

Group Transfer Polymerization of Alkyl (meth)acrylates

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

BY

BISWAJIT SANNIGRAHI

DIVISION OF POLYMER CHEMISTRY
NATIONAL CHEMICAL LABORATORY
PUNE 411 008

DEDICATED TO MY PARENTS

RR

ACKNOWLEDGMENT



It gives me immense pleasure to record my deep sense of gratitude to Dr. S. Sivaram, Head, Polymer Chemistry Division, National Chemical Laboratory, Pune, for his valuable and inspiring guidance in abundant measure throughout my pursuance of this work.

I take this opportunity to express my gratitude to Dr. P. P. Wadgaonkar, Dr. J. C. Sehra, Dr. J. A. Raj, Dr. (Mrs) B. Garnaik, Dr. R. A. Kulkarni and Dr. S. Chakrapani for their valuable advice and suggestions. I wish to thank my colleagues Dr. A. Dasgupta, Radhakrishnan, Pradeep, Nabin, Anjana, Soumen, Sukhen, Rajesh and Dr. N. K. Singha for their co-operation and support during these years.

I also thank Dr. R. Mani, Dr. B. B. De, Dr. A. G. Saikh, Dr. V. S. Iyer, Dr. S. S. Reddy, Dr. D. Bhaskaran, Dr. Avadhani, Dr. T. K. Bera, Sruti, Subarna, Balumurgan, Saptarshi, Raghu, Mahua, Biswaprasad, Parag, Ramanathan, Bindusree and all my senior colleagues of polymer chemistry Division for their timely help during the course of my stay at NCL.

My thanks are due to Dr. M. Nandy, Sourav, Sanjeeb, Dr. S. Chaudhury, Manas and Deepanita, Dr. R. K. Roy and Purnima, Parthasarathi, Dr. Sujit Baran, Soumen, Debasis, Anjan, Mrinal, Amit, Rajat, Asis, Debiprasad, Dr. R. Amin, Sunil, Surajit, Anil, Abhijit, Priyabrata, Suvendhu, Madan, Tapas, Dr. D. Bhattacharia, Dilip, Dr. A. Bhoumik, Krishanu, Depu, Faizul, Tusar, Milind, Selvaraj, Anil, Bharat, C. N. Selvam, Dr. Selvam, Ravi, Basant, Chengal, Dr. R. K. Prasad and all my friends at NCL for their encouragement.

I wish to express my gratitude to few of my earlier teachers, M. B. Panda (Lakshmisagar Primary School), N. Chakraborty (Purusottampur High School), D. Chatterjee (Ramsagar High School), A. P. Kundu (Bankura Christian College) for their encouragement.

I am thankful to Professor A. B. Sannigrahi, IIT, Kharagpur, for his timely advice.

I am indebted to my parents, brothers and sisters, for advice, support and freedom given to me.

Finally, my thanks are due to the council of Scientific and Industrial Research, New Delhi for the award of a research fellowship and the Director, NCL, for permission to submit the work in the form of a thesis.

Biswajit Sannigrahi
Biswajit Sannigrahi

CERTIFICATE

This is to certify that the work incorporated in the thesis entitled "Group Transfer Polymerization of Alkyl (meth)acrylates" submitted by Biswajit Sannigrahi was carried out by him under my supervision at the National Chemical Laboratory. Such material as has been obtained from other sources has been duly acknowledged in the thesis.

Date: May 26, 1997

National Chemical Laboratory

Pune 411 008

S. Sivaram
(Dr. S. Sivaram)

Research Guide

CONTENTS

GLOSSARY	i
ABSTRACT	iii
LIST OF TABLES	v
LIST OF FIGURES	viii
<u>GROUP TRANSFER POLYMERIZATION OF ALKYL (METH)ACRYLATES</u>	
CHAPTER-I	
<u>GROUP TRANSFER POLYMERIZATION: A CRITICAL REVIEW</u>	
1.1 INTRODUCTION	1
1.2 MONOMERS FOR GTP	2
1.2.1 Alkyl methacrylates	2
1.2.2 Alkyl acrylates	3
1.2.3 Functional group bearing acrylic monomers	4
1.2.4 Miscellaneous monomers	7
1.3 INITIATORS FOR GTP	8
1.3.1 MTS	8
1.3.2 Functional group containing MTS	9
1.3.3 Nonacetal initiators	13
1.3.4 Metal containing initiator	14
1.3.5 Bifunctional initiators	14
1.4 CATALYSTS FOR GTP	15
1.4.1 Nucleophilic catalysts	15
1.4.2 Electrophilic catalysts	18
1.5 POLYMERIZATION METHODS	19
1.5.1 Monomer purification	19
1.5.2 Initiator / catalyst purification	20
1.5.3 Nature of solvents	20
1.5.4 Effect of pressure	21
1.5.5 Livingness enhancing agents	21
1.6 KINETICS AND MECHANISM	22
1.6.1 Techniques of kinetic measurements	22
1.6.2 Kinetics of alkyl methacrylate polymerization	22
1.6.2.1 General kinetic features	22

1.6.2.2	Effect of monomer concentration	27
1.6.2.3	Effect of temperature	28
1.6.2.4	Effect of catalyst concentration	29
1.6.2.5	Effect of initiator concentration	31
1.6.2.6	Chain transfer / chain terminations mechanism	32
1.6.3	Kinetics of alkyl acrylate polymerizations	37
1.6.3.1	General kinetic features	37
1.6.3.2	Effect of monomer concentration	37
1.6.3.3	Effect of temperature	37
1.6.3.4	Effect of initiator/ catalyst	37
1.7	MECHANISM OF GTP	38
1.7.1	Associative mechanism	38
1.7.2	Dissociative mechanism	39
1.7.3	Similarities/ differences between GTP/ anionic mechanism	42
1.7.4	Stereochemistry of GTP	43
1.8	POLYMER SYNTHESIS THROUGH GTP	45
1.8.1	Homopolymers	45
1.8.2	Random copolymers	45
1.8.3	Block copolymers	48
1.8.4	Macromonomers	51
1.8.5	Telechelics	53
1.8.6	End functionalized polymers	53
1.8.7	Star and branched polymers	55
1.8.8	Graft/ comb polymers	57
1.8.9	Other polymer architecture	59
1.9	APPLICATIONS OF GTP	61
1.10	PATENT LITERATURE	62
1.11	REFERENCES	64
CHAPTER-II		
<u>SCOPE AND OBJECTIVES OF THE PRESENT STUDY</u>		70
CHAPTER-III		
<u>EXPERIMENTAL METHODS IN GTP</u>		74
3.1	INTRODUCTION	74
3.2	MATERIALS	74

3.3	PURIFICATION OF MONOMERS	74
3.4	PURIFICATION OF SOLVENTS	75
3.5	PREPARATION OF CATALYSTS	76
3.6	PURIFICATION OF INITIATOR/ CATALYSTS	77
3.7	METHODS OF POLYMERIZATION AND COPOLYMERIZATION	77
3.8	METHODS FOR KINETICS EVALUATION	80
3.9	CHARACTERIZATION OF POLYMER	81
3.10	REFERENCES	83

CHAPTER-IV

HOMOPOLYMERIZATIONS OF HIGHER ALKYL METHACRYLATES

4.1	INTRODUCTION	84
4.2	RESULTS AND DISCUSSION	84
4.2.1	Homopolymerization of Alkyl methacrylates	85
4.2.2	Kinetics of Alkyl methacrylate polymerization	93
4.2.2.1	Effect of catalyst concentration	95
4.2.2.2	Effect of initiator concentration	97
4.2.2.3	Effect of monomer concentration	99
4.2.2.4	Effect of temperature	100
4.2.2.5	Molecular weight and molecular weight distribution	103
4.3	CONCLUSIONS	105
4.4	REFERENCES	106

CHAPTER-V

COPOLYMERIZATION OF METHYL METHACRYLATE (MMA) WITH HIGHER ALKYL METHACRYLATE (LMA)

5.1	INTRODUCTION	107
5.2	RESULTS AND DISCUSSION	108
5.2.1	Random copolymerization of MMA with LMA	108
5.2.1.1	Reactivity ratios	108
5.2.1.2	Sequence distribution by ^{13}C NMR	114
5.2.1.3	Molecular weight and molecular weight distribution	126
5.2.2	Block copolymerization of MMA with LMA	131
5.2.3	Thermal properties of random and block copolymers	137
5.3	CONCLUSIONS	139
5.4	REFERENCES	140

CHAPTER-VI

GROUP TRANSFER POLYMERIZATION OF MMA USING ALKALI METAL BIBENZOATES/ CROWN ETHER COMPLEXES

6.1	INTRODUCTION	142
6.2	RESULTS AND DISCUSSION	143
6.2.1	GTP OF MMA USING ALKALI METAL BIBENZOATES/ CROWN ETHER COMPLEXES	143
6.2.2	GTP OF MMA USING POTASSIUM BIBENZOATE/18-CROWN-6	145
6.2.2.1	Effect of catalyst concentration	147
6.2.2.2	Effect of crown ether to catalyst ratio	148
6.2.2.3	Effect of temperature	149
6.2.3	KINETICS OF GTP OF MMA USING ALKALI METAL BIBENZOATE/ CROWN ETHER COMPLEXES	150
6.2.3.1	Effect of catalyst concentration	151
6.2.3.2	Effect of initiator concentration	153
6.2.3.3	Effect of temperature	155
6.2.3.4	Effect of monomer concentration	157
6.2.3.5	Molecular weight and molecular weight distribution	159
6.3	DISCUSSION	161
6.4	CONCLUSIONS	163
6.5	REFERENCES	164

CHAPTER-VII

GTP OF N-PHENYL MALEIMIDE

7.1	INTRODUCTION	165
7.2	RESULTS AND DISCUSSION	165
7.2.1	Homopolymerization of N-phenyl maleimide	165
7.2.1.1	GTP of N-PMI using TBABB as catalyst and MTS as initiator	170
7.2.1.2	GTP of N-PMI using Lewis acid catalyst	171
7.3	DISCUSSION	172
7.3	REFERENCES	173

CHAPTER-VIII

<u>SUMMARY AND CONCLUSIONS</u>	174
--------------------------------	-----

<u>SYNOPSIS</u>	178
-----------------	-----

LIST OF PUBLICATIONS	
----------------------	--

GLOSSARY

2-EHA	2-Ethylhexyl acrylate
2-EHMA	2-Ethylhexyl methacrylate
BA	Butyl acrylate
BMA	Butyl methacrylate
BzMA	Benzyl methacrylate
DEMA	N,N-Diethylmethyl acrylamide
DMA	Decyl methacrylate
DMAEM	(N,N-Dimethylamino)ethyl methacrylate
EA	Ethyl acrylate
E_a	Arrhenius energy of activation
EGDMA	Ethylene glycol dimethacrylate
EMA	Ethyl methacrylate
EPB	Ethyl-2-phenyl-2-buteneoate
Et_4NCN	Tetraethylammonium cyanide
GMA	Glycidyl methacrylate
k_{app}	Apparent rate constant of propagation
k_p	Rate constant of propagation
LMA	Lauryl methacrylate
MAN	Methacrylonitrile
MMA	Methyl methacrylate
MTS	(1-Methoxy-2-methyl-1-propenoxy)trimethyl silane
NPM	N-Phenyl maleimide
PDMS	Poly(dimethylsiloxane)
PMMA	Poly(methyl methacrylate)
PPNHF ₂	Bis(triphenylphosphoranylidene)ammonium bifluoride
t-BMA	tert-Butyl methacrylate
TASF ₂ SiMe ₃	Tris(dimethylamino)sulfonium difluotrimethylsilicate
TASHF ₂	Tris(dimethylamino)sulfonium bifluoride
TBA	tert-Butyl acrylate
TBA2-NO ₂ PhO	Tetrabutylammonium 2-nitrophenolate
TBAB	Tetrabutylammonium benzoate

RR

TH-1098

TBABB	Tetrabutylammonium bibenzoate
TBABOAc	Tetrabutylammonium biacetate
TBACN	Tetrabutylammonium cyanide
TBAF	Tetrabutylammonium fluoride
TBA _m -CB	Tetrabutylammonium m-chlorobenzoate
THFMA	Tetrahydrofuryl methacrylate
THPMA	Tetrahydropyryl methacrylate
TMS-HEMA	2-(Trimethylsiloxy)ethyl methacrylate
TMS-MA	Trimethylsilyl methacrylate
TMSB	Trimethylsilyl benzoate
TMSCB	Trimethylsilyl 3-chlorobenzoate
TPSHF ₂	Tris(piperidino)sulfonium bifluoride
VBM	Vinyl benzyl methacrylate

ABSTRACT

This thesis presents results on the polymerization of alkyl methacrylates by group transfer polymerization. Homopolymers of methyl methacrylate (MMA), butyl methacrylate (BMA) and lauryl methacrylate (LMA) have been successfully synthesized in the molecular weight range of 30-50,000 with controlled molecular weight and narrow polydispersity. MMA was purified by the treatment of triisobutyl aluminium whereas BMA and LMA were purified with bis(dimethylamino)dimethyl silane in presence of tetrabutylammonium fluoride.

Random and block copolymers (using sequential monomer addition) of MMA and LMA have been synthesized in the molecular weight range of 40-50,000 by GTP over a wide composition range (LMA content = (20-80) mol%) using tetrabutylammonium bibenzoate (TBABB) as catalyst and 1-methoxy-1-(trimethylsiloxy)-2-methyl-1-propene (MTS) as initiator in tetrahydrofuran (THF) at room temperature. The absolute molecular weight of the copolymers were determined by SEC/ MALLS. The observed molecular weights were higher by a factor of 1.1-1.4 relative to the targeted molecular weights. However, polydispersities were very narrow (1.02-1.1). Use of trimethylsilyl benzoate as “livingness enhancer” improved the livingness of the first block and the block copolymer with no detectable contamination of homopolymer have been synthesized. The reactivity ratios of MMA and LMA under GTP conditions were also determined (r_1 (MMA) = 1.38 ± 0.11 and r_2 (LMA) = 0.68 ± 0.10). ^{13}C NMR spectra (75.5 MHz) of the copolymers were analyzed in terms of sequence distribution and relative stereochemical configuration of monomer units along the macromolecular chains. The values of concentration of M- and L-centered triads, determined experimentally from the analysis of $\alpha\text{-CH}_3$ and C=O resonance signals, were in good agreement with those calculated statistically, taking into consideration the terminal copolymerization model and Bernoullian distribution of stereoregularity. Complete degradation of the copolymers at 400°C in TGA indicates that degradation occurs exclusively by depolymerization. Only one T_g was observed in the case of both random and block copolymers of MMA and LMA which confirms the existence of single phase in the copolymers.

GTP of MMA has been carried out using potassium benzoate in presence of 18-crown-6 as catalyst and MTS as initiator in THF at room temperature. Broader polydispersity and lower initiator efficiency were observed for the polymers prepared using KBB/ 18-C-6 compared to the polymers prepared using TBABB catalyst. To understand the effect of counteraction in GTP, kinetic studies were performed under identical conditions using both the catalysts. KBB/ 18-C-6 was characterized by a larger induction period and lower overall reaction rate compared to TBABB. Fractional reaction order with respect to catalyst and initiator concentration were observed in case of KBB/ 18-C-6 indicating low silicophilicity of the benzoate ion associated with K^+ / 18-C-6 counteraction.

List of Tables

1.1	Effect of Catalyst and Solvent on the GTP of MMA	3
1.2	Polymerization of Acrylic Monomers by GTP	3
1.3	GTP of Functional Monomers using MTS Initiator	6
1.4	GTP of Miscellaneous Monomers	7
1.5	Effect of Structure of the Initiators on Polymerization of MMA	9
1.6	GTP of MMA using Different Functional Initiators	13
1.7	Effect of Nucleophilic Catalysts on the GTP of MMA	17
1.8	Effect of Electrophilic Catalysts for the GTP of EA	18
1.9	Synthesis of Star Polymers in Presence of LE Agents	22
1.10	Comparison of E_a and $\log A$ Values Determined by GTP and Anionic Methods	29
1.11	Reaction Order w.r.t. Catalyst Concentration in GTP of MMA	30
1.12	Comparison of the Tacticities of PMMA Prepared in THF by GTP and Anionic Polymerization using Different Counterions	43
1.13	Homopolymerization of Higher Alkyl Methacrylates via GTP	45
1.14	Reactivity Ratios for Various Alkyl Methacrylate Monomer Pairs using GTP	46
1.15	Random Copolymers Prepared by GTP	47
1.16	Block Copolymers Prepared by GTP	51
1.17	Functional Terminators for GTP	55
1.18	Representative Patent Literature on Group Transfer Polymerization	63
3.1	dn/dc Values of Random and Block Copolymers	82
4.1	GTP of MMA in THF using MTS Initiator and TBABB Catalyst at 25 ⁰ C	87
4.2	GTP of BMA Purified by Treatment with TIBAL	88
4.3	GTP of BMA Purified by the Treatment with MTS (BMA = 10.41 mol, [BMA] ₀ = 1.57 M, C ₀ = 6.19 x 10 ⁻⁶ mol, I ₀ = 2.95 x 10 ⁻⁴ mol)	89
4.4	GTP of BMA Purified by the Treatment with BDMAS/ TBAF (BMA = 10.41 mol, [BMA] ₀ = 1.57 M, = x 10 ⁻⁴ mol)	90
4.5	GTP of LMA in THF Purified by the Treatment with BDMAS/ TBAF system at 25 ⁰ C ([LMA] ₀ = 0.86 mol/L)	92
4.6	Effect of Catalyst Concentration on the Rate of Polymerization at 25 ⁰ C ([MMA] ₀ = 1.17 M, [I] ₀ = 1.23x10 ⁻² M, [M] ₀ /[I] ₀ = 95, solvent : THF)	96
4.7	Reaction Order with Respect to Catalyst and Initiator Concentrations in the GTP of MMA in THF under Different Reaction Conditions	97

4.8	Effect of Initiator Concentration on the Rate of Polymerization at 25 ⁰ C ([MMA] ₀ = 1.17 M, [C] ₀ = 1.28 x 10 ⁻⁴ M, solvent : THF)	98
4.9	Effect of Monomer Concentration on the Rate Constant ([I] ₀ = 1.23 x 10 ⁻² mol/L, [C] ₀ = 1.28 x 10 ⁻⁴ M, solvent : THF)	100
4.10	Effect of Temperature on the Rate of Polymerization ([MMA] ₀ = 1.17 M, [I] ₀ = 1.23x10 ⁻² M, [M] ₀ /[I] ₀ = 95, [C] ₀ = 1.28 x 10 ⁻⁴ M, Solvent : THF)	103
5.1	Statistical Copolymerization of MMA (M ₁) and LMA (M ₂) at low Conversions at 0 ⁰ C	108
5.2	Calculation of η and ξ Values According to Kelen and Tudos	113
5.3	Composition Data and Conditional Probabilities P _{ij} for the Copolymerization at Low Conversion of Methyl Methacrylate (M) with Lauryl Methacrylate (L)	115
5.4	Assignment of the α-CH ₃ Resonance to Sequences of M- and L-Centered Triads	118
5.5	Experimental and Calculated Pentad Probabilities for Poly(Methyl Methacrylate) Samples using GTP	123
5.6	Experimental and Calculated Pentad Probabilities for Poly(Lauryl Methacrylate) Samples using GTP	124
5.7	Stereochemical Configuration of M-Centered Pentads Determined from the Analysis of the C=O Resonance Signals	124
5.8	Stereochemical Configuration of L-Centered Pentads Determined from the Analysis of the C=O Resonance Signals	125
5.9	Statistical Copolymerization of MMA (M ₁) and LMA (M ₂) at High Conversion in THF at 24 ⁰ C	131
5.10	Results of Block Copolymers of MMA (M ₁) and LMA (M ₂)	133
5.11	Effect of Livingness Enhancer on the Block Copolymerization of MMA (M ₁) and LMA (M ₂)	134
6.1	GTP of MMA using Alkali Metal Bibenzoate/ Crown Ether Complex Catalyst in THF (M ₀ 0.094 mol, C ₀ = 14.2 x 10 ⁻⁶ mol, I ₀ = 6.89 x 10 ⁻⁴ mol)	144
6.2	GTP of MMA using TBABB and KBB/ 18-C-6 Catalyst (I ₀ = 6.89x10 ⁻⁴ mol)	146
6.3	GTP of MMA using KBB/ 18-C-6 Catalyst at Different Catalyst Cocentrations in THF (M ₀ = 0.094 mol, I ₀ = 6.89 x 10 ⁻⁴ mol, CE/C = 1)	148
6.4	Effect of Crown Ether to Catalyst Ratio on GTP of MMA using KBB/ 18- C-6 Catalyst in THF (MMA = 0.094 mol, C ₀ = 35.5 x 10 ⁻⁶ mol, I ₀ = 6.89 x 10 ⁻⁴ mol)	148
6.5	GTP of MMA using KBB/ 18-C-6 Catalyst at Low Temperature at 15 ⁰ C in THF (MMA = 0.047 mol, C ₀ = 17.25x10 ⁻⁶ mol, I ₀ = 3.4x10 ⁻⁴ mol)	150

6.6	Effect of Catalyst Concentration on the Rate of Polymerization at 25 ⁰ C ([MMA] ₀ = 1.17 M, [I] ₀ = 1.23x10 ⁻² M, [M] ₀ /[I] ₀ = 95, solvent : THF)	152
6.7	Effect of Initiator Concentration on the Rate of Polymerization at 25 ⁰ C ([MMA] ₀ = 1.17 M, solvent : THF)	153
6.8	Effect of Temperature on the Rate of Polymerization ([MMA] ₀ = 1.17 M, [I] ₀ = 1.23x10 ⁻² M, [M] ₀ /[I] ₀ = 95, solvent : THF)	155
6.9	Comparison of Energy of Activation and Frequency Factor using Different Catalysts	157
6.10	Effect of Monomer Concentration on the Rate of Polymerization at 25 ⁰ C Constant ([I] ₀ = 1.23 x 10 ⁻² mol/L, solvent: THF)	158
7.1	GTP of N-Phenyl Maleimide in THF	170
7.2	Effect of Temperature on 1:1 Adduct Formation (M ₀ = 8.7 x 10 ⁻⁴ mol, I ₀ = 12.3 x 10 ⁻⁴ mol, C ₀ = 13.2 x 10 ⁻⁵ mol)	171
7.3	GTP of N-Phenylmaleimide using ZnBr ₂ Catalyst in CH ₂ Cl ₂ at 25 ⁰ C	171

List of Figures

3.1	Apparatus used for vacuum distillation	79
3.2	Apparatus used for conducting polymerization	79
3.3	Apparatus used for kinetic measurement	80
4.1	SEC-RI for poly(methyl methacrylate)s a) entry 1, Table 4.1; b) entry 2, Table 4.1; c) entry 3, Table 4.1.	86
4.2	SEC-RI for poly(butyl methacrylate) (entry 2, Table 4.3)	89
4.3	SEC-RI for poly(butyl methacrylate) (entry 2, Table 4.4).	91
4.4	SEC-RI for poly(lauryl methacrylate)s a) entry 1, Table 4.5; b) entry 2, Table 4.5; c) entry 3, Table 4.5.	92
4.5	SEC-RI for PMMA at different conversions	94
4.6	First-order time-conversion plots for the GTP of MMA with MTS initiator and TBABB catalyst in THF as a function of catalyst concentration: ● = K-5, ▲ = K-24, ■ = K-25	96
4.7	Bilogarithmic plot of the apparent rate constants vs. catalyst concentrations	97
4.8	First-order time-conversion plots for the GTP of MMA with MTS initiator and TBABB catalyst in THF as a function of initiator concentration: ● = K-5, ▲ = K-29, ■ = K-31	98
4.9	Bilogarithmic plot of the apparent rate constants vs. initiator concentration	99
4.10	First-order time-conversion plots for the GTP of MMA with MTS initiator and TBABB catalyst as a function of monomer concentration: ● = K-33, ▲ = K-36, ■ = K-36.	100
4.11	First-order time-conversion plots for the GTP of MMA with MTS initiator and TBABB catalyst in THF as a function of temperatures: ● = K-10, ▲ = K-11, ■ = K-5.	101
4.12	Arrhenius plot for the polymerization rate constants in the GTP of MMA with MTS initiator and TBABB catalyst	103
4.13	Number average degree of polymerization as a function of monomer conversion in THF with MTS initiator and TBABB catalyst	104
4.14	Polydispersity as a function of monomer conversion in the GTP of MMA with MTS initiator and TBABB catalyst	105
5.1	¹³ C NMR spectra in TCB of random copolymer at low conversion: PMMA-co-PLMA (feed ratio 60-40 mol%) (entry 3, Table 5.1)	109
5.2	SEC-RI of random copolymers at low conversion	110
5.3	Copolymerization diagram for the monomer system MMA and LMA	111

5.4	Determination of the monomer reactivity ratios for the GTP of MMA and LMA according to the Kelen and Tudos method, $\alpha = 0.75$	112
5.5	^{13}C NMR spectra (75.5 MHz) of the $\alpha\text{-CH}_3$ side groups of M-L copolymers	117
5.6	Schematic representation of M centered triads of methyl methacrylate--lauryl methacrylate copolymers	119
5.7	Variation of tactic sequences with M molar fraction in the copolymer. The points are experimental results from the $\alpha\text{-CH}_3$ resonance signals: mm = ●; rm.mr = ▲; rr = ■	121
5.8	^{13}C NMR spectra (75.5 MHz) of the C=O side groups of M-L copolymers	122
5.9	M centered pentad sequence probabilities as a function of P_m : mmmm = ●; mmmr = ▲; mmmr = ▼; rmmr = ◆; mmrr = ■; rrrm = ○; mrrm = Δ; rrrm = ∇; rmrr = ◇; mrrr = □	125
5.10	L centered pentad sequence probabilities as a function of P_m : mmmm = ●; mmmr = ▲; mmmr = ▼; mmrr = ◆; mrrm = ■; rrrm = ○; mrrm = Δ; rrrm = ∇; rmrr = ◇; mrrr = □.	126
5.11	SEC-RI of random copolymers at quantitative conversion: a) entry 1, Table 5.9, b) entry 2, Table 5.9, c) entry 3, Table 5.9, d) entry 4, Table 5.9 and e) entry 5, Table 5.9	127
5.12	^1H NMR spectra (in CDCl_3) of random copolymer: PMMA-co-PLMA (feed ratio 60-40 mol%) (entry 3, Table 5.9)	128
5.13	SEC-MALLS of random copolymer: PMMA-co-PLMA (feed ratio 52:48 mol%) (entry 3, Table 5.9)	130
5.14	SEC-RI for a) homopolymer before chain extension, b) block copolymer after chain extension: I) entry 1, Table 5.10, II) entry 2, Table 5.10, III) entry 3, Table 5.10, IV) entry 4, Table 5.10 and V) entry 5, Table 5.10	132
5.15	SEC-RI for a) PLMA before chain extension, b) PLMA-b-PMMA copolymer after chain extension (entry 1, Table 5.11) (without 'livingness enhancer').	133
5.16	SEC-MALLS of block copolymer: PMMA-b-PLMA (feed ratio 50:50 mol%) (entry 3, Table 5.10).	135
5.17	^1H NMR spectra (in CDCl_3) of block copolymer: PMMA-b-PLMA (feed ratio 50:50 mol%) (entry 3, Table 5.10)	136
5.18	TG curve of copolymer	138
6.1	SEC-RI for a) PMMA prepared using Na ₄ -NP/ DB18-C-6 catalyst b) PMMA prepared using KBB/ 18-C-6 catalyst	144
6.2	SEC-RI for a) PMMA prepared using KBB/ 18-C-6 catalyst b) PMMA prepared using TBABB catalyst	145

6.3	SEC-RI for a) PMMA prepared using KBB/ 18-C-6 catalyst in toluene b) PMMA prepared using TBABB catalyst in toluene	146
6.4	SEC-RI for PMMA prepared using different catalyst concentration a) entry 1, Table 6.3 b) entry 2, Table 6.3 c) entry 3, Table 6.3 d) entry 4, Table 6.3	147
6.5	SEC-RI for PMMA using different CE/C ratio a) entry 1, Table 6.4 b) entry 2, Table 6.4	148
6.6	SEC-RI for PMMA prepared at 15 ⁰ C using different CE/C ratio a) entry 1, Table 6.5 b) entry 2, Table 6.5 c) entry 3, Table 6.5	149
6.7	Time vs. conversion plots for the GTP of MMA: ■ = TBABB; ● = KBB/ 18-C-6	150
6.8	First-order time-conversion plots for the GTP of MMA using KBB/ 18-C-6 catalyst as a function of catalyst concentrations. TBABB: ● = K-37; ▲ = K-43; ■ = K-26	151
6.9	Bilogarithmic plots of the apparent rate constants vs. catalyst concentrations.	152
6.10	First-order time-conversion plots for the GTP of MMA as a function of initiator concentrations: KBB/ 18-C-6: ● = K-22; ▲ = K-43; ■ = K-21	154
6.11	Bilogarithmic plot of the apparent rate constant vs. initiator concentrations.	154
6.12	First-order time-conversion plots for the GTP of MMA using KBB/ 18-C-6 catalyst as a function of temperatures. TBABB: ● = K-13; ▲ = K-12; ■ = K-14	155
6.13	Arrhenius plot for apparent rate constants in the GTP of MMA using KBB/ 18-C-6 catalyst (■)	156
6.14	First-order time-conversion plots for the GTP of MMA using KBB/ 18-C-6 as a function of monomer concentrations. TBABB: ● = K-38; ▲ = K-43; ■ = K-40	158
6.15	Polydispersity as a function of monomer conversion in the GTP of MMA in THF using MTS initiator and KBB/ 18-C-6 catalyst (■)	159
6.16	Number average degree of polymerization as a function of monomer conversion in the GTP of MMA in THF using MTS initiator and KBB/ 18-C-6 catalyst: ● = P _n (calcd.), ■ = P _n (obs.)	160
6.17	Plots (1/k _{app} vs. 1/[I] ₀) according to eq. 6.3 for estimation of k _p and K [*]	163
7.1	¹ H NMR spectrum of poly(N-PMI) (entry 1, Table 7.1)	166
7.2	¹³ C NMR spectrum of poly(N-PMI) (entry 1, Table 7.1)	167
7.3	IR spectrum of poly(N-PMI) (entry 1, Table 7.1)	168
7.4	SEC-RI for N-PMI polymer (entry 1, Table 7.1)	169

TH-1098

CHAPTER-I

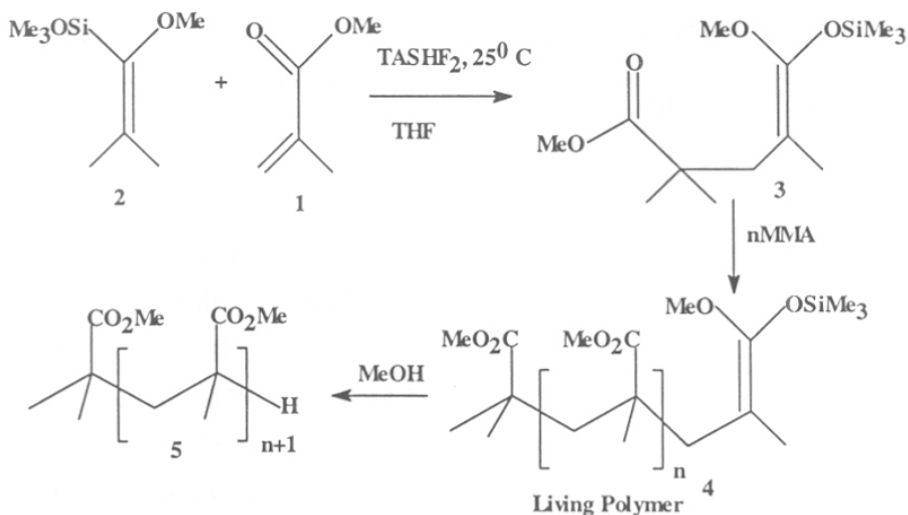
GROUP TRANSFER POLYMERIZATION: A CRITICAL REVIEW

1.1 INTRODUCTION

Controlled synthesis of polymers of acrylic and methacrylic esters with predictable molecular weights, narrow polydispersity and well defined molecular architecture is of fundamental as well as practical significance. For the controlled synthesis of acrylic polymers many excellent initiators have been reported, which includes, biphenyl sodium¹, t-BuMgBr coupled with MgBr₂ or R₃Al^{2,3}, metalloporphyrin of aluminum⁴, (1,1-diphenyl hexyl) lithium/LiCl⁵, and lanthanide complexes⁶. Amongst these, initiators based on ketene silyl acetals have proved to be one of the most attractive method for preparing poly(alkyl methacrylate)s with controlled molecular structure.

Group Transfer Polymerization (GTP) is a relatively new technique for the polymerization of acrylic monomers discovered by the scientists at DuPont⁷⁻¹⁰ in 1983. The technique gives "living" polymers (polymers that are capable of further increase in molecular weight upon the addition of additional monomer) at room temperature or above. This is in distinct contrast to the anionic polymerization of (meth)acrylic monomers which can be performed satisfactory only at low temperatures (below -50°C). Although GTP works best for (meth)acrylates, other monomers such as acrylates, acrylonitrile, maleimide and vinyl ketone can also be polymerized. Since block and graft copolymers have found increasing use as elastomers, compatibilizers, adhesives and components of high performance finishes, there has been a great emphasis on development of new synthetic methods for the preparation of well characterized block and graft copolymers. GTP appears to overcome some of the major disadvantages of other types of polymerization for preparation of well defined functional block copolymers. For example, although anionic polymerization of styrene and butadiene has been carried out commercially, the anionic polymerization of methacrylate monomer is difficult due to the low temperatures (-50°C) required to maintain the "living" conditions.

GTP is an example of Michael addition of silyl ketene acetal to α,β -unsaturated carbonyl compound. **Scheme 1.1** illustrates the polymerization of methyl methacrylate (MMA) **1** with (1-methoxy 2-methyl 1-propenoxy) trimethyl silane (MTS) **2** as the initiator in the presence of anionic or Lewis acid catalysts. The trimethylsilyl is transferred from the initiator and the growing chain end to the incoming monomer (hence the name GTP).



Scheme 1.1: GTP of MMA using MTS as initiator and TASHF₂ as catalyst

GTP initiator in presence of catalyst is very sensitive to protonic impurities (moisture, alcohol etc.). Presence of these impurities renders the initiator inactive and results in loss of molecular weight control. This is especially true when high molecular weight polymers are desired. Thus, ensuring that monomer, solvent and catalyst are pure and dry enables one to successfully prepare (meth)acrylate homo- and copolymers of desirable molecular weight.

1.2 MONOMERS FOR GTP

The original patent literature on GTP¹¹ identifies several monomers. The process is particularly applicable to polymerizations of α,β -unsaturated esters, especially methacrylates and acrylates.

1.2.1 Alkyl methacrylate

(Meth)acrylates are the most suitable monomers for GTP and can produce polymers with narrow molecular weight distributions at room temperature. Most of the common and commercially available methacrylates have been successfully polymerized^{12,13}. Methacrylates with bulky ester groups often polymerize more slowly than does MMA. MMA has been polymerized using many different conditions (**Table 1.1**).

Table 1.1: Effect of Catalyst and Solvent on the GTP of MMA

Sr. No.	Initiator	Catalyst	Solvent	$\bar{M}_n \times 10^{-3}$ (Theory)	$\bar{M}_n \times 10^{-3}$ (GPC)	\bar{M}_w/\bar{M}_n	Ref.
1	2	TBAF,H ₂ O	THF	60.0	62.3	1.15	13
2	2	TASHF ₂	THF	10.1	10.2	1.17	13
3	2	ZnBr ₂	ClCH ₂ CH ₂ Cl	3.4	6.02	1.20	13
4	65	TASHF ₂	THF	5.1	28.6	3.61	13
5	65	Et ₄ NCN	CH ₃ CN	3.07	11.8	1.64	13
6	71	TBACN	THF	50.0	48.1	1.34	14
7	2	TBABOAc	THF	4.78	4.86	1.32	15
8	2	TBAB	THF	4.78	4.50	1.38	15
9	2	(Ph ₄ P) ₂ HF ₂	THF	28.4	43.0	1.32	16

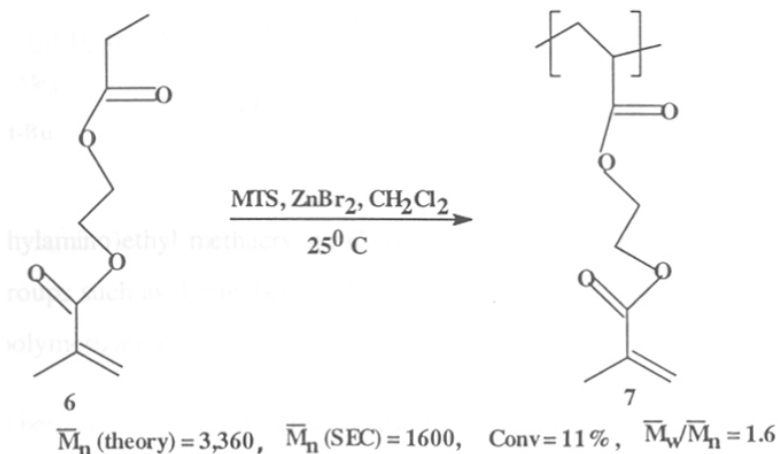
1.2.2 Alkyl acrylate

Acrylates polymerize more rapidly than methacrylates and give polymers with a lower degree of control over molecular weights and relatively broader molecular weight distribution¹².

Table 1.2: Polymerization of Acrylic Monomers by GTP

Sr No	Mono mers	Initiator	Catalyst	Solvent	$\bar{M}_n \times 10^{-3}$ (Theory)	$\bar{M}_n \times 10^{-3}$ (SEC)	\bar{M}_w/\bar{M}_n	Ref
1	PBA	2	HgI ₂	Hexane	9.34	8.62	1.04	21
2	PEA	2	HgI ₂	Toluene	9.34	9.91	1.18	21
3	PEA	2	HgI ₂	CH ₃ CN	4.5	4.09	1.74	21
5	PEA	2	ZnBr ₂	ClCH ₂ CH ₂ Cl	10.1	17.0	1.57	18
6	PEA	38	ZnI ₂	ClCH ₂ CH ₂ Cl	1.2	1.25	1.10	13
7	PBA	2	i-Bu ₂ AlCl	ClCH ₂ Cl	2.66	2.37	1.06	18
8	PEA	2	(i-Bu ₂ Al)O	Toluene	2.1	1.33	1.19	13
9	PBA	MeSSiMe ₃	TASHF ₂	CH ₃ CN	1.0	1.5	1.44	22
10	PEA	2	ZnI ₂	ClCH ₂ Cl	--	10.00	1.1	20
10	PBA	MTS	TASHF ₂	THF	23.8	27.2	2.16	13

To some extent this problem can be overcome using Lewis acid catalysts¹⁸. The difference in reactivity between acrylates and methacrylates is illustrated by the polymerization of acryloyloxyethyl methacrylate (Scheme 1.2) to give a polyacrylate with pendent methacrylate residues^{17,18}. The cause of molecular weight broadening in the GTP of acrylates may be due to cyclotermination¹⁹ which has been observed for methacrylates or the migration of the trimethylsilyl group from the oxygen atom to the α -carbon atom of the chain end¹³. Lewis acids are the preferred catalysts for acrylate polymerizations¹³ (Table 1.2).



Scheme 1.2: Relative reactivity of acrylate and (meth)acrylate monomers

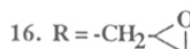
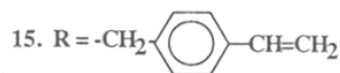
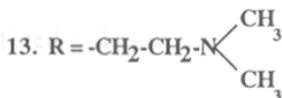
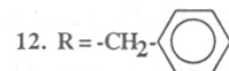
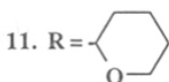
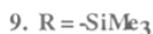
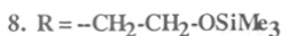
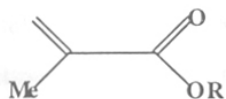
1.2.3 Functional group bearing acrylic monomer

Active hydrogen compounds interfere with GTP and stop chain growth if present in amount greater than the initiator concentration. To make polymers with pendant hydroxyl or carboxyl groups, it is necessary to protect these groups.

Polymer with pendant hydroxyl group was prepared by using 2-(trimethylsilyloxy) ethyl methacrylate (TMS-HEMA, **8**)²³ as the monomer. The trimethyl silyl group was removed from the polymer by treating with methanolic tetrabutylammonium fluoride (TBAF).

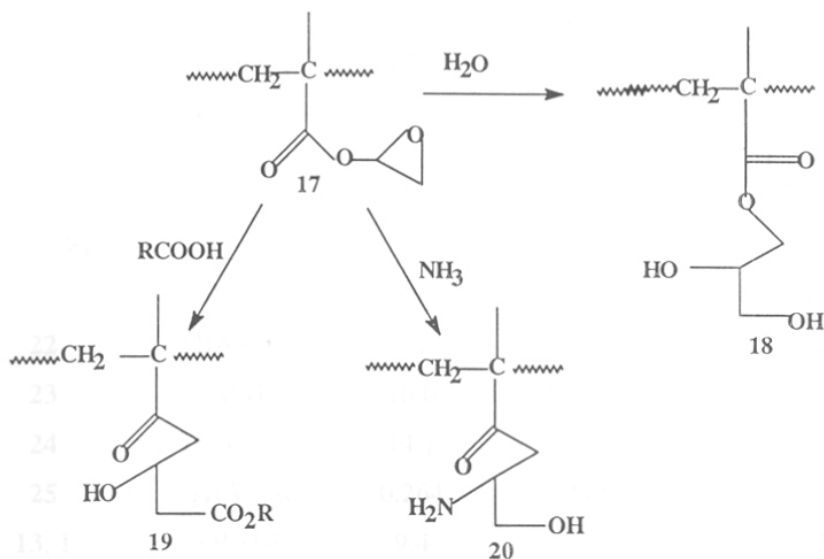
Various protected monomer approaches have been used to make polymers with methacrylic acid by GTP. Use of trimethylsilyl methacrylate (TMS-MA, **9**)²⁴ was limited to copolymers with low acid concentration, apparently because of competition between the monomer and chain ends for the available catalyst. Other protected monomers that have been used are t-butyl methacrylate (t-BMA, **10**)²⁴, tetrahydropyranyl (THPMA, **11**)²³ and benzyl

methacrylate (BzMA, **12**)^{24,25}. In most cases, copolymers rather than homopolymers were prepared. The t-butyl group from the polymer was cleaved by hydrolysis in presence of p-toluene sulfonic acid at 80°C. Benzyl group was deprotected from poly(BzMA) by hydrogenation using Pd/C catalyst.



(N,N-dimethylamino)ethyl methacrylate (DMAEM, **13**)²³ has been polymerized by GTP. Functional groups such as 4-vinylbenzyl (**14**)²⁶, allyl (**15**)¹³, glycidyl (**16**)²⁷ which interfere in many ionic polymerization reactions are inert to GTP.

GTP of vinyl benzyl methacrylate (VBM) cause the methacrylate double bond to polymerize to the exclusion of styrenic double bond. The broad molecular weight distribution of VBM homopolymer was due to the competing thermal polymerization of the styrenic double bond.




Scheme 1.3 Functionalization reactions of PGMA

So, it was necessary to copolymerize with another monomer (in order to decrease the proximity of styrenic double bonds) and to use low temperatures in order to completely prevent any thermal reaction.

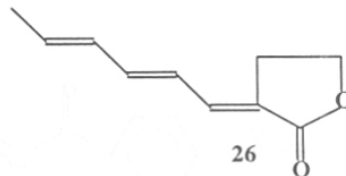
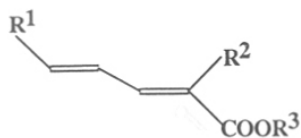
Glycidyl methacrylate was polymerized without interference from the epoxy groups provided the temperature was below 0° C. The epoxy group could then be functionalized to give functional polymers (Scheme 1.3).

Polyunsaturated monomers⁷, namely, **21**, **22**, **23**, **24**, **25**, **26**, undergo GTP to give polymers with main chain double bonds. Different functional (protected or unprotected) monomers polymerized by GTP have been listed in Table 1.3.

Table 1.3: GTP of Functional Monomers using MTS Initiator.

Sr. No.	Monomer	Catalyst	$\bar{M}_n \times 10^{-3}$ (Theory)	$\bar{M}_n \times 10^{-3}$ (GPC)	\bar{M}_w/\bar{M}_n	Functionality	Ref
1	8	TBABB	4.76	4.75	1.41	-OH	23
2	9	TBABB	--	--	--	-COOH	24
3 ^d	10 (20%) BMA(80%)	TASF ₂ SiMe ₃	--	16.4	1.07	-COOH	24
4	12	TBAF	14.0	12.0	1.07	-COOH	25
5	11	TBABB	4.76	4.12	1.1	-COOH	23
6 ^a	14	TASHF ₂	4.81	8.25	1.1	-CH=CH ₂	26
7 ^d	15 (11%),BMA (32%), 1 (57%)	TASHF ₂	--	3.8	1.07	-CH=CH ₂	13
8 ^{c,d}	16 (13%) 1 (87%)	CsHF ₂	--	4.77	1.3		27
9	21	TBAOAc	5.7	37.0	3.3	Allyl	7
10	22	TBA _m -CB	7.7	33.9	1.81	Allyl	7
11	23	TASHF ₂	16.0	52.0	4.43	Allyl	7
12 ^b	24	TBA _m -CB	14.1	18.7	1.97	Allyl	7
13	25	TBAOAc	0.264	7.24	1.51	Allyl	7
14 ^d	13 , 1	TBABB	9.4	8.25	1.07	-N(Me) ₂	23

a. Reaction temperature was 0°C. b. Reaction temperature was 35°C. c. Solvent was glyme. d. All were block copolymers.



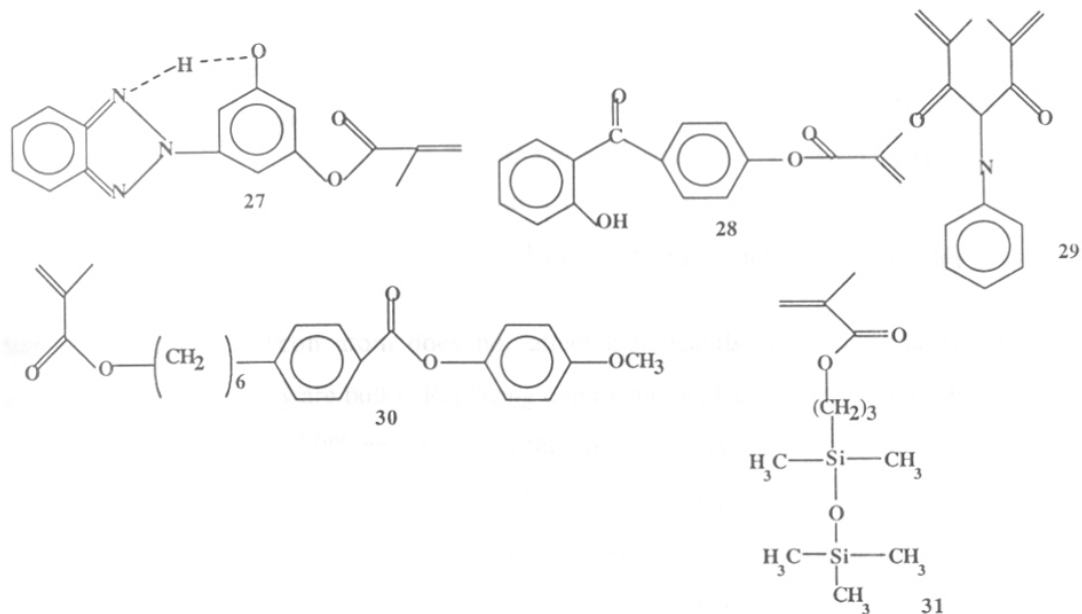
21. R¹ = R² = H; R³ = Me
22. R¹ = H; R² = R³ = Me
23. R¹ = H; R² = Me; R³ = Et
24. R¹ = Me; R² = H; R³ = Et
25. R¹ = COOEt; R² = H; R³ = Et

1.2.4 Miscellaneous monomers

The ability to polymerize unusual monomers have lead to the preparation of a variety of novel materials²⁸⁻³⁰. Two different groups have polymerized monomers of mesogenic groups by GTP for the preparation of polymers having liquid crystalline characteristics. Pugh and Percec³¹⁻³³ prepared polymers containing both mesogenic and nonmesogenic electron donor and electron acceptor groups. In addition, Kredur et al.³⁴ further examined the synthetic utility of GTP for the preparation of liquid crystalline poly(alkyl methacrylate). Polymerization results are given in **Table 1.4**.

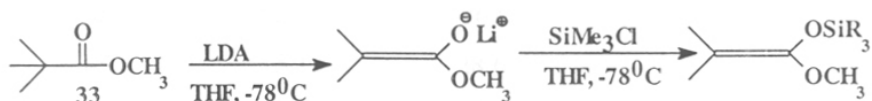
Table 1.4: GTP of Miscellaneous Monomers

Sr.No.	Monomer	Catalyst	$\bar{M}_n \times 10^{-3}$ (Theory)	$\bar{M}_n \times 10^{-3}$ (SEC)	\bar{M}_w / \bar{M}_n	Ref.
1	27	TASHF ₂	--	2.94	1.36	28
2	28	TASHF ₂	--	10.93	1.07	28
3	29	TASF ₂ SiMe ₃	--	--	--	30
4	30	TASHF ₂	20.0	15.1	1.6	34
5	31	TASHF ₂	--	18.6	2.93	29
6 ^a	32	TASHF ₂	10.12	8.16	1.05	32



1.3 INITIATORS FOR GTP

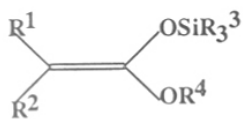
Synthesis of ketene silyl acetals, in general, have been reported in the literature since 1907³⁵. The first recognized ketene trialkylsilyl acetal was prepared by the reaction of trimethyl silane and MMA by Petrov³⁵ in 1959. Ketene silyl acetals since then have been prepared by various methods which yield varying amounts of C- and O-silylated product. **Scheme 1.4** illustrates the preparation of silyl ketene acetals. This route involves the preparation of silyl ketene acetals from anions of acetates and trimethyl chlorosilane (TMSCl). The anion is formed by addition of Lithium diisopropyl amide (LDA) to an ester, followed by the addition of TMSCl^{35,36}. A diverse number of initiators have been effectively employed in GTP.



Scheme 1.4: Synthetic routes to ketene silyl acetals

1.3.1 (1-Methoxy-2-methyl-1-propeneoxy) trimethyl silane (MTS)

The most common and preferred initiator for GTP is 1-methoxy-1-(trimethylsiloxy)-2-methyl prop-1-ene (MTS)⁷.



$$2. \quad R^1 = R^2 = R^3 = R^4 = H$$

$$34. \quad R^1 = R^2 = R^4 = Me; \quad R^3 = Et$$

$$35. \quad R^1 = R^2 = R^4 = Me; \quad (R^3)_3 = Me_2t-C_4H_9$$

$$36. \quad R^1 = R^2 = R^4 = Me; \quad (R^3)_3 = Me_2t-C_{18}H_{37}$$

$$37. \quad R^1 = H; \quad R^2 = R^3 = R^4 = Me$$

$$38. \quad R^1 = R^2 = R^3 = Me; \quad R^4 = (CH_2)_2-OSiMe_3$$

Substitution on the silicon atom does not affect significantly the molecular weight and polydispersity unless they are bulky. Replacing one methyl with octadecyl group (36) reduces the initiator efficiency to 90% and increases the polydispersity to 2.07. However, replacing one methyl by t-butyl group (35) results in loss of \bar{M}_n and increases the polydispersity to 2.12. Furthermore, the rate of polymerization is also reduced¹³. An initiator with $R_1 = H$, $R_2 = R_3 = R_4 = Me$ (37) exhibits reduced efficiency of 70%. However, polydispersity is ~ 1.4 . Possibly the catalyst used may have catalyzed isomerization of the O-silyl initiator to less active C-silyl compound (Table 1.5).

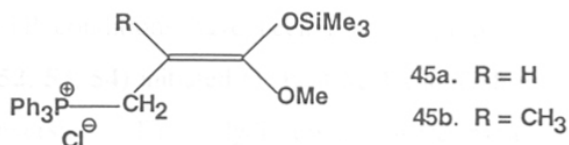
Table 1.5: Effect of Structure of the Initiators on Polymerization of MMA

Sr. No.	Initiator	$\bar{M}_n \times 10^{-3}$ (Theory)	$\bar{M}_n \times 10^{-3}$ (SEC)	$\bar{M}_w \times 10^{-3}$ (SEC)	\bar{M}_w/\bar{M}_n
1	2	60	53.7	85.38	1.59
2	34	10.1	10.2	14.7	1.45
3	35	1.99	17.9	37.9	2.12
4	36	7.6	8.28	17.1	2.07
5	37	10.1	14.2	21.1	1.48
6	38	123	262	371	1.42
7	65	5.1	28.6	103	3.61
8	66	2.1	13.0	54.0	4.0
9	67	10.1	47.5	188	3.96

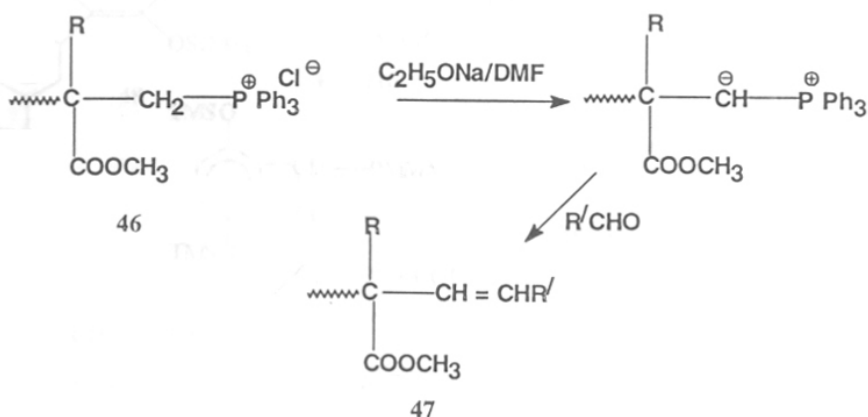
1.3.2 Functional group containing initiators

Polymers with reactive functionality on one or both chain ends can readily be introduced by using an initiator bearing functional group or groups (in the masked form if reactive towards

cations. The phosphonium cation was postreacted to make functional polymers. Polydispersity of the polymers were higher because the reactivity for a nucleophilic attack was reduced in the initiators substituted by the triphenylphosphonium group with electron withdrawing property.



The macromolecular phosphonium salts could be converted with sodium ethanolate into



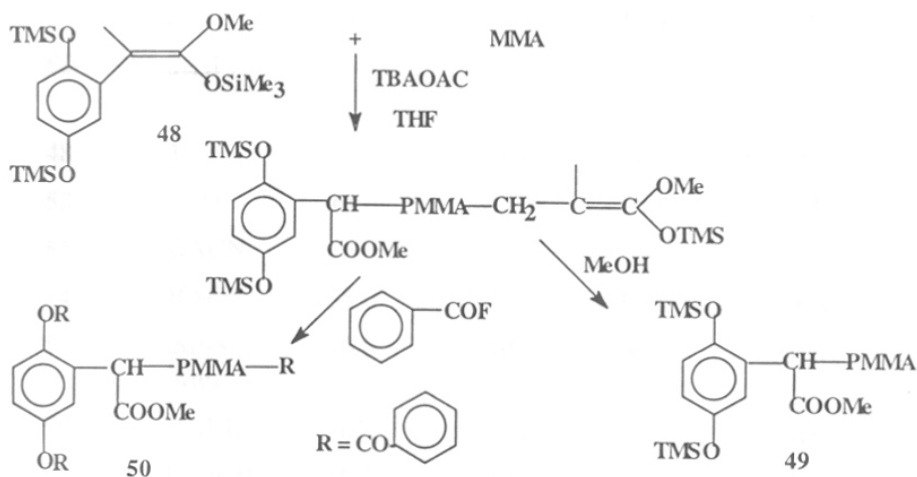
Scheme 1.7: Synthesis of vinyl group terminated macromonomer

the corresponding macromolecular ylides and by a subsequent Wittig reaction with an aldehyde into a macromonomer (Scheme 1.7).

Initiator 48⁴⁰ was used to initiate the GTP of MMA to macromonomers with aromatic hydroxyl functions. Tetrabutylammonium acetate was used as catalyst in order to avoid cleavage of the phenolic TMS protective groups by the well known fluoride or bifluoride catalyst. The molecular weight of the protected macromonomer was proportional to the ratio of monomer to initiator. However, a dependence on polydispersity of the resulting polymer on the rate of monomer addition was found. Slow or discontinuous monomer addition resulted in the broadening of polydispersity. This means that some undesired reactions occurred in the monomer starved system and the system was not living (Scheme 1.8).

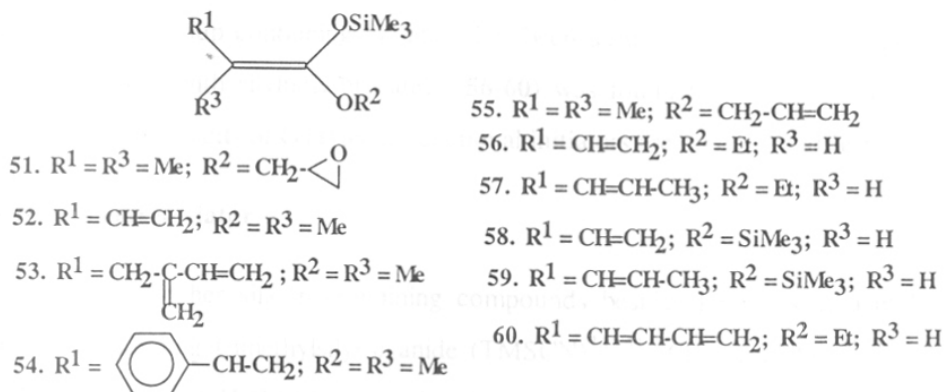
Epoxy functional initiator **51**²⁷ was used to make functional polymers. This approach places an epoxy functional group at the end of every chain. The epoxy group can be reacted with conventional epoxy based resins to make branched or triblock polymers.

A variety of initiators bearing functional groups such as vinyl, allyl, styrenyl⁴¹ etc. which are not reactive under GTP conditions have been used to prepare acrylic macromonomers. Functional initiators (**52**, **53**, **54**) initiated GTP of MMA in THF using TPSHF₂ or TBACN with quantitative conversions. The polydispersities were broader (1.2-1.7) than those expected from a real living system.




Scheme 1.8: Synthesis of PMMA macromonomers with phenolic functionality by GTP

Asami et al⁴⁰ also used the vinylbenzyl functional group containing initiator (**54**) for MMA polymerization. This initiator worked best at low temperature about 0°C using TASF₂SiMe₃ catalyst.



Attempts have been made to prepare vinyl group substitution at the alkoxy group of silyl ketene acetals (**55**) but their activity in GTP has not been examined in detail.

Table 1.6: GTP of MMA using Different Functional Initiators

Sr. No.	Initiator	Catalyst	$\bar{M}_n \times 10^{-3}$ (Theory)	$\bar{M}_n \times 10^{-3}$ (GPC)	\bar{M}_w/\bar{M}_n	Functionality	Ref
1	39	TASHF ₂	--	21.0	1.03	-OH	37
2	40	TASHF ₂	--	21.0	1.03	-COOH	38
3	43	TASHF ₂	7.57	7.05	1.03	-PO ₃ H ₂	13
4 ^a	45	ZnBr ₂	3.04	3.38	1.78	-PO ₃ H ₂	39
5	51	CsHF ₂	--	--	--		27
6	48	TBAOAc	--	3.1	--	-Ph(OH) ₂	40
7	52	TPSHF ₂	15.0	11.2	1.45	Allyl	43
8	53	TBACN	15.0	16.76		Allyl	41
9	54	TBACN	15.0	19.2	1.31	-Ph-CH=CH ₂	41,42
10 ^b	55	TASF ₂ Si Me ₃	10.0	10.7	1.1	Allyl	43
11	56	TBABB	6.1	7.06	1.8	Allyl	43
		TBAmCB	15.1	19.0	1.34		
12	57	TBABB	10.1	9.76	1.46	Allyl	43
13	58	TBABB	1.45	2.17	1.29	Allyl	43
14	59	TASHF ₂	3.1	3.91	1.17	Allyl	43
15	60	TBABB	5.15	20.1	1.12	Allyl	43
		TBAmCB	5.12	5.91	1.15		

a. Solvent was CH₂Cl₂. b. Temperature was 0^oC. c. Solvent was CH₃CN.

A variety of allyl group containing initiators has been used by Hertler et al⁴³. The rate of initiation of MMA with silylpoly(enolate)s (**56-60**) was found to be faster than with silyl ketene acetals. The results of GTP using functional initiators are given in Table 1.6.

1.3.3 Non acetal initiator

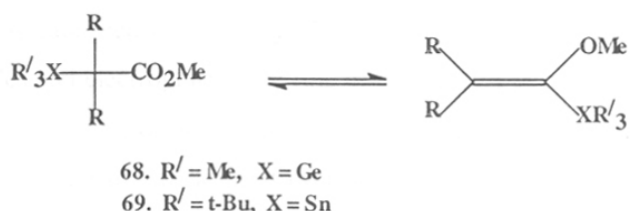
There are several other silicon containing compounds besides ketene silyl acetals which initiate GTP including trimethylsilyl cyanide (TMSCN)^{7,13,44} (**61**), R₁SSiMe₃^{11,13} (**62**, R₁ = Me, **63**, R₁ = Ph, CH₂CH₂OSiMe₃), tetrabutylammonium thiolates (**64**)⁴⁵, Me₃SiCH₂CO₂Et

(65)¹³, Me₃SiCH₂CO₂t-Bu (66)¹³, Me₂C(CN)SiMe₃ (67)¹³. In general these initiators exhibit low efficiency and give polymer with high polydispersity. They act by generating ketene acetal upon addition to the monomer. The product of initiation may undergo isomerization.

1.3.4 Metal containing initiators

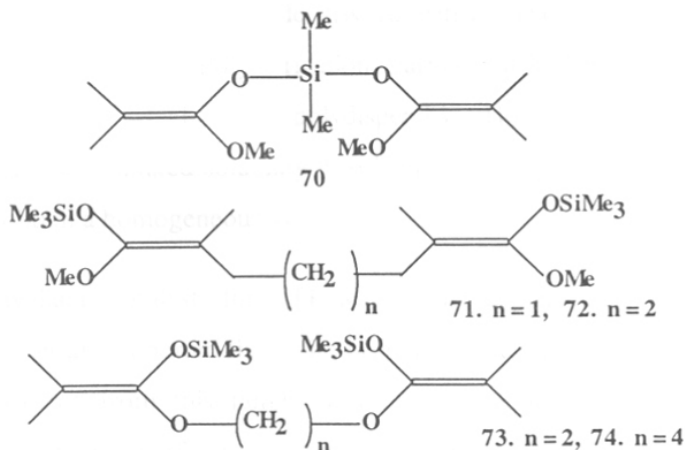
α -Trimethylsilyl, stannyl and germanyl esters can initiate GTP but provide poorer control over molecular weight and polydispersity⁴⁶. It has been suggested that the primary step is the rearrangement of ketene silyl acetal and that the slow rate of this process, and consequent slow initiation, is responsible for broad polydispersity¹³.

Titanium enolate has been reported to initiate GTP at low temperatures⁴⁷.



1.3.5 Bifunctional initiator

Bifunctional initiators have utility in the preparation of A-B-A triblock copolymers by reducing the synthesis from a three to two step procedure. Sogah⁴⁸ described the use of a bifunctional initiator, **70**, to prepare ladder polymers. However, no details are available. This initiator should initiate two chains which would be separated after termination of the reaction. A typical structure of a bifunctional initiator is one with terminal silyl ketene acetal groups linked by β -methyl groups or α -alkoxy groups. Choi and coworkers⁴⁹ have synthesized bifunctional initiators **71**, **72** and used them in the synthesis of A-B-A triblock copolymer. Steinbrecht and Bandermann⁵⁰ also studied the polymerization using initiators **71** and **73**. Using tetrabutylammonium cyanide catalyst in THF, PMMA was successfully prepared from **71** with complete conversion and $\bar{M}_w/\bar{M}_n = 1.15-1.41$. The bifunctionality of the initiator **73** was confirmed by hydrolyzing a polymer to obtain a material with half the molecular weight.



1.4 CATALYSTS FOR GTP

The GTP process is catalyzed by a variety of reagents which fall into two general classes, namely, nucleophiles and electrophiles. The role of the catalyst in polymerization mechanism appears to change depending on its nature. Electrophilic catalysts such as Lewis acid have been proposed to activate the monomer towards nucleophilic attack by ketene silyl acetal chain ends. Nucleophilic catalysts are believed to coordinate to the silicon atom of the initiator or the propagating chain end producing a pentacoordinate intermediate that is more reactive towards coordination with an incoming monomer¹⁰.

1.4.1 Nucleophilic catalysts

Fluoride and bifluoride compounds have been successfully employed as catalyst in the GTP of alkyl methacrylates^{50,52,13}. The original catalyst tris(dimethylamino)sulfonium bifluorotrimethyl silicate ($\text{TASF}_2\text{SiMe}_3$) displayed a high activity and works best at low temperatures (-78°C). Hydrolysis of this catalyst yields TASHF_2 , a crystalline solid, which is most frequently employed as the catalyst⁵³. Counterions of the anion determine the solubility of the salt. Catalysts such as TASHF_2 and potassium bifluoride (KHF_2) are soluble in solvents having high polarity (acetonitrile and dimethyl formamide). When solvents of lesser polarity are employed with these catalysts, a cosolvent is necessary. Despite the low solubility of TASHF_2 , in THF, the polymerization of MMA with a heterogeneous mixture of solid TASHF_2 in THF has been demonstrated to yield controlled molecular weight and narrow polydispersity polymers¹³.

Alternative nucleophilic catalysts include tris (dimethylamino) sulfonium cyanide¹³ and tetraethylammonium cyanide^{13,54}. Polymerizations carried out in THF again resulted in good control over molecular weight and polydispersity. However, counterions like the tetraethylammonium have limited solubility in solvents of low polarity. Hence a cosolvent is typically used to obtain a homogeneous system¹³.

The breadth of available catalysts for GTP was further expanded by DuPont scientists in 1987, when Dicker et al.¹⁵ reported the utility of numerous oxy-anions to catalyze GTP. The expanded catalysts list from this family of oxyanions included carboxylate, phenolate, sulfonate, phosphonate and perfluoro alkoxide. The list was further expanded by the ability to prepare a series of bioxyanions from the stoichiometric reaction of the oxy-anions and their conjugate acids. Simple mono-oxyanionic salts such as tetrabutylammonium bibenzoate, are prepared for example, by reaction of aqueous TBAOH with PhCOOH in a 1/2mol ratio. These catalysts are soluble in polar solvents such as THF. Molecular weight control and narrow polydispersities are achieved for a range of oxyanions catalysts. It has been noted however, that a number of parameters influence the activity of the catalysts. Firstly the counterion is influential. It has been proposed that co-ordinating cations such as sodium in sodium acetate, complex strongly to the anion making the anion less available for interaction with the silyl ketene acetal functionality. Hence, in order to achieve more control over polymerization process, the use of noncoordinating cations, like TAs⁺ and tetraalkylammonium etc. are recommended. In addition, preliminary investigations show that crown ether complexes too strongly with coordinating counterions, like K⁺, freeing the anion to serve as a catalyst⁵⁵ (**Table 1.7**).

Secondly, the polymerization temperatures appears to affect the catalytic activity of these catalysts. GTP is efficiently catalyzed at low temperatures (-78⁰C) with bifluoride catalysts.

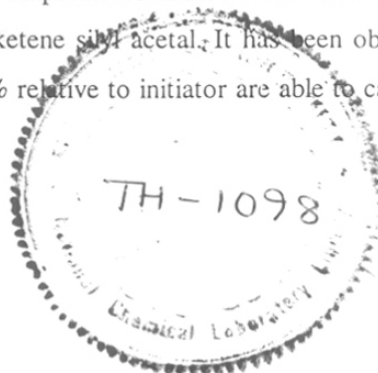
Yet, it is not only the most basic oxyanions catalysts, like acetates, that have been reported (within this class of compounds) to catalyze GTP at low temperature. Certain oxyanions catalysts are ineffective for GTP at room temperature, although, at elevated temperature they become active catalysts¹⁵.

Table 1.7: Effect of Nucleophilic Catalysts on the GTP of MMA

Sr. No.	Catalyst	Solvent	$\bar{M}_n \times 10^{-3}$ (Theory)	$\bar{M}_w \times 10^{-3}$ (SEC)	\bar{M}_w / \bar{M}_n (SEC)	Ref.
1	TASF ₂ SiMe ₃	THF, -78 ⁰ C	2.04	1.12	1.56	7
2	TASHF ₂	THF	4.1	3.80	1.06	13
3	TPSHF ₂	THF	--	--	--	50
4	KHF ₂	DMF	5.1	5.95	1.11	13
5	TBAF, H ₂ O	THF	15.1	17.5	1.14	13
6	TASCN	9% DMF in THF	10.1	10.5	1.14	13
7	Et ₄ NCN	9% DMF in THF	10.1	11.5	1.06	13
8	TASN ₃	CH ₃ CN	3.70	3.0	1.03	7
9	TBA4-NO ₂ B	THF	4.80	4.47	1.51	23
10	TBA4-CNB	THF	4.80	4.08	1.49	23
11	TBA3-CIB	THF	4.80	4.34	1.18	23
12	TBAB	THF	4.80	4.50	1.38	23
13	TBA2-NO ₂ PhO	THF	9.50	6.41	1.14	23
14	TBAPhO	THF	4.80	3.34	2.62	15
15	TBABAc	THF	4.80	4.45	1.28	23
16	TBABB	THF	4.78	4.68	1.06	23
17	TBA3-CIBB	THF	4.78	4.65	1.03	23
18	TBAB4-NO ₂ PhO	THF	4.78	4.85	1.04	23
19	PPNHF ₂	THF	10.0	12.1	1.15	56

The range of nucleophilic reagents which catalyze GTP permits the tailoring of the polymerization to selected reaction conditions, i.e., temperatures and solvents. The level of catalyst is calculated with respect to the moles of ketene silyl acetal. It has been observed that nucleophilic catalyst at levels less than 0.1 mol% relative to initiator are able to catalyze GTP.

RR



1.4.2 Electrophilic catalyst

The use of electrophilic catalysts for GTP is limited in comparison to the studies employing nucleophilic catalysts. The Lewis acid catalysts such as zinc halides, dialkylammonium halides and dialkylammonium oxide, are more efficient in the polymerizations of alkyl acrylates than anionic catalysts⁵⁷. The reaction conditions must be more strictly defined when employing Lewis acids to catalyze GTP. For example, donor solvents must be avoided during polymerization. Halogenated alkanes and aromatic hydrocarbons are preferred solvents. The aluminum catalysts have been used to catalyze GTP in acetonitrile with no apparent inhibitory effects; for example, Hertler et al.⁵⁸ investigated the utility of various zinc halides. The best molecular weight control was observed with zinc iodide while zinc chloride was poor. Zinc halides effectively catalyze GTP at room temperature whereas aluminum catalysts are more sensitive (Table 1.8).

Table 1.8: Effect of Electrophilic Catalysts for the GTP of EA

Sr.No.	Catalyst	Solvent	$\bar{M}_n \times 10^{-3}$ (Theory)	$\bar{M}_n \times 10^{-3}$ (SEC)	\bar{M}_w / \bar{M}_n (SEC)	Ref.
1	ZnCl ₂	Toluene	4.1	5.8	1.96	13
2	ZnBr ₂	(ClCH ₂) ₂	10.1	17.0	1.57	13
3	ZnI ₂	CH ₂ Cl ₂	3.36	3.3	1.03	13
4	Et ₂ AlCl	CH ₂ Cl ₂ , -78 ⁰ C	2.1	2.34	1.17	18
5	(i-Bu ₂ Al) ₂ O	Toluene	2.1	1.33	1.19	18
6	HgI ₂	Toluene	9.34	9.91	1.18	59

Electrophilic catalysts e.g. zinc halides, are required at levels of 10 mol% relative to the monomer. Aluminum catalysts are used about 10 mol% based on the initiator⁶⁰. Although it has been proposed that the Lewis acid catalysts complex with the carbonyl oxygen of the incoming monomer⁵⁸, it is not clear why such high concentrations of catalysts are required to polymerize inherently more reactive acrylate monomers.

1.5 POLYMERIZATION METHODS

1.5.1 Monomer purification

Methacrylate ester monomers ($C > 2$) are usually prepared by transesterification of methyl methacrylate with the corresponding alcohol and are often contaminated with traces of alcohol which is difficult to remove and interfere with GTP and anionic polymerization. Thus, commercially available methacrylate monomers contain the following protonic impurities: i) moisture, ii) alcohol, iii) hydroquinone (the inhibitor) and iv) methacrylic acid. For controlled polymerization a reduction in the levels of these impurities is necessary. Presence of trace impurities in the system results in severe broadening of polydispersities (>1.5), less than quantitative yields and uncontrolled molecular weight.

Calcium hydride (CaH_2) is currently the established purification agent for methacrylate monomers. Traces of moisture, inhibitor and methacrylic acid can be removed by stirring over CaH_2 and subsequent distillation. However, CaH_2 does not react with higher alcohols ($C > 2$) as reported by Allen et al.⁶¹. Conventional organic alcohol scavengers such as calcium chloride (CaCl_2) and 5⁰A molecular sieves fail to remove higher alcohols ($C > 2$). Thus, removal of alcohol is the major problem in the purification of higher methacrylates.

Allen et al.⁶¹ reported that the alcohol impurity can be adequately removed by the reactions with aluminum alkyls. Narrow polydispersities (1.05-1.16) associated with non-terminating polymerization in the molecular weight range 50-70,000 have been observed with diphenylhexyl lithium initiated polymerization of MMA purified from trialkylaluminums (TMA, TEA etc.). However, this method of purification was found unsuitable for higher methacrylates (bp $> 160^\circ\text{C}/760$ mmHg). Under the condition of distillation (static vacuum with heating) trialkylaluminum also codistills with the monomer. Trialkylaluminum is reported to interfere with GTP initiator⁶². Use of adsorbent alumina to remove trialkylaluminum is preferred in case of such high boiling acrylate monomers.

Sogah et al.¹³ have used methacryloyl chloride as purification agent for the removal of alcohol from lauryl methacrylate (LMA). The full potentiality of this method has not been judged as LMA purified by this method was used to prepare only low molecular weight polymers ($\bar{M}_n \sim 2000$).

Citron⁶³ reported the use of aminosilane compounds as purification agent for removal of alcohol, moisture etc. from alkyl methacrylates. Silyl amine readily silylate alcohol and the products are not harmful for GTP. Typically, 0.01 to 3% (by weight) is added to the solvent or monomer before or just at the start of polymerization. It is preferred, but not necessary, that about 10- 2000 ppm of polymerization catalyst also be present during scavenging. Scavenging of the ingredients by treatment with silyl amine prior to polymerization can be carried out under an inert atmosphere (e.g. nitrogen) so as to avoid introducing more poisons, such as water. Scavenging before polymerization can be carried for few minutes to several days, depending on the particular scavenger chosen. Although the temperature is not critical, the lower the temperature the slower the reaction. Solvents, monomers and any other ingredients should preferably first undergo a preliminary purification so that very large amounts of scavengers are not needed. Such methods of purification include passage over activated aluminum and removal of moisture by azeotropic distillation.

1.5.2 Initiator/ catalyst purification

Initiators are normally purified by distillation under reduced pressure. The most commonly used MTS initiator can be distilled at bp 45 °C /15 mmHg .

The solid catalysts are normally purified by recrystallisation. $TASF_2SiMe_3$ was recrystallised from a mixture of acetonitrile/THF⁷. $TASHF_2$ ¹³ was also purified following the same procedure and dried under vacuum. Tetraalkylammonium salts are purified by recrystallisation from dry THF and dry diethyl ether.

1.5.3 Nature of solvent

Suitable solvents for GTP are aprotic liquids in which the monomer, initiator and cocatalyst are sufficiently soluble for reaction to occur; that is, the materials are dissolved at any concentrations employed. Suitable solvents⁶⁴ include ethyl acetate, toluene, bromobenzene, dimethoxy ethane, N,N-dimethyl formamide, tetramethyl sulfone, diethyl ether, N,N-dimethyl acetamide, acetonitrile and tetrahydrofuran. Tetrahydrofuran (THF) is the preferred solvent when a cocatalyst with active species containing an anion is used. When the cocatalyst is zinc compound, suitable solvents are limited to hydrocarbons and chlorinated hydrocarbons,

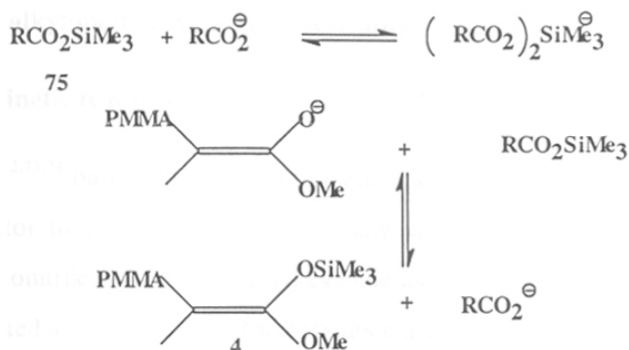
preferably dichloromethane or 1,2-dichloroethane. Acetonitrile is silylated under GTP conditions and is not recommended⁶⁵⁻⁶⁷.

1.5.4 Effect of pressure

Without catalysts, silyl ketene acetals are inactive as initiator at atmospheric pressure. Under very high pressures (6000-15000 atmospheres), MMA and ethyl acrylate were polymerized in presence of MTS initiator. However, there was no control of molecular weight and conversion was low⁶⁸.

1.5.5 Livingness enhancing agents

To synthesize well defined block and star polymers, it is desirable to find ways to increase or enhance the 'livingness' of the GTP chain ends during polymerization. Addition of few percentage of trimethylsilyl ester⁶⁹ whose pK_a value is equal to or lower than the pK_a value of the catalyst used in the polymerization, increases the longevity of the living chain end. The preferred concentration of the "livingness enhancement agent" (LE agent) is in the range of 0.1 to 200 moles per mole of catalyst. Use of LE agent leads to higher molecular weight, lower polydispersity, better control and predictability of molecular weight. The star branched polymers are prepared by terminating living PMMA chain ends with ethylene glycol dimethacrylate (EGDMA). Results of polymerization in terms of conversions, molecular weight etc. are summarized in **Table 1.9**. These examples show that improvements in molecular weight control, conversion and unattached arms are dependent on both the nature of LE and amount of LE.



Scheme 1.9: Mechanism of silyl carboxylates livingness enhancer in GTP

Table 1.9: Molecular Weight Results of GTP Star Polymers in Presence of LE Agents

Sr. No.	TMSCB (%) ^a	TMSAC (%) ^a	TBACB (%) ^a	TBAAC (%) ^a	$\bar{M}_n \times 10^{-3}$ (arms)	$\bar{M}_n \times 10^{-3}$ (star)	Unattached Arms (wt%)
1	0.00	0.00	0.00	1.82	100.0	Very High	Indeterminate
2	0.00	4.92	0.00	1.76	20.0	110.0	32
3	0.00	2.29	0.00	1.87	Very Low	180.0	Indeterminate
4	0.00	14.77	0.00	1.50	21.0	60.0	56
5	0.00	0.00	1.42	0.00	13.0	61.0	50
6	0.00	8.68	1.71	0.00	40.0	320.0	90
7	4.70	0.00	0.00	1.89	11.0	105.0	21

The beneficial action of “livingness enhancer” is proposed to be the result of a complex formation of the carboxylate ester with the catalyst and providing a means of supplying it continuously at a low concentration. They may also scavenge trace amounts of anionic chain end (Scheme 1.9).

1.6 KINETICS AND MECHANISM

1.6.1 Apparatus and experimental techniques

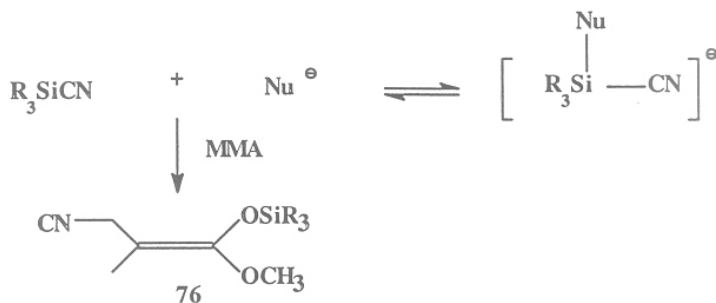
Stirred tank reactor⁷⁰ has been used by Muller et al for over all kinetics measurement. Stop flow FT-IR method has been used by Brittain⁷¹ to measure rate of initiation and first or second propagation step.

1.6.2 Kinetics of alkyl methacrylate polymerization

1.6.2.1 General kinetic features

Bandermann et al^{72,73,74} published a series of kinetic results for the GTP of MMA in which the ratio of initiator to catalyst was systematically varied. The initial investigations were carried out in acetonitrile with trimethylsilyl cyanide as the initiator and TASF₂SiMe₃ as the catalyst (documented as coinitiator)⁷². Their results indicate that the concentration of catalyst influences the degree of control achieved during polymerization. For a given initiator concentration, the conversion to polymer as well as molecular weight of the final polymer

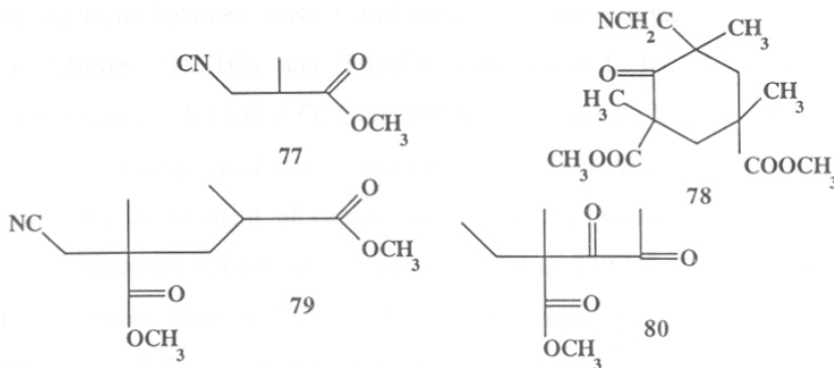
both go through a maximum as the catalyst concentration is increased⁷². The effect of initiator to catalyst concentration was unclear due to the presence of an induction period. The induction period was attributed to the complexation of catalyst and the initiator. It was proposed that the initiator complexed more strongly than the propagating chains. Therefore, until the trimethyl silyl cyanide initiator is consumed by addition to monomer forming an active ketene silyl acetal, a slower polymerization rate was observed as an induction period (Scheme 1.10).



Scheme 1.10: Conversion of TMSCN to silyl ketene acetal by the reaction with MMA in the presence of catalyst

In order to examine the effect of catalyst concentration on the mechanism of GTP, studies were performed with an expanded list of initiator and catalyst sets⁷²⁻⁷⁴. Kinetic experiments using either $\text{TASF}_2\text{SiMe}_3$ or tetraethylammonium cyanide (Et_4NCN) in combination with either trimethylsilyl cyanide or [(1-methoxy-2-methyl)-1-propenyloxy]trimethylsilane (MTS), were performed in acetonitrile^{72,74}. In all cases the GTP of MMA deviated from the living system. Studies employing chromatographic techniques and NMR identified the side reactions responsible for the observed deviation from living behavior⁷⁴.

In the GTP of MMA using MTS as the initiator and Et_4NCN as the catalyst, the first side reactions detected were attributed to the anionic oligomerization of MMA initiated by Et_4NCN . The addition reaction of the monomer with the catalyst results in the loss of “active” catalyst for polymerization. Sitz et al.⁷⁴ resolved a number of species using chromatographic techniques, which are illustrated below.



These species arise from the familiar termination reaction in the classical anionic polymerization of MMA. Further studies, confirmed by NMR, elucidated side reactions involving the MTS initiator. These side reactions involve the isomerization of MTS to its carbon silylated form. Furthermore, both these species react with acetonitrile in the presence of nucleophilic catalyst to generate $\text{Me}_3\text{SiCH}_2\text{CN}$ and methyl isobutyrate. Since the active chain ends have the same structure as MTS, according to the proposed associative mechanism, it is assumed that severe terminations can occur in GTP due to this exchange. This results in loss of active centers. Therefore, complete conversion and molecular weight control cannot be obtained under all experimental conditions. Finally, it was determined that MTS could react with Et_4NCN forming trimethylsilyl cyanide, an initiator for GTP.

Further support for these side reactions was elucidated with trimethylsilyl cyanide/ $\text{TASF}_2\text{SiMe}_3$ and trimethylsilyl cyanide/ Et_4NCN systems⁷⁴. Though $\text{TASF}_2\text{SiMe}_3$ does not undergo oligomerization reaction with MMA in acetonitrile, both the catalysts, $\text{TASF}_2\text{SiMe}_3$ and Et_4NCN show similar behavior with respect to initiation and propagation reactions, and to the termination reactions of the propagating chain with solvent. It was concluded from these studies, that the living character of GTP in acetonitrile depends strongly on the catalyst concentration. At high initiator and low catalyst concentrations, propagation is faster than termination. At higher catalyst concentrations, termination reactions become dominant, limiting the maximum conversion, loss of molecular weight control and causing an apparent broadening of polydispersity.

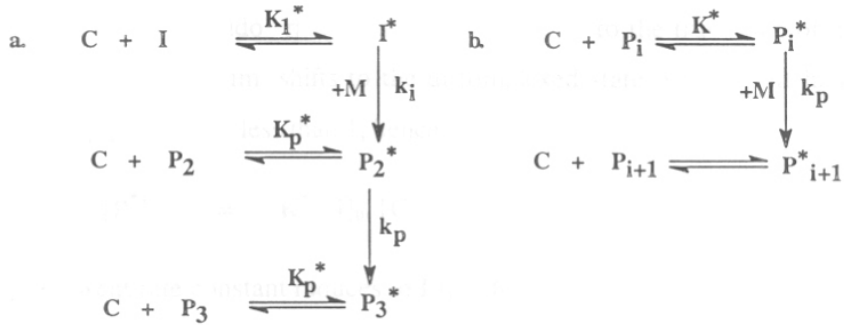
To further examine the effect of catalyst activation in GTP, Sitz and Bandermann⁷² selected catalysts that would not require the use of acetonitrile, hence reducing the chances of

termination reactions between solvent and initiator or the propagating chain ends. THF soluble $\text{TPSF}_2\text{SiMe}_3$, TPSHF_2 and TBACN were studied. In all cases, the catalyst concentration necessary for rapid GTP of MMA are extremely low and the reaction rate increased with increasing catalyst concentration. Though it was reported that molecular weight was nearly independent of catalyst concentration, indicating a living system, side reactions were observed in each of the catalyst systems. TPSHF_2 , for example, not only promoted the isomerization of MTS to its carbon silylated product, but also caused the oligomerization of MTS and releasing Me_3SiF . Consequently, the number of active centers decreased causing deviations from living behavior. For these reasons the TBACN system was examined. This is less active in the oligomerization of MTS. However it is known that cyanide anions can initiate the polymerization of MMA. It was shown that neither of these reactions occur to any appreciable extent during the GTP of MMA and hence, they can be neglected under these conditions.

Systematic evaluation of the molar ratio of initiator to catalyst were also performed. From these investigations a number of unusual anomalies were noticed which cause deviation from the living behavior. In view of this acetonitrile is considered to be an unacceptable solvent for GTP.

Kinetic Scheme

To gain deeper insight into the mechanism of GTP, Muller et al⁷⁵⁻⁷⁸, addressed key mechanistic questions through kinetic investigations. Their aim was to determine the reaction order with respect to the concentration of reagents of polymerization, namely, monomer, initiator and catalyst. Assuming the rate of propagation is faster than the rate of termination, Mai and Muller proposed a kinetic scheme consistent with the DuPont's proposed associative mechanism^{75,76} (**Scheme 1.11a**). Noting that initiator and living chain end have the same structure the scheme is simplified (**Scheme 1.11b**).



Scheme 1.11: General kinetic scheme for GTP

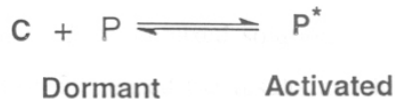
The change in monomer concentration for a living system with time for such a kinetic scheme can be written as Eq. 1.1.

$$\ln([M]_0/[M]) = k_p \cdot [P^*] \cdot t = k_{app} \cdot t \quad \text{Eq. 1.1}$$

$$\text{where } k_{app} = k_p \cdot \frac{K^* \cdot [I]_0}{1 + K^* \cdot [I]_0} [C]_0 \quad \text{Eq. 1.2}$$

$$= \text{const.} [I]_0^\beta \cdot [C]_0 = k'_{p^*} [C]_0 \quad \text{Eq. 1.3}$$

For the above kinetic scheme, the important factor to note is the parameter β . The value of β corresponds to two limiting cases. If the equilibrium is shifted to the right side, represented by the pentacoordinate complex, which will also be addressed as activated (*), then the product of ($K^* \times [I]_0$) is much greater than 1, hence ; the concentration of activated species (P^*) is equal to the concentrations of catalyst $[C]_0$. The apparent rate constant subsequently reduces to Eq. 1.4.



$$K^* \cdot [I]_0 \gg 1 \quad \text{then} \quad \beta = 0.$$

$$\text{and } k_{app} = k_p \cdot [C]_0 = k'_{p^*} [C]_0 \quad \text{Eq. 1.4}$$

Rearranging Eq. 4, the “pseudo” rate constant (k_p') equals to the true rate constant (k_p). Alternatively, if the equilibrium shifts to the uncomplexed state, i.e. the left hand side, the product of ($K^* \times [I]_0$) is much less than 1, hence:

$$[P^*] = K^* \cdot [I]_0 \cdot [C]_0 \quad \text{Eq. 1.5}$$

In turn, the apparent rate constant reduces to Eq. 1.6

$$K^* \cdot [I]_0 \ll 1 \quad \text{then} \quad \beta = 1 \quad \text{and} \quad K_{app} = k_p \cdot K^* \cdot [I]_0 \cdot [C]_0 \quad \text{Eq. 1.6}$$

Rearranging Eq.s 1.2 and 1.3 for this limiting case the “pseudo” rate constant is a function of the initial initiator concentration (Eq. 1.7).

$$k_p' = k_{app} / [C]_0 = k_p \cdot K^* \cdot [I]_0 \quad \text{Eq. 1.7}$$

The apparent rate constant is dependent on the value of β , which may lie between zero and unity depending on the activation equilibrium of initiator or the growing chains.

In summary, if GTP follows the kinetic scheme proposed by Mai and Muller, then it was predicted that the reaction order should be first order with respect to monomer and catalyst, whereas the kinetic order with respect to initiator, β is expected to be $0 < \beta < 1$. This dependence of order on the rate of propagation has been defined by Eq. 1.8.

$$R_p = \text{const.} \times [M]_0^\alpha \cdot [I]_0^\beta \cdot [C]_0^\gamma \quad \text{Where } \alpha = 1, 0 < \beta < 1 \text{ and } \gamma = 1 \quad \text{Eq. 1.8}$$

Kinetic investigations were performed to elucidate the reaction order with respect to the initiator, monomer and catalyst. An important detail to note is the order of the addition of the reagents employed in this studies. For all of experiments, a solution of catalyst in THF (without acetonitrile) was charged to premixed solution of initiator and the monomer in THF. The order of the addition influenced the results and hence, becomes a factor in the conclusions stated by Muller et al^{76,77}.

1.6.2.2 Effect of monomer concentration

The kinetic scheme, described above, predicts a linear dependence with respect to monomer concentration. Muller et al investigated the reaction order dependence with respect to two different alkyl methacrylates; methyl methacrylate and t-butyl methacrylate. For the GTP of

both monomers using TASHF₂ as the selected catalyst and MTS, as the initiator; it was reported that the kinetic order (α) observed is first order with respect to monomer concentration. Variations from the ideal behavior were noted in the first order time-conversion plots. Deviation from linearity were observed in the later stages of the polymerization of MMA, indicating the presence of termination reactions^{75,77}. The deviations are much more pronounced for t-butyl methacrylate, rendering the determination of the rate constants difficult. The higher termination for t-BMA was attributed to the lower polymerization rate constant.

1.6.2.3 Effect of temperature

Muller et al.⁷⁶⁻⁷⁸ examined the temperature dependence of rate constants in THF using TASHF₂ for the GTP of MMA and t-BMA. The temperature range spanned from ambient to -82°C. To avoid induction periods, all of the experiments of temperature studies were performed at fairly high catalyst concentration. For the GTP of MMA, induction period became more pronounced as the temperature decreased. With increased propagation rate, ideal first order behavior was observed leading to complete conversion. For t-BMA, "induction period" were not observed except below -20°C. However, termination was much more evident at ambient temperatures rendering the determination of rate constant difficult. This could be due to residual t-butanol present from the synthesis of monomer.

From the maximum slopes of the first order time conversion plots (k_{app}) and assuming $K^* \cdot [I]_0 \gg 1$ based on the reaction order with respect to initiator ($\beta = 0$) the rate constants were calculated. If the assumption $K^* \cdot [I]_0 \gg 1$ does not hold, the reported data does not represent the lower limit of the rate constants from the Eq. 1.9.

For general case $(0 < \beta < 1)$

$$k_p' = k_p \cdot \frac{K^* \cdot [I]_0}{1 + K^* \cdot [I]_0} < k_p \quad \text{Eq. 1.9}$$

From the temperature study, an Arrhenius plot was constructed for the determination of the energy of activation (E_a) and the frequency factor (A). For both monomers, the Arrhenius plot was linear yielding direct evidence for existence of only one active species during the polymerization^{76,77}. Muller compared the E_a and log A of these two monomers polymerized

by GTP to the value obtained by anionic polymerization in THF with different counterions. The similar nature of these values shown in **Table 1.10** indicates similar mechanism for the two process. For the associative mechanism proposed by Webster et al.⁷, it was cited that the coordination of carbonyl group of the approaching monomer to the hypervalent silicon atom would require much higher activation entropies. This translates into lower frequency exponents. Based on the activation parameters, it was proposed by Muller et al. that the monomer addition is more likely a two step process. Thus, the rate determining step is the addition of a vinyl group to the activated initiator or the chain end. This process is subsequently followed by the transfer of silyl group to the newly formed enolate (**Scheme 1.18**). Though one can anticipate the formation of a free enolate as the propagating center, this seems to be highly improbable based on the lower rate constant relative to those determined for anionic with free or cryptated anions. The proposed addition of monomer via a two step associative process for GTP is very similar to anionic and free radical polymerization process.

Table 1.10: Comparison of E_a and $\log A$ Values Determined by GTP and Anionic Methods

Sr.No.	Counterions	E_a (KJ/mol)	$\log A$	k_p
1	GTP (TASHF ₂)	16.9	6.8	56
2	Free anion	--	--	2,100
3	Na ⁺ , 222	--	--	270
4	Cs ⁺	19.5	7.3	30
5	K ⁺	19.3	7.2	2
6	Na ⁺	18.3	7.0	34
7	Li ⁺	24.0	7.4	2

1.6.2.4 Effect of catalyst concentration

Muller and coworkers have generated a significant amount of information regarding TASHF₂ as a catalyst. Some studies using benzoate anions have also been reported^{76,77}. It is important to reiterate here that acetonitrile was not employed in the polymerization involving TASHF₂;

hence derivations from the linearity were not directly attributed to side reactions with solvent as shown by Bandermann et al.⁷³.

The propagation reaction for GTP was predicted to be first order with respect to catalyst concentration. Two plots are represented to demonstrate more effectively the effect of catalyst concentration on the polymerization rate⁷⁸. The first order time-conversion plots for the polymerization of MMA indicated that as the catalyst concentration was reduced, the apparent rate of polymerization decreased. At lower catalyst concentrations, slight induction periods were observed prior to the linear increases in the reaction rates. The linearity of the bilogarithmic plot with a slope of 1.17 indicates that reaction order with respect to TASHF₂ catalyst is one, as predicted from the kinetic scheme (Scheme 1.11a). It was also reported that the “pseudo” rate constants (k_p') for the catalyst concentrations having the induction periods calculated from the Eq. 1.3, were smaller than expected. Two probable explanations were offered^{73,74}. First, deactivation of the active centers during the induction period would decrease the k_p' from the calculated value. This explanation will be addressed in further details when the order with respect to the initiator concentration is addressed. In a private communication to Muller et al. from DuPont it was disclosed that a kinetic order of 2 for initial stage of polymerization (oligomers to trimers) was found⁷⁷. It was presumed that this is due to a pre-equilibrium of fluoride ions from bifluoride and would be responsible for the observed induction period.

Initial results were reported for the polymerization of MMA with TAS bibenzoate. Though the reaction order with respect to monomer was again first order, the order with respect to

Table 1.11: Reaction Order w.r.t. Catalyst Concentration in GTP of MMA

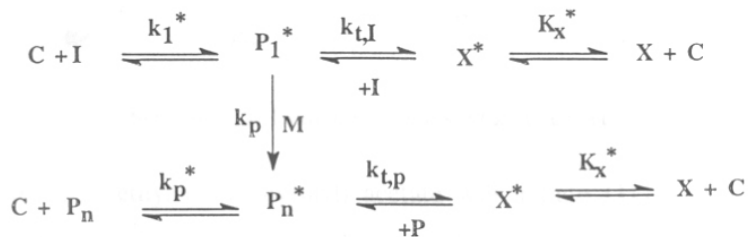
Sr. No.	Catalyst	[M] ₀ mol/L	[I] ₀ mol/L	[P] ₀ mol/L	Solvent	Temp. °C	Reaction order	Ref
1	TASHF ₂	0.18	1x10 ⁻³	2x10 ⁻⁵	THF	20	1.17	76
2	TBABB	0.125	0.25	1.25x10 ⁻³	THF	27	0.3	71
3	TPSHF ₂	0.125	0.25	2.5x10 ⁻⁵	THF	27	2.0	71
4	TASHF ₂	0.125	0.25	2.5x10 ⁻⁵	THF	27	2.1	71
5	TPSB	0.125	0.25	2.5x10 ⁻⁵	THF	27	1	71
6	TBABB	--	--	--	--	--	1	79

catalyst concentration was reported to be in the range between -0.3 to 1.0, depending on the reaction conditions and catalyst nature. The rate as well as reaction orders with respect to different catalysts are given in **Table 1.11**.

1.6.2.5 Effect of initiator concentration

For the defined kinetic scheme, the reaction order (β) with respect to the initiator concentration was cited to be very influential in defining the relationship of the true rate constant (k_p) to the “pseudo” rate constant (k_p'). It was defined that the value of β varied between zero to unity depending on the activation equilibrium between dormant polymer chains and activated polymer chains.

In order to gain more insight into activation equilibrium, the influence of initiator concentration was studied^{76,77}. The influence of the concentration of MTS was reported for two different nucleophilic catalysts; bifluoride and oxyanions. For the polymerization of MMA in presence of TASHF₂, the first order time conversion plots were characterized by slight induction periods when high initiator concentrations are employed⁷⁶. Linearity was observed with slight non-linearity at longer times and was attributed to the termination of growing chains. Using a bilogarithmic plot, the reaction order was determined to be -0.27, which was not consistent with defined kinetic **Scheme 1.11a**. According to Mai and Muller, this negative order dependence indicated that the initiator is inhibiting the reactions; hence, they revised the original kinetic scheme to account for this anomaly⁷⁶ (**Scheme 1.12**). According to this scheme, an inactive species is generated that is capable of binding to the catalyst resulting in lower apparent rate constants. It was proposed that the induction periods observed may be related to this phenomenon.



Scheme 1.12: Deactivation of initiator in presence of excess initiator

As mentioned in the previous section, the polymerization of MMA using TAS benzoate was reported⁷⁵. Though the reaction order with respect to MTS concentration was not explicitly defined, a reaction order of unity with respect to MTS concentration was documented. This



indicates that the equilibrium was shifted to the left hand side resulting in fewer activated species present at any given time. The reaction was proposed to be considerably slower than for the bifluoride catalyst system. The rate constant for propagation could not be accurately determined since equilibrium constants (K^*) were not known and because of the ambiguous behavior of the reaction order with respect to the catalyst concentration.

1.6.2.6 Chain transfer and chain termination mechanism

1.6.2.6a Chain termination mechanism

GTP being living polymerization method requires that termination should be negligible on the time scale of polymerizations. But GTP is not devoid of inherent terminations. Two termination reactions have been identified for GTP of acrylates and methacrylates: isomerization and backbiting.

Isomerization: Silyl ketene acetal in presence of GTP catalyst, can isomerize to C-silylated ester (Scheme 1.12). For example, MTS isomerizes to methyl (trimethylsilyl) isobutyrate. Presumably the same reaction occurs with the propagating chain.

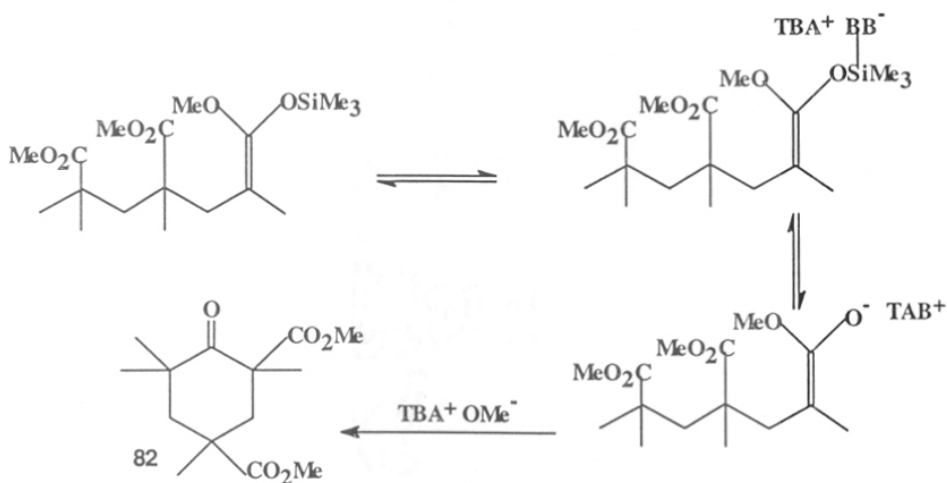


Scheme 1.12: Isomerization of silyl ketene acetal

α -Silylated ester, e.g. ethyl (trimethylsilyl) acetate will initiate GTP of MMA. Observed molecular weights are much greater than those for the rapid initiations and polydispersities are large. From this it was concluded that initiation is much slower than propagation¹³. Because isomerization is reversible, O to C isomerization is not a true termination. However,

it effectively removes isomerized species from the pool of active chains; in the terminology of free radical polymerization, this represents retardation.

Backbiting: The cyclization (Scheme 1.13) is an intermolecular nucleophilic attack by the silyl ketene acetal on the backbone ester. The propensity of a GTP oligomer to self terminate is demonstrated by 85% isolated yield of 2,4-(dicarbomethoxy)-2,4,6,6-tetramethylcyclohexanone (**82**) from the overnight reaction of 0.05 mol of MMA and 0.025 mol of MTS, in THF using 0.00125 mol of TBABB as catalyst. The occurrence of cyclization in GTP argues



Scheme 1.13: Termination by intramolecular cyclization

for the involvement of ester enolate intermediates which are active centers in anionic polymerization^{80,81}.

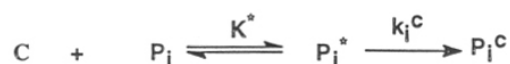
Scheme 1.13 depicts a proposed mechanism where the first step is catalyst complexation to form a pentacoordinate siliconate. The siliconate then may dissociate to form an enolate paired with counteraction of the anionic catalyst; cyclization of the enolate leads to termination of chain end.

Chain end evidence: PMMA prepared using GTP was characterized by Matrix-Assisted Laser Desorption Ionisation Time of Flight Mass Spectrometry (MALDI-TOF-MS)⁸². MALDI-TOF-MS clearly shows that the major species as corresponding to a hydrogen end-group on both ends of the polymer, however, there is also a small amount of end-group

cyclization evidenced by the peaks at 31 amu below the major peaks, i.e. loss of MeO⁻ as would be expected for cyclic termination of the chain end.

Kinetics of cyclization

The kinetics of cyclization have been studied for GTP oligomers prepared from MMA. Rates are based on the following model.



If it is assumed that the catalyst complex, P_i^* , achieves a steady state concentration, and that the rate of catalyst complexation is faster relative to the rate of cyclization (k_i^c), then the rate of reaction is given by :

$$\frac{d[P_i]}{dt} = \frac{k_i^c \cdot K^* \cdot [P_i] \cdot [C]_0}{1 + K^* \cdot [P_i]} \quad \text{Eq. 1.10}$$

The integrated form of this equation depends on the magnitude of the equilibrium constant (K^*). Muller and coworkers⁷⁶ have shown that $K^* \gg 1$ for bifluoride while $K^* \ll 1$ for oxyanion catalysts (bibenzoate, benzoate). This conclusion was made based on the kinetic rate order with respect to initiator concentration for MMA addition. Therefore, there are two limiting cases in the form of equations.

$K^* \cdot [P_i] \gg 1$; for bifluorides, this leads to

$$[P_i] = [P_i]_0 - k_i^c \cdot [C]_0 \cdot t \quad \text{Eq. 1.11}$$

$K^* \cdot [P_i] \ll 1$; oxyanions, this leads to

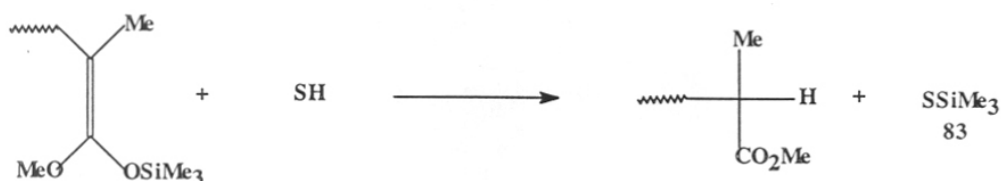
$$\ln ([P_i] / [P_i]_0) = -k_i^c \cdot K^* \cdot [C]_0 \cdot t \quad \text{Eq. 1.12}$$

Thus, the rate of disappearance of living ends by cyclization follows pseudo zero order for bifluorides. Bifluorides are strongly bound to the silicon so that the concentration of catalyst complex remains constant during the process. When “[P_i]₀-[P_i]” is plotted versus t , a straight line is obtained for at least the first half life of bifluorides catalyzed cyclization.

In contrast, the rate of living end disappearance in the presence of oxyanion catalysts follows first order kinetics in accordance with **Eq. 1.12**.

1.6.2.6b Chain transfer

The other major common reaction in polymerization system is chain transfer. Hertler established that carbon acids with $Pk_a < 25$ are transfer agent in GTP^{83,84} whereas carbon acids with $Pk_a < 18$ (e.g. malonate esters), terminate GTP. Known transfer agent S-H donate a hydrogen to the propagating chain and the residue is silylated, **Scheme 1.15**, species S-SiMe₃ is an efficient initiator.



Scheme 1.15: Chain transfer to SH

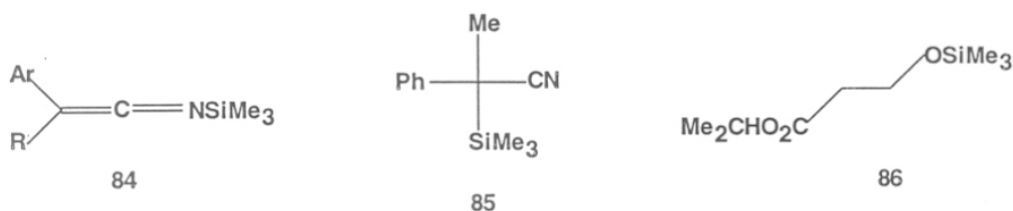
Chain transfer activity was detected by SEC. \bar{M}_n was substantially lower than the predicted value for initiation by silyl ketene acetal alone. Additional evidence for chain transfer was obtained by the use of labelled chain initiator or labeled chain transfer agent followed by end group analysis of the polymer.

Among the compounds that were found to have chain transfer activity in GTP of methyl methacrylate are benzyl cyanide, α -phenylpropionitrile, 2-(β -naphthyl) propionate, methyl phenyl acetate, methyl(p-methoxy phenyl) propionitrile, methyl- α -phenyl propionate, indene, fluorene and γ -thiobutyrolactone. Of these chain transfer agents α -phenyl propionate, gave best overall results in terms of efficiency and freedom from interference with catalyst activity. To facilitate the comparison of effectiveness of chain transfer agents and reaction conditions, chain transfer constant were estimated from the SEC measurement of \bar{M}_n . Transfer constants, the dimensionless ratio of rates of chain transfer to rates of polymerization, were calculated from the equation **Eq. 1.13**.

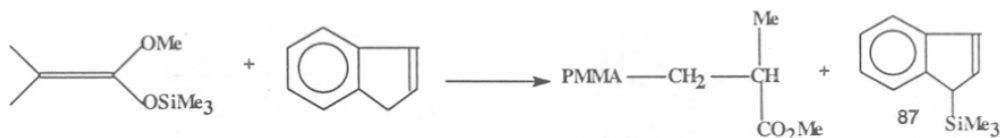
$$1/X_n = 1/X_{n,0} + C_t ([RH] / [M]) \quad \text{Eq. 1.13}$$

in which X_n = observed degree of polymerization in the presence of chain transfer agent, RH, $X_{n,0}$ = predicted degree of polymerization in the absence of RH, calculated as [(moles of monomer + moles of initiator)/moles of initiator]Y, where Y is the observed conversion to polymer (Y = 1 for 100% conversion), C_t = transfer constant to transfer agent, RH, $[RH]$ = moles of RH and $[M]$ = moles of monomer.

Mechanism of transfer by aryl-substituted nitrile are unknown but it has been suggested that N-silyl ketene imines (**84**) may be the active species formed; transfer probably leads to **85** as a kinetically controlled product⁸⁵. Silylation of phenyl propionate gave the C-silylated (**86**) which even in the presence of high catalyst concentration give low rates of polymerization and is unlikely to be active intermediate (**86**) and might interchange in the presence of catalyst.



Using protected hydroxyl initiators (**39**) the propagations of chains derived from initiator and from transfer agent residues were identified. These proportions may vary with the catalyst used. In the case of α -phenyl propionitrile transfer does not involve reaction of the active intermediate from transfer with hydrogen in isobutyrate residues in the dead polymer. The chain transfer agent (**86**) itself provides a protected hydroxyl label and its use gives terminal functionality by chain transfer. Comparative experiments derived from initiator and transfer agent varied as in **Scheme 1.16** and in support, it was shown that **87** will initiate polymerization.



Scheme 1.16: Chain transfer to Indene

1.6.3 Kinetics of alkyl acrylate polymerization

1.6.3.1 General kinetics features

Recently, Muller and coworkers⁸⁶ have studied the kinetics of n-butyl acrylate with Lewis acid catalyst, HgI_2 , in toluene. When HgI_2 is used as a catalyst, only 10 mol% of the Lewis acid based on initiator concentration is needed. Dicker et al has suggested that HgI_2 activates the initiator, i.e. acts like a nucleophilic catalyst. Thus, data have been treated according to equations derived for nucleophilic catalysis.

1.6.3.2 Effect of monomer concentration

The reaction order with respect to monomer concentration was unity like methacrylate polymerization catalyzed by nucleophilic catalyst.

1.6.3.3 Effect of temperature

As expected, the rate of polymerization increased with temperature and at the same time induction periods decreased. From the Arrhenius plot, the apparent activation energy, $E_{a,app} = 42.5$ kJ/mol is obtained. Nevertheless, a comparison with GTP of MMA in THF catalyzed by TAS bibenzoate yields the same activation energy ($E_{a,app} = 42.1$ kJ/mol). This is another indication that the mechanisms are similar.

1.6.3.4 Effect of initiator concentration

With increasing initiator concentration, the rates of polymerization increase and the induction periods decrease. The bilogarithmic plot for the apparent rate constants, k_{app} vs. initiator concentration $[I]_0$ gives a slope of 1.13. This indicates that the kinetic order with respect to initiator concentration is approximately unity, although a higher order cannot be excluded.

1.6.3.5 Effect of catalyst concentration

Increasing HgI_2 concentrations lead to increased rates of polymerization and decreased induction periods. The bilogarithmic plot of the apparent rate constants of the propagation, k_{app} vs. initial catalyst concentrations $[C]_0$ resulting in a straight line with a slope of 0.92. This indicates that the reaction is of first-order with respect to catalyst concentration.

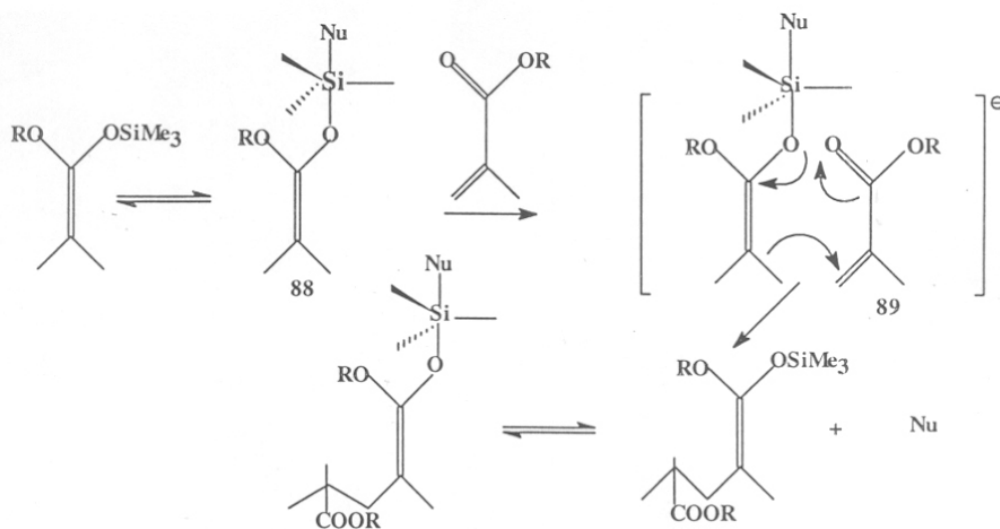
1.7 MECHANISM OF GTP

While there is no dispute about the synthetic utility of GTP, there is no unanimous agreement on the mechanism of polymerization. There are no detailed mechanistic studies of GTP catalyzed by Lewis acids. Therefore, the focus of this mechanistic discussions will be limited to catalysis by anions.

Several mechanisms might be written for GTP. The principal mechanistic question is whether GTP takes place by an associative mechanism or dissociative mechanism.

1.7.1 Associative Mechanism

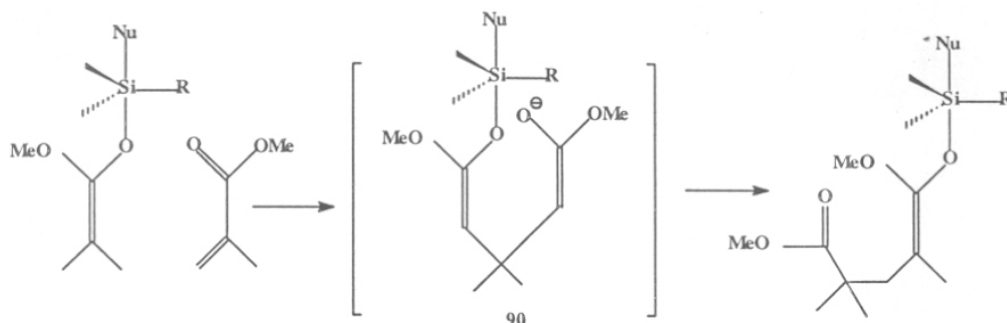
Based on the mechanistic studies using trapping and labelling experiments, Webster et al.^{7,66} proposed an intramolecular transfer mechanism for GTP, in which the silyl group is directly transferred from the initiator or propagating chain end to the carbonyl oxygen of incoming monomer via a hypervalent silicon intermediate. **Scheme 1.17** illustrated the activation of the silicon atom by a nucleophile to provide a pentacoordinated species and this intermediates then reacts with MMA forming a hexacoordinated silicon intermediate; C-C bond formation and migration of trimethyl group to the carbonyl of the incoming monomer. The important



Scheme 1.17: Associative mechanism of GTP proposed by DuPont group

distinction in this mechanism is that silyl exchange among the growing chains is excluded; hence the identity of the silicon of the initiator molecules remains invariant throughout the growth of the polymer chains .

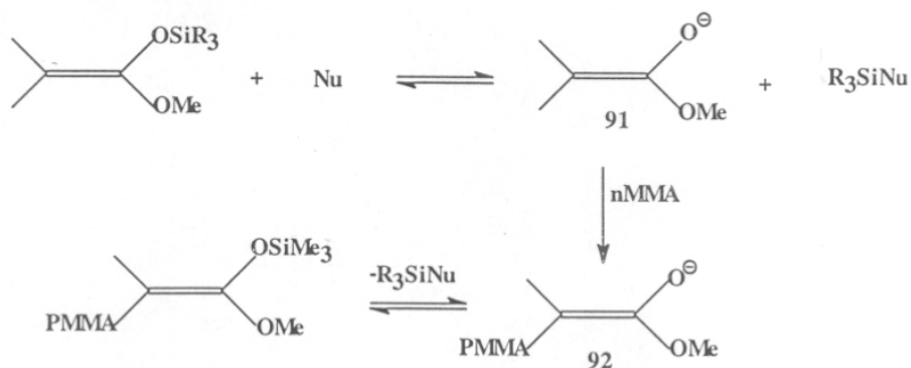
This concerted mechanism was later modified by Muller⁷⁹ to a two step associative mechanism (Scheme 1.18) where the C-C bond formation proceeds silyl migration⁵⁷.



Scheme 1.18: Two step associative mechanism of GTP proposed by Muller

1.7.2 Dissociative Mechanism

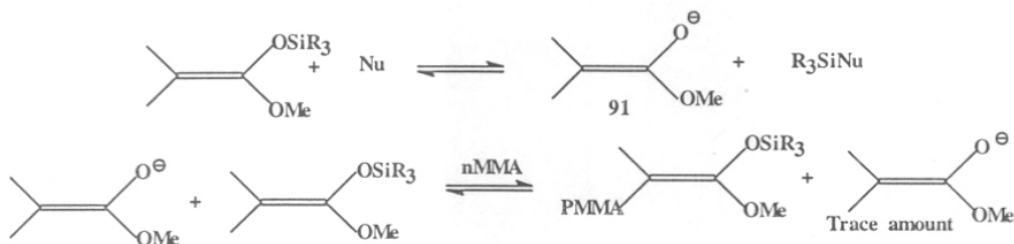
Despite the report that fluorosilane was not formed in a reversible dissociative step and silyl group exchange is not involved, detailed aspects of the GTP mechanism are not yet well elucidated. Two plausible dissociative mechanisms have been illustrated in Scheme 1.19 and 1.20.



Scheme 1.19: Reversible dissociative mechanism of GTP

The first scheme represents a reversible dissociative mechanism in which the nucleophile reversibly cleaves the trialkylsilyl group from the initiator generating the ester enolate. The

ester enolate is the propagating species, which, upon repeated addition of monomer, yield a polymeric carbanion. Upon resilylation, the ketene trialkyl silyl acetal fragment is regenerated at the polymeric chain end.



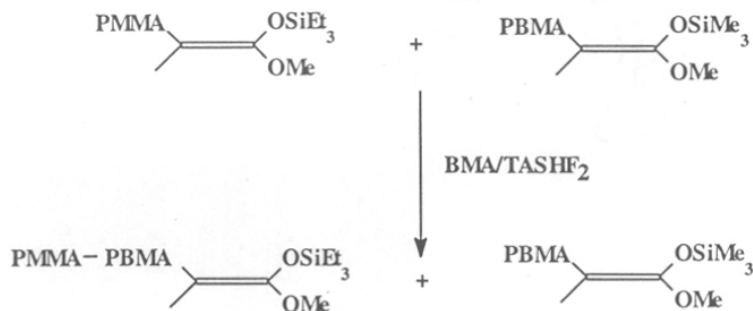
Scheme 1.20: Irreversible dissociative mechanism of GTP

In the other dissociative mechanism the trialkylsilyl group is irreversibly cleaved from the initiator. The associative mechanism involves the direct transfer of the silyl group from the initiator or propagating chain end to the incoming monomer unit via hypervalent silyl intermediate. All these mechanisms ultimately result in the presence of a ketene silyl acetal at the chain end. The existence of this moiety was confirmed using ¹³C NMR and capping reactions^{37,87}. Recognizing, however, that the important distinction between the mechanisms exist with the trialkylsilyl group, Farnham and Sogah set out to dismiss the two dissociative mechanisms.

In the associative mechanism the trialkylsilyl group is not exchanged between the chains; i.e. the identity of the silicon atom remains invariant throughout the polymerization. Under GTP reaction conditions, the formation of fluorosilanes in a reversible dissociative step (Scheme 1.19) was dismissed by labelled silyl fluoride exchange experiments using catalyst quencher such as spiro silane and silver nitrate^{87,88}.

Other results, however, reveal that living oligomers and silyl ketene acetals exchange silyl groups in the presence of a nucleophilic catalyst. This indicates that the resilylation of ester enolates by other silyl ketene acetals (monomeric or oligomeric) may be facile and pronounced at early stage of polymerization. More importantly it was observed that no silyl group exchange between living species occurred. Using two “living” homopolymers of PMMA and PBMA, double labelling experiments were performed to address this mechanistic question concerning the difference between the relative rates of silyl group exchange and

intermolecular transfer during propagation^{87,88}. It was shown that silyl group exchange does not occur between living PMMA and PBMA chain ends, which support an “intermolecular” silyl transfer mechanism (**Scheme 1.21**). Though competition between the propagation rate and the rate of silyl group exchange between the initiator and living oligomers may be evident, it was concluded that the mechanism of propagation is independent of the degree of polymerization and changes in the mechanism of polymerization are inconsistent with the fact that the initiator controls the molecular weight.



Scheme 1.21: Double labelling experiments indicating absence of exchange of silyl groups

Further support for the associative mechanism of polymerization was found in model studies. Silicon differs from carbon in its ability to expand its valency shell and form five or six coordinate compounds⁸⁹⁻⁹¹.

Based on labelling studies and model compound, the exclusive operation of two dissociative mechanisms were eliminated in favor of the proposed associative mechanism. It is pertinent to note that these studies appear to have been conducted with only one of the possible family of catalysts.

The source of possible problems in the “double exchange” experiments has been proposed by Matyjaszewski⁹². It was suggested that the normal exchange rates between silyl endgroups could have been slowed down because of some incompatibility between PMMA and PBMA chains (concentrations appear to have been = 13 wt%). He also pointed out that the double labelling experiments do not exclude the possibility of fast reversible ionizations occurring in a solvent cage around the chain ends with monomer adding at this point. This process would be induced by the presence of the nucleophile which, as in the original mechanism suggested, hops from chain-end to chain-end, randomizing the process. Whatever may be the exact

details, it is clear that the theory of anionic addition of monomer cannot still be excluded. A more sophisticated method for the determination of exchange rates would, no doubt, be useful in bringing better clarity to the problem.

If the results are correct, the mechanism for the nucleophilic catalysts of GTP must be different for different catalysts; mild nucleophile such as TASF_2 , $\text{Bu}_4\text{N}^+\text{F}^-;\text{H}_2\text{O}$ and $\text{Bu}_4\text{N}^+\text{ACOHOAC}^-$ catalyzing associative GTP; strong nucleophiles such as, Bu_4N^+ methylfluorenone, $\text{TASF}_2\text{SiMe}_3$ and TBAOAc catalyzing dissociative GTP⁹³.

1.7.4 Similarities/ differences between GTP/ Anionic

A considerable body of experimental evidence is now available which is consistent with an alternate mechanistic hypothesis that ester enolate anions are the propagating intermediates in group transfer polymerization of alkyl methacrylates⁹⁴.

1. Although GTP exhibits living polymerization, a termination reaction is observed which involves a chain end cyclization reaction to form a cyclohexanone-type chain end; this process is analogous to the termination product of ester enolate anions in corresponding anionic polymerizations.
2. Chain transfer is observed to carbon acids which have pK_a values in the range of 18-25 for methyl methacrylate GTP. Estimates of the pK_a of the conjugate acid of ester enolate anions range from 24.5 to 27-28 in aqueous solution to 30-32 in dimethyl sulfoxide. This chain process is analogous to the tetrabutylammonium fluoride catalyzed silylation of aldehyde and ketone with ethyl (trimethylsilyl)acetate for which an ester enolate anion intermediate has been postulated
3. The stereochemistry of GTP for methyl methacrylate is not unique as originally claimed; it is essentially similar to that observed for anionic polymerization when the counteranions are similar. Thus the stereochemistry of the polymer obtained with either the cesium or tetrabutylammonium cations as counterions from the silicon mediated process (GTP) is essentially the same as that observed for the polymer obtained from the corresponding anionic polymerization in the absence of silyl ketene acetal (Table 1.12). This suggests that similar intermediates are involved in anionic and group transfer polymerization.

Table 1.12: Comparison of the Tacticities of PMMA Prepared in THF by GTP and Anionic Polymerization using Different Counterions

Process	Counterion	Tacticity		
		mm	mr	rr
Anionic	Cs ⁺	10	52	38
		10	56	34
GTP	Cs ⁺	12	53	35
Anionic	Bu ₄ N ⁺	5	39	56
GTP	Bu ₄ N ⁺	5	42	53

4. Very small amount (10^{-6} moles) of ester enolate anions can function as “nucleophilic catalyst” for living anionic GTP. The proposed rapid intermolecular exchange of the nucleophilic catalyst (ester enolate anions for the system) among silyl acetal chain ends, which is required to account for the observed narrow molecular weight distributions, suggests that it is not necessary to propose the existence of any other propagating intermediates other than ester enolates

5. The monomer reactivity ratios for GTP are similar to the monomer reactivity ratios observed for anionic polymerization.

6. The energies of activation and frequency factors for GTP and anionic polymerization of methyl methacrylate are very similar. It is significant to note, however, that no kinetic comparisons are available for the same counterions.

1.7.5 Stereochemistry of GTP

The addition of monomer to the propagating chain end gives rise to the resulting microstructure in both anionic and GTP mechanisms. As addressed previously, the observed microstructure in the anionic polymerization method is readily influenced by the appropriate choice of initiator, solvent and temperature. This is particularly important in the anionic preparation of polymers with specific chemical and mechanical properties. It has been reported that the stereochemistry of PMMA prepared by GTP is independent of solvent¹². It is, however, influenced by the nature of the catalyst and polymerization temperature though

not to the degree reported for anionic polymerization. For Lewis acid catalysts, the GTP of MMA was reported to give PMMA with a ratio of a 2:1 syndiotactic triads to heterotactic triads regardless of solvent or temperature⁵⁸. The anionic catalyzed GTP of MMA at ambient temperature yields PMMA with nearly 1:1 syndiotactic to heterotactic composition. Performing isothermal polymerization studies with TASHF₂ and TASF, the precise determination of the effect of temperature on microstructure of PMMA in THF has been determined^{13,95,96}. As the temperature of the polymerization decreased the syndiotacticity increases.

From the triad and diad composition information more insight into the stereochemistry of polymerization mechanism was obtained⁹⁵. It has been determined that the polymerization follows Bernoullian statistics, and hence the configuration of the last monomer unit of the propagating chain end influences the addition of next monomer unit. The triad information obtained compares well with the data obtained for anionic polymerization of MMA with free anions or with cryptated sodium as the counterion. This conflicts with the concerted associative mechanism for GTP, where high stereo selectivity would be assured. It does, however, provide favorable support to the two step associative mechanism, where the primary role of catalyst can be determined to activate the α -carbon of the acetal to attack polarized vinyl group of monomer.

Further studies into the stereopolymerization of monomers by GTP has involved the E/Z isomerization of the ketene silyl acetal initiator or chain end. Initial studies reported by Brittain⁹⁷, elucidated that E/Z stereoisomerization of the chain ends was competitive with propagation for TPSHF₂ as the selected catalyst, resulting in the observed Bernoullian statistics for the GTP of MMA. However, the E/Z stereoisomerization was slow for TBABB and one would predict non-Bernoullian statistics though this has not been the case observed. Brittain proposed the stereochemical behavior of Z and E chain ends to be similar and the favored mechanism of E/Z stereoisomerization to be a reversible Michael reaction giving rise to the Bernoullian propagation statistics.

1.8 POLYMER SYNTHESIS THROUGH GTP

1.8.1 Homopolymers

GTP is applicable, in general, to α,β -unsaturated acrylic ester monomers. (Meth)acrylates are better suited to be polymerized by GTP than acrylates. Most of the common, commercially available methacrylates and acrylates have been successfully polymerized (either homo or copolymerized). Acrylates are more reactive than methacrylates. Thus, Lewis acid catalysts are preferred catalysts for their polymerization. The reported data of homopolymerization of various alkyl (meth)acrylates are given in **Table 1.13**. However, synthetic conditions for obtaining controlled polymerization have not been established for a wide range of alkyl methacrylates. The higher alkyl methacrylates are generally difficult to purify to the level of purity required for GTP. In the literature, purification methods are not well defined, especially for higher (meth)acrylates.

Table 1.13: Homopolymerization of Higher Alkyl Methacrylates via GTP

Sr. No.	Monomer	Initiator	Catalyst	$\bar{M}_n \times 10^{-3}$ (Theory)	$\bar{M}_n \times 10^{-3}$ (GPC)	\bar{M}_w/\bar{M}_n	Ref
1	BMA	2	TBABB	56.9	67.6	1.13	23
2	2-EHMA	2	TBABB	56.0	41.6	1.30	23
3	10	2	TBABB	--	33.2	1.31	98
4	15	2	TASHF ₂	5.2	8.3	1.21	49
5	DEMA	70	TBOAc	9.4	8.25	1.07	99
6	8	2	TBABB	4.76	4.75	1.41	23
7	11	2	TBABB	4.76	4.12	1.10	23
8	THFMA	2	TASHF ₂	--	7.32	1.10	101
9	NPM	2	TBABB	3.30	10.9	3.7	100
10	12	2	TBAF	84	72.5	1.08	25

1.8.2 Random copolymers

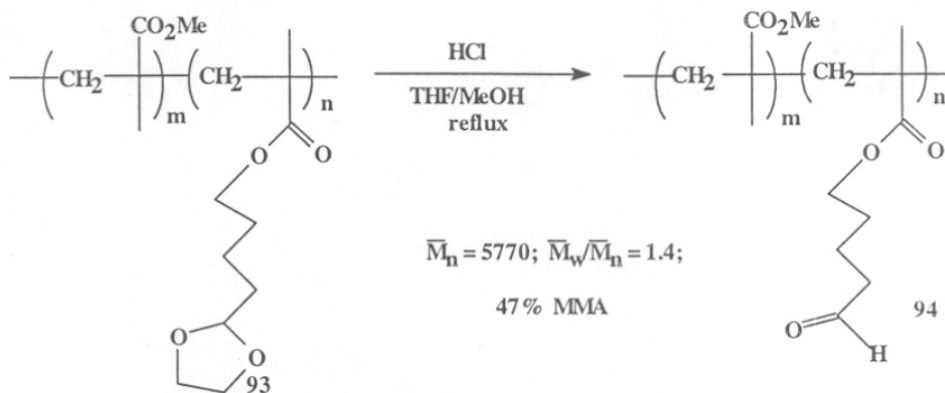
Since GTP is a living polymerization method, controlled molecular weight copolymers can also be synthesized. Random copolymers of MMA, BMA¹⁰² and glycidyl methacrylate (GMA) have been prepared with narrow polydispersity ($\bar{M}_w/\bar{M}_n = 1.1$)¹³. The copolymer of

BMA and GMA shows two T_g 's, namely, at -13 and $+47^\circ\text{C}$, indicating block copolymer formation. Reactivity ratios have been determined for a variety of GTP monomer pairs^{87,103-106} (Table 1.14). These values are consistent with the reported order of monomer reactivity: Acrylonitrile > methacrylonitrile > acrylates > dionates > methacrylate. Random copolymers via GTP are only possible for monomers within a single structural family; if the reactivity

Table 1.14: Reactivity Ratios for Various Alkyl Methacrylate Monomer Pairs using GTP.

Sr.No.	M_1	M_2	Solvent	Catalyst	r_1	r_2	Ref.
1	1	EMA	THF	TASHF ₂	1.36 ± 0.13	0.51 ± 0.06	102
2	1	EMA	THF	TASHF ₂	1.58 ± 0.23	0.40 ± 0.14	104
3	1	n-BMA	THF	TASHF ₂	0.48 ± 0.03	0.26 ± 0.03	105
4	1	9	THF	TASHF ₂	4.59 ± 0.35	0.16 ± 0.06	87
5	1	DMA	THF	TASHF ₂	1.66 ± 0.14	0.48 ± 0.03	103
6	1	MAN	THF	TASHF ₂	0.12 ± 0.12	2.69 ± 0.87	104
7	EMA	MAN	THF	TASHF ₂	0.16 ± 0.16	3.75 ± 0.70	104
8	14	BMA	THF	TASHF ₂	2.35	0.08	106

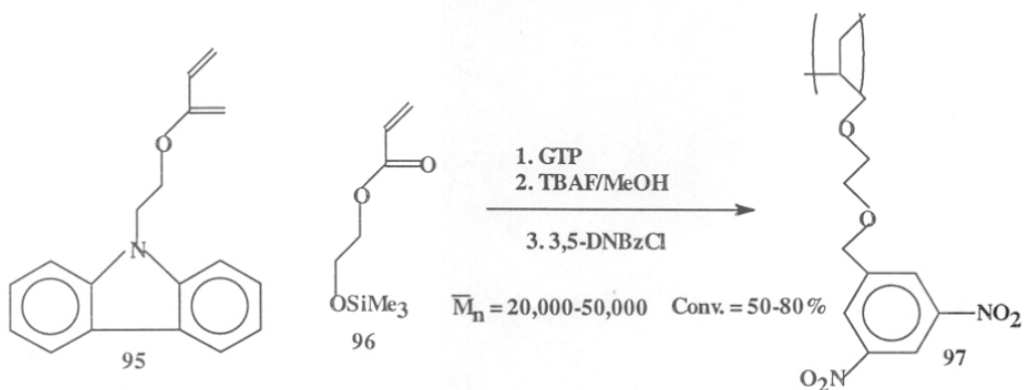
differs too greatly (e.g. methacrylonitrile and MMA), then block copolymers will result. Pugh and Percec²⁶ made random copolymers of MMA and p-vinyl benzyl methacrylate. Sogah and Webster⁵⁷ prepared a random copolymer (93) which contained pendent aldehyde



Scheme 1.22: Synthesis of copolymer with pendant aldehyde group

groups using MMA and 5-methacryloxyvaleraldehyde (protected as the acetal) which can be deprotected (**Scheme 1.22**) to produce a copolymer with pendent aldehyde group (**94**).

Electron donor and acceptor groups were incorporated into random acrylates copolymers. Epple and Schneider¹⁰⁷ prepared copolymers from **95** and **96** (**Scheme 1.23**) using n-butyl acrylate and methyl acrylate (MA). The trimethylsilyl group of the copolymer prepared from **96** was removed with TBAF; reaction of the pendent hydroxy with 3,5-dinitro benzoyl (3,5-DNBzCl) afforded an acrylate copolymer containing electron donor group (**Scheme 1.23**).



Scheme 1.23: Preparation of copolymer containing electron donor group

Table 1.15: Random Copolymers Prepared by GTP

Sr. No.	Monomers			Initiator	Catalyst	$\bar{M}_n \times 10^{-3}$ (Theory)	$\bar{M}_n \times 10^{-3}$ (GPC)	$\frac{\bar{M}_w}{\bar{M}_n}$	Ref.
	A	B	C						
1	1(35)	NBMA(65)		2	TASHF ₂	20.21	22.21	1.11	13
2	1(58)	NBMA(17)	16(25)	2	TASHF ₂	4.09	4.29	1.10	13
3	1	14		2	TASHF ₂	4.81	16.99	1.10	26
4	1(75)	DMA(25)		2	TASHF ₂	80.6	127.0	1.06	111
5	1(78)	EMA(22)		2	TASHF ₂	100.0	142.0	1.27	111
6	14	11		2	TASHF ₂	--	19.0	1.10	101
7	1(81)	30(19)		2	TASHF ₂	40.0	96.0	1.60	34

Random copolymers of mesogenic methacrylate 6-[4-(4-methoxy phenoxy carbonyl) phenoxy] hexyl methacrylate (**30**) were prepared with MMA to study the feasibility of GTP for the synthesis of liquid crystalline polymers³⁴. Random copolymers prepared by GTP are given in **Table 1.15**.

1.8.3 Block Copolymers

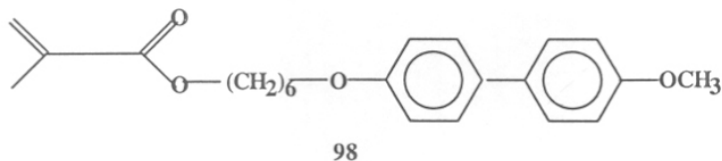
Since block copolymers have found increasing commercial use as elastomers, impact modifiers and adhesives, there has been a growing emphasis on new synthetic methods for their preparation^{108,109}. Block copolymer structures are produced when extended sequences of one monomer are linked to extended sequence of another chemically dissimilar monomer. The sequential arrangement of these chemically dissimilar sequence for varying repeating structures to be synthesized: AB diblock, ABA triblock, $(AB)_n$ multiblock.

Though many synthetic methods have been employed, the sequential addition of monomers via living polymerization is one of the most useful techniques. In the absence of termination reactions, this sequential addition methods inherently allow for the synthesis of well defined block copolymers of predictable molecular weight and block architecture. Regardless of the method employed, namely, sequential addition of monomers, use of difunctional initiators or coupling of living polymers, living polymerization technique for the preparation of block copolymers are limited by two factors¹¹⁰.

1. The monomers involved must be polymerized to a high degree of conversion by the selected polymerization technique.
2. The propagating species generated by the first monomer must be capable of rapidly initiating the polymerization of the succeeding monomer.

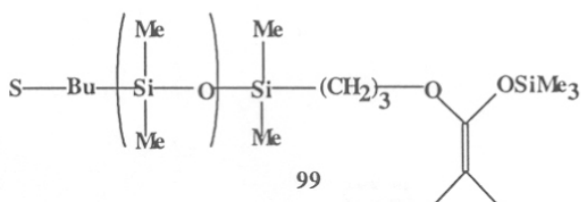
The sequential monomer additions technique was employed for PMMA-b-PLMA, PMMA-b-PBMA-poly(allyl methacrylate)¹³, PMMA-b-PGMA²⁷, PMMA-b-poly(dimethylamino) ethyl methacrylate or poly(tetrahydropyranyl)⁵⁸, PMMA-b-PEMA¹¹¹, PMMA-b-PDMA¹¹¹, PMMA-b-Pt-BMA²⁴, PMMA-b-PTMSMA²⁴. The tetrahydropyranyl group, t-Bu and TMS in TMSMA on deprotection give carboxylic acid. Hofft and Spinger¹¹² prepared AB block copolymers of MMA and mesogenic monomer.

The difunctional initiator technique was used to prepare A-B-A triblock copolymer of MMA/MA, allyl methacrylate/MMA, 2-hydroxy ethyl methacrylate/allyl methacrylate, BMA/MMA⁵⁰, poly(MMA-co-2-hydroxyethyl methacrylate)-b-PLMA-b-poly(MMA-co-2-hydroxyethyl methacrylate).



Rifle and coworkers^{113,114} prepared both A-B-A triblock and A-B diblock polymers composed of n-butyl vinyl ether and MMA using a combination of living cationic polymerization with GTP.

McGrath¹¹⁵ prepared GTP macroinitiator **99** and used it in the polymerization of MMA under GTP conditions to give poly(dimethylsiloxane)-b-PMMA.

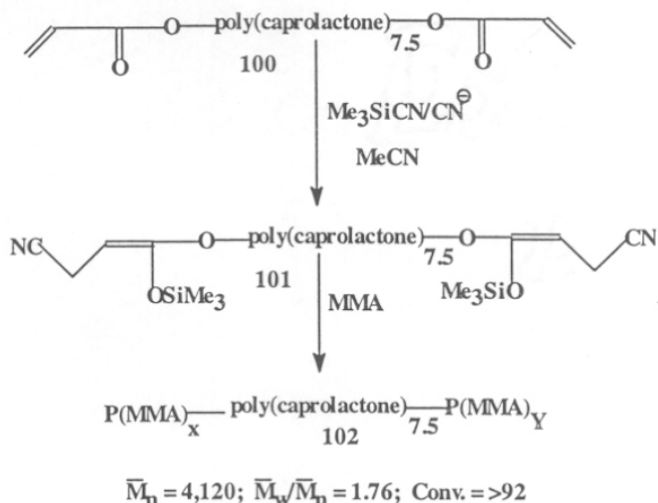


The other approach to block copolymer synthesis is to prepare and use terminally functionalized block. Eastmond and Grigor⁴⁰ terminated a PMMA chain prepared by GTP with bromine; free radical polymerization of styrene was initiated using redox chemistry to afford an A-B-A triblock (from combination of radicals) and A-B diblock (disproportionation) polymers.

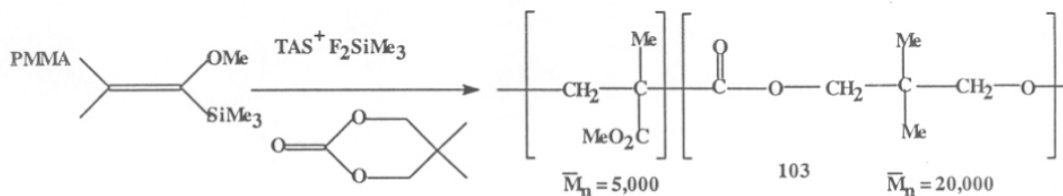
Sogah and coworkers¹³ synthesized PMMA-b-poly(caprolactone)-b-PMMA by hydroxy ended poly (caprolactone)acryloyl chloride (**Scheme 1.24**). Addition of trimethylsilyl cyanide to the acrylate generated a bifunctional initiator which was used in polymerization of MMA.

Hocker and coworker¹¹⁵ prepared PMMA-b-poly(2,2-dimethyl trimethylene carbonate) by reacting the carbonate monomer with a living polymer prepared via GTP (**Scheme 1.25**).

Few example of A-B type block copolymers are available in the recent literature consisting of two different methacrylic block. Examples are PMMA-b-poly(acrylate)⁴⁷, PMMA-b-PEA¹⁰⁹, PMMA-b-poly(2-ethylhexyl acrylate)¹¹⁰ and PMMA-b-PTMA¹¹⁰, PMMA-b-PBA¹¹¹. To the living PMMA chain end, acrylic ester was added. The molecular weight controls were poor and polydispersities were broad. Polymerization results are given in **Table 1.16**.



Scheme 1.24: Synthesis of block copolymers of MMA and caprolactone by GTP



Scheme 1.25: Synthesis of block copolymer of MMA and 2,2'-dimethyl trimethylene carbonate by GTP

Since GTP is not completely free from self terminating reaction, the block copolymers prepared by GTP always contain some percentage of unreacted homopolymer contamination. Addition of few percentage (optionally, 5 to 25 moles per mole of catalyst) of 'livingness enhancer' (Sec. 1.5.6) helps to control the molecular weight and the polydispersity of the block copolymer by suppressing the termination reaction. For example, the block copolymerization of GMA and MMA in the absence of 'livingness enhancer' results in a polymer of broad polydispersity ($\bar{M}_w/\bar{M}_n = 4.67$) which is bimodal comprising of 6% of low molecular weight fraction and 94% of high molecular weight fraction. The same polymer

when synthesized in the presence of 'livingness enhancer' exhibits a lower molecular weight tail ($\bar{M}_w/\bar{M}_n = 1.98$).

Table 1.16: Block Copolymers Prepared by GTP

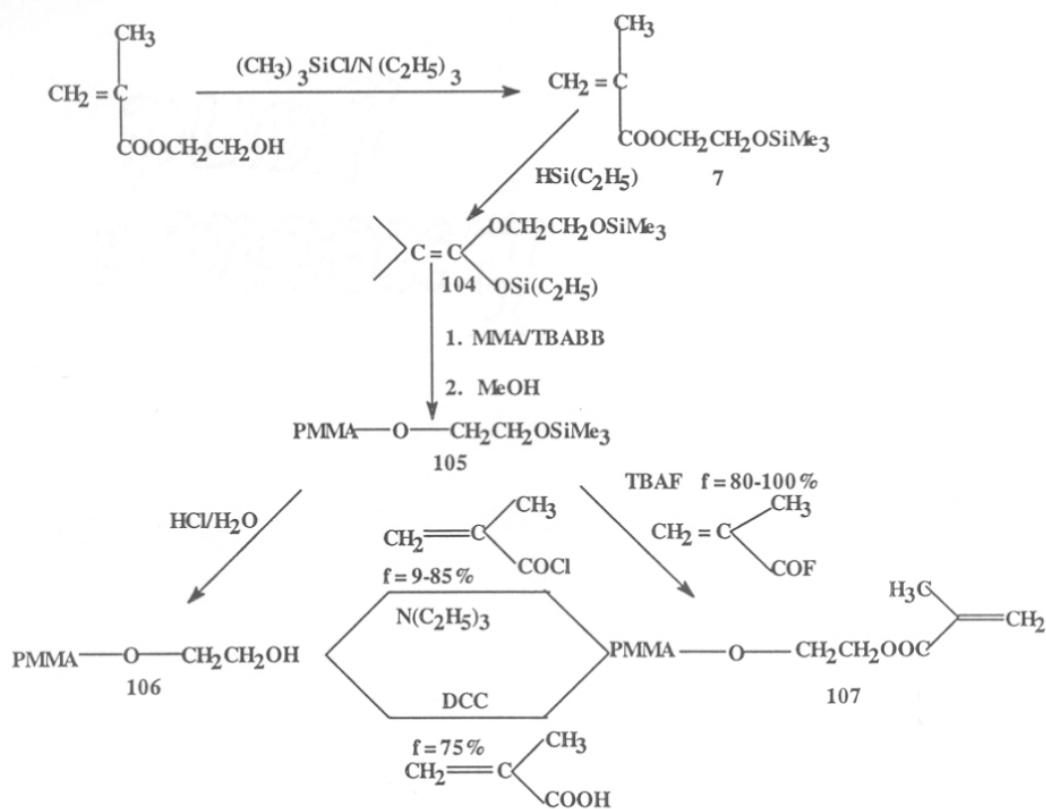
Sr. No.	Monomers		Initiator	Type	$\bar{M}_n \times 10^{-3}$ (Theory)	$\bar{M}_n \times 10^{-3}$ (GPC)	\bar{M}_w/\bar{M}_n	Ref
	A	B						
1	1(25)	2-EHMA (75)	2	A-B	--	41.50	1.30	13
2	1(90)	LMA(90)	2	A-B	7.14	6.65	1.06	13
3	LMA (10)	1(90)	2	A-B	7.12	6.54	1.14	13
4	1(40)+ 7(30)	LMA(30)	72	AB-C- AB	13.8	9.34	1.20	13
5	NBMA	MMA	72	A-B-A	--	7.2	1.21	101
6	BMA	TMBA	71	A-B-A	9.0	9.3	1.47	119
7	TBMA	MMA	72	A-B-A	4.5	4.3	1.34	119
8	MA	MMA	71	A-B-A	--	7.29	1.31	101
9	1(10)	DMA(90)	2	A-B	135.0	185.0	1.18	111
10	BMA	TMS-HEMA	72	A-B-A	43.6	51.2	1.39	120
11	MMA	THPMA	2	A-B	8.6	7.73	1.08	23
12	MMA	DMAEM	2	A-B	9.44	8.69	1.07	23
13	MMA	2-EHA	2	A-B	12.2	18.2	2.09	117
14	MMA	TBA	2	A-B	10.9	15.9	1.91	117
15	MMA	BzMA	2	A-B	-	42.8	1.05	24
16	MMA	TBMA	2	A-B	-	20.6	1.34	24
17	MMA	EA	2	A-B	9.5	11.1	2.33	116

1.8.4 Macromonomers

Macromonomers are defined as low molecular weight polymers, generally $\bar{M}_n \sim 1000$ to 10,000, carrying a polymerizable group at one chain end¹²¹. The most commonly occurring functional groups are either styrenic or (meth)acrylic ester type.

GTP technique has been used to make a variety of macromonomers. Two processes can be used to synthesize macromonomers. One, is to use an initiator that has a functional group that will polymerize under free radical conditions but not under GTP conditions. Asami and coworkers¹²² adopted this method.

In another approach the 'living' PMMA chains obtained by GTP technique have been terminated with electrophilic reagents such as methacryloyl fluoride¹²³, p-vinyl benzyl tosylate¹²², however, the functional yields are not acceptable (functionality 0.7).



Scheme 1.27: Synthesis of methacryloyl terminated macromonomer by GTP

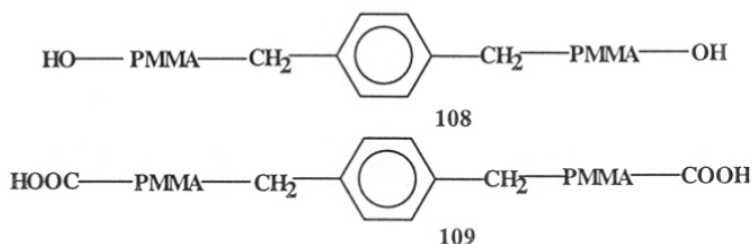
McGrath's¹²⁴ and Muller's¹²⁵ group have synthesized methacryloyl terminated PMMA macromonomer by GTP technique employing GTP initiator containing silyl protected hydroxyl group, namely, 2-methyl-1-triethylsiloxy-1-(2-trimethylsiloxy) ethoxy-1-propene. The ω -trimethylsiloxy PMMA obtained was deblocked to generate the hydroxyl functional group which was then reacted with methacrylic acid or methacryloyl chloride. In the

presence of tetrabutylammonium fluoride, methacryloyl fluoride was directly converted to ω -methacryloyl PMMA (Scheme 1.27).

1.8.5 Telechelics

Living polymerization permits the synthesis of telechelics, i.e. polymers with terminal units at both ends of the chain¹²⁶. Reactive terminal units may be introduced by using selected initiator or termination reactions (Sec.1.3.2, Sec. 1.8.6).

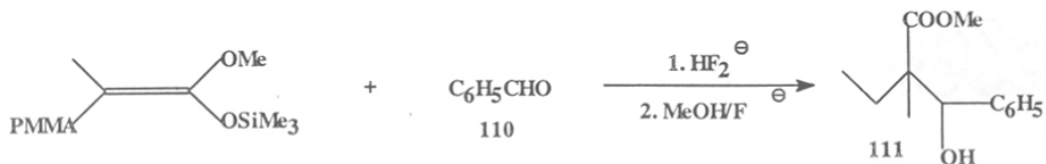
For optimal functionality, a polymerization must often be terminated before monomer consumption is complete. Termination reactions may require catalysis. While a nucleophilic weak catalyst is chosen for polymerization and to minimize termination, a stronger nucleophilic catalyst may be required for effective termination. When polymerization was initiated by a protected hydroxyl or carboxyl initiator, telechelic α,ω -diol or diacid was produced⁴⁶. The best coupling agent for the silyl ketene acetal ended polymer appears to be terephthaloyl fluoride¹²⁷.



1.8.6 End functionalized polymers

Functionality can be introduced into the polymer by using either functional monomer (Sec 1.2.3) or functional initiator (Sec 1.3.2). Another way of introducing functionality is the termination of living GTP chain end with a suitable electrophile. For example, reaction of PMMA chain ends with benzaldehyde gives, after hydrolysis, a polymer with benzhydryl alcohol group^{37,13} (Scheme 1.28).

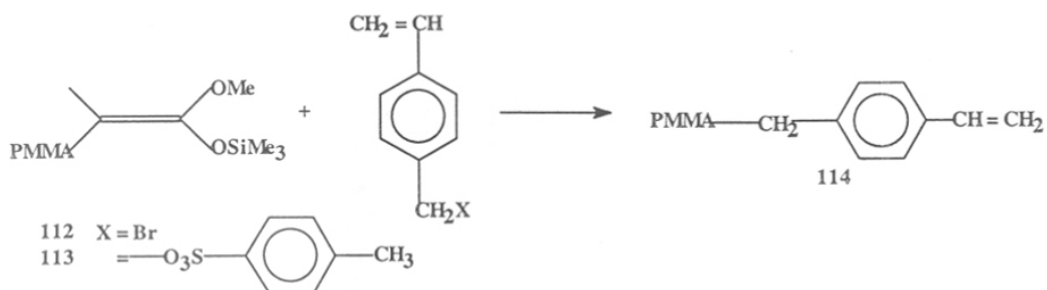
PMMA formed by GTP was functionalized by the reaction with bromine to give PMMA-Br³⁸ which initiated free radical polymerization of styrene.



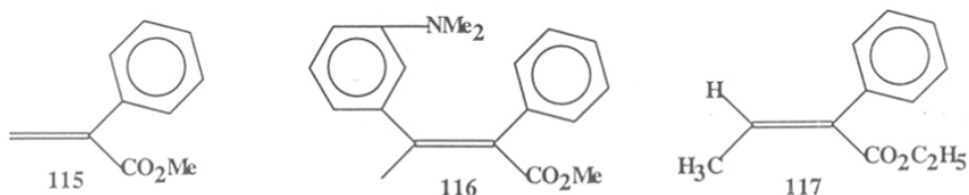
Scheme 1.28: Reaction of GTP chain end with benzaldehyde

Terminations of living ends of PMMA formed by GTP with vinyl benzyl bromide or tosylate to prepare vinyl benzyl PMMA macromonomer⁴² has been reported (Scheme 1.29).

A living functionalization method for GTP was developed by Quirk et al¹²⁸ using sterically hindered monomers. The monomers used for functionalizations were methyl-2-phenyl propenoate (MPHA), methyl-E-3-(2-dimethyl aminophenyl)-2-phenyl acrylate (AMPA) and ethyl-2-phenyl-2-butenolate (EPB). MPHA undergoes oligomerization at -78°C but only monoaddition was observed at room temperature. Various functional groups such as $-\text{NR}_2$, $-\text{OMe}$, $-\text{X}$ (Br, I, Cl), $-\text{COOMe}$ etc. could be introduced into poly (alkyl methacrylates) via substituents on the aromatic ring.



Scheme 1.29: Synthesis of vinyl benzyl terminated PMMA



The functionalization efficiency decreased to 0.6 when functionalizations were carried with two molar equivalents of EPB. This suggested the inclusion of a nonliving process. A possible nonliving process which lower the functionality could be chain transfer reactions of the living polymer chain ends with the acrylic hydrogen in EPB. Variables such as catalyst

concentration, temperature etc. could influence functionalization efficiency. In order to obtain high functionality, catalyst levels should be kept as low as possible. Therefore, a catalyst concentration of 0.1 mol% based on initiator was used. Functionalization reactions would be favored at low temperatures near 0°C since chain terminations are minimized at low temperatures (Table 1.17).

Table 1.17: Functional Terminators for GTP

Sr. No.	Terminator	Solvent	$\bar{M}_n \times 10^{-3}$ (Theory)	$\bar{M}_n \times 10^{-3}$ (GPC)	\bar{M}_w/\bar{M}_n	f (%)	Functional Group	Ref
1	110	THF	3.3	2.8	1.04	90	-OH	37
2	Br ₂	CH ₃ CN	6.1	12.79	1.29	98	-Br	38
3	112	THF	3.0	3.25	1.05	63	-C ₆ H ₅ CH=CH ₂	42
4	113	THF	3.0	4.38	1.06	73	-C ₆ H ₅ CH=CH ₂	42
5	115	THF	2.1	3.60	1.05	88	-C ₆ H ₅	128
6	116	THF	2.1	2.20	1.06	93	-C ₆ H ₅ N(CH ₃) ₂	128
7	117	THF	2.1	1.90	1.03	95	-C ₆ H ₅	128

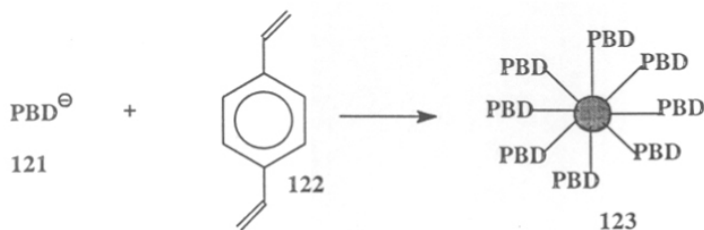
1.8.7 Star Polymers

The term “star” polymer denotes a polymer with branches emanating from a common source or core. The first star polymers were synthesized by coupling living polymers with polyfunctional tie molecules for example, living polystyrene with SiCl₄¹²⁹ (Scheme 1.30). Later it was discovered that treatment of a living polymers with a divinyl monomer would



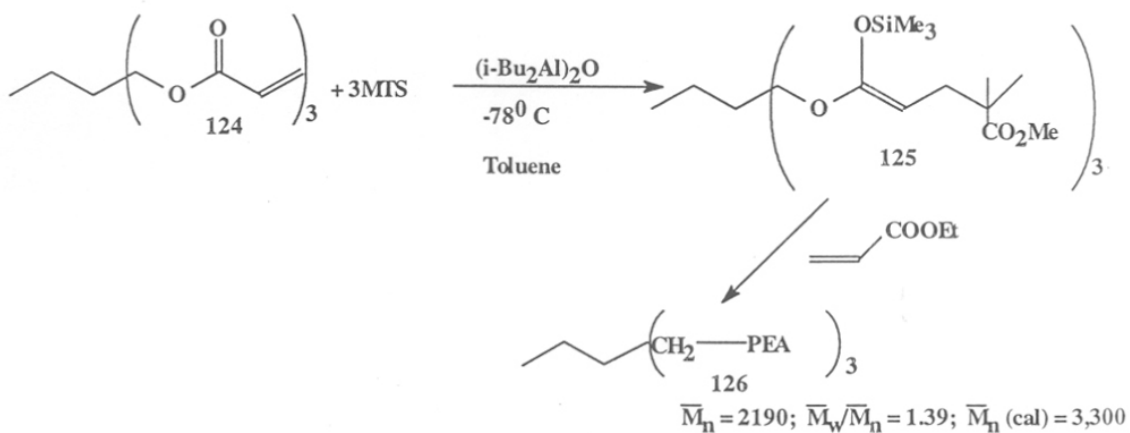
Scheme 1.30: Synthesis of four-armed star polymer by termination method

crosslink the end of the polymer to form a core with several hundred arms emanating into solution. Example of this kind of star polymers formation were first reported for polybutadiene¹³⁰ (Scheme 1.31).



Scheme 1.31: Synthesis of star polymer by terminating living chain end with a difunctional monomer

For acrylic star polymers, GTP is the preferred method. Branched polymers can be synthesized using GTP by i) polymerizing monomer with polyfunctional initiator (core first approach), ii) end capping the living methacrylate chain end with multifunctional terminating agent and iii) core formation of difunctional methacrylate by living monofunctional methacrylate (arm first method). Three and four-armed poly (ethyl acrylate) star polymers has been demonstrated with tri and tetra functional initiators⁹. The procedure is illustrated for a three-armed star (Scheme 1.32). Trimethanol propane triacetate **124** is treated with 3 (MTS) to form initiator **125**, which is used to initiate ethyl acrylate to give a three armed star **126**.



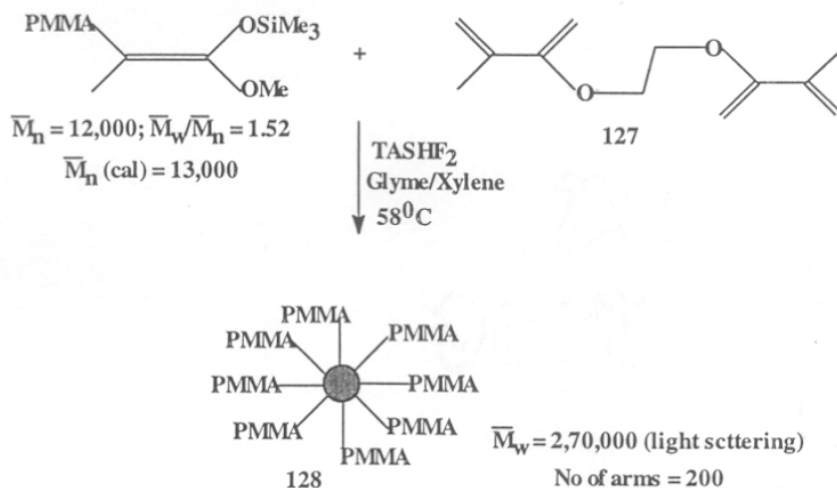
Scheme 1.32: Synthesis of acrylic star polymer by core first method

Spinelli¹³¹ has reported the synthesis of multiarmed star polymers with tightly crosslinked cores by reacting the living GTP chain end with a difunctional methacrylate (**127**) (e.g. ethylene glycol methacrylate) (Scheme 1.33). These stars, **128**, are similar in structure to NAD (Sec. 1.9.5) but have lower molecular weights. The arms, which radiate out from the core, may be, homopolymers, copolymers, or block polymers and may have functional

groups attached anywhere along the chain. Number of arms can be varied by changing the ratio of initiator to difunctional monomer. A star polymer of 200 arms has been obtained when the ratio of initiator to difunctional monomer was 0.25. Free arm content is not completely avoidable in such polymerizations. However, the details regarding polydispersity and free arm contents were not reported.

A systematic study of star polymerizations of MMA, EMA and hydroxyl protected HEMA was reported by Simms¹³². Simms concluded that the time lag between arm formation and core formation dictates the free arm content.

The structure of PMMA/EGDMA star branched microgels were investigated recently by Burchard et al¹³³. It was found that the ratio of the hydrodynamic volumes of star-branched microgel to linear polymers at the same molecular weight is dependent on the number of arms, but does not depend on arm molecular weight.



Scheme 1.33: Synthesis of PMMA star polymer by arm first method

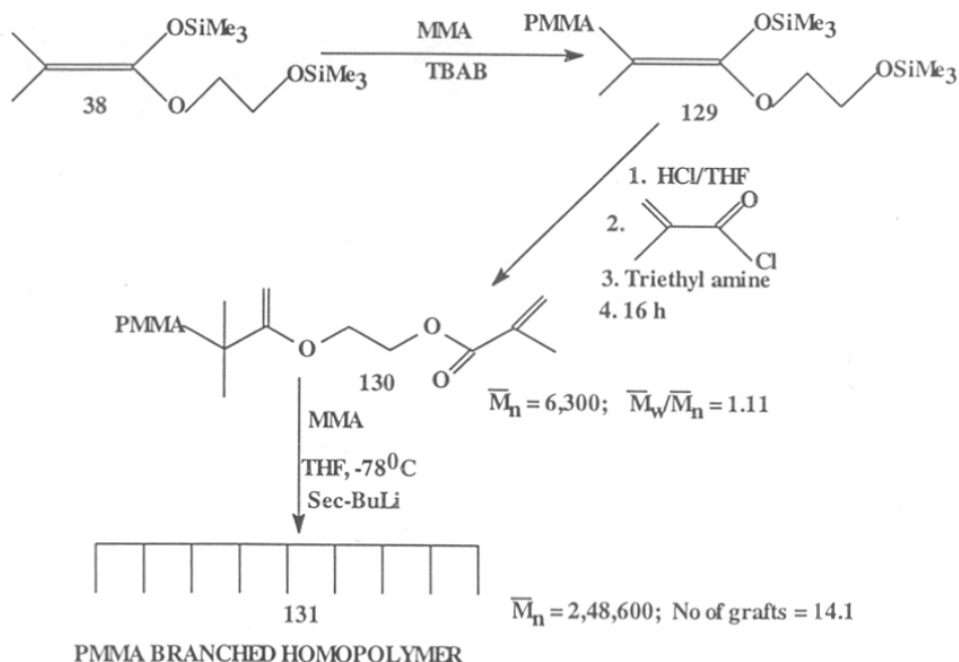
1.8.8 Graft / comb Polymers

Graft / comb polymers are made by homopolymerization or copolymerization of macromonomers. The macromonomers are obtained by living polymerization or by conversion of a functionalized polymer end to an end containing a polymerizable functional group (Sec. 1.8.4).

Graft or comb polymers have been made by two routes. First, macromonomers are made by other methods and copolymerized by GTP. Secondly, macromonomers are prepared by GTP and homo- or copolymerized by some other methods.

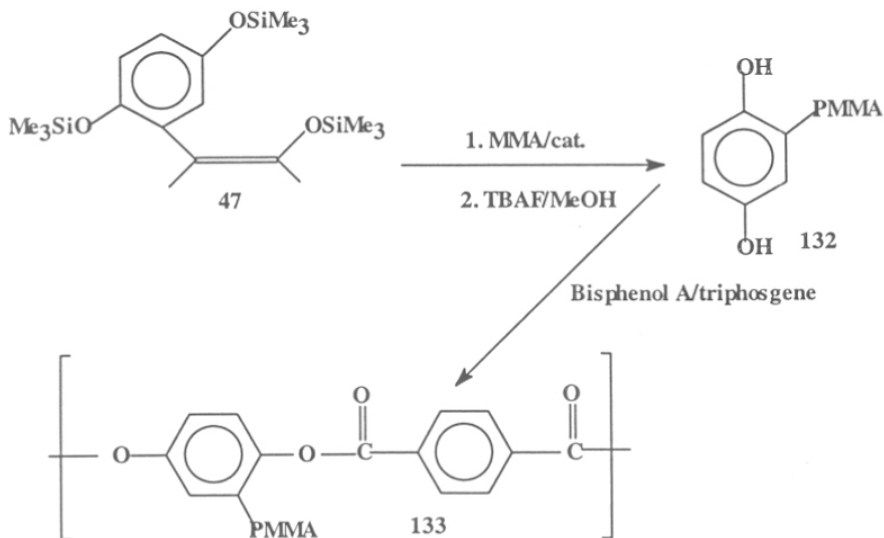
Asami et al.¹³⁴ prepared methyl methacrylate-terminated polystyrene(PS) via anionic method. The polystyrene macromonomer was homopolymerized via GTP to give oligo(MMA-g-PS) and was copolymerized with MMA to afford PMMA-g-PS. McGrath et al.¹²⁴ prepared a poly (dimethylsiloxane) macromonomer via anionic polymerization and used in the synthesis of PMMA-g-PDMS.

Wittkoski and Bandermann⁴¹ used initiators **53** and **54** to synthesize macromonomers which were then copolymerized with styrene using free radical conditions to give polystyrene-g-PMMA. McGrath and coworkers¹²⁴ initiated the polymerization of MMA with **39**; removal of the trimethyl group and reaction of the hydroxy end-group with methacryloyl chloride afforded macromonomer **130** (Scheme 1.34).



Scheme 1.34: Synthesis of PMMA branched homopolymer by GTP

Heitz and Webster¹³⁵ made graft polymer via condensation using phenolic macromonomer prepared by GTP (Scheme 1.35).

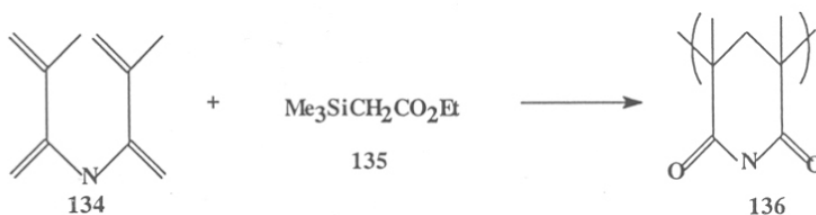


Scheme 1.35: Synthesis of graft polymer via condensation using phenolic macromonomer prepared by GTP

Hertler, Sogah and Boettcher¹³⁶ generated GTP initiating sites on crosslinked polystyrene beads prepared from chloromethylated polystyrene. MMA was successfully grafted on to the polymeric support with very little formation of engrafted PMMA. Jenkins and coworkers¹³⁷ made a graft polymer by generating GTP initiating sites on a random copolymer of styrene and (2-isobutyloxy) ethyl methacrylate which was prepared by free radical polymerization. The isobutyryloxy pendent groups were converted to silyl ketene acetal which initiated the GTP of MMA. However, it was difficult to assess the efficiency of the grafting process.

1.8.9 Other polymer architectures by GTP

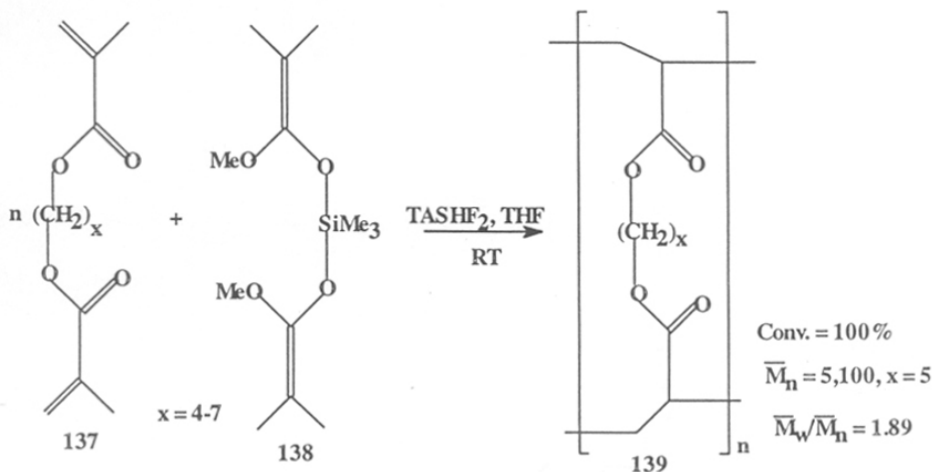
When a difunctional acrylic monomer with a connector group that is small is polymerized by GTP, a soluble uncrosslinked polymer is obtained by cyclic polymerization.



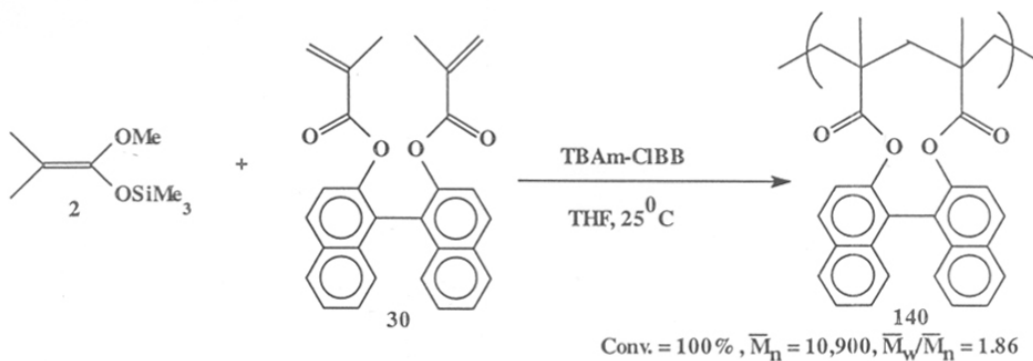
Scheme 1.36: Cyclic polymerization of N-phenyldimethyl acrylamide by GTP

Thus polymerization of *N*-phenyldimethyl acrylamide by GTP process gives **136**¹³⁸ (Scheme 1.36). The molecular weight of the polymer obtained was rather low.

If the spacer between the two methacrylate groups is 4 to 7 methylene units **137**, a soluble polymer is still formed if a difunctional initiator **138** and dilute conditions are used. A monofunctional initiator gives a crosslinked polymer. Thus a ladder structure **139** has been proposed for these polymers¹³⁹ (Scheme 1.37).



Scheme 1.37: Synthesis of ladder polymer from difunctional monomer and initiator by GTP



Scheme 1.38: Cyclopolymerization by GTP

GTP of the chiral monomer, 2,2'-bis(methacryloxy) methyl-1,1'-binaphthyl (**30**) occurred exclusively via cyclization mechanism³¹ (Scheme 1.38). The biphenyl moiety, due to its convergent and rigid structure facilitates faster cyclization (intramolecular) relative to propagation (intermolecular), control both the geometry of the resulting cyclic silyl ketene

acetal and the mode of monomer addition and provide the possibility for inducing a conformationally ordered structure (e.g., helix, as seen in polymethacrylates that contain bulky side groups). The broad polydispersities of the polymer may be partly due to differences in reactivity of diastereomeric 'living' ends.

1.9 APPLICATIONS

Free radical polymerization is still the method of choice to prepare high molecular weight acrylic polymers. GTP provides an alternate method to prepare controlled molecular weight and narrow polydispersity polyalkyl (acrylates). However, the silyl ketene acetal initiators used in GTP are expensive. Therefore, GTP is expected to find use in specialty applications where polymers with well defined compositions and molecular weights are desired.

1.9.1 Coating

Polymers with controlled structures²⁷, i.e., polymers that are branched, block or having narrow polydispersity (\bar{M}_w/\bar{M}_n), can be used to improve the properties of coating systems. These improvements include higher solid, better hardness/flexibility, better pigment dispersion and improved appearance. This increase in solids of the polymer at constant viscosity results in increased solids and lower volatile organic content (VOC) of formulated coatings.

1.9.2 Photoresists

Random copolymers of benzyl methacrylate and tetrahydropyranyl methacrylate have been used to make chemically amplified positive tone photoresists¹⁴⁰.

Block and random copolymers resists were prepared from t-BMA and SiMA (31) by Ober et al.¹⁴¹. The low absorption at 193 nm and high resistance to oxygen ion etching of these copolymers make them attractive candidate for 193 nm wavelength resist.

1.9.3 Pigment dispersion

Block copolymers are known to be better pigment dispersants than conventional, random copolymers¹⁴². GTP can be used to easily make new types of block polymers that are superior pigment dispersants.

These resins are composed of a block A or adsorbing group and a block of B or solubilizing groups. The B block is often polymerized first and is usually PMMA or PBMA. Once the B monomers have polymerized, the A monomers are added to the reaction to form a distinct block. The A block, for example, can be GMA. The epoxy group of GMA can be converted into an adsorbing group via reaction with any of a number of carboxylic acids or amines (Scheme 1.3).

1.9.4 Synthesis of NAD

Through GTP, MA macromonomers can be prepared with a wide variety of compositions. One of the end use of macromonomer is the synthesis of Non Aqueous Dispersions (NAD). These NAD's are microgel like acrylic particle and are made by copolymerizing with other acrylic and styrene monomers. The macromonomer chain is soluble in the polymerization solvent but the monomers, once polymerized, are not. This results in an insoluble particle with a core, that may or may not be crosslinked, that is stabilized by macromonomer.

1.9.5 Rheology control agent in NAD

The macromonomer display a very desirable non-Newtonian behavior over a range of concentrations. Their viscosities drop as shear increases. The control is almost Newtonian. The pseudo-plasticity of the macromonomer based NAD enables it to be useful as a rheology control agent in coating and ink applications¹⁴³.

1.9.6 Toughening agents for coating

Acrylic star polymers can be made through GTP. One of the possible end use applications for stars is in toughening of plastics and coatings. Hydroxyl functional stars can be added to other polyols and co-crosslinked. This produces two phase films which can be clear, flexible and moderately hard when the proper choices of star and modifying polyols are made. The choice of crosslinking agent seems less important, since essentially the same result can be achieved with a variety of cross-linking agents.

1.10 PATENT LITERATURE

Group transfer polymerization is still in the stage of development. Different advantages, particularly, in the preparation of star polymers, have been explained in many of the patents.

In some of the patents, the flexibility of the method in preparation of different acrylic polymer architectures, functional polymers etc. have been described (Table 1.18).

Table 1.18: Representative Patent Literature of Group Transfer Polymerization

Patent No.	C.A.No.	Name of Company	Features
EP 293,871	111: 25,003b	Ciba-Geigy A.G.	Light stabilized star shaped microparticles
US 4, 656, 226	107: 23, 910p	E.I.DuPont	Acrylic pigment dispersant
PCT 8, 600, 626	105: 24, 811c	E.I.DuPont	Acrylic star polymers
US 4, 939, 211	113: 192, 227a	E.I.DuPont	Conversion of SKA terminated living polymers to phosphonate capped polymer
US 4, 906, 713	113: 60, 098z	E.I.DuPont	Acrylic ladder polymers
EP 379, 942	114: 25, 256y	Dow Chemical Co.	Preparation of photo crosslinked imide group-terminated polymers
US 4, 845, 156	112: 119, 613y	E.I.DuPont	Preparation of macromonomers
EP 258, 065	109: 129, 894t	E.I.DuPont	Preparation of hybrid acrylic star polymers
US 627, 913	105: 24, 811c	E.I.DuPont	Preparation of acrylic star branched polymers
US 5, 162, 467	118: 39, 608j	E.I.DuPont	Zeolite catalyzed GTP of acrylates
PCT 8, 909, 236	112: 140, 016r	E.I.DuPont	Catalysts for GTP
EP 278, 668	110: 39, 526r	E.I.DuPont	Initiator system for polymerization of polar monomer or maleimides
US 4, 940, 760	114: 24, 781d	E.I.DuPont	Supported catalysts for GTP
US 4, 605, 716	105: 227, 555v	E.I.DuPont	Lewis base catalyzed polymerization of acrylic monomers in polar solvents
US 4, 528, 389	104: 6, 306s	E.I.DuPont	Pentacoordinate silyl enolates used as initiators
Ger.Offer DE 3, 832, 466	111: 174, 866n	Korea Advanced Institute of Science and Technology	Bisiloxanes for the preparation of copolymers
EP 276, 976	110; 76, 281c	E.I.DuPont	Monomers and initiators for GTP
EP 244, 953	108: 205, 280m	E.I.DuPont	Enhanced livingness of polymerization using silylated oxyanions

1.11 REFERENCES

- 1 L.J.Fetters, *J.Polym.Sci.*, **C26**,1 (1969).
- 2 K.Hatada, K.Ute, K.Okamoto and T.Kitayama, *Polym.J.*, **20**, 505 (1986).
- 3 T.Kitayama, T.Shinozaki, E.Masuda, M.Yamamoto and K.Hatada, *Polym.Bull.*, **23**, 2618 (1988).
- 4 M.Kuroki, T.Aida and S.Inoue, *J.Am.Chem.Soc.*, **113**, 5903 (1991).
- 5 S.K.Varsheny, J.P.Houtekeer, R.Fayt, R.Jerome and P.Teyssie, *Macromolecules*, **23**, 2618 (1990).
- 6 H.Yasuda, H.Yamamoto, K.Yokokawa, A.Nakamura and S.Make, *Polym.Prepr.Jap.*, **23**, 2618 (1990).
- 7 O.W.Webster, W.R.Hertler, D.Y.Sogah, W.B.Farnham and T.V.Rajanbabu, *J.Am.Chem.Soc.*, **105**, 5706 (1983).
- 8 W.J.Brittain, *Rubber Chem. Technol.*, **65**, 580 (1992).
- 9 O.W.Webster and B.C.Anderson, "New Methods for Polymer Synthesis" (Ed. W.J.Mijs) Plenum Press: New York, Chap.1, pp1-32 (1992).
- 10 G.C.Eastmond and O.W. Webster, "New Methods of Polymer Synthesis", Ed. J.R.Ebdon, Blakie, Glasgow, Chap.2, pp23(1992).
- 11 W.B.Farnham and D.Y.Sogah, US Patent 4414372 (1983).
- 12 O.W.Webster in "Encyclopedia of Polymer Science and Engineering", J.I.Kroschwitz. Ed. Wiley-Interscience, New York, Vol.7, 580 (1987).
- 13 D.Y.Sogah, W.R.Hertler, O.W.Webster and G.M.Cohen, *Macromolecules*, **20**, 1473 (1987).
- 14 R.P.Quirk and G.P.Bidinger, *Polym.Bull.*, **22**, 63 (1989).
- 15 I.B.Dicker, G.M.Cohen, W.B.Farnham, W.R.Hertler, E.D.Lignis and D.Y.Sogah, *Polym.Prepr.(Am.Chem.Soc., Div.Polym.Sci.)*, **28**(2), 106 (1987).
- 16 A.Pickering and A.J.Thorne, *U.S.Patent* 4,791,181 (1988).
- 17 D.Y.Sogah, W.R.Hertler and O.W.Webster, *Polym.Prepr.(Am.Chem.Soc., Div.Polym.Chem.)*, **25**(2), 3 (1984).
- 18 W.R.Hertler, D.Y.Sogah, O.W.Webster and B.M.Troost, *Macromolecules*, **17**, 1415 (1984).
- 19 W.J.Brittain and I.B.Dicker, *Macromolecules*, **22**, 1054 (1984).
- 20 L.Xu and W.Lei, *Chin. J.Polym.Sc.*, **7**, 299(1989).
- 21 I.B.Dicker, *Polym.Prepr. (Am.Chem.Soc., Div.Polym.Chem.)*, **29**(2), 114 (1988).
- 22 M.T.Reetz, R.Ostarek, K.E.Piejko, D.Arlt and B.Boemer, *Angew.Chem., Int.Ed.Engl.*, **25**, 1108(1986).
- 23 I.B.Dicker, G.M.Cohen, W.B.Farnham, W.R.Hertler, E.D.Lagnis and D.Y.Sogah, *Macromolecules*, **23**, 4034 (1990).

- 24 S.P.Rannard, N.C.Billingham, S.P.Armes and J.Mykytiuk, *Eur.Polym.J.*, **29**, 407 (1993).
- 25 J.Mykytiuk, S.P.Armes and N.C.Billingham, *Polym.Bull.*, **29**(1), 139 (1992).
- 26 C.Pugh and V.Percec, *Polym.Bull.*, **14**(2), 109 (1985).
- 27 J.A.Simms and H.J.Spinelli, *J.Coat.Technol.*, **57**, 125 (1987).
- 28 P.M.Gomez and H.N.Neidlinger, *Polym.Prepr.(Am.Chem.Soc., Div.Polym.Chem.)*, **28**(1), 2099 (1987).
- 29 S.Stinson, *Chem.Eng.News*, **4**, 43 (1987).
- 30 J.J.Kozakiewski, N.S.Kurose, D.R.Draney, S.H.Huang and J.Falzone, *Polym.Prepr.(Am.Chem.Soc., Div.Polym.Chem.)*, **28**(2), 347 (1987).
- 31 T.Nakano and D.Y.Sogah, *J.Am.Chem.Soc.*, **117**, 534 (1995).
- 32 A.H.Gabor and C.K.Ober, *Chem.Mater.*, **8**, 2272 (1996).
- 33 C.R.Pugh and V.Percec, *Polym.Prepr.(Am.Chem.Soc., Div.Polym.Sci)*, **26**(2), 303 (1985).
- 34 W.Krueder and O.W.Webster, *Macromol.Chem., Rapid Commun.*, **7**, 5 (1986).
- 35 C.Ainsworth, F.Chen, Y.Kuo, *J.Organomet.Chem.*, **46**, 59 (1972).
- 36 Y.Kita, J.Haruta, J.Segawa and Y.Tamura, *Tetrahedron Lett.*, **44**, 4311 (1979).
- 37 D.Y.Sogah and O.W.Webster, *J.Polym.Sci., Polym.Lett.*, **21**, 927 (1983).
- 38 O.W.Webster, W.R.Hertler, D.Y.Sogah, W.B.Farnham and T.V.Rajanbabu, *J.Macromol.Sci., Chem.*, **A21**, 943 (1984).
- 39 W-P. Shen, W-D.Chu, M-F.Yang and L.Wang, *Makromol. Chem.*, **190**, 3061 (1989).
- 40 G.C.Eastmond and J.Grigor, *Makromol. Chem., Rapid commun.*, **7**, 375 (1986).
- 41 R.Witkowski and F.Bandermann, *Makromol.Chem.*, **190**, 2173 (1989).
- 42 R.Asami, Y.Kondo and M.Takaki, *Polym.Prepr.(Am.Chem.Soc., Div.Polym.Chem)*, **27**(1), 186 (1986).
- 43 W.R.Hertler and T.V.Rajanbabu, *Polym.Prepr.(Am.Chem.Soc., Div.Polym.Chem.)*, **29**(2), 71 (1988).
- 44 F.Bandermann and H.D.Speikman, *Makromol.Chem., Rapid Commun.*, **6**, 335 (1985).
- 45 M.T.Ritz and R.Ostarek, *J.Chem.Soc., Chem.Commun.*, 213 (1988).
- 46 O.W.Webster, U.S.Patent 4,417,403 (1983).
- 47 M.T.Reetz, *Pure Appl. Chem.*, **67**, 1785 (1985).
- 48 D.Y.Sogah, *Polym.Prepr.(Am.Chem.Soc., Div.Polym.Chem.)*, **29**(2), 3 (1988).
- 49 H.Yu, W.Choi, K.Lim and S.Choi, *Macromolecules*, **21**, 2389 (1988).
- 50 K.Steinbrecht and F.Bandermann, *Makromol.Chem.*, **190**, 2193 (1989).
- 51 K.Ikeda, K.Achiwa and M.Sekiya, *Tetrahedron Lett.*, **24**(43), 4707 (1983).
- 52 Y.Kita, J.Segawa, J.Haruta, T.Fujii and Y.Tamura, *Tetrahedron Lett.*, **21**, 3779 (1980).

- 53 W.J.Middleton, *Org.Synth.*, **60**, 221 (1986).
- 54 H.D.Speikman and F.Bandermann, *Makromol.Chem.*, **189**, 437 (1988).
- 55 J.Miller, A.D.Jenkins, E.Tsartolia, D.R.M.Walton, J.Stejeskal and R.Kratochvi, *Polym.Bull.*, **20**, 247 (1988).
- 56 D.T.Martin and S Bywater, *Makromol.Chem.*, **193**, 1011 (1992).
- 57 O.W.Webster and D.Y.Sogah, in "Recent Advances in Mechanistic and Synthetic Aspects of Polymerization.", M.Fontanille and A.Guyot, Eds., NATO ASI Ser. C 215, Reidel Dordrecht, p3-21 (1987).
- 58 W.R.Hertler, D.Y.Sogah and O.W.Webster, *Macromolecules*, **17**, 1417 (1984).
- 59 W.Schubert and F.Bandermann, *Makromol.Chem.*, **190**, 2721 (1989).
- 60 O.W.Webster, *Polym.Prepr.(Am.Chem.Soc.Div.Polym.Chem.)*, **27**(1), 161 (1986).
- 61 R.D.Allen, T.E.Long and J.E.McGrath, *Polym.Bull.*, **15**, 127 (1986).
- 62 K.Marnoka, H.Banno and H.Yamamoto, *Syn.Lett.*, 253 (1991).
- 63 J.D.Citron, U.S.Patent 477116(1988); Chem. Abstr., **110**, 76288k (1989).
- 64 O.W.Webster, U.S.Patent 4,508,880 (1985).
- 65 W.R.Hertler, *Polym.Prepr.(Am.Chem.Soc., Div.Polym.Chem.)*, **27**(1), 165(1986).
- 66 F.Bandermann, H.P.Sitz and H.D.Speikman, *Polym.Prepr.(Am.Chem.Soc., Div.Polym.Sci.)*, **27**(1), 169 (1986).
- 67 F.Bandermann and H.D.Speikman, *Makromol.Chem., Rapid Commun.*, **6**, 336 (1985).
- 68 D.Y.Sogah, W.R.Hertler, I.B.Dicker, P.A.Depra and J.R.Butera, *Makromol.Chem., Macromol.Symp.*, **33**, 75 (1990).
- 69 L.V.Schneider and I.B.Dicker, U.S.Patent 4,736,003 (1988).
- 70 V.Warzelhan, G.Lohr, H.Hocker and G.V.Schulz, *Makromol.Chem.*, **179**, 2211 (1978).
- 71 W.J.Brittain, *J.Am.Chem.Soc.*, **110**, 7440 (1988).
- 72 F.Bandermann and H.D.Speikman, *Polym.Prepr. (Am.Chem.Soc., Div.Polym.Chem.)*, **27**(1), 169 (1986).
- 73 H.D.Sitz and F.Bandermann, in "Recent Advances in Mechanism and Synthetic Aspects of Polymerization".; M.Fontanille and A.Guyot, Eds., NATO ASI Ser. C 215, Reidel Dordrecht, p.49(1987).
- 74 H.D.Steiz, H.D.Speikamp and F. Bandermann, *Makromol.Chem.*, **189**, 429 (1988).
- 75 P.A.Mai and A.H.E.Muller, *Makromol.Chem., Rapid Commun.*, **8**, 247 (1987).
- 76 P.A.Mai and A.H.E.Muller, *Makromol.Chem., Rapid Commun.*, **8**, 99 (1987).
- 77 A.H.E.Muller, in "Recent Advances in Mechanism and Synthetic Aspects of Polymerization", M.Fontanille and A.Guyot, Eds., NATO ASI Ser. C 215, Reidel, Dordrecht, p23 (1987).
- 78 M.A.Doherty, F.Gores, P.A.Mai and A.H.E.Muller, *Polym.Prepr.(Am.Chem. Soc.*,

- Div. Polym. Chem.*), **29**(2), 73 (1988).
- 79 A.H.E.Muller, *Makromol. Chem., Macromol. Symp.*, **32**, 87 (1990).
- 80 W.J.Brittain and I.B.Dicker, *Makromol. Chem., Macromol. Symp.*, **67**, 351 (1993).
- 81 Y.kita, H.Yausa, J.Haruta, J.Segwa and Y.Tamura, *Synth. Commun.*, 1089 (1982).
- 82 D.R.Maloney, K.H.Hunt, P.M.Lloyd, A.V.G.Muir, S.T.Richards, P.J.Derrick and D.M.Haddleton, *J. Chem. Soc., Chem. Commun.*, 561 (1995)
- 83 W.R.Hertler, *Macromolecules*, **20**, (1987).
- 84 W.R.Hertler, *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)*, **28**(1), 108 (1987).
- 85 W.R.Hertler, D.A.Dixon, E.W.Mathews, F.Davidson and F.G.Kitson, *J. Am. Chem. Soc.*, **109**, 6532 (1987).
- 86 R.Zhuang and A.H.E.Muller, *Macromolecules*, **28**, 8035 (1995).
- 87 D.Y.Sogah and W.B.Farnham, In "*Organosilicon and Bioorganosilicon Chemistry*", H.Sakurai, Ed; John Wiley and Sons: New York, Chap. 20 (1985).
- 88 W.B.Farnham and D.Y.Sogah, *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)*, **27**(1), (1986).
- 89 J.Cella, J.Cargioli and E.Williams, *J. Organomet. Chem.*, **186**, 77 (1980).
- 90 W.B.Farnham and J.F.Whitney, *J. Am. Chem. Soc.*, **106**, 3992 (1984).
- 91 R.J.P.Corrio, in "*Recent Advances in Mechanistic and Synthetic Aspects of Polymerization*", M.Fontanille and A.Guyot, Eds., NATO ASI Ser. C 215, Reidel Dordrecht, p49 (1987).
- 92 K.Matyjaszewski, *New Polym. Mater.*, **2**, 115 (1990).
- 93 O.W.Webster, *Makromol. Chem. Macromol. Symp.*, **67**, 339 (1993).
- 94 R.P.Quirk, J.Ren and G.Bidinger, *Makromol. Chem., Macromol. Symp.*, **67**, 351 (1993).
- 95 A.H.E.Muller and M.Stikler, *Makromol. Chem., Rapid Commun.*, **7**, 575 (1986).
- 96 K.G.Banerjee and T.E.Hogen-Esch, *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)*, **28**(2), 320 (1987).
- 97 W.J.Brittain, *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)*, **29**(2), 320 (1988).
- 98 A.M.Hellstern, J.M.DeSimone and J.E.McGrath, *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Sci.)*, **29**(1), 148 (1988).
- 99 M.Eggert and R.Fritag, *J. Polym. Sci. Part-A, Polym. Chem.*, **32**(5), 803 (1994).
- 100 A.Saito and D.A.Tirrel, *Polym. J.*, **26**, 169 (1994).
- 101 W.R.Hertler, D.Y.Sogah, F.A.Raymond, R.D.Bauer, C.T.Chang, G.M.Taylor and L.E.Stillwing, *Makromol. Chem., Macromol. Symp.*, **64**, 137 (1992).
- 102 W.R.Hertler, *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)*, **27**(1), 165 (1986).
- 103 M.Augenstein and M.A.Muller, *Makromol. Chem.*, **191**, 2151 (1990).
- 104 H.Catagil and A.D.Jenkins, *Eur. Polym. J.*, **27**, 651 (1991).

- 105 A.D.Jenkins, E.Tsortolia, D.R.M.Walton, J.Stejskal and P.Kratochvil, *Polym.Bull.*, **20**, 97 (1988).
- 106 H.Catagil, N.Uyanik and C.Erbil, *Polymer*, **33**, 655 (1992).
- 107 U.Epple and H.A.Schneider, *Polymer*, **31**, 961 (1990).
- 108 F.P.Boether, *J.Macromol.Sci., Chem.*, **A 22**(5-7), 665 (1985).
- 109 J.E.McGrath, *J.Chem.Ed.*, **58**, 914 (1981).
- 110 G.Odian, "*Principle of Polymerization*", 2nd, Ed.; John-Wiley and Sons; New York 1981.
- 111 M.A.Muller, M.Augenstein and H.Punnewibb, *New Polym.Mater.*, **2**(4), 135(1991).
- 112 M.Hefft and J.Spinger, *Makromol.Chem., Rapid Commun.*, **11**, 397 (1990).
- 113 A.Varma, A.Neilson, J.M.Bronk, J.E.McGrath and J.S.Riffle, *Makromol.Chem., Macromol.Symp.*, **47**, 239 (1991).
- 114 A.Varma, A.Neilson, J.E.McGrath and J.S.Riffle, *Polym.Bull.*, **23**, 563 (1990).
- 115 W.Hovestadt, A.J.Muller, H.Kent and H.Hocker, *Makromol.Chem., Rapid Commun.*, **11**, 270 (1990).
- 116 B.Masar, P.Vlcek, J.Kriz and Kovarova, *Makromol. Chem.*, **195**, 1435 (1993).
- 117 B.Masar and P.Vlcek, *Makromol. Chem. Phys.*, **196**, 671 (1994).
- 118 Urban Schmalbroch and F.Bandermann, *Makromol. Chem.*, **194**(9), 2543 (1993).
- 119 W.J.Choi, Y.B.Kim, S.K.Kwon, K.T.Lim and S.K.Choi, *J.Polym.Sci.A-1*, **30**, 2143 (1992).
- 120 W.J.Choi, S.K.Kwon, K.T.Lim and S.K.Choi, *Polym.Bull.*, **30**, 401 (1993).
- 121 E.J.Goethal, in "*Telechelic Polymer: Synthesis and Applications*", CRC press BocaRaton, (1989).
- 122 R.Asami, Y.Kondo and M.Takaki in "*Recent Advances in Anionic Polymerization*", T.E.Hogen-Esch and J.Smid, Eds., Elsevier, New York, p. 381(1987).
- 123 G.M.Cohen, *Polym.Prepr. (Am.Chem.Soc., Div.Polym.Chem.)*, **29**(2), 46 (1988).
- 124 J.M.DeSimone, A.M.Hellstern, E.J.Siochi, S.D.Smith, T.C.Ward, V.J.Krukonic and J.E.McGrath, *Makromol. Chem., Macromol. Symp.*, **32**, 21 (1990).
- 125 W.Radke and A.H.E.Muller, *Makromol. Chem., Macromol. Symp.*, **54/55**, 583 (1992).
- 126 Y.Yamashito, in "*Chemistry and Industry of Macromonomers*", Heidelberg, Huthig and Wepf Verlag, (1993).
- 127 D.M.Wiles and S.Bywater, *J.Polym.Sci.*, **2**(B), 1175 (1964).
- 128 R.P.Quirk and J. Ren, *Polym.Int.*, **32**, 205 (1993).
- 129 B.J.Bauer and L.J.Fetters, *Rubber Chem.Technol.*, **51**, 406 (1978).
- 130 M.K.Martin, *Diss. Abstr. Int.*, B1982, **40**, 1867 (1980).
- 131 H.J.Spinelli, U.S.Patent 627, 913 (1984) *Chem.Abstr.* **105**, p24811c.

- 132 J.A.Simms, *Rubber Chem.Technol.*, **64**(2), 139 (1991).
- 133 P.Lang, M.S.Burchard, N.S.Wolfe and H.J.Spinelli, *Macromolecules*, **24**, 1306 (1991).
- 134 R.Asami, M.Takaki and Y.Moriyama, *Polym.Bull.*, **16**, 125 (1986).
- 135 T.Heitz and O.W.Webster, *Makromol. Chem.*, **192**, 2463 (1991).
- 136 W.R.Hertler, D.Y.Sogah and F.P.Boettcher, *Macromolecules*, **23**, 1264 (1990).
- 137 A.D.Jenkins, E.Tsartolia, D.R.M.Walton, J.Horska-Jenkins, P.Kratochvil and J.Stejskal, *Makromol. Chem.*, **191**, 2511 (1990).
- 138 J.J.Kozakiewicz, N.S.Kurose, D.R.Daney, S.Y.Huang and J.Falzone, *Polym.Prepr. (Am.Chem.Soc., Div.Polym.Chem.)*, **28**(1), 347 (1987).
- 139 D.Y.Sogah, *Polym.Prepr. (Am.Chem.Soc., Div.Polym.Chem.)*, **29**(1), 3 (1988).
- 140 G.N.Taylor, L.E.Stillwagon, F.M.Houlihan, T.M.Wolf, D.Y.Sogah and W.R.Hertler, *Chem.Mater.*, **3**, 1031 (1991).
- 141 A.H.Gabor, L.C.Prutte and C.K.Gabor, *Chem.Mater.*, **8**, 2282 (1996).
- 142 H.L.Jakubauskas, *J. Coat.Technol.*, **58**, 71 (1986).
- 143 H.J.Spinelli, *Adv.Org.Coat.Sci.Technol.Ser.*, **12**, 34 (1990).

CHAPTER-II

OBJECTIVES OF THE PRESENT INVESTIGATIONS

2.1 INTRODUCTION

The technique of group transfer polymerization (GTP) is found to be most suitable for (meth)acrylate monomers¹⁻³. This technique provides “living” polymers (controlled \bar{M}_w , narrow polydispersity and chain ends capable of further growth upon addition of additional monomer) at room temperature. The “living” nature of the GTP chain ends offers a potentially useful method for the synthesis of a variety of methacrylate polymers with controlled structures and architectures. Examples are block copolymers⁴, macromonomers⁵, telechelics⁶, end functionalized polymers⁷, star-branched polymers⁸ and graft polymers⁹.

The nature of the catalyst plays an important role in determining the rate of polymerization and polymer polydispersity. Incomplete monomer conversion and higher polydispersities are obtained when high catalyst concentrations are used. Typically less than 0.1 mol% based on the initiator is recommended. Apart from its effect on the rate of polymerization, it is proposed that the catalyst also affects the mechanism of polymerization. Weak nucleophiles such as HF_2^- , bibenzoate etc. presumably catalyze GTP by an “associative” mechanism whereas strong nucleophiles such as acetate, methyl fluorenides etc. catalyzed GTP by “dissociative” mechanism^{10,11}.

The present investigation has been undertaken with the following objectives.

a. There are a number of reports in the literature on the random and block copolymers of methyl methacrylate (MMA) with higher alkyl methacrylates¹. However, the copolymerization of MMA with lauryl methacrylate (LMA) has not been systematically examined. Copolymers of LMA are expected to exhibit interesting properties on account of its comb like structures. Controlled synthesis of such copolymers are not possible by anionic technique since LMA has limited solubility in solvents such as THF below 0°C. Living anionic polymerization of alkyl methacrylates is only feasible at very low temperatures, typically below -40°C. GTP is the **only potential** method for synthesizing narrow polydispersity random and block copolymers of MMA and LMA. Therefore, a study aimed at the synthesis of high molecular weight (~50,000) copolymers of LMA and MMA, over a wide range of compositions using GTP was undertaken.

b. The counteranions associated with GTP chain ends are generally large with diffuse charge distribution. Examples are tris(dimethyl amino)sulfonium (TAS)³, tris (piperidinio)sulfonium (TPS)³ or tetraalkylammonium (R₄N⁺)³. Alkali metal cations have been less studied in GTP. In early studies KHF₂ was examined as catalyst; however, in view of its insolubility in THF, solvents such as acetonitrile or DMF had to be used. Acetonitrile has since been shown to have an unfavorable effect on GTP as it reacts with the initiator and the active chain ends. To improve the solubility of these salts in the preferred solvent, namely THF, complexation with crown ethers or ethylene glycol are resorted to. In view of the proven success of tetrabutyl ammonium bibenzoate as a GTP catalyst, we undertook a study of potassium bibenzoate as GTP catalyst. To promote solubility, this catalyst was used in presence of 18-crown-6. The features of group transfer polymerization such as rate, conversion, molecular weight and polydispersity using this catalyst was elucidated.

This approach also enables a comparison between GTP and classical anionic polymerizations. Recently Teysse and coworkers¹² showed that diphenyl methyl sodium, complexed with dibenzo-18-crown-6, showed living characteristics in toluene at 0°C. Therefore, in both the processes, namely GTP catalyzed by potassium bibenzoate/18-C-6 and anionic polymerization initiated by diphenyl methyl sodium/ DB-18-C-6, an alkali metal cation solvated by a bulky crown ether could be the counterion.

c. In addition to acrylates and methacrylates, GTP has been used to polymerize acrylonitrile, methacrylonitrile, N,N-dimethyl acrylamide and substituted lactones. In general, poor control and broad molecular weight distributions are reported for monomers other than methacrylic esters using GTP techniques with anionic catalysts. However, relatively less is known regarding the polymerizability of monomers containing 1,2-dicarbonyl groups (e.g. maleimides) using GTP initiator. Therefore, a study of polymerization of N-phenyl maleimide using group transfer initiators was undertaken.

2.2 APPROACHES

2.2.1 Synthesis of homopolymers and copolymers of alkyl methacrylates.

2.2.1.1 Various purification methods of higher alkyl methacrylates (BMA, LMA etc.) were explored.

2.2.1.2 Random copolymers of LMA and MMA were synthesized and the reactivity ratios of these two monomers were determined under GTP conditions.

2.2.1.3 Block copolymers of LMA and MMA were synthesized and the effect of livingness enhancer (trimethylsilyl benzoate) on the molecular weight and polydispersity was studied.

2.2.1.4 The effect of concentration of initiator, monomer, catalyst as well as temperature and the nature of the alkyl groups on the rate of polymerization was studied.

2.2.1.5 Copolymers were characterized by SEC-RI and SEC-MALLS.

2.2.1.6 Sequence determination and statistics of copolymerization were examined by ^{13}C NMR.

2.2.2 Potassium bibenzoate/18-crown-6 complex catalyzed GTP of MMA.

2.2.2.1 The effect of concentration of catalyst, crown ether to catalyst ratio, crown ether to initiator ratio, solvent and temperature on the molecular weights and polydispersities were studied.

2.2.2.2 The rates of reactions were evaluated as a function of concentration of catalyst, initiator and monomer and temperature.

2.2.3 Homopolymerization of NPM and copolymerization with MMA.

2.2.3.1 Conditions for the homopolymerization of NPM were standardized using Lewis acid catalyst and TBABB catalyst.

2.3 REFERENCES

- 1 G.C.Eastmond and O.W.Webster, "New methods of polymer synthesis," Ed. J.R.Ebdon, Blackie, Glasgow, chap.2, p.23,1992.
- 2 O.W.Webster and B.C.Anderson, "New methods for polymer synthesis," Ed. W.J.Mijs Plenum press: New York, chap.1, p.1 (1992).
- 3 W.J.Brittain, *Rubber Chem.Technol.*, **65**, 580 (1992).
- 4 O.W.Webster, W.R.Hertler, D.Y.Sogah, W.B.Farnham and T.V.Rajanbabu, *J.Am.Chem.Soc.*, **105**, 5706 (1983).
- 5 D.Y.Sogah and O.W.Webster, *J.Polym.Sci., Lett.Ed*, **21**, 927 (1983).
- 6 K.Steinbretch and F.Bandermann, *Makromol.Chem.*, **190**, 2183 (1989).
- 7 R.P.Quirk and J.Ren, *Makromol.Chem.Macromol.Symp.*, **88**, 17 (1994).
- 8 J.A.Simms, *Rubber Chem.Technol.*, **64**(2), 139 (1991).
- 9 J.A.DeSimone, A.M.Hellstern, E.J.Siochi, S.D.Smith, T.C.Ward, P.M.Gallenger, V.J.Krukonis and J.E.McGrath, *Makromol.Chem.Macromol.Symp.*, **32**, 21 (1990).
- 10 S.Bywater, *Makromol.Chem.Macromol.Symp.*, **67**, 339 (1993).
- 11 O.W.Webster, *Makromol.Chem.Macromol.Symp.*, **67**, 365 (1993).
- 12 S.K.Varshney, R.Jerome, P.Bayard, C.Jacob, R.Fayt and P.Teyssie, *Macromolecules*, **25**, 4457 (1992).

CHAPTER-III

EXPERIMENTAL METHODS IN GTP

3.1 INTRODUCTION

GTP is a living polymerization method which make it possible to control polymer properties such as molecular weight, polydispersity, chain end functionalizations, polymer architecture etc. of acrylic and methacrylic polymers¹.

The active centers in GTP are susceptible to terminations by protic sources; all reagents and solvents should be carefully purified and dried (**Chap-I, Sec. 1.5**).

In this chapter, purification methods of reagents, methods of preparation of catalysts, polymerization process, kinetics measurement techniques have been discussed.

3.2 MATERIALS

Sodium metal, calcium hydride, benzophenone, n-butyl lithium (1.6 M in hexane), bis(dimethylamino) dimethylsilane (BDMAS) and tetrabutyl ammonium fluoride (TBAF) (1.0 M in THF) were procured from Aldrich, USA and were used as received. Adsorbent alumina, G-87 grade (IPCL, Baroda) was activated under nitrogen at 400⁰C in a furnace for 4 h. Triisobutylaluminum (TIBAL) (Schering AG, Germany) was used as received. 18-Crown-6 (Aldrich, USA) was dried under vacuum (0.001 mmHg) for 3 h prior to use. Methyl methacrylate (MMA) was obtained from Gujarat State Fertilizer Corporation, Baroda, India. Butyl methacrylate (BMA), lauryl methacrylate (LMA) and N-phenyl maleimide (NPM) were purchased from Aldrich, USA. S.D.Fine Chemicals, Bombay supplied all solvents, tetrahydrofuran (THF), dichloromethane (CH₂Cl₂), toluene etc.

3.3 PURIFICATION OF MONOMERS

3.3.1 MMA

Methyl methacrylate (MMA) was passed through activated alumina (G-87) column to remove inhibitor, moisture and alcohol, stirred over CaH₂ for 8 h, vacuum distilled at 10⁻³ mm of Hg and stored under nitrogen at 0⁰C. MMA was then transferred into a nitrogen filled monomer purification apparatus (**Fig. 3.1**) via cannula. MMA was degassed to ensure removal of oxygen and then TIBAL was added dropwise to the cooled MMA until bright yellow complex formed². It was subsequently distilled under vacuum (10⁻³ mm of Hg) and used immediately for polymerization.

3.3.2 BMA

Purification of BMA by treatment with MTS

BMA was passed through activated alumina column and stirred over CaH_2 for 8 h and distilled (bp $67^\circ\text{C}/15$ mmHg). Finally, BMA (28 mL) was added with MTS (0.2 mL) and stirred at 60°C for 1 h and distilled (bp $67^\circ\text{C}/15$ mmHg) prior to use in the polymerization.

Purification of BMA by treatment with BDMAS/TBAF

BMA (30 mL) distilled over CaH_2 was syringed into a two necked flask and treated with BDMAS (0.3 mL) and TBA (0.1 mL)³. The contents of the flask were heated at 50°C for 1 h with stirring and distilled (bp $67^\circ\text{C}/15$ mmHg).

3.3.3 LMA

Lauryl methacrylate (LMA) was passed through activated alumina (G-87) column, stirred over CaH_2 for 8 h and distilled (bp $142^\circ\text{C}/4$ mmHg). To approximately 30 mL of LMA was added with 0.3 mL of BDMAS and 0.1 mL of TBAF and stirred at 50°C for 1 h. The monomer was distilled under reduced pressure (bp $142^\circ\text{C}/4$ mmHg).

3.3.4 NPM

N-phenyl maleimide (Aldrich) was recrystallized several times from cyclohexane and dried by repeated azeotropic distillation with toluene.

3.4 PURIFICATION OF SOLVENTS

3.4.1 THF

Tetrahydrofuran (THF) was purified by refluxing over fresh sodium benzophenone complex (a deep purple color indicating moisture free solvent). It was further distilled over poly(styryl) lithium under reduced pressure (10^{-3} mm of Hg) immediately before use (Fig. 3.1). THF thus purified typically showed moisture level < 20 ppm as measured by Karl Fisher titration.

3.4.2 TOLUENE

Toluene was refluxed over sodium-benzophenone complex for several hours and distilled under nitrogen. Finally some amount of toluene was transferred into the distillation apparatus (Fig. 3.1) and poly(styryl) lithium was added until the color of the solvent turned red and distilled under reduced pressure (10^{-3} mm of Hg).

3.4.3 CH₂Cl₂

Methylene chloride (CH₂Cl₂) was distilled over CaCl₂ and then refluxed for 48 h over CaH₂ and distilled. After degassing with nitrogen, it was stirred over CaH₂ for several hours and distilled under vacuum (10^{-3} mmHg).

3.5 PREPARATION OF CATALYSTS AND TRIMETHYL SILYL BENZOATE

3.5.1 TETRABUTYLAMMONIUM BIBENZOATE

Tetrabutylammonium bibenzoate (TBABB), was prepared from benzoic acid and aqueous tetrabutylammonium hydroxide (TBAOH)⁴. Into a separatory funnel was added 10.0 g (0.082 mol) of benzoic acid and 80 mL of 40% aqueous TBAOH. The mixture was shaken until homogeneous then extracted with 3x50 mL of CH₂Cl₂. To the combined extracts was added 10.0 g of benzoic acid and the solution was dried over MgSO₄, filter and stripped. The residual solid was dissolved in 250 mL of warm THF and the volume was reduced to 125 mL under aspirator pressure. To the partly crystallizing mixture was added 250 mL ether (in parts) and the mixture was allowed to stand overnight. The product was filtered, washed with ether and dried under vacuum; mp 102-104°C (lit⁴ mp 102°C).

3.5.2 POTASSIUM BIBENZOATE

Potassium bibenzoate (KBB) was prepared by cooling an alcoholic solution of one mole of benzoic acid and 0.5 mol of potassium hydroxide. The crystals consisted of extremely thin flakes⁵. The complex of KBB with 18-Crown-6 was made by dissolving KBB in melted 18C6.

3.5.3 SYNTHESIS OF TRIMETHYLSILYL BENZOATE

Trimethylsilyl benzoate was prepared according to the literature procedure⁶. To 1 g (8.19×10^{-3} mol) benzoic acid, 2 mL (9.47×10^{-3} mol) hexamethyldisilazane was added slowly with

stirring. The addition was exothermic. The mixture was heated to 85⁰C for 1 h and then fractionally distilled under reduced pressure (50⁰C/1 mmHg). Yield was 94%.

3.6 PURIFICATION OF INITIATOR AND CATALYSTS

3.6.1 INITIATOR

[(1-Methoxy-2-methyl-1-propenyl)oxy]trimethylsilane (MTS) (Aldrich, USA) was distilled over CaH₂ (bp 35⁰C /15 mmHg) after stirring under nitrogen.

3.6.2 CATALYSTS

Catalysts were dried under high vacuum (10⁻³ mmHg) for couple of hours before use in the polymerizations.

3.7 METHODS OF POLYMERIZATION AND COPOLYMERIZATION

General remark: All glass-wares were predried at 120⁰C for at least 24 h, assembled hot and cooled under a stream of purified nitrogen. All manipulations were conducted under a nitrogen atmosphere by using standard benchtop inert atmosphere techniques.

3.7.1 HOMOPOLYMERIZATION OF METHACRYLATES USING TBABB CATALYST

The GTP of alkyl methacrylate monomers was carried out in a 250 mL three necked round bottom flask (Fig. 2.2). The flask containing a magnetic stirring bar was assembled under N₂ while hot.

The solid catalyst, TBABB, (1-2 mole% based on initiator) (0.006g, 0.012 mmol) was added to the polymerization flask and then the solvent THF was transferred via cannula. The amount of solvent charged was based on the weight of the monomer. The desired amount of MTS (0.11g, 0.63 mmol) was added into the flask using a microsyringe and the reaction mixture was stirred well, allowing sufficient time (5 minutes) for initiator and catalyst to form a complex. Finally, monomer (9.4g, 94 mmol) was added dropwise via syringe while stirring was continued. An exothermicity (5-20⁰C) was observed indicating the onset of the polymerization. Polymerization was continued for 3 h and then reaction was terminated by

adding 1-2 mL of methanol. The solvent layer was decanted off and the polymer was dried in vacuum at 60°C for 24 h (9.4g, 100%conversion).

3.7.2 HOMOPOLYMERIZATION OF MMA USING KBB/ 18-CROWN-6 AS THE CATALYST

To a 250 mL round bottom flask (Fig. 2.2) fitted with a septum, a thermowell and a stopper, under nitrogen, were added THF (30 mL), KBB/ 18-C-6 (0.14 mmol) in THF solution and bis(dimethylamino) dimethylsilane (0.16g, 1 mmol). After stirring for 30 minutes, MTS (0.12g, 0.69 mmol) in THF solution was added via a syringe. After 5 minutes, MMA (9.4g, 94 mmol) was added via cannula. An exothermic reaction occurred. The reaction was quenched after 3 h by addition of methanol. The polymer was precipitated in excess methanol, the layer was decanted off and the polymer dried at 60°C/ 1 mm of Hg till constant weight. Yield was 9.4 g (100% conversion).

3.7.3 BLOCK COPOLYMERIZATION

A 250 mL round bottom flask (Fig. 2.2) equipped with a magnetic stirring bar, a thermowell and a rubber septum was charged with THF (50 mL), MTS (0.07g, 0.4 mmol) and TBABB (0.004g, 0.008 mmol). The molar ratio of catalyst to initiator was 1:50. Trimethylsilyl benzoate (10 µL, 0.044 mmol) was added as "livingness enhancer". The solution was stirred at 25°C for 5 min. Thereafter LMA (9.1g, 36 mmol) was added slowly over a period of 10 min. A 3°C temperature rise was observed. The mixture was stirred for 3 h and a 5 mL pick out was removed and quenched in methanol. This sample of homopoly(lauryl methacrylate) was used for determining conversion, molecular weight and polydispersity. Another portion of catalyst, TBABB (0.004g, 0.008 mmol) dissolved in THF (2 mL) was added to the reaction flask followed by addition of MMA (3.3g, 33 mmol) at 25°C. The temperature rose from 25°C to 33°C. Polymerization was continued for 3 h and was terminated by adding 2 mL of methanol. The viscous mixture was diluted with THF (50 mL) and then poured into methanol to precipitate the polymer. The precipitate was collected by filtration, dried and weighed to give 12.4 g (100% conversion) of the copolymer.

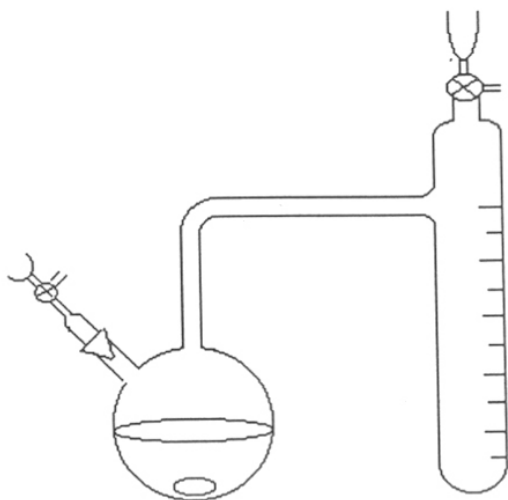


Fig.3.1: Apparatus used for vacuum distillation

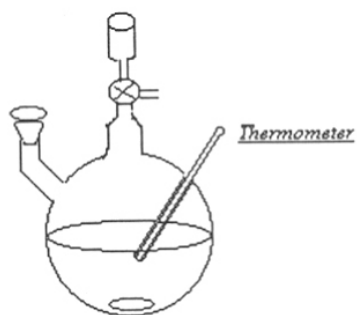


Fig. 3.2: Apparatus used for conducting polymerization

3.7.4 RANDOM COPOLYMERIZATION

To a stirred mixture of MTS (0.068g, 0.4 mmol) and TBABB (0.004g, 0.008 mmol) in 50 mL THF were added a mixture of MMA (3.2g, 32 mmol) and LMA (8.68g, 34 mmol) over a period of 10 min at 24°C. The temperature rose from 24°C to 36°C. Precipitation in methanol and evaporation of solvent gave a 11.8 g (100% conversion) of the random copolymer.

3.8 METHODS FOR EVALUATION OF POLYMERIZATION KINETICS

Kinetic experiments were performed in a jacketed reactor comprising of a stirring bar, glass ampoules for monomer, initiator, catalyst and solvent, a measuring burette connected to the reaction flask and a glass tube fitted with a Teflon valve for withdrawing samples (Fig. 3.3). The apparatus was assembled hot under nitrogen and flame dried under high vacuum (10^{-3} mm of Hg). After cooling, the vacuum was closed and the whole system was filled with purified nitrogen. Initially, little nitrogen was taken into reaction flask for equilibration. The

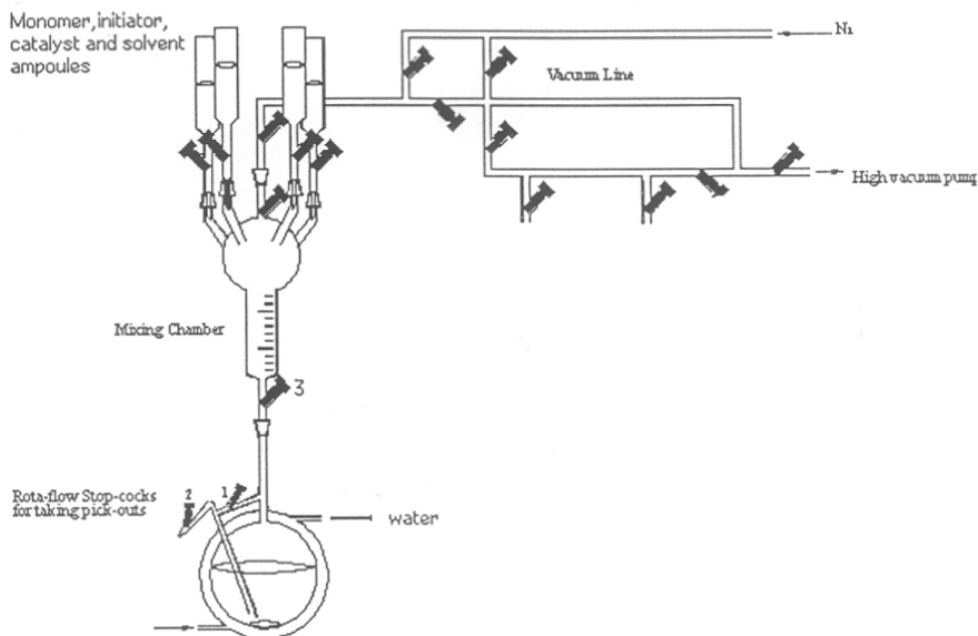


Fig.3.3: Apparatus used for kinetic measurement

nitrogen line was closed. Through using stopcock S₅ and the excess pressure of nitrogen was released through the bubbler by opening stopcocks S₄ and S₆. Therefore, S₄ and S₃ were closed and S₅ was opened to create a pressure difference and solvent THF was transferred to the reaction flask by opening the stopcock S₃. In a similar fashion, the catalyst solution was added to THF, followed by the addition of calculated amount of monomer and finally, MTS was added rapidly. The stop-watch was also started simultaneously. After predetermined period of elapsed time samples were withdrawn and terminated in methanol. Monomer conversions were determined gravimetrically.

3.9 CHARACTERIZATION OF POLYMERS

3.9.1 DETERMINATION OF MOLECULAR WEIGHT USING SEC-RI

The number average molecular weight (\bar{M}_n) and polydispersity of PMMA were determined using Waters Gel Permeation Chromatography model GPC/ALC 150C equipped with refractive index detector using μ -styragel columns (10^5 , 10^4 , 10^3 , 500, 100 \AA) at 30°C and THF as eluant (0.5% weight solution in THF, flow rate 1 mL/min or 2 mL/min). Monodisperse PMMA was used for calibration.

3.9.2 DETERMINATION OF ABSOLUTE MOLECULAR WEIGHT USING GPC-MALLS

Size exclusion chromatography (SEC) measurements were done using a Waters GPC 150C equipped with a R401 refractive index detector (Waters) and a mutiangle laser light scattering (MALLS) detector from Wyatt Technology. The mobile phase used was THF; columns were a series of five 30 cm columns packed with a crosslinked μ -polystyrene gel with nominal porosities of 10^5 , 10^4 , 10^3 , 500 and 100 \AA . The columns were housed in an oven maintained at 30°C. The eluent (0.5% weight solution in THF, flow rate 1 mL/min) from the column was directed through a DAWN-F MALLS scattering and then through R401 RI detector to avoid subjecting fragile refractometer cell to high back pressure. The outputs of the DAWN-F and the R401 were directed to an IBM AT and the output of the R401 was also directed to an IBM XT through as HPIB intelligent interface. Software (Aurora) from Wyatt Technology was used to perform calculations.

3.9.3 DETERMINATION OF dn/dc VALUES

A Brice-Phoenix, Model BP-2000V, differential refractometer was used for the precise measurement of the differential refractive index increment (dn/dc) for each polymer at 25⁰C in THF. The values measured were quite small, ranging from 0.076 to 0.088 (Table 3.1).

Table 3.1: dn/dc Values of Random and Block Copolymers

Sr.No.	Copolymer type	MMA/LMA (mol ratio)	dn/dc
1	Random	80/20	0.086
2	Random	60/40	0.084
3	Random	52/48	0.081
4	Random	40/60	0.081
5	Random	23/77	0.078
6	Block	80/20	0.083
7	Block	60/40	0.088
8	Block	50/50	0.079
9	Block	40/60	0.085
10	Block	20/80	0.076

3.9.4 DETERMINATION OF COPOLYMER COMPOSITIONS BY ¹H NMR

The compositions of the copolymers were determined by ¹H NMR using a Bruker 200 NMR MHz spectrometer at 30⁰ C in CDCl₃ (conc. 4 mg/mL) using a 5 mm diameter NMR tube.

3.9.5 DETERMINATION OF COPOLYMER COMPOSITIONS BY ¹³C NMR

The compositions of the copolymers at low conversions were determined by ¹³C NMR. ¹³C NMR spectra were recorded at 75.5 MHz (Bruker MSLG-300) spectrometer at 393⁰ K. The sample concentration was 15% W/V in 1,2,4-trichlorobenzene (TBC) and C₆D₆ was used as locking agent. Spectra were obtained by using BROADBAND decoupling and pulse delay of 2 s, 0.4 Hz/point, corresponding to a spectral width 25,000 and a data length of 16 K. The flip angle and acquisition time were 60⁰ C and 1.3 s respectively.

3.4 REFERENCES

- 1 G.C.Eastmond, O.W.Webster, "*New Methods of polymer synthesis*", Ed. J.R.Ebdon, Blackie, Glasgow, 1992, chap.2, p.23.
- 2 R.D.Allen, T.E.Long and J.E.McGrath, *Polym. Bull.*, **15**, 127 (1986).
- 3 J.D.Citron, *U.S.Patent* 4771116 (1988); *Chem. Abstr.*, **110**, 76288k (1989).
- 4 I.B.Dicker, G.M.Cohen, W.B.Farnham, W.R.Hertler, E.D.Lagnis and D.Y.Sogah, *Macromolecules*, **23**, 4034 (1990).
- 5 J.M.Skinner, G.M.D.Stewart and J.C.Speakman, *J.Chem.Soc.*, 180 (1954).
- 6 N.S.Fedotov, V.L.Kozlikov, V.F.Mironov (USSR), *Zh. Obshch. Khim.*, **40**(12), 2589 (1970).

CHAPTER-IV

HOMOPOLYMERIZATION OF ALKYL METHACRYLATES

4.1 INTRODUCTION

Silyl ketene acetals and other organosilicon compounds initiate the Group Transfer Polymerization (GTP) of polar monomers such as methacrylates, acrylates, acryl amides etc. in presence of either nucleophilic (HF_2^- , CN^- , F^- , PhCOO^- , OAc^- , PhO^- etc.) or electrophilic (Lewis acid) catalysts through a living polymerization mechanism^{1,2}. Therefore, it has the important advantages associated with living polymers, including the capability to give polymers with narrow polydispersity, the ability to control molecular weight by the ratio of monomer to initiator and the ability to synthesize polymers with predetermined architecture.

Methacrylates are the best suited class of monomers for initiating GTP and can produce polymers with narrow polydispersity. Most of the common and commercially available methacrylates are either homopolymerized or copolymerized with methyl methacrylate (MMA), examples being BMA, DMA, LMA etc.. An advantage to GTP is that methacrylates with functional groups which are sensitive to anionic or radical polymerization conditions can be used. Examples include 4-vinylbenzyl methacrylate, allyl and sorbyl methacrylates, and glycidyl methacrylate. Polymerizations involving GMA are generally performed below 0°C to obtain best results. Active hydrogens interfere with GTP, so that methacrylic acid or hydroxyethyl methacrylate must be protected with trimethyl silyl groups prior to polymerization. Another way to incorporate acid groups is by use of tetrahydropyranyl methacrylate; acidic hydrolysis of the polymers gives pendent carboxylic acid.

In this chapter, the homopolymerization of methyl methacrylate (MMA), butyl methacrylate (BMA) and lauryl methacrylate (LMA) will be discussed. The rates of polymerization have been determined with respect to concentration of catalyst, initiator, monomer as well as temperature and nature of the alkyl groups.

4.2 RESULTS AND DISCUSSION

Under ideal conditions, there are no termination steps in living polymerization process provided high purity conditions are maintained. As in the anionic mechanism, GTP is susceptible to termination by the presence of reactive protonic impurities. In the presence of reactive protonic impurities the trimethylsilyl group is cleaved from the initiator, or the propagating chain end, thus resulting in the termination of the living polymerization. Initial

investigations were centered around meeting the purity requirements of reagents; solvent, monomers, initiator and catalysts, for the living polymerization of alkyl methacrylates by GTP.

The purification of all reagents are described in **Chapter-III**. Anionic polymerization of alkyl methacrylates using 1,1-diphenylhexyllithium (DPHL) as the initiator at -78°C allows for the titration of impurities present in the solvent and 1,1-diphenylene prior to the charge of organolithium. This results in knowing the exact concentration of the initial active concentration of initiator without the complication of impurities. In GTP, titration of trace impurities present in solvent, initiator and catalyst is not possible prior to monomer addition. Thus, using syringe techniques and relying on the purification of reagents, a methodology to prepare alkyl methacrylate polymers by GTP was established.

4.2.1 Homopolymerization of alkyl methacrylates

4.2.1.1 GTP of MMA with MTS as initiator and bioxanion as catalyst in THF

As a first step, the GTP of MMA in THF with MTS as the initiator and tetrabutylammonium bibenzoate (TBABB) as catalyst was studied. The mole ratio of the catalyst relative to initiator was lower (at maximum 2 mol%) as recommended by Dicker et al.⁴ for improved molecular weight and polydispersity control. A number of polymers were prepared using a wide range of monomer/initiator ratios. Monomer was added slowly to the reaction mixture. This produced polymers with a relatively narrow polydispersity ($\bar{M}_w/\bar{M}_n = 1.15$). However, occasionally polydispersity values as high as 1.25 were observed for no apparent reason (**Fig. 4.1**). Number average molecular weights were consistently 10-15% higher than those calculated from the monomer to initiator ratio. Part of this discrepancy could be due to the fact that all polymers were isolated by precipitating in methanol and oligomers of lower molecular weight are not precipitated under these conditions. Polymerization results are given in **Table 4.1**.

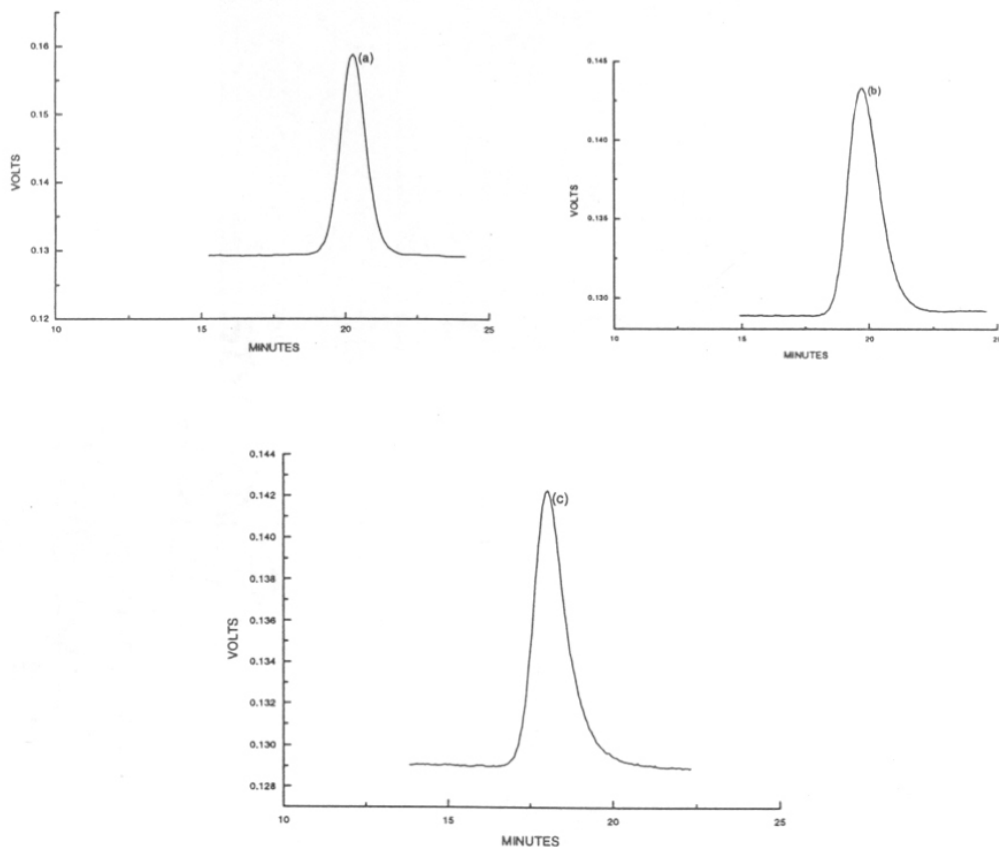


Fig. 4.1: SEC-RI for poly(methyl methacrylate)s a) entry 1, Table 4.1; b) entry 2, Table 4.1; c) entry 3, Table 4.1.

TBABB is an effective catalyst to initiate the polymerization of MMA producing relatively sharp polydispersity polymers of controlled molecular weight. The general mechanism is clear, since the catalyst needs to be only a small percentage of the initiator, whereas the molecular weight is determined by the initiator itself, the presence of active chain ends of some type is required in labile equilibrium with a large number of silylated chain ends. The dependence of the degree of polymerization (\bar{DP}_n) on $[M]_0/[I]_0$ requires that all chains participate in growth, and the narrow polydispersity observed requires that the active and inactive chain ends interchange rapidly on the time scale of polymerization. These requirements were described many years ago by Gee et al.³ in sodium alcoholate/alcohol initiated polymerization of ethylene oxide in 1,4-dioxane. A mixture of inactive -OH and active -ONa chain ends were produced, since the presence of alcohol was required to

solubilize the sodium alkoxides. Under the above conditions, a narrow polydispersity polymer with a number average degree of polymerization $DP_n = [M]/([ROH] + [RONa])$ was obtained. In GTP active chains are derived from the initiator. Therefore the relationship simplifies to $\bar{DP}_n = [M]/[I]_0$ or $[M]/([I]_0 + [C]_0)$ if some initiator I is destroyed by the catalyst. The discoverers of the GTP process have preferred a mechanism which involves a nucleophile (HF_2^- or B^-) exchanging rapidly between inactive $=(\text{OCH}_3)(\text{OSiMe}_3)$ end-groups, chain growth only occurring when an end-group is activated by the nucleophile.

Table 4.1: GTP of MMA in THF using MTS Initiator and TBABB Catalyst at 25°C

Sr. No.	$M_0 \times 10^2$ (mol)	$[M]_0$ (mol/L)	$C_0 \times 10^6$ (mol)	$I_0 \times 10^4$ (mol)	Conv. (%)	\bar{M}_n (Calcd)	\bar{M}_n (SEC)	\bar{M}_w / \bar{M}_n (SEC)
1.	9.0	2.27	13.4	6.9	100	12,200	14,720	1.16
2.	8.0	2.35	5.3	4.7	100	17,094	22,625	1.25
3.	18.3	2.34	5.97	2.95	100	62,000	72,500	1.15

Dicker et al.⁴ reported the GTP of MMA with MTS initiator and TBABB catalyst. Monodisperse PMMA ($\bar{M}_w / \bar{M}_n = 1.16$) with good molecular weight control ($I_{\text{eff}} = > 90$) were obtained. Polydispersity and molecular weight control obtained during the present study are similar to those reported earlier (Table 4.1, entry 1).

Bandermann et al.⁵ studied extensively the GTP of MMA in THF with MTS initiator and TBABB catalyst, changing the catalyst concentrations and initiator concentrations. In all cases, controlled molecular weights PMMA ($I_{\text{eff}} = > 95$) with broad polydispersities ($\bar{M}_w / \bar{M}_n = 1.3-1.8$) were reported.

The better catalytic activity of bioxyanions towards molecular weight control and polydispersity stems from the fact that they only serve as sources of low concentrations of monoxy anions by dissociation to a carboxylic acid and a monoxy anion. Because of low concentration of catalyst, the loss of initiator or living chain ends will be small.

On the other hand, the catalytic influence of oxyanions can also be explained on the basis of the ideas of Quirk and Biding⁶. These authors propose a rapid reversible complexation of small concentration of enolate anions with silyl ketene acetals to explain the living nature of GTP. In the case of monoxy anions the catalysts could react with silyl ketene acetal to

generate free enolate anions and a trimethylsilyl carboxylate. If this reaction is assumed to be reversible the rate decreasing influence of the external addition of silylesters can easily be understood. Silylesters should shift the equilibrium to the left side of the reaction, thus reducing the concentration of the free enolate anions, active in polymerization and the probability of chain termination would be reduced.

4.2.1.2 GTP of BMA with MTS as initiator and bioxanion as catalyst in THF

Commercially available BMA generally contains the following impurities: a) moisture b) n-butanol c) hydroquinone monomethylether (inhibitor) and d) methacrylic acid. Unless the reduction in the level of these impurities is successfully achieved, controlled polymerization of BMA is difficult.

Table 4.2: GTP of BMA Purified by Treatment with TIBAL

Sr.No.	$[M]_0 \times 10^1$ (M)	$[I]_0 \times 10^4$ (mol)	Conv. (%)	\bar{M}_n (Calcd)	\bar{M}_v^a
1	1.38	17.62	99	5,200	12,800
2	1.51	9.15	90	9,880	22,650
3	1.66	4.74	NR ^b	19,000	----
4	2.80	18.45	97	11,800	22,300

a. Viscosity measurements were carried out in CHCl_3 at $30 \pm 0.01^\circ\text{C}$ and \bar{M}_v , calculated using Mark-Houwink equation and the values of the parameters, $K = 4.47 \times 10^{-5}$, $a = 0.8$. b. NR = no reaction.

Initially, we attempted the use of TIBAL for the purification of BMA⁷. The use of TIBAL was found to be unsatisfactory because GTP results were erratic and irreproducible (Table 4.2). This was attributed to the fact that BMA has relatively higher boiling point (bp $160\text{--}163^\circ\text{C}/760$ mmHg) which is close to that of TIBAL (bp $86^\circ\text{C}/10$ mmHg). During distillation under static vacuum (10 mmHg) with heating at 50°C , some TIBAL codistilled with BMA. TIBAL is reported to interfere with the GTP initiator⁸.

Therefore, a search for an alternative purification technique was initiated. As n-butanol and water are the likely major impurities in BMA, a reagent which reacts with n-butanol and water but does not react with BMA was sought. Accordingly, MTS, the GTP initiator itself,

was used as scavenger since MTS is known to readily silylate phenols, acids and alcohols under mild conditions⁹ and the resulting silylether derivatives and the by-product methylisobutyrate should be inert under GTP conditions. Furthermore, in the absence of a catalyst, MTS does not react with methacrylic monomers. The results on GTP of BMA purified by this method are given in Table 4.3. In every instance, polymerization proceeded with quantitative conversions (100%).

Table 4.3: GTP of BMA Purified by the Treatment with MTS (BMA = 10.41 mol, [BMA]₀ = 1.57 M, C₀ = 6.19 x 10⁻⁶ mol, I₀ = 2.95 x 10⁻⁴ mol)

Sr. No.	Conv. (%)	$\bar{M}_n \times 10^{-3}$ (Calcd)	$\bar{M}_v \times 10^3$	$\bar{M}_n \times 10^{-3}$ (SEC)	\bar{M}_w / \bar{M}_n (SEC)
1	100	50.0	40.4	36.6	1.18
2	100	50.0	55.6	42.5	1.21
3	100	50.0	40.0	39.2	1.23

The observed molecular weights were lower than expected molecular weight indicating the presence of excess MTS (Table 4.3, entry 3).

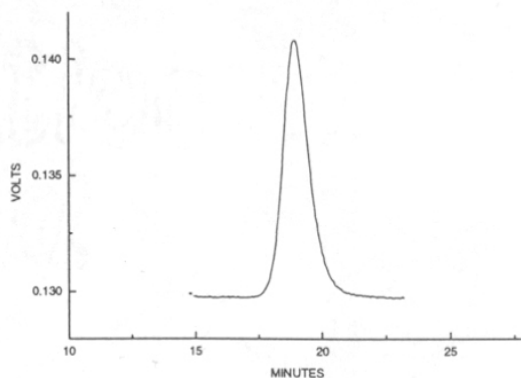


Fig. 4.2: SEC-RI for poly(butyl methacrylate) (entry 2, Table 4.3).

In an independent study it was found that MTS does not react with protic substances (water, n-butanol, phenol etc.) in the absence of a nucleophile. Based on these observations, it was concluded that MTS does not function as a scavenger. Therefore, MTS is not a useful reagent for the deactivation of protic impurities present in alkyl methacrylate monomers.

Bis(dimethylamino) dimethylsilane (BDMAS), in presence of a nucleophile catalyst such as tetrabutylammonium fluoride (TBAF) is reported to efficiently and quantitatively silylate -OH groups⁹. The products of the reaction between an alcohol and BDMAS are the corresponding dialkoxy dimethylsilane and dimethylamine¹⁰ (Eq. 4.1).



Dialkoxy dimethylsilane is not expected to interfere in GTP.⁴¹ Hence it was decided to use BDMAS/ TBAF system as a scavenger for the impurities present in higher alkyl methacrylate monomers.

The results on the polymerization of BMA purified by the treatment with BDMAS/ TBAF system are shown in **Table 4.4**. In every case, conversion was quantitative. However, the observed molecular weights were always higher than the theoretical molecular weights but polydispersities were narrow (1.2-1.3) (**Fig. 4.3**).

Table 4.4: GTP of BMA Purified by the Treatment with BDMAS/TBAF System

(BMA = 10.41 mol, [BMA]₀ = 1.57 M)

Sr. No.	I ₀ x 10 ⁴ (mol)	C ₀ x 10 ⁶ (mol)	Conv. (%)	$\bar{M}_n \times 10^{-3}$ (Calcd)	$\bar{M}_v \times 10^{-3}$	$\bar{M}_n \times 10^{-3}$ (SEC)	\bar{M}_w / \bar{M}_n (SEC)
1	8.9	18.1	100	15.00	26.00	18.75	1.22
2	2.95	6.19	100	50.08	94.00	79.20	1.19
3	2.95	6.19	100	50.0	97.00	79.80	1.23
4	2.95	6.19	100	50.08	83.10	72.60	1.21

It can be concluded that the treatment of BMA with BDMAS/ TBAF system is a satisfactory method for the purification of BMA. Further improvements are, however, needed to obtain "controlled" polymerization, especially in the high molecular weight range ($\bar{M}_n = 50,000$ and above).

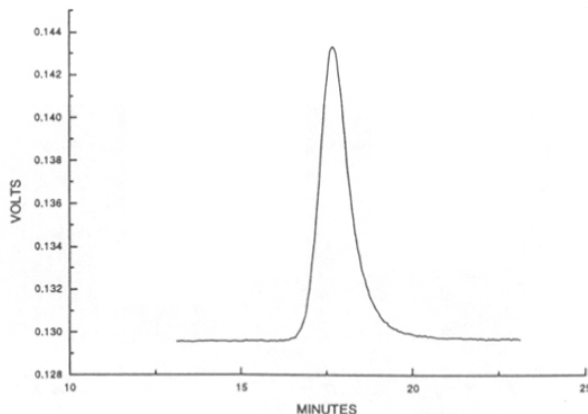


Fig. 4.3: SEC-RI for poly(butyl methacrylate) (entry 2, Table 4.4).

4.2.1.3 GTP of LMA with MTS as initiator and bioxanion as catalyst in THF

The methods of purification of MMA for GTP are well known in the literature. This generally involves a final treatment of MMA with TIBAL to a persistent yellowish color followed by distillation under dynamic vacuum at room temperature. Attempts to purify LMA by a similar method proved unsuccessful. LMA has a higher boiling point (142°C/ 4 mmHg) and even under a dynamic vacuum of 10^{-3} mm of Hg it can be distilled only with heating. It was found that this procedure invariably resulted in polymerization of LMA. Since BDMAS could be used to purify BMA, a similar approach was tried with LMA.

Polymerization of LMA was performed in THF with MTS as initiator and TBABB (2 mol% based on MTS) as catalyst. The results are shown in **Table 4.5**. Polymerization with good control on molecular weight and reasonable polydispersities could be obtained upto \bar{M}_n of 15000. Attempts to synthesize homopolymer with $\bar{M}_n > 30,000$ led to loss of molecular weight control and broadening of polydispersity (**Fig. 4.4**). We attribute this to interfering impurities present in the monomer and the limitation of the purification methods.

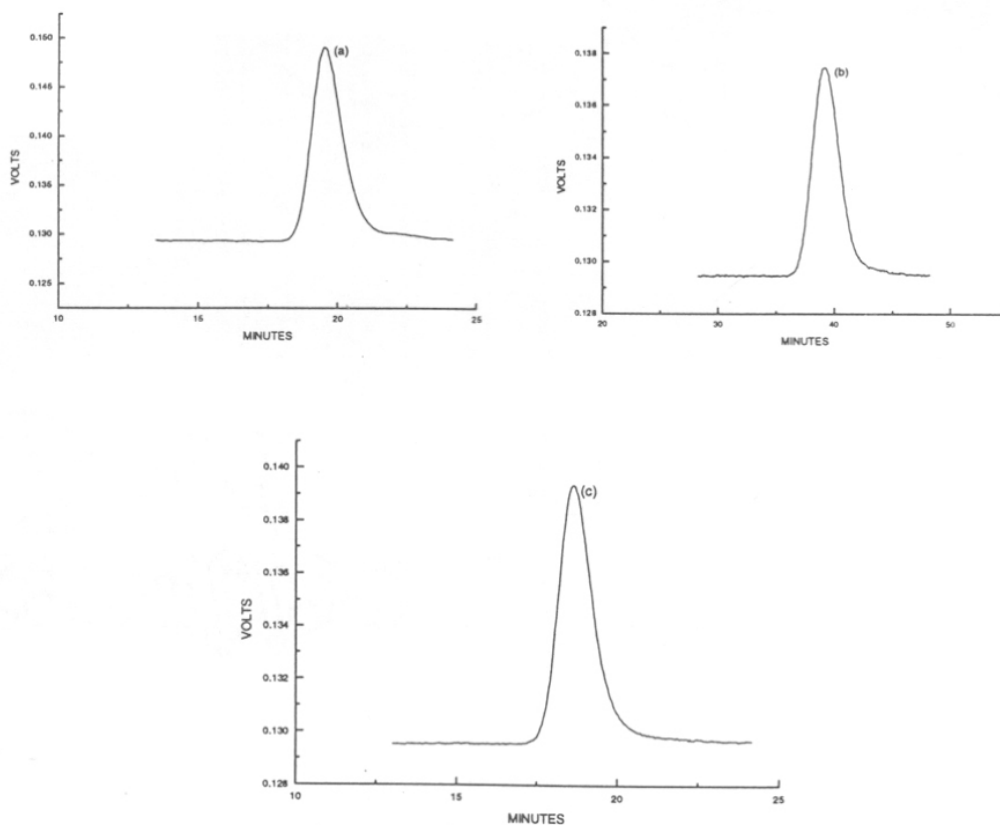


Fig. 4.4: SEC-RI for poly(lauryl methacrylate)s a) entry 1, Table 4.5; b) entry 2, Table 4.5; c) entry 3, Table 4.5.

Table 4.5: GTP of LMA in THF Purified by the Treatment with BDMAS/ TBAF System at 25⁰C ([LMA]₀ = 0.86 mol/L)

Sr.No.	$M_0 \times 10^2$ (mol)	$[C]_0 \times 10^6$ (mol)	$[I]_0 \times 10^4$ (mol)	Conv. (%)	\bar{M}_n (Calcd)	\bar{M}_n (SEC)	\bar{M}_w / \bar{M}_n (SEC)
1.	3.94	7.2	5.9	100	16,950	20,600	1.18
2.	3.90	7.6	6.6	100	15,090	17,120	1.26
3.	5.63	6.5	4.77	100	30,000	41,000	1.32

4.2.2 KINETICS OF ALKYL METHACRYLATE POLYMERIZATION

In order to get further insight into the polymerization mechanism of MMA by GTP, kinetic investigations were undertaken. A number of investigations, including kinetic and labelling studies, have been conducted to establish the mechanism of GTP. These studies predominantly focus on nucleophilic catalysts, in particular fluoride and bifluoride catalysts. These have inherently lower solubility in THF and require presence of a polar solvent such as acetonitrile.

Our present work entailed investigation of the GTP of MMA in the presence of MTS as initiator and TBABB as catalyst. The bibenzoate catalysts, in comparison to the traditional fluoride catalysts, are soluble in THF. However, kinetic studies with TBABB have not been performed extensively. With this soluble catalyst and a suitably designed polymerization reactor we explored the effect of catalyst, initiator and monomer concentrations as well as temperature on the rate of polymerization.

Methodology and sample analysis

The kinetic investigations were carried out in a controlled temperature polymerization reactor and the conditioning process of this reactor is described in **Chapter-III**. The use of such reactor permits the study of the influence of catalyst, initiator and monomer concentrations, solvent and temperature on the rate of polymerization while maintaining stringent reaction conditions for the polymerization. GTP exhibits a detectable exotherm even with very dilute solutions. Hence, it was necessary to restrict the polymerization exotherm in order to isolate the effects of different variables on the reaction that may be overshadowed or complicated by variations in reaction temperature. The reactor was equipped with water circulating bath for precise control of temperature of polymerization. Thus, it was possible to independently determine the effect of catalyst level, monomer and initiator concentration on the polymerization rate and consequently the effect of temperature at a constant catalyst level.

To examine these variables, samples were removed from the reactor with time through a glass tube fitted with a Teflon valve into a measuring cylinder containing methanol of measured amount. These samples were transferred to round bottom flask and evacuated

under high vacuum. This enables the conversion of monomer to polymer. The samples at different conversions were analyzed by SEC. As evident from the SEC traces (Fig. 4.5) the eluogram shift to lower elution volumes with time. This is indicative of increasing molecular weight with conversion of monomer to polymer.

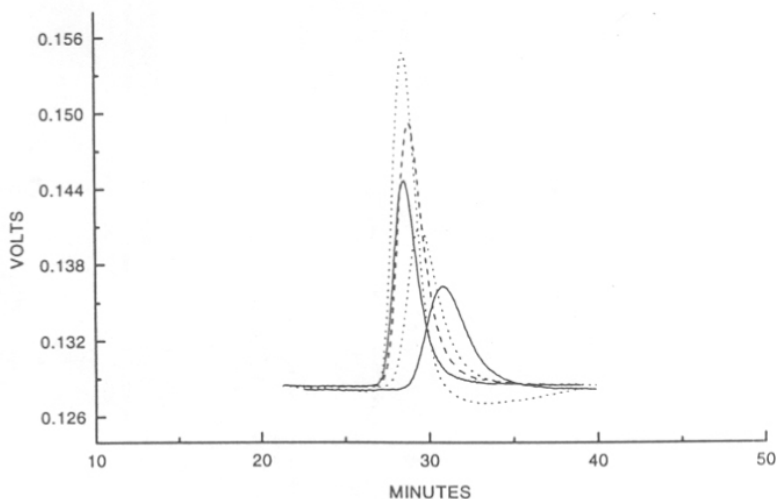


Fig. 4.5: SEC-RI for PMMA at different conversions

This experimental procedure was repeated at various concentrations of initiator, catalyst, monomer and at different temperatures. The results obtained is presented in the following sections and compared with the results obtained by other investigators. Indeed, it is important to preface the discussion of the kinetic results with a mention of the ability to compare results. Each investigator has been working with a different mode of addition of reactants, variable concentrations types of reactants and different methods of analysis. Therefore, direct comparisons is difficult and may be questionable but some correlations concerning the various trends may be possible.

Introduction to the kinetic results

At a constant temperature, the rate of any reaction is expressed in terms of the existing concentration of the reactants. For GTP, using the kinetic scheme established by Mai and

Muller⁷ for the DuPont associative mechanism, the rate of polymerization can be expressed as Eq. 4.2.

$$R_p = -d[M]/dt = k_p[M]^\alpha \cdot [I]_0^\beta \cdot [C]_0^\gamma \quad \text{Eq. 4.2}$$

The degree of dependence of rate of propagation on reaction concentration is known as the kinetic order of the reaction. The kinetic order of a reaction is determined experimentally and represents the fitting of the experimental data to the rate equation for the reaction in question. The magnitude of each exponent is commonly stated as the order of reaction of that species^{1a-15}. Determination of the order of reaction in each reactive species requires the determination of the initial rate at various concentrations of reactants: monomer, catalyst and initiator. Putting Eq. 4.3 into logarithmic form,

$$\log(-d[M]/dt) = \log k_p + \alpha \log[M] + \beta \log[I]_0 + \gamma \log[C]_0 \quad \text{Eq. 4.3}$$

it becomes evident that using a bilogarithmic plot one can elucidate the reaction order with respect to specific reactive species. It was our aim to elucidate the order of reaction with respect to MMA monomer, TBABB catalyst and MTS initiator.

4.2.2.1 Dependence of reaction rate on catalyst concentration

Our studies began with the investigation of the dependence of reaction rates on catalyst concentration (Table 4.6). The concentration of catalyst, TBABB was varied from 1.28×10^{-4} to 2.57×10^{-4} M. Each experiment was conducted at 25°C. The order of addition of reagents was as follows. First catalyst was added to the polymerization solvent THF, followed by the addition of calculated amount of monomer and finally initiator was added very fast. Fig. 4.6 illustrates the first order plots for the conversion of monomer at various catalyst concentrations.

The apparent rate constant (k_{app}) for each catalyst concentration was determined using the methods of initial rates.

Following from equations 4.2 and 4.3, a bilogarithmic plot of the apparent rate constants obtained from the maximum slope, i.e. initial rates, of the first order time-conversion curves vs the various catalyst concentrations was constructed (Fig. 4.7).

Table 4.6: Effect of Catalyst Concentration on the Rate of Polymerization at 25⁰C
 ([MMA]₀ = 1.17 M, [I]₀ = 1.23x10⁻² M, [M]₀/[I]₀ = 95, Solvent : THF)

Run No.	[C] ₀ x 10 ⁴ mol/L	[C] ₀ x 10 ² / [I] ₀	K _{app} min ⁻¹	Induction Period min
K-5	1.28	1.04	0.189	0.52
K-24	1.93	1.57	0.377	0.15
K-25	2.57	2.10	0.700	0.05

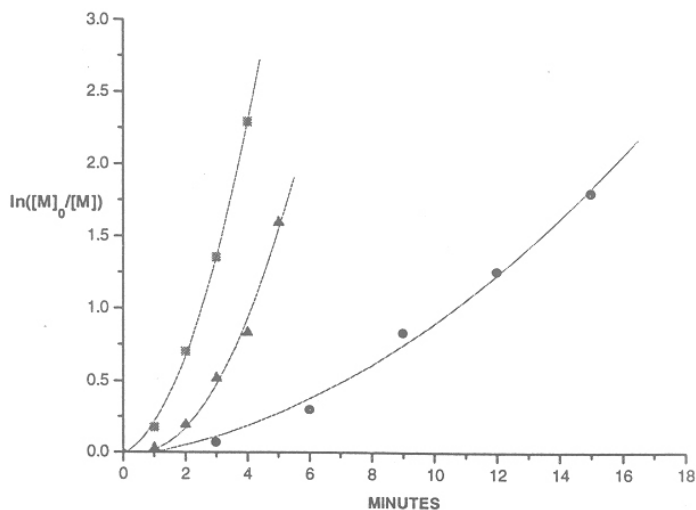


Fig. 4.6: First-order time-conversion plots for the GTP of MMA with MTS initiator and TBABB catalyst in THF as a function of catalyst concentration: ● = K-5, ▲ = K-24, ■ = K-25

It is difficult to directly compare these results to those reported by other investigators since the catalyst system and concentrations are different. **Table 4.7** lists some of the information reported by Brittain and Muller et al. It is important to note, that our results as those of Muller, reflect average propagation rates, unlike the study conducted by Brittain which focused on isolating the reaction order dependence of various catalysts on initiation and first propagation steps. It is also again apparent from this summary of data, that each investigator is evaluating GTP with varied conditions: reagents and their purity, concentration of reagents, temperature and mode of addition. These variables make it difficult to accurately compare experimental data.

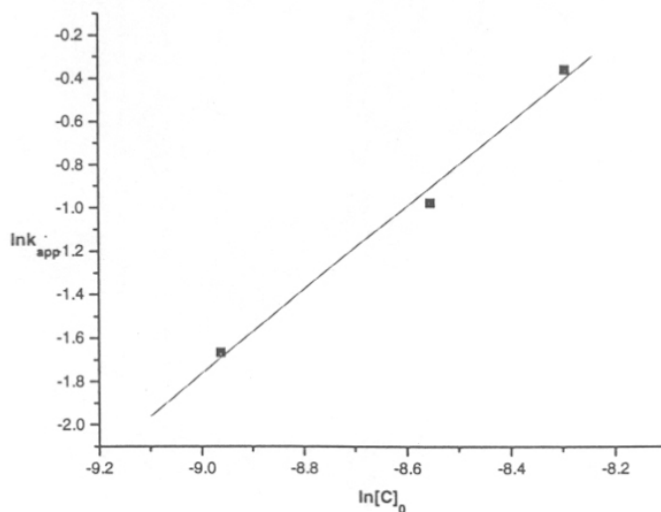


Fig. 4.7: Bilogarithmic plot of the apparent rate constants vs. catalyst concentrations

Table 4.7: Reaction Order with respect to Catalyst and Initiator Concentrations in the GTP of MMA in THF under Different Reaction Conditions

Catalyst	$[M]_0$ mol/L	$[I]_0$ mol/L	$[P]_0$ mol/L	T °C	Reaction order w.r.t. initiator	Reaction order w.r.t. catalyst	Ref.
TASHF ₂	0.18	0.001	2×10^{-5}	20	-0.27	1.17	12
TBABB	0.125	0.25	1.25×10^{-3}	27	--	0.30	16
TPSHF ₂ ^a	0.125	0.25	2.5×10^{-5}	27	--	2.00	16
TPSB ^b	0.125	0.25	2.5×10^{-5}	27	--	1.00	16
TASHF ₂	0.125	0.25	2.5×10^{-5}	27	--	2.10	16
TASB ^c	--	0.005	--	--	1.00	--	18
TBABB	--	--	--	--	--	1.00	17

a. Tris(piperidino)sulfonium bifluoride, b. Tris(piperidino)sulfonium benzoate, c. Tris(dimethylamino)sulfonium benzoate

4.2.2.2 Effect of initiator concentration

In the same manner as described above the reaction order with respect to initiator concentration was evaluated for the GTP of MMA. The concentration range spanned from

1.23×10^{-2} to 2.15×10^{-2} M. Results are given in **Table 4.8**. Again the first order plots for these concentrations were constructed and the apparent rate constants were determined via slope method (**Fig. 4.8**). With increasing initiator concentrations, 'induction period' at the beginning of the reaction diminished.

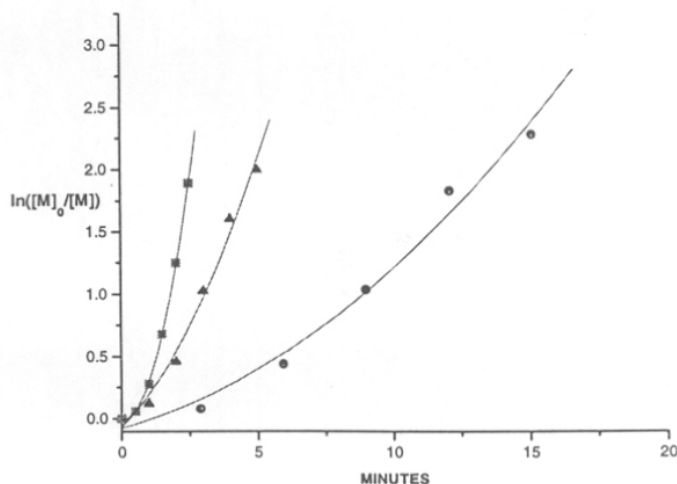


Fig. 4.8: First-order time-conversion plots for the GTP of MMA with MTS initiator and TBABB catalyst in THF as a function of initiator concentration: ● = K-5, ▲ = K-29, ■ = K-31

Fig. 4.9 shows a plot of $\log k_{app}$ vs $\log [I]_0$. A value of 1.97 is obtained for β representing the reaction order with respect to MTS concentration while maintaining a constant initial concentration of the TBABB catalyst.

Table 4.8: Effect of Initiator Concentration on the Rate of Polymerization at 25°C
 ($[MMA]_0 = 1.17$ M, $[C]_0 = 1.28 \times 10^{-4}$ M, solvent : THF)

Run No.	$[I]_0 \times 10^2$ mol/L	$[C]_0 \times 10^2 /$ $[I]_0$	$[M]_0 / [I]_0$	K_{app} min^{-1}	Induction Period min
K-5	1.23	1.04	95	0.192	0.52
K-29	1.85	0.69	63	0.489	0.05
K-31	2.15	0.60	54.4	0.600	0.02

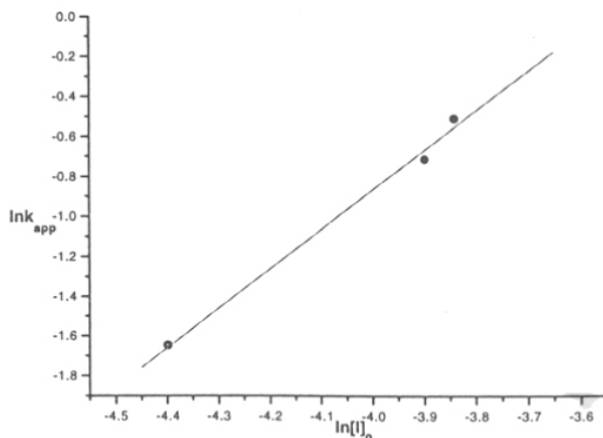


Fig. 4.9: Bilogarithmic plot of the apparent rate constants vs. initiator concentration

Muller et al.¹³ reported a value of +1 for β in a concentration range $1.3 \times 10^{-4} - 5.3 \times 10^{-4}$ M for MTS using TASB. The concentration of the catalyst used in this study was not reported. Therefore comparison to this data is difficult.

4.2.2.3 Dependence of rate constant on monomer concentration

The effect of monomer concentration on the reaction rates was studied (Table 4.9). In each set all parameters were kept constant, with the exception of monomer concentration $[M]_0$ ($1.65 < [M]_0 > 0.85$ mol/L). Fig. 4.10 shows first order time conversion plots. The plots are nonlinear initially due to induction period. Deviations from linearity observed in the later stages of polymerization is likely indicating the presence of termination reactions. The extent of termination also depends on the initial monomer concentration. An increase of termination was observed for $[M]_0 < 1.65$ mol/L and $[M]_0 > 0.85$ mol/L rendering the determination of the initial slope, k_{app} , difficult and reducing its accuracy. The complex dependence of termination on monomer concentration may be the result of different coexisting termination mechanism.

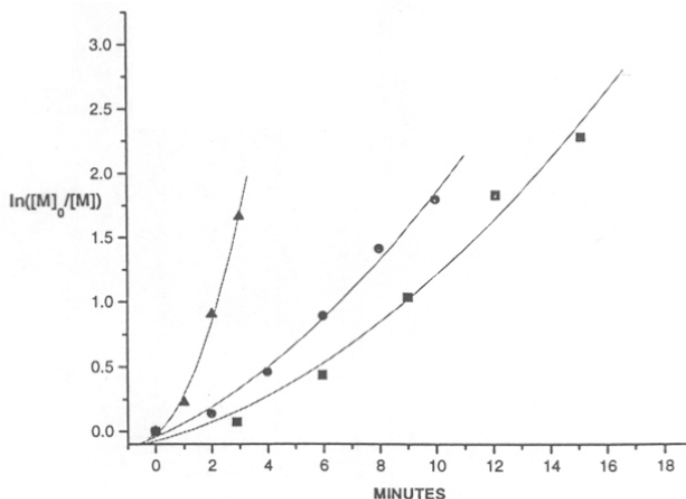


Fig. 4.10: First-order time-conversion plots for the GTP of MMA with MTS initiator and TBABB catalyst as a function of monomer concentration: ● = K-33, ▲ = K-36, ■ = K-36.

Table 4.9: Effect of Monomer Concentration on the Rate Constant
 ($[I]_0 = 1.23 \times 10^{-2}$ mol/L, $[C]_0 = 1.28 \times 10^{-4}$ M, solvent : THF)

Run No.	$[M]_0$ mol/L	$[C]_0 \times 10^2 /$ $[I]_0$	$[M]_0 / [I]_0$	K_{app} min^{-1}	Induction Period min
K-36	0.85	1.04	69	0.717	0.05
K-5	1.17	1.04	95	0.189	0.47
K-33	1.65	1.04	134	0.226	0.37

4.2.2.4 Dependence of propagation rate on temperature

By varying the temperature of a chemical reaction one can elucidate information regarding the energy of activation under a certain set of reaction conditions. It must be kept in mind when considering a mechanism such as GTP, that a catalyst is required and, by its nature, serves to lower the energy of activation for the reaction without itself being permanently altered. Thus, experiments to elucidate the global E_a for GTP of MMA with TBABB and MTS were carried out with constant concentrations of reagents. Reaction rates were measured at temperatures, 15° , 25° and 35°C using TBABB catalyst. As described previously

the first order time-conversion plots were constructed from which the apparent rate constants (k_{app}) were obtained (Fig. 4.11). In every case, induction period was observed and induction period decreased with increasing temperature. Results are given in Table 4.10.

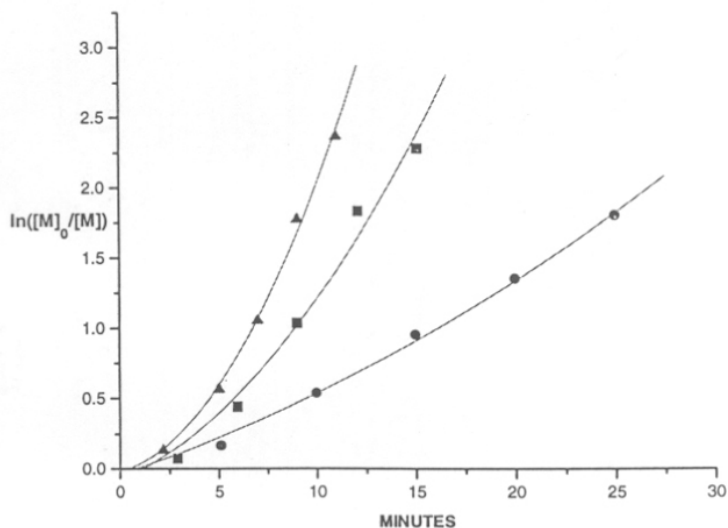


Fig. 4.11: First-order time-conversion plots for the GTP of MMA with MTS initiator and TBABB catalyst in THF as a function of temperatures: ● = K-10, ▲ = K-11, ■ = K-5.

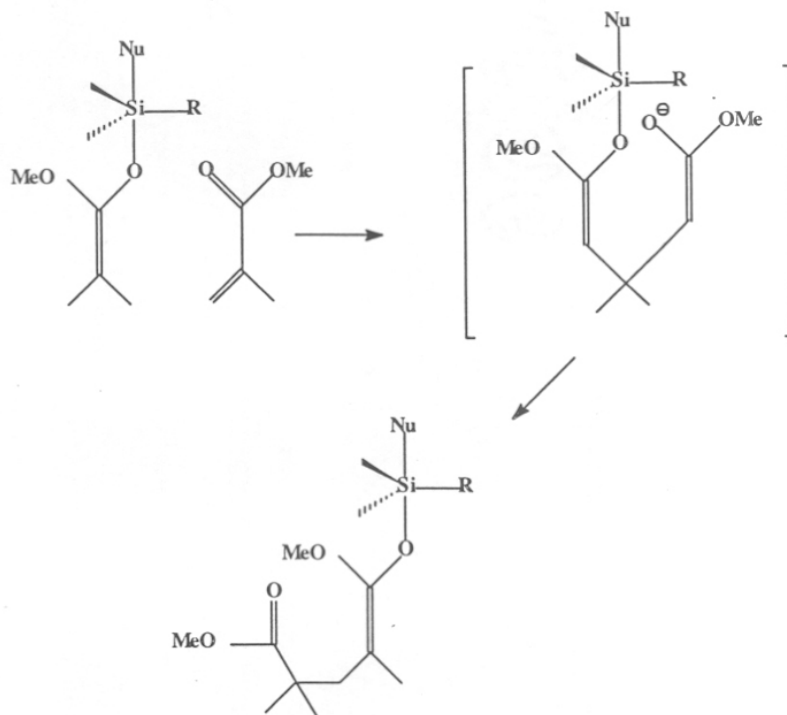
Subsequently, an Arrhenius plot for the polymerization rate constants was constructed (Fig. 4.12). As demonstrated by Mai and Muller^{12,19} using TASHF₂ as the selected catalyst, the linearity of the plot using TBABB renders evidence for the existence of only one active species. The E_a determined from the slope of Arrhenius plot (Eq. 4.4) was 42.2 kJ/mol.

$$\log(k_{app}) = -(E_a/RT) + \log A \quad \text{Eq. 4.4}$$

A value of 16.9 kJ/mol was reported by Mai and Muller using TASHF₂ as the selected catalyst. Since TBABB is a weaker base, one would predict the global E_a for TBABB at a given concentration to be higher than that obtained for TASHF₂.

Muller has also compared the E_a (TASHF₂) to the global E_a reported for the anionic polymerization of MMA using various counterions. Based on the relative similarity of the E_a and stereochemistry between anionic (using a free anion, bulky or strongly solvated

counterions) to the reported GTP value using TASHF₂, Muller proposed a two step “associative” mechanism of monomer addition for GTP (Scheme 4.1). Though the value obtained for the global E_a using TBABB is similar to that reported by Mai and Muller, a direct comparison to anionic and free radical mechanism is difficult.



Scheme 4.1: Mechanism of GTP as reported by Mai and Muller

In free radical and anionic mechanisms, variations in temperature and solvent may lower the E_a by causing the reaction to occur at a faster rate, however GTP is catalyzed. Therefore, the effect of temperature and solvent is negligible. A catalyst does not operate by making the uncatalyzed reactions faster but introduces a different, more favorable pathway²⁰. From the limited number of kinetic investigations conducted at this point, it is difficult to eliminate either the concerted “associative” mechanism or the two step “associative” mechanism or an alternative pathway.

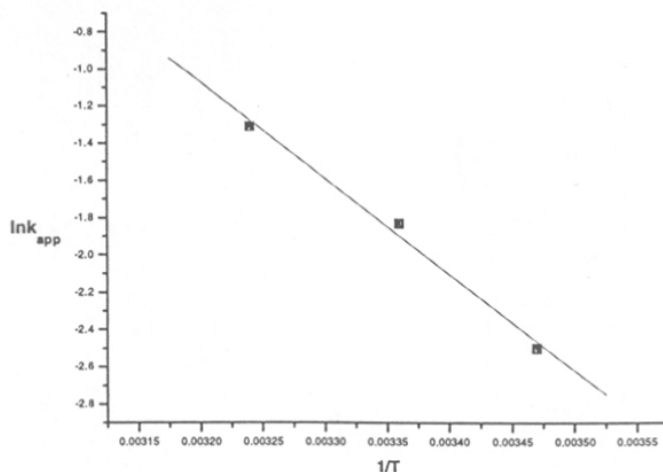


Fig. 4.12: Arrhenius plot for the polymerization rate constants in the GTP of MMA with MTS initiator and TBABB catalyst

Table 4.10: Effect of Temperature on the Rate of Polymerization ($[MMA]_0 = 1.17$ M, $[I]_0 = 1.23 \times 10^{-2}$ M, $[M]_0/[I]_0 = 95$, $[C]_0 = 1.28 \times 10^{-4}$ M, solvent : THF)

Run No	T ⁰ C	$[C]_0 \times 10^2 / [I]_0$	K_{app} min ⁻¹	Induction Period min
K-10	15	1.04	0.084	1.12
K-5	25	1.04	0.189	0.52
K-11	35	1.04	0.258	0.25

4.2.2.5 Molecular weight and molecular weight distribution

A unique molecular weight distribution arises with some polymerization mechanisms in the absence of terminating side reactions and under the conditions of fast initiation relative to propagation. By its living nature, the active centers in GTP should grow at the same time and add monomers at equal rates. From kinetic arguments which invoke a constant concentration of active centers, $[P^*]$, (Eq. 4.5)

$$-d[M]/dt = k_p \cdot [M] \cdot [P^*] \quad \text{Eq. 4.5}$$

the kinetic chain length, ν , for GTP can be described by Eq. 4.6²¹.

$$v = ([M]_0 - [M])/[P^*] - 1 = \langle i_n \rangle \approx \langle i_w \rangle \quad \text{Eq. 4.6}$$

It follows that the polymers should have molecular weight distributions which approximate the Poisson distribution.

The polydispersity for a Poisson MWD is found to be

$$\bar{M}_w / \bar{M}_n = 1 + (i_n - 1)/i_n^2 \approx 1 + 1/i_n \quad \text{Eq. 4.7}$$

From the kinetic investigations, the molecular weight distribution can be followed as a function of conversion (Fig. 4.13).

Plotting the molecular weight distribution vs conversion, a relatively insignificant narrowing of the polydispersity is observed as the chain length increased with conversion. These results are consistent with the nature of living polymerizations, though deviation is observed in the molecular weight vs conversion plots (Fig. 4.14). The deviation from linearity through zero on both axes has been attributed largely to the initial induction period observed in the polymerization, gravimetry for percent conversion and SEC for the \bar{M}_w and \bar{M}_n . A method

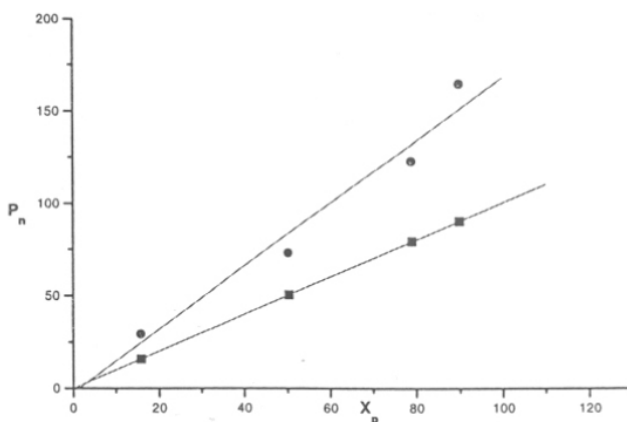


Fig. 4.13: Number average degree of polymerization as a function of monomer conversion in THF with MTS initiator and TBABB catalyst

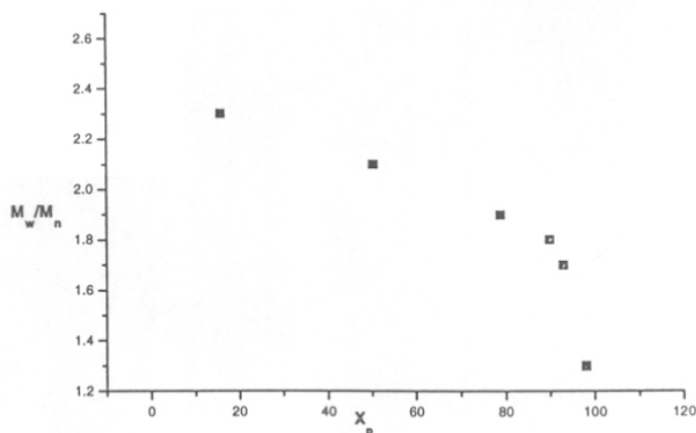


Fig. 4.14: Polydispersity as a function of monomer conversion in the GTP of MMA with MTS initiator and TBABB catalyst

such as vapor phase osmometry, VPO, may permit a more accurate determination of \bar{M}_n than SEC for low molecular weight or low conversion samples. Though PMMA standards were employed for the calibration, at low conversions during any given kinetic run, sample analysis by SEC may have been beyond the column separation limits. Therefore, it is difficult to accurately compare the values of \bar{M}_n and \bar{M}_w obtained from this relative method to the conversion data.

4.3 CONCLUSIONS

BDMAS in presence of TBAF is a satisfactory purification agent to purify higher alkyl methacrylates such as BMA, LMA etc. To prepare very high molecular weight polymers (>100 000) further investigations in terms of purification are necessary.

It is difficult to make any definitive statements regarding the kinetics of GTP from these studies. It does appear, however, that the kinetic expression may be more complex than that originally proposed and significantly dependent on the level of catalyst. That is, at higher levels of catalyst, the rate determining step may be strictly the addition of monomer. At very low concentrations of catalyst one would predict that the decomposition rates of activated initiator or activated chain end would be the rate determining step. However, at moderate catalyst levels, both the decomposition and propagation step may become partially rate

limiting (k_{-1} and $k_p[M]$ are comparable) and then the kinetic expression is more complex. Again, it is difficult to compare the results of the limited number of kinetic investigations between various investigators due to the variations in concentration of reactants and products, mode of addition of reagents, physical conditions; pressure, temperature and viscosity. However, with more systematic studies, bridges between the data may be formed and provide a basis for making comparisons and mechanism deductions.

4.4 REFERENCES

- 1 G.C.Eastmond and O.W.Webster, "New Methods of Polymer Synthesis", Ed. J.R.Ebdon, Blakie, Glasgow, 1992, chap. 2, p23.
- 2 W.J.Brittain, *Rubb.Chem.Technol.*, **65**, 580 (1992).
- 3 G.Gee, W.C.E.Higginson and G.T.Merral, *J.Chem.Soc.*, 1345 (1959).
- 4 I.B.Dicker, G.M.Cohen, W.B.Farnham, W.R.Hertler, E.D.Lagnis and D.Y.Sogah, *Macromolecules*, **23**, 4034 (1990).
- 5 U.Schmalbrock and F.Bandermann, *Macromol.Chem.*, **194**, 2543 (1993).
- 6 R.P.Quirk and G.P.Bidinger, *Polym.Bull.*, **22**, 63 (1989).
- 7 R.D.Allen, T.E.Long and J.E.McGrath, *Polym. Bull.*, **15**, 127 (1986).
- 8 K.Marnoka, H.Banno and H.Yamamoto, *Syn.Lett.*, 253 (1991).
- 9 E.W.Colvin, "Silicon in organic Synthesis", Butterworth, London (1981).
- 10 J.D.Citron, U.S.Patent 4771116 (1988); *Chem. Abstr.*, **110**, 76288k (1989).
- 11 F.F.Denes, A.Sahil, H.P.Keller and E.S.Kovats, *Anal.Chem.*, **51**, 1 (1979).
- 12 P.M.Mai and A.H.E.Muller, *Macromol.Chem.Rapid Commun.*, **8**, 99 (1987).
- 13 J.M.Moore, R.G.Pearson, "Kinetics and Mechanism", John Wiley and Sons; New York, chap.1(1981).
- 14 J.H.Espenson, "Chemical Kinetics and Mechanisms", McGraw Hill; New York, p.5 (1981).
- 15 J.F.Bunnett, in "Investigation of Rates and Reaction Mechanisms of Reactions", Ed. C.F.Bernasconi; John Wiley and Sons; New York, Part-1, chap.11 (1986).
- 16 W.J.Brittain, *J.Am.Chem.Soc.*, **110**, 7440 (1988).
- 17 A.H.E.Muller, *Makromol.Chem.Macromol.Symp.*, **32**, 87 (1990).
- 18 M.A.Doherty, F.Gores, P.M.Mai and A.H.E.Muller, *Polym. Prepr.(Am.Chem.Soc., Div.Polym.Chem.)*, **29**(2), 73 (1988).
- 19 A.H.E.Muller, in "Recent Advances in Mechanism and Synthetic Aspect of Polymerization", M.Frontanille and A.Guyot, Eds.; NATO ASI Series215; D.Reidel Publishing Dortect, Holland p23 (1987).
- 20 J.R.Keeffe and A.J.Kresge, in "Investigation of Rates and Reaction Mechanisms of Reactions", Ed. C.F.Bernasconi; John Wiley and Sons; New York,1986, Part-1, chap.10.
- 21 T.C.Ward, *J.Chem.Ed.*, 867 (1981).

CHAPTER-V

**COPOLYMERIZATION OF METHYL METHACRYLATE (MMA) WITH
HIGHER ALKYL METHACRYLATE (LMA)**

5.1 INTRODUCTION

Group transfer polymerization (GTP) is a convenient method to prepare methacrylate and acrylate polymers with narrow polydispersity at room temperature¹. For the GTP of methacrylates, polar solvents and nucleophilic catalysts (e.g. bifluorides or bibenzoates) are most suitable for obtaining a "living" polymerization. The "living" nature of the GTP chain ends offers a potentially useful method for the synthesis of a variety of methacrylate polymers with controlled structures and architectures. Examples are block copolymers², macromonomers³, telechelics⁴, end functionalized polymers⁵, star branched polymers⁶ and graft copolymers⁷.

There are a number of reports in the literature on the random and block copolymerization of methyl methacrylate with higher alkyl methacrylates. Sogah⁸ and coworkers demonstrated the synthesis of random copolymers of methyl methacrylate (MMA) with butyl methacrylate, and butyl methacrylate with glycidyl methacrylate as well as block copolymers of MMA with butyl methacrylate, 2-ethylhexyl methacrylate and lauryl methacrylate. However, these copolymers had relatively low molecular weights and short block segment length ($\bar{M}_n < 10,000$, PLMA block molecular weight < 2000) and limited to a narrow range of compositions. Moller⁹ and coworkers examined the random and block copolymerization of MMA with ethyl methacrylate and decyl methacrylate. They prepared copolymers with $\bar{M}_n > 100,000$ and polydispersities in the range of 1.1-1.3 using TASHF₂ as catalysts. Billingham¹⁰ and coworkers prepared block copolymers of MMA with benzyl methacrylate using tetrabutylammonium bibenzoate as catalysts with $\bar{M}_n > 40,000$ and polydispersities in the range of 1.05 -1.10.

Copolymers of methyl methacrylate with higher alkyl methacrylates, such as, lauryl methacrylate (LMA) exhibit interesting properties on account of its comblike structures. Controlled synthesis of such copolymers is not possible by anionic techniques since LMA has limited solubility in solvents such as tetrahydrofuran below 0°C. Living anionic polymerization of alkyl methacrylates is feasible only at very low temperatures. Thus, GTP is the only potential synthetic method for preparing narrow polydispersity random and block copolymers of MMA with LMA.

In this chapter the synthesis of random and block copolymers of MMA and LMA are discussed. Reactivity ratios of MMA and LMA under GTP conditions has been determined. Sequence of monomer incorporation in the polymer at low conversion has been determined by ^{13}C NMR. Thermal stability of random and block copolymers of MMA and LMA has also been examined.

5.2 RESULTS AND DISCUSSION

5.2.1 Random Copolymerization of MMA with LMA

5.2.1.1 Reactivity ratios

Chemical composition data for the copolymerization of LMA and MMA are given in **Table 5.1**. Polymerization reactions were quenched after a short period of time to restrict the monomer conversions below 20% and the compositions of the copolymers were determined by ^{13}C NMR (**Fig. 5.1**).

Table 5.1: Statistical Copolymerization of MMA (M_1) and LMA (M_2) at Low Conversions^{a,b,c,d} at 0°C

Sr.No.	$[M_1]$ molL ⁻¹	$[M_2]$ molL ⁻¹	Conv. %	\bar{M}_n calcd	\bar{M}_n SEC RI	\bar{M}_w/\bar{M}_n SEC RI
1	0.68	0.67	16.0	1,600	6,371	1.23
2	0.17	0.80	23	2,000	5,957	1.39
3	0.44	0.70	20.0	2,000	5,376	1.38
4	0.84	0.54	17.0	1,710	7,430	1.33

a. Molecular weights were determined by SEC-RI using PMMA standards. b. THF was used as solvent. c. $[I]_0 = 0.02 \text{ molL}^{-1}$ for all cases. d. $[C]_0 = 3.85 \times 10^{-3} \text{ molL}^{-1}$ for all cases.

The number average molecular weight determined by SEC using PMMA standards were considerably higher than those calculated theoretically for a living polymerization, indicating a non-linear dependence of \bar{M}_n with conversion. Secondly, polydispersities are also broader compared to the polymer after complete conversion (**Fig. 5.2**).

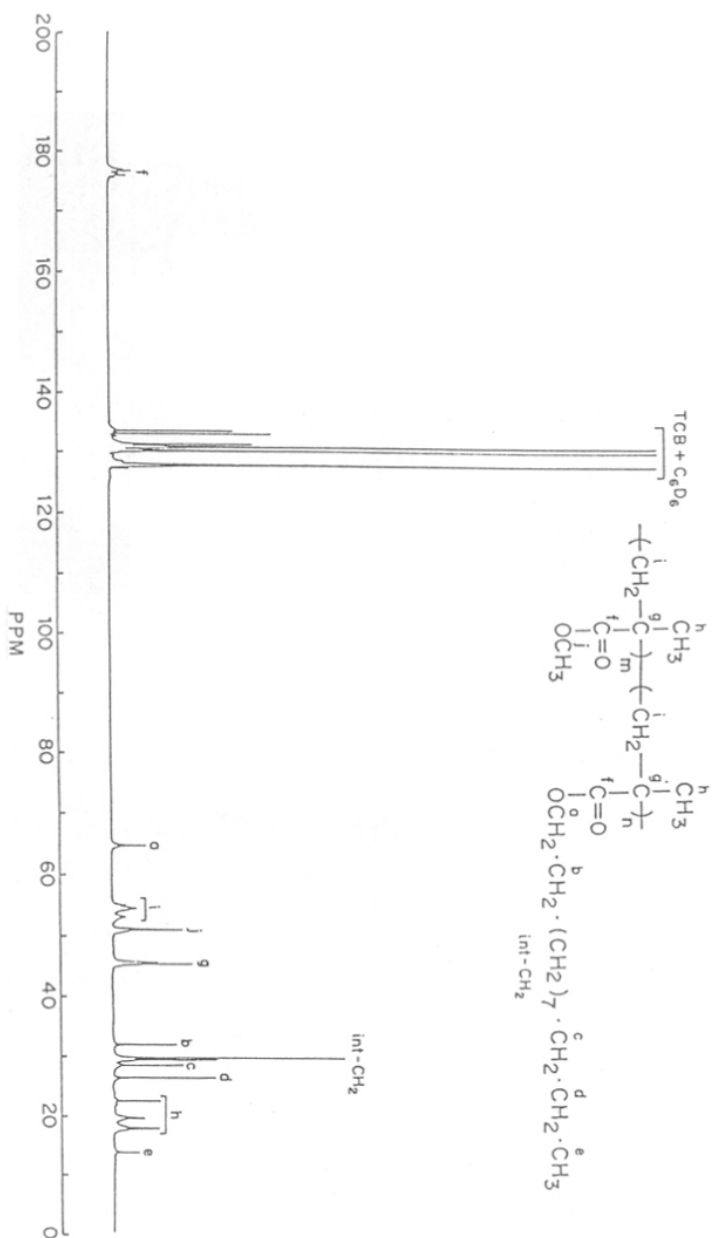


Fig. 5.1: ^{13}C NMR spectra in TCB of random copolymer at low conversion: PMMA-co-PLMA (feed ratio 60-40 mol%) (entry 3, Table 5.1)

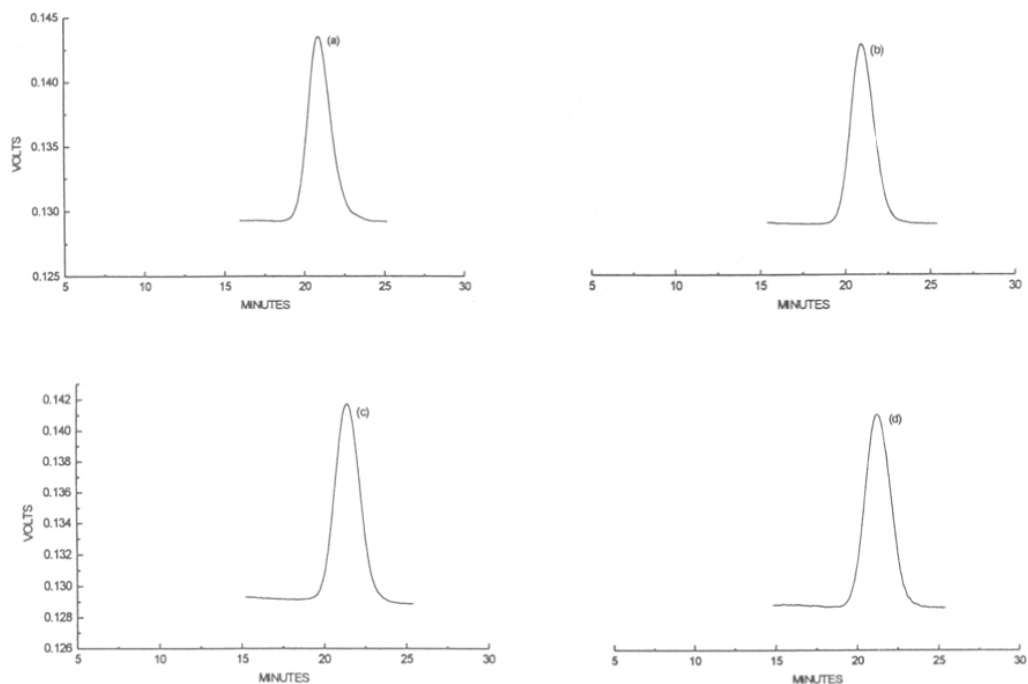


Fig. 5.2: SEC-RI of random copolymers at low conversion

Both observations are in agreement with results presented in the literature¹¹. The observed non-linear dependence of \bar{M}_n upon conversion and the broad MWD's at low conversions have been explained in terms of an equilibrium between a 'dormant' and 'activated' form of the living polymer. Activation of polymer chain is believed to proceed via coordination of the nucleophilic catalyst to the silicon atom. Recently slow initiation was proposed to cause induction periods and the aforementioned non-linear behavior of \bar{M}_n vs. conversion.

As it can be shown from the copolymerization diagrams in **Fig. 5.3**, MMA is significantly more reactive than LMA in group transfer copolymerization.

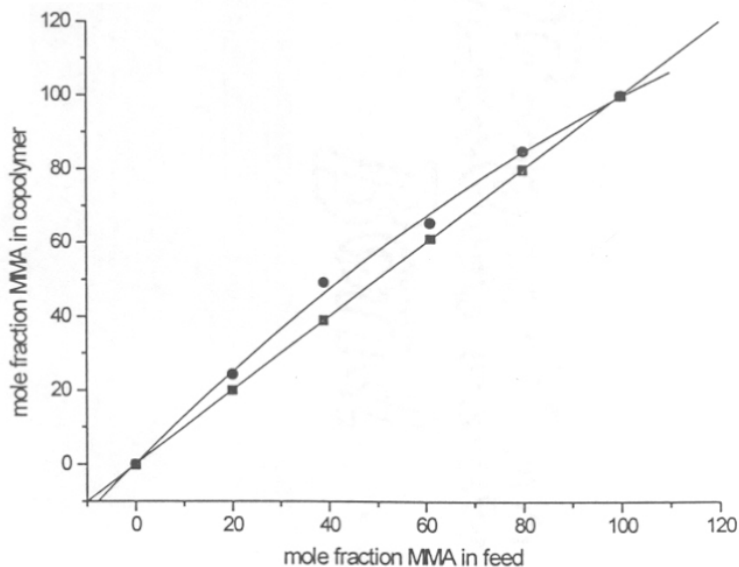


Fig. 5.3: Copolymerization diagram for the monomer system MMA and LMA: ● = obs.; ■ = calcd.

Monomer reactivity ratios were evaluated according to the method of Kelen and Tudos¹² (Table 5.2):

$$\eta = (r_1 + r_2/\alpha)\xi - r_2/\alpha$$

$$\text{with } \eta = G/(\alpha+F); \quad \xi = F/(\alpha+F)$$

$$G = a - a/b; \quad F = a^2/b$$

$$a = M_1/M_2 \quad \text{and} \quad b = m_1/m_2$$

m_1, m_2 = mole fraction of monomers in the copolymer from ¹H NMR

M_1, M_2 = mole fraction of monomers in the feed

α is the geometric mean of the lowest and highest F values. The plot of η vs ξ is linear (Fig. 5.4).

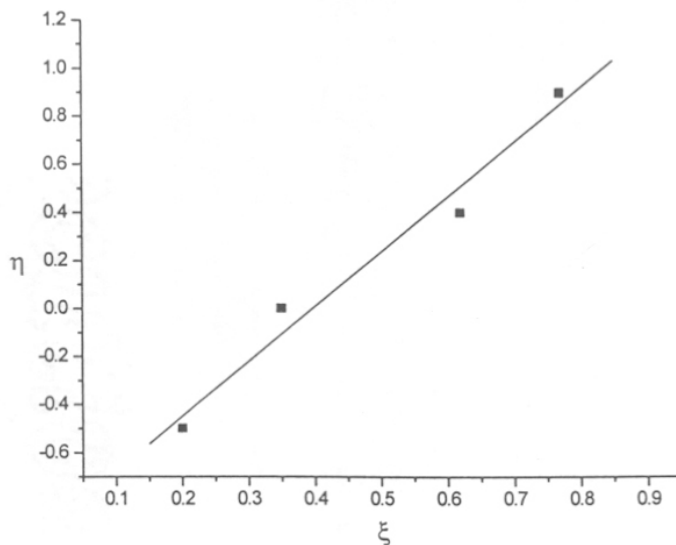


Fig. 5.4: Determination of the monomer reactivity ratios for the GTP of MMA and LMA according to the Kelen and Tudos method, $\alpha = 0.75$.

From slope and intersection with the ordinates r_1 and r_2 values were determined as $r_1(\text{MMA}) = 1.38 \pm 0.11$ and $r_2(\text{LMA}) = 0.68 \pm 0.10$.

In the radical copolymerization of MMA and LMA in 1,1,2-trichloro-1,2,2-trifluoroethane at 60°C reactivity ratios do not differ significantly from unity ($r_1(\text{MMA}) = 1.21 \pm 0.12$ and $r_2(\text{LMA}) = 0.84 \pm 0.10$)¹³. The results for group transfer copolymerization, however, show reactivity ratios differing markedly from unity. Moller and coworkers⁹ have determined the reactivity ratios for the copolymerization of MMA and DMA ($r_1(\text{MMA}) = 1.66 \pm 0.14$ and $r_2(\text{DMA}) = 0.48 \pm 0.03$). These ratios are close to those found for anionic copolymerization with sodium as a counterion at -90°C ($r_1(\text{MMA}) = 1.5 \pm 0.4$ and $r_2(\text{DMA}) = 0.72 \pm 0.2$). Although reactivity ratios are a complex function of mechanism, as well as of reaction conditions, the author concluded that GTP and anionic polymerizations proceed via similar mechanisms. The active centers in both GTP and anionic polymerization are more sensitive to the monomer structure compared to radical copolymerization. Thus, direct comparison between anionic and GTP mechanisms are not possible for this pair of monomers (MMA and LMA) because reactivity ratios of MMA and LMA are not available under anionic polymerization conditions.

Table 5.2: Calculation of η and ξ Values According to Kelen and Tudos

Sr. No.	M_1 mol%	M_2 mol%	$a = \frac{M_1}{M_2}$ mol %	m_1 mol %	m_2 mol%	$b = \frac{m_1}{m_2}$ m ₁ /m ₂	a/b	G $a - (a/b)$	F a^2/b	$\alpha + F$	η $G/\alpha + F$	ξ $F/\alpha + F$
1	80.0	20.0	4.0	84.9	15.1	5.6	0.7	3.3	2.8	3.6	0.90	0.77
2	39.0	61.0	0.6	49.1	50.9	1.0	0.6	0	0.4	1.2	0	0.35
3	61.0	39.0	1.6	65.4	34.6	1.9	0.8	0.8	1.3	2.0	0.40	0.65
4	20	80	0.25	24.3	75.7	0.32	0.8	-0.5	0.2	1.0	-0.50	0.20

 $\alpha = 0.75$

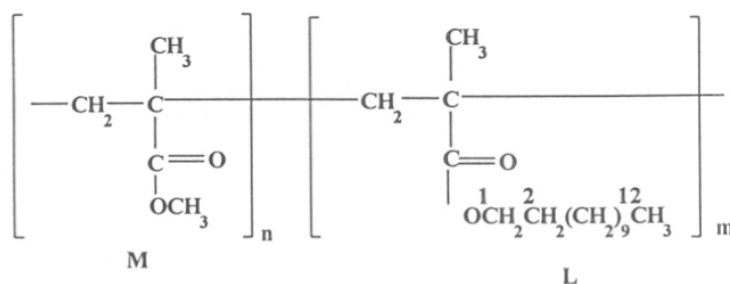
5.2.1.2 Sequence Distribution by ^{13}C NMR

^{13}C NMR spectroscopy is an important tool for the analysis of chemical structure, morphology, orientation and molecular dynamics of a polymer chain¹⁴ all of which have an effect on material properties. The properties of a copolymer depend both on the chemical nature of the repeating units and on their arrangement within the polymer chain.

Detailed microstructural analysis of acrylic ester copolymers synthesized by GTP has not been reported before in the literature. The detailed microstructure of these copolymers using ^{13}C NMR spectroscopy has been examined.

RESULTS AND DISCUSSION

The GTP of MMA with LMA in solution of THF, using TBABB as catalyst and MTS as initiator at room temperature, gives rise to the formation of homogeneous random copolymers with a statistical distribution of monomer units along the polymer chain which corresponds to the chemical structure outlined in **Scheme 5.1**.



Scheme 5.1: Structure of copolymer of MMA and LMA

The average molar composition of different copolymer samples prepared at conversions < 15% was determined from the analysis of the corresponding ^1H NMR spectra (**Table 5.3**). The composition of copolymers were determined from the ^{13}C spectra.

The copolymer composition was determined from the analysis of the signal assigned to the $-\text{OCH}_3$ group (δ 51.39) of M units and $-\text{OCH}_2$ group (δ 64.21) of L units. These signals appear as very sharp peaks in the spectra of copolymer and are in agreement with those obtained from ^1H NMR spectra.

Fig. 5.4 corresponds to the application of the composition data depicted in Table 5.3 to the linearization methods of the copolymer composition equation proposed by Kelen and Tudos¹².

Table 5.3: Composition Data and Conditional Probabilities P_{ij} for the Copolymerization at Low Conversion of Methyl Methacrylate (M) with Lauryl Methacrylate (L)

Feed F_M^a	f_M^a (copolymer)		P_{ML}	P_{LM}
	$^1\text{H NMR}$	$^{13}\text{C NMR}$		
0.190	0.267	0.243	0.755	0.256
0.390	0.501	0.491	0.531	0.484
0.608	0.641	0.654	0.318	0.695
0.795	0.838	0.848	0.157	0.850

a. F_M and f_M are the molar fraction of methyl methacrylate in the monomer feed and in the copolymer samples respectively.

The microstructure and stereochemical configuration of copolymers prepared with different feed composition were determined from the exhaustive analysis of NMR resonance signals since the decoupled ^{13}C NMR spectra provide excellent and accurate information of the chemical composition and stereochemical configuration of copolymer chain segments. In this analysis, the statistical distribution of M- and L- centered sequences were determined from the conditional probabilities P_{ML} and P_{LM} (and $P_{MM} = 1 - P_{ML}$, $P_{LL} = 1 - P_{LM}$) (Table 5.3). These values were calculated based on the classical terminal model for copolymerization¹⁵. The parameters P_{ij} ($i, j = M, L$) are the conditional probabilities for the addition of monomer units j to reactive i ends¹⁶.

The $\alpha\text{-CH}_3$ resonance of PLMA (Fig. 5.5) is shifted towards lower field compared to that of PMMA because of the long aliphatic character of the ester group in PLMA.

Effectively, the $\alpha\text{-CH}_3$ resonance of both M and L units present a complex pattern with seven distinguishable peaks, whose intensities change with the average composition of copolymer samples (Fig. 5.5). A detailed analysis of these signals leads to the assignment of peaks I and IV as due to the rr and $rm + mr$ triads in PMMA; in addition, the intensity of these signals increase with the increasing molar fraction of M in the copolymer. The

expanded ^{13}C NMR decoupled spectra of the $\alpha\text{-CH}_3$ carbon resonance signals of homopolymers M and L as well as those of several M-L copolymer samples of various compositions is shown in **Fig. 5.5**. The $\alpha\text{-CH}_3$ group is present in the chemical structure of both mesomeric units, but, as previously reported¹⁷ in the case of PMMA (M in **Fig. 5.5**), this group gives three resonances at 17.58, 18.75 and 21.73 ppm from TMS, which have been assigned to iso (mm), hetero (mr + rm), and syndiotactic (rr) triads in order of increasing field¹⁸.

The $\alpha\text{-CH}_3$ group of PLMA also shows three resonance signals at 17.81, 19.45 and 21.61 ppm from TMS, which have been assigned to mm, mr + rm and rr tactic triads in order of increasing field, since these values are close to those reported for the resonance of the $\alpha\text{-CH}_3$ in PMMA¹⁷⁻¹⁹.

The (rr) and (rm + mr) resonances of PLMA (17.81 and 19.45 δ), appear at somewhat lower field than those of the PMMA, (rr) at 17.58 and (rm + mr) at 18.50 δ . However, the resonance signal assigned to isotactic (mm) sequences has almost similar chemical shift for both the polymers (21.60 δ). This means that the $\alpha\text{-CH}_3$ side group in isotactic sequences shows very little sensitivity to short chain and long chain aliphatic character of the ester groups. This is reasonable since the diamagnetic carbonyl centers are as far as possible from the $\alpha\text{-CH}_3$ group of the central unit in the triad (**Fig. 5.6**). On the other hand, it is easily seen from **Fig. 5.5** that the separation between tactic signals of PMMA is noticeably higher, ($\delta_{\text{mm}} - \delta_{\text{mr}}$) \cong $\delta_{\text{mr}} - \delta_{\text{rr}} \cong 1.71$ ppm, than that of PLMA ($\delta_{\text{mm}} - \delta_{\text{mr}}$) \cong $\delta_{\text{mr}} - \delta_{\text{rr}} \cong 1.54$ ppm. This means that except for (mm) sequences, the chemical shift of M and L units is sensitive to the composition and the stereochemical configuration of the neighboring units in sequences of triads.

In this sense, for a complete description of the monomers sequence distribution and relative stereochemical configuration in terms of M- and L-centered triads it is necessary to take into consideration as many as 10 different triads with a central M unit which may be magnetically distinguishable as is shown in the scheme of **Fig. 5.6**. Similarly, 10 triads with a central L unit must also be considered. It is well known that the sensitivity of the $\alpha\text{-CH}_3$ resonance to tacticity arises from the diamagnetic effects of the carbonyl ester group of the neighboring units on the $\alpha\text{-CH}_3$ residue of the methacrylic central unit¹⁴.

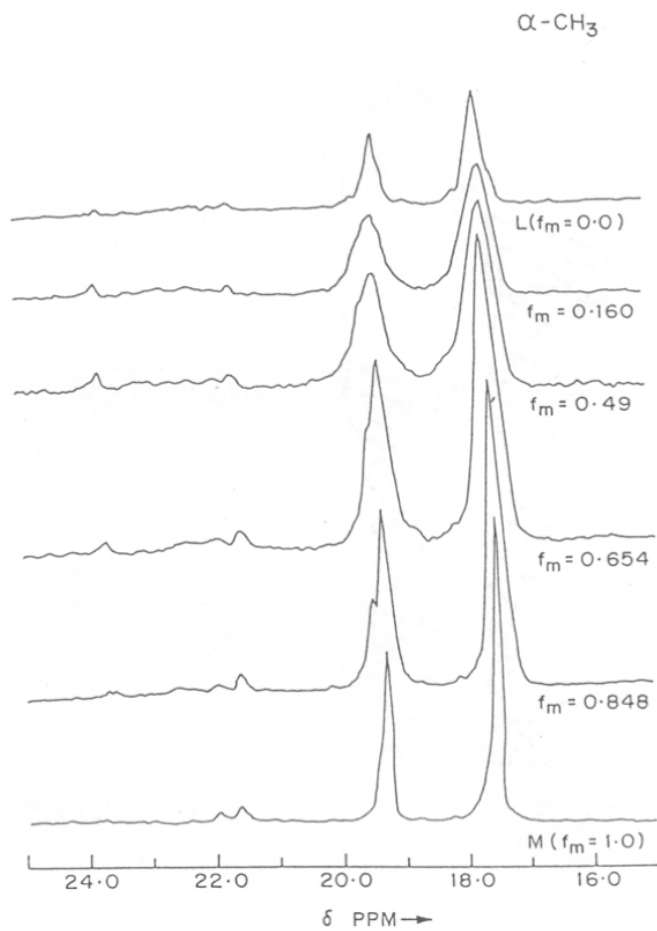


Fig. 5.5: ¹³C NMR spectra (75.5 MHz) of the α -CH₃ side groups of M-L copolymers

Fig. 5.6 as well as molecular models clearly show that the diamagnetic effects of neighboring units on the α -CH₃ central unit for MML or LMM (rr) triads are different from those of MMA (rr) triads or LML (rr) triads and according to the difference in the chemical shifts (rr) sequences of both M and L homopolymers, it may be expected that the cosyndiotactic heterotriads or LMM (rr) give a resonance signal between those of the homopolymers.

Table 5.4: Assignment of the α -CH₃ Resonance to Sequences of M- and L-Centered Triads^a

Spectral Signal No	Chemical Shift, ppm	Copolymer Composition	Sequence Configuration
I	17.46	MMM	rr
		MLM	
		MML	
II	18.10	LMM	rr
		LLM	
		MLL	
III	18.63	LML	rr
		LLL	
		MMM	
IV	19.27	MML	mr + rm
		LMM	rm
		LML	mr
		LML	mr + rm
V	19.83	MML	mr
		LMM	rm
		LLM	mr
		MLL	rm
VI	20.13	LMM	mr + rm
		LLM	rm
		LLM	rm
VII	21.50-21-90	a	mm

^a The signals considered in this interval correspond to all the possible isotactic triads independent of their composition.

Therefore, we tentatively assign the peak II to this kind of triad as is indicated in Table 5.4. Also it can be easily understood that α -CH₃ of central M unit of MML or LMM triads with

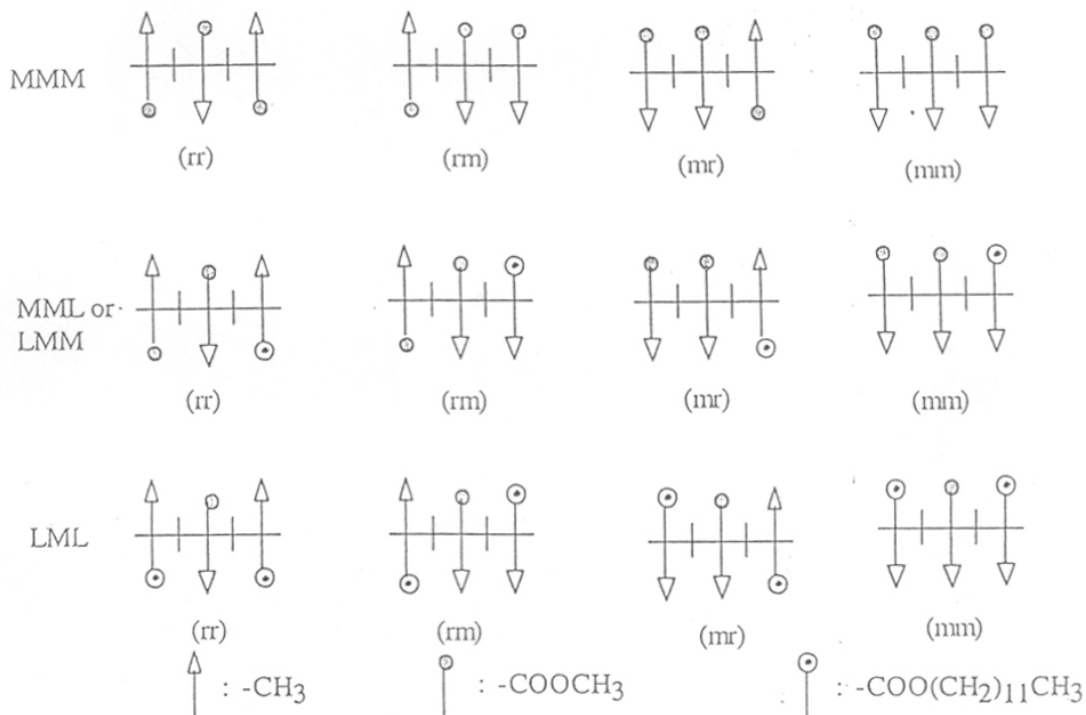


Fig. 5.6: Schematic representation of M centered triads of methyl methacrylate--lauryl methacrylate copolymers

the stereochemical configuration (rr) have the same magnetic and spatial arrangement as the MLL (rr) triads, so we have included these in the signal II.

On the same basis, it may be expected that the LML (rr) sequence has the same chemical shift as the syndiotactic triad of homopolymer L and that the MLM (rr) should be similar to the syndiotactic triad of homopolymer M (see **Fig. 5.6 & Table 5.4**).

Based on similar arguments we have assigned peak V to the contribution of sequences reported in **Table 5.4**. The experimental data obtained from NMR spectra are in good agreement with the contribution of the corresponding sequences calculated statistically.

The molar concentration of M- and L-centered sequences with statistical sequence distribution and stereochemical configuration of copolymer chains have been analyzed and correlated statistically according to the reactivity ratio reported, the conditional probability P_{ij} quoted in **Table 5.3** and the average composition of the copolymer samples. This analysis has been carried out by making the following assumptions.

- a) With respect to the chemical composition of copolymer sequences, it is assumed that copolymerization reaction is described by the terminal unit model^{20,21}.
- b) From a stereochemical point of view, it is assumed that the configurational sequence distribution may be described according to Bernoullian statistics with the isotactic parameters σ_{MM} , σ_{ML} , σ_{LM} and σ_{LL} as defined by Bovey²² and Coleman²³, where σ_{ij} is the probability of generating a meso diad between an *i* ending growing species and incoming *j* monomer.

Values $\sigma_{MM} = 0.52$ and $\sigma_{LL} = 0.52$ have been considered for the statistical distribution of units in pure MMM and LLL triads. These value correspond to the isotacticity parameters of M and L homopolymers and have been determined from the analysis of the α -CH₃ resonances of PMMA and PLMA, considering the Bernoullian distribution of tactic sequences. These coisotacticity parameters σ_{ML} and σ_{LM} are not accessible directly, but it is reasonable to assume that $\sigma_{ML} = \sigma_{LM} = \sigma^*$ ^{24,25}. In this way we have determined this parameter by comparison of the integrated intensities of peak I & II of the α -CH₃

resonances (assigned as indicated in **Table 5.4**) for several copolymer samples. The application of well known statistical relations gives a value of $\sigma_{ML} = \sigma_{LM} = 0.30$.

Fig. 5.7 shows the variation of the concentration of tactic sequences (independently of their chemical composition), with the average molar fraction M in the copolymer chain. It clearly shows that there is a slight increase of the coheterotactic sequences with increasing the molar fraction of M in the copolymer samples, but, in any case, from a stereochemical point of view one can conclude that there is a random distribution of tacticity following the classical Bernoullian triad.

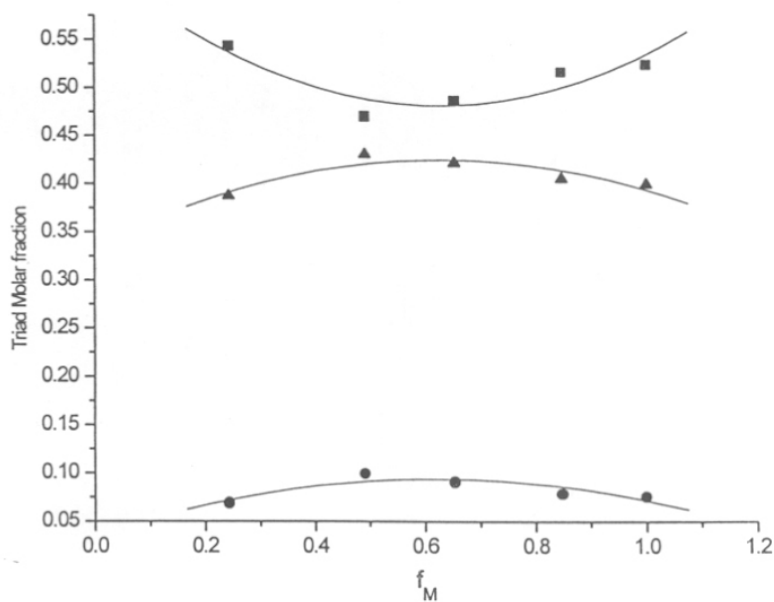


Fig. 5.7: Variation of tactic sequences with M molar fraction in the copolymer. The points are experimental results from the α -CH₃ resonance signals: mm = ●; rm.mr = ▲; rr = ■.

Carbonyl Carbon Resonance Signals

We have also examined the validity of the statistical model, from the analysis of the complex pattern of the carbonyl carbon resonance signals. **Fig. 5.8** shows the spectra of the C=O resonances for four copolymer samples of different composition, together with those of corresponding M and L homopolymers. The calculated and observed peak intensities are

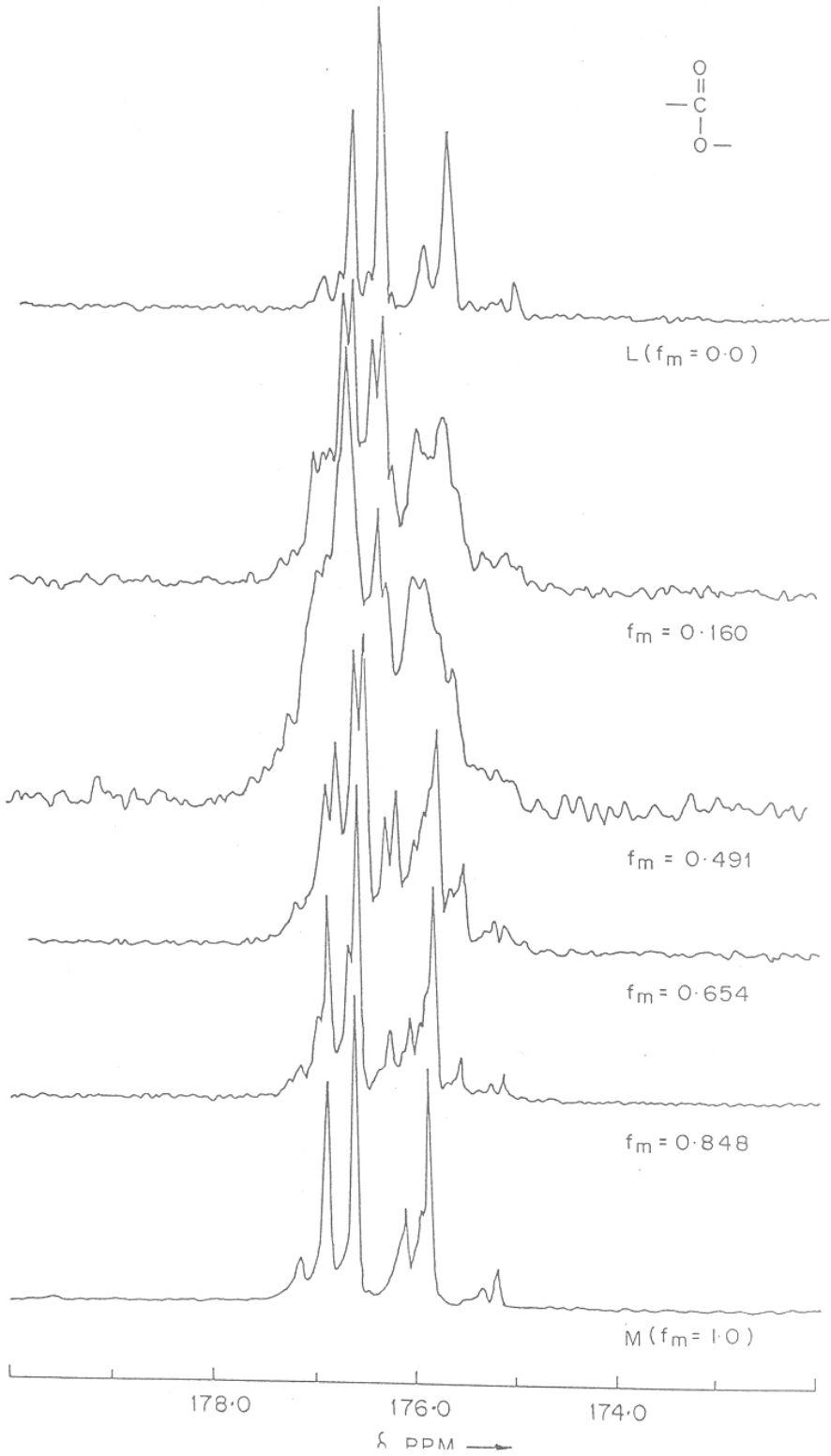


Fig. 5.8: ^{13}C NMR spectra (75.5 MHz) of the C=O side groups of M-L copolymers

compared in **Table 5.5** and **Table 5.6** for PMMA and PLMA respectively. They agree well with each other indicating that the pentad distributions in the samples obey Bernoullian statistics. The C=O resonances of PLMA reveals that this group presents a resonance pattern very similar to that of PMMA. The assignment of PLMA was carried out in terms of tactic pentads in the same manner as for PMMA^{18,19}.

Table 5.5: Experimental and Calculated Pentad Probabilities for Poly (Methyl Methacrylate) Samples using GTP

¹³ C	C=O	Pentads	ppm	Observed	Calculated
		mrrm	177.12	0.044	0.039
		rrrm	176.86	0.204	0.209
		rrrr	176.59	0.277	0.276
		rmrm	176.46	0.084	0.080
		mrmm	176.09	0.089	0.80
		rrmm	175.94	0.216	0.210
		rrmr	175.85	0.015	0.030
		rmmm	175.71	0.014	0.030
		mmmm	175.46	0.20	0.006
		rmmr	175.32	0.035	0.039

Calculation from intensity of C=O group. P_m is calculated from intensity of mm triad of α -CH₃ group of PMMA.

The spectra of copolymers (**Fig. 5.7**) when compared with those of the homopolymers M and L reveal that they correspond to the superposition of both spectra, but with intensities according to the average molar composition of copolymer chains. This means that the C=O resonances of M and L-centered sequences are not sensitive to the chemical composition and distribution of monomeric units but are sensitive to the relative stereochemical configuration of copolymer segments in terms of sequences of tactic pentads. On this basis, the chemical shifts of signals assigned to tactic pentads centered in M units, together with the molar fraction of sequences for copolymers with different average molar fraction of M, are listed in **Table 5.7**.

Table 5.6: Experimental and Calculated Pentad Probabilities for Poly (Lauryl Methacrylate) Samples using GTP

^{13}C	C=O	Pentads	ppm	Observed	Calculated
		mrrm	177.0	0.036	0.040
		rrrm	176.77	0.205	0.209
		rrrr	176.49	0.283	0.273
		rmmr	176.32	0.089	0.080
		mrmm	176.01	0.068	0.031
		rrmr	175.78	0.188	0.209
		rrmm	175.55	0.058	0.080
		rmmm	175.29	0.014	0.028
		mmmm	175.23	0.020	0.010
		rmmr	175.10	0.037	0.040

Table 5.7: Stereochemical Configuration of M-Centered Pentads Determined from the Analysis of the C=O Resonance Signals

Tactic Pentad	Chemical Shift, ppm	f_M (Copolymer)			
		0.243	0.491	0.654	0.848
mrrm	177.33	0.039		0.017	0.049
			0.087		
mrrr	177.21	0.048		0.065	0.083
rrrm	177.00	0.172	0.221	0.235	0.202
rrrr	176.63	0.393	0.433	0.436	0.362
rmmr	-	-	-	-	-
mmrr	-	-	-	-	-
rmrr	176.00	0.204	0.216	0.158	0.197
mrrm	175.33	0.052	0.043	0.032	0.032
mmmr	175.13	0.052	-	0.038	0.073
rmmr	174.95	0.038	-	0.016	-
mmmm	-	-	-	-	-

Table 5.8: Stereochemical Configuration of L-Centered Pentads Determined from the Analysis of the C=O Resonance Signals

Tactic Pentad	Chemical Shift, ppm	f_L (Copolymer)			
		0.152	0.346	0.509	0.757
mrrm	176.88	0.173	0.137	0.221	0.152
rrrm	176.59	0.270	0.214		0.244
rrrr	176.25	0.129	0.193	0.263	0.356
rmmr	175.97	0.066	0.092	0.194	-
mmrr	175.90	0.093	0.108		0.077
rmrr	175.83	0.188	0.146	0.201	0.074
mrrm	175.71	0.014	0.042		0.096
mmmr	175.59	0.055	0.057		-
rmmr	175.38	0.011	0.009	0.120	-
mmmm	-	-	-	-	-

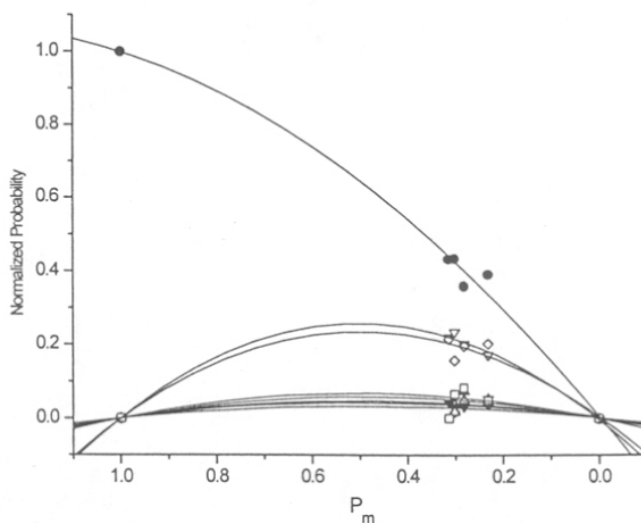


Fig. 5.9: M centered pentad sequence probabilities as a function of P_m : mmmm = ●; mmmr = ▲; mrrm = ▼; rmmr = ◆; mmrr = ■; rrrm = ○; mrrm = △; rrrm = ▽; rmrr = ◇; mrrr = □.

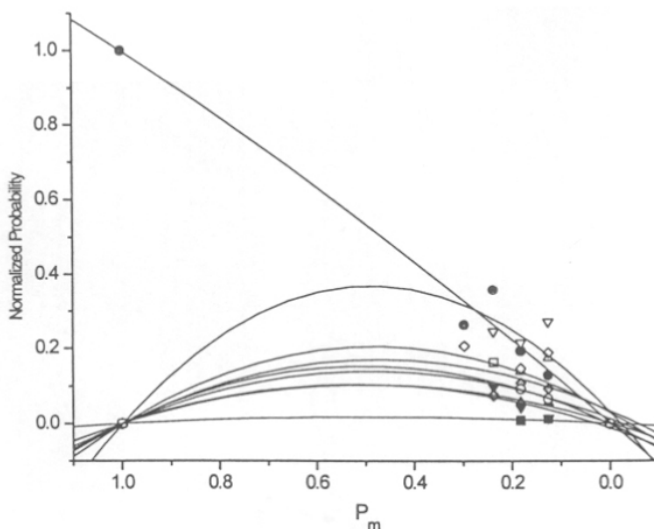


Fig. 5.10: L centered pentad sequence probabilities as a function of P_m : mmmm = ●; mmmr = ▲; mrmr = ▼; mmrr = ◆; rmmr = ■; rrmr = ○; mrrm = △; rrrm = ▽; rmrr = ◇; mrrr = □.

Similarly, Table 5.8 reports the corresponding values for L-centered sequences. In this case, the overlapping between 176.50 and 175.80 ppm with the more intense syndiotactic L-centered sequences (see Fig. 5.7) does not permit us to determine the contribution of isotactic M centered sequences. Therefore, the values collected in Table 5.8 for these sequences have been calculated statistically according to the model described before; nevertheless, their contribution to the whole system can be disregarded in practice.

Fig. 5.9 and Fig. 5.10 show pentad sequence probabilities as a function of P_m . The pentad graphs are well compared with the literature¹⁴.

5.2.1.3 Molecular Weight and Molecular Weight Distribution

Methyl methacrylate (MMA) and lauryl methacrylate (LMA) are both important commercial monomers. The copolymerization is interesting for two reasons. First, the product is high polymer with usable physical properties. Second, when copolymerizing monomers of similar electronic structure but with different pendent groups such as higher and lower methacrylates, the effect of bulk side chains on monomer sequence can be isolated and studied. Random copolymers of LMA and MMA were synthesized in

quantitative conversion over a wide composition range (Table 5.9). The copolymers were characterized by SEC. Molecular weights and polydispersities were determined by comparison with standardized PMMA samples. The copolymers gave smooth single-peak SEC curves (Fig. 5.11).

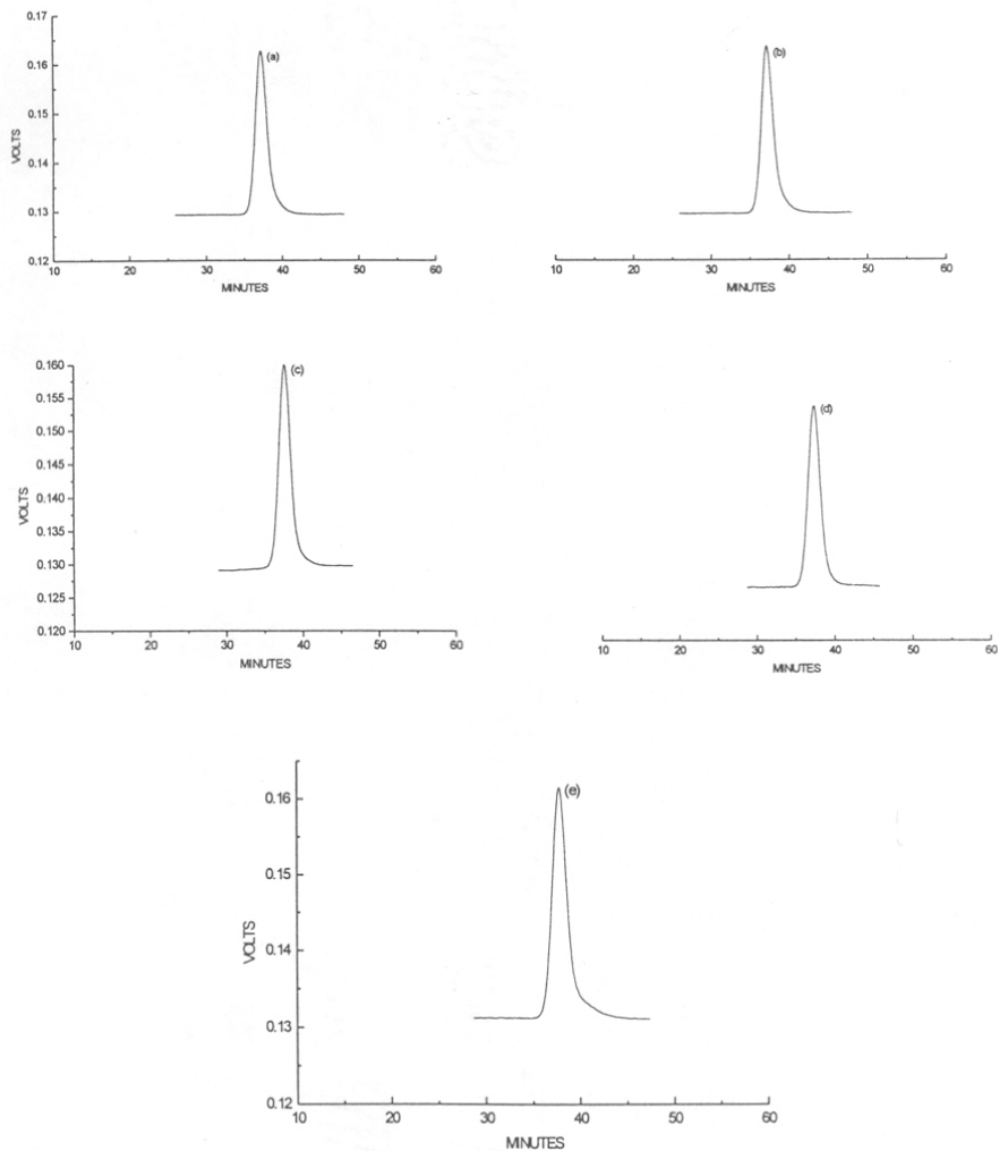


Fig. 5.11: SEC-RI of random copolymers at quantitative conversion: a) entry 1, Table 5.9, b) entry 2, Table 5.9, c) entry 3, Table 5.9, d) entry 4, Table 5.9 and e) entry 5, Table 5.9.

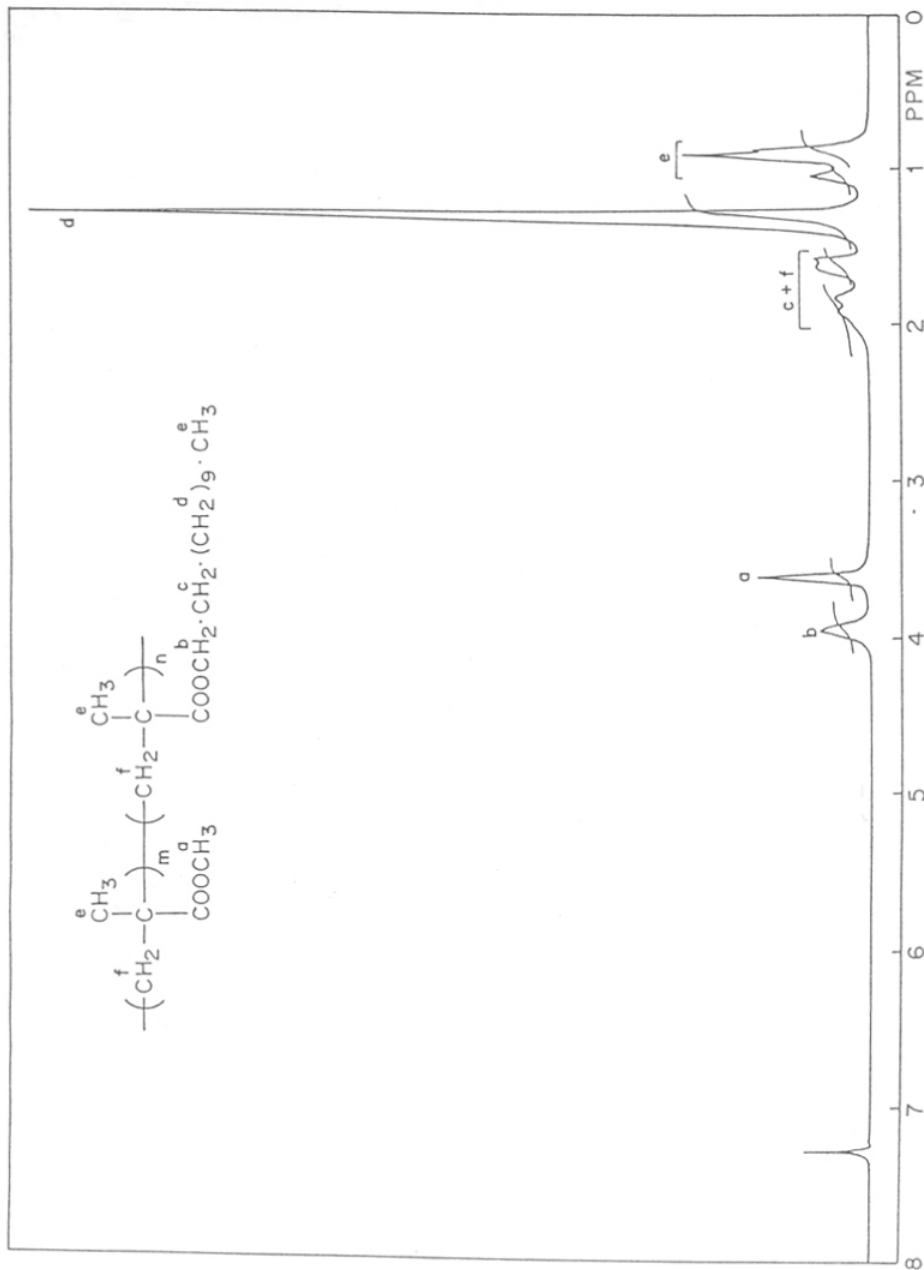


Fig. 5.12: ^1H NMR spectra (in CDCl_3) of random copolymer: PMMA-co-PLMA (feed ratio 60-40 mol%) (entry 3, Table 5.9)

The compositions of copolymers determined by NMR were close to the feed ratio of the monomers. A typical NMR spectrum of the random copolymer is shown in Fig. 5.12.

The characterization of the molecular weight and polydispersity of synthetic copolymers by SEC is difficult because of the lack of appropriate samples for calibration of the column. Frequently a series of molecular weights of similar polymer (PMMA), for example) is used for calibration and molecular weight averages are reported 'relative to poly(methyl methacrylate)'. Absolute methods such as colligative methods or light scattering are time-consuming, require large amount of sample, and give no information about polydispersity.

Light scattering detectors that interface with an SEC have been introduced in recent years to address these problems²⁶⁻³⁰. These instruments differ from the classical light scattering instrument design in several ways: a). optics and detectors are usually fixed, b). sample flows through scattering cell, and c). very small scattering volumes (0.1 μL) are used. When used with SEC, light scattering (LS) provide a direct measurement of the molecular weight from the scattered intensity of the eluting sample. The most recent LS detector introduced commercially provides a range of as many as 18 scattering angles, so that as many as 19 individual chromatograms are obtained with each injection; one for each scattering angle plus the refractive index (or absorption) chromatogram. With these data, the angular dependence of the scatter intensity may be determined at each elution volume. In principle, with multi-angle detectors, the root-mean-square radius of gyration (R_G) may then be obtained as a function of elution volume. This presents the appealing possibility of being able to measure R_G vs. M over a decade of M with as little as a few milligrams of sample for a broad distribution polymer.

The LS chromatograms obtained for copolymers were independent of scattering angles, with the exception that the lower angles were more noisy. Molecular weights at each elution volume were calculated by averaging over all the scattering angles measured. The scattered intensity is proportional to CM so that the intensity is larger in the high M -portion of the distribution. In fact, the SEC/ LS technique is very advantageous in detection of very small fractions of high M species, such as aggregates or branched molecules which are not detectable by any other solution technique. Conversely, intensity in the low M portion of the

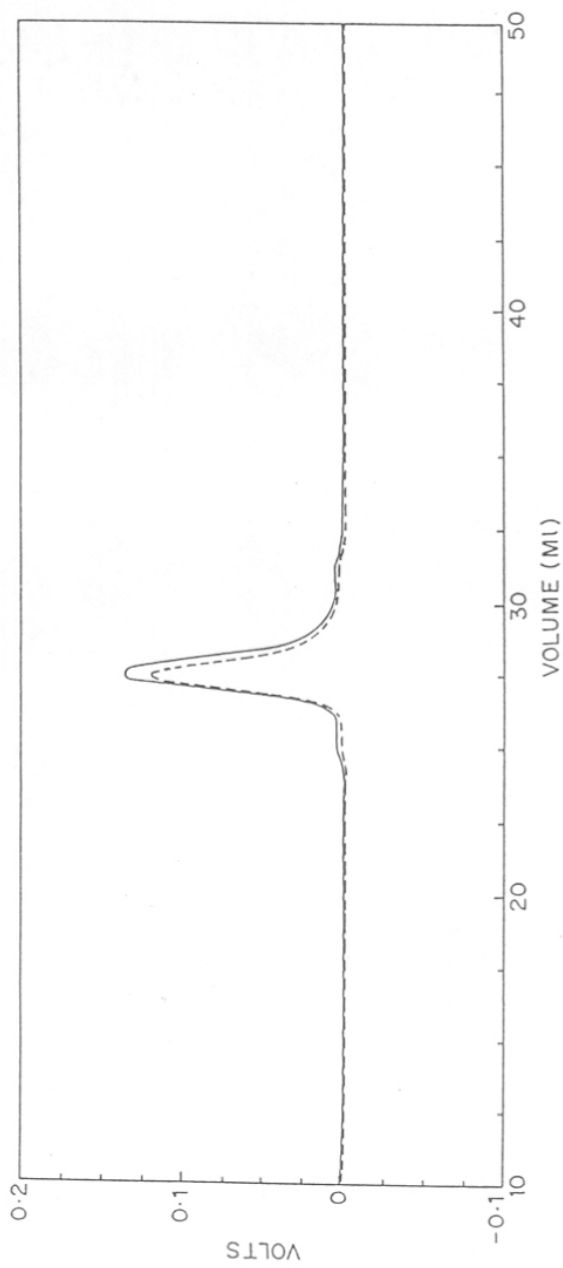


Fig. 5.13: SEC-MALLS of random copolymer: PMMA-co-PLMA (feed ratio 52:48 mol %)
(entry 3, Table 5.9)

distribution can be quite small, and molecular weight averages that primarily reflect the low M contribution, such as \bar{M}_n , may be erroneously large.

The technique of SEC/LS has been used to determine molecular weight and polydispersity of a series of copolymers with as little as 3 mg of sample. Though the values of dn/dc are quite low, scattered intensities were large enough compared to THF to measure accurately the molecular weight and polydispersity (Table 5.9, Fig. 5.13).

Table 5.9: Statistical Copolymerization of MMA (M_1) and LMA (M_2) at High Conversion using SEC-MALLS^{a,b,c,d} at 24^oC

Sr. No.	[M_1] molL ⁻¹	[M_2] molL ⁻¹	M_1/M_2 feed	M_1/M_2 NMR	\bar{M}_n SEC RI	\bar{M}_w/\bar{M}_n SEC RI	\bar{M}_n SEC MALLS	\bar{M}_w/\bar{M}_n SEC MALLS	I_{eff}^c (%)
1	1.37	0.35	80/20	78/22	49,500	1.16	40,800	1.03	77
2	0.82	0.56	60/40	58/42	51,200	1.16	45,800	1.02	70
3	0.60	0.63	52/48	56/44	44,100	1.14	42,250	1.05	74
4	0.41	0.66	40/60	38/62	49,840	1.14	46,990	1.03	67
5	0.18	0.79	23/77	27/73	40,100	1.20	46,960	1.05	67

a. In every case conversion was 100%. b. $[I_0] = 0.007 \text{ molL}^{-1}$ c. $[C]_0 = 1.5 \times 10^{-4} \text{ molL}^{-1}$ d. THF was used as solvent. e. $I_{eff} = (\bar{M}_{nca}/\bar{M}_{nSEC}) \times 100$.

5.2.2 Block Copolymerization of MMA with LMA

Living PLMA chains, prepared in presence of trimethylsilylbenzoate (livingness enhancer), were used to initiate block copolymerization of MMA by sequential monomer addition technique. Since the degree of purity of LMA was suspected to be lower than MMA, the synthesis of LMA block was performed first to avoid the contamination of "dead" homopolymer in the final block copolymer³¹. Deactivation of the catalyst, either by initiator or polymer or both is reported to lead to incomplete monomer conversion in GTP³². So in every block copolymerization second lot catalyst was added before the addition of the second monomer.

The second monomer was added after ensuring complete conversion of the first monomer. Addition of a few percent of trimethylsilyl benzoate increased the 'livingness' of the chain

end by complexing with the catalyst and providing a means of supplying it continuously at low concentration³³. This effect could be seen from the extent of molecular weight control and polydispersity of both the initial PLMA block and the final copolymer (Table 5.10) (Fig. 5.14).

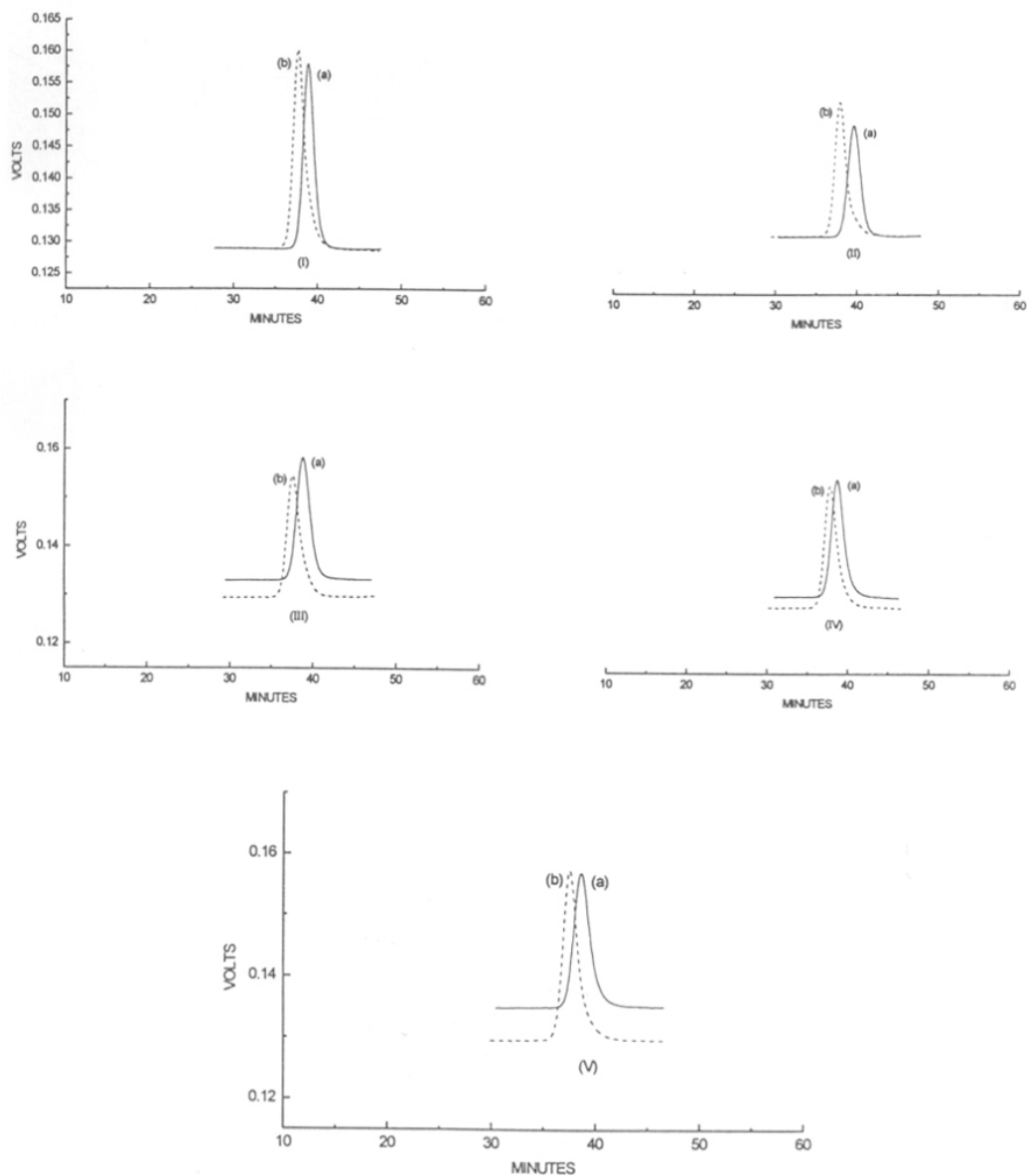


Fig. 5.14: SEC-RI for a) homopolymer before chain extension, b) block copolymer after chain extension: I) entry 1, Table 5.10, II) entry 2, Table 5.10, III) entry 3, Table 5.10, IV) entry 4, Table 5.10 and V) entry 5, Table 5.10.

Table 5.10: Results of Block Copolymers of MMA (M_1) and LMA (M_2)^a

Reaction	type	M_1/M_2 feed	M_1/M_2 NMR	\bar{M}_n	\bar{M}_w/\bar{M}_n	\bar{M}_n	\bar{M}_w/\bar{M}_n	I_{eff}^b (%)
				SEC RI	SEC RI	SEC MALLS	SEC MALLS	SEC MALLS
1	Homo PMMA			27,300	1.08			
	Block	80/20	82/18	41,100	1.13	37,900	1.05	90
2	Homo PLMA			21,100	1.10			
	Block	60/40	60/40	41,000	1.11	37,000	1.06	85
3	Homo PLMA			28,280	1.14			
	Block	50/50	49/51	43,390	1.14	44,600	1.03	75
4	Homo PLMA			28,660	1.14			
	Block	40/60	42/58	41,880	1.12	41,100	1.03	80
5	Homo PLMA			29,120	1.14			
	Block	20/80	21/79	43,950	1.14	44,800	1.03	71

a. In every case conversion was 100%. b. $I_{\text{eff}} = (\bar{M}_{\text{nCAL}}/\bar{M}_{\text{nSEC}}) \times 100$

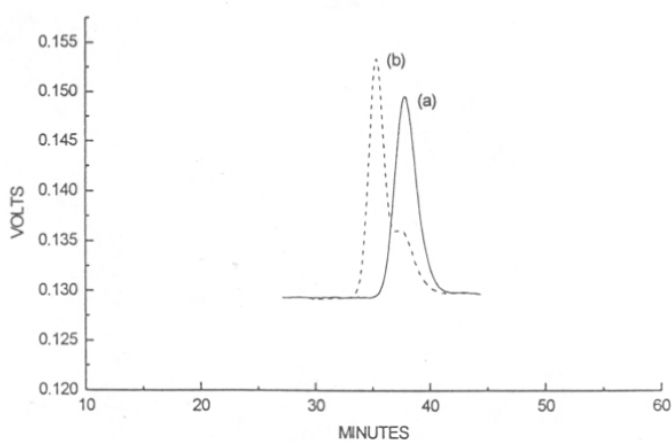


Fig. 5.15: SEC-RI for a) PLMA before chain extension, b) PLMA-b-PMMA copolymer after chain extension (entry 1, Table 5.11) (without 'livingness enhancer').

Table 5.11: Effect of Livingness Enhancer on the Block Copolymerization of MMA (M_1) and LMA (M_2)^a

Reaction	Type	M_1/M_2 feed	M_1/M_2 NMR	\bar{M}_n SEC RI	\bar{M}_w/\bar{M}_n SEC RI
1 ^b	Homo			39,831	1.20
	PLMA				
	Block	50/50	51/49	57,792	2.00
2 ^c	Homo			28,280	1.14
	PLMA				
	Block	50/50	49/51	43,390	1.14

a. Target molecular weights were same in both the cases. b. Without livingness enhancer. c. With livingness enhancer.

The same copolymer synthesized without trimethylsilyl benzoate showed bimodal polydispersity i.e. $\bar{M}_w/\bar{M}_n = 2.0$ (Fig 5.15) (Table 5.11).

The \bar{M}_n of PLMA homopolymers were determined by SEC-RI using PMMA standards since their molecular weights were below the detection limit of MALLS detector. The \bar{M}_n as determined by SEC were generally higher than the calculated value, but, polydispersities were very narrow (1.1-1.15). Absolute molecular weights of the block copolymers were determined using SEC-MALLS. In each polymerization, SEC molecular weight was higher than calculated molecular weight but polydispersities were very narrow (1.02-1.06).

All the copolymers gave elution curves which were single sharp peaks with no shoulders, (Fig. 5.16) implying that the products were true copolymers. No homopolymer contamination could be detected in SEC.

The compositions of all block copolymer samples were determined by ¹H NMR (Fig. 5.17) and were found to be the same as those calculated from the amount of monomers feed used for copolymerization.

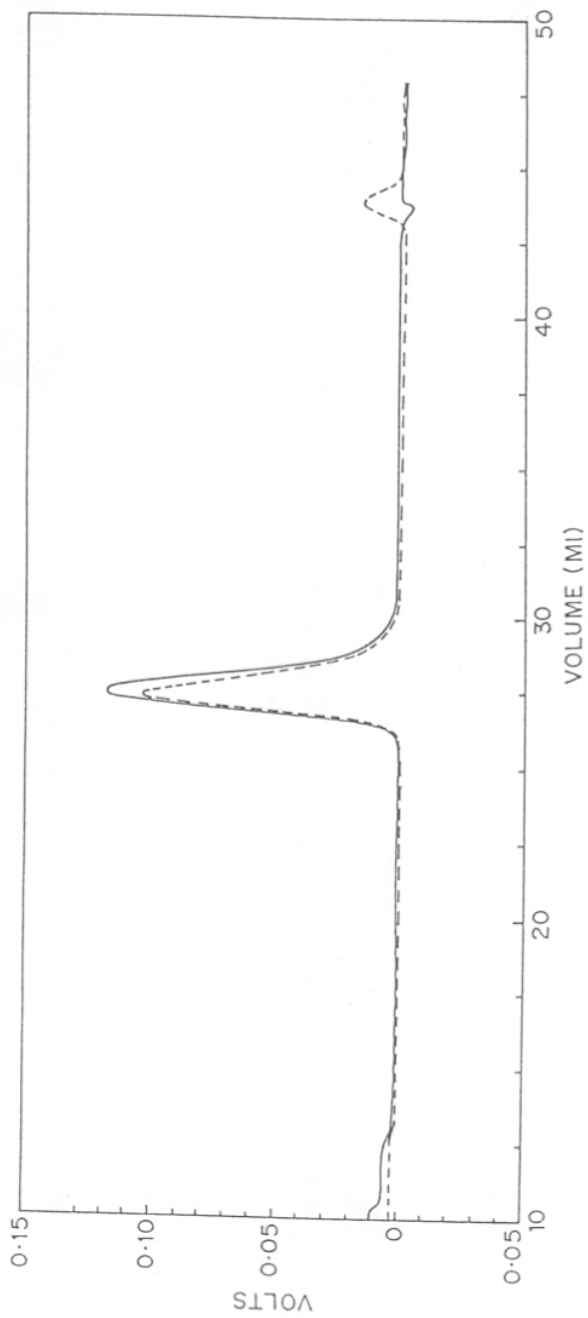


Fig. 5.16: SEC-MALLS of block copolymer: PMMA-b-PLMA (feed ratio 50:50 mol%) (entry 3, Table 5.10).

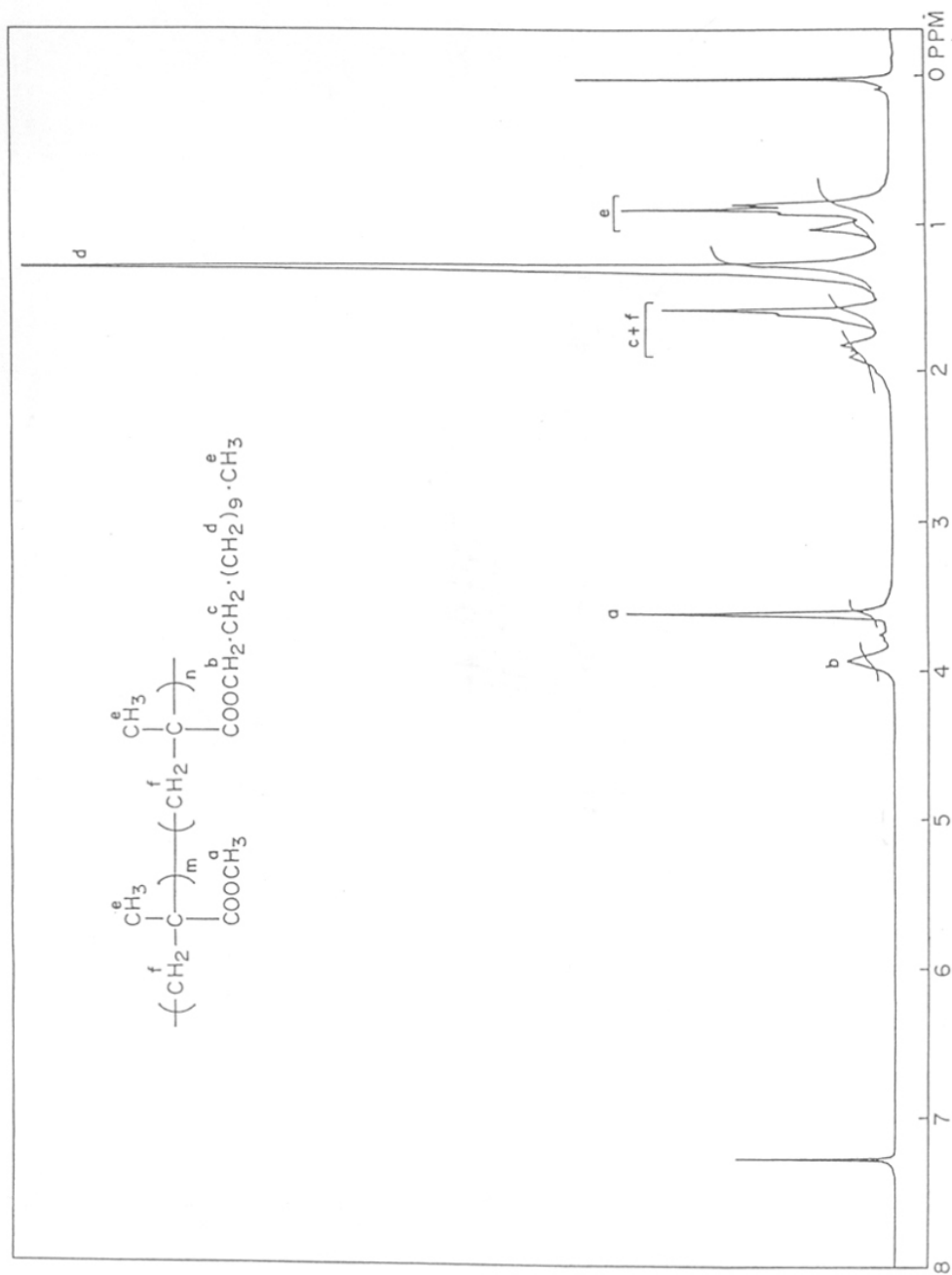


Fig. 5.17: ^1H NMR spectra (in CDCl_3) of block copolymer: PMMA-b-PLMA (feed ratio 50:50 mol %) (entry 3, Table 5.10)

The I_{eff} for block copolymer increased from 0.71 to 0.90 with increasing PMMA block length. This is presumably due to the partial deactivation of the polymer chain end due to impurities present in LMA monomer.

5.2.3 Thermal Properties of Random and Block Copolymers

In order to investigate the effect of comonomer (i.e. MMA) on the thermal stabilities of poly(lauryl methacrylate) (PLMA), thermogravimetric studies were carried out.

The thermal degradation of PMMA and its copolymers has been extensively investigated. The sole product of degradation of PMMA is monomer which is produced by reverse polymerization (depolymerization) reaction. However, the degradation of PMMA is very much dependent on the mode of polymerization and the presence of comonomer units in the backbone³⁴. For example when PMMA prepared by free radical polymerization is subjected to a programmed rate of heating it undergoes depolymerization in two stages³⁴. The first stage of degradation is due to initiation at unsaturated chain ends, and occurs below 300⁰ C. The second stage of degradation observed at high temperature is due to initiation by random scission of the backbone. One step degradation is observed in PMMA prepared by anionic and group transfer polymerization.

The degradation behavior of copolymers of MMA depends largely on the nature of the comonomers³⁴. If the comonomer is another methacrylate, which also undergoes depolymerization, then unzipping will continue to produce MMA and the corresponding monomer. This behavior has been demonstrated with linear ester side groups (ethyl and n-propyl methacrylate). Monomers are the sole product of degradation up to a temperature of 400⁰ C in copolymers of MMA and iso-octyl or isodecyl methacrylate³⁴. For the copolymer of MMA and LMA, degradation was completed at 400⁰C indicating depolymerization (Fig. 5.17).

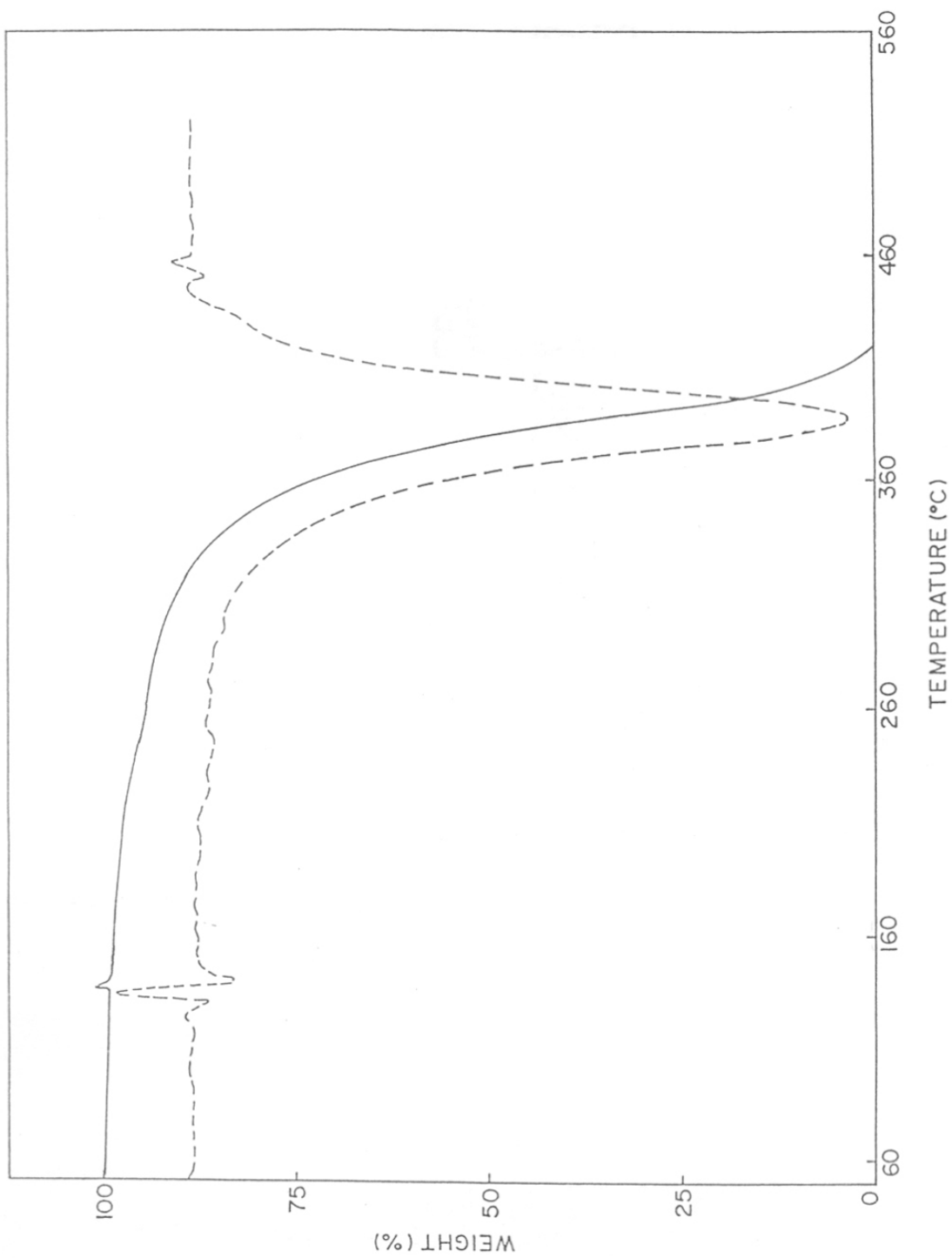


Fig. 5.18: TG curve of copolymer (entry 3, Table 5.10)

5.3 CONCLUSIONS

Random and block copolymers MMA and LMA with \bar{M}_n in the range of 50,000 and with narrow polydispersities (1.02-1.10) were successfully synthesized over a wide composition range. The absolute molecular weights of random and block copolymers determined by SEC-MALLS were higher by a factor of 1.1-1.4 relative to targeted molecular weights. A lesser degree of control over molecular weights was observed when LMA content was higher in the monomer feed ratio, implying termination by impurities present in LMA. Use of livingness enhancer, namely, trimethylsilylbenzoate improved the molecular weight control and polydispersity of the PLMA and the final block copolymer. The r_1 and r_2 values for the statistical copolymerization of MMA (M) with LMA (L) were determined as r_1 (MMA) = 1.38 ± 0.11 and r_2 (LMA) = 0.68 ± 0.10 . ^{13}C NMR spectra of the copolymers were analyzed in terms of sequence distribution and relative stereochemical configuration of monomer units along the macromolecular chains. The values of concentration of M- and L-centered triads, determined experimentally from the analysis of $\alpha\text{-CH}_3$ and C=O resonance signals, were in good agreement with those calculated statistically, taking into consideration the terminal model and Bernoullian distribution of stereoregularity.

5.4 REFERENCES

- 1 G.C.Eastmond, O.W.Webster, "New Methods of polymer synthesis", Ed. J.R.Ebdon, Blackie, Glasgow, 1992, chap.2,p.23.
- 2 O.W.Webster, W.R.Hertler, D.Y.Sogah, W.B.Farnham and T.V.Rajanbabu, *J. Am. Chem. Soc.*, **105**, 5706 (1983).
- 3 D.Y.Sogah and O.W.Webster, *J.Polym.Sci.Lett.Ed.*, **21**, 927 (1983).
- 4 K. Steinbrecht and F. Bandermann, *Makromol. Chem.*, **190**, 2183 (1989).
- 5 R.P.Quirk and J.Ren, *Makromol. Chem. Macromol. Symp.*, **88**, 17 (1994).
- 6 J.A.Simms, *Rubber Chem. Technol*, **64(2)**, 139 (1991).
- 7 J.A.DeSimone, A.M.Hellstern, E.J.Siochi, S.D.Smith, T.C.Ward, P.M.Gallanger, V.J.Krukonis and J.E.McGrath, *Makromol. Chem. Macromol. Symp.*, **32**, 21 (1990).
- 8 D.Y.Sogah, W.R.Hertler, O.W.Webster and G.M.Cohen, *Macromolecules*, **20**, 1473 (1987).
- 9 M.A.Moller, M.Angenstein, E.Dumont and H.Punnewibb, *New Polym. Mater.*, **2(4)**, 135 (1991).
- 10 S.P.Rannard, N.C.Billingham, S.P.Armes and J.Mykytiuk, *Eur. Polym. J.*, **29**, 407 (1993).
- 11 A.H.E.Muller, in M.Fontnille and A.Guyot (Eds),in "Recent Advances in Mechanistic and Synthetic Aspects of Polymerization", NATO ASI Series C, 1987, Vol.125. p.23.
- 12 T.Kelen and F.Tudos, *J. Macromol. Sci. Chem. Ed.*, **A9**, 1 (1975).
- 13 G.A.Stahl, *J. Polym. Sc. Polym. Chem. Ed.*, **17**, 1883 (1979).
- 14 F.A.Bovey, "Nuclear Magnetic Resonance Spectroscopy", 2nd Ed.; Academic Press: New York, 1987.
- 15 A.D.Jenkins, in "Reactivity, Mechanism and Structure in Polymer Chemistry", A.D.Jenkins, A.Ledwith, Ed.; Wiley: London, 1974.
- 16 J.L.Koenig, *Chemical Microstructure of Polymer Chains*; Wiley-Interscience: New York 1980.
- 17 R.Chujo, K.Hatada, R.Kitamura, T.Kitayama, H.Sato and I.Tanaka, *Polym.J.*, **19**, 413 (1987).
- 18 I.R.Peat and W.F.Reynolds, *Tetrahedron Lett.*, **14**, 1359 (1972).
- 19 T.Konishi, Y.Tamai, M.Fujii, Y.Einaga and H.Yamakawa, *Polym.J.*, **21**, 329 (1989).
- 20 F.R.Mayo and F.M.Lewis, *J.Am.Chem.Soc.*, **66**, 1594 (1944).
- 21 T.Alfrey(Jr.) and G.Goldfinger, *J.Chem.Phys.*, **12**, 205 (1944).
- 22 F.A.Bovey, *J.Polym.Sci.*, **62**, 197 (1962).
- 23 B.Coleman, *J.Polym.Sci.*, **31**, 155 (1958).
- 24 R.Russel and J.C.Galin, *J.Macromol.Sci., Chem.*, **A11 (2)**, 347 (1977).

- 25 K.Ito, S.Iwase, K.Umehara and Y.Yamashita, *J.Macromol.Sci., Chem.*, **AI**, 891 (1967).
- 26 W.Kaye and A.J.Havlik, *J.Appl.Opt.*, **12**, 541 (1973).
- 27 A.C.Quano and W.Kaye, *J.Polym.Sci., Polym.Chem.Ed.*, **12**, 1151 (1973).
- 28 C.Jackson, L.Nillson and P.J.Wyatt, *J.Appl.Polym.Sci.*, **43**, 99 (1989).
- 29 S.H.Kim and P.M.Cotts, *J.Appl.Polym.Sci.*, **42**, 217 (1991).
- 30 P.M.Cotts and A.C.Quano, in *Microdomains in Polymer Solutions* (Ed.P.Dubon), Plenum Press, New York, Ch7, (1975).
- 31 D.M.Haddleton, A.V.G.Muir, J.P.O'Donnel and D.L.Tworse, *Polym. Prepr.(Am.Chem.Soc., Div.Polym.Chem.)*, **34(2)**, 564 (1993).
- 32 M.A.Doherty, F.Gores, P.M.Mai and A.H.E.Muller, *Polym. Prepr.(Am.Chem.Soc., Div.Polym.Chem.)*, **29(2)**, 73 (1988).
- 33 L.V.Schneider and I.B.Dicker, EP 244,953 (1987); *Chem.Abstr.*, **108**:205280m (1988).
- 34 I.K.Varma, M.Varma Nair, V.K.Karan and D.S.Varma, *Thermochimica Acta*, **142**, 189 (1989).

CHAPTER-VI

**GROUP TRANSFER POLYMERIZATION OF MMA USING ALKALI
METAL BIBENZOATES/CROWN ETHER COMPLEXES**

6.1 INTRODUCTION

Group transfer polymerization (GTP) is a technique for initiating a “living” polymerization of acrylate and methacrylate monomers at room temperature¹. The initiator most commonly used is 1-methoxy-1-(trimethylsiloxy)-2-methyl-1-propene (MTS). For the GTP of methacrylate, polar solvents (THF) and nucleophilic catalysts (e.g. bifluorides, benzoates, bibenzoates etc.) are most suitable. The associated cations are generally large and diffused examples being tris(dimethylamino) sulfonium² (TAS), tris(piperidino) sulfonium³ (TPS), or tetraalkylammonium⁴ (R_4N^+). Tetraalkylammonium salts of oxyanions and bioxyanions derived from carboxylates and phenolates have assumed importance in the recent years as nucleophilic catalysts for GTP⁵. Bioxyanions were judged to be superior catalysts because of their ease of preparations, crystallinity, nonhygroscopic nature and uniformly good polymerization results with a wide variety of monomers. The superiority of bioxyanions over monooxyanions has been attributed to the ability of bioxyanions to serve as a source of low concentration of monooxyanions via dissociative equilibrium.

The nature of the catalyst plays a significant role in determining both the rate of polymerization and polymer molecular weight distribution. Incomplete monomer conversions and higher polydispersities were obtained when high catalyst concentrations were used. Typically less than 0.1 mol% of catalyst based on the initiator is recommended. Apart from its effect on the rate of polydispersity it was proposed that the catalyst also affects the mechanism of polymerization. Weak nucleophiles such as HF_2^- , bibenzoate etc. presumably catalyze GTP by an “associative” mechanism whereas strong nucleophiles such as acetate, methylfluorenone etc. catalyze GTP by a “dissociative” mechanism^{6,7,8}.

The use of simple alkali metal cations has been far less studied in GTP. Potassium hydrogen bifluoride has been examined as a catalyst for GTP; however, in view of its insolubility in THF, solvents such as acetonitrile or DMF had to be used². Acetonitrile has since been shown to have an unfavorable effect on GTP as it reacts with the initiator and the active chain ends. To enhance the solubility of these salts in the preferred solvent, namely, THF, complexation with crown ethers or polyethylene glycols were attempted. Potassium acetate in presence of polyethylene glycol is a very poor catalyst for GTP⁹. Less than quantitative conversions were reported. No molecular weight or polydispersity data was presented.

Potassium hydrogen bifluoride and 18-crown-6 was investigated as GTP catalyst in THF¹⁰. Under these conditions, 100% conversion was obtained. However, polydispersity was in the range of 1.4-1.8 and there was no molecular weight control. Potassium acetate/18-crown-6 in acetonitrile was studied as catalyst for GTP by Miller et al.¹¹. No experimental data was presented. The polydispersity was very broad (~ 1.9).

In view of the proven benefits of tetrabutylammonium bibenzoate as catalyst, a study of the use of potassium bibenzoate as the GTP catalyst has been undertaken. Solubility of the catalyst was promoted by addition of 18-crown-6.

In this chapter, effect of catalyst, initiator and monomer concentration, crown ether to catalyst ratio, temperature, nature of crown ether and nature of alkali metal on the molecular weight controls and polydispersities of PMMA obtained by GTP initiated by MTS will be discussed. The kinetics of GTP of MMA with alkali metal bibenzoate and the tetrabutyl ammonium bibenzoate will be compared. The mechanism of polymerization catalyzed by alkali metal bibenzoate has been elucidated.

6.2 RESULTS AND DISCUSSION

6.2.1 GTP OF MMA USING ALKALI METAL BIOXYANIONS/CROWN ETHER COMPLEXES

The feasibility of GTP of MMA has been investigated using sodium and potassium salts of bioxyanions derived from carboxylates and phenolates. Sodium bibenzoate (NaBB) or potassium bibenzoate (KBB) failed to catalyze GTP of MMA in the absence of crown-ether in view of their insolubility in THF. Sodium bis-4-nitrophenolate (Na4NP) in presence of dibenzo-18-crown-6 (DB-18C6) (1:2) catalyzed the GTP of MMA. However, the reaction was incomplete and control over molecular weight was poor and polydispersity was broad (MWD > 2.0) (Table 6.1, Fig. 6.1).

NaBB and KBB in presence of DB-18-C-6 again failed to catalyze the GTP of MMA. Complete conversion, good molecular weight control and relatively broad polydispersity have been observed for the GTP of MMA catalyzed KBB in presence of 18-crown-6 (18-C-6). Since KBB can easily be prepared and 18-C-6 is commercially available and easy to

handle, the factors which might affect the efficiency and dispersity of the polymerization were further investigated.

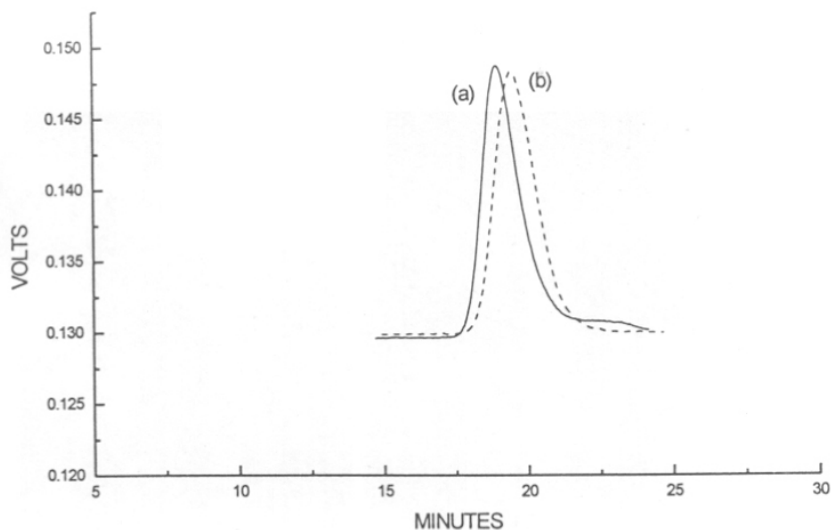


Fig. 6.1: SEC-RI for a) PMMA prepared using Na4-NP/ DB18-C-6 catalyst b) PMMA prepared using KBB/ 18-C-6 catalyst

Table 6.1: GTP of MMA using Alkali Metal Bibenzoate/ Crown Ether Complex Catalyst in THF ($M_0 = 0.094$ mol, $C_0 = 14.2 \times 10^{-6}$ mol, $I_0 = 6.89 \times 10^{-4}$ mol)

Catalyst	CE/C	Conv.%	$\bar{M}_n \times 10^{-3}$ SEC	\bar{M}_w / \bar{M}_n	I_{eff}^a
KBB	--	0	--	--	0
NaBB	--	0	--	--	0
Na4-NP/ DB-18-C-6	1	60	14.10	2.08	38
NaBB/ DB-18-C-6	1	0	--	--	0
NaBB/ 18-C-6	1	0	--	--	0
KBB/ 18-C-6	1	100	19.20	1.40	75

6.2.2 GTP OF MMA USING POTASSIUM BIBENZOATE/18-CROWN-6 COMPLEXES

Alkali metal (Na^+ , K^+) bibenzoates are insoluble in THF, a preferred solvent for GTP. However, they could be rendered soluble by complexation with a suitable crown ether. Potassium bibenzoate catalyzes the GTP of MMA in THF when it is complexed with 18-C-6. When the anion and solvent effects are not strong, the cation-cavity size compatibility is the main consideration for M^{2+} crown interaction. Based on this consideration 18-C-6 was chosen as the complexing agent for K^+ .

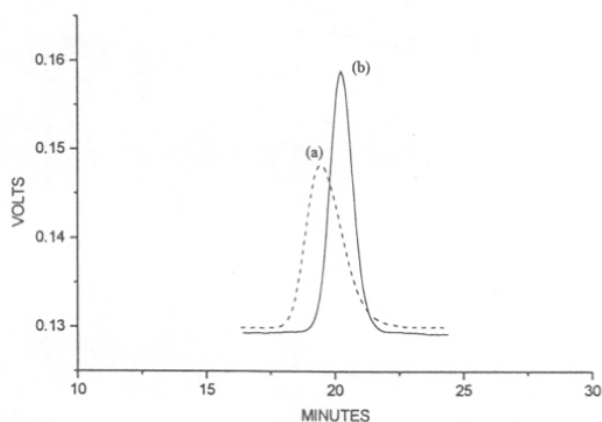


Fig. 6.2: SEC-RI for a) PMMA prepared using KBB/ 18-C-6 catalyst b) PMMA prepared using TBABB catalyst

The catalyst concentration used was 2 mol% based on initiator. The reaction system was scavenged free of impurities by addition of bis(dimethylamino) dimethylsilane which has been reported to be a very effective scavenger of impurities in GTP¹². All reactions were accompanied by an appreciable exotherm. The conversions were quantitative and good control over molecular weights were obtained. For comparisons, MMA was also polymerized using TBABB as catalyst under identical conditions. When TBABB was used, the rise of the exotherm from 30⁰C to 50⁰C was very much faster compared to KBB/ 18-C-6. The polydispersity of PMMA prepared using KBB/ 18-C-6 was broader than obtained using TBABB (Table 6.2). It is clear from SEC chromatogram that the broadening of

polydispersity in the case of KBB/ 18-C-6 was caused by a significant low molecular weight tailing (Fig. 6.2).

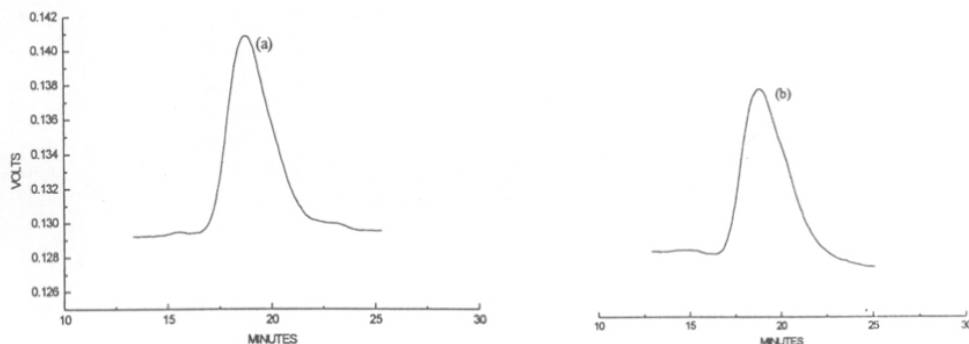


Fig. 6.3: SEC-RI for a) PMMA prepared using KBB/ 18-C-6 catalyst in toluene b) PMMA prepared using TBABB catalyst in toluene

To avoid competitive solvation of cation by crown ether and THF, the polymerizations of MMA using KBB/ 18-C-6 was performed in toluene. A comparative experiment was also performed with TBABB. The results (Table 6.2) showed that in both cases, toluene caused a broadening of polydispersity and the loss of molecular weight control (Fig. 6.3). This indicates that catalyst transfer is slow in a solvent of low polarity such as toluene.

Table 6.2: GTP of MMA using TBABB and KBB/ 18C6 Catalyst ($I_0 = 6.89 \times 10^{-4}$ mol)

Catalyst	MMA mol	CE/C	$C_o \times 10^6$ mol	Solvent	Conv. %	$\bar{M}_n \times 10^{-3}$ SEC	$\frac{\bar{M}_w}{\bar{M}_n}$	I_{eff}^a
TBABB	0.084	---	13.8	THF	100	14.3	1.14	90
KBB/ 18-C-6	0.094	1	14.2	THF	100	19.2	1.40	75
TBABB	0.094	---	13.8	Toluene	100	20.1	2.52	50
KBB/ 18-C-6	0.094	2	35.5	Toluene	100	18.9	2.41	56

a. $I_{eff} = \bar{M}_n(cal) \times 100 / \bar{M}_n(obs)$

6.2.2.1 Effect of catalyst concentration

KBB/ 18-C-6 catalyzed the GTP of MMA when the catalyst concentration was 1 mol% based on the initiator. It has been earlier reported that higher catalyst concentration may impart incomplete conversions due to termination¹³. However, 100% conversions were obtained even when the catalyst concentration was as high as 5 mol%. With increasing catalyst concentration the rate of initiation was expected to increase there by reducing the induction period. This results in improvement in the polydispersity (Fig. 6.4).

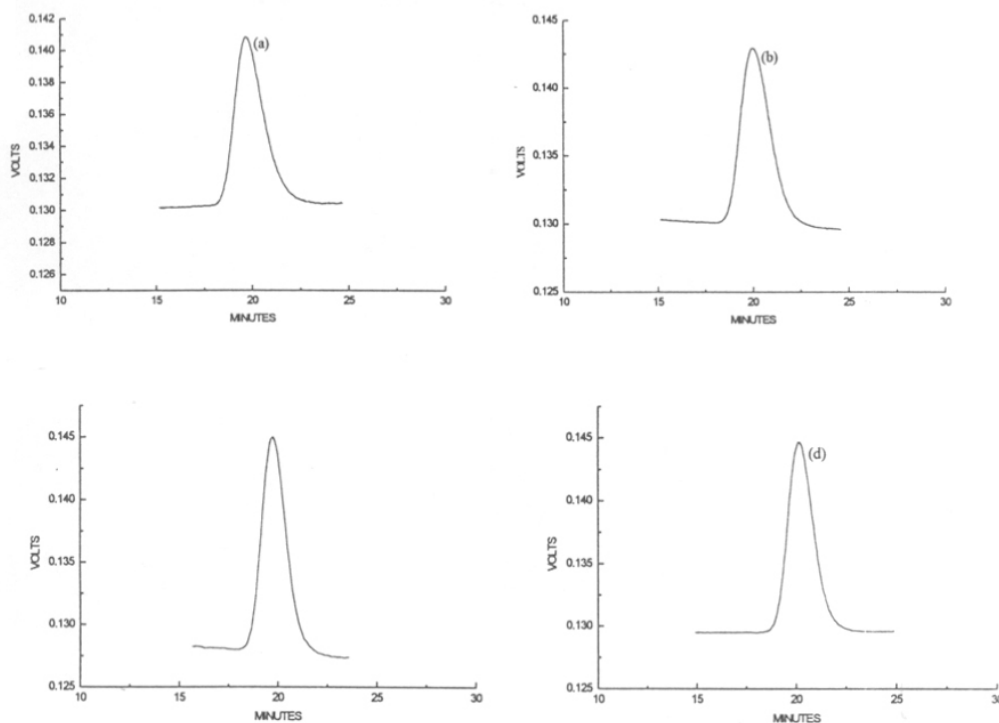


Fig. 6.4: SEC-RI for PMMA prepared using different catalyst concentration a) entry 1, Table 6.3 b) entry 2, Table 6.3 c) entry 3, Table 6.3 d) entry 4, Table 6.3

The lowest polydispersity values (1.25) were obtained at a catalyst concentration of 5 mol% based on the initiator. In case of TBABB it was established that good control over molecular weight and polydispersities are obtained using 1-2 mol% based on the initiator. Results are given in Table 6.3.

Competing equilibria, namely complexation-decomplexation equilibrium for CE/C complex and catalyst-initiator activation equilibrium, affect counterion availability. Hence, the larger than usual amount of catalyst required could be partially, thus, explained.

Table 6.3: GTP of MMA using KBB/ 18-C-6 Catalyst at Different Catalyst Concentrations in THF ($M_0 = 0.094$ mol, $I_0 = 6.89 \times 10^{-4}$ mol, $CE/C = 1$)

Sr. No.	$C_0 \times 10^6$ Mol	Conv.%	$\bar{M}_n \times 10^{-3}$ (SEC)	\bar{M}_w / \bar{M}_n	I_{eff}^a
1	7.1	100	19.5	1.41	78
2	14.2	100	20.6	1.40	75
3	35.5	100	19.5	1.25	78
4	53.25	100	20.4	1.27	75

$$a. I_{eff} = \bar{M}_n(cal) \times 100 / \bar{M}_n(obs)$$

6.2.2.2 Effect of crown ether to catalyst ratio

K^+ forms a very stable 1:1 complex with 18-C-6¹⁴. Increase in the crown ether to catalyst ratio beyond 1:1 did not significantly improve either the degree of molecular weight control or polydispersity (Fig. 6.5).

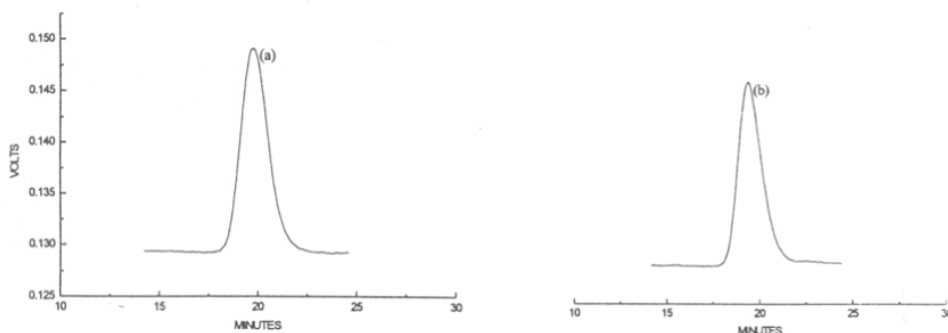


Fig. 6.5: SEC-RI for PMMA using different CE/C ratio a) entry 1, Table 6.4 b) entry 2, Table 6.4

Table 6.4: Effect of Crown Ether to Catalyst ratio on GTP of MMA using KBB/ 18-C-6 Catalyst in THF ($MMA = 0.094$ mol, $C_0 = 35.5 \times 10^{-6}$ mol, $I_0 = 6.89 \times 10^{-4}$ mol)

Sr. No.	CE/C	Conv.%	$\bar{M}_n \times 10^{-3}$ SEC	\bar{M}_w / \bar{M}_n	I_{eff}^a
1	2	100	18.2	1.34	80
2	4	100	23.8	1.30	62

$$a. I_{eff} = \bar{M}_n(cal) \times 100 / \bar{M}_n(obs)$$

At very high CE/C ratio (4), the initiator efficiency was reduced to 62%. Experimental data are given in **Table 6.4**.

6.2.2.3 Effect of crown ether to catalyst ratio at low temperature(15⁰C)

GTP is not especially sensitive to temperature. Reaction may be performed below, at or above ambient, upto ~100⁰C. It is reported that unwanted side reactions increase with increasing temperature. On the contrary, induction periods increases with decreasing temperature.

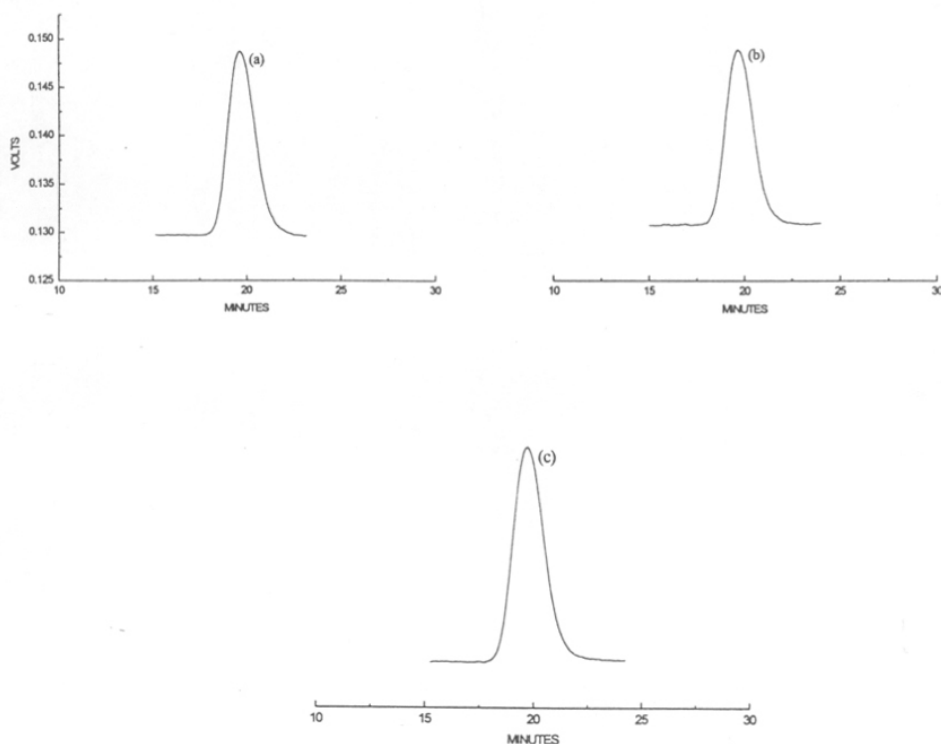


Fig. 6.6: SEC-RI for PMMA prepared at 15⁰ C using differnt CE/C ratio a) entry 1, Table 6.5 b) entry 2, Table 6.5 c) entry 3, Table 6.5

The GTP of MMA initiated by MTS in presence of KBB/ 18-C-6 was examined at 15⁰C with varying crown ether to catalyst ratio. However, no significant improvement in molecular weight control and polydispersity are observed (**Table 6.5, Fig. 6.6**).

Table 6.5: GTP of MMA using KBB/ 18-C-6 Catalyst at Low Temperature at 15⁰ C in THF (MMA = 0.047 mol, C₀ = 17.25x10⁻⁶ mol, I₀ = 3.4x10⁻⁴ mol)

Sr. No.	CE/C	Conv.%	$\bar{M}_n \times 10^{-3}$ SEC	\bar{M}_w / \bar{M}_n	I ^a _{eff}
1	1	100	19.0	1.38	82
2	2	100	19.5	1.34	78
3	4	100	18.9	1.34	82

a. I_{eff} = $\bar{M}_n(\text{cal}) \times 100 / \bar{M}_n(\text{obs})$

6.2.3 KINETICS OF GTP OF MMA USING ALKALI METAL BIBENZOATES/ CROWN ETHER COMPLEXES

A study of the kinetics of GTP of MMA with KBB/ 18-C-6 was undertaken. Kinetic experiments were performed in a specially designed apparatus (Chapter-III), which enabled addition of all components of a GTP in sequence at a constant temperature. The course of the reaction was followed gravimetrically. A typical time-conversion plot for both the catalysts is shown in Fig. 6.7.

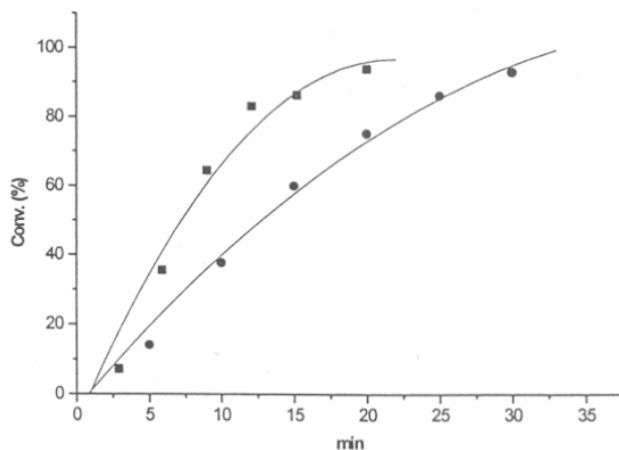


Fig. 6.7: Time vs. Conversion plots for the GTP of MMA: ■ = TBABB; ● = KBB/ 18-C-6

Appreciable induction period was observed in both the cases. As expected, the polymerization showed a first order dependence on monomer concentration.

6.2.3.1 Effect of catalyst concentration

We started our studies with the investigation of the dependence of reaction rates on catalyst concentration (Table 6.6). $[C]_0$ was varied from 2.21×10^{-4} to 8.87×10^{-4} mol/L (i.e. 1.79 to 7.72 mol% with respect to initiator concentration), all the other parameters being kept constant. Fig. 6.8 shows the first order plots for the conversion of monomer. In every case, low reaction rates are observed initially (induction period) followed by a rate increase in a linear manner. Finally, the rates decrease again, indicating the presence of termination reactions. The apparent rate constants were estimated from the maximum slope of the first-order time-conversion plots. Nevertheless, monomer conversion always was complete.

Fig. 6.9 shows a plot of $\ln k_{app}$ vs $\ln[C]_0$. Linearity is good with a slope of 0.45. This indicates the order of the reaction with respect to catalyst concentration.

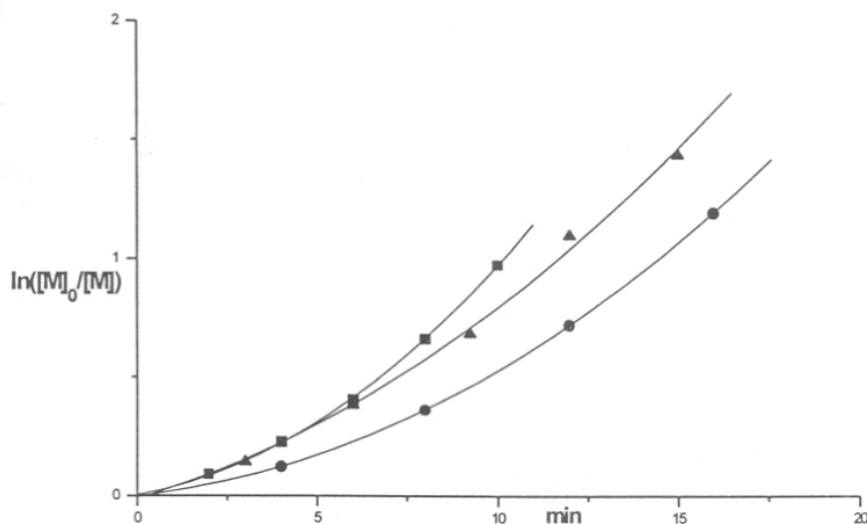


Fig. 6.8: First-order time-conversion plots for the GTP of MMA using KBB/ 18-C-6 catalyst as a function of catalyst concentrations. TBABB: ● = K-37; ▲ = K-43; ■ = K-26

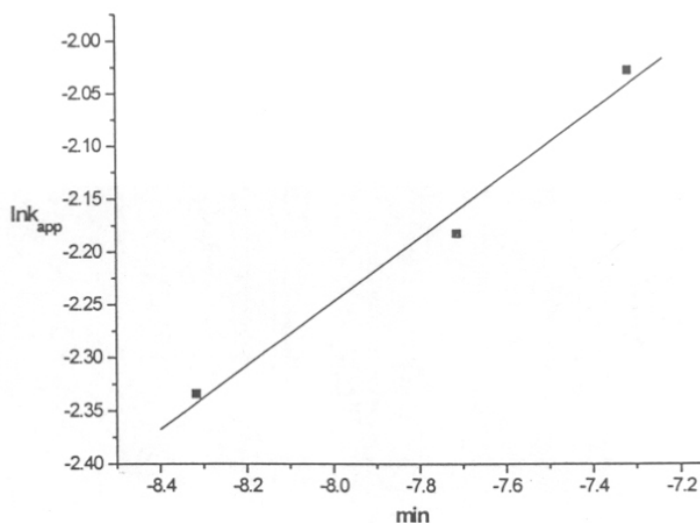
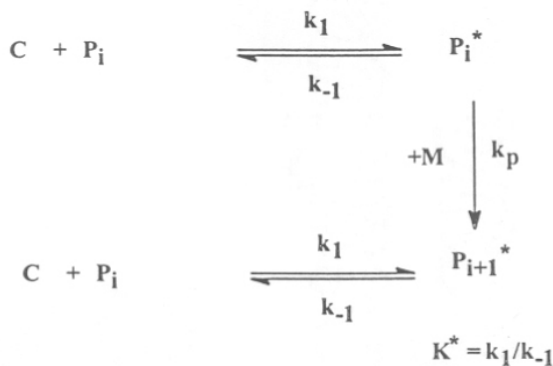


Fig. 6.9: Bilogarithmic plots of the apparent rate constants vs. Catalyst concentrations.

Table 6.6: Effect of Catalyst Concentration on the Rate of Polymerization at 25⁰C ([MMA]₀ = 1.17 M, [I]₀ = 1.23x10⁻² M, [M]₀/[I]₀ = 95, solvent : THF)

Run No	[C] ₀ × 10 ⁴ mol/L	[C] ₀ × 10 ² / [I] ₀	K _{app} min ⁻¹	Induction Period min
K-37	2.21	1.79	0.098	3.35
K-43	4.43	3.60	0.120	1.62
K-26	6.65	5.40	0.125	1.32
K-27	8.87	7.20	0.084	2.90

The rate order of catalyst varies depending on catalyst structure. **Scheme 6.1** implies a rate order of 1. This has been observed for TPS benzoate¹⁷. However, conflicting values of the rate order for TBA bibenzoate have been reported. Muller¹⁸ reported the expected value of 1 while Brittain¹⁷ reported a rate order of 0.3. Muller¹⁵ observed a first order dependence on bifluoride concentration. In contrast, Brittain¹⁷ found a second order dependence on bifluoride catalyst.



Scheme 6.1: Kinetic Scheme proposed by Muller et al.

Bandermann et al.³ has also observed a second order dependence on bifluoride catalyst. We have found a second order rate dependence on TBA bibenzoate catalyst (1.9) (Chapter-IV) and fractional order (0.45) dependence on KBB/ 18-C-6 complex catalyst system. These differing rate orders for catalysts reveal the complexity of GTP. Different concentration ranges may explain the difference.

6.2.3.2 Effect of initiator concentration

In a second set of experiments the influence of initiator concentration ($0.92 \times 10^{-2} < [\text{I}]_0$ mol/L $> 2.4 \times 10^{-2}$) on the rate of reaction was investigated (Table 6.7). Fig. 6.10 shows first-order time-conversion plots of these experiments. With increasing initiator concentrations, 'induction period' at the beginning of the reaction diminished.

Table 6.7: Effect of Initiator Concentration on the Rate of Polymerization at 25⁰C
 ([MMA]₀ = 1.17 M, solvent : THF)

Run No	[C] ₀ × 10 ⁴ mol/L	[I] ₀ × 10 ² mol/L	[C] ₀ × 10 ² / [I] ₀	[M] ₀ / [I] ₀	K _{app} min ⁻¹	Induction Period min
K-22	4.43	0.92	4.81	127	0.104	2.38
K-43	4.43	1.23	3.60	95	0.119	1.62
K-21	4.43	2.40	1.84	63	0.218	0.25

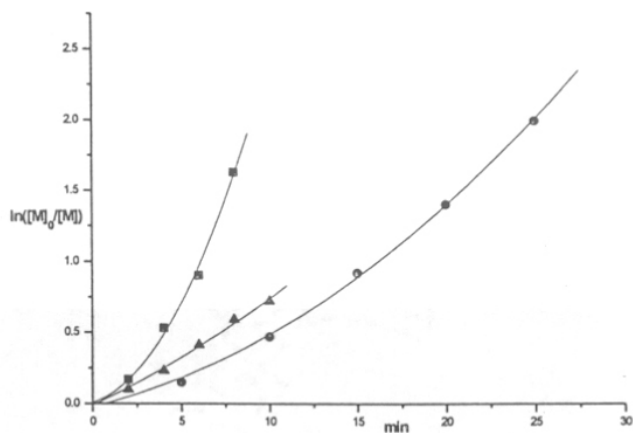


Fig. 6.10: First-order time-conversion plots for the GTP of MMA as a function of initiator concentrations: KBB/ 18-C-6: ● = K-22; ▲ = K-43; ■ = K-21

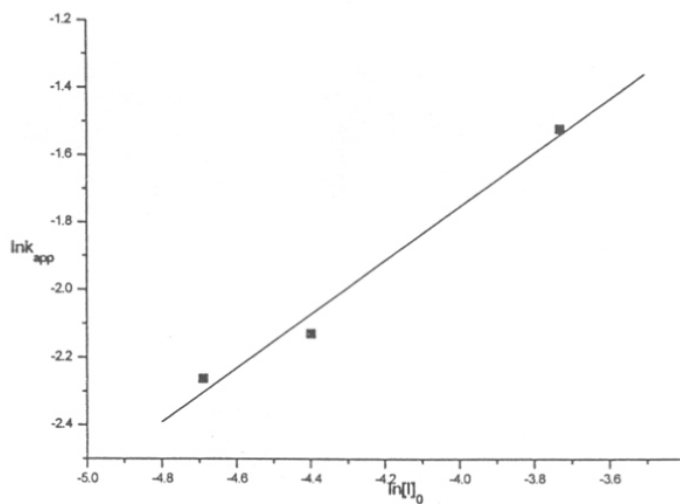


Fig. 6.11: Bilogarithmic plot of the apparent rate constant vs. Initiator concentrations.

Fig. 6.11 shows a plot of $\ln k_{app}$ vs $\ln [I]_0$. The slope of the curve (0.79) is the order of the reaction with respect to initiator concentration.

6.2.3.3 Effect of temperature

Kinetic experiments were conducted at temperatures, 15^o, 25^o and 35^oC. Fig. 6.12 shows time-conversion plots. Induction period was observed in all cases and it was more pronounced with decreasing temperature. For all the runs, the apparent rate constants were determined from the maximum slope the first order time-conversion plots. All these runs lead to complete monomer conversion.

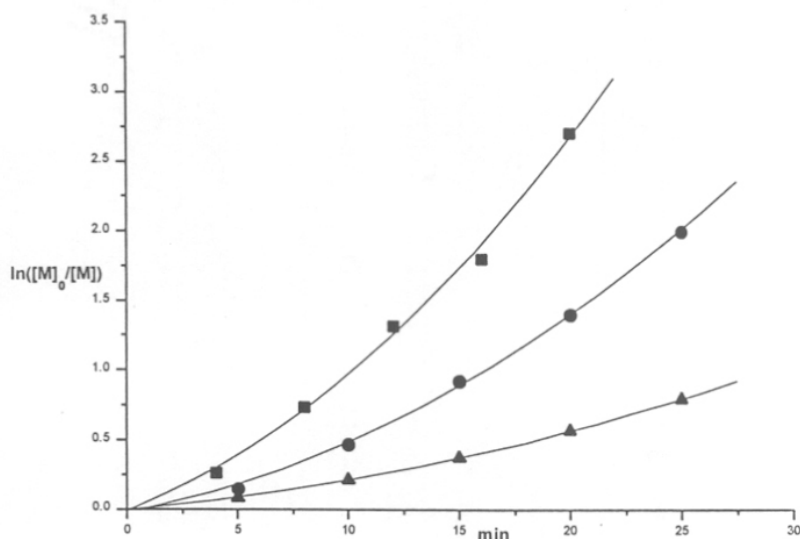


Fig. 6.12: First-order time-conversion plots for the GTP of MMA using KBB/ 18-C-6 catalyst as a function of temperatures. TBABB: ● = K-13; ▲ = K-12; ■ = K-14

Table 6.8: Effect of temperature on the rate of polymerization ($[MMA]_0 = 1.17$ M, $[I]_0 = 1.23 \times 10^{-2}$ M, $[M]_0/[I]_0 = 95$, solvent : THF)

Run No	T ^o C	$[C]_0 \times 10^4$ mol/L	$[C]_0 \times 10^2 /$ $[I]_0$	K_{app} min ⁻¹	Induction Period min
K-13	15	4.43	3.60	0.042	4.45
K-12	25	4.43	3.60	0.101	3.23
K-14	35	4.43	3.60	0.159	2.11

Fig. 6.13 shows the corresponding Arrhenius plot of $\ln k_{app}$ vs $1/T$. A linear plot is obtained giving an activation energy of $E_a = 56.6$ kJ/mol and a pre-exponential factor $\ln A = 20.1$.

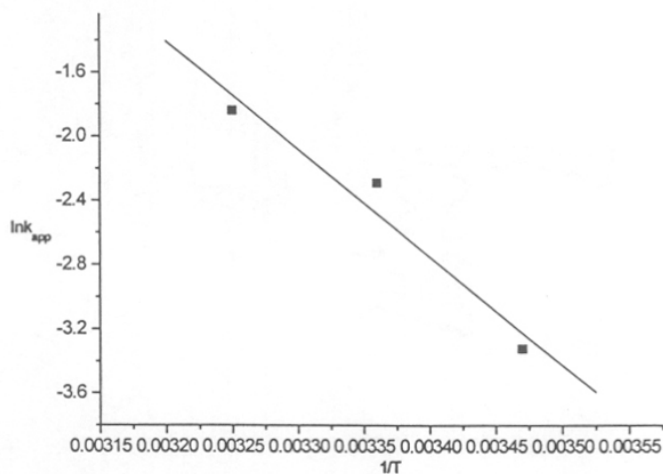
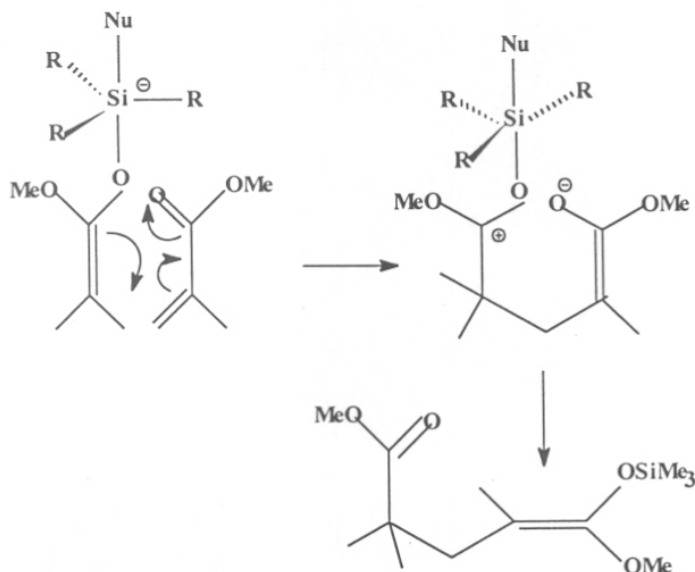


Fig. 6.13: Arrhenius plot for apparent rate constants in the GTP of MMA using KBB/ 18-C-6 catalyst

Muller et al.¹⁸ examined the temperature dependence of rate constants in THF using TASHF₂ for the GTP of MMA and tBMA. They determined the energy of activation (E_a) and frequency factor (A) from Arrhenius plots. For both monomers, the Arrhenius plots were linear indicating the existence of single active species during the polymerization.

The temperature dependence of the rate constants in THF using TBABB and KBB/ 18-C-6 catalyst system for the GTP of MMA was investigated. From this study, Arrhenius plots were constructed for the determination of the energy of activation (E_a) and frequency factor (A). For both catalysts, the Arrhenius plots were linear yielding direct evidence for the existence of single active species during the polymerization.

Based on the activation parameter, it was proposed by Muller et al.¹⁶ that monomer addition is more likely a two step process. The rate determining step is the addition of a vinyl group to the activated initiator or chain end. This is subsequently followed by the transfer of a silyl group to a newly formed enolate (Scheme 6.2).



Scheme 6.2: Mechanism of GTP proposed by Muller et al.

Table 6.9: Comparison of Energy of Activation and Frequency Factor using Different Catalysts

Catalyst	E_a (KJ/mol)	$\ln A$
TASHF ₂	18.04	6.66
TBABB	43.35	15.4
KBB/ 18-C-6	56.50	20.1

The values of the energy of activation determined using the catalysts TBABB and KBB/ 18-C-6 for the GTP of MMA were higher compared to the value determined by Muller et al.¹⁶ using TASHF₂ (Table 6.9). The higher value of activation energies for KBB/ 18-C-6 and TBABB relative to TASHF₂ may be a consequence of the weaker silicophilicity of the former.

6.2.3.4 Effect of monomer concentration

In order to determine reaction rate with respect to monomer concentration, $[M]_0$ was varied from 0.85 to 1.51 mol/L (Table 6.9). Fig. 6.14 shows first order time conversion plots. The plots are nonlinear initially due to induction period. Deviations from linearity observed at

the later stages of polymerization is likely indicating the presence of termination reactions. The extent of termination also depends on the initial monomer concentration. An increase of termination is observed for $[M]_0 < 1.51$ mol/L and $[M]_0 > 0.85$ mol/L rendering the

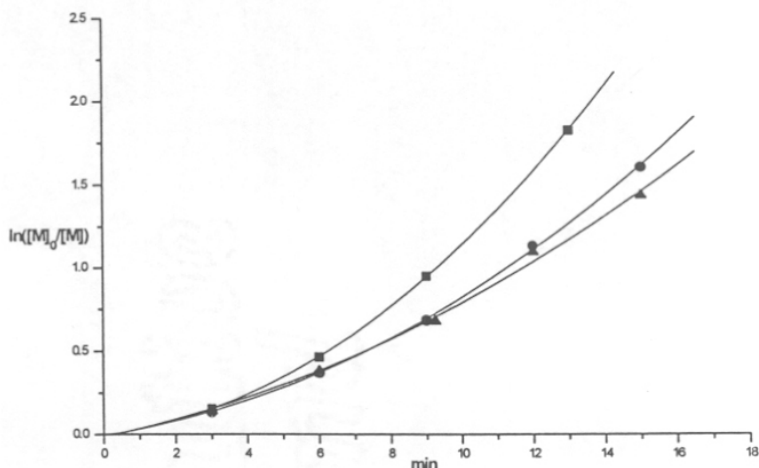


Fig. 6.14: First-order time-conversion plots for the GTP of MMA using KBB/ 18-C-6 as a function of monomer concentrations. TBABB: ● = K-38; ▲ = K-43; ■ = K-40

Table 6.10: Effect of Monomer Concentration on the Rate Constant
($[I]_0 = 1.23 \times 10^{-2}$ mol/L, solvent : THF)

Run No	$[M]_0$ mol/L	$[C]_0 \times 10^4$ mol/L	$[C]_0 \times 10^2$ / $[I]_0$	$[M]_0/$ $[I]_0$	K_{app} min^{-1}	Induction Period min
K-38	0.85	4.43	3.60	69	0.138	1.83
K-43	1.17	4.43	3.60	95	0.119	1.62
K-40	1.51	4.43	3.60	123	0.182	0.92

determination of initial slope, k_{app} , difficult and reducing its accuracy. The complex dependence of termination on monomer concentration may be the result of different coexisting termination mechanisms.

6.2.3.5 Molecular weight and molecular weight distribution

The molecular weight distributions of polymers prepared by GTP considerably depend on the mode of addition of reagents. The standard method introduced by DuPont group uses slow addition of monomer to a solution of initiator and catalyst and leads to polydispersity as low as 1.05. The actual monomer concentration is rather low.

In order to perform kinetic experiments it is favorable to add monomer in one batch. It was observed that addition of a monomer batch to a solution of initiator and catalyst leads to unsatisfactory kinetic results due to a deactivation of the initiator/catalyst system. Thus, a initiator solution was added to a premixed solution of monomer and catalyst. In these experiments the monomer concentration is high at the beginning and decreases with conversion.

When adding monomer in a batch the molecular weight distribution of the resulting polymers are broader than is expected ($\bar{M}_w/\bar{M}_n > 1.3$). Especially at low monomer conversions (i.e. high concentration of monomer) the polydispersity is very high ($\bar{M}_w/\bar{M}_n > 2$) (Fig. 6.15).

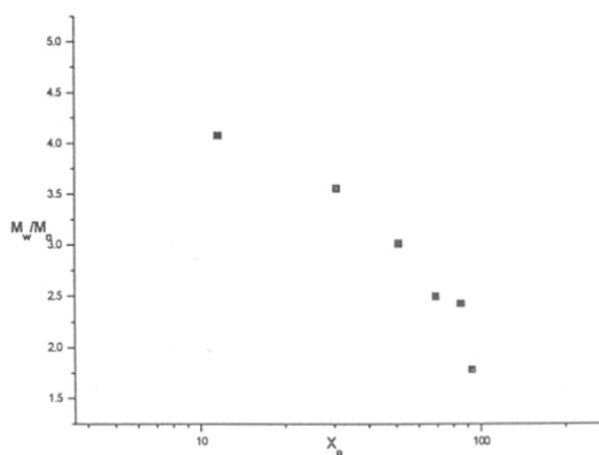


Fig. 6.15: Polydispersity as a function of monomer conversion in the GTP of MMA in THF using MTS initiator and KBB/ 18-C-6 catalyst (■)

Fig. 6.16 shows that a non-linear dependence of the number average degrees of polymerization vs conversion is observed. However, at complete monomer conversion the calculated and experimental degrees of polymerization usually agree within experimental error.

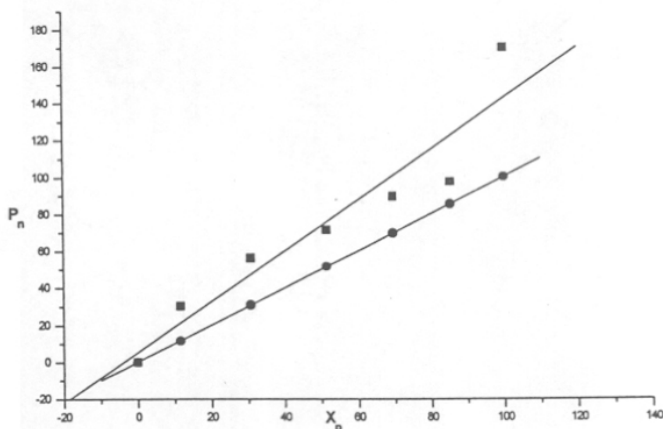


Fig. 6.16: Number average degree of polymerization as a function of monomer conversion in the GTP of MMA in THF using MTS initiator and KBB/ 18-C-6 catalyst: ● = P_n (calcd.), ■ = P_n (obs.)

In order to explain these observations it is necessary to take into account the rates of the equilibrium between dormant and activated polymers (or initiator) (Scheme 6.1).

The probability of a given activated chain to add monomer is

$$\rho = \frac{\text{rate of polymerization}}{\text{rate of deactivation}} = \frac{k_p \cdot [M] \cdot [P^*]}{k_{-1} \cdot [P^*]} = \frac{k_p \cdot [M]}{k_{-1}}$$

The number average degree of polymerization is given by

$$\rho = \frac{\text{number of polymerized monomers}}{\text{total number of polymerized chain}} = \frac{[M]_0 \cdot X_p}{[\text{Chains}]}$$

Thus, P_n/X_p is reciprocal to the actual total chain concentration at a given conversion X_p .

Two limiting cases can be discussed:

(a). fast exchange of catalyst
(low monomer concentrations):

$$k_{-1} \gg k_p \cdot [M] \\ [\text{Chains}] = [I]_0$$

$$P_n = \frac{[M]_0 \cdot X_p}{[I]_0} = P_{n,\text{th}}$$

(b). No exchange of catalyst
(high monomer concentrations)

$$k_{-1} \ll k_p \cdot [M] \\ [\text{Chains}] = [C]_0$$

$$P_n = \frac{[M]_0 \cdot X_p}{[I]_0} \gg P_{n,\text{th}}$$

As usually $[C]_0 \ll [I]_0$, the plot of P_n vs X_p will have a much higher slope for case (b) than that expected for case (a).

6.3 DISCUSSION

Potassium bibenzoate (KBB)/ 18-C-6 complex catalyzes GTP of MMA with quantitative conversion. However, KBB/ 18-C-6 catalyst system is characterized by a larger induction time, lower overall reaction rate, broader polydispersity and a lower initiator efficiency as compared to TBABB. Crown ether complexed metal salts from two types of species, namely, solvent separated ion pair and contact ion pair in a polar solvent like THF¹⁵. However, for larger cavity crown like 18-C-6 which allows the anion pairing from the axial sides, K^+ cation is forced to yield a contact ion pair for a delocalized anion¹⁵. Formation of contact ion pair decreases the nucleophilicity of anion which results in lowering of the reactivity of the catalyst. The significantly larger induction period observed with KBB/ 18-C-6 may be a consequence of the lower dissociation equilibrium of the bioxycyanion to the monoanion (eq. 6.1) or the lower silicophilicity of the carboxylate anion in case of KBB/ 18-C-6.



The molecular weight broadening in case of KBB/ 18-C-6 is associated with a significant low molecular weight tailing (Fig. 6.2) implying a lower rate of initiation compared to propagation. Additionally, in case of an alkali metal cation, competitive solvation of growing chain end by the alkali metal cation cannot be ruled out, resulting in cyclization as a result of Claisen reaction leading to low molecular weight oligomers.

To explore the role of the counteraction, Brittain measured the rate of polymerization of two salts having a common anion (TPS bibenzoate and TBA bibenzoate)¹⁷. It was concluded that the counteraction in GTP catalyst is not a significant contributor to overall reactivity, at least, when it is noncoordinating and the anion structure dominates the reactivity of the catalyst. However, our results shows that the overall rate of MMA polymerization is affected by the nature of the counteraction. These differences stem presumably from the existence of the catalyst exchange equilibrium¹⁵ (Scheme 6.1). The equilibrium constant (K^*) determines the concentration of the active centers and the apparent rate constant of propagation.

The scheme differs from the propagation step in anionic polymerization where generally only the right hand side has to be considered. In GTP, beside living chain ends dormant ones are present. Usually, catalyst concentration is much lower than initiator concentration. Thus only a small part of the polymer chains is active at a time, i.e. living chains are diluted by dormant ones. Catalyst molecules are exchanged through dynamic equilibrium (catalyst exchanged equilibrium). However, exact equilibrium constants cannot be determined because determination of molecular weights become complicated due to the presence of induction periods. Under these conditions, the first order rate constant for monomer consumption, is given by the formula:

$$\left(-\frac{1}{[M]_0} \frac{d[M]}{dt} \right) = k_{app} = \left(k_p \frac{K^* [I]_0}{1 + K^* [I]_0} \right) [C]_0 \quad (\text{eq. 6.2})$$

Rearranging we find, $1/k_{app} = 1/k_p [C]_0 + 1/k_p [C]_0 K^* .1/[I]_0$ (eq. 6.3)

By plotting $1/k_{app}$ vs $1/[I]_0$, the values of K^* and k_p can be determined from the abscissa and the ordinate, respectively. The equation is consistent with KBB/ 18-C-6 catalyst system giving a positive intercept, indicating $K^* \sim 20.88 \text{ M}^{-1}$, $k_p \sim 23.4 \text{ M}^{-1}\text{s}^{-1}$ or $1403.8 \text{ M}^{-1}\text{min}^{-1}$ (Fig. 6.17).

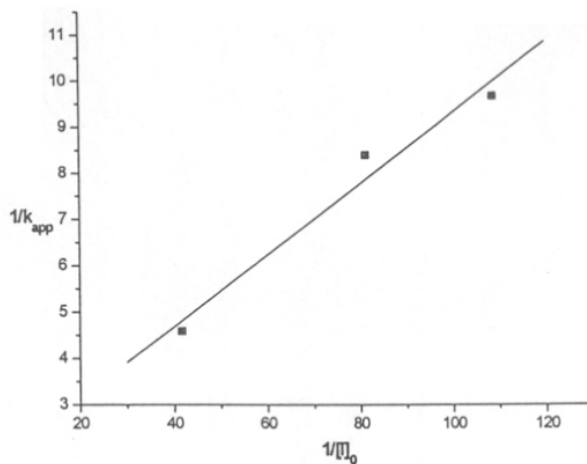


Fig. 6.17: Plots ($1/k_{app}$ vs. $1/[I]_0$) according to eq. 6.3 for estimation of k_p and K^*

6.4 CONCLUSIONS

Potassium bibenzoate in presence of 18-C-6 forms a soluble catalyst which activates the group transfer polymerization of methyl methacrylate in THF in presence of MTS as initiator. The alkali metal counteraction causes a reduction in the rate of the polymerization. The initiator efficiency is lower than that observed for a metal free counteraction, namely, tetrabutylammonium bibenzoate. Based on the observed kinetics, it is concluded that the bibenzoate ion associated with K^+ / 18-C-6 counteraction is a poorer silicophile causing a reduction in the rate of initiation.

6.5 REFERENCES

- 1 G.C.Eastmond, O.W.Webster, "New Methods of Polymer Synthesis", Ed. J.R.Ebdon, Blakie Glasgow 1992 ch.2.
- 2 D.Y.Sogah, W.R.Hertler, O.W.Webster G.M.Cohen, *Macromolecules*, **20**, 1473 (1987).
- 3 W.Schubert. H.Sitz and F.Bandermann,, *Macromol. Chem.*, **190**, 2193 (1989).
- 4 I.B.Dicker, G.M.Cohen, W.B.Farnham, W.R.Hertler, E.D.Lagnis and D.Y.Sogah, *Macromolecules*, **23**, 1473 (1990).
- 5 U.Schmalbrock and F.Bandermann, *Makromol. Chem.*, **194**, 2543 (1993).
- 6 R.P.Quirk and G.P.Bidinger, *Polym. Bull.*, **22**, 63 (1989).
- 7 S.Bywater, *Makromol. Chem. Macromol. Symp.*, **67**, 339 (1993).
- 8 O.W.Webster, *Makromol. Chem. Macromol. Symp.*, **67**, 339 (1993).
- 9 S-S.P.Choi and C-W.Niu, *MRL. BULL. Res. Div.*, **2**, 33 (1987).
- 10 J.Miller, A.D.Jenkins, E.Tsartolia, R.M.D.Walton, J.Stejskal and R.Kratochvi, *Polym. Bull.*, **20**, 247 (1988).
- 11 A.D.Jenkins and D.M.Morrison, *Makromol. Chem. Rapid Commun*, **12**, 653 (1991).
- 12 J.D.Citron, U.S.Pat. 4771116 to E.I.dupont de Nemours and Company; *Chem. Abstr.*, **110**, 76288k (1989).
- 13 W.J.Brittain, *Rubber Chem. Technol.*, **65**,580 (1992).
- 14 A.M.Bajaj and N.S.Poonia, *Coordination Chem. Rev.*, **87**, 55 (1988).
- 15 P.A.Mai and A.H.E.Muller, *Makromol. Chem. Rapid Commun.*, **8**, 99 (1987).
- 16 P.A.Mai and A.H.E.Muller, *Makromol. Chem. Rapid Commun.*, **8**, 247 (1987).
- 17 W.J.Brittain, *J.Am.Chem.Soc.*, **110**, 7440 (1988).
- 18 A.H.E.Muller, *Makromol. Chem. Macromol. Symp.*, **32**, 87 (1990).

CHAPTER VII

GROUP TRANSFER POLYMERIZATION OF N-PHENYL MALEIMIDE

7.1 INTRODUCTION

Group transfer polymerization (GTP) has been successfully used for the preparation of methacrylate polymers with precisely controlled molecular weights, polydispersities and macromolecular architectures¹⁻³. Sogah and coworkers³ have reported that GTP is useful for polymerization of acrylates, N,N-dimethyl acrylamide, acrylonitrile, methacrylonitrile and α -methylene- γ -butyrolactone. In general, poor molecular weight control and broad polydispersities have been reported for monomers other than methacrylate esters using GTP techniques with anionic catalysts. Thus, Lewis acids are preferred catalysts for acrylate polymerizations.

Vinyl monomers possessing one carbonyl group can be polymerized with appropriate GTP initiators and catalyst. However, relatively less is known regarding the polymerizability of monomers featuring 1,2-dicarbonyl substituted (e.g. N-phenyl maleimide) using GTP initiators⁴⁻⁶. Anionic polymerization of such monomers (N-phenyl or alkyl maleimides) have been reported in the literature⁷⁻⁹. Alkali metal tert-butoxide, Grignard reagents and organozinc halides as well as butyllithium can polymerize N-PMI. Insoluble polymer with low yield has been obtained in the polymerization of N-PMI using butyllithium initiator in THF. The polymerization initiated with potassium tert-butoxide in THF afforded poly(N-PMI) in quantitative yield with controlled molecular weight and narrow polydispersity. These results indicate that initiator of low basicity offers stable propagating species in the anionic polymerization of N-PMI.

In this chapter the results of homopolymerization of N-phenyl maleimide under different reaction conditions have been discussed.

7.2 RESULTS AND DISCUSSION

7.2.1 Homopolymerization of N-PMI

The GTP of N-PMI was carried out with both type of catalysts e.g. nucleophilic (TBABB, TBAF), electrophilic (ZnI_2 , $ZnBr_2$). The homopolymers obtained were yellow powders which were normally soluble in THF, dimethyl sulphoxide (DMSO), DMF and dichloromethane and insoluble in chloroform, ether, alcohol and hydrocarbon solvents. The polymers were characterized by 1H NMR, ^{13}C NMR, IR and SEC.

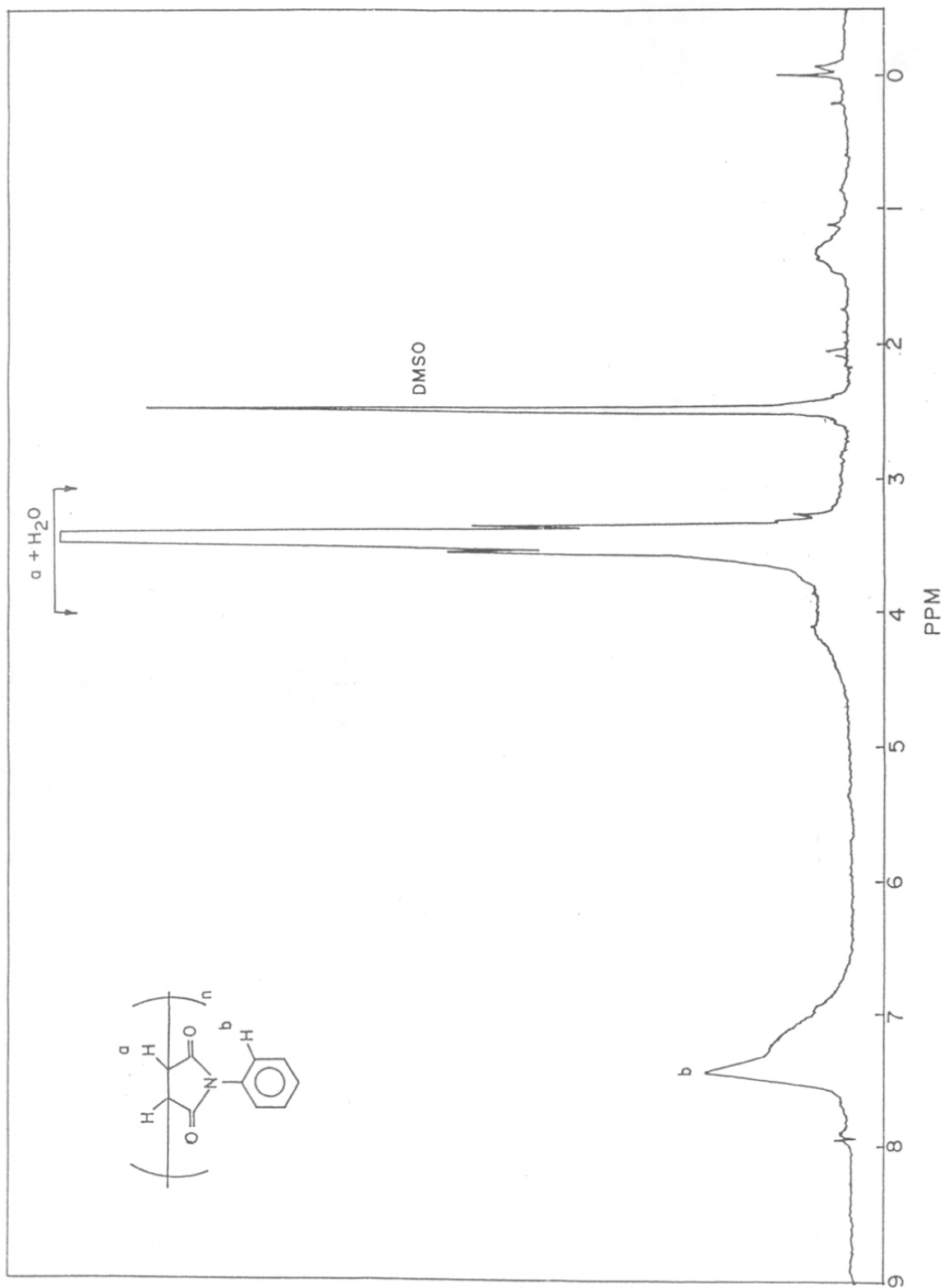


Fig. 7.1: ^1H NMR spectrum of poly(N-PMI) (Sr.No. 1, Table 7.1)

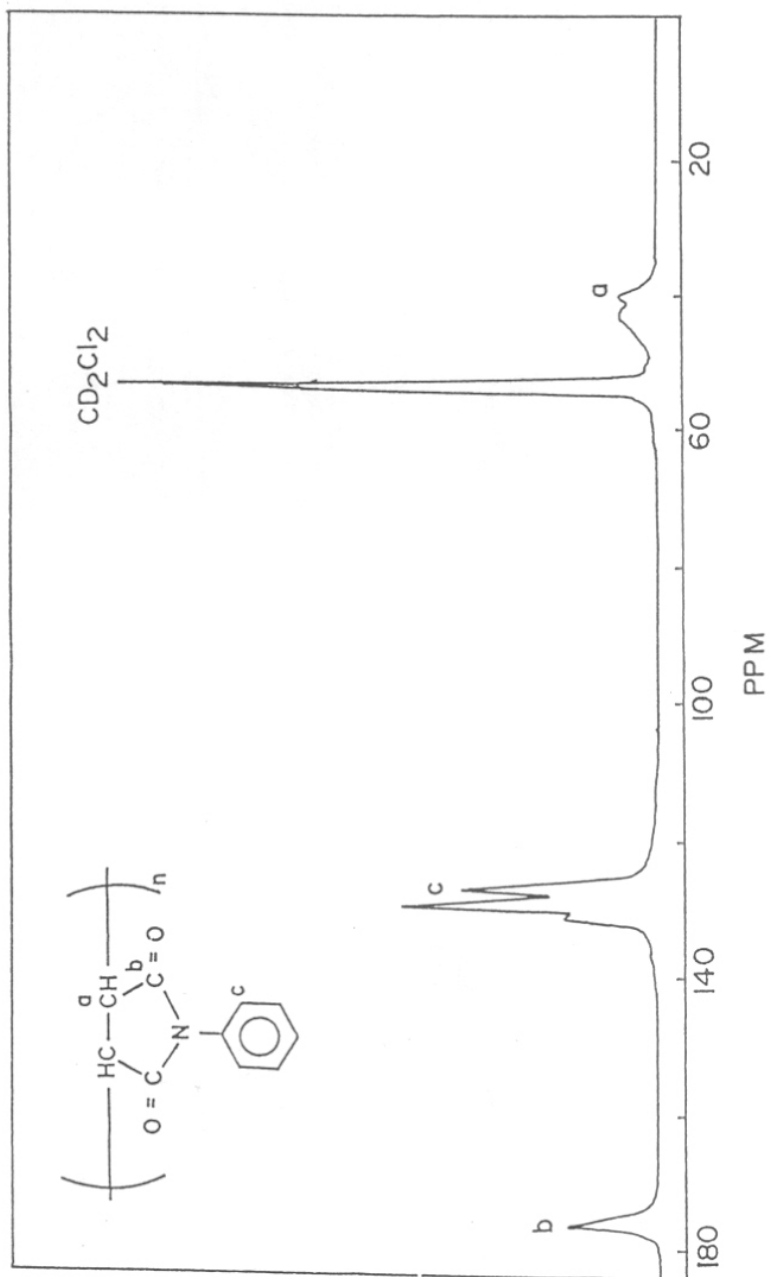


Fig. 7.3: IR spectrum of poly(N-PMI) (Sr.No. 1, Table 7.1)

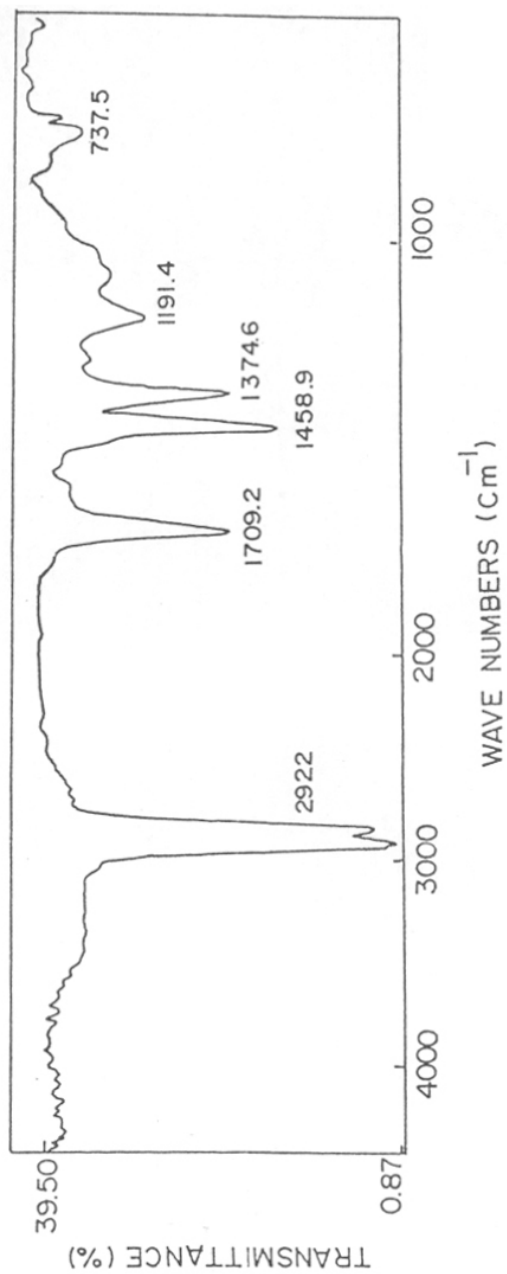


Fig. 7.2: ^{13}C NMR spectrum of poly(N-PMI) (Sr.No. 1, Table 7.1)

Fig. 7.1 shows a typical ^1H NMR spectrum of poly(N-PMI) prepared by GTP (Sr.No. 1, Table 7.1). The broad signal observed from 6.0 to 8.0 ppm is associated to phenyl protons. The methine protons in the polymer main chain appear at 3.0 to 5.0 ppm. The breadth of these signals is attributed to the stiffness of the main chain. Two peaks observed in the region at 1.0 to 1.75 ppm are due to the methyl protons of the initiator moiety.

Fig. 7.2 shows a typical ^{13}C NMR spectrum of poly(N-PMI) prepared by GTP(Sr.No. 1, Table 7.1). The signals assigned to the carbonyl and phenyl carbons of poly(N-PMI) are observed at 176.0 ppm and from 125.0 to 132.0 ppm respectively. The broadened signal from 38.0 to 48.0 ppm is assigned to the methine carbons in the polymer main chain. The broadening of the methine carbons reflects the complex microstructure of the main chain.

Fig. 7.3 shows a typical IR spectrum of poly(N-PMI) prepared by GTP(Sr.No. 1, Table 7.1). The absorption bands due to the imide ring are observed at 1709.2 (C=O), 1374.6 (C-N-C) and 1191.4 (C-N-C) cm^{-1} . The absorption bands assigned to the aromatic ring are observed at 2922 (CH), 1458.9 (C=C) and 737.5 cm^{-1} (monosubstituted). The strong ethylenic CH stretch at 840 cm^{-1} , which is the characteristic of N-PMI monomer, is absent, indicating that monomer and polymer have been effectively separated.

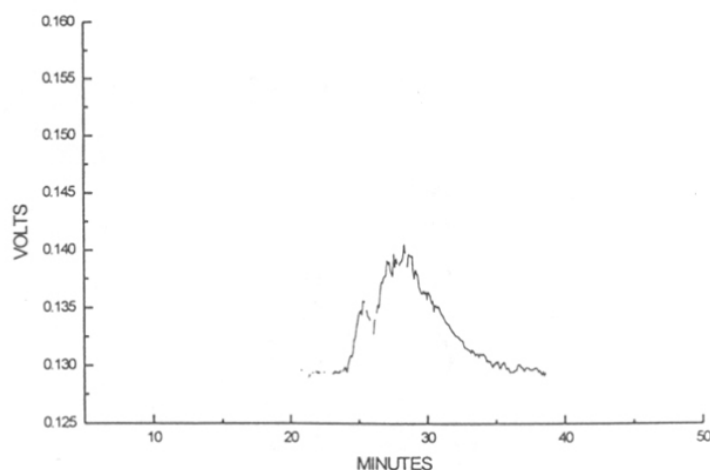


Fig. 7.4: SEC-RI for N-PMI polymer

Fig. 7.4 shows a typical SEC trace of poly(N-PMI) prepared by GTP (Sr.No. 1, Table 7.1). Narrow polydispersity could not be achieved under the experimental conditions attempted.

7.2.1.1 GTP of N-PMI using TBABB as catalyst and MTS as initiator

MTS in presence of TBABB catalyst initiated the GTP of N-PMI. Less than quantitative yield, poor molecular weight control and broad polydispersity have been observed in each polymerization experiment (Table 7.1). At higher molecular weight range, both molecular weight control and conversion were very poor.

The effect of catalyst concentration on conversion, polydispersity and molecular weight control was investigated. At high catalyst concentration (10 mol% based on initiator), the conversion was quantitative for low molecular weight polymer. However, there was no control on molecular weight and polydispersity was broad (4.0) (Sr.No. 4, Table 7.1).

Polymerization was conducted at different temperatures (-40°C to 25°C) (Table 7.1). Decreasing the polymerization temperature to -40°C caused a reduction in yield without improvement in molecular weight control or polydispersity. In all cases, irrespective of temperature and catalyst concentration, polymers showed broad polydispersity indicating significant deviation from the living polymerization conditions. This may be due to the fact that the rate of propagation is faster than the rate of initiation.

Table 7.1: GTP of N-Phenylmaleimide in THF

Sr. No.	$M_0 \times 10^3$ mol	$I_0 \times 10^4$ mol	$C_0 \times 10^6$ mol	Temp. $^{\circ}\text{C}$	Conv. %	\bar{M}_n Calcd.	\bar{M}_n SEC	\bar{M}_w / \bar{M}_n SEC
1	10.0	24.6	45.1	25	70	800	1,220	2.04
2	5.0	4.92	10.2	25	90	1,940	5,340	2.16
3	10.0	6.17	12.0	25	70	2,300	6,440	2.00
4	8.67	4.92	51.2	25	97	3150	1190	4.01
5	11.6	4.92	10.2	25	55	3,560	10,540	2.64
6	5.0	4.92	12.0	-10	63	1860	10,450	2.30
7	8.67	4.92	12.0	-40	30	3150	-	-

In order to obtain livingness as well as control over molecular weights for GTP of N-PMI, attempts have been made to make 1:1 adduct of initiator and monomer at various temperatures. Surprisingly, at all temperatures investigated, there was no 1:1 adduct formation, rather high molecular weight polymers were obtained.

Table 7.2: Effect of Temperature on 1:1 Adduct Formation ($M_0 = 8.7 \times 10^{-4}$ mol, $I_0 = 12.3 \times 10^{-4}$ mol, $C_0 = 13.2 \times 10^{-5}$ mol)

Sr. No.	Temp. °C	Conv. %	\bar{M}_n SEC	\bar{M}_w / \bar{M}_n SEC
1	25	50	3,220	2.94
2	0	40	3,640	2.56
3	-20	20	3,440	2.70

7.2.1.2 GTP of N-PMI using Lewis acid catalyst

Attempts were made to polymerize N-PMI by GTP using zinc bromide ($ZnBr_2$) as catalyst and MTS as initiator in dichloromethane at 25°C. Monomer addition was exothermic and temperature increased from 25°C to 30°C. Conversion was poor (< 30%) and the polymer was insoluble (Table 7.3). The inefficiency of $ZnBr_2$ as catalyst has been attributed due to its insolubility in CH_2Cl_2 .

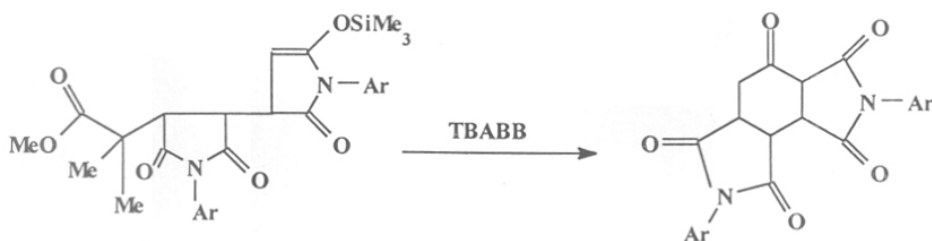
Table 7.3: GTP of N-Phenylmaleimide using $ZnBr_2$ Catalyst in CH_2Cl_2 at 25°C

Sr. No.	$M_0 \times 10^3$ mol	$I_0 \times 10^4$ mol	$C_0 \times 10^5$ mol	Conv. %
1	5.85	4.93	5.0	30
2	1.0	6.19	6.5	20

Experiments were carried out by dissolving $ZnBr_2$ in diethyl ether and using the conditions mentioned in Table 7.3. Under these conditions, the color of the reaction mixtures changed from light brown to purple. However, no polymers were obtained.

7.3 DISCUSSION

Saito et al⁵ reported GTP of N-PMI using MTS initiator and TBABB catalyst. They also synthesized the copolymers of MMA and N-PMI. In each case, polymer was obtained with incomplete conversion, uncontrolled molecular weight and broad polydispersity ($\bar{M}_w/\bar{M}_n > 2.0$). These observations lead to the conclusion that these polymerization reactions do not exhibit the characteristics of living polymerization. Raj et al⁶ also presented similar results. The results of the present study are also similar to those reported by other authors. Incomplete conversion can be attributed to termination reactions. A probable termination reaction is cyclization of chain end as shown in **Scheme 7.1**.



Scheme 7.1: Cyclization of chain end in the GTP of N-PMI

The reason for broad polydispersity is due to the faster rate of propagation compared to initiation. To avoid induction periods, attempts were made to prepare 1:1 adduct of initiator and monomer at different temperatures. However, all the reactions resulted only in polymer and no adduct could be isolated. In order to suppress the rate of propagation as well as termination, livingness enhancer, namely, trimethylsilyl benzoate, was used in the polymerization. Surprisingly, the resulting polymers were insoluble. THE observed behavior of N-PMI in GTP can be best understood in terms of the relative basicity of the initiating and propagating enol ethers. The silyl enol ether derived from N-PMI is significantly more basic, because of the conjugation with both an oxygen and a nitrogen atom. Consequently propagation rates are much faster than initiation.

7.4 REFERENCES

- 1 O.W.Webster, W.R.Hertler, D.Y.Sogah, W.B.Farnham and T.V.Rajanbabu, *J.Am.Chem.Soc.*, **105**, 5706 (1983).
- 2 W.J.Brittain, *Rubber Chem.Technol.*, **65**, 580 (1992).
- 3 D.Y.Sogah, W.R.Hertler, O.W.Websterand G.M.Cohen, *Macromolecules*, **20**, 1473 (1987).
- 4 A.Saito and D.A.Tirrel, *Polym.Prepr. (Am.Chem.Soc., Div.Polym.Chem.)*, **34(1)**, 152 (1993).
- 5 A.Saito and D.A.Tirrel, *Polym.J.*, **26**, 169 (1994).
- 6 D.J.A.Raj, B.B.De and S.Sivaram, "Polymer Science Recent Advances", I.S.Bhardwaj Eds., p294 (1994).
- 7 T.Hagiwara, J.Mizota, H.Hamana and T.Narita, *Makromol.Chem., Rapid Commun.*, **6**, 169 (1985).
- 8 T.Hagiwara, M.Takeda, H.Hamana and T.Narita, *Makromol.Chem.,Rapid Commun.*, **8**, 167 (1987).
- 9 T.Hagiwara, T.Shimizu, T.Someno, T.Yamagashi, H.Hamana and T.Nortia, *Macromolecules*, **21**, 3324 (1988).

CHAPTER-VIII

SUMMARY AND CONCLUSIONS

SUMMARY AND CONCLUSIONS

Group transfer polymerization (GTP) has been successfully employed for the synthesis of poly(alkyl methacrylate). MMA was purified by the treatment of triisobutyl aluminium and subsequent distillation under vacuum (10^{-3} mmHg). PMMA of molecular weight upto 60,000 has been synthesized with good molecular weight control and narrow polydispersity ($\bar{M}_w/\bar{M}_n = 1.25$). Attempts to purify BMA and LMA by similar method proved unsuccessful. Therefore, a search for an alternate purification technique was initiated. Bis(dimethylamino)dimethylsilane, in presence of a nucleophilic catalyst such as tetrabutylammonium fluoride (TBAF) is reported to react efficiently with moisture and alcohol. Hence, it was decided to use BDMAS/ TBAF system as a scavenger for the impurities present in higher alkyl methacrylate monomers. This purification system enables us to prepare PBMA and PLMA upto 30,000 molecular weight with good molecular weight control and narrow polydispersity ($\bar{M}_w/\bar{M}_n = 1.25$). Attempts to prepare higher molecular weight causes loss of molecular weight control.

GTP is the only potential synthetic method for preparing narrow polydispersity random and block copolymers of MMA and LMA because LMA has low solubility in THF below room temperature. Random polymer of molecular weight $\sim 50,000$ with narrow polydispersity ($\bar{M}_w/\bar{M}_n = 1.20$) have been synthesized in quantitative conversion over a wide composition range (LMA content = (20-80) mol%). Block copolymers were prepared by sequential monomer addition technique. Living PLMA chains, prepared in the presence of trimethylsilyl benzoate (livingness enhancer), initiated the block copolymerization of MMA. Presence of trimethylsilyl benzoate in the system increased the livingness of the chain end by complexing with the catalyst and providing a means of supplying it continuously at low concentration. This effect has been observed from the extent of molecular weight control and polydispersity of both the initial PLMA block and the final copolymer ($\bar{M}_w/\bar{M}_n = 1.15$). The same polymer synthesized without trimethylsilyl benzoate showed bimodal distribution ($\bar{M}_w/\bar{M}_n = 2.0$).

The determination of absolute molecular weights of copolymers by SEC is difficult because of the lack of appropriate samples for calibration of the column. Use of SEC/ MALLS

technique has been made to determine the absolute molecular weights of random and block copolymers of MMA and LMA.

The relative reactivities of MMA and LMA were also determined. The polymerization reactions were quenched after a short period of time to restrict the conversion below 20% and the composition of the copolymers were determined by ^{13}C NMR. Monomer reactivity ratios were determined according to the method of Kelen and Tudos (r_1 (MMA) = 1.38 ± 0.11) and r_2 (LMA) = 0.68 ± 0.10).

^{13}C NMR spectra of methyl methacrylate (M)-lauryl methacrylate (L) copolymers were analyzed in terms of sequence distribution and relative stereochemical configuration of monomer units along the macromolecular chains. The values of concentration of M- and L-centered triads, determined experimentally from the analysis of $\alpha\text{-CH}_3$ and C=O resonance signals, were in good agreement with those calculated statistically, taking into consideration the terminal copolymerization model and Bernoullian distribution of stereoregularity, with the statistical parameters P_{ij} determined from the reactivity ratios and coisotacticity parameters $\sigma_{\text{MM}} = 0.52$, $\sigma_{\text{LL}} = 0.52$, $\sigma_{\text{ML}} = \sigma_{\text{LM}} = \sigma^* = 0.30$.

Potassium bibenzoate (KBB) in presence of 18-C-6 catalyzes the GTP of MMA at room temperature using MTS initiator. Polymerization proceeds to quantitative conversion with good molecular weight control and relatively broader polydispersity ($\bar{M}_w/\bar{M}_n = 1.40$). The effect of catalyst concentration, crown ether to catalyst ratio, temperature etc. on the polydispersity have been studied. The lowest polydispersity value ($\bar{M}_w/\bar{M}_n = 1.25$) was obtained at catalyst concentration of 5 mol% based on the initiator concentration.

To understand the role of counteranions in the GTP of MMA, kinetic studies were conducted using KBB/ 18-C-6 and TBABB catalysts under identical conditions. Lower rate constants and higher induction periods were observed for the reactions catalyzed by KBB/ 18-C-6 compared to TBABB catalyst. Fractional orders of reaction were obtained with respect to catalyst concentration (0.45) and initiator concentration (0.79) for KBB/ 18-C-6 catalyst system. In case of TBABB, the orders of the reaction with respect to catalyst and initiator concentration were 1.91 and 2.0 respectively. Reaction rates were also measured at different temperatures and Arrhenius plots were constructed. The value of activation energies were determined as 56.0 KJ/mole and 42.3 KJ/mole for KBB/ 18-C-6 and TBABB

catalyst respectively. The higher value of activation energy may be a consequence of the weaker silicophilicity of the former.

GTP of N-phenyl maleimide has been carried out using MTS initiator and TBABB catalyst in THF at room temperature. These reactions do not exhibit the characteristics of living polymerization. Incomplete conversion, poor molecular weight control and broad polydispersities were observed.

In conclusion, purification method involving BDMAS in presence of TBAF allows to prepare homopolymers and copolymers of higher alkyl methacrylates ($C > 2$) with superior control on molecular weights and narrow polydispersities of $\bar{M}_n = 30-50,000$. Use of 'livingness enhancer', namely, trimethylsilyl benzoate improved the molecular weight control and polydispersity of initial PLMA and final block copolymer of MMA and LMA prepared by GTP using TBABB catalyst and MTS initiator. The reactivity ratios of MMA and LMA were determined as $r_1(\text{MMA}) = 1.38 \pm 0.11$ and $r_2(\text{LMA}) = 0.68 \pm 0.10$ under GTP conditions. Triad sequence distributions and relative stereochemical configuration of monomer units along the macromolecular chain determined from the analysis of $\alpha\text{-CH}_3$ and C=O resonance signals follow Bernoullian distribution of stereoregularity.

Potassium bibenzoate in presence of 18-C-6 can catalyze the GTP of MMA in THF at room temperature using MTS initiator. Low initiator efficiency and broad polydispersity were observed for polymers prepared using KBB/ 18-C-6 catalyst compared to those prepared using TBABB catalyst. Kinetic studies indicate a lower silicophilicity of the bibenzoate anion associated with K^+ / 18-C-6 compared to bibenzoate ion associated with TBA^+ . This causes a reduction in the rate of initiation.

Scope for Future Work

The present study has identified a number of new areas of research which may be very fruitful. The major areas which deserve further attention are highlighted below.

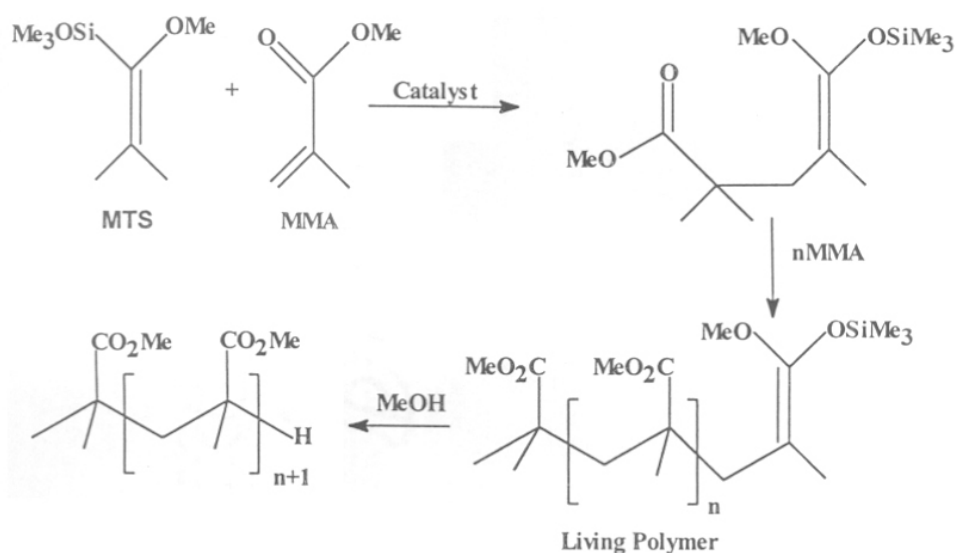
- a. Further in depth studies are necessary to elucidate the role of 'livingness enhancer' with a wide variety of catalysts and its applicability to the synthesis of newer block copolymers.
- c. Block copolymers of MMA and LMA have been synthesized over a wide composition range. Further studies are necessary to characterize its solution and rheological properties.
- d. Additional kinetic studies of GTP are necessary, particularly, with varying the mole ratio of initiator to catalyst. It may be possible to define, for a selected catalyst, the region in which the rate of monomer addition is no longer the rate determining step.
- e. Kinetics of the GTP of various alkyl acrylate monomers to elucidate the role of Lewis acid catalysts and define a connecting GTP mechanism for nucleophilic and electrophilic catalysts needs to be examined.
- f. Some preliminary experiments have been carried out using N-phenyl maleimide (N-PMI) monomer. More detail studies to establish living polymerization of this monomer by GTP are necessary through judicious selection of catalyst and initiator.

SYNOPSIS

The thesis entitled “Group Transfer Polymerization of Alkyl (meth)acrylates” consists of seven chapters and chapter VIII summarizes the work reported in the thesis.

Introduction

Group transfer polymerization (GTP), discovered in 1983, represents a new method for controlled synthesis of complex macromolecular structures¹⁻³. GTP is based on the fact that silyl ketene acetals can be activated by nucleophilic catalysts to undergo a Michael addition reaction with methacrylates. The reaction regenerates the silyl ketene acetals at the chain end; iteration of the process leads to the polymer (Scheme 1).



Scheme 1

Although the GTP method works best for methacrylates, other monomers such as acrylates, acrylonitrile, maleimide and vinyl ketones can be polymerized. This technique gives “living” polymers (controlled Mw, narrow molecular weight distribution and chain ends capable of further growth upon the addition of additional monomer) at room temperature. The “living” nature of the GTP chain ends offers a potentially useful method for the synthesis of a variety of methacrylate polymers with controlled structures and architectures. Examples are block copolymers⁴, macromonomers⁵, telechelics⁶, end functionalized polymers⁷, star-branched polymers⁸ and graft polymers⁹.

The nature of the catalyst plays an important role in determining the rate of polymerization and polymer molecular weight distribution. Incomplete monomer conversion and higher polydispersities are obtained when high catalyst concentrations are used. Typically less than 0.1 mol% based on the initiator is recommended. Apart from its effect on the rate of polymerization, it is proposed that the catalyst also affects the mechanism of polymerization. Weak nucleophiles such as HF_2^- , bibenzoate etc. presumably catalyze GTP by an “associative” mechanism whereas strong nucleophiles such as acetate, methyl fluorenides etc. catalyzed GTP by “dissociative” mechanism^{10,11}. The present investigation has been undertaken with a view to understand some of the features of GTP as described below.

a. There are a numbers of reports in the literature on the random and block copolymers of MMA with higher alkyl methacrylates¹. However, the copolymerization of MMA with LMA has not been systematically examined. Copolymers of LMA exhibit interesting properties on account of its comb like structures. Controlled synthesis of such copolymers are not possible by anionic technique since LMA has limited solubility in solvents such as THF below 0°C. Living anionic polymerization of alkyl methacrylates is only feasible at very low temperatures, typically below -58°C. GTP is the only potential method for accessing narrow molecular weight distribution random and block copolymers of MMA and LMA. Thus, a study aimed at synthesis of copolymers of LMA and MMA, over a wide composition range using GTP was undertaken.

b. The associated counteranions with the nucleophiles are generally large with diffuse charge. Example are tris(dimethylamino)sulfonium (TAS)³, tris(piperidinio)sulfonium (TPS)³ or tetraalkylammonium (R_4N^+)³. Alkali metal cations have been less studied in GTP. In early studies KHF_2 was examined as catalyst; however, in view of its insolubility in THF, solvents such as acetonitrile or DMF had to be used. Acetonitrile has since been shown to have an unfavorable effect on GTP as it reacts with the initiator and the active chain ends. To improve the solubility of these salts in the preferred solvent, namely THF, complexation with crown ethers or ethylene glycol are resorted to. In view of the proven success of tetrabutyl ammonium bibenzoate as a GTP catalyst, we undertook a study of potassium bibenzoate as GTP catalyst. To promote solubility, this catalyst was used in presence of 18-crown-6. The features of the polymerization using this catalyst was elucidated.

c. In addition to acrylates and methacrylates, GTP has been used to polymerize acrylonitrile, methacrylonitrile, N,N-dimethyl acrylamide and substituted lactones. In general, poor control and broad molecular weight distributions are reported for monomers other than methacrylic esters using GTP techniques with anionic catalysts. However, relatively less is known regarding the polymerizability of monomers containing 1,2-dicarbonyl groups (e.g. maleimides) using GTP initiator. Therefore, a study of polymerization of N-phenyl maleimide using group transfer initiators was undertaken.

Objectives of the present investigation

a. The present study is aimed at examining the possibility of synthesizing high molecular weight random and block copolymers of LMA and MMA over a wide composition range. Another objective of this work is to study the relative reactivity of the two monomers under GTP conditions.

b. The objective of this work is to study the role of counterions other than quaternary ammonium ions on the rate, molecular weight control, conversion and polydispersity in the GTP of MMA.

This approach also enabled a comparison between GTP and classical anionic polymerizations. Recently Teyssie and coworkers¹² showed that diphenyl methyl sodium, complexed with dibenzo-18-crown-6, showed the living characteristics in toluene at a temperature as high as 0°C. Therefore, in both the process, namely GTP catalyzed by potassium benzoate/18C6 and anionic polymerization initiated by diphenyl methyl sodium/DB-18C6, an alkali metal cation solvated by a bulky crown ether could be the counterion.

c. The objective of this work is to synthesize homopolymer of NPM under GTP conditions and copolymers with MMA.

Chapter I

This chapter provides a detailed survey of the literature on Group Transfer Polymerization.

Chapter II

The objective and scope of the present investigation is described in this chapter.

Chapter III

This chapter contains information regarding the source of materials used, general purification methods for the reagents, methods for preparation of catalysts, homo- and copolymerization techniques and general characterization techniques.

Chapter IV

This chapter deals with the homopolymerizations of alkyl methacrylates (MMA, BMA, LMA etc.) in THF using GTP initiator, MTS and TBABB as catalyst. The reaction rate decreases with increasing size of the substituted alkyl group. To understand the influence of parameters, namely, catalyst concentration, initiator concentration, monomer concentration and temperature, kinetics of polymerizations have been studied varying one parameter at a time.

Chapter V

This chapter deals with the synthesis of random and block copolymers of MMA and LMA using GTP initiator, MTS and TBABB catalyst at room temperature over a wide composition range [LMA (20-80) mol%]. To understand the effect of livingness enhancer (trimethylsilyl benzoate) polymerization has been carried out with and without livingness enhancer. Reactivity ratios are calculated according to the Kelen-Tudos method. Molecular weights are determined by SEC using RI detector and PMMA standard. To determine the absolute molecular weight by SEC using MALLS detector, dn/dc values are measured. Compositions of the monomers in the copolymers are determined by 1H NMR.

Chapter VI

This chapter deals with the GTP of MMA using potassium bibenzoate/18-crown-6 complex catalyst and MTS initiator in THF at room temperature. The molecular weight distributions have been found broad (1.40) in comparison to the polymer prepared using TBABB catalyst. The influence of catalyst concentration, crown ether to catalyst ratio and

temperature on the molecular weight distribution has been examined. To get deeper insight in the polymerization of MMA catalyzed by KBB/ 18-C-6, kinetics studies are carried out with respect to catalyst concentration, initiator concentration, monomer concentration and temperature.

Chapter VII

This chapter deals with the investigation of group transfer polymerization of N-phenyl maleimide using MTS initiator. The reactions are very fast when anionic catalysts are used in THF. Thus, these polymerizations are carried out in presence of $ZrBr_2$ (Lewis acid) in CH_2Cl_2 .

Chapter VIII

This chapter summarizes the results and describes the salient conclusions of the investigations reported in the thesis.

a. Random and block copolymers of LMA and MMA with \bar{M}_n in the range of 50,000 and with narrow molecular weight distributions (1.02-1.10) are successfully synthesized over a wide composition range. The absolute molecular weights of random and block copolymers are higher by a factor of 1.1-1.4 relative to the targeted molecular weights. A lesser degree of control over molecular weights is observed when LMA content is higher in the monomer feed ratio, implying impurities present in LMA. Use of livingness enhancer, namely, trimethylsilyl benzoate improve the molecular weight control and molecular weight distribution of the homo PLMA and the final block copolymer. The r_1 and r_2 values of LMA and MMA are as $r_1(\text{MMA}) = 1.38 \pm 0.11$ and $r_2(\text{LMA}) = 0.68 \pm 0.10$.

b. Potassium bibenzoate in presence of 18-C-6 catalyzes the GTP reaction. Catalyst concentration influences the molecular weight distribution of PMMA. The lowest polydispersity value (1.25) is obtained at a catalyst concentration of 5 mol% based on the initiator concentration. Kinetic investigation show fractional order dependence of reaction rate with respect to catalyst concentration (0.45) and initiator concentration (0.75). This implies association of the catalyst with the propagating center. The Arrhenius energy of activation is found to be 56.28 KJ/mole.

c. NPM can be polymerized by GTP initiators and incorporated into the statistical copolymer with MMA. These reactions do not exhibit the characterizations of living polymerizations. Thus, incomplete conversion, poor molecular weight control and broad molecular weight distributions are obtained .

References

- 1 G.C.Eastmond and O.W.Webster, "New Methods of Polymer Synthesis," Ed. J.R.Ebdon, Blackie, Glasgow, chap.2, p.23 (1992).
- 2 O.W.Webster and B.C.Anderson, "New Methods for Polymer Synthesis," (Ed. W.J.Mijs) Plenum press: New York, chap.1, p1 (1992).
- 3 W.J.Brittain, *Rubber Chem.Technol.*, **65**, 580 (1992).
- 4 O.W.Webster, W.R.Hertler, D.Y.Sogah, W.B.Farnham and T.V.Rajanbabu, *J.Am.Chem.Soc.*, **105**, 5706 (1983).
- 5 D.Y.Sogah and O.W.Webster, *J.Polym.Lett.Ed*, **21**, 927 (1983).
- 6 K.Steinbretch and F.Bandermann, *Makromol.Chem.*, **190**, 2183 (1989).
- 7 R.P.Quirk and J.Ren, *Makromol.Chem.Macromol.Symp.*, **88**, 17 (1994).
- 8 J.A.Simms, *Rubber Chem.Technol.*, **64**(2), 139 (1991).
- 9 J.A.DeSimone, A.M.Hellstern, E.J.Siochi, S.D.Smith, T.C.Ward, P.M.Gallenger, V.J.Krukonis and J.E.McGrath, *Makromol.Chem.Macromol.Symp.*, **32**, 21 (1990).
- 10 S.Bywater, *Makromol.Chem.Macromol.Symp.*, **67**, 339 (1993).
- 11 O.W.Webster, *Makromol.Chem.Macromol.Symp.*, **67**, 365 (1993).
- 12 S.K.Varshney, R.Jerome, P.Bayard, C.Jacob, R.Fayt and P.Teyssie, *Macromolecules*, **25**, 4457 (1992).

LIST OF PUBLICATIONS

- 1 Group Transfer Polymerization of Methyl methacrylate Catalyzed by Potassium Bibenzoate/ 18-Crown-6 Complexes.
B. Sannigrahi, P. P. Wadgaonkar, J. C. Sehra and S. Sivaram
Polymer Science, Recent Advances, I.S.Bhardwaj (editor), 1994,1,p.124
- 2 Copolymerization of Methyl methacrylate with Lauryl methacrylate using Group Transfer Polymerization.
B. Sannigrahi, P.P. Wadgaonkar, J.C. Sehra and S. Sivaram
J.Polym.Sc., Polym.Chem.Ed. (in press)
- 3 Kinetics of Group Transfer Polymerization of Methyl methacrylate using Potassium Bibenzoate/18-Crown-6 Complexes.
B. Sannigrahi and S. Sivaram
Macromolecular Chemistry and Physics (Communicated)
- 4 Microstructural Analysis of Methyl methacrylate--Lauryl methacrylate Copolymers using ^{13}C Nuclear Magnetic Resonance Spectroscopy.
B. Sannigrahi and B. Garnaik
Macromolecules (Communicated)
- 5 Group Transfer Polymerization: A Critical Review
B. Sannigrahi and S. Sivaram
J.Macromol.Sci. (Rev. Macromol. Chem. Phys.) (Communicated)