine dihalide is useful as halogenation, dehydration and condensation reagent¹⁶. It has been used in the preparation of water and temperature sensitive compounds like imidoyl bromide¹⁷.

1.2.1.4 Sulphur containing agent

Polymeric sulphur reagents are used for epoxidation of aldehydes¹⁸ and oxidation of primary and secondary alcohol to ketone¹⁹. Selective mono oxidation of diols to monoaldehyde is achieved by using polymeric thioanisole dichloride²⁰.

1.2.1.5 Halogenating agent

Poly(N-halo maleimide) is used for bromination and oxidation of olefins²¹ and ketones²². Polymeric aryl iodine difluoride is effective in the preparation of the gem-difluoride from alkenes in excellent yield²³.

1.2.1.6 Protecting groups

Functional polymer is used to block (protect) a reactive group in a difunctional reagent. The other reactive group of the reagent could then be suitably modified. 3-amino phenyl boronic acid grafted to carboxymethyl cellulose was used to complex numerous oligonucleotides containing free diol²⁴. Polystyrene boronic acid was used as an efficient and selective protecting group for cis diol of glycosides²⁵. Crosslinked polystyrene anchored dimethyl and diphenyl chlorosilanes effectively protect hydroxyl group²⁶. Benzyl p-nitrobenzyl carbonate derivative of polystyrene protects amino group²⁷.

1.2.2 POLYMERIC CATALYSIS

It is a conventional catalytic species, but supported on a polymeric backbone. It can be recycled many times without appreciable loss in activity²⁸.

1.2.2.1 Ion exchange resins

Ion exchange resins are used primarily for the removal of large concentrations of contaminant from aqueous solutions. The work-up process is simplified and number of separation steps are reduced without posing corrosion problems. These are also used to catalyse various chemical reactions. Poly(styrene sulphonic acid) is used for hydrolysis of esters²⁹, enamines³⁰ and amides³¹. Poly(acrylic acid) is used in

hydrolysis³² and esterification³³. poly(vinyl pyridine) is used in acylation³⁴ and acetalisation of carbonyl compounds and in esterification of carboxylic acids³⁵. Anion exchange resins are used as supported phase transfer catalysts³⁶.

1.2.2.2 Lewis acids and super acids

Impregnation of water sensitive Lewis acids in hydrophobic polymer protects them against hydrolysis by atmospheric moisture. The polymer imparts catalytic strength to the reactant resulting in higher yields of desired product. The impregnated Lewis acid is made accessible by swelling the resin with a suitable solvent. Aluminium chloride impregnated in Nafion and polystyrene has been used as a mild catalyst for the formation of ethers³⁷, esters³⁸ and acetals³⁹. Polymers with strong protonic acid group on impregnation with Lewis acid attain acidity to the level of superacids. Polystyrene sulphonic acid with aluminium chloride⁴⁰ and copolymer of perfluoroalkane sulphonic acid in combination with aluminium chloride⁴¹ are used as strong and efficient acid catalysts.

1.2.2.3 Hydrolysis and decarboxylation

Synthetic polymers with pendant imidazole groups resemble histidine present in the active site of hydrolysing enzymes. These polymers are used to catalyse hydrolysis of esters and amides. Polysoaps, with the characteristics of conventional micelles, and polyelectrolytes are reactive polymers with a polar or charged moiety. They are excellent activating reagents. Decarboxylation is enhanced in the presence of fully quaternised polyethylenimines containing dodecyl derivative⁴². Poly(crown

ether)s and polyglymes behave as typical polycations. In salt solution of alkali these interact with alkali picrates, methyl orange, p-nitrophenolate, phenolphthalein⁴³ and are efficient decarboxylation catalysts⁴⁴.

1.2.2.4 Phase transfer catalysts

Phase transfer catalysts bring reactants from different phases together by transfer of one reactant into the other phase or to the interface. These compounds can form ion pairs with anions or complex with cation of a salt. Organophilic onium salt from functional polymer enables its use as phase transfer catalyst. Catalytic activity is enhanced with increase in the distance of catalyst from polymer via spacer arm⁴⁵.

1.2.2.5 Transition metal catalysts

Polymer supported transition metal catalysts have been used as catalysts for a wide range of reactions of olefins such as hydrogenation⁴⁶, hydroformylation⁴⁷, carbonylation⁴⁸ etc. Homogeneous transition metal catalysis suffers from corrosion, instability due to dimer formation, cost and difficulty in recovery from reaction mixture. In polymers having transition metals, the active sites are kept apart to decrease the scope of dimerisation. Multiple catalysis is possible by loading two different catalysts on the same polymer enabling sequential multistep synthesis. Selectivity of catalyst can be increased by controlling steric environment of the catalyst. These are ideal academic catalyst supports. The support is inert hydrocarbon. Hence, it is free from unwanted side reactions. Uniformity achieved in polymeric catalyst offers synthesis ease vis-a-vis organometallic catalyst. Polymers can give high densities of active sites for binding catalytic groups. Efficient use of reactor volume is possible.

1.2.2.6 Immobilised enzymes

Immobilisation of enzymes on a solid support offers better stability and repeated use which makes it commercially viable system. Though enzymes are highly specific natural catalysts, their cost, stability, and operation are deterring factors for use of native extracellular enzymes. Immobilisation of enzyme by adsorption, entrapment, crosslinking or covalent binding are known. Functional polymers are instrumental in covalently binding of enzyme. In this technique, functional groups of amino acids of enzymes which are not part of active site, are reacted with functional polymers to covalently bind it. Amino group of lysine, carboxyl groups on aspartic and glutamic acid, phenol group on tyrosine, mercapto group on cysteine, hydroxyl group on serine, threonine and tyrosine, imidazole group on histidine and indole group on tryptophan are of particular interest. The choice of reaction parameters are restricted by the risk of denaturation during immobilisation.

1.2.2.7 Polymeric initiators

Photo⁴⁹, azo⁵⁰, anionic⁵¹ and cationic⁵² initiators covalently bound to polymer initiates the polymerisation of vinylic monomers. Unlike other polymeric reagent, separation of initiator from the polymer formed poses difficulty. They are more useful for the preparation of graft copolymers in converting initiating site into grafting site.

1.2.3 POLYMER AIDED SEPARATIONS

Active group on polymer can be used to bind one or more species out of a mixture of different species. The binding is possible by ionic, covalent or by entrapment/absorption.

1.2.3.1 Metal ion separations

Winning of metal ions from complex sources in hydrometallurgical recovery, industrial and waste water treatment systems are possible through polymers. Tailor making specific metal selective ligands attached to polymeric carriers is the approach selected. Styrenes, acrylates, vinylpyridines and vinylimidazoles are typical examples. 1-Vinyl-4,5-dicarboxy imidazole and 2-styryl-4,5-dicarboxylic acid imidazole were polymerised in the presence of 5 percent divinylbenzene⁵³. Hydroxyimines and hydroxyoximes are also important for chelation of transition metal ions. 5-vinyl salicylaldehyde and 4,4'-divinyl(-2,2'-ethylene) bis(nitrilo methylidene)diphenol were copolymerised with styrene to form schiff base chelates which form Co(II) polymeric complex⁵⁴. Acrylates, methacrylates and their corresponding acid chlorides are converted to functional monomers. Polyacrylamide gels, incorporating imino diacetate groups, were made by aminomethylation of the N-methylol polyacrylamide with sodium iminodiacetate⁵⁵. These polymers show high stability constants with bivalent ions like Ca, Mn, Hg, Zn and Cu. Copolymers of glycidyl methacrylate are also used. Aminated derivatives of benzocrown ethers are reacted with acrylamide and then polymerised to get functionality with high selectivity⁵³.

1.2.3.2 Separation of chiral molecules

Natural and synthetic chiral polymers are used as chiral stationary phases for chromatographic separation of enantiomers. Amino acid enantiomers are separated by ligand exchange chromatography wherein a chiral bidentate ligand is immobilised on a support and a transition metal ion is added to mobile aqueous phase. Linear polyacrylamide with L-proline and copper⁵⁶ is one such system.

Natural polymers like microcrystalline cellulose triacetate⁵⁷, cellulose tribenzoate⁵⁸, natural cellulose⁵⁹, bovine serum albumin⁶⁰ and synthetic polymers such as isotactic poly(triphenylmethyl methacrylate)⁶¹ are also used as stationary phase.

1.2.3.3 Gas separation

Some polymer-metal complexes can absorb and desorb gas molecules. This is used in the selective concentration of desired gas. Iron or cobalt tetrapyrrole complexes⁶² are oxidised by adsorbed oxygen. Thus such irreversible gas adsorptions are prevented by incorporation onto a polymer.

1.2.3.4 Solvent purification

Solvent purification without distillation is achieved to get high purity solvent used for analytical purposes. Polymer bound borohydride was used to purify ethanol reducing aldehyde impurities⁶².

1.2.3.5 Affinity chromatography

Affinity chromatography, a well known protein purification technique since early 1970s, is an adsorption technique due to interaction of molecules in solution with functional groups on a chromatographic adsorbent. This relies on highly specific molecular interactions such as biological recognition. The polymer used is an inert matrix with a component hooked on for biological recognition system. A number of biopolymers such as agarose^{63,64}, dextran⁶⁵ and cellulose⁶⁶ are used as is or with suitable modification.

Synthetic organic polymers have been used extensively. These include polyacrylamide^{67,68}, Poly(hydroxyalkyl methacrylate)⁶⁹ and polyamides⁷⁰. They are

suitably modified for activation or for coupling ligand. These are generally cyanogen bromide, carbonyl diimidazole/ chloroformate, sulphonyl chloride, periodate, glutaraldehyde, triazine chloride etc.

1.2.4 CONTROLLED RELEASE

Controlled release technology deals with the protection of biologically active agent and permit its continuous release to the desired target site at controlled rate. The bioactive substance such as drugs⁷¹, fertilizers⁷², herbicides⁷³, molluscides⁷⁴ are either embedded in the polymer matrix or covalently bound to the polymer. The continuous release is by erosion, diffusion or hydrolysis of covalent bond. The principle is used in anti-fouling paints to slowly release chemical to restrict growth of marine organisms on the painted surfaces of submerged ships, buoys etc.⁷⁵ Similar formulations are used in preservation of wood from biodegradation⁷⁶.

1.2.5 POLYMERIC FOOD ADDITIVES

Increasing needs for nontoxicity of the food additives have led to the use of functional polymers to enhance product quality, appearance, texture, flavour etc.. Functional groups of food additives are attached to properly selected functional polymer molecule. This produces additive of larger dimensions which cannot be absorbed through digestive tract. They cannot pass through membranes of liver kidney and are excreted in the faeces without any metabolism, thereby reducing toxicity. Food dyes derivatised with poly(methacrylamide) are used as food colorant⁷⁷. Food products such as oils and fats deteriorate on exposure. Generally phenolic antioxidants are used to delay rancidity. Toxicity of phenolic derivatives and loss due to evaporation makes it less effective. Polymerisation of

α -(2-hydroxy-3,5 dialkylphenyl) ethylvinyl benzene gives a better antioxidant. It is less volatile due to high molecular weight. It cannot be absorbed in intestinal walls⁷⁸. High temperature food additive is prepared by polymerising divinyl benzene with phenolics using aluminium catalyst⁷⁹.

1.3 FUNCTIONAL POLYELECTROLYTES:

Most linear functional as well as crosslinked insoluble polymers hitherto discussed, operate in organic solvents. Isolated from these are the water soluble ionizing functional polymers. These find applications as dispersing and drilling mud additive, flocculant and sequestrant. In these, additional complexity arise from the electrolytic character. Anomalous viscosity dependence on concentration due to electrostatic interaction, ionisation of weak and strong electrolyte and counterion binding are the prominent additional features.

Applications of relevance to the present study are: (i) antistatic agent (ii) flocculant (iii) detergent (iv) scale inhibitor (v) corrosion inhibitor (vi) dispersant (viii) sequestering agent

1.3.1 SCALE INHIBITORS

Polyacrylates inhibit scale formation preferentially in the nucleation period while organophosphonates act at the level of crystal growth in being adsorbed on crystal faces.

Polyacrylate completely neutralised with sodium can be used as such. Though organo phosphonates is 10 times more effective to polyacrylates, poly acrylate is preferred above 100°C due to greater thermal stability. It shows low toxicity and

low rise of eutrophication⁸⁰. Acrolein-acrylic acid copolymer stabilises supersaturated solutions by inhibiting crystallisation of calcium carbonate, calcium sulphate, calcium oxalate, ferric oxide and other salts in industrial treatment. A 3-10 ppm dose of the copolymer permits in large measure, avoidance of scale formation in installations using these treated waters. 1:9:90 acrolein, acrylic acid and allyl alcohol copolymers saponified with sodium hydroxide was useful as detergent builder and scale inhibitor⁸¹. Property of poly(maleic acid) as a boiler scale inhibitor was improved by copolymerising with acrylic acid. It showed 103 per 100 part of polymer of iron and 42 magnesium as compared with polymaleic acid 76 and 39 for iron and magnesium respectively⁸².

1.3.2 SEQUESTERING AGENTS

Sequestration is the formation of soluble metal complex. Sequesterants differ from chelants and flocculants in deactivating the metal ion without phase separation. Natural polymeric sequestrants such as heparin are known. Inorganic sequestrants are widely used. The use of sequestrants may be classified as under: i) Dissolving precipitates. ii) precipitation prevention. iii) Suppress ionic form of metal ions solution. iv) The use of actual chelate as such in contradistinction to metals or ionic forms. v) Alter crystallisation behaviour⁸³.

Oligomeric copolymers of sodium vinyl oxy acetate, acrylate allyloxy acetate and allyloxy malonate sequester bivalent ions of calcium, copper, cadmium, mercury and disperse manganese dioxide. These biodegrade under aerobic condition and are better detergent builders vis-a-vis ethylene diamine tetra acetate (EDTA) or NTA triphosphate⁸⁴.

Poly(α -hydroxy acrylic acid) and its sodium salt were useful as sequestering agent

or detergent builders^{85,86}. Copolymer of 2-chloro acrylic acid and chloro maleic anhydride hydroxylated in boiling water to give lactonised polymer or sodium salt was superior detergent builder to sodium salt of acrolein acrylic acid copolymer⁸⁷. Low molecular weight copolymers of acrylic acid-acrylamide have good calcium sequestering capacity. It decreases surface tension of the calcium solution⁸⁹. Combination of poly(acrylic acid) and poly(ethylene oxide) in water had calcium and iron sequestering capacity⁹⁰. Polyacrylic acid on treatment with 2-phosphonobutane 1,2,4 tricarboxylic acid⁹¹ inhibits calcium sulphate scaling. Poly(α -hydroxy acrylic acid) was used as complexing agent for calcium and lime⁹². Copolymers of acrylic acid and hydroxy acrylic acid were used as a builder in detergent containing dodecyl benzene sulphonate, ethoxylated tallow fatty alcohol and tallow soap⁹³. Poly (α -hydroxy carboxylic acid) prepared by polymerising allyl alcohol and acrylic acid had good calcium blocking capacity. Precipitation inhibiting capacity at 1 ppm level was 96.5 percent⁹⁴. It could also be used as peroxide stabilizer⁹⁵. A poly(hydroxy carboxylate) prepared by canizzaro reaction of acrolein-acrylic acid copolymer was a biodegradable sequestering agent⁹⁶.

1.4 COPOLYMERS OF ACROLEIN, ACRYLIC ACID AND METHACRYLIC ACID

Functional polyelectrolytes formed by copolymerisation of acrolein with acrylic acid or methacrylic acid are used in various applications. The properties having relevance to the present study and some of the applications are briefly discussed here.

1.4.1 BIOLOGICAL ACTIVITY

Synthetic poly(carboxylic acids) are biologically active⁹⁷. Poly(acrylic acid) gives complete protection against Semillki Forest virus⁹⁸ and reduces pox count for vaccinia virus infection by 55 percent⁹⁹. The biological activity was molecular weight dependent with optimum activity in the molecular weight range 6000-15,000. Above 25,000 it is too toxic to be biocompatible. In mice it increased the survival time against lethal doses of Mengo virus and sarcoma 180 ascitis tumour. Incorporation of acrolein imparted antialgal property to methacrylic acid-allylic acid copolymer¹⁰⁰.

1.4.2 ENZYME IMMOBILISATION

Enzymes can be immobilised onto the polymers containing carboxylic groups by various coupling reactions via amino groups of the protein. The carboxyl groups are activated as acyl azide, acid anhydride and active ester by condensation reagents and four centered condensation reaction¹⁰¹. The carboxyl group is converted to methyl ester and reacted with hydrazine hydrate to form hydrazide. This, on reaction with aqueous sodium nitrite gives the azide. The azide can be reacted with amino group of enzyme under mildly alkaline pH¹⁰²⁻¹⁰⁷.

Carbodiimides react with carboxyl groups at mild acidic pH (4.75-5) to form O-acyl isourea derivative¹⁰⁸. N-alkyl-5-phenyl isoxazolium salts (Woodward K reagent) and N-ethoxy carbonyl-1-ethoxy-1,2-dihydroquinidine (EEDO) are other activating coupling reagents.

Polymers with aldehyde pendent groups react with amino groups on the protein to form aminol, azomethine and aldimine linkages. The method has limited applications due to instability and reversibility of the bond formed.

Acrolein copolymerised with N-vinyl pyridine was used in immobilisation of trypsin via imine bond formation¹⁰⁹. Polyacrolein microspheres were used in derivatisation of proteins, with desferroxamine like ligands under physiological pH¹¹⁰. Acrolein-methacrylic acid copolymer microspheres prepared by γ radiation were derivatised with 1,6-diaminohexane and coupled with carbodiimide. It was used in scanning electron microscope for localisation of antigen receptors on cell surfaces¹¹¹. Acrolein- N-vinyl pyrrolidone copolymer was used to immobilise corynebacterium simplex used in the transformation of steroids¹¹². Lipoprotein lipase was immobilised on polyacrolein with or without oligo glycine as spacer¹¹³.

Aldehyde group is modified by reacting with alcohol, amine, bisulphite and oxime derivatives. Bisulphite derivative of acrolein-acrylic acid copolymer was prepared by reacting with sulphur dioxide¹¹⁴. Alternatively, insoluble compositions of the copolymers were converted into bisulphite derivatives with aqueous sulphurous acid. Polymer derivative containing less than 57 mole percent acrylic acid were soluble in water but copolymers with acrylic acid more than 57 mole percent were insoluble. The decomposition of dried derivatives during storage was prevented by its conversion to sodium salt¹¹⁵.

Polymers with nonthrombogenic surface were prepared by grafting polyethylene with bisulphite derivative of acrolein-acrylic acid copolymer and exposing to UV or γ radiation¹¹⁶. This property was also exploited as a blood anticoagulant. The copolymer was treated with sulphur dioxide to form α hydroxy sulfonic acid derivative. Storage stability was enhanced by neutralisation as sodium salt¹¹⁷. This was less active than heparin, a natural anticoagulant but had longer duration of action. No toxicity was observed both *in vivo* and *in vitro* in rabbits¹¹⁸. Copolymers of acrylic acid azide¹¹⁹ and acrolein, methacrolein with other monomers were used

678.01:541.8(043)
GAD

TH-651

for similar applications¹²⁰.

Acrolein-acrylic acid copolymer was used in aqueous suspension polymerisation of vinyl chloride to inhibit deposition of polymer on reactor surface and to increase yield¹²¹. Polyacrolein modified with triethanolamine at 40-80°C was useful as copper absorbant¹²². Polyacrolein derivatised with hydroxyl amine hydrochloride was used to remove heavy metal such as iron and copper from fruit juices and alcoholic beverages^{123,124,125}.

1.4.3 SCALE PREVENTION

Homopolymer or copolymers of methacrylic acid were found to be useful in scale prevention in desalination apparatus¹²⁶. Copolymers of acrolein-acrylic acid copolymer stabilises supersaturated solutions by inhibiting crystallisation of calcium carbonate, calcium sulphate, calcium oxalate, ferric oxide and other salts in industrial treatment. A 3-10 ppm dose of the copolymer permits in large measure, avoidance of scale formation¹²⁷.

1.4.4 ANTICORROSIVE PROPERTY

Life of cutting tools was enhanced and surface quality of metals improved when the fluid contained water soluble 5 weight percent bisulphite derivative of acrolein-acrylic acid copolymer, and 1 percent of calcined soda¹²⁸. Copolymers of acrolein and hydrazine derivative formed water resistant and corrosion resistant coating¹²⁹.

Acrolein-acrylic acid copolymers prepared by oxidative polymerisation were condensed with formaldehyde as in cannizzaro reaction treated with sodium borohydrate. The polymer was a moisturiser and improved moisture retention and

rehydration of skin¹³⁰. A copolymer of acrylic acid, acrolein and allyl alcohol saponified with sodium hydroxide at 70°C gives detergent builders and scale inhibitor¹³¹. A similar copolymer of methacrylic acid, acrolein and allyl alcohol exhibited calcium sequestration capacity¹³².

1.4.5 POLYMERISATION AND ITS CHARACTERISTICS

Though acrolein is easily polymerised at room temperature, copolymerisation is sensitive to presence of comonomer^{133,134}. The rate in the radiation polymerisation of acrolein at -78°C was found to increase with the addition of acrylic acid¹³⁵. Effect of hydrophobic and hydrophilic interaction on copolymerisation of acrylic acid and methacrylic acid in the presence of polymer of hydrophobic and hydrophilic vinyl monomer indicated formation of hydrophobic areas in the water phase. Polymerisation proceeded in these areas. The less hydrophilic areas preferentially incorporating less hydrophilic monomer and more hydrophilic area more hydrophilic monomer¹³⁶. In copolymerisation of acrylic acid with vinyl acetate, reactivity of acrylic acid was minimum at pH 4.3. At a specific pH, the reactivity increased with increasing cation concentration due to strong ion pair formation¹³⁷. Addition of upto 2 percent of Copper or cobalt methacrylate in the copolymerisation of methacrylic acid with methyl methacrylate decreased the reaction rate and reactivity ratio of methacrylic acid dropped from 0.68 to 0 due to complexation¹³⁸.

1.5 COPOLYMERISATION AND MONOMER REACTIVITIES

Copolymerisation reactions involve the simultaneous incorporation of two or more monomers in the same chain during polymerisation. The composition of the copolymer is generally found to be different from that in the reactant feed. Different models have been put forth to visualise the mechanism of copolymerisation. These differ in assumptions regarding mechanism of addition of growing chains and the factors influencing them. First attempt at a quantitative, comprehensive theory of copolymerisation was made by Dostal¹³⁹. It was established quantitatively by Mayo and Lewis¹⁴⁰.

LIST OF SYMBOLS

M_1 and M_2 = Monomer 1 and monomer 2.

M_1^0 and M_2^0 = Mole fractions of the monomers 1 and 2 in initial feed

$\sim M_1^*$ and $\sim M_2^*$ = Growing polymer radicals with terminals M_1 and M_2 .

m_1 and m_2 = Mole fraction of the monomer 1 and 2 in the copolymer respectively.

r_1 and r_2 = Reactivity ratios of monomers 1 and 2.

$[M_1]$ and $[M_2]$ = Concentrations of monomers 1 and 2 in feed

$d[M_1]/d[M_2]$ = Relative rate of addition of the two monomers

P_{11} , P_{12} , P_{22} and P_{21} = Probabilities of addition of monomers

w_1 and w_2 = Weight fraction of all M_1 and M_2 sequences.

$$F_1 = [M_1]/[M_2]$$

$$f_1 = m_1/m_2$$

$$X_1 = \frac{M_1}{M_1 + M_2}$$

$$Y_1 = \frac{m_1}{m_1 + m_2}$$

$$k = m_2[M_1] / m_1[M_2]$$

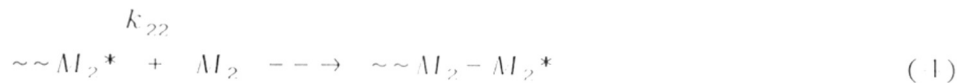
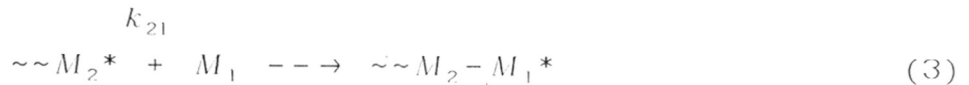
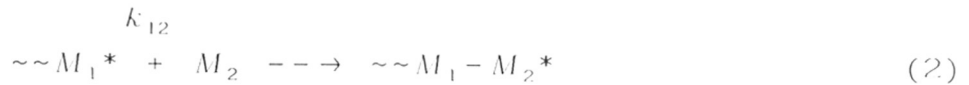
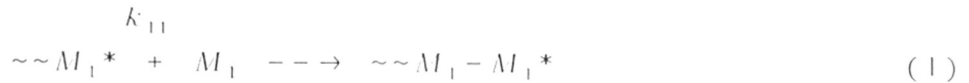
N = Number of experiments performed

MFC = Mole Fraction Conversion

WFC = Weight Fraction Conversion

1.5.1 COPOLYMER COMPOSITION EQUATION

The following four principal, mutually competitive, propagation reactions are well recognised[139-147] in binary free radical copolymerisations.



where M_1 and M_2 are monomers and $\sim M_1^*$ and $\sim M_2^*$ are the corresponding growing polymer radicals with terminal M_1 and M_2 free radical centres. The rate of consumption of monomers M_1 and M_2 are given by:

$$-\frac{d[M_1]}{dt} = k_{11}[M_1][M_1^*] + k_{21}[M_1][M_2^*] \quad (5)$$

$$\frac{d[M_2]}{dt} = k_{22}[M_2][M_2^*] + k_{12}[M_2][M_1^*] \quad (6)$$

It is assumed that, under isothermal conditions, a steady state for the free radical concentration^{140,145-147} is reached wherein:

$$k_{21}[M_2^*][M_1] = k_{12}[M_1^*][M_2] \quad (7)$$

The differential form of the polymer composition equation is then arrived at as:

$$\frac{d[M_1]}{d[M_2]} = \frac{[M_1]}{[M_2]} \cdot \frac{[r_1[M_1] + [M_2]]}{[[r_2][M_2] + [M_1]]} \quad (8)$$

The monomer reactivity ratios, $r_1 = k_{11}/k_{12}$ and $r_2 = k_{22}/k_{21}$ are the kinetic parameters of importance in copolymerisations. These measure the relative rate of addition of a radical to its own monomer vis a vis addition of the same radical to the comonomer. $[M_1]$, $[M_2]$, are molar concentrations of the two monomers in feed and $d[M_1]/[M_2]$ is the relative rate of addition of the two monomers to the growing chain. At relatively low conversions the latter may be approximated to mole ratio of respective monomers in the copolymer.

This differential form of copolymer composition equation has also been derived on the basis of probability of monomer addition. This quantifies the correctness of four basic competitive reactions [equations (1) to (4)] assumed in the kinetic treatment of binary copolymerisations.

The probability of addition of monomer M_1 to a chain radical $\sim M_1^*$ is:

$$P_{11} = \frac{k_{11}[M_1] \cdot [M_1]}{k_{11}[M_1] \cdot [M_1] + k_{12}[M_1] \cdot [M_2]} = \frac{r_1[M_1]}{r_1[M_1] + [M_2]} = [1 - P_{12}]$$

Similarly,

$$P_{12} = \frac{[M_1]}{r_1[M_1] + [M_2]} = [1 - P_{11}] \quad (10)$$

$$P_{21} = \frac{[M_1]}{[M_1] + r_2[M_2]} = [1 - P_{22}] \quad (11)$$

$$P_{22} = \frac{r_2[M_2]}{[M_1] + r_2[M_2]} = [1 - P_{21}] \quad (12)$$

The probability of occurrence of a sequence of 'n' repeat units of species M₁ in a copolymer chain is:

$$P_{M_1} = P_{11}^{n-1} \cdot P_{12} \quad (13)$$

The weight fraction of all M₁ sequences is:

$$W_1 = \frac{P_{12}}{P_{11}} \sum_n n P_{11}^n = \frac{1}{P_{12}} \quad (14)$$

Likewise, the weight fraction of all M₂ sequences is:

$$W_2 = \frac{1}{P_{21}} \quad (15)$$

The composition of the copolymer is given by:

$$\begin{aligned} \frac{d[M_1]}{d[M_2]} &= \frac{r_1}{r_2} = \frac{1/P_{12}}{1/P_{21}} \\ &= \frac{(r_1[M_1] + [M_2])/[M_2]}{(r_2[M_2] + [M_1])/[M_1]} \end{aligned} \quad (16)$$

$$\frac{d[M_1]}{d[M_2]} = \frac{[M_1]}{[M_2]} \cdot \frac{[r_1[M_1] + [M_2]]}{[r_2[M_2] + [M_1]]} \quad (17)$$

1.5.2 SIGNIFICANCE OF REACTIVITY RATIOS

The composition of the instantaneously formed copolymer can be predicted from the binary copolymer equation. Similarly, reactivity ratios of comonomers can be estimated from a knowledge of monomer concentrations in the feed and the copolymer composition. The reactivity parameters can predict distribution of the monomers in the formed copolymer. The mean sequence length, average block length of either monomer, can also be predicted. Since reactivity ratio is the ratio of reaction rates between similar species vis-a-vis dissimilar ones, it predicts the nature of the formed copolymer. Reactivity ratio r_1 greater than unity arises from preferential addition of M_1 to the growing radical M_1^* . This indicates tendency to form blocks of M_1 . Reactivity ratio r_1 less than unity denotes preferential addition of M_2 to the growing radical M_1^* . Zero reactivity ratio indicates the incapability of the monomer to form block of M_1 . The copolymerisation system is said to be ideal if product of the two reactivity ratios is unity. The two radical species show similar preferences in their relative reactivities towards the two monomers. Here, the reactive end group on growing chain has no influence on

the rate of addition. If both r_1 and r_2 are zero, the monomers alternate along the chain regardless of monomer feed composition. In reality, most copolymerisations are intermediate between ideal and the alternating cases. i.e. $0 < r_1$ and $r_2 < 1$. If both r_1 and r_2 are less than one, there exists a specific monomer feed ratio which generates copolymer of identical composition. This is termed as azeotropic composition.

1.5.3 METHODS OF ESTIMATING REACTIVITY RATIOS

A number of methods for determining the reactivity ratios have evolved^{140,148-159} and been reviewed^{155,159}. Different statistical treatments and numerical modifications, varying in accuracy and ease of operation, have been suggested to predict the reactivity ratios within a narrow confidence region^[**].

1.5.3.1 Mayo-Lewis method

The differential form of Mayo and Lewis¹⁴⁰ equation is expressed as:

$$r_2 = \frac{[M_1]}{[M_2]} \left[\frac{m_2}{m_1} \left(1 - \frac{r_1 [M_1]}{[M_2]} \right) - 1 \right] \quad (18)$$

Each experiment of specific monomer feed-copolymer composition yields a straight line of r_2 as a function of r_1 . The coordinates of the best weighted point of intersection of several experimental lines represent r_1 and r_2 . This is known as the intersection method of Mayo-Lewis plot. The 'best point of intersection' is invariably spread over an area and large uncertainties lie in the evaluation of r_1 and r_2 .

1.5.3.2 Fineman-Ross method

A graphical method was developed by Fineman and Ross¹⁴⁹. In this, the differential copolymer composition equation is modified and linearised. The copolymer composition equation may be expressed as:

$$f_1 = F_1 \cdot \frac{r_1 F_1 + 1}{r_2 + F_1} \quad (19)$$

wherein $F_1 = [M_1]/[M_2]$ and $f_1 = m_1/m_2$

Linearisation evolves two independent equations:

$$\frac{(f_1 - 1)}{F_1} = r_1 - \left(\frac{f_1}{F_1^2} \right) r_2 \quad (20)$$

$$\frac{F_1(1 - f_1)}{f_1} = r_2 - \left(\frac{F_1^2}{f_1} \right) r_1 \quad (21)$$

F_1 and f_1 are computed from the monomer feed and copolymer composition data respectively. Plot of $(f_1 - 1)/F_1$ against f_1/F_1^2 from equation (20) yields r_2 as slope and r_1 as intercept. The plot of $F_1(1-f_1)/F_1$ against F_1^2/f_1 from equation (21) yields r_1 and r_2 as slope and intercept respectively. These equations are unsymmetrical with respect to r_1 and r_2 . The experimental data are unequally weighted. The data obtained under extreme experimental conditions [very low $[M_2]$ in equation (20) and very low $[M_1]$ in equation (21)] have the greatest influence on slope of the lines drawn. The method does not account for extent of reaction and neglects the drift in monomer concentration as reaction proceeds. The method

was corrected by a statistical treatment^{160,161} to take into account the relative experimental accuracy in the estimation of copolymer composition. The parameters defined were as follows:

\overline{F}_1 and \overline{f}_1 are mean of all F_1 and f_1 values respectively.

$$SR = \sum (f_1 - \overline{f}_1)^2 - b \sum (F_1 - \overline{F}_1)(f_1 - \overline{f}_1) \quad (22)$$

$$S = \sqrt{(SR/n-2)} \quad (23)$$

$$SE(b) = \frac{S}{\sqrt{\sum (F_1 - \overline{F}_1)^2}} \quad (24)$$

where $SE(b)$ is standard error in calculation of slope and

$$SE(b_0) = S \sqrt{\frac{1}{n} + \frac{\overline{F}_1^2}{\sum (F_1 - \overline{F}_1)^2}} \quad (25)$$

$SE(b_0)$ is standard error in calculation of intercept. A 95 percent confidence interval is given as

$$\Delta r_1 = SE(b) \times t_{0.95} \quad (26)$$

and

$$\Delta r_2 = SE(b_0) \times t_{0.95} \quad (27)$$

The "Student distribution function", $t_{0.95}$, is the value at 95 percent confidence limit at $(n-2)$, number of experiments is 'n'.

1.5.3.3 Mayer-Lowry method

An equation was proposed by Skeist¹⁶² to relate reactivity ratios to the change in composition of monomer mixture during copolymerisation. A general formulation was developed, which required graphical or numerical evaluations. Mayer and Lowry¹⁶³ developed analytical solution to Skeist's equation for binary copolymerisation. Substituting $M = M_1 + M_2$ and $X_1 = M_1 / (M_1 + M_2)$ and differentiating yielded:

$$\begin{aligned} \frac{dX_1}{dM_1} &= \frac{1}{M} \left[\frac{dM_1}{dM} - \frac{M_1}{M} \right] \\ &= \frac{1}{M} (F_1 - f_1) \end{aligned} \quad (28)$$

Integration of this equation (28) yields Skeist's equation:

$$\ln \frac{M}{M_0} = \int_{X_{10}}^{X_1} \frac{1}{(F_1 - X_1)} dX_1 \quad (29)$$

On integration, right side of the equation (29) yields:

$$X = \frac{M}{M_0} = \left[\frac{X_1}{X_{10}} \right]^a \left[\frac{X_2}{X_{20}} \right]^b \left[\frac{X_{10} - \delta}{X_1 - \delta} \right]^y \quad (30)$$

where,

$$\alpha = \frac{r_2}{(1 - r_2)}$$

$$\beta = \frac{r_1}{(1 - r_1)}$$

$$\gamma = \frac{(1 - r_1 r_2)}{(1 - r_1)(1 - r_2)}$$

$$\delta = \frac{1 - r_2}{(2 - r_1 - r_2)}$$

This equation enables the estimation of copolymer composition with respect to change in monomer feed composition. Victor Mayer¹⁶⁴ used this equation to develop a method of determining reactivity ratios from a knowledge of copolymer composition and conversion data. In this procedure, a specific value of r_2 was chosen. Values of x were calculated for this r_2 for various r_1 ranging from 0 to 1. r_1 was plotted against x . When x became less than M/M_0 , interpolation between the least and the preceding value of x was repeated till agreement within desired narrow limits was achieved. Thus, experimental value of M/M_0 was obtained for a known initial monomer composition. The values of r_1 were estimated for different values of r_2 such that x nearly equals the experimentally obtained M/M_0 values. These values of r_1 and r_2 represent one line corresponding to a given feed composition. A series of lines of r_1 and r_2 were obtained for specific feed compositions differing only in degrees of conversion. These lines are more or less parallel to each other. Similarly, another set of lines were drawn for different sets of feed composition. The two sets of lines intersect each other. The region of intersection of these lines is the region of reactivity ratios within a specific confidence limit. Rearrangement of this equation yields Mayo-Lewis equation. So

these methods are similar. However, the Mayo-Lewis treatment determines monomer reactivity ratios from widely varying monomer feed ratios as a function of conversion, whereas Mayer's treatment should be more amenable to the detection and interpretation of deviation from this presumed ideal copolymerisation behaviour. This approach is used to study the copolymerisation behaviour at moderately high conversions which is not feasible with the Mayo-Lewis approach.

1.5.3.4 Tidwell-Mortimer method

A non-linear least-squares procedure was proposed, by fitting the experimental mole fraction of the copolymer to theoretical curves in the form developed by Skeist, i.e. m_2 vs M_2 . Theoretical curves were computed on the basis of an initial approximate estimate of the reactivity ratios. From this selected point, by successive iterations sum of the square of the mean square deviation was minimised. This method eliminated the serious subjective element in the selection of the best point of intersection on the Mayo-Lewis plot.

1.5.3.5 Yezrielev-Brokhina-Roskin method

An improved form of linearisation was provided which eliminated the dissymmetry of the two Fineman-Ross equations (20) and (21). The two unsymmetrical equations of Fineman-Ross were coupled to yield a symmetrical equation,

$$\frac{F_1 r_1}{\sqrt{f_1}} - \frac{\sqrt{f_1} r_2}{F_1} = \sqrt{f_1} - \frac{1}{\sqrt{f_1}} \quad (31)$$

The method yields very reliable r_1 and r_2 values even at relatively higher (20 percent) conversions. The monomer concentration used in the computation is the average of values at the start and the concentration at the time of termination of the reaction. This, copolymer composition and weight fraction conversion are used in the calculation [a17]. This method yields graphical as well as analytical solution. The differential form of the copolymer composition equation.

$$\frac{d[M_1]}{d[M_2]} = \frac{[M_1]}{[M_2]} \cdot \frac{[r_1[M_1] + [M_2]]}{[[r_2][M_2] + [M_1]]}$$

may be expressed as:

$$\begin{aligned} K &= \frac{r_1[M_1] + [M_2]}{r_2[M_2] + [M_1]} \\ &= \frac{d[M_1]}{d[M_2]} \cdot \frac{[M_2]}{[M_1]} \\ &\sim \frac{m_1}{m_2} \cdot \frac{[M_2]}{[M_1]} \end{aligned}$$

where $d[M_1]/d[M_2]$ and m_1/m_2 are the monomer mole ratios in the incremental copolymer formed and $K = m_2[M_1]/m_1[M_2]$. Equation (2) becomes:

$$Kr_2[M_2] + K[M_1] = r_1[M_1] + [M_2] \quad (32)$$

dividing by $[M_2]$,

$$Kr_2 + KF_1 = r_1F_1 + 1 \quad (33)$$

$$\text{or } KF_1 - 1 = r_1 F_1 - Kr_2 \quad (34)$$

Dividing equation (34) by K yields:

$$F_1 - \frac{1}{K} = \frac{F_1}{K} r_1 - r_2 \quad (35)$$

Similarly, dividing equation (34) by F_1 yields:

$$\frac{1}{F_1} - K = \frac{K}{F_1} r_2 - r_1 \quad (36)$$

The Fineman-Ross equations (20,21) are interconvertible by multiplying equation (20) with $-K/F_1$ and equation (21) with $-F_1/K$ respectively. The YBR method derives a symmetric equation with respect to r_1 and r_2 by multiplying equations (20) and (21) by $\sqrt{K/F_1}$ and $\sqrt{F_1/K}$ respectively.

$$\sqrt{KF_1} - \frac{1}{\sqrt{KF_1}} = r_1 \sqrt{\frac{F_1}{K}} - r_2 \sqrt{\frac{K}{F_1}} \quad (37)$$

Substituting f_1/F_1 for K in equation (37) and rearranging, we get,

$$\frac{F_1}{\sqrt{f_1}} r_1 - \sqrt{\frac{f_1}{F_1}} r_2 = \sqrt{f_1} - \frac{1}{\sqrt{f_1}} \quad (38)$$

This linearisation was symmetrical with respect to r_1 and r_2 . Solution for r_1 and r_2 is obtained in the following manner:

Equation (37) on multiplication by $\sqrt{F_1}/K$ and \sqrt{K}/F_1 gives,

$$r_1 F_1 / K - r_2 = F_1 - 1 / K \quad (39)$$

$$r_2 K / F_1 - r_1 = 1 / F_1 - K \quad (40)$$

These equations on summation to N data points become:

$$r_1 A_1 - r_2 N = C_1 \quad (41)$$

$$-r_1 N + r_2 A_2 = C_2 \quad (42)$$

where

$$A_1 = \sum \frac{F_i}{K_i}$$

$$A_2 = \sum \frac{K_i}{F_i}$$

$$C_1 = \sum \left(F_i - \frac{1}{K_i} \right)$$

$$C_2 = \sum \left(K_i - \frac{1}{F_i} \right)$$

N = number of experiments.

Equations (41) and (42) can be resolved for r_1 and r_2 . Multiplication of equation (41) by N and equation (42) by A_1 , followed by addition and rearrangement yields:

$$r_1 A_1 N - r_2 N^2 = C_1 N \quad (43)$$

$$-r_1 A_1 N + r_2 A_1 A_2 = C_2 A_1 \quad (44)$$

$$r_2 (A_1 A_2 - N^2) = A_1 C_2 + N C_1 \quad (45)$$

$$r_2 = \frac{A_1 C_2 + N C_1}{A_1 A_2 - N^2} \quad (46)$$

Similarly,

$$r_1 = \frac{C_1 A_2 + N C_2}{A_1 A_2 - N^2} \quad (47)$$

The mean square error in the determination of the monomer reactivity ratios is evaluated through the method of least squares by substituting in equation (21) the r_1 and r_2 values obtained from equations (46) and (47).

$$\Lambda^2 = \frac{\sum_{i=1}^N \Delta_i^2}{N - 2}$$

where

$$\Delta_i^2 = (r_1 \sqrt{F_i/K_i} - r_2 \sqrt{K_i/F_i} - \sqrt{K_i F_i} + 1 / \sqrt{K_i F_i})^2$$

Thus, the expression for mean square error in the determination of r_1 and r_2 is:

$$\Delta_{r_1}^2 = \frac{\Delta^2 A_2}{A_1 A_2 - N^2}$$

$$\Delta_{r_2}^2 = \frac{\Delta^2 A_1}{A_1 A_2 - N^2}$$

The exact values of r_1 and r_2 are then:

$$r_1 = \frac{C_1 A_2 + N C_2}{A_1 A_2 - N^2} + \sqrt{\frac{\Delta^2 A_2}{A_1 A_2 - N^2}} \quad (18)$$

$$r_2 = \frac{C_2 A_1 + N C_1}{A_1 A_2 - N^2} + \sqrt{\frac{\Delta^2 A_1}{A_1 A_2 - N^2}} \quad (19)$$

The method gives very balanced average parameters inspite of any stray experimental error in a set of data. The method was theoretically predicted for experiments carried to very low conversions (<5 percent). It gives fairly accurate values of reactivity ratios even at conversions as high as 20 per cent¹⁶⁵.

The range of applicability increases to higher conversions (>25%) if average monomer feed values, as defined by Joshi¹⁵⁹, are used in the computation.

The average feed values are estimated as given below:

$$MFC = WFC \cdot \frac{M_2^0 b + (1 - M_2^0)}{m_2 b + \alpha(1 - m_2)} \quad (50)$$

where MFC and WFC are the mole fraction and weight fraction conversions respectively, a and b are the molecular weights of monomers, M_1 , M_2 and m_2 are the mole fractions of the monomer 2 in the initial feed, its average mole fraction in the feed and its average mole fraction in the copolymer respectively.

1.5.3.6 Joshi-Joshi method

This method is based on Mayo Lewis-plot. Best point representing r_1 and r_2 was statistically calculated as the closest point to all experimental lines. The coordinates of the point of intersection is a weighted, linear and least square solution. The method derived initially for differential form was extended to integral equation. The r_1 and r_2 were preliminarily estimated by YBR differential method using average monomer feed values. The values of r_1 and r_2 arbitrarily represent a point on the hypothetical r_2 versus r_1 plot of Mayo-Lewis differential equation³¹. This is the same as the best point of intersection of the several lines representing r_2 versus r_1 . Using this best point, coordinates of the point of intersection of the normal to the i^{th} line were estimated. The new coordinates of the point of intersection to a line on the Mayo-Lewis plots were designated $(r_1)_i$ and $(r_2)_i$. The values of r_1 and r_2 around the best point were marginally altered with an auxiliary constant, $Z = 0.1$, to obtain three values of P ,

$$P = \frac{1 - r_1}{1 - r_2} \quad (51)$$

The Mayo-Lewis integrated equation was solved in the significant region using these three values of P as r_2 versus r_1 plot. The portion of each integral curve representing points obtained from the three values of P were approximated as root

mean square straight lines. The slopes $m = F^2 / f$ and intercepts [$C = F(1/f - 1)$] were computed. These new slopes (m) and intercept (c) were treated in a manner akin to the differential YBR procedure and the final values of r_1 and r_2 with their standard deviations were obtained.

1.5.3.7 Braun-Brendlein-Mott method

Procedures, discarded due to tedious and complicated calculations, were examined afresh with the advent of computers. A simple method of this kind was developed by Braun, Brendlein and Mott¹⁶⁶. The program is based on curve fitting of Mayo-Lewis differential copolymerisation equation. The copolymer composition equation was transformed into:

$$Y = \frac{(r_1 - 1)X^2 + X}{(r_1 + r_2 - 2)X^2 + (2 - 2r_2)X + r_2} \quad (52)$$

where $Y = \frac{m_1}{m_1 + m_2}$ and $X = \frac{M_1}{M_1 + M_2}$. The copolymer composition is governed by r_1 when

m_2 exceeds m_1 and by r_1 when m_2 is less than m_1 . The data was grouped into two sets comprising of m_1 values less than m_2 (set 1) and m_1 values greater than m_2 (set 2).

Two values of Y emerge. One, Y_{calc} , calculated by equation (52), and the other, Y_{actual} from analysis of the copolymer formed. The difference between Y_{actual} and Y_{calc} was minimised to less than 0.001 by successive iterations. The values of r_1 and r_2 were altered by small increments to arrive at a more exact and reportable r_1 and

r_2 values. The accuracy of reactivity ratio is dependent on the precision of copolymer analysis. Hence, the analysis method is questionable if the polymer analysis is not precise.

1.5.3.8 Kelen-Tudos method

A graphical semi-empirical procedure was proposed^{157,158,167-169}, to overcome the shortcomings of Fineman-Ross linearisation. This provides accurate values of r_1 and r_2 by analytical solution.

Arbitrary parameters ' η ' and ' ξ ' were defined as:

$$\eta = G / \alpha + H$$

$$\text{and } \xi = H / \alpha + H$$

$$\text{where } G = F(F - 1) / f$$

$$\text{and } H = F^2 / f.$$

The linear equation obtained was:

$$\eta = r_1 + \frac{r_2}{\alpha} \cdot \xi - \frac{r_2}{\alpha} \quad (53)$$

A large number of binary copolymerisation systems have been predicted by this method. A straight line is obtained by plotting η as a function of $\xi(0, 1)$. This linearity testifies to the applicability of copolymer composition equation and the simple two parameter model implicit in it. Extrapolation to $\eta = 0$ and $\eta = 1$ yield $-r_2 / \alpha$ and r_1 as the respective intercepts. The proper choice of α governs uniform distribution of the experimental data. α can be chosen as 1 for a monomer pair with nearly identical reactivity ratios. When reactivities of two monomers are

markedly different or data is not uniformly distributed, then α is chosen considering the entire experimental range of composition for both polymer and comonomers. If H_M and H_m are the highest and the lowest values of F, $\alpha = \sqrt{H_M \cdot H_m}$ affords the optimum distribution of the data. Using least squares method r_1 and r_2 values may be derived as:

$$r_1 = \frac{\sum \eta \cdot \xi (N - \sum \xi) - \sum \eta (\sum \xi - \sum \xi^2)}{N \sum \xi^2 - (\sum \xi)^2} \quad (54)$$

$$r_2 = \frac{\sum \eta \cdot \xi \sum \xi - \sum \eta \sum \xi^2}{N \sum \xi^2 - (\sum \xi)^2} \quad (55)$$

Kelen-Tudos modified this equation for high conversion by redefining F and G as:

$$H = \frac{m_1}{m_2} \left[\frac{\log z_1}{\log z_2} \right]^2 \quad (56)$$

and

$$G = \left[\frac{m_1}{m_2} - 1 \right] \left[\frac{\log z_1}{\log z_2} \right] \quad (57)$$

where $z_1 = M_1 / M_{10}$ and $z_2 = M_2 / M_{20}$

This procedure does not suffer from reindexing error. This modification can be used with relatively high conversions. It gives the data symmetrically located

along the interval of the independent variable and gives a visual evaluation of the applicability. The confidence limit for this extended KT method is a function of Student's distribution for n experiments at $n-2$ degrees of freedom and at the desired probability level.

1.5.3.9 Shawki-Hamielec method

A method to estimate the reactivity ratios from composition data based on non-linear regression was developed by Shawki and Hamielec¹⁷⁰ from Mayer-Lowry equation [equations (29) and (30)]

$$\ln \frac{M}{M_0} = \int_{f_{10}}^{f_1} \frac{1}{(F_1 - f_1)} df_1 \quad (29)$$

$$X = \frac{M}{M_0} = \left[\frac{f_1}{f_{10}} \right]^\alpha \left[\frac{f_2}{f_{20}} \right]^\beta \left[\frac{f_{10} - \delta}{f_1 - \delta} \right]^\gamma \quad (30)$$

The conversion X is related to F_1 (the cumulative average mole fraction of M_1 in the copolymer formed up to that conversion) by the following relationship:

$$f_1 = \frac{f_{10} - F_1 X}{1 - X} \quad (38)$$

Given the value of the conversion X , $\ln(1-X)$ is calculated. A stepwise numerical integration algorithm is successively applied to the right side of the equation while the upper limit of integration is incremented. Thus, starting from f_{10} , f_1 is progressively decreased if monomer M_1 is the more reactive component or increased

otherwise. At each point, the value of $1/(F_1 - f_1)$ is computed using the equation,

$$F_1 = \frac{r_1 f_1^2 + f_1 f_2}{r_1 f_1^2 + 2 f_1 f_2 + r_2 f_2^2} \quad (59)$$

This is the midpoint of the interval of the two f_1 values that makes the right side of equation (46), just exceed in absolute value the left side of the equation is taken as the solution of the equation. Hence, the corresponding value of the average cumulative copolymer composition F_1 , is obtained. The residual in each experimental run is taken as the difference between the value of F_1 thus calculated and that measured experimentally. The values of reactivity ratios that minimise sum of the squares of these residuals of all observations are then found by nonlinear least-squares regression method developed by Marquardt¹⁷¹. This method combines the Gauss linearisation technique and method of the steepest descent. The method assumes that all experimental errors are associated only with the measured copolymer composition. The error in measuring the conversion is much smaller than that in the measurement of copolymer composition. This method collects data at intermediate conversion levels. It does not assume constant composition during the course of reaction.

1.5.3.10 Kuo-Chen method

Kuo J.F. and Chen C.Y. suggested a linearisation method based on a different integrated form of the copolymer composition equation and a graphical method based on instantaneous copolymer composition. The integrated method estimated

the reactivity ratios by fitting the overall weight conversion of the copolymerisation and cumulative copolymer composition¹⁷².

The equations (5) and (6) were integrated to yield

$$-\frac{d[M_1]}{dt} = k_{11}[M_1][M_1^*] + k_{21}[M_1][M_2^*] \quad (5)$$

$$-\frac{d[M_2]}{dt} = k_{22}[M_2][M_2^*] + k_{12}[M_2][M_1^*] \quad (6)$$

$$M_1 = M_{10} \exp[-(k_{11}M_1^* + k_{21}M_2^*)t] \quad (60)$$

and

$$M_2 = M_{20} \exp[-(k_{12}M_1^* + k_{22}M_2^*)t] \quad (61)$$

since the magnitudes in the parentheses for many a systems was of the order of magnitude of 10^{-7} per minute the equations were linearised to

$$M_1 = M_{10} [1 - (k_{11}M_1^* + k_{21}M_2^*)t] \quad (62)$$

$$M_2 = M_{20} [1 - (k_{12}M_1^* + k_{22}M_2^*)t] \quad (63)$$

approximating by steady state assumption

$$k_{21}[M_2^*][M_1] = k_{12}[M_1^*][M_2]$$

and rearranging a new integrated form of copolymer equation was derived as:

$$\frac{(M_{10} - M_1)}{(M_{20} - M_2)} = \frac{M_{10}(r_1 M_1 + M_2)}{M_{20}(M_1 + r_2 M_2)} \quad (64)$$

substituting

$$Z_1 = \frac{M_{10} - M_1}{(M_{10} - M_1) + (M_{20} - M_2)} = 1 - Z_2 \quad (65)$$

and rearranging:

$$\frac{Z_2 X_{10} X_2 - Z_1 X_{20} X_1}{Z_1 X_{20} X_2} = r_2 - \frac{Z_2 X_{10} X_1}{Z_1 X_{20} X_2} r_1 \quad (66)$$

The values of r_1 and r_2 are obtained by linear least squares or graphic method.

In another graphic method¹⁷³, Y_1 is substituted for $m_1/(m_1 + m_2)$ and X_1 is substituted for $M_1/(M_1/M_2)$ the equation becomes:

$$X_1 = 1 - X_2 = \frac{r_1 Y_1^2 + Y_1 Y_2}{r_1 Y_1^2 + 2Y_1 Y_2 + r_2 Y_2^2} \quad (67)$$

$$\frac{Y_1}{X_1} = \frac{r_1 Y_1^2 + 2Y_1 Y_2 + r_2 Y_2^2}{r_1 Y_1^2 + Y_1 Y_2} \quad (68)$$

$$\lim_{Y_1 \rightarrow 0} Y_1 / X_1 = r_2 \quad (69)$$

equation (67) is rearranged as

$$X_2 = \frac{Y_1 Y_2 + r_2 Y_2^2}{r_1 Y_1^2 + 2Y_1 Y_2 + r_2 Y_2^2} \quad (70)$$

hence

$$\frac{Y_2}{X_2} = \frac{r_1 Y_1^2 + 2Y_1 Y_2 + r_2 Y_2^2}{Y_1 + r_2 Y_2} \quad (71)$$

$$\lim_{Y_1 \rightarrow 0} Y_2 / X_2 = 1$$

combining equation (68) and (71)

$$\lim_{Y_1 \rightarrow 0} \frac{Y_1 / X_1}{X_2 / Y_2} = \lim_{Y_1 \rightarrow 0} Y_1 Y_2 / X_1 X_2 = r_2 \quad (72)$$

Similarly,

$$\lim_{Y_1 \rightarrow 1} Y_1 / X_1 = 1$$

and

$$\lim_{Y_1 \rightarrow 1} Y_2 / X_2 = r_1$$

Hence

$$\lim_{Y_1 \rightarrow 1} Y_1 Y_2 / X_1 X_2 = r_1 \quad (73)$$

$Y_1 Y_2 / X_1 X_2$ is plotted against Y_1 . The graph is extrapolated to the two extremes of $Y_1 = 0$ and $Y_1 = 1$, to arrive at $r_1 (Y_1 = 0)$ and $r_2 (Y_1 = 1)$ values. The authors also developed a method for predicting composition of the copolymer from similar data. The method predicted a marginal change in reactivity with change in monomer feed compositions. Further, it was claimed that the reactivity ratio changed with conversion for a given comonomer composition. A method for predicting composition without determining the reactivity ratios was proposed¹⁷⁴.

To summarise, the Mayo-Lewis treatment of free radically propagated copolymerisation kinetics is presupposed in all these derivations. These take into account only the interactions between growing polymer radicals and monomers, and ignore the interactions occurring between free monomer molecules. The effect of conversion is also ignored. Extensive calculations are required. These do not give a quantitative estimate of error and require subjective estimate of the best intersection to arrive at reactivity ratios.

1.5.4 PARAMETERS AFFECTING REACTIVITY RATIOS

The reactivity ratios, of a given monomer pair, are altered by experimental conditions. The four principal mutually competitive propagating reactions are altered non-uniformly by the changed environment. The parameters affecting these reactions to an appreciable extent are:

1.5.4.1 Mechanism of polymerisation

Some monomers are polymerisable by different mechanisms. Monomer like styrene is susceptible to polymerisation by cationic, anionic or radical species. The specific

reaction rates for these species differ dramatically. Solvent and temperature also influence, but to a lesser degree. Reactivity ratios for methyl acrylate-acrylonitrile system investigated with different mechanisms are presented in the Table 1.

1.5.4.2 Hydrogen ion concentration

The behaviour of free radicals in aqueous media are considerably influenced by the pH of the media. The investigation of copolymerisation kinetics in water is restricted to water-soluble unsaturated acids, their derivatives and amines. The kinetic investigation necessitates a preliminary knowledge of the electro-chemical properties of monomer and the homo/copolymer. The copolymerisation behaviour is complicated by additional factors such as dissociation, specific and nonspecific binding of counter-ions, electrostatic and hydrophobic interactions which come into play. The polymerisation rate of methacrylic acid in ion free aqueous solutions, with hydrogen peroxide as the initiator, decreased with increase in the pH of the system¹⁷⁵, attaining a near zero value at pH 5.5. It was observed that un-ionised monomer alone took part in the polymerisation¹⁷⁵. The effect of pH on the rate of polymerisation of acrylic and methacrylic acids has been studied in detail by Blauer^{176,177}. Similar effects operate in the binary copolymerisations. Alfrey, Overberger and Pinner¹⁷⁸ observed, in binary copolymerisations of methacrylic acid-diethyl amino ethyl methacrylate as ionising monomers leading to the preparation of the polyampholytes, that the copolymer composition depended markedly on the pH of the medium. At pH 1.2, the reactivity ratios are 0.98 and 0.90 respectively. While at pH 7.2, the values are 0.08 and 0.65 respectively. This reversal in the observed reactivity ratios is due to the ionisation of carboxyl group in methacrylic acid. A copolymerization study has been carried out by Kabanov

Table-1
 Reactivity ratios for different mechanism-Acrylonitrile-Methyl acrylate

acrylonitrile	methylacrylate	conditions
4.80	0.10	25°C, $\text{RuH}_2\text{P}(\text{Ph}_3)_4$, toluene
0.69	1.04	50°C, redox, emulsion
2.40	0.20	-70°C, BuLi
0.76	0.43	50°, Ir_2O_3 , 3×10^8 Pa
1.00	0.83	60°C, radical

et al¹⁷⁹ for a system with one of the monomers ionisable. The acrylic acid-acrylamide system was investigated in the acidic pH range by Cabaness et al.¹⁸⁰. A gradual reversal in reactivity ratios of both monomers was observed. These investigations were carried out over a narrow pH range, in alkaline¹⁷⁹ and acidic region¹⁸⁰. Study of methacrylic acid-N vinyl pyrrolidone system, over a wide pH range, with and without addition of a strong electrolyte has been carried out by Ponrathnam et al¹⁸¹. This is presented in Table 2.

1.5.4.3 Solvent

G.Saini¹⁸² studied the effect of solvent on monomer reactivity ratios. The acrylamide-styrene system was investigated in dioxane, ethanol and 7:3 mixture of 1,4-dioxane-ethanol. H.Fujihara et al.¹⁸³ investigated copolymerisation of styrene-methyl methacrylate in benzene, dioxane, dichloromethane, N,N dimethyl formamide, acetonitrile, ethanol and phenol. Some of the systems were investigated at two different temperatures. The data is presented in Table 3. Similar observations are reported in later communications^{184,185}

1.5.4.4 Concentration

Matsubara et al.¹⁸⁶ observed effect of concentration on the reactivity ratios of styrene-N- methyl pyridazinone and styrene- N-phenyl pyridazinone in Figure 1. The systems were investigated in bulk and in solvents like acetic acid, phenol, ethanol and benzene at differing concentrations. The change in reactivities was attributed to reduced collisions between monomer molecules arising from solvation of the monomers. Similar effect of concentration in gaseous phase due to different pressure was observed¹⁸⁷ in ethyl acrylate-acrylonitrile system.

Table-2
Effect of pH and addition of strong electrolyte

Medium pH	methacrylic acid	acrylamide
4	2.84	0.20
4 with 1 M NaCl	1.84	0.35
6	0.19	0.55
6 with 1 M NaCl	0.22	0.76
10	0.38	0.51
10 with 1 M NaCl	0.52	0.24

Table 3
Effect of solvents and mixture of the solvents

Monomer	Dioxane	Dioxane-Ethanol	Ethanol
acrylamide r ₁	1.38	0.59	0.30
styrene r ₂	1.27	1.13	1.44
acrylamide r ₁	2.45	0.82	0.44
methyl-methacrylate r ₂	2.55	2.53	2.60

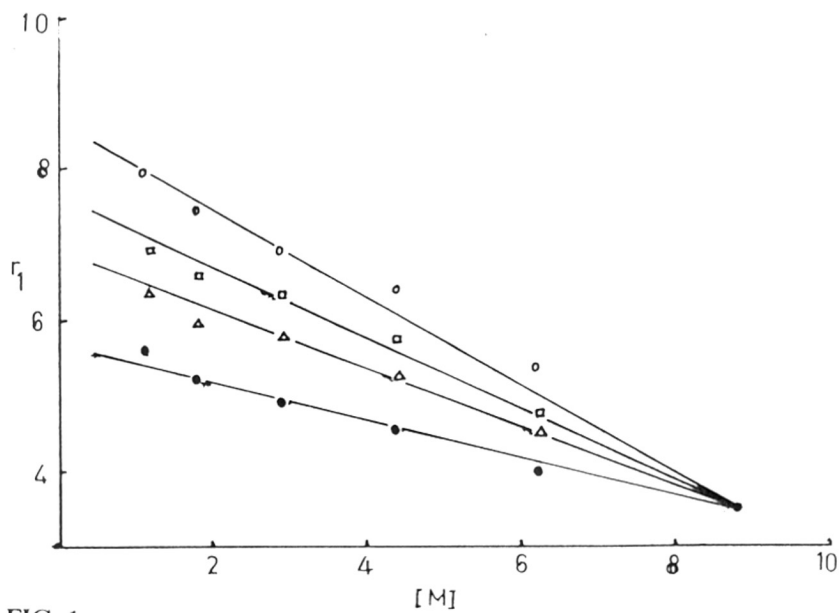


FIG. 1

EFFECT OF MONOMER CONCENTRATION

REACTIVITY RATIO OF STYRENE WITH N-PHENYL PYRIDAZENONE

- BENZENE
- Δ ETHANOL
- ◻ PHENOL
- ◊ ACETIC ACID

1.5.4.5 Temperature

Effect of temperature on the reactivity parameter was pointed out by H. Fujihara et al.¹⁸³⁻¹⁸⁴ in styrene-methyl methacrylate system. In Table 4, the change in reactivity ratios is presented for the copolymerisation in dioxane, acetonitrile and ethanol. Similar solvent and temperature effects are reported for styrene-N,N dimethyl acrylamide system. At elevated temperatures, the rate enhancement of all the reactions might be nonlinear. This could alter the relative rate, resulting in the change in reactivity ratios. This change in some cases is prominent but the same is marginal for monomer pairs with uniform enhancement in the reaction rate.¹⁸⁴⁻¹⁸⁶

1.5.4.6 Initiator system

The effect of different initiators on the reactivity ratios due to different mechanisms is discussed earlier. In some radical copolymerisations, change in reactivity due to different initiator has been reported. Redox initiator is operative at relatively lower temperatures than benzoyl peroxide or azo bis-isobutyro nitrile. These changes could be attributed to the change in reaction temperature. Jelinek¹⁸⁸ et al. have reported dependence of reactivity ratios on the redox initiator systems at 40⁰C. The effect of initiator system on reactivity ratios is presented in Table 5.

Table-4
 Copolymerization of Styrene (r_1) and Methyl methacrylate (r_2)

Solvent	Temperature	r_1	r_2
Benzene	80	0.62	0.59
1,4 Dioxane	60	0.48	0.54
1,4 Dioxane	80	0.52	0.60
Dichloromethane	80	0.50	0.63
N,N Dimethylformamide	80	0.55	0.58
Acetonitrile	60	0.52	0.54
Ethanol	60	0.40	0.45
Ethanol	80	0.41	0.41
Phenol	80	0.29	0.38

Table-5
Effect of initiator system

Redox system	Acrolein	Acrylamide
	r ₁	r ₂
K ₂ S ₂ O ₈ -AgNO ₃	1.67	0.16
K ₂ S ₂ O ₈ -Na ₂ S ₂ O ₅	1.59	1.99
Me ₃ COOH-FeSO ₄	2.07	0.31

1.6 SCOPE OF WORK

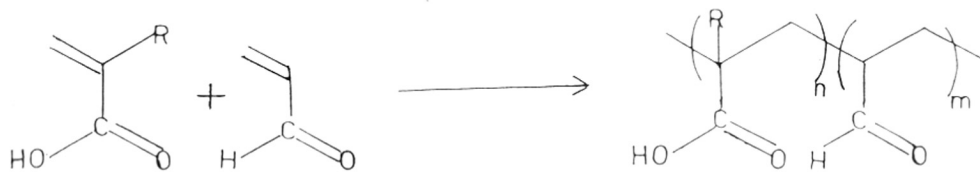
Functional polyelectrolytes are water-soluble polymers bearing labile functional groups together with ionic moieties. Copolymers of acrylic/ methacrylic acid with acrolein are examples of functional polyelectrolytes. Copolymers of ionising monomers and functional monomers offer scope to be suitable for sequestration, enzyme immobilization etc. The properties of the copolymers vary with its monomer composition and monomer distribution along the chain. It is possible to tailor make functional hydrophilic copolymers with specific sequence length distribution of the two comonomers, from a knowledge of relative reactivities of the two monomers. The functional polyelectrolytes offer ease of modification into polymers with desired property profiles suitable for metal chelation.

1.6.1 COPOLYMERISATION

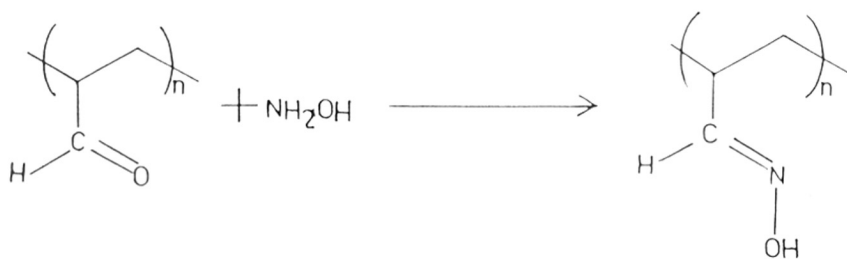
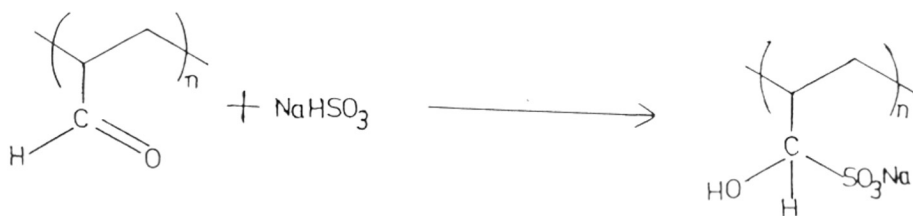
The comonomer mole ratios in the feed stream are not replicated in instantaneously formed copolymer. This is dependent on the relative abilities of the monomers towards self and cross additions. Reactivity ratios are the measures of the two tendencies. Hence reactivity ratios of the systems must be determined. The reactivity ratios vary with reaction conditions such as reaction temperature, solvent etc. The reactivity ratios in aqueous solution copolymerisation of ionising monomers are influenced by pH, ionic strength of the medium, ionisation and co-operative hydrophobic interactions. Hence, acrylic acid-acrolein and methacrylic acid-acrolein copolymerisations were studied at different pH, at a constant temperature. The reaction is presented in Figure 2(a). The reactivity ratios of the systems were determined using Yezrielev, Brokhina, Roskin (YBR) and Kelen, Tudos (KT) procedures.

FIG. 2

a) COPOLYMERISATIONS



b) DERIVATISATIONS



Anomalous behaviour was observed in the aqueous copolymerisation of acrolein with acrylic acid. The instantaneously formed copolymer immediately separates out as a coacervate from feed streams wherein the acrolein concentration exceeds a critical limit. This effect alters the apparent reactivity ratio of acrolein. The effect of homogeneous and heterogeneous media on the reactivity ratios were investigated.

1.6.2 SYNTHESIS

Copolymerisations of acrylic and methacrylic acids with acrolein were conducted at 30^oC using a redox initiator to optimise the reaction parameters such as monomer and initiator concentrations, nonsolvent type etc. Once standardised, a series of copolymerisations were conducted.

1.6.3 CHARACTERISATION

Aldehyde, a reactive group, undergoes self addition and with carboxylic acid group present in the copolymer. In a functional polymer, the content and distribution of free aldehyde group along the copolymer chain are of particular interest. Influence of feed composition and mean sequence length on the amount of free aldehyde group was studied by solid state C¹³ NMR using Cross Polarization/ Magic Angle Spinning (CP/MAS) technique.

1.6.4 SEQUESTRATION

Sequestration is formation of soluble metal complex. Sequestering agents differ from chelating and flocculating agents in deactivating the metal ion without phase separation. Naturally occurring polymeric sequestering agents such as heparin are

known, and inorganic sequestrants are widely used. A study of synthetic polymers as sequestering agents reveals importance of control over distribution of sequestering groups in the polymer. The copolymers were derivatised with hydroxylamine hydrochloride and sodium bisulphite. It is shown in the Figure 1(b). The amount corresponded to the aldehyde concentration in the copolymers. These derivatised copolymers were studied for calcium sequestering capacity. The sequestering capacity of the copolymer is dependent on the degree of dissociation of the ionizing group, which in turn is affected by pH of the media. The study was carried out in the 4 to 11 pH range.

1.6.5 MODIFICATION WITH PHENOLS

Novel phenolic resins were synthesised. Copolymers (0.8 moles of aldehyde) were reacted with 1 mole of phenol and m-cresol to form novolac type resins. It is shown in Figure 3. The reactions were catalysed insitu by pendent carboxylic groups. For comparative evaluation, styrene-acrolein copolymers were synthesised and reacted with m-cresol. Curing behaviour of these polymers and m-cresol-formaldehyde systems of similar concentration were studied with hexamethylene tetramine using differential scanning calorimeter.

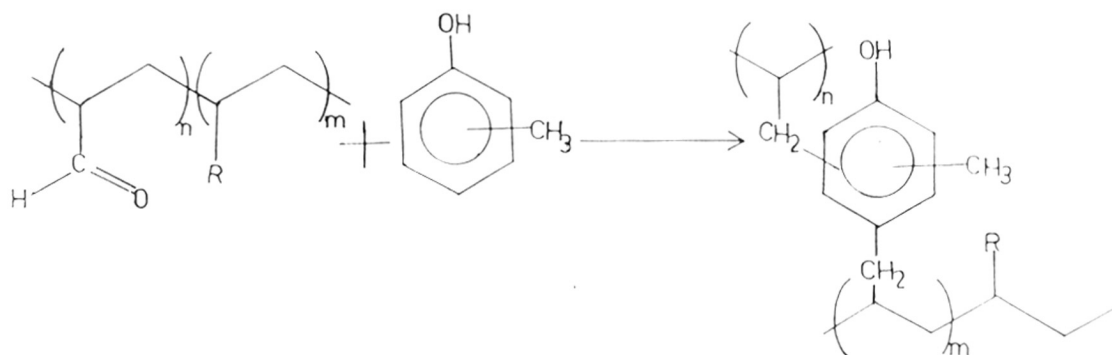


FIG. 3

DERIVATISATION WITH PHENOL TO FORM NOVOLAK TYPE POLYMERS

CHAPTER II

EXPERIMENTAL

2.1 MATERIALS

(i) Acrylic acid

Empirical formula	$C_3H_4O_2$
Molecular weight	72.06
Density	1.051 gm/mL
B.P.	139°C

Acrylic acid (propenoic acid) was obtained from Fluka A/G, Switzerland. It was freed from inhibitor by distillation at reduced pressure, under nitrogen blanket. Freshly distilled acrylic acid was used in all the copolymerisation experiments.

(ii) Methacrylic acid

Empirical formula	$C_4H_6O_2$
Molecular weight	86.09
Density	1.015 gm/mL
B.P.	163°C

Methacrylic acid (2-methyl propenoic acid) was obtained from Fluka A/G, Switzerland. It was purified by distillation at reduced pressure under nitrogen blanket. Freshly distilled methacrylic acid was used as a monomer in all the copolymerisations.

(iii) Acrolein

Empirical formula	C_3H_4O
Molecular weight	56.06
Density	0.839 gm/mL
B.P.	53°C

Acrolein (2-propenal or acrylaldehyde) was obtained from Fluka A/G, Switzerland. It was purified by distillation under nitrogen blanket. Freshly distilled acrolein was used as a monomer in all the copolymerisations.

(iv) Styrene

Empirical formula	C_8H_8
Molecular weight	104.15
Density	0.909 gm/ml
B.P.	145-46°C

Styrene was obtained from Fluka A/G, Switzerland. It was freed from inhibitor by washing sequentially with 5 weight percent sodium hydroxide (thrice) and distilled water till free from hydroxide ions. It was then dried over calcium chloride and distilled at reduced pressure under nitrogen blanket. Freshly distilled styrene was used for copolymerisations.

(v) Potassium hydrogen phthalate

Empirical formula	$C_8H_5O_4K$
Molecular weight	204.2

Potassium hydrogen phthalate was obtained from M/S. Loba Chemie, Bombay (India). It was used as the primary standard to estimate normality of sodium hydroxide used in potentiometric titration.

(vi) Potassium persulphate

Empirical formula $K_2S_2O_8$

Molecular weight 270.33

Analytical reagent grade potassium persulphate was obtained from M/S Loba Chemie, Bombay (India). It was recrystallised from deionised water. It was used as a component of the redox initiator system in the aqueous copolymerisations.

(vii) Sodium sulphite

Empirical formula Na_2SO_3

Molecular weight 126.04

Analytical reagent grade sodium sulphite was obtained from M/S. Loba Chemie, Bombay (India). It was recrystallised from hot water. It was used as a component of redox initiator system for the copolymerisations.

(viii) Hydroquinone

Empirical formula $C_6H_6O_2$

Molecular weight 110.11

M.P. 173°C

Hydroquinone was obtained from M/S. Loba Chemie, Bombay (India). It was used to terminate the copolymerisations. It was also used to inhibit polymerisation of the vinyl monomers during storage.

(ix) **Hexamethylene tetramine**

Empirical formula	$C_6H_{12}N_4$
Molecular weight	140.19
M.P.	280°C

Hexamethylene tetramine (HMTA or hexa) was obtained from M/S. Loba Chemie, Bombay (India). It was used in the curing studies of novolak type polymers.

(x) **Calcium acetate**

Empirical formula	$C_4H_6O_4Ca.H_2O$
Molecular weight	158.17

Calcium acetate was obtained from M/S. Loba Chemie, Bombay (India). It was used in determining calcium sequestering capacity of the polymers.

(xi) **Sodium oxalate**

Empirical formula	$C_2O_4Na_2$
Molecular weight	134.0

Sodium oxalate was obtained from Fluka A/G, Switzerland. It was used as an indicator in determining calcium sequestration capacity of the polymers.

(xii) Hydroxylamine hydrochloride

Empirical formula	NH_4OCl
Molecular weight:	69.49
M.P.	159°C (decomposes)

Hydroxylamine hydrochloride was obtained from Fluka A/G, Switzerland. It was used to derivatise aldehyde groups to form oxime.

(xiii) Sodium bisulphite

Empirical formula	NaHSO_3
Molecular weight	104.06

Sodium bisulphite was obtained from M/S. Loba Chemie, Bombay (India). It was used for derivatising aldehyde group on polymer.

(xiv) Potassium hydroxide

Empirical formula	KOH
Molecular weight	56.11

Potassium hydroxide was obtained from M/S. Loba Chemie, Bombay (India). It was used as a secondary standard, to adjust the pH of copolymerisation media and to convert the copolymers into potassium salt in the carboxylic acid estimation.

(xv) Sulphuric acid

Empirical formula	H ₂ SO ₄
Molecular weight	98.08

Sulphuric acid was obtained from M/S. Loba Chemie, Bombay (India). It was used for converting potassium salt of copolymers into potassium sulphate for analysing copolymer compositions.

xvi) Phenol

Empirical formula	C ₆ H ₆ O
Molecular weight	94.11
M.P.	40-42°C
B.P.	182°C

Phenol was obtained from Fluka A/G, Switzerland. It was used in the derivatisation of acrolein-methacrylic acid copolymer to form novolak type resin.

(xvii) m-Cresol

Empirical formula	C ₇ H ₈ O
Molecular weight:	108.14
M.P.	32-34°C
B.P.	202°C

m-Cresol was obtained from Fluka A/G, Switzerland. It was used in the derivatisation of acrolein-methacrylic acid copolymer to form novolak type resin.

(xviii) 1,4-Dioxane

Empirical formula	$C_4H_8O_2$
Molecular weight	88.11
Density	1.034 gm/mL
B.P.	100-102°C

1,4-dioxane was obtained from M/S. Loba Chemie, Bombay (India). It was kept over ferrous sulphate to make it peroxide-free, kept over sodium wire and distilled out. It was used as solvent for the copolymerisation of acrolein with styrene.

(xxiv) Acetone

Empirical formula	C_3H_6O
Molecular weight	58.08
B.P.	56°C

Acetone of differing purity levels was obtained from M/S.Loba Chemie, Bombay(India).It was used as solvent, nonsolvent and in the investigation of molecular association.

(xxv) Methanol

Empirical formula	CH_4O
Molecular weight	32.04
B.P.	64.6°C

It was used as a component of nonsolvent system for acrolein methacrylic acid copolymer as well as to precipitate potassium salt of the copolymer.

(xxvi) **Petroleum ether (60-80)**

Petroleum ether was obtained from M.M. Supplier, Pune (India). It was used as a component in the nonsolvent system for copolymers.

(xxvii) **Benzoyl peroxide (BPO)**

Empirical formula	$C_{14}H_{10}O_4$
Molecular weight	242.23
M.P.	105°C (decomposes)

Benzoyl peroxide was obtained from M/S. Loba Chemie, Bombay (India). It was used as initiator in the copolymerisation of acrolein with styrene.

(xxviii) **p-Toluene sulphonic acid (PTSA)**

Empirical formula	$C_7H_8O_3S$
Molecular weight	190.22
M.P.	103-106°C

PTSA was obtained from Fluka A/G, Switzerland. It was used as an acid catalyst in the condensation reaction of acrolein styrene copolymer with m-cresol.

(xxix) **Hydrochloric acid**

Empirical formula	HCl
Molecular weight	36.46

Hydrochloric acid was obtained from M/S. Loba Chemie, Bombay(India). It was used in adjusting pH of the copolymerisation reaction media and in potentiometric titrations.

(xxx) **Sodium hydroxide**

Empirical formula NaOH

Molecular weight 40.0

Sodium hydroxide was obtained from M/S. Loba Chemie, Bombay (India). It was used in adjusting pH for calcium sequestration investigation and in potentiometric titrations.

(xxxii) **Sodium chloride**

Empirical formula NaCl

Molecular weight 58.44

It was obtained from M/s. Loba Chemie, Bombay (India). Analytical reagent grade sodium chloride was used as a strong electrolyte in the calcium sequestration studies of selected copolymers.

(xxxiii) **Potassium bromide**

Empirical formula KBr

Molecular weight 119.01

Spectroscopy grade potassium bromide was obtained from Aldrich Chemical Company, Inc., USA. It was used to form sample pellets to estimate infrared absorbances.

xxxiii) Nitrogen gas

The gas was made oxygen-free by bubbling it through Fieser's solution (sodium salt of anthraquinone sulphonic acid in potassium hydroxide.)

2.2 COPOLYMERISATIONS

The following aqueous copolymerisations were conducted at differing constant pH:

(i) Aqueous solution copolymerisation of acrolein with acrylic acid and (ii) acrolein with methacrylic acid at differing constant pH.

The copolymerisations were terminated at moderately low conversions to study the monomer reactivity ratios for the systems.

(iii) Aqueous solution copolymerisations of acrolein with methacrylic acid taken to high conversions.

These copolymers were investigated for calcium sequestration. Additionally, the copolymers were modified with phenols. The persulphate-sulphite red-ox pair was used to initiate the copolymerisation.

(iv) Copolymerisation of acrolein with styrene in 1,4-dioxane using benzoyl peroxide (BPO) as initiator.

These polymers were reacted with m-cresol to prepare novel novolak type resins.

2.2.1 Stock Solutions

The following stock solutions were accurately prepared to avoid weighing error.

2.2.2 Copolymerisation of acrolein-acrylic acid

The reaction vessel used for conducting copolymerisation is depicted in Figure 4. The isothermal reactions were conducted in a thermostatted water bath maintained at $30.0 \pm 0.1^\circ\text{C}$. Total reaction volume was set at 50 mL. Acrylic acid and acrolein were taken in various proportions like 1:9, 2:8,..., 8:2 and 9:1. Acrylic acid in the required amounts was pipetted out from stock solution. The pH of the reaction was adjusted to required value using hydrochloric acid and potassium hydroxide stock solutions. In different sets of reactions, the pH was maintained at 1, 3, 5, and 7 respectively. Thus, pH of 1 was established with 1 molar hydrochloric acid and pH 3, 5 and 7 were established with 1, 5 and 10 molar potassium hydroxide solutions respectively. Required amounts of acrolein was pipetted out and deionised water was added to make the volume upto 46 mL. Another set was run without controlling the pH of the reaction medium through external additions. The total monomer concentrations in the five sets of copolymerisations was identical at 4 molar. In a sixth set, experiments were studied without pH control and the total monomer concentration was 1 Molar. The reaction vessels were flushed for 15 minutes with oxygen-free nitrogen. 2 mL each of 0.125 molar solution of potassium persulphate and sodium sulphite were sequentially added to initiate copolymerisations. The reaction vessels were stoppered and thermostated at $30.0 \pm 0.1^\circ\text{C}$. The reaction time was adjusted between 2-3 hours to maintain the weight percent conversion below 35 percent. After the desired reaction time, the copolymerisation was terminated by the addition of 2 mL of 0.25 molar hydroquinone solution in acetone. The copolymers were quantitatively precipitated with 7:1 v/v acetone/petroleum ether mixed

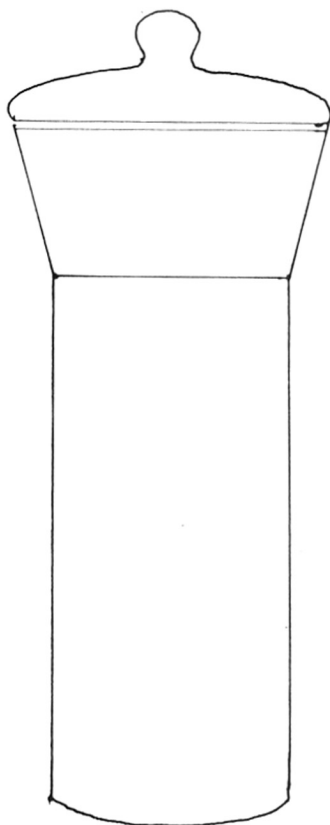


FIG. 4
REACTION VESSEL USED FOR CONDUCTING
COPOLYMERISATION AT LOW CONVERSION

- (i) Acrylic acid: A 4 molar stock solution was prepared by weighing out 72.06 gm of acrylic acid and making up the volume to 250 mL with deionised water. A 1 molar stock solution was prepared by weighing out 18.015 gm of acrylic acid and making up the volume to 250 mL with deionised water.
- (ii) Methacrylic acid: A 4 molar stock solution was prepared by weighing out 86.09 gm and making up the volume to 250 mL with deionised water.
- (iii) Sodium sulphite: 0.125 molar stock solution was prepared by weighing 0.7878 gm and making up the volume to 50 mL with deionised water.
- (iv) Potassium persulphate: 0.125 molar stock solution was prepared by weighing 1.733 gm and making up the volume to 50 mL with deionised water.
- (v) Hydroquinone: A 0.250 molar stock solution was prepared by weighing 2.7528 gm and making the volume upto 100 mL with acetone.
- (vi) Potassium hydroxide: A 10 molar solution was prepared by weighing 140 gm and making up the volume to 250 mL with deionised water. Stock solutions of 1 and 5 molarity were prepared from the 10 molar solution. The molarities were estimated against the primary standard potassium hydrogen phthalate solution. The solutions were used to adjust pH of the copolymerisation media.
- (vii) Hydrochloric acid: A 1 molar stock solution was prepared from 21 mL of 12 molar concentrated solution and making up the volume to 250 mL. The solution was used to adjust pH of the copolymerisation media.

nonsolvent system, filtered through weighed sintered crucibles and dried to constant weight under reduced pressure at room temperature to estimate the weight fraction conversion.

2.2.3 Copolymerisation of acrolein-methacrylic acid

Methacrylic acid stock solution in the required amounts was pipetted out into stoppered reaction vessels. The pH of the reaction was maintained at pH 1, 3, 5, and 7. The pH of the solution was adjusted to the required value with the addition of either hydrochloric acid or potassium hydroxide stock solutions, as presented in section 2.2.2. Required amounts of acrolein was pipetted out and deionised water was added to make up the volume to 46 mL. The total monomer concentrations in the four sets of copolymerisations was kept identical at 4 molar. The reaction vessels were flushed with oxygen-free nitrogen for 15 minutes. 2 mL each of 0.125 molar solution of potassium persulphate and sodium sulphite were added to initiate the copolymerisations. The reaction vessels were stoppered and thermostated at $30.0 \pm 0.1^\circ\text{C}$. The reaction time was adjusted between 2-3 hours to maintain the weight percent conversion below 35 percent. After the desired reaction time, the copolymerisation was terminated by the addition of 2 mL of 0.25 molar hydroquinone solution in acetone. The copolymers were quantitatively precipitated with 5:1:1 v/v acetone/methanol/petroleum ether mixed nonsolvent system, filtered through weighed sintered crucibles and dried to constant weight under reduced pressure at room temperature to estimate the weight fraction conversion.

2.2.4 High conversion copolymerisation of methacrylic acid-acrolein (MAC series)

In a stirred tank reactor depicted in Figure 5, required amount of methacrylic acid was taken in deionised water. The pH of the solution was adjusted to 1 with appropriate amount of hydrochloric acid. Corresponding amount of acrolein was added and the total monomer concentration was set at 4 molar. The reaction vessel was flushed with nitrogen for 15 minutes. Red-ox initiator system sodium sulphite-potassium persulfate was added. Combined initiator concentration was 0.015 molar. The copolymerisation was taken to high conversion. The reaction was stopped using hydroquinone solution in acetone. The copolymer formed was precipitated with dry acetone, dissolved in water and reprecipitated in acetone and dried under reduced pressure at room temperature. Poly(acrylic acid) and poly(methacrylic acid) were prepared under similar experimental conditions. Copolymers with acrolein mole fraction exceeding 0.40 crosslink on drying. Hence, copolymers of following compositions were synthesised: MAC 5, MAC 10, MAC 20, MAC 30 and MAC 40 with 2.5, 5.2, 10.31, 28.1, 40.0 mole percent acrolein respectively.

2.2.5 Acrolein-styrene copolymerisation

In a stirred round bottom flask required amount of acrolein, styrene and benzoyl peroxide were stirred in 1,4-dioxane and copolymerised at 80°C. In a typical copolymerisation reaction, 1 gm (0.5 percent) benzoyl peroxide was dissolved in 0.46 mole (48.12 gm) of styrene. It was added to 0.54 mole (30.15 gm) of acrolein

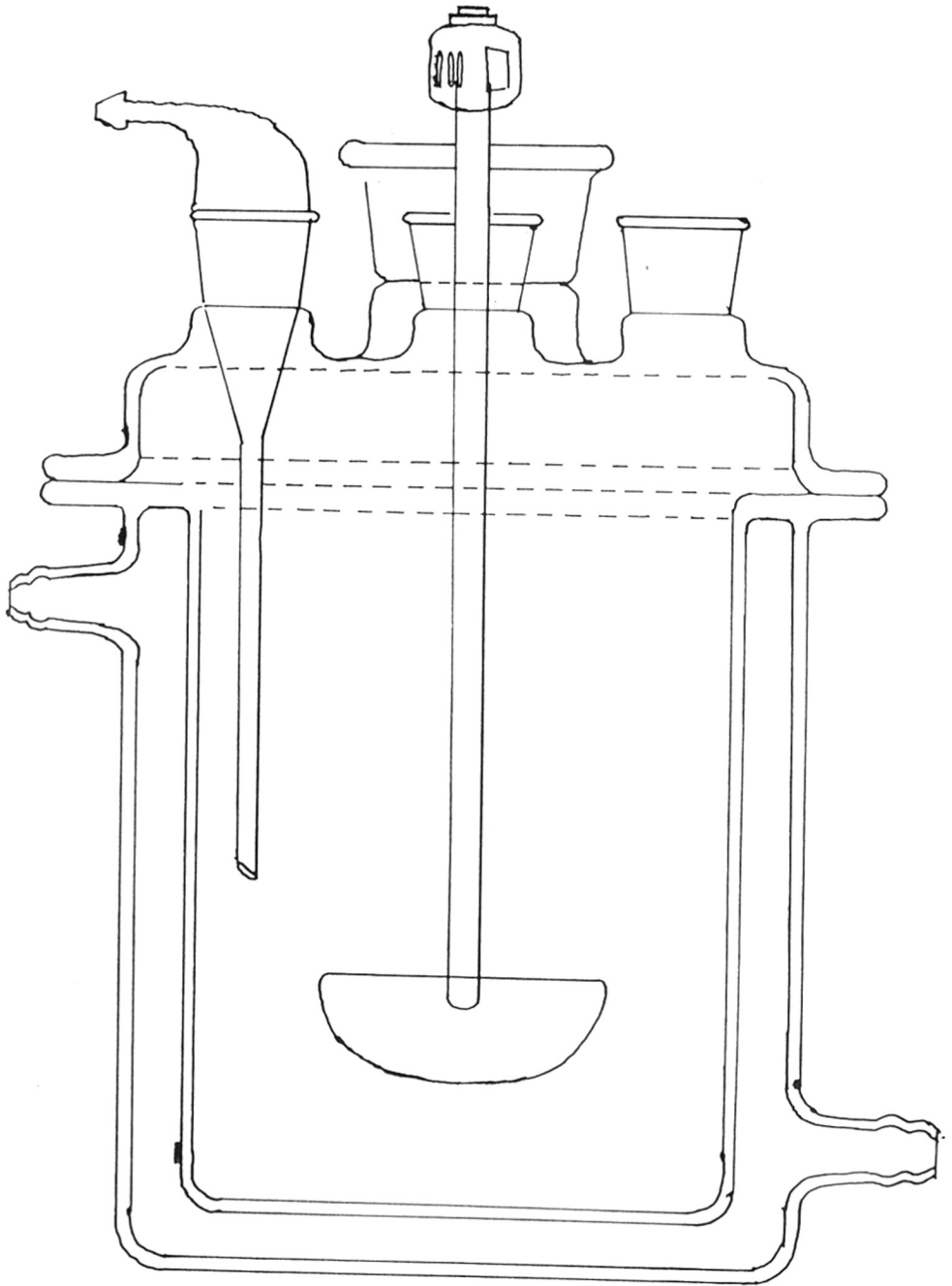


FIG. 5

REACTION VESSEL FOR COPOLYMERISATION AT HIGH CONVERSION

dissolved in 200 mL of 1,4-dioxane. Copolymerisation was conducted under purified nitrogen blanket at constant rate of stirring at 80°C for 3 hours. The reaction was terminated by introducing hydroquinone solution in dioxane. The copolymer was precipitated with methanol, dissolved in 1,4-dioxane and reprecipitated.

2.3 Copolymer analysis

The copolymers were analysed for compositions relative to the two monomers.

2.3.1 Acrolein-acrylic acid copolymers

The copolymers formed in section 2.2.2 were analysed for carboxylic content. An exact weight of copolymer (~ 100 mgm) was allowed to react for 16 hours with 20 mL of 1.0 molar aqueous potassium hydroxide solution. The copolymer was converted quantitatively into the corresponding potassium salt, precipitated with acetone/methanol mixture, and washed to remove the excess potassium hydroxide. The potassium salt was converted quantitatively into potassium sulphate with concentrated sulphuric acid and analysed by flame photometry to estimate potassium and hence acrylic acid content of the copolymer. Reliability of the procedure was estimated by analysing poly(acrylic acid) and polyacrolein as well as synthetic mixtures of the two homopolymers. The results were reproducible with an accuracy of more than 98.5 percent. The data is presented in Tables 6-17.

2.3.2 Acrolein-methacrylic acid copolymers

The copolymers formed in section 2.2.3 were similarly analysed. An exact weight of copolymer (~ 100 mgm) was allowed to react for 16 hours with 20 mL 1.0

Table-6

Copolymerisation of acrolein-acrylic acid

pH: not controlled,

Initiator: $K_2S_2O_8 = 5 \times 10^{-3} \text{ M}$, $Na_2SO_3 = 5 \times 10^{-3} \text{ M}$

Temperature: $30 \pm 0.005^\circ \text{C}$

Total monomer concentration = 4 M, Homogeneous phase

Sample	Acrylic acid g.	Acrolein g	Initial pH	Mole fraction acrolein	polymer weight g	Weight fraction conversion	Final pH	Mole fraction acrolein polymer
AC-20	11.5656	2.3826	2.26	0.209	2.3712	0.170	2.33	0.707
AC-30	9.9515	3.3636	2.30	0.303	3.2356	0.243	2.40	0.783
AC-35	9.2381	3.9242	2.33	0.353	2.3297	0.177	2.43	0.782
AC-40	8.6472	4.7763	2.37	0.425	1.0336	0.077	2.45	0.777
AC-45	7.8185	5.0454	2.46	0.454	3.5247	0.274	2.54	0.810

Table-7

Copolymerisation of acrolein-acrylic acid

pH: not controlled,

Initiator: $K_2S_2O_8 = 5 \times 10^{-3}$ M, $Na_2SO_3 = 5 \times 10^{-3}$ M

Temperature: $30 \pm 0.005^\circ C$

Total monomer concentration = 4 M, Heterogeneous phase

Sample	Acrylic Acid		Acrolein		Initial		Mole fraction		Copolymer		Final		Mole fraction	
	acid g.	g.	g.	g.	pH	acrolein	acrolein	acrolein	weight g.	weight g.	conversion fraction	pH	conversion fraction	acrolein
AC-50	7.9266	5.9704	2.46	0.516	0.8894	0.064	2.47	0.819						
AC-55	6.3989	6.1666	2.51	0.553	3.5057	0.279	2.52	0.873						
AC-60	5.6855	6.7272	2.54	0.603	2.0729	0.167	2.57	0.814						
AC-65	4.9721	7.2822	2.57	0.653	1.5563	0.127	2.66	0.831						
AC-70	4.2660	7.8540	2.66	0.703	1.8786	0.155	2.65	0.825						
AC-75	3.5526	8.409	2.84	0.753	1.6501	0.138	2.72	0.815						
AC-80	2.8896	9.5470	2.84	0.810	4.7632	0.383	2.76	0.841						
AC-90	1.4412	10.7411	2.93	0.905	2.0588	0.169	2.79	0.856						

Table-8

Copolymerisation of acrolein-acrylic acid

pH: not controlled,

Initiator: $K_2S_2O_8 = 5 \times 10^{-3}$ M, $Na_2SO_3 = 5 \times 10^{-3}$ M

Temperature: $30 \pm 0.005^\circ C$

Total monomer concentration = 1 M, Homogeneous phase

Sample	Acrylic acid g.	Acrolein g.	Initial pH	Mole fraction acrolein	Polymer weight g.	Weight fraction	Final pH	Mole fraction acrolein	conversion	polymer
AC1-10	3.2401	0.2968	2.20	0.1053	0.0455	0.0129	2.25	0.7143		
AC1-15	3.0699	0.4494	2.23	0.1548	0.0439	0.0125	2.30	0.7162		
AC1-25	2.7008	0.4761	2.31	0.2621	0.0629	0.0182	2.33	0.7608		
AC1-30	2.5340	0.8393	2.32	0.2986	0.2696	0.0799	2.40	0.7645		
AC1-40	2.1612	1.1192	2.35	0.3996	0.0842	0.0257	2.45	0.7734		
AC1-45	1.9787	1.3396	2.34	0.4653	0.0543	0.0164	2.45	0.7786		

Table-9

Copolymerisation of acrolein-acrylic acid

pH: not controlled,

Initiator: $K_2S_2O_8 = 5 \times 10^{-3}$ M, $Na_2SO_3 = 5 \times 10^{-3}$ M

Temperature: $30 \pm 0.005^\circ C$

Total monomer concentration = 1 M, Heterogeneous phase

Sample	Acrylic acid g.	Acrolein g.	Initial pH	Mole fraction acrolein	Polymer weight g.	Weight fraction conversion	Final pH	Mole fraction acrolein polymer
AC1-55	1.6277	1.6415	2.35	0.5649	0.0489	0.0150	2.53	0.8428
AC1-65	1.2569	1.9416	2.40	0.6651	0.0745	0.0233	2.56	0.8448
AC1-70	1.0822	1.9586	2.50	0.6994	0.0528	0.0174	2.58	0.8999
AC1-75	0.9025	2.2393	2.52	0.7613	0.0592	0.0188	2.66	0.9144
AC1-80	0.7334	2.2384	2.58	0.7968	0.0232	0.0078	2.80	0.8220
AC1-90	0.3653	2.5266	2.78	0.8989	0.1072	0.0371	3.01	0.9361

Table-10

Copolymerisation of acrolein-acrylic acid

pH: 1.0,

Initiator: $K_2S_2O_8 = 5 \times 10^{-3}$ M, $Na_2SO_3 = 5 \times 10^{-3}$ M

Temperature: $30 \pm 0.005^\circ C$

Total monomer concentration = 4 M, Homogeneous phase

Sample	Acrylic acid	Acrolein	Initial pH	Mole fraction acrolein	Polymer weight g.	Weight fraction conversion	Final pH	Mole fraction acrolein polymer
1AC-10	12.9727	1.1955	1.00	0.1058	0.5922	0.0418	1.01	0.4882
1AC-15	11.9570	1.7890	1.02	0.1613	0.7538	0.0548	1.03	0.5477
1AC-20	11.5400	2.3910	1.00	0.2106	0.3546	0.0255	1.00	0.5798
1AC-25	10.5794	2.9845	1.02	0.2661	0.3838	0.0283	1.02	0.5831
1AC-30	10.0861	3.5780	1.00	0.3131	0.5012	0.0367	1.01	0.6593
1AC-35	9.1520	4.1800	1.02	0.3699	0.4074	0.0300	1.02	0.7000
1AC-40	8.6580	4.7735	1.00	0.4147	0.6970	0.0519	1.00	0.7120
1AC-45	7.7528	5.3755	1.00	0.4713	0.4119	0.0313	1.00	0.7425

Table-11

Copolymerisation of acrolein-acrylic acid

pH: 1.0,

Initiator: $K_2S_2O_8 = 5 \times 10^{-3} \text{ M}$, $Na_2SO_3 = 5 \times 10^{-3} \text{ M}$ Temperature: $30 \pm 0.005^\circ \text{C}$

Total monomer concentration = 4 M, Heterogeneous phase

Sample	Acrylic acid	Acrolein	Initial pH	Mole fraction acrolein	Polymer weight	Weight fraction	Final pH	Mole fraction acrolein
1AC-50	7.2536	5.9690	1.00	0.5140	0.6687	0.0506	1.00	0.7592
1AC-55	6.3298	6.5625	1.00	0.5714	0.3357	0.0260	1.00	0.8006
1AC-60	5.7749	7.1644	1.00	0.6147	0.4601	0.0356	1.01	0.8667
1AC-65	4.9229	7.7579	1.01	0.6687	0.2087	0.0165	1.01	0.8710
1AC-70	4.3381	8.3599	1.00	0.7124	0.3064	0.0241	1.00	0.7798
1AC-75	3.5292	8.9534	1.00	0.7620	0.2308	0.0185	1.00	0.8611
1AC-80	2.9042	9.5554	1.02	0.8087	0.3787	0.0304	1.02	0.8631
1AC-90	1.4669	10.7424	1.00	0.9038	0.4474	0.0366	1.01	0.8741

Table-12

Copolymerisation of acrolein-acrylic acid

pH: 3.0,

Initiator: $K_2S_2O_8 = 5 \times 10^{-3} \text{ M}$, $Na_2SO_3 = 5 \times 10^{-3} \text{ M}$

Temperature: $30 \pm 0.005^\circ \text{C}$

Total monomer concentration = 4 M, Homogeneous phase

Sample	Acrylic acid	Acrolein	Initial pH	Mole fraction acrolein	Polymer weight g	Weight fraction acrolein	Final pH	Mole fraction acrolein
3AC-20	11.5872	2.3910	3.00	0.2098	2.2033	0.1376	3.05	0.7023
3AC-30	10.3046	3.5865	3.01	0.3092	2.0722	0.1576	3.07	0.7785
3AC-35	9.5768	4.1800	2.99	0.3595	1.6245	0.1492	3.06	0.7968
3AC-40	8.8346	4.7735	3.01	0.4097	1.2671	0.0931	3.07	0.7766
3AC-45	8.0995	5.3755	3.00	0.4588	1.4568	0.1081	3.06	0.7844

Table-13

Copolymerisation of acrolein-acrylic acid

pH: 3.0,

Initiator: $K_2S_2O_8 = 5 \times 10^{-3} \text{ M}$, $Na_2SO_3 = 5 \times 10^{-3} \text{ M}$

Temperature: $30 \pm 0.005^\circ\text{C}$

Total monomer concentration = 4 M, Heterogeneous phase

Sample	Acrylic acid g.	Acrolein g.	Initial pH	Mole fraction	Polymer weight g.	Weight fraction	Final pH	Mole fraction
3AC-60	5.8945	7.1644	3.00	0.6097	0.9003	0.0689	3.07	0.8202
3AC-70	4.4173	8.3599	3.00	0.7087	0.1895	0.0148	3.08	0.8466
3AC-80	2.9400	9.5554	2.99	0.8068	0.2179	0.0174	3.08	0.8713
3AC-85	2.2122	10.1489	3.01	0.8550	0.1954	0.0158	3.09	0.8721
3AC-90	1.4700	10.7509	3.00	0.9039	0.1225	0.1000	3.09	0.8838

acrolein feed

Table-14

Copolymerisation of acrolein-acrylic acid

pH: 5.0,

Initiator: $K_2S_2O_8 = 5 \times 10^{-3}$ M, $Na_2SO_3 = 5 \times 10^{-3}$ M

Temperature: $30 \pm 0.005^\circ C$

Total monomer concentration = 4 M, Homogeneous phase

Sample	Acrylic acid g.	Acrolein g.	Initial pH	Initial Mole fraction acrolein	Copolymer weight g.	Copolymer weight fraction acrolein	Final pH	Final Mole fraction acrolein	Copolymer weight fraction conversion	Final pH	Final Mole fraction acrolein	Conversion %
5AC-15	12.2498	1.7890	4.99	0.1580	2.5943	0.1848	5.29	0.6469	0.1848	5.29	0.6469	0.6469
5AC-20	11.5294	2.3910	5.00	0.2107	0.9419	0.0677	5.22	0.650	0.0677	5.22	0.650	0.650
5AC-25	10.8090	2.9845	5.00	0.2618	1.7532	0.1271	5.20	0.676	0.1271	5.20	0.676	0.676
5AC-30	10.0884	3.5865	5.00	0.3136	1.5238	0.1114	5.22	0.703	0.1114	5.22	0.703	0.703
5AC-35	9.3678	4.1799	5.00	0.3646	1.1980	0.0884	5.31	0.717	0.0884	5.31	0.717	0.717
5AC-40	8.6472	4.7735	4.98	0.4149	0.8329	0.0621	5.30	0.743	0.0621	5.30	0.743	0.743
5AC-45	7.9266	5.3755	4.99	0.4658	0.7227	0.0543	5.28	0.789	0.0543	5.28	0.789	0.789

Table-15

Copolymerisation of acrolein-acrylic acid

pH: 5.0,

Initiator: $K_2S_2O_8 = 5 \times 10^{-3} \text{ M}$, $Na_2SO_3 = 5 \times 10^{-3} \text{ M}$

Temperature: $30 \pm 0.005^\circ\text{C}$

Total monomer concentration = 4 M, Heterogeneous phase

Sample	Acrylic acid g.	Acrolein g.	Initial pH	Mole fraction acrolein	Copolymer weight g	Copolymer weight fraction	Final pH	Mole fraction acrolein	Copolymer weight fraction	conversion %
5AC-50	7.206	5.9690	5.00	0.5157	0.7584	0.0576	5.27	0.799	0.813	0.799
5AC-55	6.4854	6.5709	5.00	0.5656	0.5688	0.0436	5.30	0.813	0.834	0.813
5AC-60	5.7648	7.1644	5.00	0.6150	0.4846	0.0375	5.30	0.841	0.893	0.834
5AC-65	5.0442	7.7664	5.00	0.6643	0.2212	0.0173	5.28	0.874	0.857	0.841
5AC-70	4.3236	8.3599	4.99	0.7131	0.2742	0.0216	5.28	0.874	0.857	0.893
5AC-75	3.6030	8.9534	5.00	0.7616	0.2067	0.0165	5.26	0.874	0.857	0.874
5AC-80	2.8824	9.5554	5.00	0.8099	0.2063	0.0166	5.26	0.857	0.857	0.857
5AC-90	1.4412	10.7509	4.99	0.9056	0.2071	0.0177	5.20	0.872	0.872	0.872

Table-16

Copolymerisation of acrolein-acrylic acid

pH: 7.0,

Initiator: $K_2S_2O_8 = 5 \times 10^{-3} \text{ M}$, $Na_2SO_3 = 5 \times 10^{-3} \text{ M}$

Temperature: $30 \pm 0.005^\circ\text{C}$

Total monomer concentration = 4 M, Homogeneous phase

Sample	Acrylic acid		Acrolein		Initial		Copolymer		Copolymer		Final		Mole fraction
	g.	g.	g.	g.	pH	fraction acrolein	weight	g	fraction	conversion	pH	fraction	
7AC-15	11.5292	2.3910	6.98	0.2105	1.5906	0.1143	7.29	0.7417					
7AC-25	10.8088	2.9930	7.04	0.2625	0.7552	0.0547	7.40	0.7334					
7AC-30	10.0882	3.5865	7.02	0.3136	0.6125	0.0448	7.59	0.7511					
7AC-35	9.3676	4.1884	6.98	0.3649	0.4300	0.0317	7.49	0.7615					
7AC-40	8.6471	4.7819	6.98	0.4155	0.5907	0.0440	7.48	0.7823					

Table-17

Copolymerisation of acrolein-acrylic acid

pH: 7.0,

Initiator: $K_2S_2O_8 = 5 \times 10^{-3}$ M, $Na_2SO_3 = 5 \times 10^{-3}$ MTemperature: $30 \pm 0.005^\circ C$

Total monomer concentration = 4 M, Heterogeneous phase

Sample	Acrylic acid g.	Acrolein g	Initial pH	Mole fraction acrolein	Copolymer weight g.	Copolymer weight fraction	Final pH	Mole fraction acrolein
7AC-45	7.9265	5.3839	6.98	0.4661	0.3533	0.0265	7.48	0.7831
7AC-50	7.2059	5.9774	6.98	0.5160	0.1569	0.0119	7.73	0.8286
7AC-55	6.4853	6.5794	6.95	0.5658	0.1882	0.0144	7.80	0.8437
7AC-65	5.0441	7.7749	6.94	0.6646	0.0988	0.0077	8.23	0.8657
7AC-70	4.3235	8.3684	6.94	0.7133	0.0889	0.0074	8.28	0.8734
7AC-75	3.6029	8.9789	6.96	0.7621	0.5706	0.0406	8.13	0.8632
7AC-90	1.4412	10.7594	6.98	0.9056	0.1611	0.0132	8.05	0.8812

molar aqueous potassium hydroxide solution to convert it quantitatively into the potassium salt of the carboxylic acid. The copolymers with aldehyde content less than 0.40 were totally soluble in the alkaline solution. They were quantitatively precipitated with methanol. Copolymers with aldehyde content exceeding 0.40 were quantitatively precipitated with acetone/methanol mixture, washed to remove the excess potassium hydroxide. The potassium salt was converted quantitatively into potassium sulphate with concentrated sulphuric acid and analysed by flame photometry to estimate the potassium and hence the methacrylic acid content of the copolymer. The reliability of the procedure was estimated by analysing poly(methacrylic acid) and polyacrolein as well as synthetic mixtures of the two homopolymers. The results were reproducible and more than 98.5 percent accurate. The data is presented in Tables 18-22.

2.3.3 Acrolein-methacrylic acid copolymer MAC series

The water soluble copolymers formed in section 2.2.4 were diluted with deionised water, and potentiometrically titrated against sodium hydroxide to estimate the carboxyl content and copolymer composition.

2.3.4 Acrolein-styrene copolymer

The copolymer formed in section 2.2.5 was analysed spectrophotometrically for styrene content. Polystyrene solution in 1,4-dioxane (1.5×10^{-3} mole of benzene moieties) was used as reference standard. 50 mgm of polystyrene copolymers were dissolved in 25 mL of 1,4-dioxane. This solution was diluted 5 fold and absorbance at 261 nm was measured. From standard calibration curve, amount of styrene moieties in the copolymer was calculated.

Table-18

Copolymerisation of acrolein-methacrylic acid

pH: not controlled,

Initiator: $K_2S_2O_8 = 5 \times 10^{-3}$ M, $Na_2SO_3 = 5 \times 10^{-3}$ M

Temperature: $30 \pm 0.005^\circ C$

Total monomer concentration = 4 M, Homogeneous phase

Sample	Methacrylic acid g.	Acrolein g.	Initial pH	Mole fraction acrolein	Polymer weight g.	Weight fraction acrolein	Final pH	Mole fraction acrolein
OMAC 90	15.4477	1.1955	2.10	0.1063	5.6209	0.3377	2.21	0.3251
OMAC 85	14.5895	1.7975	2.11	0.1592	5.8857	0.3592	2.24	0.3565
OMAC 80	13.7313	2.3910	2.12	0.2112	3.1992	0.1984	2.26	0.3621
OMAC 75	12.7831	2.9930	2.14	0.2632	3.1419	0.1980	2.32	0.3943
OMAC 65	11.1567	4.1884	2.17	0.3656	0.9277	0.0605	2.38	0.4287
OMAC 60	10.2985	4.7819	2.21	0.4163	1.1092	0.0736	2.39	0.4515
OMAC 55	9.4403	5.3839	2.24	0.4667	0.7988	0.0539	2.41	0.4722

OMAC 50	8.5903	5.9774	2.41	0.5165	0.7632	0.0524	2.63	0.5440
OMAC 35	6.0132	7.7749	2.57	0.6651	0.5329	0.0386	2.90	0.6033
OMAC 30	5.1542	8.3684	2.64	0.7137	0.8091	0.0606	2.93	0.6290
OMAC 25	4.2952	9.3265	2.77	0.7693	0.6328	0.0465	2.99	0.6727

Table-19
 Copolymerisation of acrolein-methacrylic acid

pH: 1,

Initiator: $K_2S_2O_8 = 5 \times 10^{-3} \text{ M}$, $Na_2SO_3 = 5 \times 10^{-3} \text{ M}$

Temperature: $30 \pm 0.005^\circ \text{C}$

Total monomer concentration = 4 M, Homogeneous phase

Sample	Methacrylic acid g.	Acrolein g.	Initial pH	Mole fraction acrolein	Polymer weight g.	Weight fraction acrolein	Final pH	Mole fraction conversion
1MAC-90	15.4705	1.1955	1.00	0.1060	5.6294	0.3378	1.22	
1MAC-85	14.6110	1.7975	1.00	0.1591	1.1365	0.0693	1.30	0.3365
1MAC-80	13.7515	2.3910	1.00	0.2110	2.2712	0.1407	1.18	0.3497
1MAC-75	12.8920	2.9930	1.01	0.2628	2.1747	0.1369	1.12	0.3783
1MAC-70	12.0326	3.5865	1.00	0.3140	1.7451	0.1117	1.07	0.3796
1MAC-65	11.1731	4.1884	1.01	0.3653	1.2781	0.0832	1.04	0.423
1MAC-60	10.3136	4.7819	1.00	0.4159	0.7831	0.0519	1.22	0.4386

LMAC-55	9.4542	5.3839	1.01	0.4665	0.7897	0.0532	1.21	0.4679
LMAC-50	8.6057	5.9774	1.01	0.5160	0.3889	0.0267	1.17	0.524
LMAC-45	7.7460	6.5794	1.01	0.5661	0.3137	0.0219	1.22	0.5588
LMAC-40	6.8853	7.1729	1.01	0.6154	0.3464	0.0246	1.26	0.5814
LMAC-35	6.0247	7.7749	1.01	0.6647	0.3164	0.0229	1.24	0.6033
LMAC-30	5.1640	8.3684	1.02	0.7134	0.3451	0.0255	1.22	0.6873
LMAC-25	4.3033	8.9704	1.00	0.7623	0.3640	0.0274	1.18	0.7523

Table-20

Copolymerisation of acrolein-methacrylic acid

pH: 3,

Initiator: $K_2S_2O_8 = 5 \times 10^{-3} \text{ M}$, $Na_2SO_3 = 5 \times 10^{-3} \text{ M}$

Temperature: $30 \pm 0.005^\circ \text{C}$

Total monomer concentration = 4 M, Homogeneous phase

Sample	Methacrylic acid g.	Acrolein g.	Initial pH	Mole fraction acrolein	Polymer weight g.	Weight fraction conversion	Final pH	Mole fraction conversion
3MAC 90	15.3397	1.1955	2.99	0.1068	1.0246	0.0620	2.69	0.3293
3MAC 80	13.6353	2.3910	3.00	0.2123	1.0563	0.0659	2.83	0.3854
3MAC 70	11.9309	3.5865	3.01	0.3158	0.9758	0.0629	2.98	0.4231
3MAC 60	10.2265	4.7819	3.00	0.4179	1.5748	0.1049	3.00	0.4963
3MAC 50	8.5860	5.9774	3.00	0.5167	1.2396	0.0851	3.24	0.5722
3MAC 40	6.8688	7.1729	3.00	0.6159	1.1920	0.0849	3.53	0.6218
3MAC 30	5.1516	8.3684	3.00	0.7140	0.3183	0.0237	3.60	0.6639

Table-21

Copolymerisation of acrolein-methacrylic acid

pH: 5,

Initiator: $K_2S_2O_8 = 5 \times 10^{-3}$ M, $Na_2SO_3 = 5 \times 10^{-3}$ M

Temperature: $30 \pm 0.005^\circ C$

Total monomer concentration = 4 M, Homogeneous phase

Sample	Methacrylic acid g.	Acrolein g.	Initial pH	Mole fraction acrolein	Polymer weight g.	Weight fraction conversion	Final pH	Mole fraction conversion
5MAC-85	14.4875	1.7975	5.00	0.1602	0.3893	0.0699	5.44	0.3905
5MAC-75	12.7831	2.9930	5.00	0.2645	0.7932	0.0503	5.40	0.4329
5MAC-65	11.0787	4.1884	5.00	0.3673	0.6954	0.0455	5.37	0.4611
5MAC-55	9.3743	5.3899	4.99	0.4685	0.8729	0.0591	5.50	0.5041
5MAC-45	7.7224	6.5794	5.00	0.5666	1.0998	0.0769	5.58	0.5619
5MAC-35	6.0102	7.7749	5.00	0.6652	0.5365	0.0389	5.63	0.6181
5MAC-25	4.2930	8.9704	4.99	0.7623	0.2562	0.0193	5.76	0.6546

Table-22

Copolymerisation of acrolein-methacrylic acid

pH: 7,

Initiator: $K_2S_2O_8 = 5 \times 10^{-3}$ M, $Na_2SO_3 = 5 \times 10^{-3}$ M

Temperature: $30 \pm 0.005^\circ C$

Total monomer concentration = 2 M, Homogeneous phase

Sample	Methacrylic acid g.	Acrolein g.	Initial pH	Mole fraction acrolein	Polymer weight g.	Weight fraction conversion	Final pH	Mole fraction conversion
7MAC-80	6.8728	1.1955	6.98	0.2109	1.0531	0.1305	7.40	0.4412
7MAC-75	6.4325	1.4965	6.99	0.2633	0.9827	0.1239	7.50	0.4828
7MAC-70	6.0154	1.7932	7.00	0.3139	0.9233	0.1182	7.63	0.5135
7MAC-65	5.6211	2.0942	7.01	0.3642	0.8112	0.1051	7.56	0.5529
7MAC-60	5.1626	2.3909	6.98	0.4152	0.7531	0.0997	7.59	0.5871
7MAC-55	4.7260	2.6919	6.98	0.4665	0.7076	0.0954	7.64	0.6221

acrolein

2.4 Copolymer derivatisation

The copolymers were modified by reacting the pendent aldehyde groups with different reagents as follows:

2.4.1 Oxime derivative

Aldehyde pendent group was converted into oxime, as a nonionic sequestering group, as follows: The acrolein-methacrylic acid copolymers synthesised in section 2.2.4 were dissolved in deionised water. The solution was treated with a molar equivalent of hydroxylamine hydrochloride. Thus, in a typical experiment, copolymer MAC-10 1 gm (1.54 millimole aldehyde) was dissolved in 25 mL of deionised water. 0.1069 gm (1.54 millimole) of hydroxylamine hydrochloride was dissolved in 25 mL of deionised water. The two solutions were mixed and stirred at room temperature for 10 hours. The derivatives were investigated for calcium sequestration capacity (CSC). Some of the derivatives were also investigated for CSC at a specific pH, in presence of sodium chloride.

2.4.2 Bisulphite derivative

Aldehyde group was converted into bisulphite group, an ionic sequestering group, as follows: The acrolein-methacrylic acid copolymers synthesised in section 2.2.4 were reacted with sodium bisulphite to form bisulphite adduct. In a typical experiment, 1 gm (1.54 millimole aldehyde) of copolymer MAC 30 was dissolved in 25 mL deionised water. 0.16 gm (1.54 millimole) sodium bisulphite was dissolved in 25 mL deionised water. The two solutions were mixed together

and stirred for 6 hours. The derivatives were investigated for calcium sequestration capacity. Some of the derivatives were also investigated for CSC at a specific pH, in presence of sodium chloride.

2.4.3 Novolak type derivative

The acrolein-methacrylic acid copolymers synthesised in section 2.2.4 were reacted with m-cresol and phenol to form novel ortho novolak type resins. In a typical reaction, 2 gm (10.8 millimole aldehyde) polymer MAC 40, was dissolved in 50 mL deionised water. 0.93 gm (8.64 millimole) m-cresol was added to it. The reaction mixture was stirred at 95°C for 8 hours. The reaction was catalysed by the carboxyl pendent groups in the polymer MAC 40. The polymer formed was precipitated twice in dry acetone to get rid of unreacted m-cresol.

In another reaction, 2 gm (10.8 millimole of aldehyde groups) polymer MAC 40 was dissolved in 50 mL of deionised water. 0.81 gm (8.64 millimole) phenol was added to it. The reaction mixture was stirred at 95°C for 8 hours. To avoid solubilisation of the polymer in acetone, the solution was poured gradually over 30 minutes into 500 mL of dry acetone. The precipitated polymer was reprecipitated to get rid of unreacted phenol.

Novel novolaks were synthesised from styrene-acrolein copolymers by reacting with m-cresol in 1,4-dioxane for 6 to 8 hours at 95°C using p-Toluene sulphonic acid (PTSA) as acid catalyst. The polymer thus derivatised was precipitated in methanol.

2.5 Characterisation

The various polymers and their derivatives were subjected to different characterisations as follows:

2.5.1 Free aldehyde estimation

The copolymers were derivatised by modifying the aldehyde pendent groups. Hence, aldehyde content of the polymers was estimated. Estimation of free aldehyde present in polyacrolein was first investigated. An exact amount of polyacrolein was weighed. 25 mL of 0.1 molar hydroxyl amine hydrochloride was added and kept for 16 hours. Released hydrochloric acid was potentiometrically titrated using 0.1 molar sodium hydroxide solution. This method could not be used for quantitative estimation of copolymers since pendent carboxylic groups on copolymer interfered the reaction.

2.5.2 Solid state ^{13}C NMR

Analysis in section 2.5.1 indicated that an appreciable amount of acrolein moieties were not present with free aldehyde pendent groups. Hence, the copolymers were investigated for the free aldehyde vis a vis acrolein content in the copolymer. The acrolein-acrylic acid copolymers synthesised in section 2.2.2 were characterised in the solid state by Cross Polarisation/Magic Angle Spinning (CP/MAS) NMR technique. 75.5 MHz ^{13}C CP/MAS spectra were recorded on a Bruker MSL 300 NMR spectrometer under a matched Hartmann-Hann field of 50 kHz. A contact time of 1 millisecond was used for all the measurements. The copolymers studied differed only in the composition of comonomers, The cross-polarisation parameters, which determine the observed ^{13}C signal intensities, would be similar. Hence a constant time of 1 ms can be

expected to give nearly quantitative information within the samples. A spinning speed of ~ 4 kHz was employed. The generation of spinning side bands for the carbonyl groups could not be avoided even at this spinning speed due to their larger chemical shift anisotropy (CSA) in 7.0 Tesla magnetic field. The areas of spinning side bands were also taken into account for the quantitative measurements. The peak areas were estimated with planimeter.

2.5.3 Ultra-violet spectra

Molecular association of acrolein with acrylic acid in different solvents was investigated. Stock solutions of acrylic acid and acrolein of 1 millimolar concentration were prepared in deionised water and acetone. Spectra of differing concentrations of acrolein were recorded. Retaining the acrolein concentration, acrylic acid was added to it and the spectra of the solution was recorded. Spectra of corresponding acrylic acid solution was recorded. Thus, absorbance at respective λ_{\max} were obtained.

2.5.4 Infra-red spectra

(i) Molecular association: Acrylic acid was presumed to form molecular association with acrolein which reflected in copolymerisation. Hydrogen bonding, change in carbonyl character was investigated by obtaining infra-red spectra. In the IR spectra of acrylic acid, acrolein and 1:1 mixture of acrylic acid-acrolein were recorded on a Shimadzu IR-470 spectrophotometer with sodium chloride window using 0.5 micron lead stensil. The scanning time was 12 minutes.

(ii) Characterisation: 2 mgm of polymer was thoroughly mixed with 100 mgm of oven dried potassium bromide to cast a pellet. It was scanned in the range 4000-400 cm^{-1} using blank potassium bromide pellet as a reference.

2.5.5 Potentiometric titration

Calcium sequestration properties of methacrylic acid-acrolein copolymers were found to be conformation dependent which in turn was pH dependent. To investigate into the conformations of the copolymers, potentiometric titrations were carried out in ion free water. The solutions were prepared by weighing accurately, the dry copolymers into ion free water and adding calculated amount of sodium hydroxide solution till exact neutralization. The degree of ionization at this point was equal to 1. The copolymer concentration was kept around $(3-5) \times 10^{-2}$ equivalents of the titrable groups per litre. The experiments were conducted under nitrogen blanket at $30 \pm 0.05^\circ\text{C}$ with 0.5 molar hydrochloric acid solution. Small increments of hydrochloric acid were added and the corresponding pH were recorded with a pH meter accurate to 0.05 pH unit (standardised with buffers of known pH). Titrations were carried to $\alpha = 0$. Blank titrations were carried out and the corrections, found to be negligible in the experimental pH range, were not applied. The potentiometric titrations were carried out for copolymers MAC40, MAC30, MAC20 with acrolein content 0.40, 0.28 and 0.10 respectively. The data is presented in tables 23-25.

2.5.6 Estimation of Calcium Sequestration Capacity (CSC)

Ability of methacrylic acid-acrolein copolymers to bind Ca^{+2} ion was investigated over a wide pH range. Mehrslatter's method was used. Exact amount

Table-23
Potentiometric titration of MAC-40

mL	pH	α	$3\sqrt{\alpha}$	pK_{app}
HCl				
0.05	9.59	0.9872	0.9957	7.7035
0.1	9.16	0.9744	0.9914	7.5802
0.15	8.87	0.9615	0.9870	7.4721
0.20	8.66	0.9487	0.9826	7.3928
0.3	8.37	0.9231	0.9737	7.2908
0.35	8.26	0.9103	0.9691	7.2538
0.4	8.16	0.8974	0.9646	7.2180
0.5	7.92	0.8718	0.9553	7.0875
0.6	7.77	0.8462	0.9458	7.0296
0.7	7.62	0.8205	0.9361	6.9599
0.8	7.45	0.7949	0.9263	6.8617
0.9	7.31	0.7692	0.9163	6.7871
1.0	7.21	0.7436	0.9060	6.7476
1.1	7.10	0.7179	0.8954	6.6942
1.2	6.99	0.6923	0.8846	6.6378
1.3	6.88	0.6667	0.8736	6.5790
1.4	6.77	0.6410	0.8622	6.5182
1.5	6.65	0.6154	0.8506	6.3959

1.6	6.55	0.5897	0.8386	6.3924
1.7	6.45	0.5641	0.8263	6.3380
1.8	6.33	0.5385	0.8136	6.2631
1.9	6.22	0.5128	0.8004	6.1977
2.0	6.11	0.4872	0.7869	6.1323
2.1	6.03	0.4615	0.7728	6.0969
2.2	5.93	0.4359	0.7582	6.0420
2.3	5.83	0.4103	0.7431	5.9876
2.4	5.72	0.3846	0.7272	5.9241
2.5	5.63	0.3590	0.7107	5.8818
2.6	5.57	0.3333	0.6934	5.8710
2.7	5.50	0.3077	0.6751	5.8522
2.8	5.43	0.2821	0.6558	5.8358
2.9	5.33	0.2564	0.6353	5.7924
3.0	5.25	0.2308	0.6134	5.7729
3.1	5.15	0.2051	0.5898	5.7383
3.2	5.04	0.1795	0.5641	5.7001
3.3	4.90	0.1538	0.5358	5.6404
3.4	4.73	0.1282	0.5042	5.5625
3.5	4.53	0.1026	0.4681	5.4720
3.55	4.27	0.0897	0.4477	5.2762
3.6	4.12	0.0769	0.4253	5.1992
3.7	3.78	0.0513	0.3715	5.0472
3.75	3.58	0.0385	0.3376	4.9779
3.8	3.37	0.0256	0.2949	4.9498
3.85	3.18	0.0128	0.2340	5.0665

Table-24

Potentiometric titrations data of MAC-30

mL HCl	pH	α	$3\sqrt{\alpha}$	pK _{app}
0.05	9.38	0.9868	0.9956	7.5049
0.1	8.99	0.9737	0.9911	7.4218
0.2	8.35	0.9474	0.9821	7.0947
0.3	8.29	0.9211	0.9730	7.2231
0.4	8.09	0.8947	0.9636	7.1606
0.5	7.85	0.8684	0.9541	7.0305
0.6	7.70	0.8421	0.9443	6.9730
0.7	7.53	0.8158	0.9344	6.8837
0.8	7.37	0.7895	0.9242	6.7960
0.9	7.27	0.7632	0.9138	6.7618
1.0	7.16	0.7368	0.9032	6.7128
1.1	7.02	0.7105	0.8923	6.6300
1.2	6.93	0.6842	0.8812	6.5942
1.4	6.76	0.6316	0.8580	6.5259
1.5	6.63	0.6053	0.8459	6.4444
1.6	6.49	0.5789	0.8335	6.3517
1.8	6.27	0.5263	0.8074	6.2242
1.9	6.18	0.5000	0.7937	6.1800
2.0	6.09	0.4738	0.7795	6.1358

2.1	5.96	0.4474	0.7648	6.0518
2.2	5.88	0.4211	0.7495	6.0183
2.3	5.80	0.3947	0.7336	5.9856
2.4	5.72	0.3684	0.7169	5.9541
2.5	5.62	0.3421	0.6994	5.9040
2.6	5.55	0.3158	0.6810	5.8858
2.7	5.47	0.2894	0.6615	5.8600
2.8	5.37	0.2632	0.6408	5.8172
2.9	5.29	0.2368	0.6187	5.7982
3.0	5.21	0.2105	0.5949	5.7840
3.1	5.07	0.1842	0.5690	5.7163
3.3	4.78	0.1316	0.5086	5.5995
3.4	4.59	0.1052	0.4722	5.5194
3.5	4.24	0.0789	0.4290	5.3069
3.6	3.95	0.0526	0.3748	5.2053
3.7	3.61	0.02631	0.2974	5.1782

Table-25

Potentiometric titration data of MAC-20

mL HCl	pH	α	$3\sqrt{\alpha}$	pK_{app}
0.1	9.09	0.9744	0.9914	7.5102
0.2	8.60	0.9487	0.9826	7.3328
0.3	8.31	0.9231	0.9737	7.2308
0.4	8.10	0.8974	0.9646	7.1580
0.5	7.93	0.8718	0.9553	7.0975
0.6	7.79	0.8462	0.9458	7.0496
0.7	7.59	0.8205	0.9362	6.9299
0.8	7.48	0.7949	0.9263	6.8917
0.9	7.32	0.7692	0.9163	6.7971
1.0	7.22	0.7436	0.9060	6.7576
1.1	7.12	0.7179	0.8954	6.7142
1.2	7.02	0.6923	0.8846	6.6678
1.3	6.93	0.6667	0.8736	6.6290
1.4	6.81	0.6410	0.8622	6.5582
1.5	6.70	0.6154	0.8506	6.4959
1.6	6.61	0.5897	0.8386	6.4524
1.7	6.52	0.5641	0.8262	6.4080
1.8	6.39	0.5385	0.8136	6.3231
1.9	6.26	0.5000	0.7937	6.2600

2.0	6.16	0.4872	0.7869	6.1823
2.1	6.08	0.4615	0.7728	6.1469
2.2	5.99	0.4359	0.7582	6.1020
2.3	5.90	0.4103	0.7430	6.0576
2.4	5.82	0.3846	0.7272	6.0241
2.5	5.73	0.3590	0.7107	5.9818
2.6	5.64	0.3333	0.6934	5.9410
2.7	5.57	0.3077	0.6751	5.9222
2.8	5.51	0.2821	0.6558	5.9158
2.9	5.41	0.2564	0.6353	5.8724
3.0	5.33	0.2308	0.6134	5.8529
3.1	5.25	0.2051	0.5898	5.8383
3.2	5.14	0.1795	0.5641	5.8001
3.3	5.02	0.1538	0.5358	5.7604
3.4	4.88	0.1282	0.5042	5.7125
3.5	4.59	0.1026	0.4681	5.5320
3.6	4.35	0.0769	0.4253	5.4292
3.7	4.06	0.0513	0.3715	5.3272
3.8	3.71	0.0256	0.2949	5.2898

(0.1-1 gm) of copolymer was dissolved in 50-100 ml of water. 2 mL of 2 weight percent sodium oxalate was added to it. The pH of the solution was adjusted to the required value using sodium hydroxide solution. The solution was titrated against 1 weight percent calcium acetate, till the first appearance of turbidity as end point. 1 mL of 1 weight percent Calcium acetate corresponded to 0.0632 millimoles of Ca^{++} ions. CSC was thus expressed as millimoles of calcium ions per gram of copolymer, as well as millimoles of calcium ions per millimole of monomer in the copolymer. The CSC was determined at different pH between 4 to 11 for all copolymers, the oxime and bisulphite derivatives, poly(acrylic acid) and poly(methacrylic acid). Blank titrations were conducted at each pH without the polymer by adopting a similar procedure for deionised water, hydroxyl amine hydrochloride and sodium bisulphite at respective pH. Similar analysis was carried out for some copolymers in presence of equimolar amount of sodium chloride solution at selected pH.

2.5.7 Differential Scanning Calorimeter (DSC)

Different copolymers and phenol derivative described in section 2.4.3 were characterised using DSC 30 Mettler differential scanning calorimeter. The polymer was continuously and uniformly heated from 40°C to around 350°C at the rate of 5 and 10 °C per minute. Curing behaviour of the phenolic resins with hexamethylene tetramine was studied. Typically, 4 weight percent of hexamethylene tetramine was mixed with the resin and uniformly heated upto 180°C. The temperature range over which exotherm due to curing occurred was obtained.

For a fresh sample of same composition, curing temperature was quickly attained at the rate of 100°C per minute and the isothermal curing at the attained temperature was studied.

CHAPTER III

RESULTS AND DISCUSSION

3.1 COPOLYMER OF ACROLEIN-ACRYLIC ACID

Acrolein is a versatile vinyl monomer suited to the synthesis of homo/copolymers with reactive functional groups¹⁸⁹. The pendant aldehyde group may be used as is or derivatised to generate materials suitable for affinity chromatography, metal chelation and sequestration¹⁹⁰⁻¹⁹³. The aldehyde group of acrolein may interfere in the vinyl polymerization. This reactivity is profoundly influenced by the micro-environment. A variety of structural features emerge from this interference during the polymerisation and/or due to the polycyclisation between adjacent aldehyde pendant groups in the polymer chain¹⁹⁴. In aqueous solution copolymerisation of acrolein with acrylic acid, instantaneous phase separation of copolymer is observed above a specific mole fraction of acrolein monomer in the feed¹⁹⁵. This alters the copolymer composition and monomer reactivity ratio of acrolein. The polycyclisation is interrupted by acrylic moieties entrapping a high concentration of "widowed" aldehyde groups ideally suited for derivatisation¹⁹⁶.

The composition of the copolymer chain is influenced by the ionisation of the acrylic acid comonomer. Since the properties of copolymers are related to copolymer composition and sequence distribution, the polymerisation methodologies can be suitably altered to tailor-make polymers with a variety of property profiles. Hence, the influence of pH of the reaction medium on the reactivity ratios are investigated and the emerging structural features discussed.

3.1.1 Effect of pH

A number of experiments were conducted at each pH to make unbiased estimates of monomer reactivity ratios, over a wide range of acrolein and acrylic acid mole fractions. The copolymerisation was homogeneous when the mole fraction of acrolein in the feed was below certain critical value. At higher mole fractions of acrolein in the feed, the instantaneously formed copolymer phase separated out. The experimental data were analysed separately for estimating the reactivity ratios in the two mutually exclusive homogeneous and heterogeneous regimes. All the monomer feed and copolymer composition data obtained at a particular pH were also pooled together to estimate the global feature of the system. Thus, at each pH three different sets of reactivity ratios were estimated.

Reactivity ratios were estimated using symmetrical linearisation method of Yezrielev, Brokhina and Roskin (YBR) based on differential equation¹⁵³. Mole fractions of acrolein in feed and in copolymer as well as weight fraction conversion were input. The data input for the system studied without pH control, wherein the total monomer concentration was maintained at 1 molar, is presented in Tables 6-10. The data for pH 1, 3, 5 and 7 are presented in Tables 11-18 respectively. Reactivity ratios were also estimated with Kelen-Tudos (KT) method¹⁶⁸ using average mole fraction in feed. Reactivity ratios computed are compiled in Table 26.

D'Alelio et al. investigated the copolymerisation parameters of acrolein-acrylic acid system at pH 3, 5 and 7 using AIBN as initiator¹⁹⁷. The isothermal polymerisation temperatures were 54, 75 and 80°C respectively. The precipitation was observable only at pH 5 and 7. The study revealed heterogeneity in the system.

Table-26

Reactivity ratios of acrolein acrylic acid system at various pH

pH	Points	Method	Acrylic acid r_1	Acrolein r_2
no control 1M	all	YBR	-0.102 ± 0.046	1.67 ± 0.18
		KT	-0.13	2.13
	homogeneous	YBR	-0.065 ± 0.016	3.14 ± 0.44
		KT	-0.69	3.30
	heterogeneous	YBR	-0.966 ± 0.35	1.17 ± 0.30
		KT	-1.05	1.12
no control 4M	all	YBR	$-0.152 \pm$	$0.088 \pm$
		KT	0.105	0.049
	homogeneous	YBR	-0.08	3.80
		KT	-0.063	4.33
	heterogeneous	YBR	-0.81	0.54
		KT	-1.34	0.106
1	all	YBR	-0.060 ± 0.058	1.01 ± 0.17
		KT	-0.10	1.45
	homogeneous	YBR	0.034 ± 0.011	2.28 ± 0.15

		KT	0.034	2.27
	heterogeneous	YBR	-0.898±0.18	0.67±0.13
		KT	-0.92	0.71
3	all	YBR	-0.002±0.002	1.02±0.21
		KT	-0.27	1.13
	homogeneous	YBR	-0.095±0.038	3.23±0.67
		KT	-0.10	3.23
	heterogeneous	YBR	-1.046±0.24	0.70±0.10
		KT	-1.09	0.72
5	all	YBR	-0.109±0.055	1.01±0.19
		KT	-0.15	1.65
	homogeneous	YBR	-0.030±0.006	2.84±0.12
		KT	-0.03	2.83
	heterogeneous	YBR	-0.939±0.190	0.66±0.15

7					
	all	KT	-1.00	0.73	
		YBR	-0.10±0.04	1.05±0.23	
		KT	-0.28	1.49	
	homogeneous	YBR	-0.89±0.002	3.11±0.06	
		KT	-0.089	3.11	
	heterogeneous	YBR	-0.782±0.17	0.73±0.17	
		KT	-0.85	0.80	

The nature of the reaction medium (homogeneous/heterogeneous) on the kinetic parameters was not investigated. It was presumed that solubility characteristics of growing copolymer chain do not alter the relative rates of addition of acrolein and acrylic acid to it.

3.1.2 Phase separation

Phase separations were observable in the present study at $30 \pm 0.1^\circ\text{C}$, above a critical mole fraction of acrolein in the feed. The phase separation occurred when acrolein mole fraction exceeded 0.47 at pH 1, 0.45 at pH 3 and 5 and 0.40 at pH 7. Thus, the onset of phase separation occurs at lower acrolein content at higher pH. This phase separation was observable after a time lapse, but at as low as 2 weight percent conversion. Aqueous homopolymerisation of acrolein is heterogeneous. Large sequences of acrolein in the initially formed copolymer rejected water. This phase-separation altered the reactivity ratio of acrolein. Reactivity ratios are unaltered by the heterogeneity in the copolymerisation of styrene-methyl methacrylate in methanol¹⁹⁸. Methanol, a nonsolvent for both polystyrene and poly(methyl methacrylate), does not interact with either of the two components in the copolymer. The phase separated copolymer radical is excluded from further copolymerisation. The two comonomers are soluble in methanol and the solution copolymerisation continues obeying the binary copolymer composition equation. Thus, assumptions of the instantaneous copolymer composition equation were not violated throughout the copolymerisation of styrene-methyl methacrylate.

3.1.3 Copolymerisation in presence of nonsolvent

Effect of introducing nonsolvent in heterophase copolymerisation of acrylic acid with methyl methacrylate was investigated by Slavitskaya et al¹⁹⁹. The copolymerisations were taken to moderate conversion. The reaction was homogeneous in bulk. Introduction of cyclohexane, a solvent for acrylic acid and methyl methacrylate but nonsolvent for the respective homopolymers, introduces heterogeneity in the system. This alters the composition of the instantaneously formed copolymer and results in increase in the relative rate of addition of acrylic acid into the copolymer chain. This was attributed to a selective sorption of acrylic acid in the precipitated phase but the active polymer phase which continues to grow. Thus, the variance in the relative reactivities observed globally are in essence due to differential concentrations of the two monomers induced by this heterogeneity. The investigators observed four regimes operating (i) in bulk, (ii) 0-40 volume percent, (iii) 40-75 volume percent and (iv) 75-90 volume percent cyclohexane. In the presence of 40-75 volume percent cyclohexane (relative to monomers), the reaction at moderate conversions occurred primarily in the polymer phase and was initiated by the trapped polymer radicals. This reaction within the polymer phase became less apparent with further increase in cyclohexane volume (70-90 volume percent). The polymerisation was initiated by adsorbed microradicals at the phase boundary. The reaction tended towards the bulk copolymerisation. It may be concluded that the trapped polymer radical becomes less solvated with increase in the relative volume of cyclohexane. The solvated polymer phase selectively absorbs acrylic acid and induces its polymerisation thereby introducing the anomalous behaviour.

3.1.4 Absorption of monomer

Selective sorption of acrylonitrile and methacrylic acid around the polymer molecule was observed in homogeneous radical copolymerisation with styrene²⁰⁰. The dependence of copolymer composition on copolymer molecular weight was caused by selective sorption of the monomers by macromolecular coils of different molecular weights. In copolymerisation systems exhibiting such a dependence, the thermodynamic quality of the monomer mixture as a solvent for the copolymer decreased with increasing polymer molecular weight and the system approached theta conditions. Under such conditions, the effect of selective sorption was pronounced. In acrylonitrile-styrene and methacrylic acid-styrene systems, acrylonitrile and methacrylic acid content in the copolymer increased with increasing molecular weight of previously formed copolymer.

The anomalous behaviour observable in styrene-methyl methacrylate and acrylic acid-methyl methacrylate were induced by the addition of nonsolvents for both monomers. In acrylic acid-acrolein system, poly(acrylic acid) is water soluble while polyacrolein is insoluble. Additionally, copolymer formed from monomer feed rich in acrylic acid swells in water as a coacervate while copolymer formed from acrolein rich feed, phase separates. Increase in the dilution of the two monomers from 4 to 1 molar in water, without pH control, resulted in decrease in the reactivity ratio of acrolein. This points to an interaction of water with monomer molecules.

3.1.5 Molecular interactions

Molecular association of acrylic acid, acrolein and solvent was investigated by ultraviolet (UV) and infra-red (IR) spectroscopy. Carbonyl stretching frequency

for acrylic acid was at 1699 cm^{-1} and that for acrolein was at 1724 cm^{-1} . Carbonyl stretching frequencies observed for 1:1 molar mixture of the two monomers were at 1689 and 1724 cm^{-1} respectively. There was a shift in the carbonyl stretching frequency of acrylic acid indicating change in carbonyl character of the acrylic acid due to the association with acrolein. Kabanov reported similar molecular association in methacrylic acid-N vinyl pyrrolidone system²⁰¹.

UV absorption of mixtures of acrolein and acrylic acid was investigated in water and acetone. The experimental data are presented in Tables 27 and 28. Aqueous solution of acrolein absorbs with λ_{max} at 234 nm while absorbance of acrylic acid is marginal. Addition of acrylic acid to this acrolein solution decreased its absorbance. This decrease was more enhanced at 6:4 mole ratio of acrolein:acrylic acid (Table 27). The decrease was less dramatic at other mole ratios. This could be due to molecular association of acrylic acid with acrolein. This association decreases the concentration of free acrolein molecules taking part in $\pi \rightarrow \pi^*$ transition. Thus, the molecular association was dependent on relative concentration of the two species. Solvent molecules play an important role in this association. Water and acrylic acid are polar and protic while acrolein is aprotic, less polar. Acrylic acid interacts with water through hydrogen bonding. Similar investigations were carried out using acetone as a solvent. The investigations were possible at concentrations ten times higher than that in aqueous solution. Here, the absorbance of acrolein ($\lambda_{\text{max}} = 337\text{ nm}$) was not depressed by the addition of acrylic acid (Table 28). Molecular association responsible for reduction in carbonyl character of acrolein and acrylic acid is absent. Acetone may interact with both the monomers and being in large excess keep the two monomers far apart to restrict the molecular association.

Table-27

U.V. investigation for the study of molecular association.

Aqueous solution; absorption at 333 nm

No	Acrolein(AC) X $10^{-3}M$	Acrylicacid (AA) X $10^{-3}M$	Abs(AC)		Abs(AC+AA)	A-B
			A	B		
1	1.7825	7.2925	0.054	0.049	0.006	0.006
2	3.5650	5.4694	0.106	0.092	0.014	0.014
3	4.4563	4.5579	0.126	0.114	0.012	0.012
4	5.3475	3.6463	0.145	0.138	0.007	0.007
5	7.1300	1.8231	0.184	0.178	0.006	0.006

Table-28

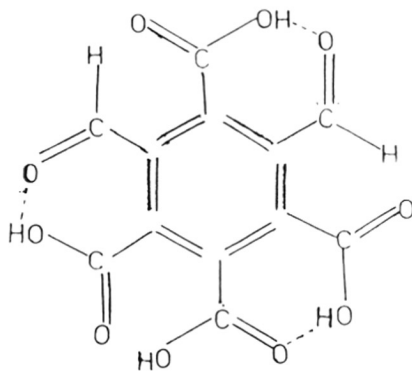
U.V. investigation for the study of molecular association.
acetone solution, absorption at 337-341 nm

No	Acrolein(AC) X 10 ⁻² M	Acrylic acid(AA) X 10 ⁻² M	Abs(AC) A	Abs(AC+AA) B	A-B
1	0.4600	4.5142	0.123	0.123	0.000
2	1.3802	3.5111	0.321	0.322	-0.001
3	3.2205	1.5047	0.748	0.746	+0.002
4	4.1407	0.5015	960	0.961	-0.001

UV measurements were conducted with dilute solutions. IR study was conducted with undiluted monomer mixture and the copolymerisations were investigated in between these two extremes, at 4 molar concentration. At this concentration, nature of molecular association may vary with change in relative proportion of the two monomers. The plurimolecular aggregates formed between the monomers due to molecular association are similar to micelles. The double bond may orient inwards with ionised and hydrophilic groups facing the solvent molecules as depicted in Figure 6. Global feed concentrations of the two monomers may not be reflected in the "plurimolecular aggregate". Relative proportions of monomers in these aggregates will be dependent on feed mole ratio and molarity of the solution. Initially, aggregate with higher acrolein content is miscible with water. As the polymerisation proceeds in the aggregate, heterogeneity is enhanced resulting in complete phase separation.

The critical composition of acrolein above which phase separation took place was dependent on the pH of the medium. At lower pH, acrylic acid is un-ionised. This allows other un-ionised hydrophilic moieties into the aggregate, rendering the aggregate homogeneous even at relatively higher (global) concentration of acrolein. This observation is in agreement with the copolymer composition data at various pH.

The turbidity could be the onset of precipitation leading to the phase separation of copolymer. Monomers can diffuse into the precipitated but active copolymer even after phase separation, thereby continuing copolymerisation in the precipitated phase concurrently with solution copolymerisation. Kinetic expression for this reaction becomes complicated. The instantaneous copolymer composition



IN UN-IONISED ACRYLIC ACID

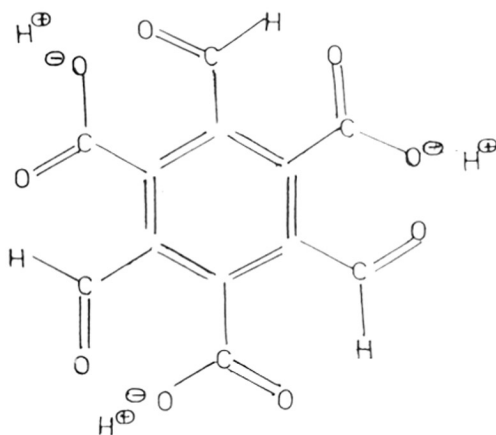


FIG. 6

MOLECULAR ASSOCIATION OF ACRYLIC ACID AND ACROLEIN
IN IONISED ACRYLIC ACID

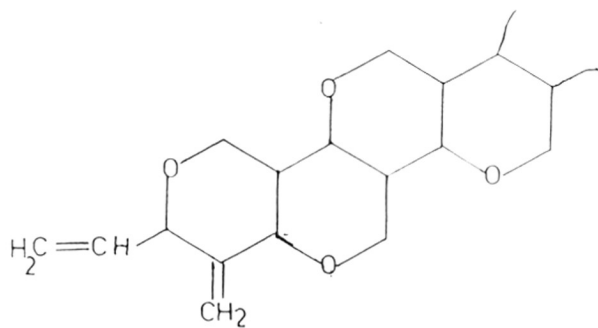
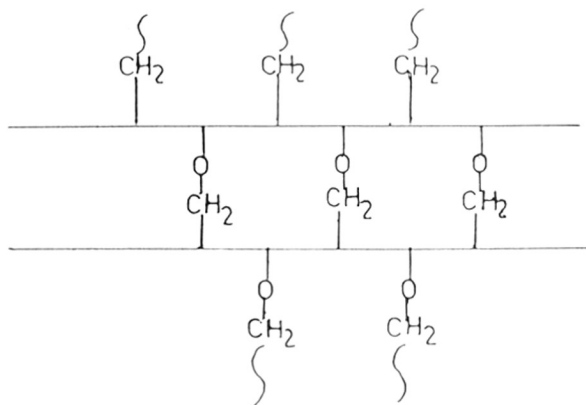
equation derived from simple four mutually competing reactions would not be applicable to the heterogeneous system. Thus, the reactivity ratio calculated for heterogeneous reactions are misleading. This accounts for negative reactivity ratios presented in Table 26 for acrylic acid in the precipitative range. Further, considering the entire concentration range including the heterogeneous range for the estimation of reactivity ratios are inexact. It is observed from Table 26, that reactivity ratios are independent of the method of estimation only in homogeneous range while it is markedly different in heterogeneous range. Hence calculation ought to be restricted only to the copolymerisations in the homogeneous range.

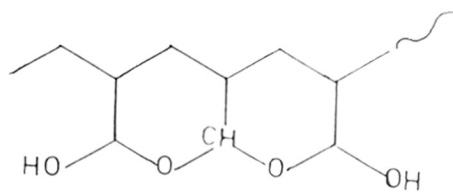
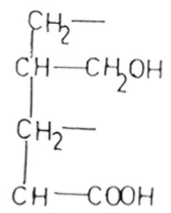
The reactivity ratio of acrylic acid is positive at pH 1. At that pH, acrylic acid is un-ionised. Growing polymer chain with terminal ionised acrylic acid moiety would repel ionised acrylic acid molecule. This would decrease the rate of self-addition (k_{11}) of acrylic acid to the growing end thereby decreasing reactivity ratio of acrylic acid with increase in pH.

Reactivity ratio of acrolein was less at pH 1, increased at pH 3, then it decreased at pH 5 and again increased at pH 7. In D'Alelio's¹⁹⁴ study a gradual increase in reactivity ratio of acrolein was observed. In a similar study of weakly ionisable monomer (acrylic acid) with a hydrophilic un-ionisable one (acrylamide), the reactivity ratio of acrylamide decreased with increase in pH but increased again at pH 10. In our study, general trend such as gradual decrease/increase could not be observed. As could be seen from Figure 7, acrylic acid-acrolein system could not be investigated beyond pH 7, since aldehyde group present in acrolein takes part in the chain growth making kinetic estimates untenable²⁰¹⁻²⁰⁴.

FIG. 7

INTER/INTRAMOLECULAR CYCLISATIONS IN POLYACROLEIN

7a7b

7c7d

3.1.6 Effect of counterion

Ionisation of acrylic acid introduces another monomer (acrylate anion). This gives rise to another interesting aspect to the investigation. Effect of metal methacrylate was studied by Gonyukh et.al¹³⁸. Addition upto 2 mole percent of copper or cobalt methacrylate in copolymerisation of methacrylic acid with methyl methacrylate decreased reaction rate and induction period. Reactivity ratio of methacrylic acid dropped from 0.68 to 0. This was attributed to complexation by these ions.

Reactivity ratio of ionized acrylate differs from that of acrylic acid. Reactivity ratios for acrylic acid-acrylamide in homogeneous aqueous copolymerisation with different counter ions is presented in Table 29. Reactivity ratios of acrylic acid and acrylamide were 1.43 and 0.60 respectively. This differs from 0.84 and 1.40 observed for potassium acrylate-acrylamide system and 0.35 and 1.10 for sodium acrylate-acrylamide system under similar conditions. Thus, addition of a base, for pH adjustment of weakly ionisable monomer like acrylic acid, introduces another species which is effectively a third monomer. The reaction can no longer be treated as a binary copolymerisation but is a ternary system.

3.1.7 Nonlinearity in the system

Fineman and Ross plots at pH 1 and that without pH control at 4 molar are presented in Figure 8,9. Ideally the data should be linear, yielding reactivity ratios as slope and intercept of the straight line. The data without control of pH showed two distinct regimes. In homogeneous regime, data is linear. The data for hetero-

Table-29

Effect of counter ion on reactivity ratio of acrylic acid.

Counterion	Acrylamide r_1	Acrylic acid r_2
hydrogen	0.6	1.43
potassium	1.4	0.84
sodium	1.1	0.35

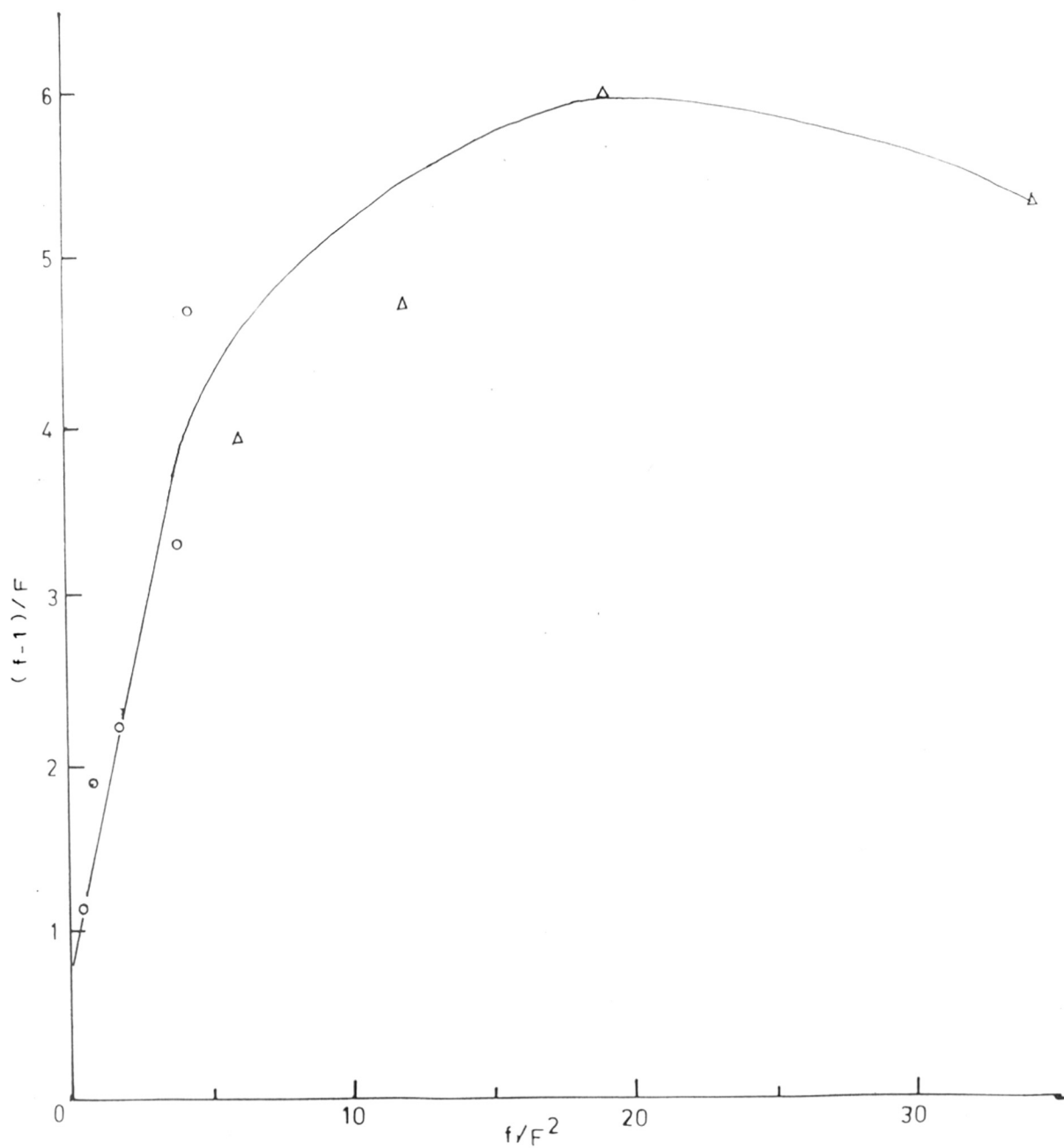


FIG. 8

FINEMAN-ROSS PLOT FOR ACROLEIN-ACRYLIC ACID, NO pH CONTROL.

○ HOMOGENEOUS RANGE

△ HETEROGENEOUS RANGE

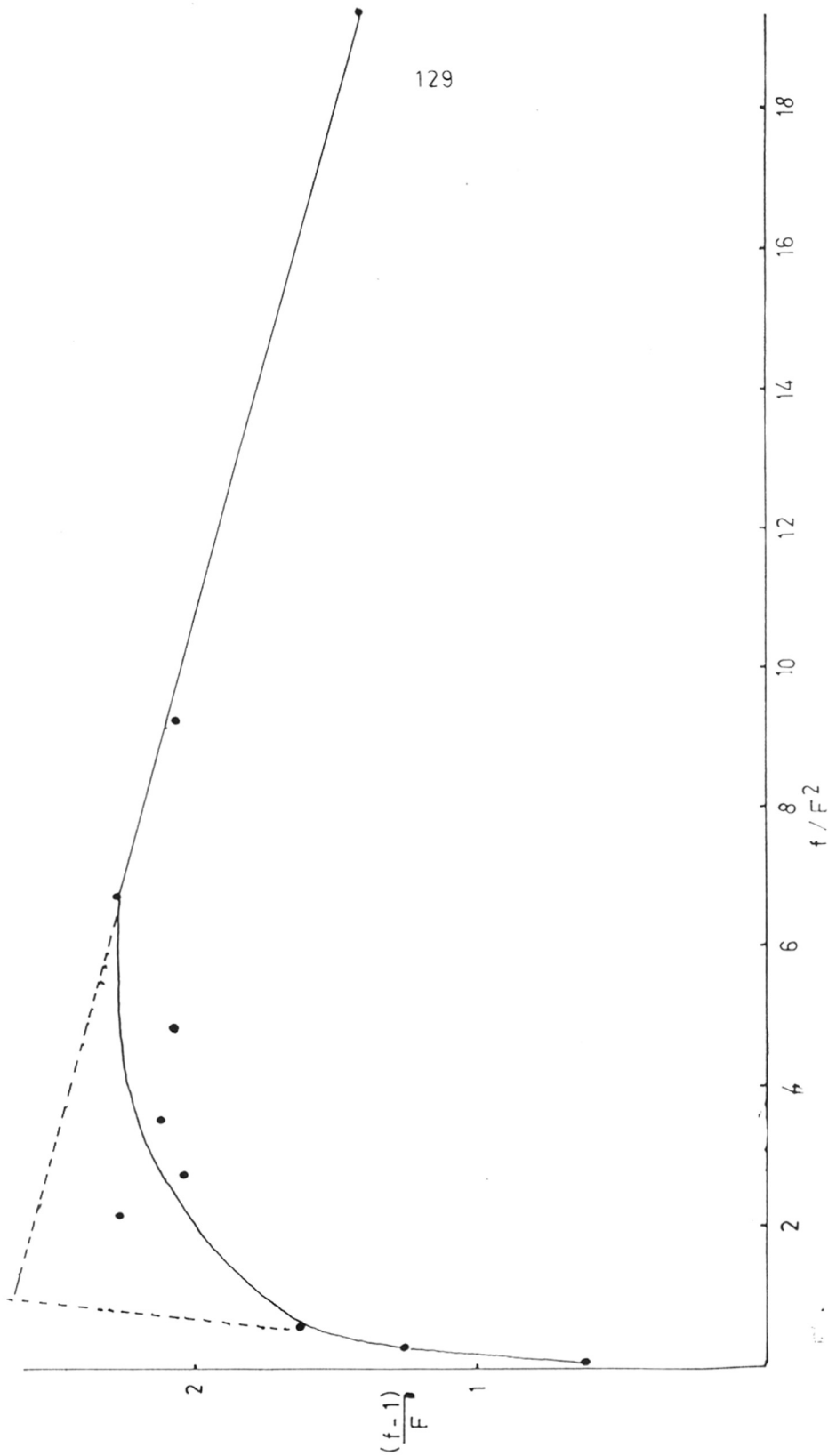


FIG. 9
FINEMAN-ROSS PLOT FOR ACROLEIN-ACRYLIC ACID AT pH 1

geneous range is another straight line. Combined data is nonlinear. At pH 1, similar linearity for the two distinct regions is observed. The concentration near phase separation is nonlinear. Overall data is nonlinear.

Our system resembles the class II type cationic copolymerisations¹⁵⁸, monomer pairs described by J.P.Kennedy et. al¹⁵⁸. Nonlinearity is observed in these systems due to following reasons:

- 1) In the kinetic sense, the system contains more than two monomers and/or more than two active centers.
- 2) The reactivity ratios change with feed ratio since effect of medium is not internally compensated due to unequal solvent interaction with the two monomers.
- 3) The monomer reactivities are significantly different. In the present case, at pH 1, reactivity of acrolein is 66 times that of acrylic acid. In such cases, validity of the steady state assumption is questionable.

$$k_{12} [M_1^*] [M_2] = k_{21} [M_2^*] [M_1]$$

Radical initiation is less selective than ionic initiation and yields many true copolymers. Kennedy¹⁵⁸ predicted that in free radical copolymerisations, many monomer pairs accepted to yield true copolymer pairs could in reality be treated as class II pairs. Aqueous copolymerisation of acrylic acid-acrolein is one such example.

3.1.8 Conclusions

The anomaly in the copolymerisation could arise because of one or many of the following factors:

- (a) monomeric aggregation dependent on relative comonomer composition.
- (b) nonuniform interactions of the two monomers with the solvent

(c) selective sorption of one of the monomers around the growing polymer chain. The conventional methods to estimate reactivity ratio may not be applicable and the data ought to be treated as ternary system.

3.2 Solid state C^{13} NMR

C^{13} NMR in solid state using CP/MAS technique was obtained to investigate free aldehyde content in the copolymer. The analysis of polymer using routine methods for aldehyde was not possible due to interference of carboxyl group present in the polymer. Moreover, aldehyde content in polyacrolein was found to be less than 20 percent of the theoretical aldehyde content due to inter/intra molecular cyclisation. Amount of free aldehyde on the polymer is critical for the desired properties required for sequestration.

3.2.1 Peak assignment

The solid state ^{13}C -NMR spectra of polyacrolein, poly(acrylic acid) and an acrolein-acrylic acid copolymer are presented in Figure 10. The copolymer spectrum consists of four peaks:

1. ~ 40 ppm: $(-CH_2-CHR-)_n$ from polymer backbone
2. ~ 99 ppm: hemiacetal and acetal linkages
3. ~ 180 ppm: carboxylic groups from acrylic acid
4. ~ 203 ppm: free aldehyde groups of acrolein

Solid state ^{13}C CP/MAS NMR gives semiquantitative estimates of the relative concentration. The curve integrations are not the same for all functional groups. However, an estimate of relative populations can be made within similar structural elements in a copolymer series. The areas under the peak for various structural

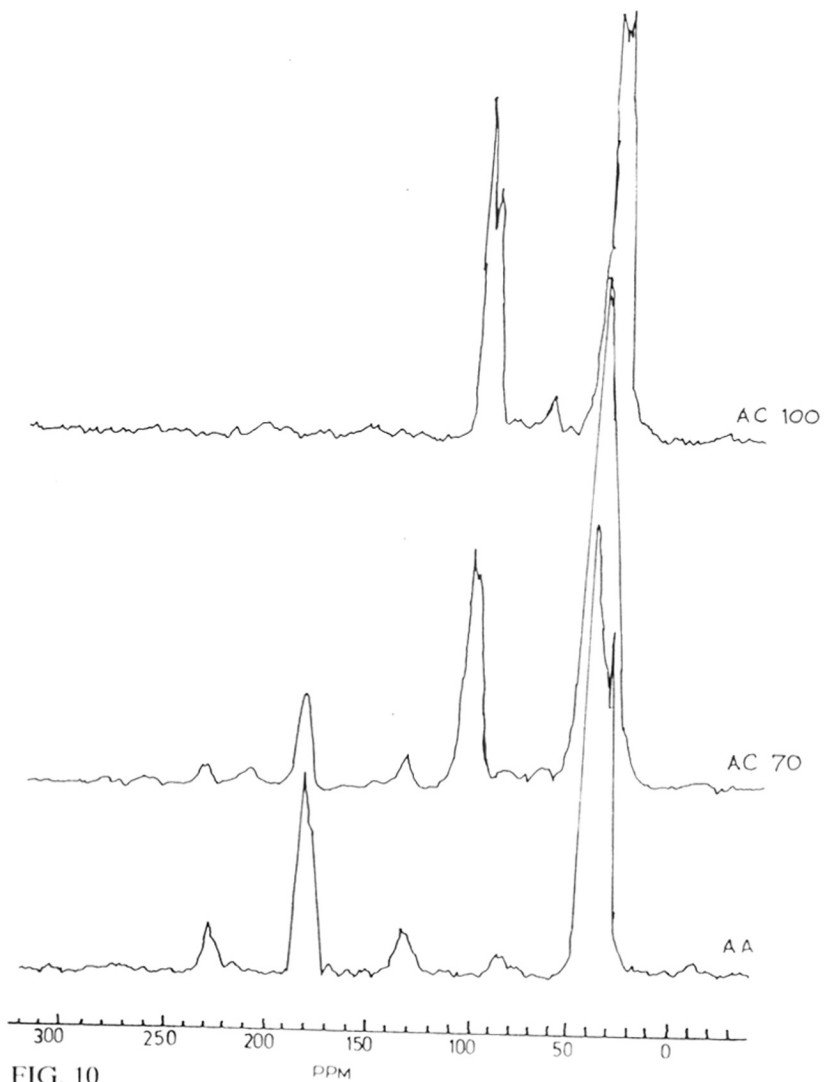


FIG. 10

SOLID STATE ^{13}C NMR OF

AA: ACRYLIC ACID HOMOPOLYMER

AC70: ACROLEIN-ACRYLIC ACID COPOLYMER

AC100: ACROLEIN HOMOPOLYMER

elements are presented in Table 30. The ratio of peak area of aldehyde to hemiacetal is presented in Table 31. It reveals that the relative concentration of free aldehyde groups increases with a decrease in acrolein content in the copolymer chain.

3.2.2 Effect of mean sequence length

The concentration of acrolein in feed, copolymer and mean sequence length are presented in Table 31. The mean sequence length " μ " of acrolein was calculated using the relation:

$$\mu = r_1 \frac{[M_1]}{[M_2]} + 1 \quad (73)$$

where r_1 = reactivity ratio of acrolein, and M_1 and M_2 are moles of acrolein and acrylic acid in the feed respectively. The relation between the mean sequence length of acrolein moieties, the free aldehyde concentration and the mole fraction of acrolein in the feed are presented in Figure 11.

Free aldehyde concentration in the copolymer decreases with an increase in the sequence length of acrolein moieties. Thus, the relative placements of aldehyde and carboxylic groups along the copolymer chain alters the cyclisation reactions of aldehyde groups. The intramolecular polycyclisation occurs only in the presence of adjacent aldehyde groups giving rise to ladder type structure. Incorporation of acrylic acid interrupts this reaction. As a result, the relative concentration of isolated free aldehyde group increases with an increase in acrylic acid mole fraction in the feed.

Table-30
 Peak Areas of Solid State ^{13}C CP/MAS NMR Signals of Acrolein-
 Acrylic acid Copolymer

Sample No.	Area			
	~ 40 ppm (cm^2)	~ 99 ppm (cm^2)	~ 181 ppm (cm^2)	~ 203 ppm (cm^2)
AA 100	8.89	-	2.49	-
AC 10	5.11	0.09	1.51	0.03
AC 25	4.90	0.56	1.20	0.17
AC 45	9.71	2.10	1.48	0.41
AC 55	5.48	1.20	0.83	0.12
AC 70	5.32	1.60	0.53	0.14
AC 85	5.58	2.11	0.31	0.16
AC 100	8.67	3.77	-	0.27

Table-31

Mean Sequence Length of Acrolein in Copolymers

Sample No.	Mole Fraction		Mean Sequence Length	$\frac{\text{area 203}}{\text{area 99@}}$
	In Feed	In Polymer		
AC 10	0.1050	0.6819	1.4458	0.33
AC 25	0.2523	0.7067	2.2823	0.30
AC 45	0.4535	0.8098	4.1535	0.20
AC 55	0.5534	0.8725	5.7089	0.10
AC 70	0.7030	0.8249	9.9950	0.088
AC 85	0.8518	-	21.8419	0.076

@ Ratio of area of peaks corresponding to 203 ppm and 99 ppm respectively.

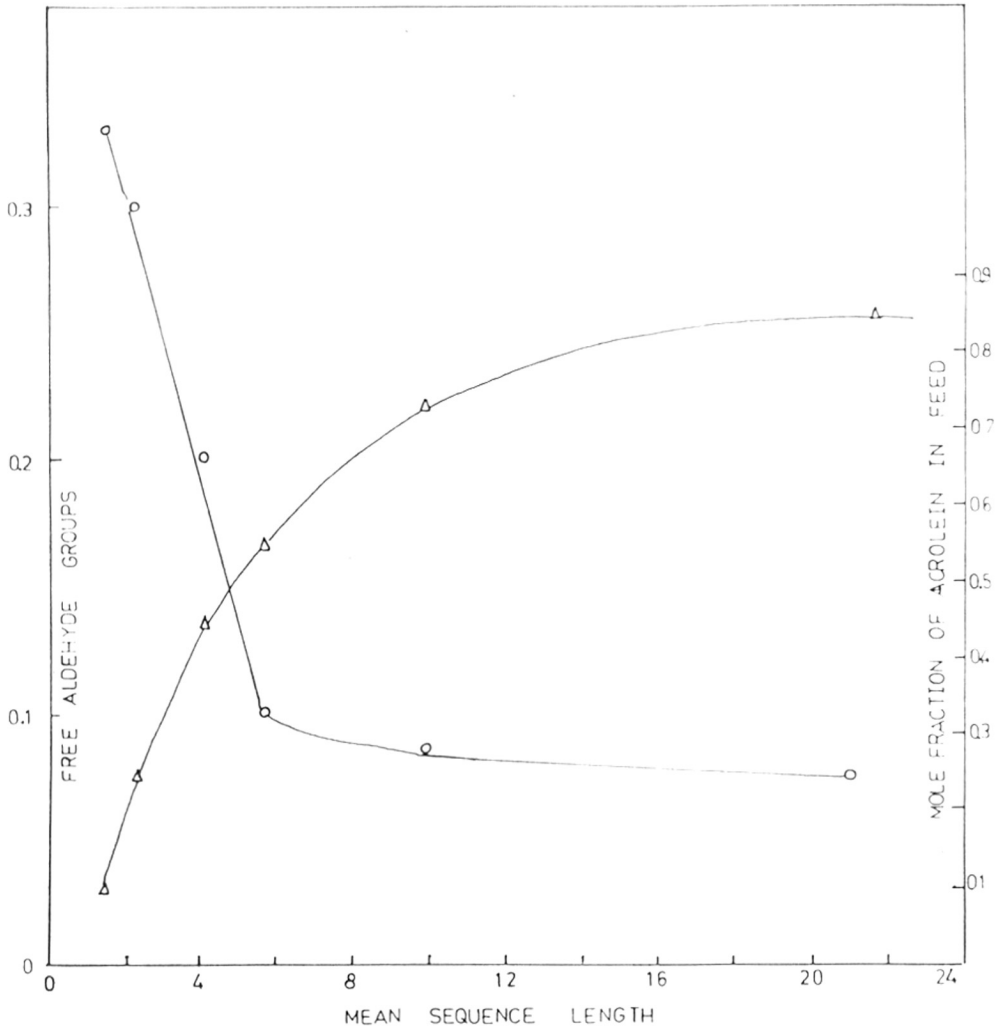


FIG. 11

MEAN SEQUENCE LENGTH VS MOLE FRACTION OF ACROLEIN
IN FEED

MEAN SEQUENCE LENGTH VS FREE ALDEHYDE

3.2.3 Effect of acrolein in feed and polymer

The variance of free aldehyde concentration with acrolein mole fraction in feed/polymer, presented in Figure 12, reveals that the free aldehyde concentration decreases linearly with increase in acrolein fraction in the copolymer. The free aldehyde content in the copolymer shows three distinct regions in relation to acrolein concentration in the feed. In the high acrylic acid feed region (acrolein mole fraction in feed up to 0.25), the aldehyde content in the copolymer gradually decreases with increase in the acrolein mole fraction. In the second region (acrolein mole fraction in feed upto 0.55) this change is very rapid. In the third region, with high relative concentration of acrolein, (acrolein mole fraction in feed 0.55-1.0), the decrease is again very gradual. This is probably due to differences in global and local concentrations of acrolein in the vicinity of the growing copolymer chain. Acrylic acid forms multimolecular aggregates in aqueous solution. The relative concentration of the two monomers in the hydrogen bonded multimolecular aggregates around the growing chain would be different from their global concentrations in the reaction mixture, generating the observed trend.

3.3 CHARACTERISATION USING INFRA-RED SPECTROPHOTOMETER

3.3.1 Characterisation of bisulphite of polyacrolein

IR spectra of poly(acrolein bisulphite) as shown in Figure 13 exhibits important signals as follows:

3472:(sharp), Intermolecularly hydrogen bonded single bridge compound,

2944:(sharp), C-H stretching of alkane backbone

~2550: (weak) S-H stretching

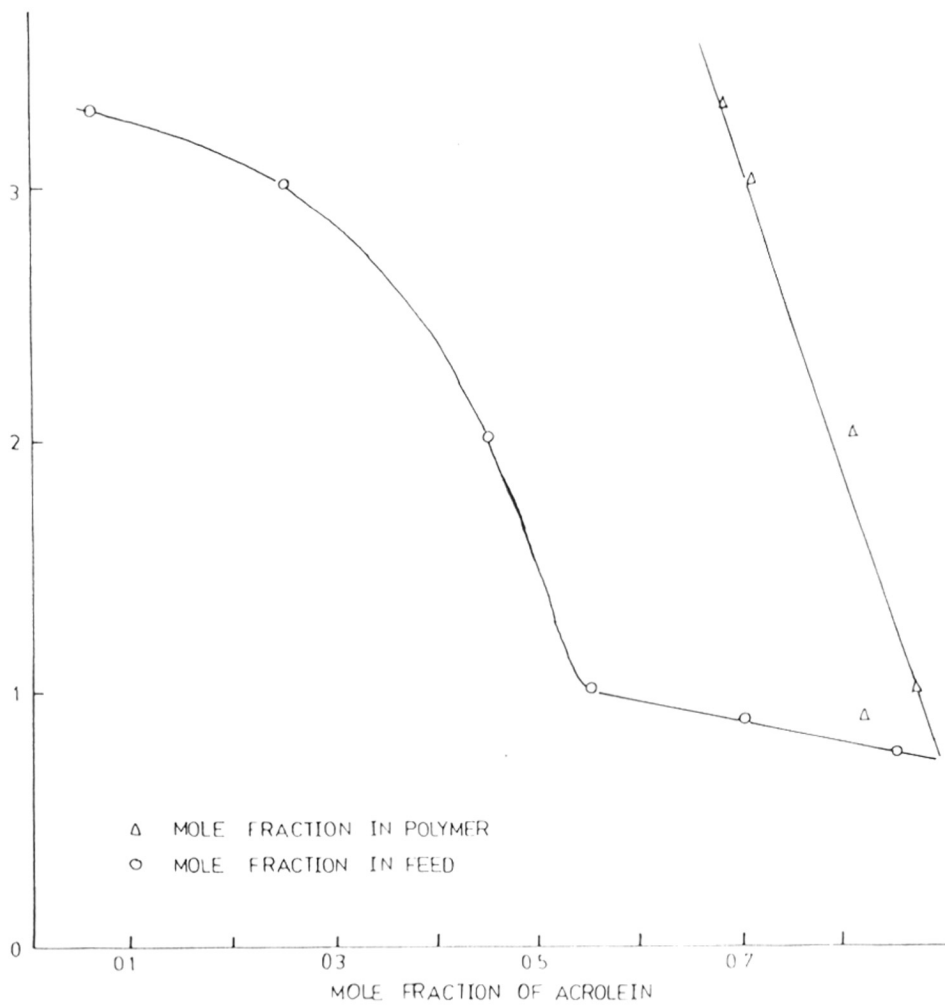


FIG. 12

MOLE FRACTION(S) Vs AMOUNT OF FREE ALDEHYDE GROUPS

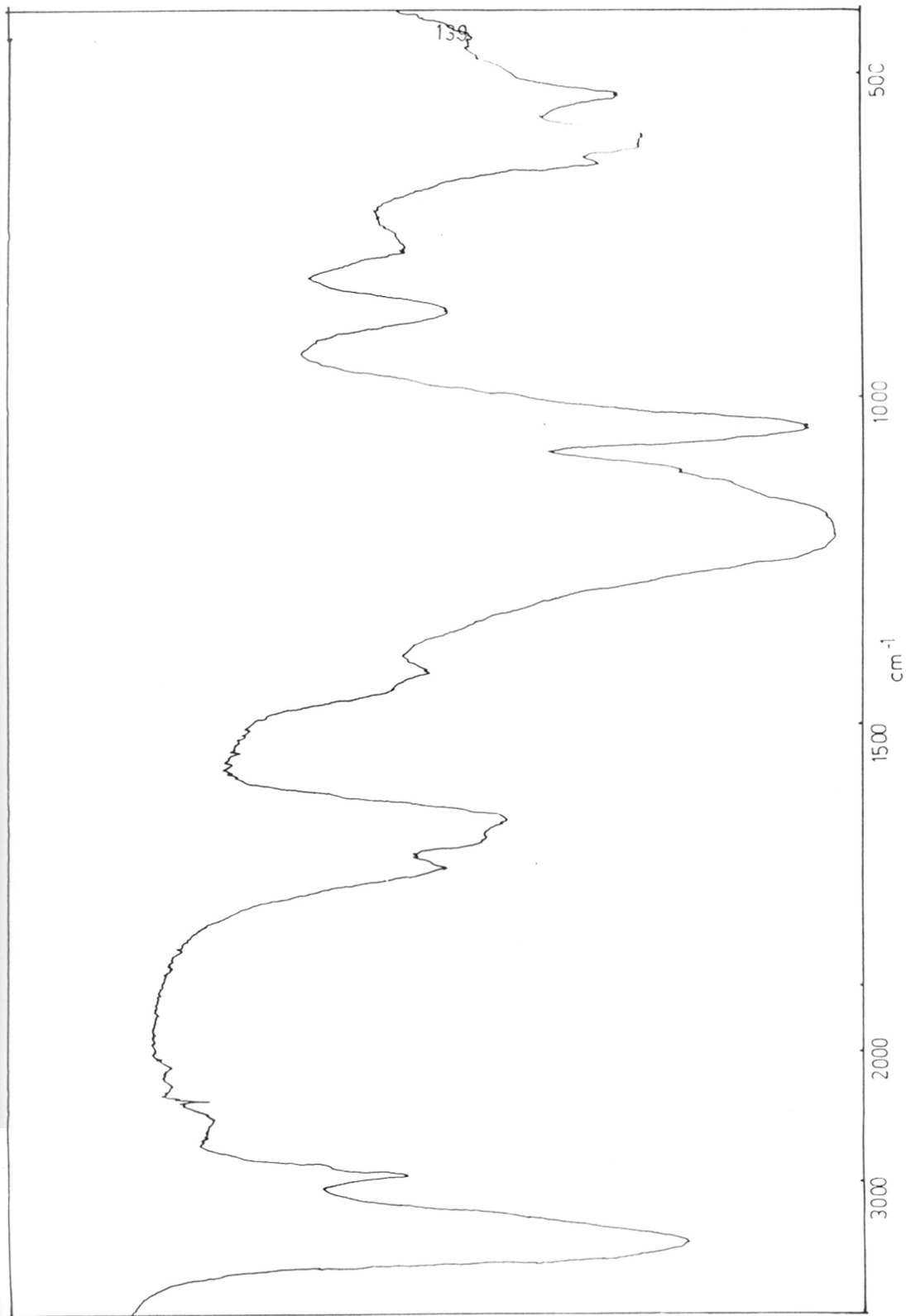


FIG. 13
IR SPECTRA OF POLY(ACROLEIN BISULPHITE)

1718:saturated aliphatic aldehyde stretching

1417:(sharp) and 1203:(sharp), S-O stretching for sulfite

1049.6: (sharp), C-O stretching for primary hydroxyl or ether

592:(medium) C-O-C stretching as in ethers and acetals

3.3.2 Characterisation of oxime of polyacrolein

IR spectra of poly(acrolein oxime) as shown in Figure 14 exhibits some of the important signals as follows:

3360: (strong broad), polymeric association of hydrogen bonded

Hydroxyl group

2928:(sharp) C-H stretching of alkane backbone

1721:saturated aldehyde stretching

1606:C=N stretching

1056:(sharp), C-O stretching for primary hydroxyl or ether

3.3.3 Acrolein-acrylic acid copolymers

The copolymers exhibit different signals in homogeneous (Figure 15) and heterogeneous reactions (figure 16) respectively. In heterophase reactions, AC-55, AC-70 and AC-85 signal at 3375-3420 cm^{-1} due to OH stretching and in the range 2850-2920 cm^{-1} due to CH stretching bands are prominent. Carbonyl stretching band at 1710-1720 cm^{-1} is also prominent. CH bending vibrations at 1425-1450 cm^{-1} are present. In homogeneous polymerisations the copolymers formed show

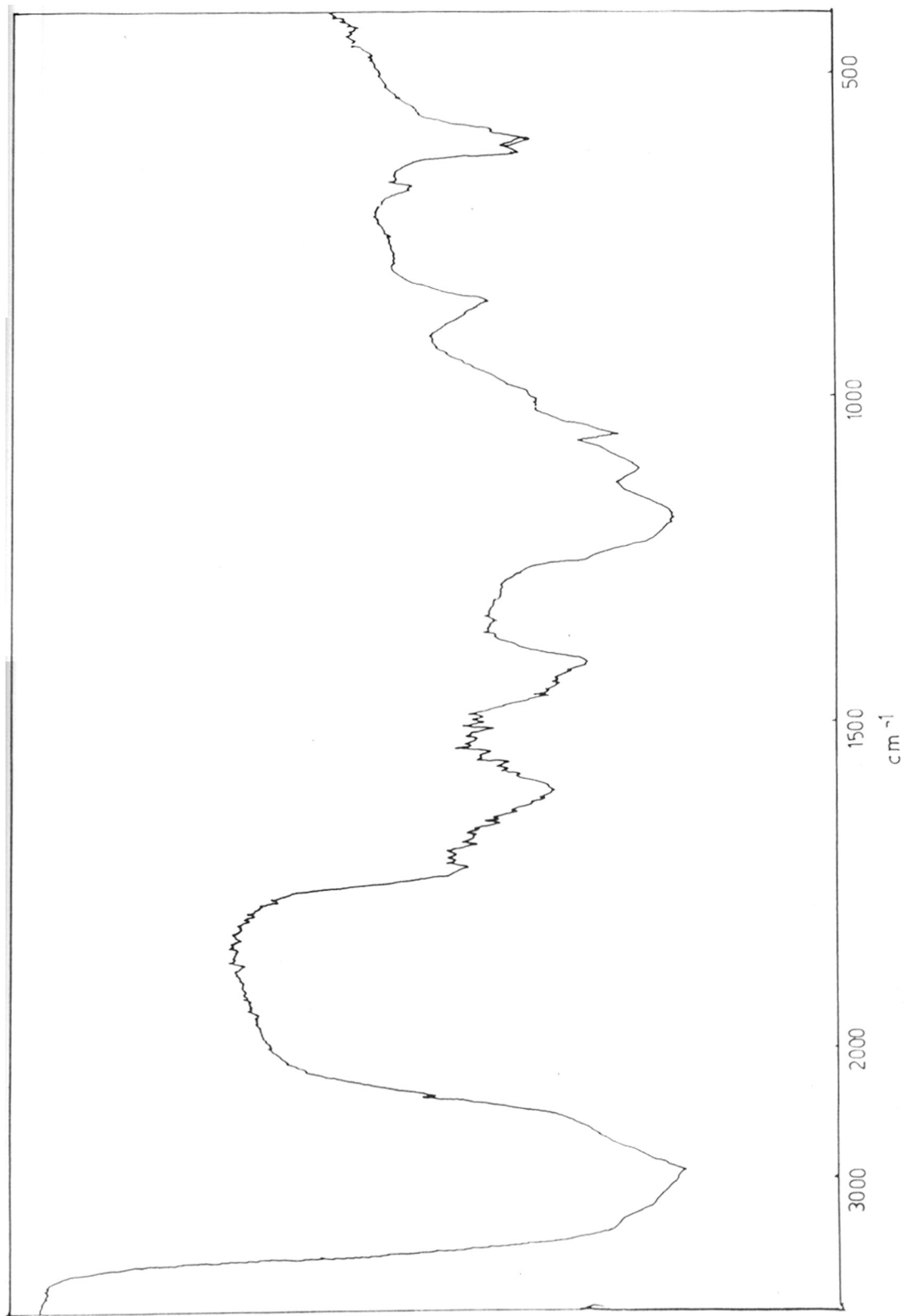


FIG. 14
IR SPECTRA OF POLY(ACROLEIN OXIME)

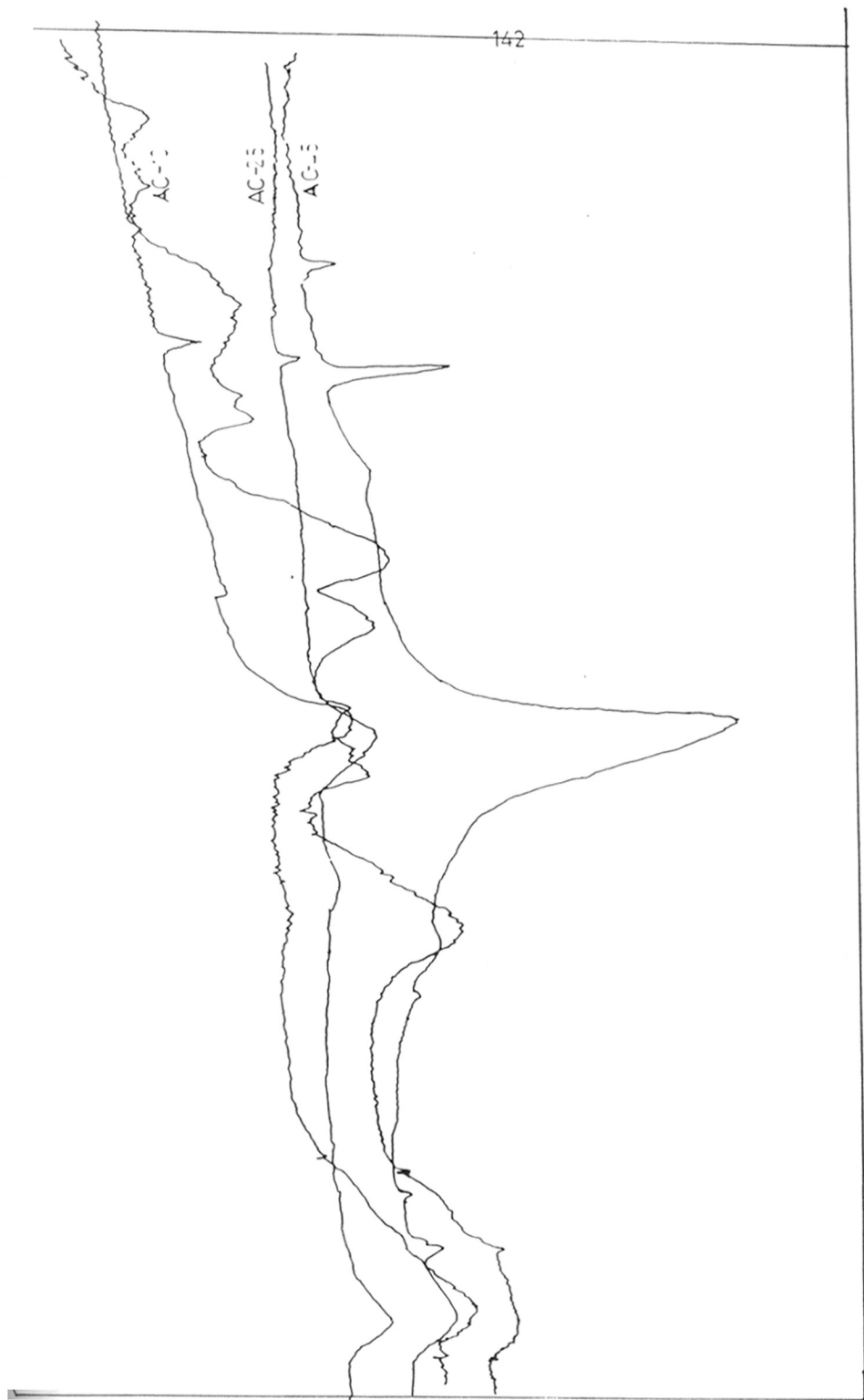


FIG. 15
IR SPECTRA OF ACROLEIN-ACRYLIC ACID COPOLYMERS IN HOMOGE-
NEOUS PHASE

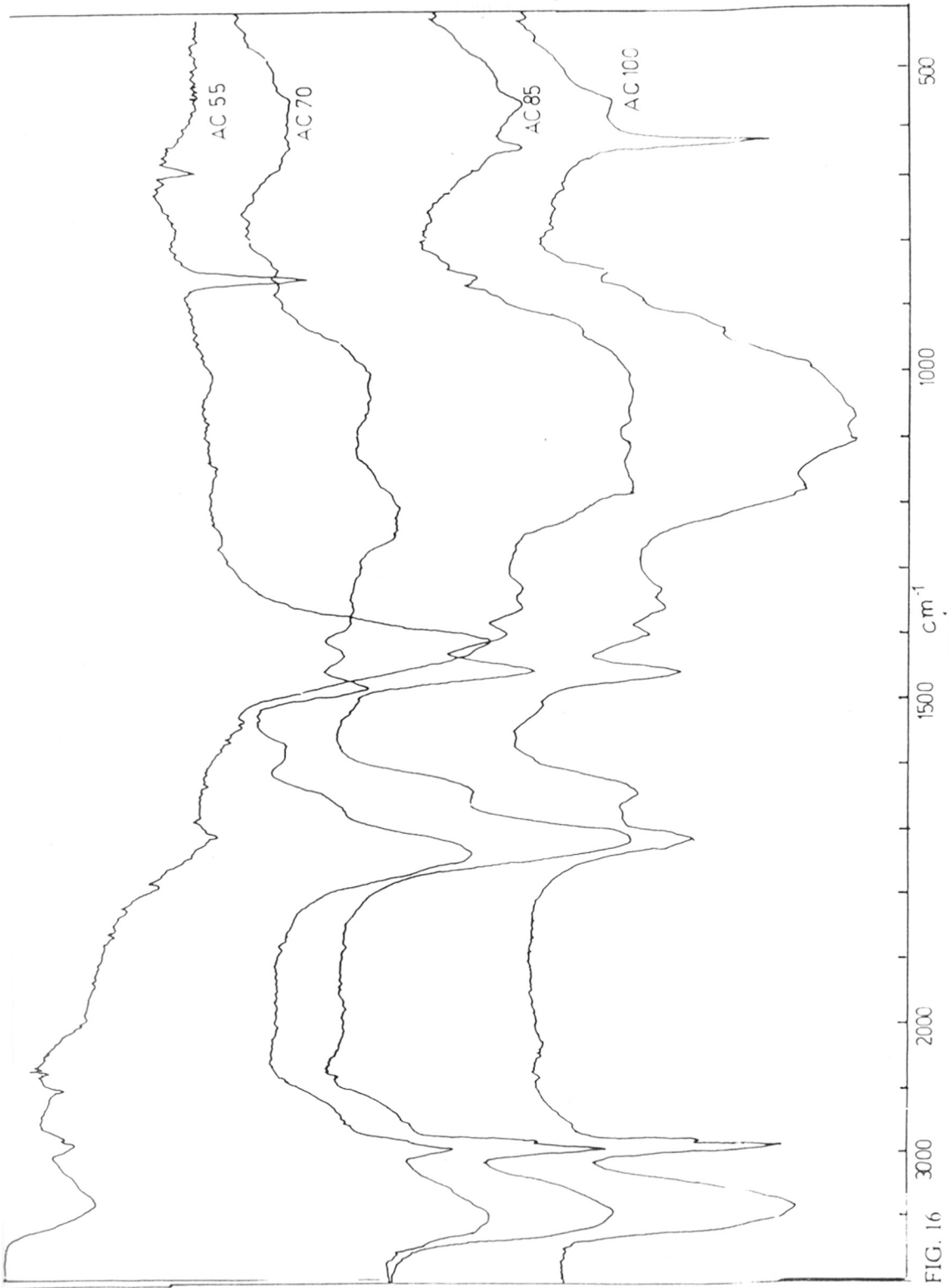


FIG. 16

IR SPECTRA OF ACROLEIN-ACRYLIC ACID COPOLYMERS IN HETEROGE-

broad spectra with only three prominent peaks near $3375\text{-}3425\text{ cm}^{-1}$ in the range $1430\text{-}1460\text{ cm}^{-1}$ due to CH bending of CH_2 and near 725 and 877 cm^{-1} due to presence of CH_2 .

3.4 COPOLYMERS OF ACROLEIN-METHACRYLIC ACID

Aqueous solution copolymerisations of acrolein-methacrylic acid were carried out at differing constant pH. Phase separation was observed during copolymerisation of acrolein-acrylic acid above a critical concentration of acrolein. It was presumably because of hydrophobicity of polyacrolein blocks in the copolymer. Methacrylic acid is hydrophobic as compared to acrylic acid. The effect of this enhanced hydrophobicity on copolymerisation with acrolein was investigated.

The copolymerisations were homogeneous over the entire range of comonomer compositions upto pH 7. Slight turbidity appeared above 0.50 mole percent acrolein in feed. However, this turbidity did not result into precipitation even at high conversions.

The aqueous free radical solution polymerisations of ionisable monomers are profoundly influenced by ionic strength and pH of the medium. In such cases various factors like dissociation, specific and nonspecific bindings of ions, electrostatic and hydrophobic interactions are of importance. Copolymerisation of methacrylic acid with acrolein was investigated for the effect of pH on the reactivity ratios of the two monomers. The reactivity ratios are presented in Table 32. The copolymerisations were carried out at pH 1, 3, 5 and 7. The pH of the feed was not controlled in another set of reactions. Except for the reaction at pH 7, copolymerisations were conducted while maintaining total monomer concentration at 4 molar. Addition of potassium hydroxide to set pH to 7 resulted in the crystallisation of potassium methacrylate prior to copolymerisation. Copolymerisation was possible without crystallisation of potassium salt, when total monomer concentration was set at 2 molar. The system could not be evaluated beyond pH 7. In alkaline range the

Table-32

Reactivity ratios of methacrylic acid and acrolein at different pH

pH	Method	Methacrylic acid r_1	Acrolein r_2
no control	YBR	0.07 ± 0.02	0.22 ± 0.07
	KT	0.10	0.11
1	YBR	0.28 ± 0.04	0.46 ± 0.07
	KT	0.30	0.43
3	YBR	0.15 ± 0.2	0.41 ± 0.07
	KT	0.17	0.42
5	YBR	0.13 ± 0.02	0.30 ± 0.03
	KT	0.15	0.30
7	YBR	0.14 ± 0.01	1.06 ± 0.04
	KT	0.15	1.06

aldehyde group in acrolein takes part in the chain growth reaction and generates crosslinked structure. At pH 7, the feed composition with acrolein content exceeding 0.50 mole percent tended to phase separate even prior to addition of redox initiators.

3.4.1 Effect of pH

Reactivity ratio of methacrylic acid decreases with increase in pH. The trend is apparent in Figure 17. Reactivity ratio of acrolein also decreases with increase in pH. But at pH 7 it shoots to a higher value of 1.06. At that pH (initial pH 7.0 final pH 7.5) acrolein polymerises by a complicated mechanism. Another striking feature of methacrylic acid-acrolein system at this pH is stability of acrolein monomer. In acrolein-acrylic acid system over all feed composition, a slight pH shift above 7 during copolymerisation caused the precipitation of growing copolymer. In acrolein-methacrylic acid system on the other hand, the copolymerisation from feed composition upto 0.5 mole fraction of acrolein was homogeneous even as the final pH shifted to 7.64. The copolymerisation was not possible from feed compositions consisting of acrolein mole fraction exceeding 0.5 due to sudden phase separation of the monomer prior to the addition of redox initiator. Decreasing the total monomer concentration to 2 molar solubilised the monomers and the reaction proceeds as a homogeneous one. At this pH, methacrylic acid is completely ionised. Incorporation of this ionised monomer in multimolecular aggregate is less probable. This enhanced scope of self addition of acrolein is reflected in its reactivity ratio. Since ionisation and aggregations would differ, comparison of reactivity ratios

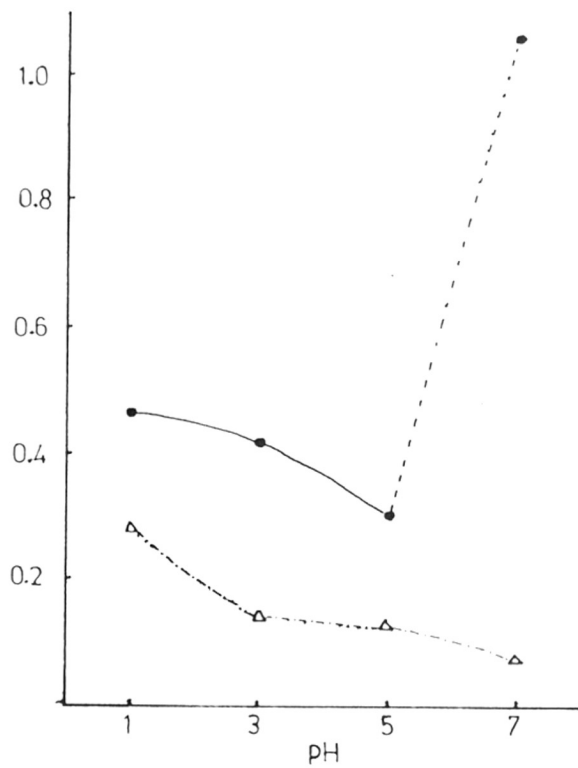


FIG. 17

REACTIVITY RATIOS AT DIFFERENT pH

- ACROLEIN
- △ METHACRYLIC ACID

estimated at different monomer concentrations will be inexact. These differences would also be reflected in the reactivity ratio as discussed in the previous chapter [1.5.4.4].

In the case of acrylamide-acrylic acid and acrylamide-methacrylic acid systems, the reactivity ratio of ionising monomers (acrylic/methacrylic acid) reduces while reactivity ratio of nonionising monomer increases. Molecular association and repulsion between ionised molecules led to the decrease in self addition of acrylic/methacrylic acid. Reactivity ratio of methacrylic acid in acrolein-methacrylic acid system is appreciably higher than the reactivity ratio of acrylic acid in acrolein-acrylic acid copolymerisation system under similar experimental conditions. Ionised monomer molecules would repel each other thereby reducing their local concentrations in the vicinity of the growing chain as well as in multimolecular aggregates. At a given pH, degree of dissociation of acrylic acid (pK 4.2) and poly(acrylic acid) (pK 6.4) are greater than that of methacrylic acid (pK 4.32) and poly(methacrylic acid) (pK 7.0) respectively. Thus, under similar conditions, methacrylic acid concentration in the local multimolecular aggregate with acrolein would be larger than that for acrylic acid. Increased hydrophobic interaction with acrolein due to the presence of methyl group in methacrylic acid would act additively to the aggregation.

3.4.2 Effect of counter-ion

Effect of counter-ion on the reactivity ratios in methacrylic acid-acrylamide system is summarised in Table 33. Monovalent and bivalent ions influence the reactivity ratio of the ionisable monomer. Bivalent ions complex with carboxylic ligand bringing two methacrylic acid molecules together to increase the relative rate of

Table-33
Effect of counterion on reactivity ratio of methacrylic acid

Counter ion	Acrylamide r_1	Methacrylic acid r_2
Hydrogen	0.12	0.25
Lithium	0.50	0.73
Sodium	0.42	0.59
Potassium	0.41	0.46
Cadmium	0.04	2.13
Calcium	0.24	0.71
Magnesium	0.20	0.92
Zinc	0.04	1.20

self addition. Thus, reactivity ratios of methacrylic acid is enhanced with the presence of multivalent ions. Only when the copolymerisation of methacrylic acid is conducted using aprotic solvent, the monomer is completely unionised. This will be a true binary system consisting of methacrylic acid and acrolein. In aqueous solution, addition of potassium hydroxide to adjust the pH generates potassium methacrylate. In strict sense it becomes a ternary copolymerisation system consisting of acrolein, methacrylic acid and methacrylate anion, excepting at pH 1 wherein the monomer is completely unionised. The aqueous solution copolymerisation without pH control is also a binary system with only a slight constraint of pH variation from 2.2 to 2.9 with the change in monomer feed composition.

3.4.3 Nonlinearity

The reactivity ratio values follow a well defined trend. The values are positive and decrease with increase in pH. When the data was used for Fineman-Ross plot, it was expected to be linear. However, the data was nonlinear. Finding best fitting line in a set of nonlinear data points in acrolein-acrylic acid yielded negative values of reactivity ratio for acrylic acid, which is meaningless. In acrolein-methacrylic acid system, the values being positive the anomaly was not as apparent as in acrolein-acrylic acid system. The Fineman-Ross plots for pH 1 and without pH control are presented in figures 18 and 19. The data is nonlinear.

The nonlinearity in the previous (acrolein-acrylic acid) system was ascribed to the anomalies described in J.P.Kennedy's classification¹⁵⁸. The nonlinearity could be due to unequal interaction of the two monomers with solvent. Water is a nonsolvent

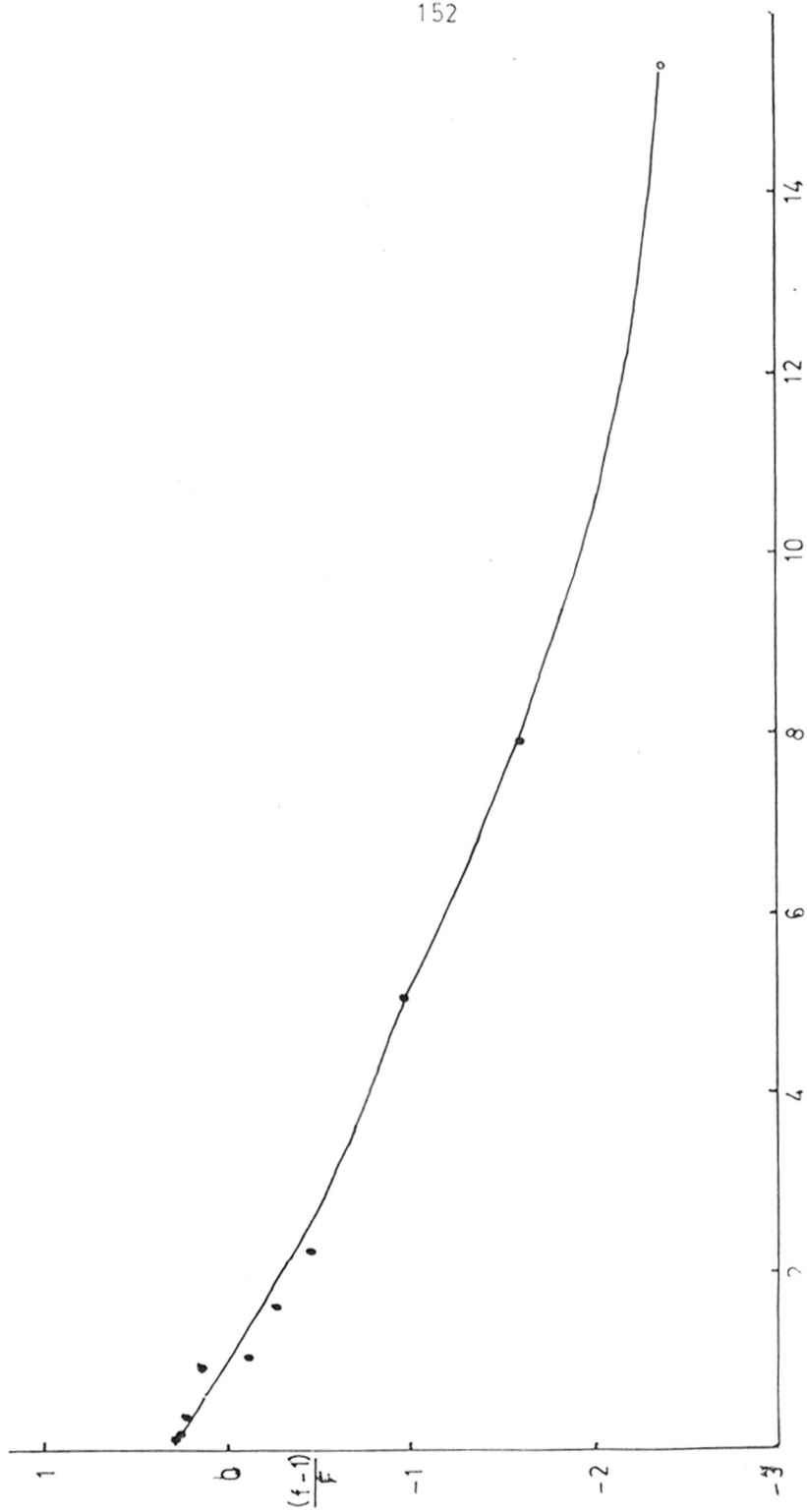
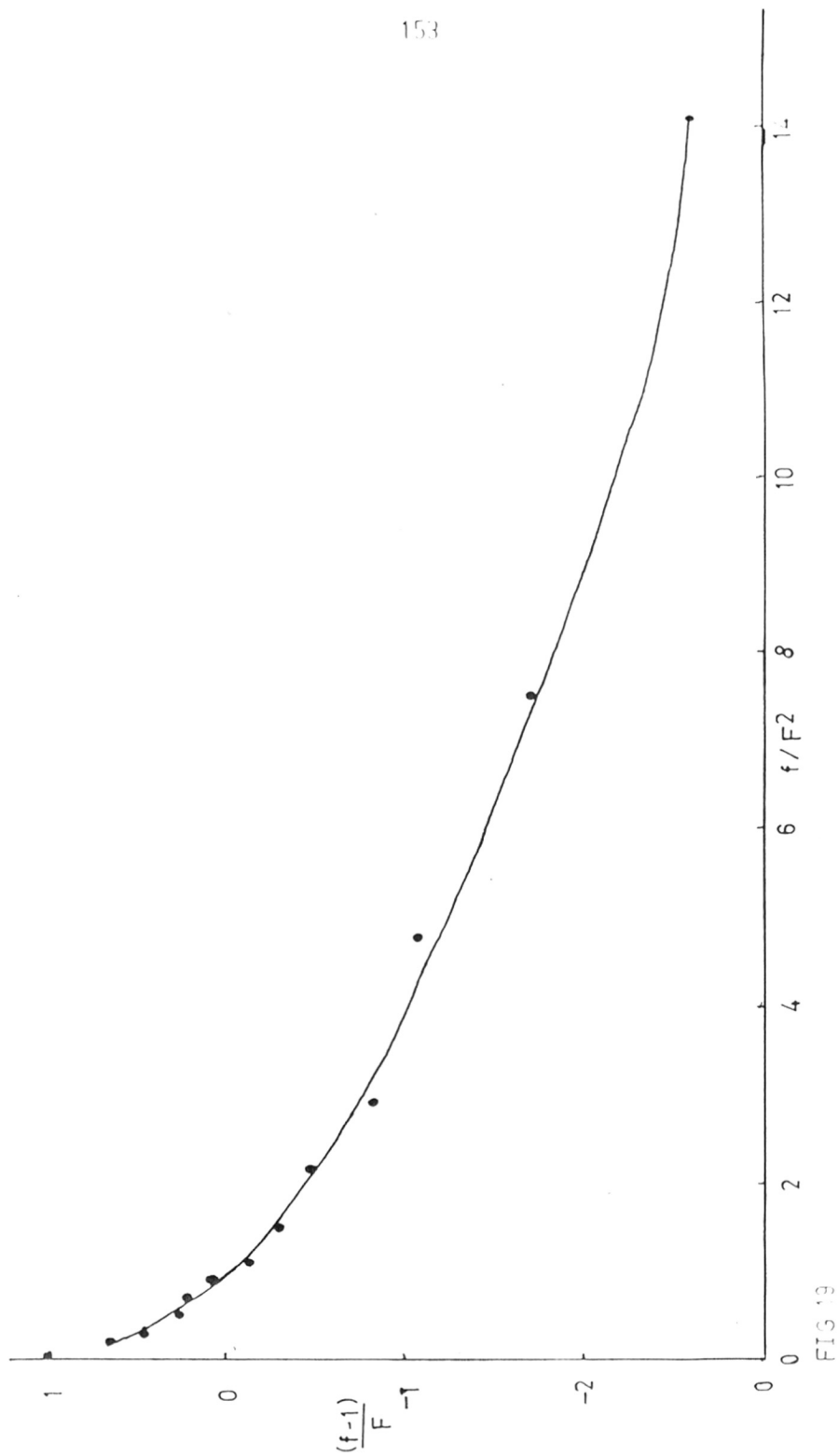


FIG. 18
FINEMAN-ROSS PLOT FOR ACROLEIN-METHACRYLIC ACID, NO pH CON-
TROL

FIG. 19
FINEMAN-ROSS PLOT FOR ACROLEIN-METHACRYLIC ACID AT pH 1

for polyacrolein but is a solvent for poly(methacrylic acid). The unequal interaction in the case of acrolein-acrylic acid system led to formation of micellar multimolecular aggregate which tended to phase separation on polymerisation. The multimolecular aggregate of acrolein-methacrylic acid did not phase separate. The hydrophobic methyl group on methacrylic acid facilitated inclusion of more methacrylic acid units with acrolein. Unequal solvent interactions and more so greater than two types of reacting species present in this system give rise to the nonlinearity. Hence, the choice of the method of estimating monomer reactivity ratios for ionisable monomers in protic solvent has to be exercised carefully, considering simplifications/approximations/assumptions in the kinetic expressions used to derive the reactivity ratios.

3.5 POTENTIOMETRIC TITRATIONS

The degree of ionisation α when the sodium salt is titrated by the acid is given by:

$$\alpha = 1 - \frac{[\text{volume of HCl added to titrate at a given pH}]}{[\text{Total volume of HCl required for titration}]}$$

The apparent pH (pK_{app}) for different values of α were computed from the equation

$$\text{pK}_{\text{app}} = \text{pH} + \log \left[\frac{1 - \alpha}{\alpha} \right]$$

The intrinsic pK (pK_0) values were obtained by extrapolation of pK_{app} versus $\alpha^{1/3}$ plots to $\alpha = 0$ as suggested by Arnold¹⁹⁵. The titration data from high α (random coil region) in the pK versus α plots were extrapolated to pK_0 by curved extrapolation. These plots for MAC-40, MAC-30 and MAC-20 are presented in figures 20,21 and 22 respectively and the data is presented in Table 23-25. The free energy

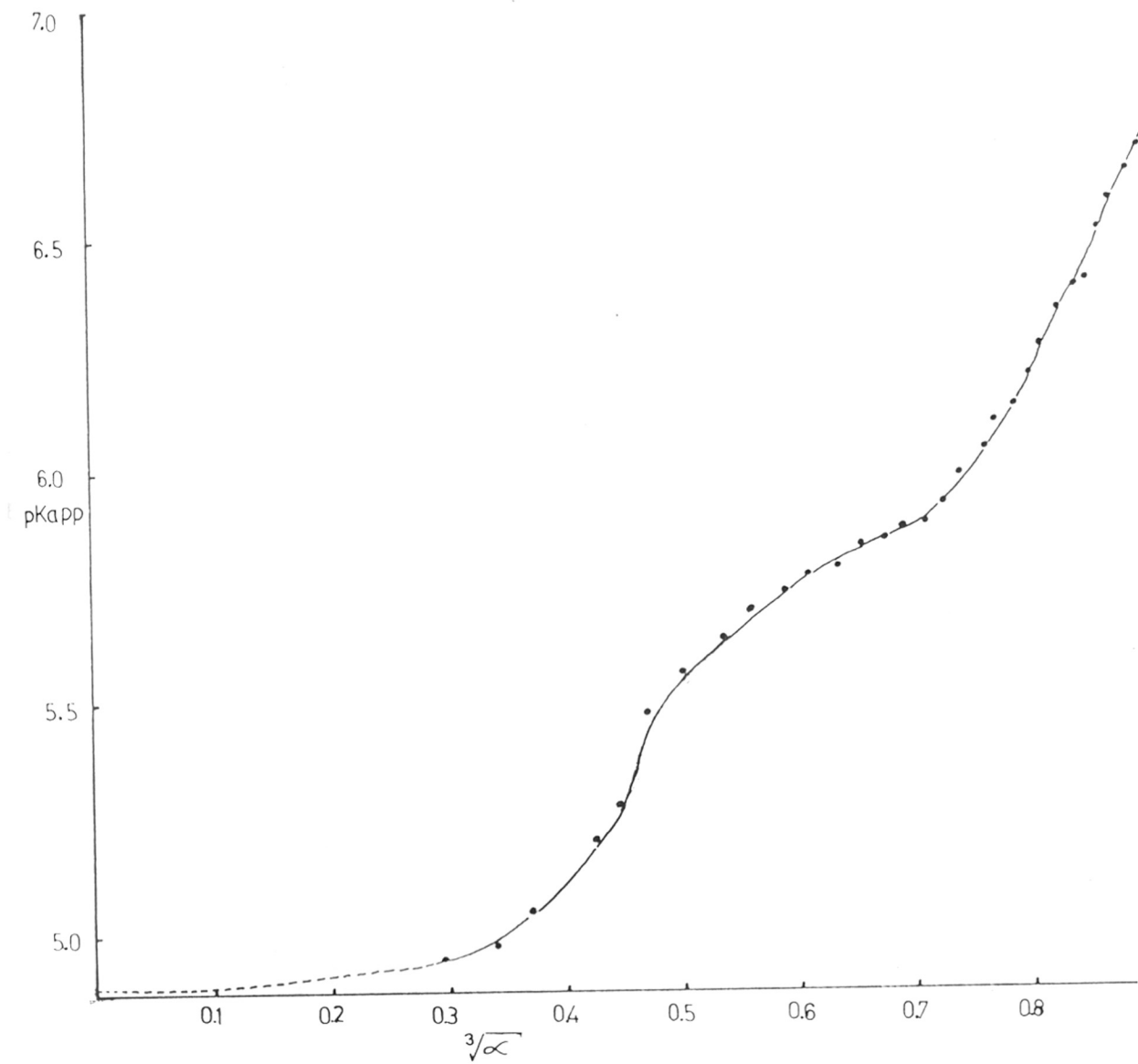


FIG. 20

POTENTIOMETRIC TITRATION OF MAC-40

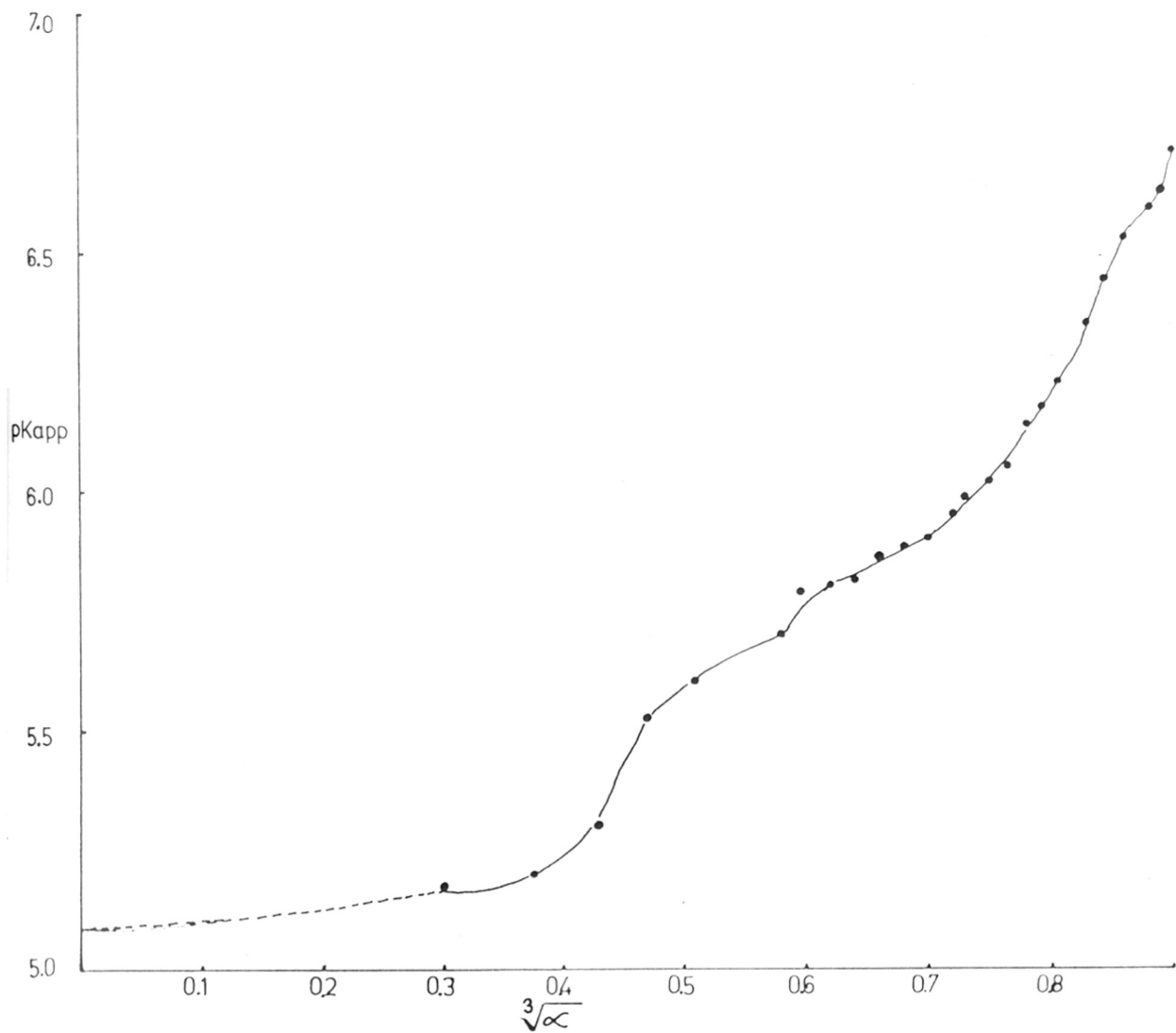


FIG. 21

POTENTIOMETRIC TITRATION OF MAC-30

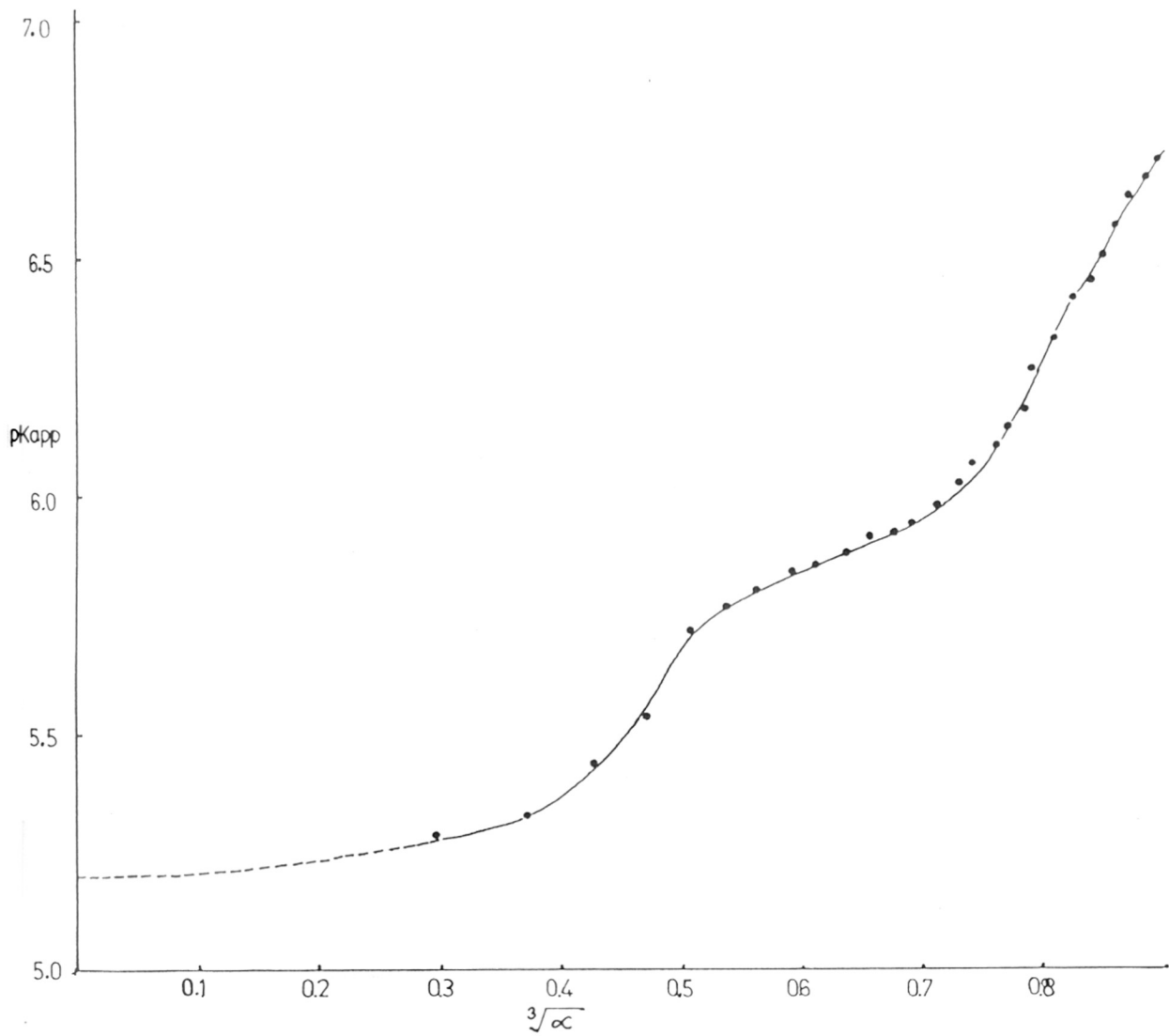


FIG. 22

POTENTIOMETRIC TITRATION OF MAC-20

of conformational transition per mole of the titratable carboxyl groups ($\Delta F^0/N$) of the uncharged expanded form was estimated by the Zimm and Rice¹⁹⁶ procedure as

$$\frac{\Delta F^0}{N} = 2.303RTA$$

where A is the area enclosed by the loop formed by the experimental titration curve, the extrapolated curve and the pK_0 on the Y axis. These plots for MAC-40, MAC-30 and MAC-20 are shown in Figures 23,24 and 25 respectively. The free energy of transition from uncharged compact globular to the uncharged expanded form for the copolymers were computed from its titration curves and presented in Table 34. The titration curves show progressive increase in the area of the loop between experimental titration curve and the extrapolated curve and pK_0 with increase in acrolein content in the polymer. This indicates gradual stabilisation of compact structure with increase in acrolein content. Thus degree of dissociation at a given pH is induced with increase in the interruption of carboxylic blocks. In MAC-40, due to "azeotropic composition" of the copolymer drastic decrease in pK_0 is observed.

3.6. CALCIUM SEQUESTRATION

Carboxylate group ionises upon neutralisation with a suitable base. The mutual ionic repulsion between these groups, when present in a polymer as pendants, causes the molecule to adopt an expanded configuration. Each polyelectrolyte molecule can be regarded as a microscopic ionic network. The counter ions are exchanged between the expanded ionic network and its surrounding external solution. Diffusion of the mobile counter ions away from the vicinity of the polyelectrolyte leads to a net negative charge within the polymer molecule. This increases the electrical

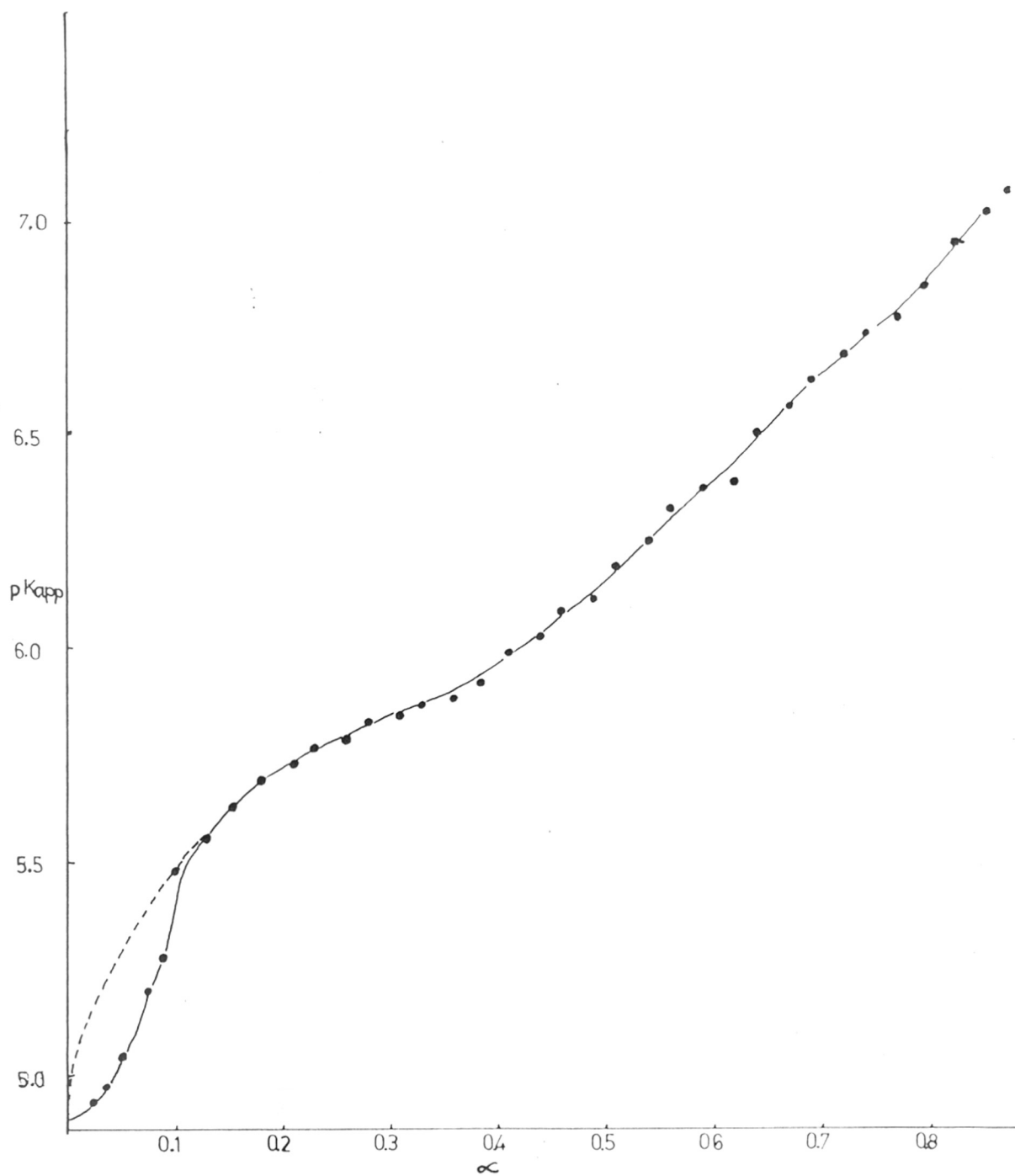


FIG. 23

POTENTIOMETRIC TITRATION OF MAC-40

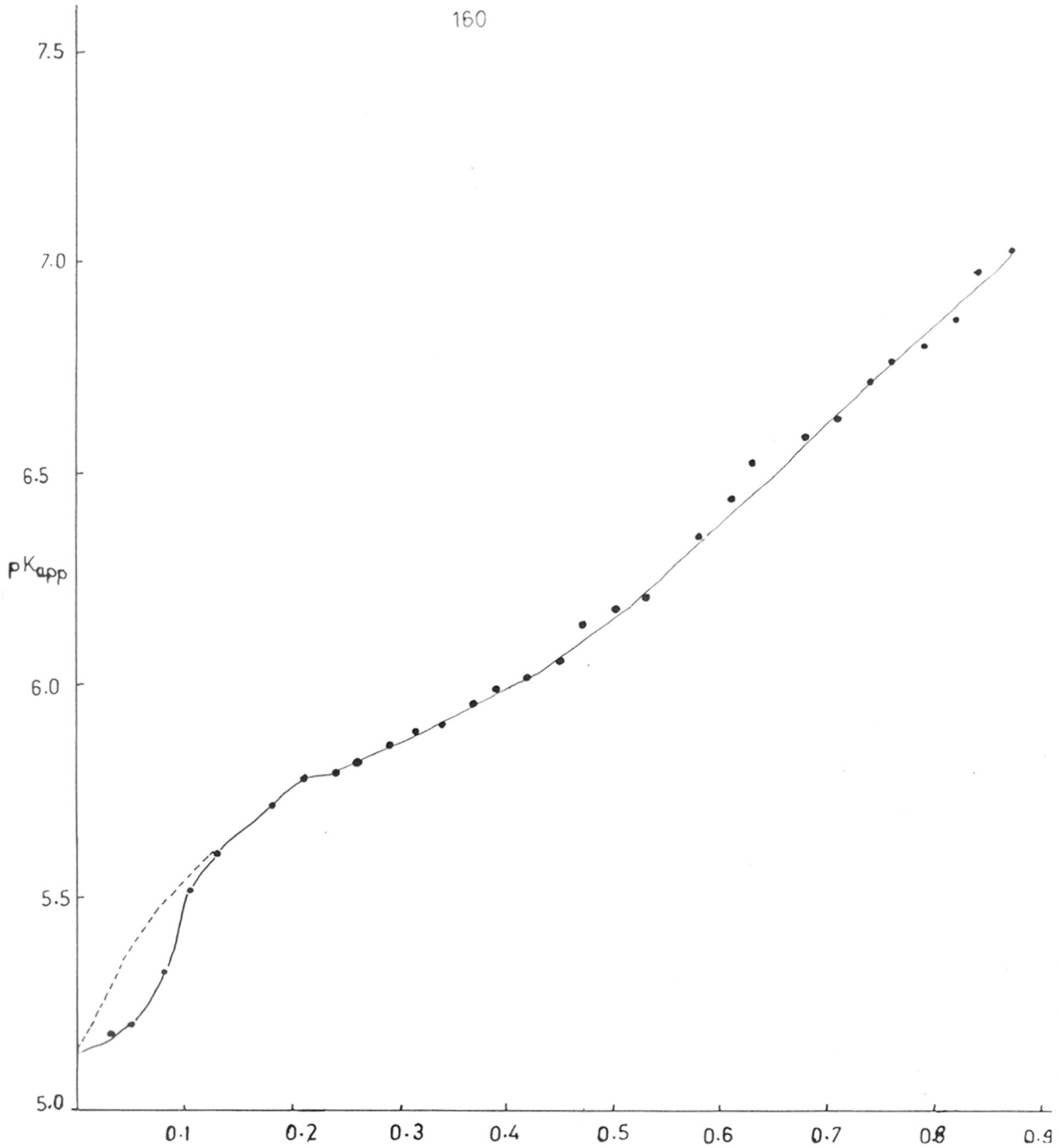


FIG. 24

POTENTIOMETRIC TITRATION OF MAC-30

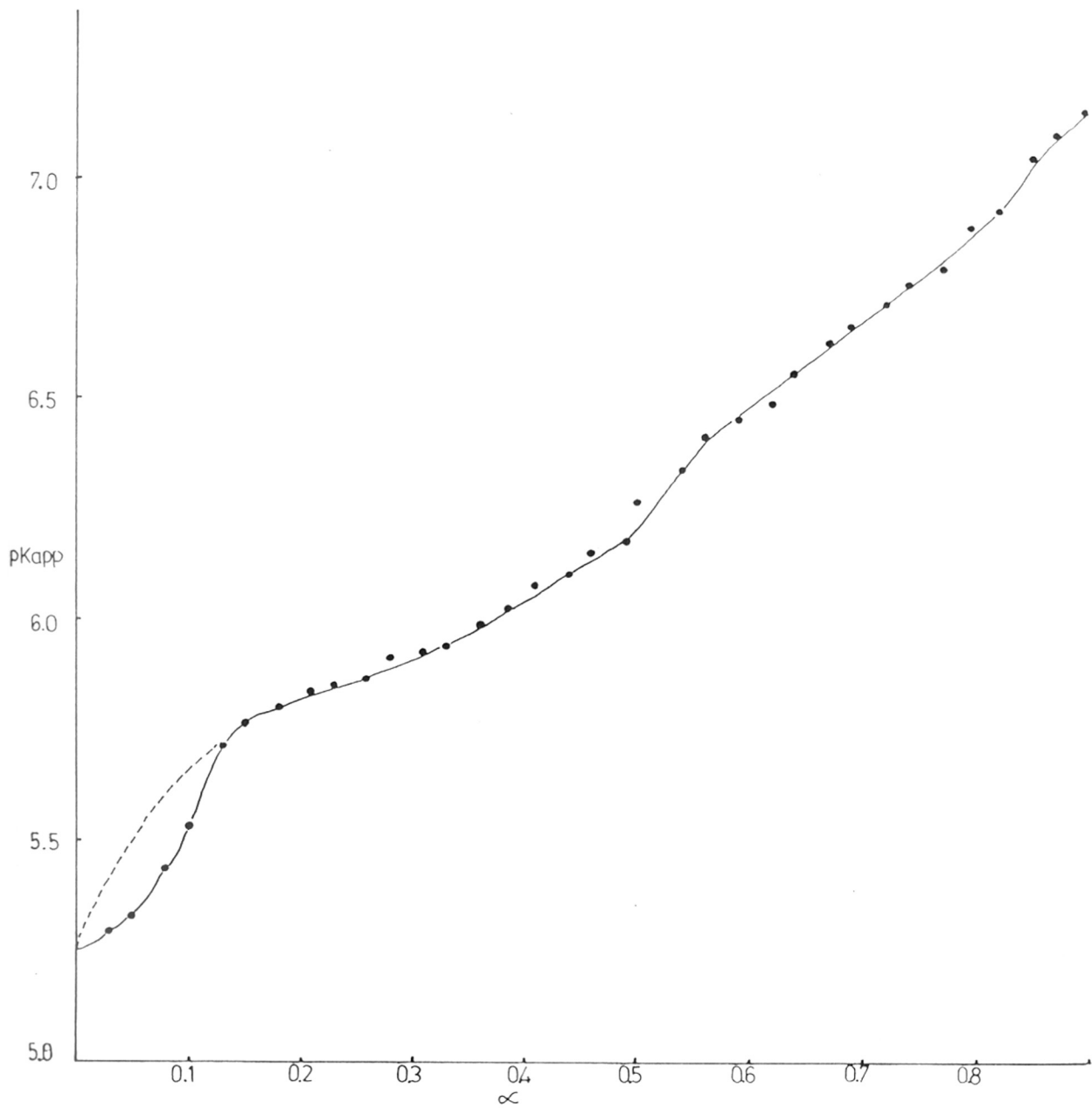


FIG. 25

POTENTIOMETRIC TITRATION OF MAC-20

Table-34pK_o and free energies of transition for acrolein-methacrylic acid copolymers

Polymer	pK _o	$\Delta F / N$ cal/mole
MAC-40	4.875	126.85
MAC-30	5.125	88.40
MAC-20	5.187	83.70
PMA	7.00	

potential within the molecule relative to its surroundings. Such conditions favour a high concentration of counter ions within the domain of the polymer molecule than in the external solution. Addition of a strong electrolyte (ion salt) such as sodium chloride to the solution causes a decrease in the extent of ionisation of the polyelectrolyte.

Poly(methacrylic acid-co-acrolein) was studied for Ca^{2+} ion sequestration capacity (CSC) at different constant pHs. Polymer molecule carrying such coordinating groups are solvated in water. The polymer molecule can form complexes with calcium ion due to the presence of coordinating carboxylic and aldehyde groups. Addition of Ca^{2+} ion beyond a certain limit (CSC), could not stabilise the complex with polymer. The excess Ca^{2+} ion reacted with sodium oxalate used as an end point indicator to form turbid calcium oxalate. The pH was adjusted using sodium hydroxide. Derivatives of Poly(methacrylic acid - co- acrolein) were formed by addition of hydroxyl amine hydrochloride and sodium bisulfite respectively. The effect of these derivatisation towards sequestering capacity were determined. Hence CSC of these reagents were determined to subtract from readings corresponding to the respective derivatised copolymers.

3.6.1 Effect of polymer composition

The CSC of the copolymer may primarily be related to the carboxylic groups. Hence, calcium sequestering capacity of poly(methacrylic acid)[PMA] was studied. Poly(acrylic acid) [PAA] was also investigated as the simplest poly(carboxylic acid). Poly(acrylic acid) exhibited a maximum capacity of 3.76 millimoles/gm at pH 10 as against that of 3.74 millimoles/gm for poly(methacrylic acid) at pH 9. This expression was misleading since this mode of expressing capacity (millimoles/gm)

does not reveal the number of calcium ions bound relative to the number of coordinating groups present in the respective polymeric sequestrant. Hence, alternatively CSC was expressed as millimoles of Ca ions/millimoles of functional groups. In this mode of expression it bears out that PMA exhibited highest capacity of 0.64 millimoles/millimoles as against 0.54 millimole/millimole for PAA. The presence of methyl groups in PMA increases the electron density around the carboxyl group through inductive effect making it a better ligand in PMA. CSC of PAA and PMA at various pH is presented in Figure 26 and the data is presented in Table 35. Also cooperative hydrophobic interaction between methyl groups, forms a polymer conformation in which methyl groups were away from solvent molecule exposing hydrophilic carboxylic groups for solvation till 30 percent ionisation. More carboxylic groups were thus made available for complexation. Increase in ionisation or neutralisation induces more carboxylic ligands for complexation. Hence for both PAA and PMA the CSC was enhanced with increase in pH upto 9 and 10 respectively. However CSC decreased with further increase in pH. Addition of potential monovalent counter-ions beyond complete neutralisation of the polyacid reduced number of free ligands available for calcium sequestration.

3.6.1.1 MAC-5

CSC of MAC-5 as a function of pH is presented in Figure 27 and data is presented in Table 36. Copolymer MAC 5 exhibited a trend similar to PMA. However, the overall capacity decreased drastically. In PMA 65 percent of carboxyl groups present were capable of complexing with Ca^{2+} . This decreased to 45 percent for copolymer MAC-5. In the copolymer, interruption of methacrylic acid by acrolein

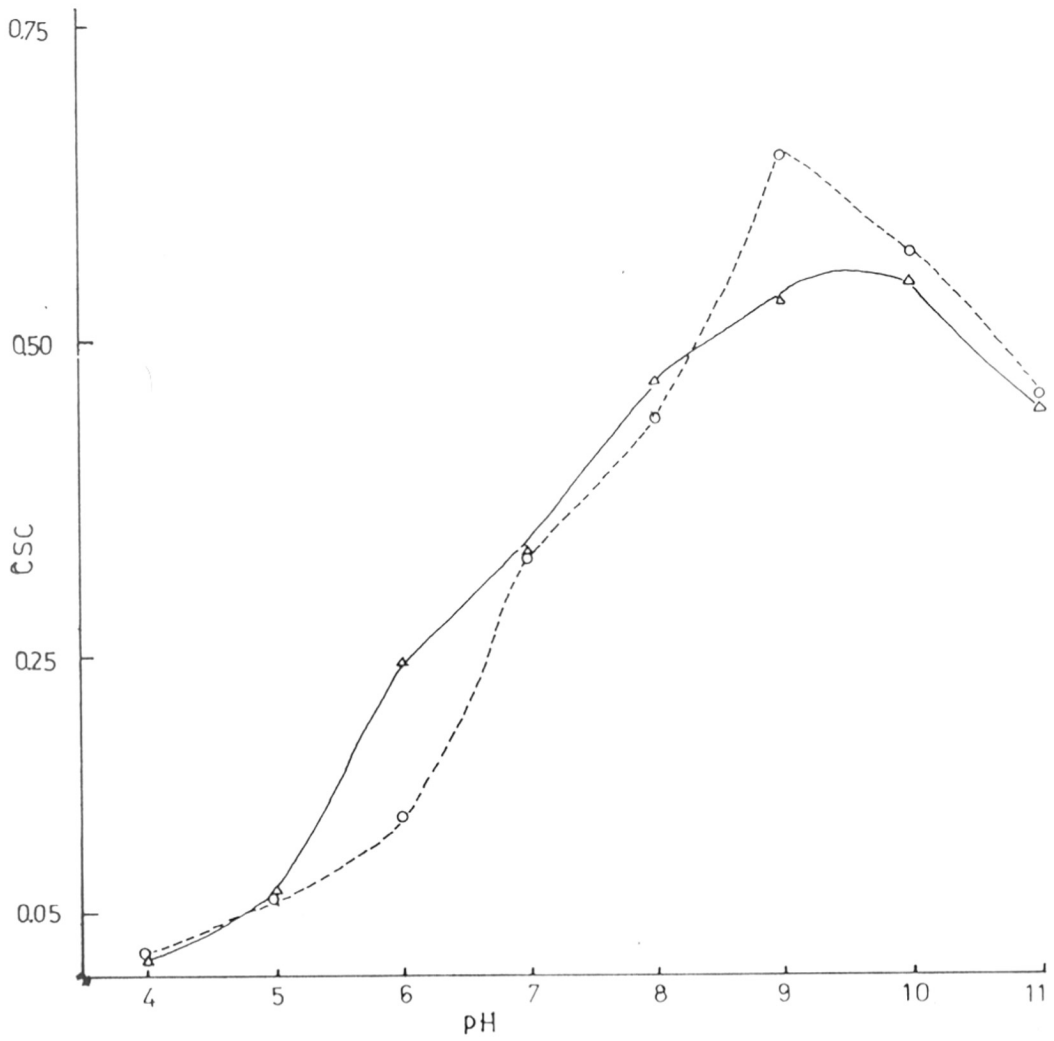


FIG. 26

CSC OF POLY(CARBOXYLIC ACID)

△ POLY(ACRYLIC ACID)

○ POLY(METHACRYLIC ACID)

Table 35

CSC of poly(acrylic acid) and poly(methacrylic acid)

pH	Poly(acrylic acid)		Poly(methacrylic acid)	
	mmole/g	mmole/mmole	mmole/g	mmole/mmole
3	0.0632			
4	0.1011	0.015	0.1068	0.018
5	0.4552	0.660	0.3161	0.0545
6	1.6944	0.244	0.7081	0.122
7	2.2760	0.328	1.8840	0.325
8	3.2497	0.468	2.5289	0.436
9	3.692	0.532	3.7428	0.645
10	3.7681	0.543	3.2750	0.565
11	3.0853	0.445	2.6427	0.456

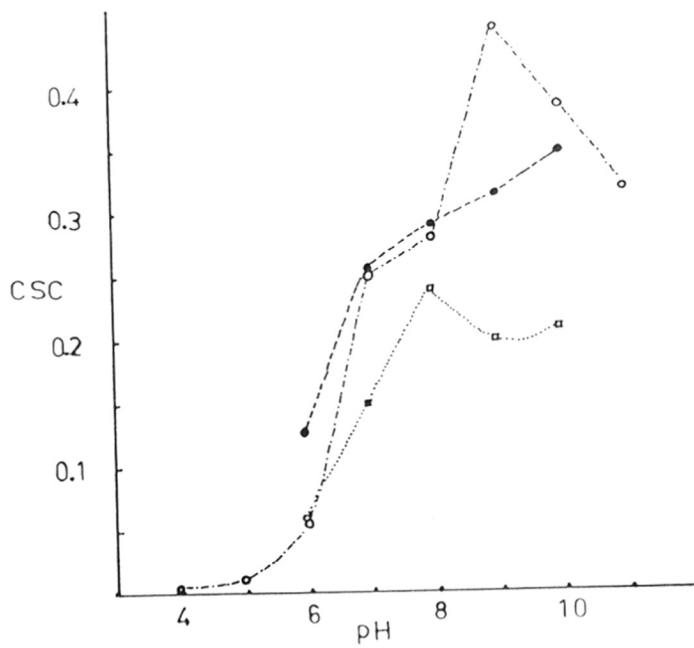


FIG. 27

CSC OF MAC-5

- POLYMER
- BISULPHITE
- OXIME

Table-36
CSC of MAC-5 and MAC-10

pH	MAC-5		MAC-10	
	mmole/g	mmole/mmole	mmole/g	mmole/mmole
4	0.0253	0.0043	0.037	0.0063
5	0.0632	0.0108	0.0759	0.0128
6	0.3161	0.0540	0.3035	0.0513
7	1.4794	0.2525	1.4541	0.2458
8	1.6438	0.2806	1.7702	0.2992
9	2.6301	0.4489	1.4541	0.2458
10	2.2507	0.3842	1.5806	0.2672
11	1.8700	0.3192	1.4789	0.2500

moieties reduces the mean sequence length of carboxyl groups. Long continuous block of carboxyl group had better solubility in water and had better sequestering ability.

3.6.1.2 MAC-10

CSC of MAC-10 as a function of pH is presented in Figure 28. The CSC varies in a zig-zag manner with pH. It increased with pH upto pH 8. It was less at pH 9, slightly higher at pH 10 and again decreased at pH 11. This behaviour is probably indicative of the cumulative effects of two different (carboxylic and aldehyde) functional groups active at differing pH.

3.6.1.3 MAC-20

CSC of MAC-20 as a function of pH is presented in Figure 29 and data is presented in Table 37. Two maxima were observed for sequestration capacity with respect to pH in copolymer MAC-20. This zigzag variation was more pronounced in this copolymer relative to MAC-10 probably due to increase in aldehyde content. Thus, second ligand (aldehyde) present in 10 mole percent is active at pH 10 wherein the carboxylate anion is less active.

3.6.1.4 MAC-30

CSC of MAC-30 as a function of pH is presented in Figure 30 and data is presented in Table 38. Copolymer MAC-30 showed an increase upto pH 8, a plateau upto pH 10 followed by a further rise at pH 11. Two maxima were not observed as in MAC-10 and MAC-20. Reduction in the sequestration capacity due to reduced

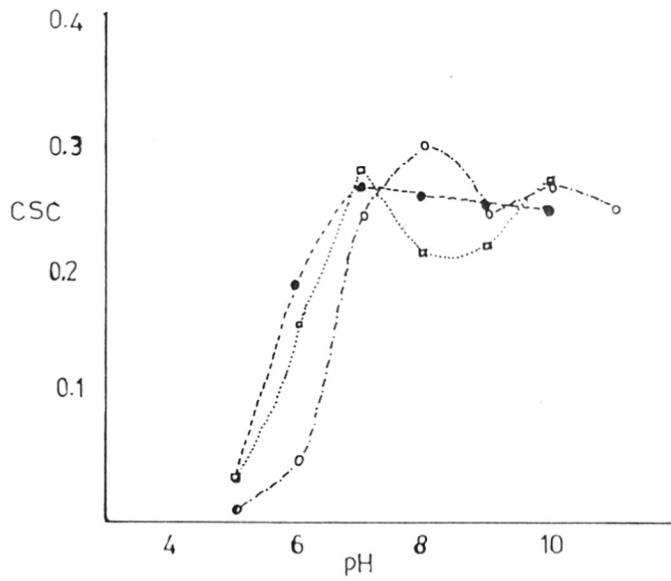


FIG. 28

CSC OF MAC-10

- POLYMER
- BISULPHITE
- OXIME

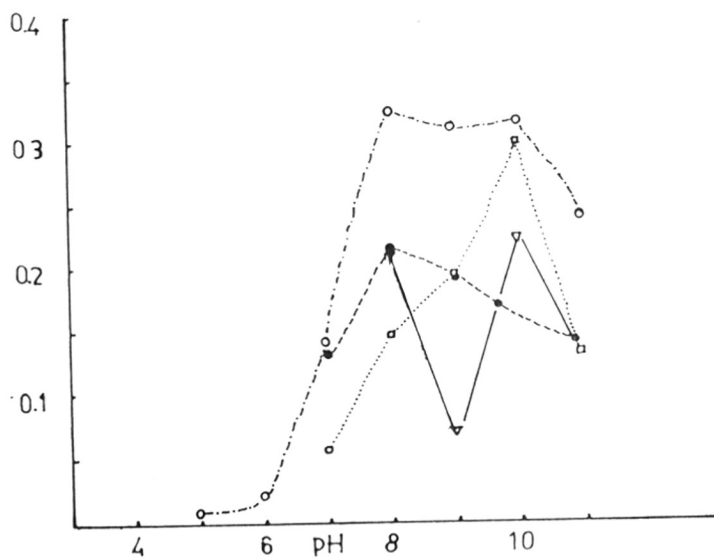


FIG. 29

CSC OF MAC-20

- POLYMER
- ◻ BISULPHITE
- OXIME
- ▽ POLYMER + NaCl

Table-37
CSC of MAC-20

pH	MAC-20		MAC-20 + NaCl	
	mmole/g	mmole/mmole	mmole/g	mmole/mmole
4	0.0253	0.0042	-	-
5	0.0569	0.0094	-	-
6	0.2908	0.0483	-	-
7	0.8472	0.1406	-	-
8	1.9599	0.3253	1.264	0.1049
9	1.8840	0.3128	0.4045	0.0335
10	1.9220	0.3190	1.3651	0.1133
11	1.4541	0.2414	0.8595	0.0713

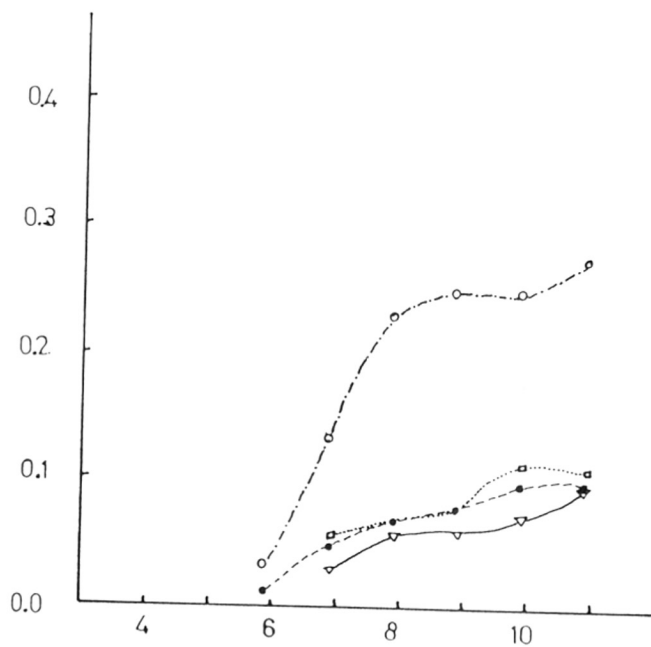


FIG. 30

CSC OF MAC-30

○ POLYMER

□ BISULPHITE

● OXIME

▽ POLYMER + NaCl

Table-38
CSC of MAC-30

pH	MAC-30		MAC-30 + NaCl	
	mmole/g	mmole/mmole	mmole/g	mmole/mmole
4	0.0190	0.0029	-	-
5	0.0569	0.0088	-	-
6	0.2023	0.0312	-	-
7	0.8472	0.1306	0.2528	0.0195
8	1.4921	0.2299	0.3539	0.0273
9	1.6059	0.2474	0.4045	0.0312
10	1.5932	0.2455	0.4550	0.0351
11	1.7576	0.2708	0.6067	0.0467

mean sequence length of methacrylic units and increase in the capacity due to the contribution of aldehyde groups tend to balance each other in the pH range of 8 to 10.

3.6.1.5 MAC-40

CSC of MAC-40 as a function of pH is presented in Figure 31 and data is presented in Table 39. Interruption of methacrylic acid sequences would be maximum for this copolymer with 40 mole percent acrolein, ought to decrease the CSC to make it the lowest in the series. This was not observed. Between pH 8 and 11 the copolymer had the highest CSC excepting MAC 5 at pH 9. This copolymer composition (MAC-40) is an azeotropic one for the system. Hence, the copolymer composition should be uniform and the distribution of monomer units along the chain ought to be random. This would not be the case with other copolymers in this series. Aldehyde may be presumed to act as a ligand in alkaline pHs by hydrating to produce two hydroxyl groups on the same carbon. This unstable hydrate would be stabilised only when coordinated in a metal complex. Hence, further addition of sodium hydroxide to increase the pH beyond 10 increased the number of complexing groups. This is reflected in the increase in CSC at pH 11.

In the present study, complete neutralisation of copolymers were achieved at pH 10. Maximum CSC in all cases should be approximately proportional to the number of sequestering groups present in the copolymer. However, this varied from 0.65 to 0.26 relative to the number of functional groups. As a general observation, polyelectrolyte remains water soluble if more than 20 percent ionisable groups are present. The remaining 80 percent of the groups should sequester 40 percent Ca^{2+} ions. The observed maximum capacity was one half of theoretical maximum

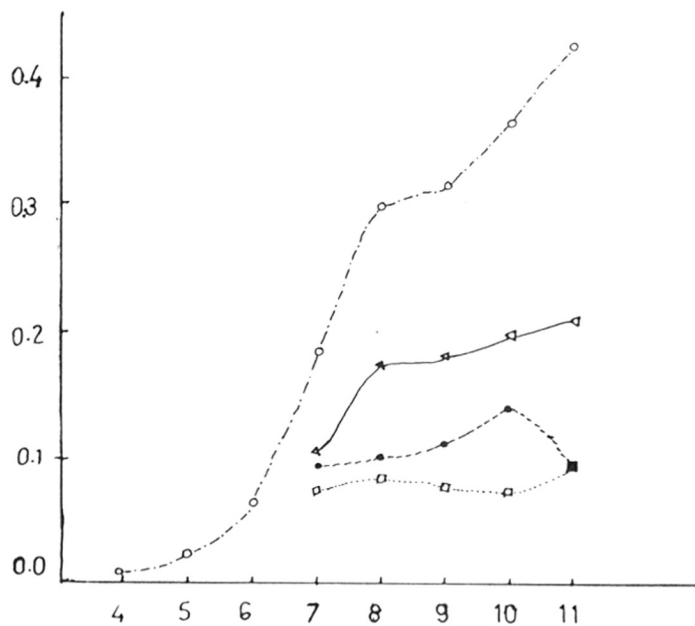


FIG. 31

CSC OF MAC-40

○ POLYMER

◻ BISULPHITE

● OXIME

◄ POLYMER + NaCl

Table-39
CSC of MAC-40

pH	MAC-40		MAC-40 + NaCl	
	mmole/g	mmole/mmol	mmole/g	mmole/mmol
4	0.0632	0.0094	-	-
5	0.1770	0.0262	-	-
6	0.4552	0.0674	-	-
7	1.2518	0.1854	0.7163	0.1061
8	2.0105	0.2978	1.1797	0.1748
9	2.1369	0.3166	1.1797	0.1797
10	2.4657	0.3654	1.3483	0.1998
11	2.8956	0.4290	1.4325	0.2122

capacity in copolymer MAC-20 and MAC-30. This was due to the nonavailability of carboxyl group arising from conformations such as random coil or globular one. To study this effect of ionising groups, the copolymers were derivatised with hydroxylamine hydrochloride to form nonionising chelating group i.e. oxime, while bisulfite was ionising chelating group.

3.6.2 Effect of pH

CSC is controlled by pH in two modes. Conformation and ionisation of copolymers are pH dependent. The copolymers change from random coil to globular conformation on ionisation with increase in pH. The conformation controls the type of ligand available for sequestration while ionisation dictates the concentration of ionisable ligand. The two factors act synergistically to control capacity of sequestration. Ease of substitution of mono-valent ion by bi-valent ion increases with the size of counterion. Hence, sodium counterion is more easily replaceable than H^+ by bi-valent calcium. Sodium salt of polymer shows greater sequestering capacity compared to the parent polyacid. In general, CSC increases with pH till complete neutralisation of the acid. CSC as a function of pH for the copolymers, the copolymers in presence of sodium chloride, their bisulphite and oxime derivatives are shown in Figure 27-31.

3.6.3 Effect of mean sequence length

The mean sequence length (MSL) of methacrylic acid in the copolymer would increase with the methacrylic acid content. The data of CSC of copolymers at its maximum capacity with MSL is presented in Table 40. It indicates that the effect of MSL of methacrylic acid would predominate in copolymers with 97.5 and 95

Table-40

Mean Sequence Length of methacrylic acid and maximum CSC

Sample	pH	Maximum CSC	Mean Seq. Length
MAC 5	9	0.4489	17.8979
MAC 10	8	0.2992	8.9311
MAC 20	8	0.3253	3.9533
MAC 30	11	0.2708	2.4284
MAC 40	11	0.4290	1.4267

mole percent methacrylic acid units MAC-5 and MAC-10 respectively. Excepting MAC-40, higher MSL corresponded to higher capacity in all the polymers. MAC-40 has the lowest MSL. The maximum capacity of this copolymer is comparable to that of MAC-5. Thus, MSL dictates CSC when contribution of aldehyde is not appreciable to compensate for the loss in capacity due to reduced MSL of carboxylic units.

3.6.4 Effect of derivatisation

Pendent aldehyde was derivatised with hydroxyl amine to form oxime and with bisulphite to form bisulphite adduct. Oxime has two nonionic ligands in nitrogen and hydroxyl group. Bisulphite adduct has two ligands, bisulphite as ionising and hydroxyl as nonionising ligand. Aldehyde is monodentate and in hydrated form may act as bidentate ligand. Aldehyde group is modified by derivatisation. The acrolein bisulphite adduct and acrolein oxime derivatives of polyacrolein were investigated for CSC to evaluate the exclusive contribution of derivative to the sequestration. The data is presented in Table 41. Poly(acrolein oxime) precipitated above pH 8. Poly(acrolein-bisulphite) had the highest CSC at pH 3 which decreased with pH till 7 but increased at pH 8 and 9. Bisulphite adduct is a strong ionising polyelectrolyte at pH 3, which contributed to the capacity. Addition of sodium hydroxide neutralised it. This reduced the number of sequestering groups. Further addition of the alkali generated sodium salt (SO_3Na) which contributed to the sequestration. In general, maximum capacity of both the derivatives were very low, not more than 4.8 mole percent. The data of CSC of both the derivatives of the copolymers is presented in Tables 42-46 respectively

Table-41

CSC of Hydroxyl amine and bisulphite derivatives of polyacrolein

pH	Poly(acrolein bisulphite)		Poly(acrolein oxime)	
	mmole/g	mmole/mmole	mmole/g	mmole/mmole
3	0.1517	0.0485		
4	0.0758	0.0243	0.1517	0.0216
5	0.0506	0.0162	0.2023	0.0288
6	0.0506	0.0162	0.2528	0.0359
7	0.0506	0.0162	0.2528	0.0359
8	0.0758	0.0243	precipitation	
9	0.1011	0.0324	precipitation	
10	0.0506	0.0162	precipitation	

Table-42
CSC of derivatives of MAC-5

pH	oxime		bisulphite	
	mmole/g	mmole/mmole	mmole/g	mmole/mmole
3	0.0632	0.0108	0.0253	0.0043
4	0.0759	0.0130	0.0379	0.0065
5	0.2276	0.0388	0.0759	0.0130
6	0.7334	0.1252	0.6828	0.1165
7	1.5174	0.2590	0.8851	0.1511
8	1.7197	0.2935	1.4162	0.2417
9	1.8461	0.3151	1.1886	0.2029
10	2.0484	0.3496	1.2645	0.2158

Table-43
CSC of derivatives of MAC-10

pH	oxime		bisulphite	
	mmole/g	mmole/mmole	mmole/g	mmole/mmole
3	0.0126	0.0021	0.0253	0.0043
4	0.0064	0.0064	0.0632	0.0107
5	0.2276	0.0385	0.2023	0.0342
6	1.1127	0.1881	0.9357	0.1582
7	1.5679	0.2651	1.6438	0.2779
8	1.5426	0.2606	1.2645	0.2138
9	1.5174	0.2565	1.3150	0.2223
10	1.4668	0.2480	1.5932	0.2693

Table-44

CSC of derivatives of MAC-20

pH	oxime		bisulphite	
	mmole/g	mmole/mmol	mmole/g	mmole/mmol
4	0.0379	0.0033	0.0379	0.0033
5	0.0506	0.0083	0.0632	0.0549
6	0.1138	0.0189	0.1264	0.0210
7	0.4931	0.0818	0.7840	0.1320
8	0.8851	0.1469	1.2897	0.2140
9	1.1886	0.1974	1.1886	0.1974
10	1.8208	0.3022	0.9610	0.1596
11	0.8093	0.1344	0.8598	0.1426

Table-45
CSC of derivatives of MAC-30

pH	oxime		bisulphite	
	mmole/g	mmole/mmole	mmole/g	mmole/mmole
4	0.0506	0.0078	0.0253	0.0039
5	0.0632	0.0097	0.0379	0.0058
6	0.0759	0.0117	0.0632	0.0097
7	0.3035	0.0468	0.3540	0.0544
8	0.4299	0.0663	0.4552	0.0701
9	0.5058	0.0779	0.5058	0.0779
10	0.6322	0.0974	0.7081	0.1092
11	0.6322	0.0974	0.6828	0.1052

Table-46
CSC of derivatives of MAC-40

pH	oxime		bisulphite	
	mmole/g	mmole/mmole	mmole/g	mmole/mmole
4	0.0632	0.0094	0.0253	0.0037
5	0.0759	0.0112	0.0506	0.0075
6	0.2276	0.0337	0.2280	0.0338
7	0.6575	0.0974	0.5311	0.0786
8	0.6828	0.1012	0.5817	0.0862
9	0.7587	0.1124	0.5564	0.0824
10	0.9610	0.1424	0.5311	0.0787
11	0.6322	0.0936	0.6575	0.0974

3.6.4.1 Bisulphite derivative

In presence of acid, bisulfite adduct reversibly transformed into the aldehyde. Hence the derivatisation may not be stable in acidic pH range. The capacity for bisulfite derivative of MAC-5, was reduced to 60 percent at pH 7 but was restored to 90 percent at pH 8 and drastically reduced to 45 and 56 percent at pH 9 and 10 respectively. The maximum CSC in bisulfite derivative of MAC-5 and MAC-20 was at pH 8, as in parent copolymer. However, the capacity reduced upon derivatisation from 0.44 to 0.24 for MAC-5, from 0.30 to 0.28 for MAC-10. MAC-10 copolymer exhibited maximum capacity at pH 8. This maxima shifted to pH 7 on derivatisation. At pH 8, the capacity of bisulfite of MAC-10 was reduced to 71 percent relative to the parent copolymer. At all other pH, it was 90 percent of the copolymer. This indicates that around 10 percent contribution in CSC arises from the aldehyde group. Thus, it implies that for MAC-10 with all other factors remaining constant, conformation remains unaltered upon derivatisation while for other copolymers this might be changing.

3.6.4.2 Oxime derivative

Oxime formation reduced the capacity of MAC-5 by 10 percent at pH 10 indicating marginal contribution of aldehyde group. At pH 9, the capacity was reduced to 70 percent. The maximum capacity of MAC-20 was marginally reduced on derivatisation from 0.32 to 0.30. In all other cases, derivatisation drastically reduced sequestering capacity by as much as 35 percent (MAC-40). The contribution of aldehyde groups to CSC are appreciable in MAC-30 and MAC-40. Here oxime

derivatisation drastically reduced the CSC. The maximum capacity shifted to higher pH in oximes relative to the bisulphite derivatives. The maximum CSC is achieved after complete neutralisation of bisulphite.

3.6.5 Presence of electrolyte

In the presence of salt, sequestration due to ionising ligands would be suppressed while that due to nonionising ligand would only be marginally affected. The differing capacities of ionising and nonionising ligands can be checked by the addition of salt to the solution. Hence, CSC of some copolymers and their derivatives were studied in 0.09 molar sodium chloride solution at selected pH. The data is presented in Table 47. In the presence of sodium chloride CSC of MAC-30 was reduced to 35 percent of its original capacity while that of MAC-20 and MAC-40 were reduced to 60 and 70 percent of the original capacity respectively. This indicates that more contribution to sequestration came from carboxylic group in MAC-20 and MAC-30. This was less in MAC-40. CSC of bisulphite of MAC-40 was unaffected, the effect was marginal for MAC-30, but reduced to 58 percent for MAC-10. Thus, contribution to CSC in MAC-40 bisulfite derivative is from nonionising ligands.

3.6.6 Conclusion

The calcium sequestering ability was dependent on:

- (a) extent of ionisation of carboxylic group,
- (b) mean sequence length of carboxylic block,
- (c) uniformity of monomer sequence distribution,
- (d) complexing ability due to aldehyde.

The resultant sequestering capacity is from the combination of these factors.

Table-47

CSC of copolymer derivatives in presence of NaCl

Sample	pH	mmol/g	mmol/mmol
MAC-5 oxime	10	0.9859	0.1683
MAC-5 oxime	11	0.9101	0.1553
MAC-10 oxime	10	0.6573	0.1111
MAC-10 bisulphite	8	0.6826	0.1154
MAC-10 bisulphite	11	0.9354	0.1581
MAC-20 oxime	10	0.9606	0.1595
MAC-20 oxime	11	0.7078	0.1175
MAC-20 bisulphite	8	0.9606	0.1595
MAC-20 bisulphite	11	0.6699	0.1112
MAC-30 bisulphite	10	0.6573	0.1013
MAC-30 bisulphite	11	0.6573	0.1013
MAC-40 bisulphite	10	0.5334	0.0796
MAC-40 bisulphite	11	0.6575	0.0974

3.7 CHARACTERISATION USING DIFFERENTIAL SCANNING CALORIMETER

Differential scanning calorimeter is uniquely suited to the studies of enthalpy changes accompanying phase changes and chemical processes. The heat of reactions is recorded as endotherm or exotherm against temperature (thermograms). Similar study can be carried out at constant temperature (isothermal). Knowledge of amount of heat liberated during the course of reaction can be utilised to estimate kinetics of curing in thermosetting resins. It is used not only for isothermal mode but also in the dynamic mode at different heating/cooling rates. The isothermal cure curve is obtained by stepwise integration of the thermogram as a function of time. It is necessary to express heats of reaction as a fraction of total heat change (H/H_0), where H is fraction of heat change and H_0 is total heat change. This is because the total heat of reaction varies with the curing temperature. The same behaviour would be expected of any thermosensitive reaction which can be stopped by lowering the reaction temperature.

3.7.1 Kinetic parameters

Rogers²⁰² method is used for obtaining kinetic parameters. The necessary data are present in a DSC curve run at constant heating rate in covered cells. The data are distances measured between the reaction curve and the base line (scanning) at associated absolute temperatures. The distance measured is proportional to the rate of heat evolution or absorption at that temperature. This rate is proportional to the rate constant. As many distances as possible are measured between the onset and maximum of the curve. The logarithm of the distance is plotted against $1/T$ in

degrees K. The best straight-line portion is chosen. The distances at the extremes, d_1 and d_2 with corresponding temperatures $1/T_1$ and $1/T_2$ are put into the equation:

$$-E = \frac{4.58 \log (d_1/d_2)}{(1/T_1) - (1/T_2)}$$

The distances enter only as a ratio, so that proportionality constants cancel. Neither mass nor heat of reaction needs to be known. The Arrhenius plot should be linear over a reasonable range. E will appear as kcal/mole. Caution must be exercised not to exceed dynamic range of the DSC and to contain the reaction and products within the sample cell. Some consideration of phase of the sample during the reaction must also be made, especially when the data are compared to literature values.

Given E from the previous calculation, the heating rate B, and the temperature at maximum, T_{\max} , it is possible to calculate the pre-exponential factor A with:

$$A = \frac{BE e^{E/RT_{\max}}}{RT_{\max}^2}$$

The method is totally independent of sample mass and is operable so long as the kinetic order of the reaction is not significantly different from 1 and the above precautions are observed.

In polyacrolein, structural features vary with the mode of polymerisation²⁰³. In the acrolein-acrylic acid copolymers structural features change with feed and copolymer composition^{19,3}. Acrolein-acrylic acid, acrolein-methacrylic acid copolymers and novolak type polymers prepared from acrolein copolymers were studied using DSC. These are presented in Figures 30-35.

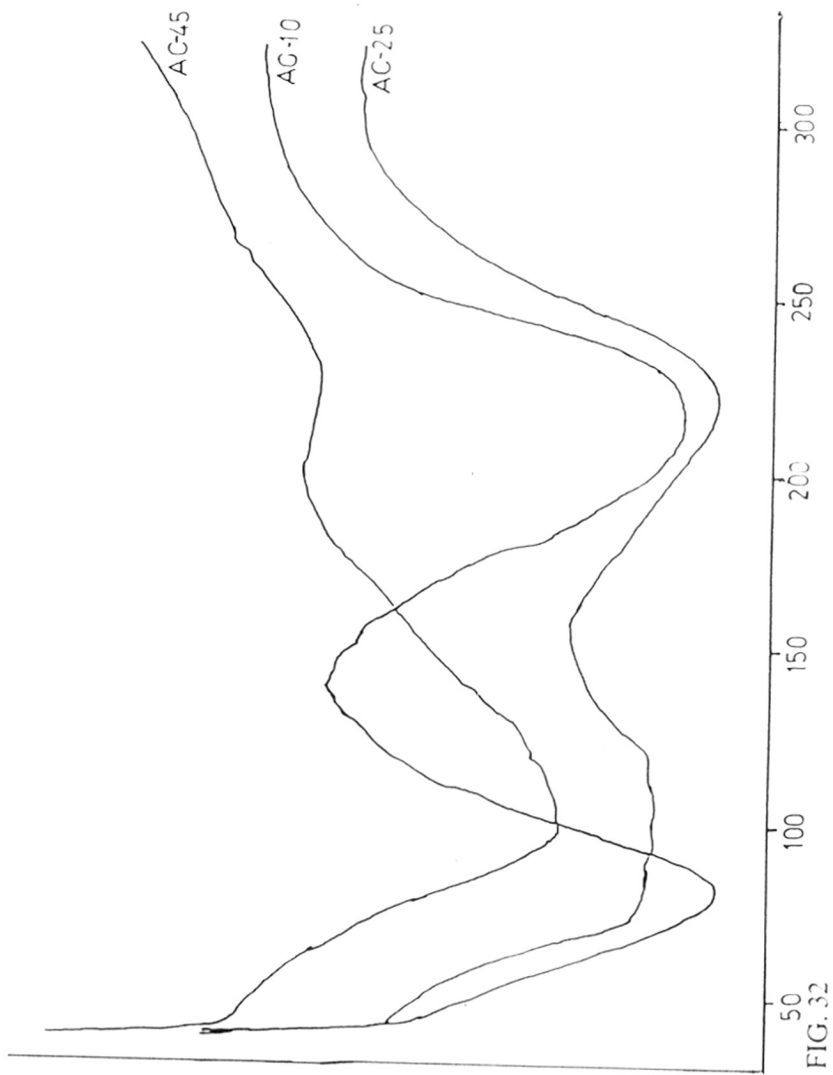


FIG. 32

THERMOGRAMS OF ACROLEIN-ACRYLIC ACID COPOLYMERS IN HOMOGENEOUS RANGE

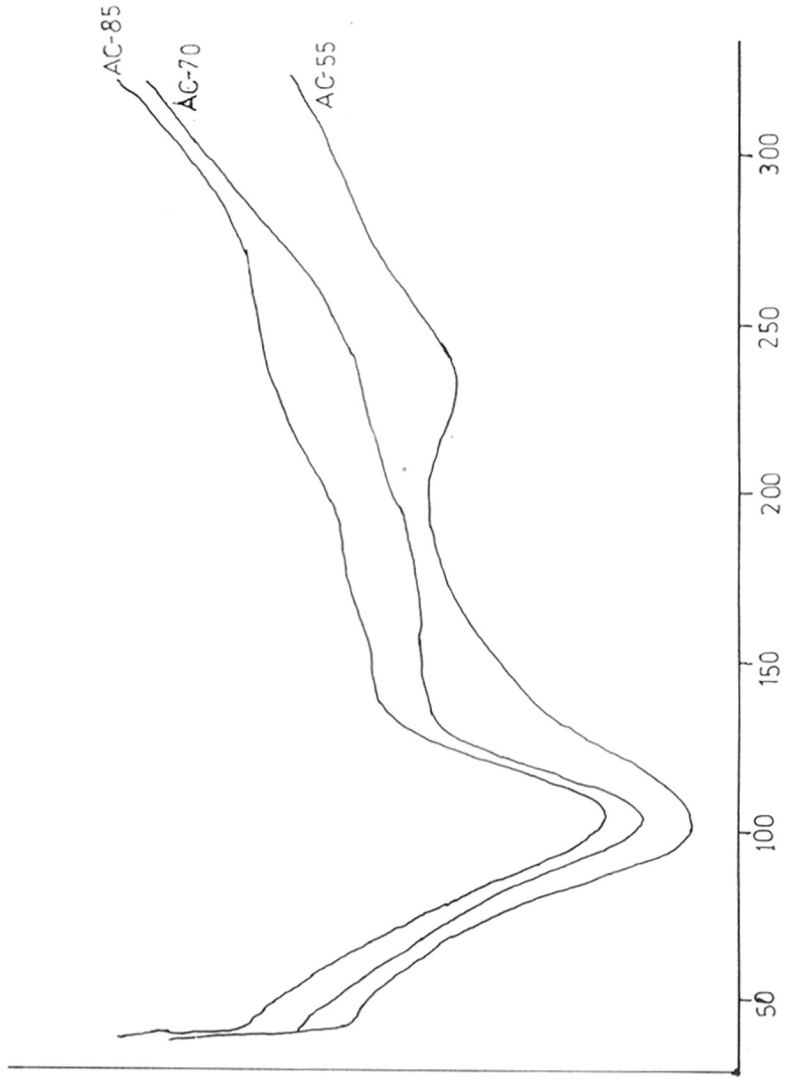


FIG. 33

THERMOGRAMS OF ACROLEIN-ACRYLIC ACID COPOLYMERS IN HETEROGENEOUS RANGE

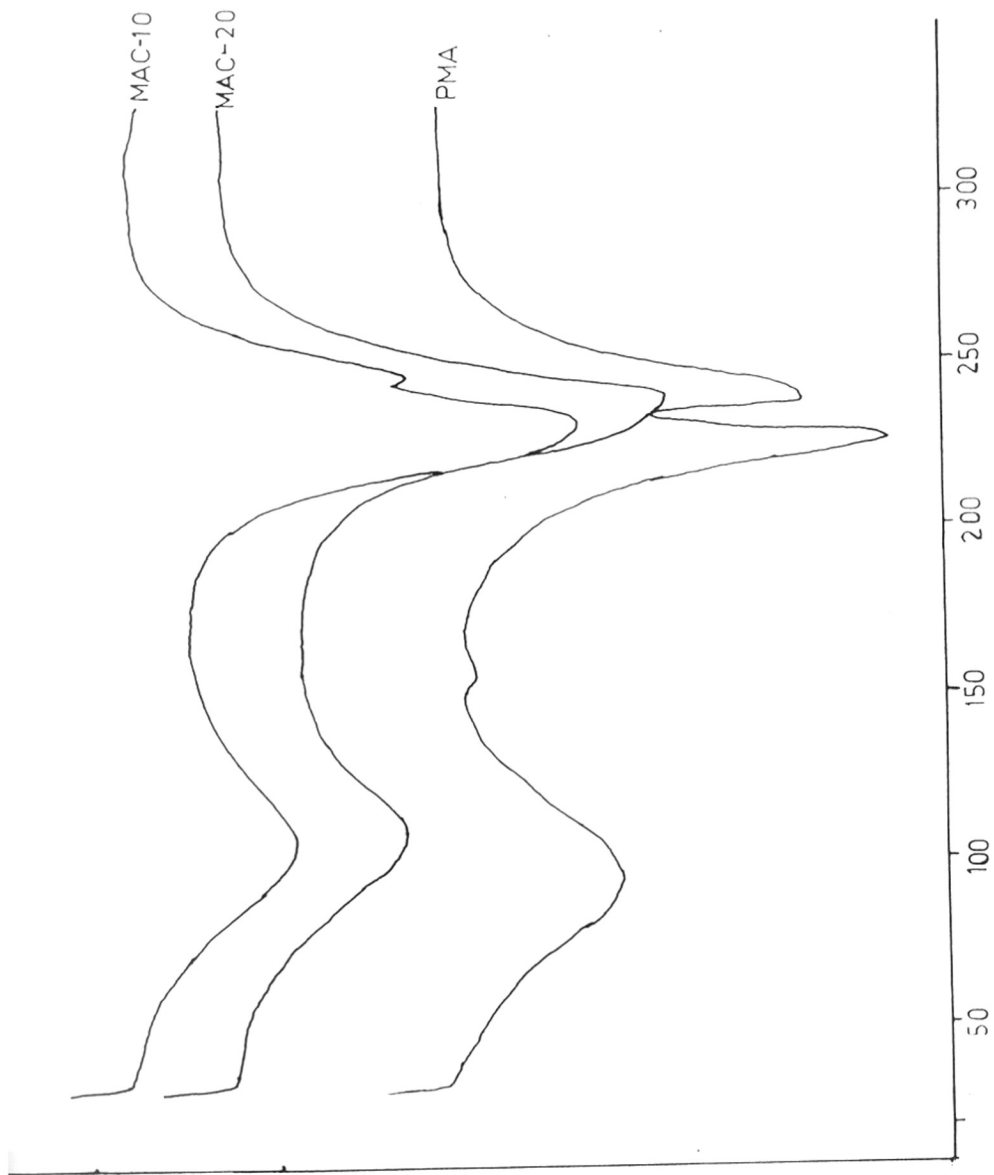


FIG. 34

THERMOGRAMS OF ACROLEIN-METHACRYLIC ACID COPOLYMERS

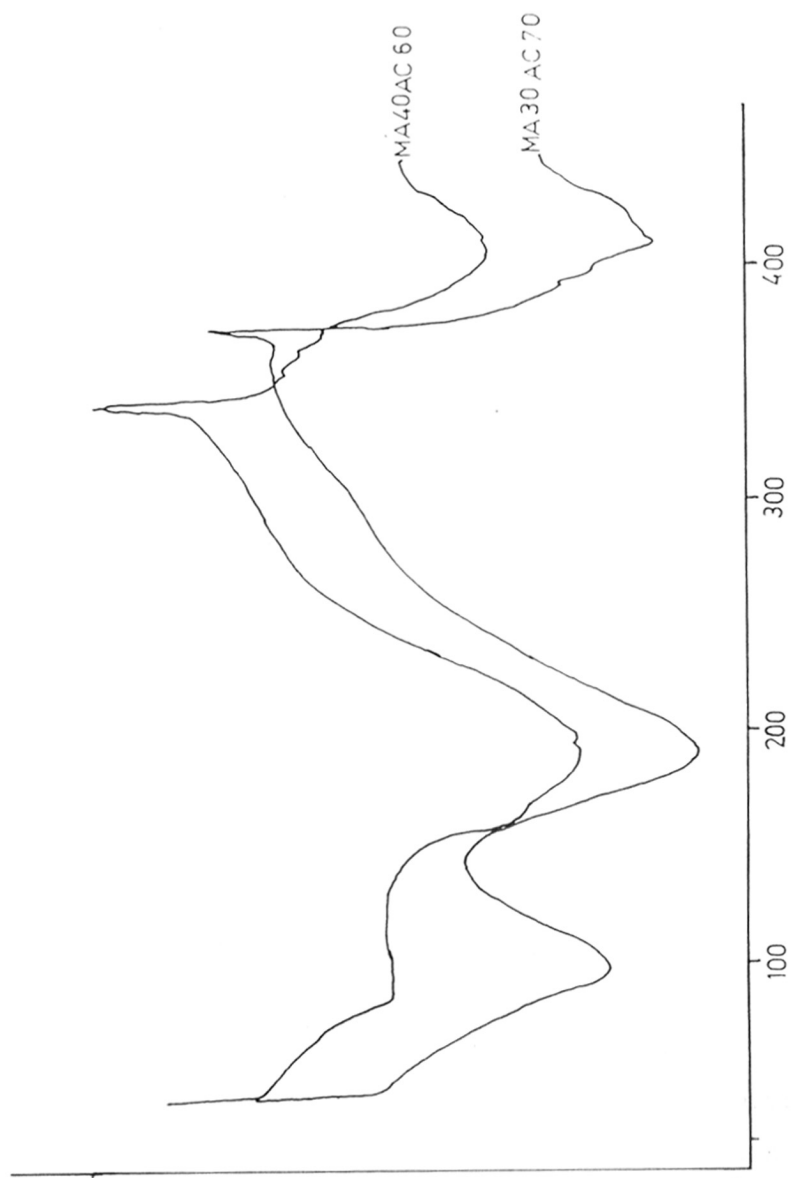


FIG. 35

THERMOGRAMS OF ACROLEIN-METHACRYLIC ACID COPOLYMERS

3.7.2 Acrolein-acrylic acid copolymer

Copolymers prepared from homogeneous reactions like AC-10, AC-25 and AC-45 show two endothermic transitions. One in the range of 80-95°C and the other in the range of 215-230°C. The polymers obtained from phase separated reactions like AC-55, AC-70 and AC-85 show transition only in the temperature range of 215-230°C. In AC-55 the low temperature transition was shifted to 100-105°C. In the case of polyacrolein, one endothermic transition at 105°C and an exothermic transition near 205°C was observed. Incorporation of upto 0.45 mole percent of acrylic acid in the copolymer shifted higher transition temperature to 230°. Incorporation of more acrylic acid in the copolymer shifted lower transition temperature to still lower side (from 105 to 80°).

3.7.3 Acrolein-methacrylic acid copolymer

Poly(methacrylic acid) shows two endothermic transitions. One near 100 and another near 225°C. The higher transition temperature goes through a maxima corresponding to 5 mole percent of acrolein in this copolymer series. Introduction of 5 mole percent of acrolein units in the polymer shifted the higher transition temperature from 225 to 240°C. Incorporation of more acrolein moieties decreased the transition to the range 175-215°C. Lower temperature transition vanished when methacrylic acid content was decreased below 60 mole percent while second transition is shifted to 175-215°C.

3.7.4 Novolaks prepared from acrolein copolymers

Phenol and m-cresol were reacted with acrolein-methacrylic acid copolymer. Similarly m-cresol was reacted with acrolein-styrene copolymer. Curing of these polymers with hexamethylene tetra amine (Hexa) was investigated. Pure hexa decomposes above 300°C. It cures the polymers in the range 120-150°C. Curing

behaviour of copolymers of 40 mole percent acrolein with styrene and methacrylic acid modified with m-cresol are presented in Figures 36 and 37 respectively. Temperature range of curing exotherms were studied with 2-8 weight percent hexa in nonisothermal mode. The isothermal curing temperatures were selected for the study. The samples were then maintained isothermally at selected temperatures. Corresponding ΔH were calculated. The curing rate was maximum at 137.5°C with 2 weight percent hexa. This temperature shifted to 135°C with increases in hexa content (4, 6 and 8 weight percent). The data is presented in Table 48-51. Such exotherms were not apparent with acrolein-methacrylic acid copolymer because the small exotherm in the curing temperature region is compensated by the highly endothermic transition displayed by the parent polymer (See Figure 36-37). Hence isothermal curing studies did not yield interpretable data.

Table-48

Curing of AC-40ST with 2 weight percent hexa

Temperature range 130-145°C

 $\Delta H = 6.8 \text{ J/gm}$ $E_a = 343 \text{ kJ/mol}$

Temperature	ΔH	ΔH	Time
°C	mJ	J/g	minutes
130.0	100	6.9	1.43
132.5	171	11.5	1.28
135.0	186	9.8	1.25
137.5	161	10.7	1.23
140.0	139	9.6	1.20
142.5	100	9.0	1.05
145.0	72	6.2	1.03

Table-49

Curing of AC-40ST with 4 weight percent hexa

Temperature range 130-145°C

 $\Delta H = 15.3 \text{ J/gm}$ $E_a = 322 \text{ kJ/mol}$

Temperature °C	ΔH mJ	ΔH J/g	Time minutes
115	67	4.3	1.60
120	390	27.4	1.95
125	609	42.7	1.88
130	1132	74.4	1.98
135	2006	156.1	2.05
140	1505	107.7	1.88
145	1047	90.3	1.55

Table-50

Curing of AC-40ST with 6 weight percent hexa

Temperature range 130-144°C

 $\Delta H = 9.05 \text{ J/gm}$ $E_a = 345 \text{ kJ/mol}$

Temperature	ΔH	ΔH	Time
°C	mJ	J/g	minutes
130.5	1423	925	2.38
132.5	889	62.9	2.15
135.0	3695	259.1	2.72
137.5	1094	89.8	1.90
140.0	1362	122.7	2.02

Table-51

Curing of AC-40ST with 8 weight percent hexa

Temperature range 130-145°C

 $\Delta H = 10.4 \text{ J/gm}$ $E_a = 356 \text{ kJ/mol}$

Temperature	ΔH	ΔH	Time
°C	mJ	J/g	minutes
130.0	678	47.6	2.25
132.5	569	34.05	2.08
135.0	1673	117.7	2.33
137.	1424	103.6	2.23
140	844	61.5	1.75

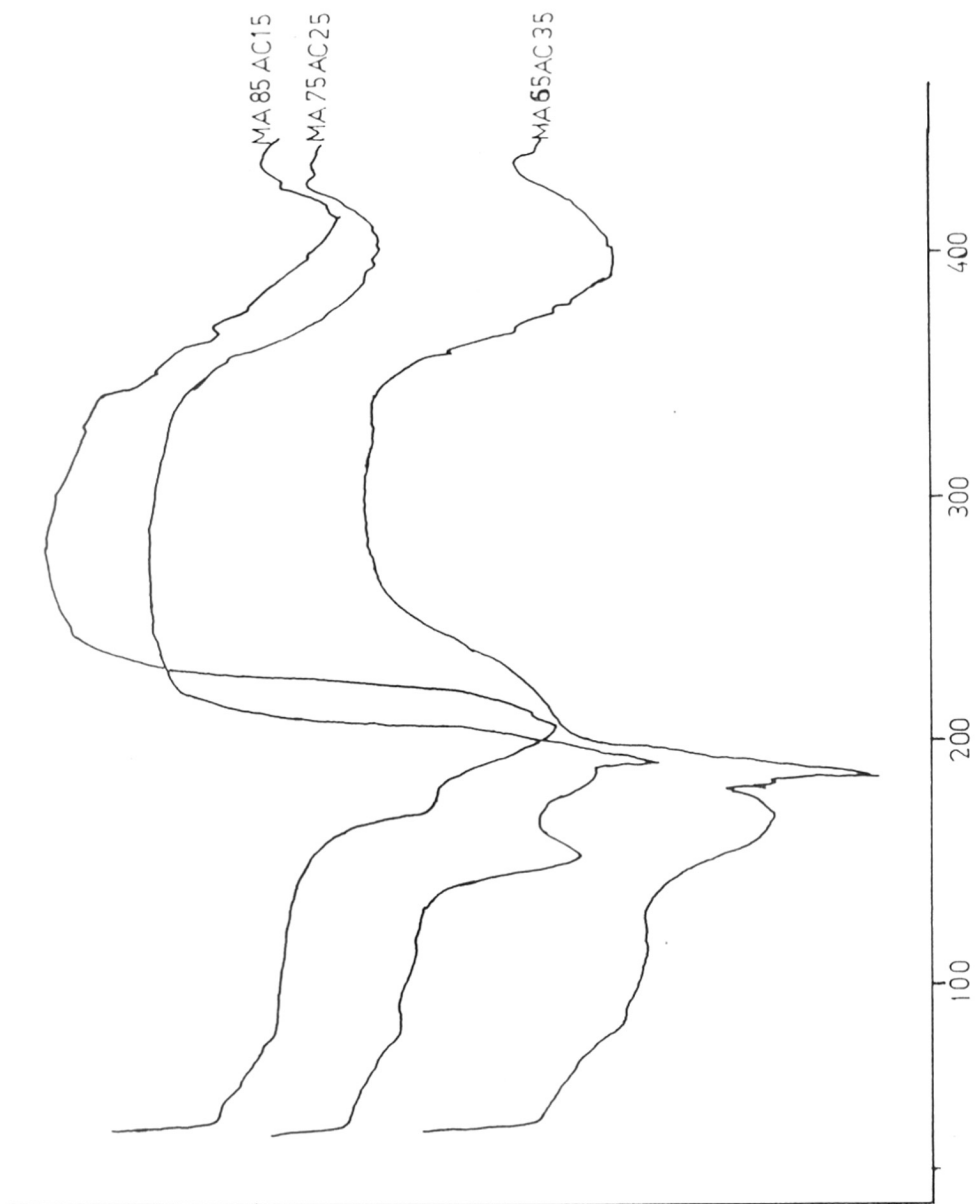


FIG. 36

THERMOGRAMS OF ACROLEIN-METHACRYLIC ACID COPOLYMERS

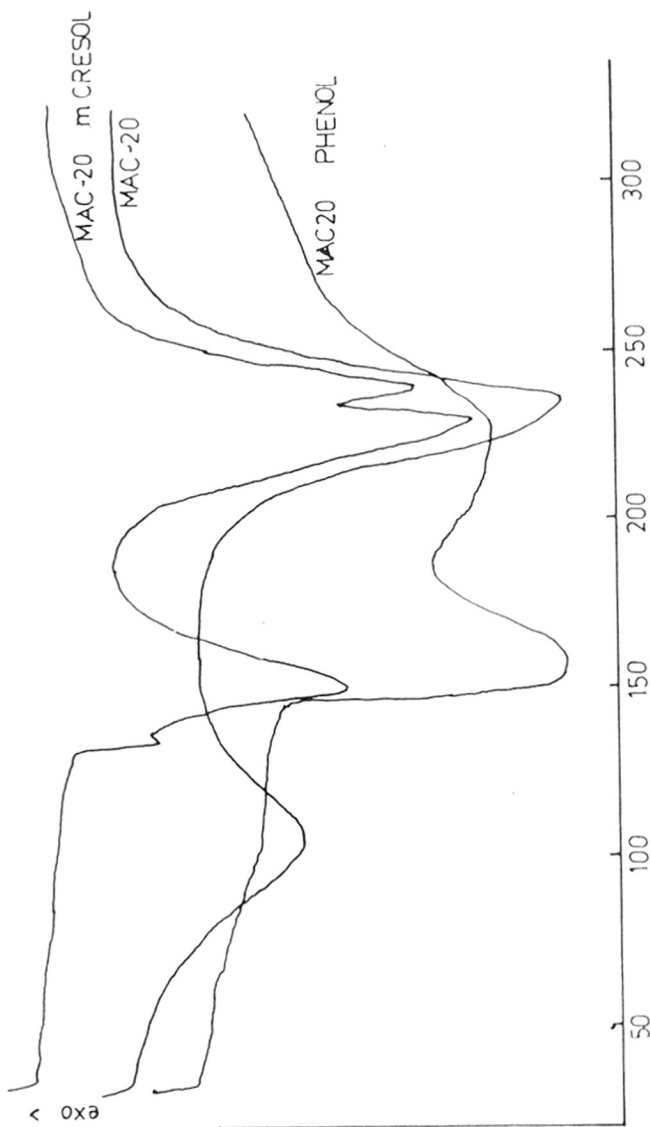


FIG. 37

THERMOGRAMS OF

ACROLEIN-METHACRYLIC ACID COPOLYMER MAC-20

NOVOLAK TYPE POLYMER WITH PHENOL

NOVOLAK TYPE POLYMER WITH CRESOL

SUMMARY
AND
RECOMENDATIONS

SUMMARY OF CONCLUSIONS AND RECOMMENDATIONS

SUMMARY

COPOLYMERISATIONS

Aqueous solution copolymerisations of acrolein with acrylic acid and methacrylic acid were initiated by redox pair of potassium persulphate-sodium sulphite at 30°C. Total monomer concentration was 4 molar. The pH of the reaction media was adjusted to 1, 3, 5 and 7 respectively. At each pH different monomer compositions such as 1:9, 2:8,..8:2, and 9:1 were varied.

In the copolymerisation of acrolein with acrylic acid, monomer composition having acrolein more than certain critical value, phase separated during the course of reaction. This critical value was dependant on the pH of the media. This phase separation affected copolymer composition and two sets of reactivity ratios were obtained. The reactivity ratios estimated from homogeneous range were found to be more reliable. Considering both the ranges of compositions for estimating reactivity ratio gives erroneous values.

In the copolymerisation of acrolein with methacrylic acid, phase separation was not observed. However, the data obtained was nonlinear. Nonlinearity in both the systems was due to violation of assumptions made for deriving expression for

reactivity ratios. This is due to nonuniform interaction of solvent with the monomers. Molecular associations form multimolecular aggregates having concentrations different to that of global concentration could be another factor. Due to formation of acrylate anion, the copolymerisation became a ternary system. Hence, use of binary copolymer composition equation for calculation of reactivity ratios is not valid.

CHARACTERISATION

NMR and Infra-red characterisation show variation in the functional group. Solid state ^{13}C NMR indicated that percentage of free aldehyde increased as interruption in acrolein blocks increased. The interruption of acrylic acid moieties reduced inter/intra molecular cyclisations of aldehyde groups from acrolein moieties. This variation in the structure was indicated by the shift in transitions of thermogram obtained from Differential Scanning Calorimeter.

CALCIUM SEQUESTRATION

Sequestering capacity of the copolymers was investigated at different pH. The capacity was found to be more in alkaline region. The calcium sequestering capacity was controlled by combination of various factors such as pH of the media, composition of the copolymer, sequence distribution of the coordinating groups.

CURING BEHAVIOUR

Curing with hexa methylene tetra amine of novolak type polymer formed from acrolein-methacrylic acid copolymers could not be quantitatively investigated since the curing exotherm was compensated by endothermic transition in the copolymer in the same temperature range.

RECOMMENDATIONS

COPOLYMERISATION

The present study on copolymerisation of a ionisable monomer with another hydrophobic monomer in aqueous medium raises doubts about relevance of applying binary copolymer composition equation for calculating reactivity ratios. Molecular association of the monomers and its effect on copolymer composition has to be investigated before selecting copolymerisation model and consequent composition equation. The phase separation occurring beyond certain critical composition of acrolein gives clues to the microenvironment formed in the multimolecular aggregates of monomer and solvent molecules. The possibility of selective absorption of a monomer around the growing polymer chain is discussed in current literature. Effect of molecular weight on the copolymer composition is also a topic of interest. In general, simplistic assumptions/approximations made in the terminal model of copolymerisation has to be checked again.

SEQUESTRATION

Sequestering capacity of the copolymer can be altered by changing composition of the copolymer. The maximum capacity of the polymer at a specific pH is due to

the coordinating groups active in that pH range. However, by modifying coordinating groups which are active in another pH range, the copolymer can be tailored to be active in the desired pH range. In electrolyte solution, capacity of ionising sequestrant is reduced. By a combination of ionising and nonionising sequestering groups in a polymer, the sequestrant can be kept active in the electrolyte solution.

REFERENCES

1. R.B.Merrifield, *J.Amer.Chem.Sci.*, **85**, 2149 (1963).
2. S.L.Regen, *Macromolecules*, **8**, 689 (1975).
3. S.L.Regen, *J.Amer.Chem.Soc.*, **96**, 5275 (1974).
4. M.Tomoi, S.Shiiki and H.Kikiuch, *Makromol. Chem.*, **187**, 357 (1986).
5. F.Montanari and P.Tundo, *J.Org. Chem.*, **46**, 2125 (1981).
6. F.Guendouz, R.Jacquier and J.Venducci, *Tet. Lett.*, **25**, 4521 (1984).
7. P.Tundo and P.Venturekko, *J.Amer.Chem. Soc.*, **101**, 6606 (1979).
8. J.M.J.Frechet, J.Warnock and M.J.Farrall, *J.Org.Chem.*, **43**, 2618 (1978).
9. J.M.J.Frechet, P.Darling, and M.J.Farrall, *J.Org.Chem.*, **46**, 1728 (1981).
10. N.M.Weinschenker, G.A.Grosby, and J.Y.Wong, *J.Org.Chem.*, **40**, 1966 (1975).
11. M.L.Hallensleben, *J.Polym. Sci. Polym. Symp.*, **47**, 1 (1974).
12. A.R.Sande, M.H.Jagdale, R.B.Mare and M.M.Salunke, *Tetrahedron Lett.*, **25**, 3501 (1984).
13. P.Hodge, E.Khoshdel, and Waterhouse, *J. Makromol. Chem.*, **185**, 489 (1984).
14. M.Bernard and W.T.Ford, *J.Org.Chem.*, **48**, 326 (1983).
15. W.Heitz and R.Michels, *Liebigs Ann. Chem.*, 227(1973).
16. M.Bernard, W.T.Ford and E.C.Nelson, *J.Org. Chem.*, 3164 (1983).
17. A.Akelah and M.El-Borai, *Polymer*, **21**, 255 (1980).
18. M.J.Farrall, T.Durst and J.M.J.Frechet, *Tetrahedron Lett.*, 203 (1979).
19. H.Yamaguchi and R.C.Schulz, *Makromol.Chem.*, **177**, 3441 (1976).
20. G.A.Crosby, N.M.Weinshenker, and H.S.Uh, *J. Am. Chem. Soc.*, **19**, 843 (1981).
21. C.Yaroslavsky and E.Katchalski, *Tetrahedron Lett.*, 5173 (1972).
22. C.Yaroslavsky, A.Patchornik and E.Katchalsky, *Tetrahedron Lett.*, 3629 (1970).
23. M.Zupana and A.Pollak, *J. Chem. Soc. Chem. Commun.*, 715 (1975).
24. H.L.Weith, J.L.Wiebers and P.T.Gilhan, *Biochemistry*, **9**, 4396 (1970).

25. J.M.J.Frechet, I.J.Nuyens and E.Seymour, *J. Amer. Chem. Soc.*, **101**, 432 (1979).
26. H.G.Tak and Q.H.Wen, *J. Chem. Soc. Chem. Commun.*, 909 (1985).
27. D.M.Dixit, and C.C.Leznoff, *J.Chem.Soc., Chem. Commun.*, 798 (1977).
28. K.Takemoto, Y.Inaki and R.M.Ottenbrite, *Functional monomers and polymers*, Marcel Dekker, Inc., N.Y. (1987)
29. Klein, J., *Makromol. Chem. Suppl.*, **5**, 155 (1981).
30. R.H.Hasek, P.G.Gott, R.H.Meen and J.C.Martin, *J. Org. Chem.*, **28**, 2496 (1963).
31. J.M.Bora, A.K.Saund, I.K.Sharma and N.K.Mathur, *Indian J. Chem.*, **14-B**, 722 (1976).
32. M.Morawetz and J.A.Shafer, *J.Phys. Chem.*, **67**, 1293 (1963).
33. J.Svec, M.Bares, J.Zajic, and J.Kalal, *Chem. Ind.*, 159 (1977).
34. J.LeGoffic, S.Sicsic, and C.Vincent, *Tetrahedron Lett.*, 2845 (1976).
35. J.I.Yoshida, J.Hashimoto and N.Kawabata, *Bull. Chem. Soc. Jpn.*, **54**, 309 (1981).
36. A.Akelah and A Moet, *Functionalized Polymers and Their Applications*, Chapman and Hall (1990).
37. G.A.Olah, A.Hussein, B.G.B.Gupta, and S.C.Narang, *Synthesis*, 471 (1981).
38. E.O.Blossey, L.M.Turner, and D.C.Neckers., *J. Org. Chem.*, **40**, 959 (1975).
39. B.Sket, and M.Zupan, *J. Macromol. Chem.*, **A-19**, 643 (1983).
40. K.M.Dooley, and B.C.Gates, *J. Polym. Sci. Polym. Chem. Ed.*, **22**, 2859 (1984).
41. G.A.Olah, P.S.Iyer, and G.K.S.Prakash, *Synthesis*, 513 (1986).
42. D.Suh, I.S.Scarpa, and I.M.Klotz, *J.Amer.Chem.Soc.*, **98**, 7060 (1976).
43. J.Smid, *Makromol. Chem.Suppl.*, **5**, 203,(1981). *Pure.Appl.Chem.* **54**, 2159 (1982).
44. S.C.Shah and J.Smid, *J.Amer.Chem.Soc.*, **92**, 5965 (1978).
45. J.M.Brown, and J.A.Jenkins, *J. Chem.Soc. Chem. Commun.*, 458 (1976).

46. J.Lieto, M.Wolf, B.A.Matrana, M.Prochazka, B.Tesche, B.C.Gates and H.Knozinger, *J.Phys.Chem.*, **89**, 991 (1985).
47. P.L.Ragg, Ger.Patents, 1, 937, 225. and 1, 937, 232 (1970).
48. D.C.Sherington and P.Hodge, Synthesis and Separations using Functional Polymers, J.Wiley and Sons. p.124 (1988).
49. S.N.Gupta, L.Thijs and D.C.Neckers, *J.Polym.Sci., Polym.Chem.*, **19**, 855 (1981).
50. R.Kerber, O.Nuyken and Steinhausen, *Makromol. Chem.*, **177**, 1357 (1976).
51. D.Braun and J.Loflund, *Makromol. Chem.*, **53**, 219 (1962).
52. M.Okada and H.Sumitomo, *Makromol. Chem.*, **162**, 285 (1972).
53. G.Manecke and R.Schlegel, *Makromol.Chem.*, **179**, 19 (1978).
54. D.Woehrle, H.Bohlen and G.Meyer, *Polym.Bull.*, **11**, 143 (1984).
56. J.Boue, R.Audebert and C.Quivoron, *J. Chromatog.*, **204**, 185 (1981).
57. K.Rimbock, F.Kastner and A.Mannschreck, *J.Chromatog.*, **329**, 307 (1985).
58. Y.Okamoto, M.Kawashima, K.Yamamoto and K.Hatada, *Chem. Lett.*, 739 (1984).
59. S.Yuasa, M.Itoh, and A.Shimada, *J.Chromatog. Sci.*, **22**, 288 (1984).
60. S.Allenamrk, S. and Bomgren, S., *J.Chromatog.*, **252**, 297 (1982).
61. H.Yuki, Y.Okamoto and I.Okamoto, *J. Am. Chem. Soc.*, **102**, 6356 (1980).
62. M.M.Cook, S.E.Wagner, R.A.Mikulski, P.R.Demko and J.G.Clements, *Polym. Preprepr., Am. Chem. Soc., Div. Polym.Chem.*, **19(2)**, 415 (1978).
63. M.Wilchek, *Angew. Makromol.*, **123/124**, 175 (1984).
64. S.Hjerten and Y.Kunquan, *J. Chromatog.*, **215**, 317 (1981).
65. P.Cuatrecasas, *Nature*, **228**, 1327 (1970).
66. J.S.Ayers, M.J.Petersen, B.E.Sheerin and G.S.Bethell, *J. Chromatog.*, **194**, 195 (1984).

67. J.K.Inman, *Methods Enzymol.*, **34**, 30 (1974).
68. R.L.Schnnar and Y.C.Lee, *Biochemistry*, **14**, 1535 (1975).
69. J.Yurkova, K.Blaha, J.Horaacek, J.Vajcner, A.Frydrychova and J.Coupek, *J. Chromatog.*, **215**, 165 (1981).
70. P.V.Sundaram, *Ann. N.Y. Acad. Sci.*, **434**, 299 (1984).
71. J.R.Domhroski, L.G.Donaruma and J.Razzano, *J.Med.Chem.*, **14**, 993 (1971).
72. R.N.Trivedi and V.Pachaiyappan, *Fert. News*, **24**(10), 19 (1979).
73. A.Akelah, M.Hassanein, A.Selim and A.Rehab, *J.Chem. Technol.Biotechnol.*, **37-A**, 169 (1987).
74. A.Akelah. and A.Rehab., *J. Mater.*, **3**, 83 (1986).
75. C.E.Carraher, D.J.Giron, W.K.Woelk, J.A.Schroeder and M.F.Fedderson, *J.Appl. Polym. Sci.*, **23**, 1501 (1979).
76. J.A.Meyer, *Wood Sci.*, **14**(2), 49 (1981).
77. Y.Ida, S.Takahashi and S.Utsumi, *Yakugaku Zasshi*, **89**(4), 517 (1969). *Chem. Abstr.*, 51214-w.(1969).
78. A.Zaffarony, US Patent 3 994 828 (1976).; *Chem Abstr.*,**89**, 60475-f(1978).
79. N.M.Weinshenker, *Polym.Prepr., Am. Chem. Soc.;Div. Polym. Chem.*, **20**(1), 344 (1979).
80. A.Girou, *Rev.Fr. Sci, Eau*, **4**(2-3), 129(1985). *Chem. Abstr.*, **104**, 74718.
81. K.Okitsu. and H.Omari, JP 62 81, 411, *Chem. Abstr.*, **108**, 6638 j
82. A.J.Testa, U.S. 3,755, 264. *Chem. Abstr.*, **80**, 4072 z.
83. R.L.Smith and P.Womersley, *Chem. Products*, **19**, 152 (1956).
84. Y.Abe, S.Matsumura and J.Takahashi, *Yukagaku*, **35**(3), 167 (1986). *Chem. Abstr.*,**104**, 209189 d.
85. R.C.DeGeiso, L.G. Donaruma and E.A.Tomie. *J.Org.Chem.*, **27**, 1424 (1962).

Anal Chem. **34**, 845 (1962).

86. Solvay el cie., Belg. 786,464. *Chem. Abstr.*, **78**, 148457 k.

87. K.Henning, Ger Offen. 2, 212, 623. *Chem. Abstr.*, **80**, 72320 d.

88. N.Van Lautem and J.Mulders, Ger. Offen. 2, 815, 148. *Chem. Abstr.*, **90**, 25164 c.

89. K.Yamada, S.Ikeda and H.Shosenji, *Yukagaku*, **28(9)**, 605 (1979). *Chem. Abstr.*, **91**, 212885 w.

90. N.I.Vassileff, US Patent 4, 085, 060. *Chem. Abstr.*, **89**, 147614 z.

91. Amjad Zahd and B.F.Goodrich, Eur. Pat. Appl. EP 171, 049 US appl 638, 155 *Chem. Abstr.*, **104**, 135835 n.

92. W.Vogt, E.Fischer and E.Auer, Ger. Offen. 2, 211, 256. *Chem. Abstr.*, **80**, 37617 j.

93. W.Vogt, Ger. Offen. 2, 327, 141. *Chem. Abstr.*, **82**, 172971 b.; Ger. Offen 2,327, 097. *Chem. Abstr.*, **82**, 172973 d.

94. K.Okitsu and H.Omori, JP 61 85, 407. *Chem. Abstr.*, **105**, 191811.

95. Haschke H. Morlock G. Kuzel P. *Chem-Ztg.* **96(4)**, 199 (1992).

96. Haschke H.; Morlock G. *Tenside Deterg.* **11(2)**, 57(1974).

97. C.G.Gebelein and C.E.Carraher, Jr., *Bioactive Polymeric Systems: An Overview*. P514.

98. A.Billeau, J.Desmyter and P.DeSomer, *J.Virol.*, **5**, 321 (1970).

99. P.DeSomer, E.Declercq, A.Billeau, E.Schonne and M.Claes, *J.Virol.*, **2**, 878 (1968).

100. K.Okitsu, H.Omori, JP 62, 81, 411.

101. Vrelblad and R. Axen. *FEBS lett.*, **18**, 254(1971).

102. F.Michael and J.Ewers, *Makromol. Chem.*, **3**, 200(1949).

103. M.A. Mitz and L.J. Summari, *Nature*, **189**, 576 (1961).
104. C.W. Wharton, E.M. Crook and K. Brocklehurst, *Eur.J.Biochem.*, **6**, 5722 (1968).
105. C.J. Epstein and C.B. Anfinsen, *J.Biol.Chem.*, **237**, 2175 (1962).
106. C.W. Wharton, E.M. Crook and K. Brocklehurst, *Eur.J.Biochem.*, **6**, 565 (1968).
107. W. Brummer, N. Hennrich, M. Klockow, H. Lang and H.D. Orth, *Eur.J.Biochem.*, **25**, 129 (1972).
108. G.J. Bartling, H.D. Brown and S.K. Chattopadhyay, *Biotechnol. Bioeng.*, **16**, 361 (1974).
109. E. Bron, A. Racois, E. Grimand, J.C. Lecoq, R.C.M. Tixier, *Makromol. Chem.*, **179**(12), 2887 (1978).
110. Margel Shlomo, Wiesel Erika, *J. Polym. Sci., Polym. Chem. Ed.*, **22**(1), 145 (1984).
111. A. Rembaum, *Can CA* 1,218, 185. *Chem Abstr.*, 107: 36202 j.
112. G. Manecke and U. Klusmann, *Angew. Makromol. Chem.*, **134**, 125 (1985).
113. Y. Hayashi and Y. Ikada, *Biotechnol. Bioeng.*, **36**(6), 593 (1990).
114. Irkutsk Inst. of Org. Chem. JP 8075406. *Chem. Abstr.*, **93**, 192049 n.
115. N.P. Roman'kova, V.Z. Annenkova, V.M. Annenkova, G.S. Ugryumova and M.G. Voronkov, *Vysokomol. Soedin. Ser B*, **20**(8), 616 (1978). *Chem. Abstr.*, **89**, 164159 x.
116. V.Z. Annenkova, N.B. Dobrova, V.M. Annenkova, S.P. Novikova, G.S. Ugryumova, N.P. Romankova and M. Voronkov, *Vysokomol. Soedin, Ser B*, **24**(8), 619 (1982).
117. V.Z. Annenkova, V.M. Annenkova, N.P. Shilyaeva and M.G. Voronkov, *Vysokomol. Soedin, Ser. A*, **27**(11), 2311 (1985).
118. V.Z. Annenkova, G.S. Ugryumova, A.T. Platonova, V.M. Annenkova,

- V.B.Kazimirovskaya, N.P.Roman'kova and M.G.Voronkov, *Khim-Farm. Zh.*, **16(4)**, 438 (1982). *Chem. Abstr.* **97**, 16846 u.
119. Y.Muraghige, JP 60,233,115. *Chem. Abstr.*, **104**, 187065.
120. Jo Yasushi JP 7884094, *Chem. Abstr.*, **89**, 186100 y.
121. A.Sabel, H.B.J.Stange and R.Kretschmer, Ger.Offen., 2,845,569. *Chem. Abstr.*, **93**, 72597 t
122. V.Z.Annenkova, V.M.Annenkova, L.G.Bagun, O.A.Triofnova and M.G.Voronkov, U.S.S.R. SU 1,265,197. *Chem. Abstr.*, **106**, 103478 y.
123. H.Kern, Ger. Offen. DE 3,545,578. *Chem. Abstr.*, **107**, 174394 z.
124. V.Z.Annenkova, A.G.Khabibulina, V.M.Annenkova, L.G.Erofeva and M.G.Voronkov, *Zh. Prikl. Khim. (Leningrad)*, **63(3)**, 641 (1990). *Chem. Abstr.*, **113**, 98186 q,
125. V.Z.Annenkova, V.M.Annenkova, L.G.Bugun, A.G.Khabibulina, M.G.Voronkov, USSR SU 1,613, 447 (1990). *Chem. Abstr.*, **114**, 208121 w.
126. Pfizer Inc. JP 60 71,094, *Chem. Abstr.*, **103**, 76038 j
127. H.Wegert, K.Stutzel, *Wau. Ind. Nuisances*, **86**, 52 (1984). *Chem. Abstr.*, **102**, 84174 v.
128. V.Z.Annenkova, A.I.Promptov, R.V.Makarov, L.N.Zhdankovich, V.M.Annenkova; N.P.Romankova, I.V.Zagoskin, G.A.Melikyan, M.G.Voronkov, U.S.S.R. SU 977, 482, *Otkrytiya, Izobret., Prom. Obratzy Tovarye znaki*, **44**, 97 (1984). *Chem. Abstr.*, **98**, 110357 c.
129. Abe Sunao; M.Aoki, T.Tsukamoto, JP 62 62, 853. *Chem. Abstr.*, **108**, 23471 s
130. R.Osberghans, J.Wasik, G.Stchlik, Ger.Patent, 2, 556, 258. *Chem. Abstr.*, **87**, 122642 c.
131. K.Okitsu, H.Omori, *Chem. Abstr.*, **108**, 6638 j.

132. K.Okitsu, H.Omori, JP 62, 53, 305. *Chem. Abstr.*, **107**, 199130 y.
133. Shim Jyong Sup, Jun Young-Sung, *Daehan Hwahak Hwoijee*, **13(4)**, 373 (1969).
134. Yasuo Kinoshita, Juichi Kobayashi, Ide Fumio, Yasuo Nakatsuka, *Kobunshi Kagaku*, **28(313)**, 430 (1971).
135. M.Kunakura, I.Kaetsu, *J.Polym.Sci., Polym. Chem. Ed.*, **23(1)**, 131 (1985).
136. Ouchi Tatsuro, et al, *J.Polym. Sci., Polym. Chem. Ed.*, **20(8)**, 2089 (1982)
137. B.Heublein, A.Burckhardt, G.Heublein, *Acta Polym.*, **39(3)**, 136 (1988).
138. E.A.Gonyukh, E.V.Kuznetsov, Kh.KhazryatovaL, V.P.Prokop'ev, M.A.Akhtmerov, *Izv.Vssh. Uchebn. Zaved., Khim.Khim. Tekhnol.* **27(9)**, 1070 (1984).
139. H.Dostal, *Monatch*, **69**, 424 (1936).
140. F.R.Mayo and F.M.Lewis, *J.Amer.Chem.Soc.*, **66**, 1594 (1944).
141. R.G.Norrish and E.F.Brookman, *Proc.Roy.Soc.*, **A163**, 205 (1937).
142. R.G.Norrish and E.F.Brookman, *Proc.Roy.Soc.*, **A171**, 147 (1937).
143. F.T.Wall, *J.Amer.Chem.Soc.*, **63**, 1862 (1941).
144. E.Jenckel, *Z.Physik.Chem.*, **A190**, 24 (1941).
145. T.Alfrey Jr. and G.Goldfinger, *J.Chem.Phys.*, **12**, 205 (1944).
146. R.Simha and H.Branson, *J.Chem.Phys.*, **12**, 253 (1944).
147. F.T.Wall, *J.Amer.Chem.Soc.*, **66**, 2050 (1944).
148. T.Alfrey, J.J.Bohrer and H.Mark, *Copolymerization, High Polymers Vol.VIII*, Interscience, New York-London, 1952, p.12.
149. M.Fineman and S.D.Ross, *J.Polym.Sci.*, **5**,259 (1950).
150. R.M.Joshi and S.L.Kapur, *J.Polym.Sci.*, **14**, 508(1954); *J.Polym.Sci.*, **19**, 582 (1956).
151. G.A.Shtraikhman, *Zh.Fiz.Khim*, **32**, 512 (1958).
152. G.R.Brown and J.G.Byrne, *Polymer*, **10**, 333 (1969).

153. A.I.Yezrielev, E.L.Brokhina, and Y.S.Roskin, *Vysokomol.Soedin.*, **a11**, 1670 (1969). *Polymer Science [U.S.S.R.]*, **11**, 1894 (1969).
154. R.M.Joshi, *J.Macromol.Sci.-Chem.*, **a7**, 1231 (1973).
155. P.W.Tidwell and G.A.Mortimer, *J.Polym.Sci.*, **A3**, 369 (1965); *J.Macromol.Sci.-Rev. Macromol.Chem.* **C4**, 281 (1970).
156. D.W.Behnken, *J.Polym.Sci.*, **A2**, 645 (1964).
157. T.Kelen and F.Tudos, *J.Macromol.Sci.-Chem.*, **A9**, 1 (1975).
158. J.P.Kennedy, T.Kelen and F.Tudos, *J.Macromol.Sci.-Chem.*, **13**, 2277 (1975).
159. R.M.Joshi and S.G.Joshi, *J.Macromol.Sci.- Chem.*, **A5**, 1329 (1971).
160. S.Sounderarajan and B.S.R.Reddy, *J.Appl.Polym.Sci.*, **43**, 251 (1991).
161. E.P.George, Box, W.G.Hunter and J.S.Hunter, *Statistics for experiments: An introduction to Design, Data Analysis and Model Building*, Wiley, N.Y. 1978.
162. Skeist, *J.Amer.Chem.Soc.*, **68**, 1781 (1946).
163. G.G.Lowry and V.E.Meyer, *J.Polym.Sci.*, **A3**, 2843 (1965).
164. V.E.Mayer, *J.Polym.Sci.*, **A1**,4 2819 (1966).
165. S.Ponrathnam, Ph.D. Thesis.
166. D.Braun, W.Brendlein and G.Mott, *Eur.Polym.J.*, **95**, 1007 (1973).
167. F.Tudos, T.Kelen, T.Foldes-Bereznich and B.J.Turcsanyi, *J.Macromol.Sci., Chem.* **A10**, 1513 (1975).
168. F.Tudos, T.Kelen; B.J.Turcsanyi and J.P.Kennedy, *J.Polym.Sci., Polym.Chem.Ed.*, **19**,1119, (1981).
169. D.Braun, W.Czerwinski,G.disselhoff, F,Tudos, T.Kelen and B.J.Turcsanyi, *Angew. Makromol. Chem.* **125**, 161 (1984).
170. S.M.Shawki and A.E.Hamielec, *J.Appl.Polym.Sci.*, **23(11)**, 3155 (1979)
171. D.L.Marquardt, *J.Soc.Ind.Appl.Math.*, **2**, 431 (1963).

172. J.F.Kuo and C.Y.Chen, *J.Appl.Polym.Sci.*, 26, 1117(1981).
173. J.F.Kuo and C.Y.Chen, *J.Appl.Polym.Sci.*, 27, 2747(1982).
174. J.F.Kuo, C.Y.Chen, S.H.Luo and T.C.Pan, *J.Appl.Polym.Sci.*, **38(3)**, 529 (1989).
175. A.Katchalsky and G.Blauer, *Trans.Faraday Soc.*, 47, 1360 (1951).
176. G.Blauer, *J.Polym.Sci.*, 11, 189 (1953).
177. G.Blauer, *Trans.Faraday Soc.*, 56, 606 (1960).
178. T.Alfrey, C.G.Overberger and S.H.Pinner, *J.Amer.Chem.Soc.*, 75, 4221 (1953).
179. V.A.Kabanov and D.A.Topchiev, *Vysokomol.Soedin*, **a13**, 1324 (1971).
Polymer Science [U.S.S.R.] 13, 1486 (1972).
180. W.R.Cabaness, T.Yen-ChinLin and C.Parkanyi, *J.Polym.Sci.*, **A1**, 9, 2155 (1971).
181. S.Ponrathnam and S.L.Kapur, *Makromol. Chem.*, 178, 1029 (1977).
182. G.Saini, A.Leoni and S.Franco, *Makromol.Chem.*, 144, 235, (1971).
183. H.Fujihara, M.Yoshihara, Y.Matsubara and T.Maeshime, *J.Macromol.Sci., Chem.*, **A13(6)**, 789 (1979).
184. H.Fujihara, M.Yoshihara and T.Maeshime, *J.Macromol.Sci., Chem*, **A14(6)**, 807 (1980).
185. J.I.Arakura, M.Yoshihara, Y.Matsubara and T.Maeshime, *J.Macromol.Sci., Chem.*, **A15(8)**, 1473 (1981).
186. Y.Matsubara, K.Enyo and M.Yoshihara, *J.Polym.Sci: Polym.Chem.Ed.* 13, 913 (1975).
187. G.Jenner and S.Aieche, *J.Polym.Sci., Polym. Chem. Ed.*, 16(5), 1017 (1978).
188. M.Jelinek, L.J.Ambroz, J.Svabik and J.Palacky, *Chem.Prum.*, 27(3), 139 (1977).
Chem.Abstr. 86,140515x.
- 189.R.C.Schulz, E.Kaiser and W.Kern., *Makromolek. Chem.*, 58, 160 (1962).

- 190.H.Batka and Altenchoepfer. Ger. Offen. Pat. 2,101,508 (1972).
- 191.P.Salvatore and R.A.Polistina. U.S. Pat. 3,730,841 (1973).
- 192.J.M.Gadgil, U.V.Nayak, C.R.Rajan, G.D.Shahapure, S.Ponrathnam, *Eur.Polym.J.*, **27(8)**, 803(1991).
- 193.J.M.Gadgil, C.R.Rajan, S.Ponrathnam, P.R.Rajamohanan, S.Ganapathy, *J.Polym.Sci.: Polym.Chem.*, **29**, 1077(1991).
- 194.G.F.D'Aleliio and T.F.Huemer, *J.Polym.Sci.*, **A1(5)**, 77(1967).
- 195.R.Arnold, *J.Colloid Sci.*, **12**, 549 (1957).
- 196.B.H.Zimm and S.A.Rice, *Mol. Phys.*, **3**, 391 (1960).
199. N.N.Slavnitskaya, Yu.D.Semchikov,A.V.Ryabov and D.N.Bort, *Vyasokomol. Soed.*, **A12:8**, 1756(1970). *Polym.Sci., USSR*, **12**, 1993(1971).
200. Simchikov Yu.D., Smirnova L.A., Bulgakova S.A., Knyazeva T.E., Sherstyankh V.I. And Slavnitskaye N.N., *Dokl. Akad. Nauk, SSSR*, **298(2)**, 411(1988).
202. R.N.Rogers and E.D.Morris, *Anal.Chem.*, **38**, 412 (1966).
203. R.C.Schulz and W.Kern, *Makromol.Chem.*, **18/19**, 4 (1956).

LIST OF PUBLICATIONS

1. Anomalous Behaviour in Copolymerizations in Aqueous Medium: Copolymerization of Acrolein with Acrylic Acid, *Eur. Polym. J.*, **27**, 803 (1991).
2. Acrolein-Acrylic Acid Copolymers: A Solid State ^{13}C -NMR Study of Free Aldehyde Groups., *J. Polym. Sci., Polym. Chem.*, **29**, 1077 (1991).
3. Acrolein-Acrylic Acid Copolymers: Effect of Phase Separation on Reactivity Ratio. (to be communicated)
4. Reactivity Ratios of Acrolein-Methacrylic Acid Aqueous Copolymerisation: Effect of pH (to be communicated)
5. Calcium Sequestration Capacity of Acrolein-Methacrylic Acid Copolymers (to be communicated)

PATENTS

1. An Improved Process for the Production of Immobilized Penicillin G Acylase Using Crosslinked Spherical Macroporous Hydroxyethyl Methacrylate Terpolymers Useful for the Preparation of 6-Amino Penicillanic Acid.
Indian Patent No. 186/90.

. A Process for the Preparation of Crosslinked Spherical Macroporous Hydrox-ethyl Methacrylate Terpolymers Beads of Controlled Pore Size Distribution for nzyme immobilization.

ndian Patent No. 185/90.