SOME STUDIES OF THE EMULSION COPOLYMERISATION OF VINYL ACETATE AND ETHYL KETHACRYLATE.

BY

AKPAN JOHN UMOUDOH

A THESIS SUBMITTED TO THE POSTGRADUATE SCHOOL, AHMADU BELLO UNIVERSITY, IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE AWARD OF DEGREE OF MASTER OF SCIENCE IN POLYMER SCIENCE AND TECHNOLOGY

DEPARTMENT OF CHEMISTRY,
FACULTY OF SCIENCE,
AHMADU BELLO UNIVERSITY,
ZARIA - NIGERIA.

SEPTEMBER, 1989

DECLARATION

I hereby declare that this thesis has been written by me and it is a record of my own researchwork. It has not been presented in any previous application for a higher degree. All sources of information are specifically acknowledged by means of references.

Akpan John Umoudoh.

CERTIFICATION

This thesis entitled, "Some Studies on the Emulsion Copolymerisation of vinyl acetate and Ethyl methacrylate by UMOUDOH, AKPAN JOHN meets the regulation governing the award of the degree of Master of Science in Polymer Science and Technology of Ahmadu Bello University and is approved for its contribution to scientific knowledge and literary presentation.

Professor J.Y. Olayemi
Chairman, Supervisory Committee
and Head of Department.

Date.

Dr. O. A. Peters
Member, Supervisory Committee

Date

Dr. F. Okieimen
External Examiner

Date

Professor D. I. Saror
Dean, Postgraduate School.

6-9-90
Date

DEDICATION

To none, but the Almighty God who has given me this opportunity in life.

ACKNOWLEDGEMENT

In acknowledging the contributors for the accomplishment of this work, my first and foremost gratitude goes to my Supervisor, Professor J.Y. Olayemi. I am indebted to him not only for initiating this research work but also for scholarly advice and guidance throughout the period of this research.

My deep appreciation also goes to Dr. O.A. Peters for his efforts and patience which enhances the successful completion of this research.

I am equally grateful to Mr David Barau of Centre for Energy Research and Training, Messrs Chris Uwadiale, A.A. Atodo, Malam Sani, Malam Musa and Mr. Buba for their unquantifiable assistance and cooperation.

Special thanks and appreciation go to Mr. A.F. Udo for showing interest in my work and offering suggestions wherever he could. Discussions with him had no doubt been fruitful.

I am also grateful to other staff members of the Chemistry Department for their assistance during the course of my laboratory work.

I should not fail to express my deepest gratitude to Mr. George A. Bisalla for typing the manuscript.

Finally, I want to thank the Almighty God for sustaining and upholding me throughout the period of preparing this thesis.

May God help us all.

A.J. Umoudoh.

ABSTRACT

The behaviour of VAc. and EMA monomers in emulsion polymerisation at 60°C with sodium lauryl sulphate emulsifier concentration (6.3×10^{-3} M/L), a constant initiator (potassium persulphate) concentration (8.3×10^{-4} M/L) was investigated. The percentage conversion of EMA, VAc to the respective polymers and viscosity average molecular weight increased with time. The viscosity average molecular weight ($\bar{M}v$) of the PEMA obtained were higher than the PVAc obtained under the same conditions and time of polymerisation.

Emulsion copolymerisation studies of EMA-PVAc matrix at 60°C have been investigated using three copolymerisation processes - batch, semi-batch and semi-batch continuous, semi-continuous. The results suggest that the semi-continuous process gave the highest percentage recovery of the suspected 'copolymerisation product'. The least percentage recovery was from the batch process.

The recovery of the copolymer itself resulted in the isolation of four fractions from the copolymerisation product: the methanol soluble i.e PVAc the methanol insoluble i.e PEMA and the expected copolymer., the ethanol insoluble i.e. PEMA., the ethanol soluble i.e the copolymer .

Melting points of the copolymerisation products were found to lie between those of the homopolymers and were found to be composition dependent.

Similarly, x-ray studies have helped to indicate that the percentage ordering and crystallinity indices of most of the copolymerisation products were between those from the amorphous component ie. PVAc and the semi-crystalline component, PEMA. Both the ordering and crystallinity indices were also observed to depend on the method and procedure of copolymerisation.

It is believed from spectroscopic studies that a methylene bridge, $-CH_2-$, between PEMA and PVAc resulted in a copolymer. Evidences include the broadening of the IR band between 1200 - 1260 cm^{-1} normally present in PVAc but absent in PEMA, the disappearance of the band between 1620 - 1660 cm^{-1} in the copolymer that is normally present in the monomers. A model structure has therefore been proposed.

Finally, the optical microscopy have established the heterogeneity in these copolymerisation products. The different processes of copolymerisation give products with different morphologies, the semi-continuous batch being more miscible than the semi-batch and batch. The morphologies of the different fractions from 'copolymerisation products' - methanol insoluble, methanol soluble, ethanol insoluble and ethanol soluble were more homogeneous than those of the products from which they were derived.

TABLE OF CONTENTS

CONTENT		PAGE
Title		i
Declaration		ii
Certification		iii
Dedication		iv
Acknowledgements		v
Abstracts		vi
Table of contents		viii
List of Tables		XV
List of Figures		xvi
List of Plates		xix
List of Appendices		xx
Abbreviations, Definitions, Glossaries and Symbols		xxi
CHAPTER ONE		
1.0	Introduction	1
1.1	General	1
1.2	Types of Copolymer	2
1.2.1	Polymer Mixtures	3
1.2.2	Random/Alternating Copolymers	3
1.2.3	Block Copolymers	3
1.2.4	Graft Copolymers	4
1.3	Reactivity Ratios and Copolymer Composition	9
1.3.1	Ideal Copolymerisation	10
1.3.2	Alternating Copolymerisation	11
1.3.3	Block Copolymerisation	12

CONTENT

		PAGE
1.4	Copolymerisation Techniques - - - - - - -	12
1.4.1	Bulk Copolymerisation - - - - - - - - - -	12
1.4.2	Solution Copolymerisation - - - - - - - -	13
1.4.3	Suspension Copolymerisation - - - - - - -	14
1.4.4	Emulsion Copolymerisation - - - - - - - -	15
1.5	Emulsion Copolymerisation Processes - - -	17
1.5.1	Batch Emulsion Copolymerisation - - - - -	17
1.5.2	Semi-Continuous Batch Emulsion Process -	18
1.5.3	Continuous Emulsion Process - - - - - - -	19
1.6	Effect of Process of Copolymerisation on rate -	21
1.7	Separation and Analysis of Heterogeneous Polymer System - - - - - - - - - - - - - -	22
1.7.1	Solvent Extraction - - - - - - - - - - - -	22
1.7.2	Fractional Precipitation Techniques - - -	23
1.7.3	Selective Precipitation Techniques - - - -	24
1.8	Analytical Methods for Qualitative and Quantitative Study of Copolymers - - - - -	24
1.8.1	Spectrophometry - - - - - - - - - - - - - -	25
1.8.2	X-ray Diffraction Methods - - - - - - - - -	26
1.8.3	Melting Point Determinations - - - - - - -	27
1.8.4	Microscopy - - - - - - - - - - - - - - - -	27
1.9	Research Aims and Objectives - - - - - - -	28
1.10	Scope of Present Work - - - - - - - - - - -	28
1.11	The Approach - - - - - - - - - - - - - - -	29

CONTENT

		PAGE
CHAPTER TWO		
2.0	LITERATURE REVIEW - - - - - - - - - - - - - -	30
2.1	General - - - - - - - - - - - - - - - - - - -	30
2.2	Copolymerisation Characteristics of Vinyl Acetate - - - - - - - - - - - - - - -	31
2.3	Graft Copolymerisation of Some Vinyl Monomers with Vinyl Polymers - - - - - - -	34
2.4	Emulsion Copolymerisation of Vinyl Acetate with n-butylacrylate - - - - - - - - - - -	37
2.5	Emulsion Copolymerisation of Methyl metha crylate with Vinyl Acetate - - - - - - -	38
2.6	Review of Methods for Synthesis of Block and Graft Copolymers - - - - - - - - - - -	39
2.6.1	Transfer Processes and Long Lived Radical Processes - - - - - - - - - - - - - - - -	39
2.6.2	Grafting with Preformed Initiating Sites on the Polymer Backbones - - - - - - - - - -	40
2.6.3	Photochemical Grafting - - - - - - - - - -	41
2.6.4	Mechanical Processes - - - - - - - - - - - -	41
CHAPTER THREE		
3.0	RESEARCH PROCEDURES - - - - - - - - - - - -	43
3.1	Homopolymerisation of Monomers - - - - - - -	43
3.1.1	Ethyl Methacrylate - - - - - - - - - - - - -	43
3.1.2	Vinyl acetate - - - - - - - - - - - - - - -	43
3.1.3	Initiator and Emulsifier - - - - - - - - - -	44
3.1.4	Nitrogen Gas - - - - - - - - - - - - - - - -	44
3.1.5	Polymerisation Studies of the Monomers - - -	44
3.1.6	Viscosity Average Molecular Weight ($\bar{M}v$) Determination of PEMA and PVAc Samples - - -	46

Chapter 3 (Contd.)

CONTENT		PAGE
3.2	Emulsion Copolymerisation of EMA and VAc Monomers - - - - - - - - - - - - - - - -	46
3.2.1	Semi-Batch Emulsion Copolymerisation - - -	47
3.2.2	Semi-Batch Continuous Emulsion Copolymerisation - - - - - - - - - - - - - - - - - -	48
3.2.3	Semi-Continuous Emulsion Copolymerisation - -	49
3.2.4	Batch Emulsion Copolymerisation - - - - - - -	50
3.2.5	Preliminary Investigation of Precipitation of Copolymerisation Product Using Various Non-Solvents - - - - - - - - - - - - - - - -	51
3.3	Preliminary Investigation of the 'Copolymerisation Product' from the Various Non-Solvents - - - - - - - - - - - - - - - -	52
3.3.1	Solubility Test - - - - - - - - - - - - - -	52
3.4	Methanol Extraction of PEMA, PVAc and their Physical Mixtures - - - - - - - - - - - - -	53
3.4.1	Ethanol Extraction of PEMA and PVAc - - - -	55
3.4.2	Methanol Extraction of 'Copolymerisation Products' - - - - - - - - - - - - - - - - -	56
3.4.3	Ethanol Extraction of 'Copolymerisation Products' - - - - - - - - - - - - - - - - - -	58
3.5.	Characterisation of Polymers - - - - - - - -	59
3.5.1	Melting Points Determinations - - - - - - -	59
3.5.2	Infra-red (IR) Spectroscopy - - - - - - - -	59
3.5.3	Nuclear Magnetic (N.M.R.) Spectroscopy - -	60
3.5.4	X-ray Analysis - - - - - - - - - - - - - - -	60
3.5.5	Optical Microscopy - - - - - - - - - - - - -	60

CONTENTS PAGE

CHAPTER FOUR

4.0	RESULTS AND DISCUSSION - - - - - - - - - -	61
4.1	Emulsion Polymerisation of EMA and VAc --	61
4.1.1	Influence of Time on Percentage Conversion of EMA, VAc, to their Respective Polymers and the Viscosity Average Molecular Weight ($\bar{M}v$) - - - - - - - - - - - - - - - - -	61
4.1.2	Comparative Study of EMA and VAc in Emulsion Polymerisation at 60°C - - - - - -	63
4.2	Emulsion Copolymerisation of EMA and VAc at 60°C for 9 Hours - - - - - - - - - - - -	66
4.2.1	Preliminary Investigation of the Recovery of Some Compolymerisation Products - - - -	66
4.3	Recovery of the Products from the Emulsion Copolymerisation of EMA, VAc Under Different Processes - - - - - - - - - - - -	69
4.3.1	Effect of Initial Time of Polymerisation of VAc ($7.0cm^3$) before Addition of EMA ($7.0cm^3$) on Percentage Recovery - - - - - - - - - -	69
4.4	Solubility Studies of the Copolymerisation Products - - - - - - - - - - - - - - - - -	72
4.5	Analysis of Physical Mixtures of PEMA, PVAc and the - - - - - - - - - - - - - - - -	72
4.6.0	Analysis of Copolymerisation Products by Extraction - - - - - - - - - - - - - - - - -	75
4.6.1	Methanol Extraction of Unbound PVAc from the Copolymerisation Products - - - - - - -	75
4.6.2	Effect of Initial Time of Polymerisation of VAc Before Addition of EMA on the MIS and MSS Composition of Copolymerisation Products - - - - - - - - - - - - - - - - -	75
4.6.3	Composition of Copolymerisation Product and the Process of Emulsion Copolymerisation	78
4.7.0	Ethanol Extraction of Unbound PEMA from the Copolymerisation Product - - - - - - - - - -	79

Chapter 4 (Contd.)

	CONTENT	PAGE
4.8.0	Melting Point Studies of the Copolymerisation Products, MIS and MSS Fractions - - - - - - - - - - - - - - - -	81
4.9.0	X-ray Studies of Homopolymers, Physical Mixtures and Copolymerisation Products - -	85
4.9.1	Percentage Ordering in the Copolymerisation Products - - - - - - - - - - - - - - - -	88
4.9.2	Percentage Ordering and Initial Time of Polymerisation of VAc Before EMA - - - -	90
4.9.3	Comparative Studies of Percentage Ordering for Physical Mixtures and the Copolymerisation Products - - - - - - - - - - - - - -	90
4.10	Crystallinity Index from Differential Intensity Measurement- - - - - - - - - --	92
4.11	Effect of Initial Time of Polymerisation of VAc on Crystallinity Index - - - - - -	93
4.12	Infrared Spectroscopy Studies of Monomers, Homopolymers and Copolymerisation Products -	95
4.12.1	Analysis of Infrared Spectrsocopy Studies of Copolymerisation Products- - - - - - - - -	102
4.12.2	Analysis of I.R. Spectroscopy Studies of Various Fractions of Copolymerisation Products - - - - - - - - - - - - - - - - - -	107
4.13	Nuclear Magnetic Resoance Studies of Monomers Polymer, Mixtures and Copolymerisation Product - - - - - - - - - - - - - - - - - -	109
4.13.1	Analysis of the n.m.r. spectra of Homopolymers, Physical Mixtures and Copolymerisation Products - - - - - - - - - - - - - -	109
4.13.2	Analysis of the n.m.r. spectroscopy of Fractions of Copolymerisation Products - - - - - - - - - - - - - - -	114
4.14	Optical Microscopy - - - - - - - - - - - -	122
4.14.1	Comparative Studies of Micrographs - - - -	122

CONTENT		PAGE
CHAPTER FIVE		
5.0	SUMMARY AND CONCLUSION - - - - - - - - - -	134
5.1	Summary -	134
5.2	Conclusion - - - - - - - - - - - - - - - - - -	136
	References - - - - - - - - - - - - - - - -	138
	Appendices - - - - - - - - - - - - - - - - -	144

LIST OF TABLES

TABLE	TITLE	PAGE
1.		
2.1	Graft Copolymerisation Involving Monomer - Polymer Pair at 70°C - - - - - - - - - - - -	34
3.1	Receipe for Polymerisation of EMA and VAc Monomers - - - - - - - - - - - - - - - - - - -	45
3.2	Initial Time of Polymerisation of VAc (batch) and Time of Copolymerisation After Addition of EMA (batch) in Minutes - - - - - - - - -	48
3.3	Initial Time of Polymerisation of VAc (batch) and Time of Copolymerisation After Dropping of EMA (continuous) at a Fixed Rate of 7.0cm^3/ hour in Minutes - - - - - - - - - - - - - - -	49
3.4	Common Receipe for Copolymerisation of Ethyl-methacrylate and Vinylacetate Monomers - - -	50
3.5	Recovery of Some 'Copolymerisation Products' from Various Non-Solvents - - - - - - - - - -	51
3.6	Methanol Extraction of PEMA and PVAc - - - -	54
3.7	Ethanol Extraction of PEMA and PVAc by Refluxing for 2 Hours at 80°C - - - - - - - - -	57
4.1	Recovery of the Same Copolymerisation Product from the Reaction Medium by Precipitation in Different Non-Solvents - - - - - - - - - - - -	67
4.2	Percentage Receovery of PEMA, PVAc, Physical Mixtures by Extraction with Methanol - - - -	73
4.3	Percentage Recovery of PEMA, PVAc and Physical Mixture from Ethanol at 80°C - - - - - - - - -	74
4.4	Percentage Ethanol Insoluble and Ethanol Soluble Fraction of the Methanol Insoluble (MIS) Fraction of Copolymerisation Product Determined by Ethanol Extraction - - - - - - - - - - - - - - - - - -	80
4.5	Variation of Melting Points of Copolymerisation Products with the Percentage of Methanol Insoluble and Methanol Soluble - - - - - - - - - -	83
4.6	Melting Point Ranges of Methanol Insoluble (MIS) and Methanol Soluble (MSS) from Various Copolymerisation Products - - - - - - - - - - - -	84
4.7	Comparison of Percentage Ordering from Calibration Curve - - - - - - - - - - - - - - -	91

LIST OF FIGURES

FIGURE	TITLE	PAGE
3.1	Schematic Diagram for Separation of 'Copolymerisation Product' into Methanol Insoluble (MIS) and Methanol Soluble(MSS) - - -	37
4.1	Kinetics of Emulsion Polymerisation of EMA ($7.0cm^3$) and VAc ($7.0cm^3$) with Constant Concentration of SLS Emulsifier (6.0×10^{-3} m/L) and Constant Potassium Persulphate Initiator Concentration (8.3×10^{-4} m/L) at 60°C - - - -	62
4.2	Variation of Viscosity Average Molecular Weight and Time of Polymerisation for EMA ($7.0cm^3$) with Initiator Concentration of 8.3×10^{-4} m/L and Emulsifier Concentration 6.3×10^{-3} m/L at 60°C - - - - - - - - - - - -	64
4.3	Variation of Viscosity Average Molecular Weight and Time of Polymerisation for VAc ($7.0cm^3$) with Initiator Concentration of 8.3×10^{-4} m/L and Emulsifier Concentration of 6.3×10^{-3} m/L at 60°C -	65
4.4	Variation of Percentage Recovery of Copolymerisation Products with Initial Time of Polymerisation of VAC ($7.0cm^3$) with Constant Emulsifier conc. of 6.3×10^{-3} m/L, constant initiator concentration of 8.3×10^{-4} m/L for batch(O), semi-batch (⊡), Semi-batch continuous (⊗), semi-continuous (⊛) emulsion copolymerisation at 60°C - - - - - - - - - - -	70
4.5	Variation of Percentage MIS, initial time of polymerisation of VAc ($7.0cm^3$) prior to additon of EMA ($7.0cm^3$) for the semi-batch continuous (⊡) and semi-batch (⊙), copolymerisation Products - - - - - - - - - - - - - - - - - -	76
4.6	Variation of Percentage MSS with initial time of polymerisation of VAc ($7.0cm^3$) prior to addition of EMA ($7.0\ cm^3$) for the semi-batch continuous (O) and semi-batch (x) copolymerisation Products - - - - - - - - - - - - - - -	77

FIGURE	T I T L E	PAGE
4.7	Variation of percentage ordering with time of polymerisation of VAc prior to addition of EMA for the semi-batch (x) and semi-batch continuous (□) copolymerisation products - - - -	89
4.8	Calibration curve for variation in percentage ordering with percentage PEMA in PEMA/PVAc mixture -	150
4.9	Variation of crystallinity index (C_i) with initial time of polymerisation of VAc prior to EMA addition for semi-batch continuous (□) and semi-batch (⊗) copolymerisation products--	94

FIGURE		PAGE
4.10a	X-ray spectrum of PEMA (LR) - - - - - - - -	86
4.10b	X-ray spectrum of PVAc (LR) - - - - - - - -	87
4.11a	I.R. spectrum of EMA monomer - - - - - - - -	96
4.11b	I.R. spectrum of VAc monomer - - - - - - -	97
4.12a	I.R. spectrum of PURE PEMA - - - - - - - -	98
4.12b	I.R. spectrum of PURE PVAc - - - - - - - -	99
4.13a	I.R. spectrum of mixture of PEMA/PVAc - -	100
4.13b	I.R. spectrum of a typical copolymerisation product - - - - - - - - - - - - - - - - - -	101
4.14a	I.R. spectrum of a typical methanol insoluble	103
4.14b	I.R. spectrum of a typical methanol soluble	104
4.15a	I.R. spectrum of a typical ethanol insoluble	105
4.15b	I.R. spectrum of a typical ethanol soluble	106
4.16a	N.M.R. spectrum of EMA monomer - - - - - -	110
4.16b	N.M.R. spectrum of VAc monomer - - - - - -	111
4.17a	N.M.R. spectrum of Pure PEMA - - - - - - -	112
4.17b	N.M.R. spectrum of Pure PVAc - - - - - - -	113
4.18a	N.M.R. spectrum of mixture of PEMA/PVAc -	115
4.18b	N.M.R. spectrum of a typical copolymerisation product - - - - - - - - - - - - - -	116
4.19a	N.M.R. spectrum of a typical methanol insoluble - - - - - - - - - - - - - - - - -	117
4.19b	N.M.R. spectrum of a typical methanol soluble - - - - - - - - - - - - - - - - -	118
4.20a	N.M.R. spectrum of a typical ethanol insoluble - - - - - - - - - - - - - - - - -	119
4.20b	N.M.R. spectrum of a typical ethanol soluble - - - - - - - - - - - - - - - - -	120
4.21	Schematic diagram for the separation of copolymerisation products - - - - - - - -	107

LIST OF PLATES

PLATES					PAGE
I:	Optical micrograph of	100%	PEMA (LR)	- - - -	123
II:	" "	"	PVAc (LR)	- - - -	123
III:	" "	of PBB_1	copolymerisation	product	124
IV:	" "	PSB_1	"	"	124
V:	" "	PBB_2	"	"	125
VI:	" "	PSB_2	"	"	125
VII:	" "	PBB_4	"	"	126
VIII:	" "	PSB_4	"	"	126
IXA:	" "	PBB_1	Methanol Insoluble	- - -	128
IXB:	" "	PBB_2	"	" - - -	128
IXC:	" "	PSB_4	"	" - - -	129
XA:	" "	PBB_1	Methanol Soluble	- - -	129
XB:	" "	PSB_2	"	" - - -	130
XC:	" "	PSB_4	"	" - - -	130
XIA:	" "	PBB_2	Ethanol Insoluble	- - -	131
XIB:	" "	PBB_4	"	" - - -	131
XIIA:	" "	PBB_2	Ethanol Soluble	- - -	132
XIIB:	" "	PSB_2	"	" - - -	132

LIST OF APPENDICES

APPENDIX		PAGE
I	Percentage recovery of copolymerisation products using batch and semi-batch processes of emulsion copolymerisation at 60°C for 9 hours - - - - - - - - - -	144
II	Percentage recovery of copolymerisation products using batch continuous and semi-continuous processes of emulsion copolymerisation at 60°C for 9 hours - -	146
III	Methanol extraction of the copolymerisation products showing the percentage methanol insoluble (MIS) and percentage methanol soluble (MSS) - - - - - - - - -	147
IV	Result from X-ray spectra of polymers and copolymerisation products at $2\theta = 43^{\circ}$	148
V	Calibration curve for percentage ordering and percentage PEMA in polymer from x-ray spectra at $2\theta = 43^{\circ}$ - - - - - - - - - -	150
VI	Crystallinity indices or degree of crystallinity of samples - - - - - - --	151
VII	Important band frequencies in (cm^{-1}) from infrared spectra of samples - - - -	152
VIII	Important N.M.R. peaks in (δ) from N.M.R spectra of monomers, polymer samples - - - - - - - - - - - - - - - - - -	157

ABBREVIATIONS, DEFINITIONS, GLOSSARIES AND SYMBOLS.

AnaLAR - Analytical Reagent grade.

Ci - Crystallinity index

'Copolymerisation product': - The product obtained from the copolymerisation of EMA and VAc at 60°C which comprises of unbound PEMA, unbound PVAc and the expected copolymer.

EIS - Ethanol Insoluble fraction: The portion of the methanol insoluble which remains insoluble when refluxed in ethanol.

EMA - Ethyl meth acrylate monomer

ES - Ethanol soluble: The portion of the methanol insoluble (MIS) which has dissolved in ethanol when refluxed.

i.r. - Infrared spectroscopy.

LR - Laboratory Reagent.

MIS - Methanol Insoluble fraction: The fraction of the 'copolymerisation product' which remains insoluble in methanol.

m/L - Mole per litre

MSS - Methanol soluble fraction: The fraction of the 'copolymerisation product' which has dissolved in methanol.

m/V - Mass per volume.

n.m.r. - Nuclear magnetic resonance spectroscopy.

PBB_1 ... PBB_7 'Copolymerisation products' obtained from semi-batch emulsion copolymerisation of EMA ($7.0cm^3$) and VAc ($7.0cm^3$) for various times of initial polymerisation of VAc before EMA addition of 30, 60, 120, 240, 300, 360 and 420 minutes.

PEMA - Poly(ethylmethacrylate) polymer.

PMMB - Copolymerisation product obtained when equal volumes of EMA, $7.0cm^3$ VAc ($7.0cm^3$) comonomer was mixed and copolymerised in batch at 60°C for 9 hours.

PSB_1.... PSB_4: 'Copolymerisation products' obtained from semi-batch continuous emulsion copolymerisation of VAc ($7.0cm^3$) in batch for 30, 60, 120 and 240 minutes before dropping EMA ($7.0cm^3$) at a fixed rate of $7.0cm^3$/hr.

PSMCMS - 'Copolymerisation product' obtained from semi-continuous copolymerisation of EMA and VAc.

PVAc - Poly(vinyl acetate) polymer.

VAc - Vinyl acetate monomer.

V/V - Volume per volume.

Chapter 1

1.0 INTRODUCTION

1.1 General

Emulsion polymerisation of vinyl monomers has been carried out for various industrial and scientific purposes. Classical emulsion polymerisation involves the use of water as diluent, water-insoluble monomer (which is dispersed in the diluent), a water-soluble initiator and an emulsifying agent. When the reaction involves only one monomer, it is referred to as homopolymerisation (simply polymerisation) and the product as homopolymer or generally referred to as polymer.

However, when there are two or more monomers with chemically different species it is copolymerisation, whilst the product is copolymer (Huggins and Herman 1952). There are possibilities of multicomponent polymerisation in emulsion (Ham, 1967). With the increase in technological advancement, scientific and industrial interest in the field of polymer synthesis is shifting increasingly from homopolymerisation to copolymerisation and therefore from polymers to copolymers.

Copolymerisation greatly increases the number of possible polymeric products which can be formulated and presents excellent possibilities for the production of resins best suited for particular application. For example, copolymerisation may impart to a single polymer molecule the desired structural qualities of two different homopolymer species. This is rarely achieved by a physical mixture, that is a blend of the two polymers. This unique characteristic arises from the fact that one material can be used to modify the properties of another material through

KASHIM IBRAHIM LIBRARY
AHMADU BELLO UNIVERSITY
ZARIA, NIGERIA.

copolymerisation. An elastomeric polymer could be used to make a plastic flexible or a soft, rubbery polymer (e.g. polyvinyl acetate) could be stiffened by incooperating molecules of rigid, brittle polymer (e.g. polyethyl methacrylate) by this method. Other advantages of copolymerisation include the following:

(a) Unlike blending, copolymerisation provides an excellent means of permenently binding short chains of one polymer onto short chains of another by chemical bonds. It is also advantageous over blending in that it eliminates the shear and temperature effects which result in degradation of individual polymers involved.

(b) Heterophase polymers may be produced with improved miscibility and compatibility different from polymer mixtures (Olabisi et al., 1979).

(c) Copolymerisation of one specie with another may impart synergistic effect on some of the properties of both components, leading to improvement on their respective homoproperties. Synergism is the enhanced action between two or more materials, e.g. polymers (Adeniyi 1986).

(d) Monomers which do not homopolymerise at all or polymerise with great difficulty are found to copolymerise easily. For example, maleic anhydride which homopolymerises with great difficulty was found to copolymerise readily with such monomers as styrene and vinyl chloride (Schildneck 1952), (Billimeyer 1970).

(e) The production of polymers with tailor-made properties not attainable by other materials but through only copolymers is made possible through copolymerisation.

1.2 Types of Copolymers

A polymeric substance consisting of molecules with large number of units of two or more chemically different types in more or less irregular

sequence is a copolymer. The relative numbers of the different units may not be the same in the different proportions of a single molecule, (Huggins and Hershan 1952). Unlike other polymer hybrids (e.g. polyblends, composites) the components in copolymer are linked by strong covalent bonds and not secondary forces e.g. Vander Waals, dipole interaction, hydrogen bonding. Polymerisation of two monomers may give a variety of products, depending on the method and conditions of reaction. These possibilities may include ordinary mixtures of the two homopolymers, graft or block copolymer. However, the most common chemical hybrids are discussed below:

1.2.1 Polymer Mixtures

These involve homopolymers with certain interfacial bonding. The possibility of producing mechanical mixtures of two individual polymers would require that each monomer should add selectively to its own type of radical in the system. (Alfrey et al., 1952). Such a case has not yet been found to exist.

1.2.2 Random/Alternating Copolymer

Random copolymers are the most common type of polymer chemical hybrids, and are composed of random arrangement of say - ABBAAAABBAAA - repeat units where A and B are different monomeric units. They are generally characterised by a statistical placement of the comonomer repeat units along the backbone of the chain. Random copolymers are the most versatile, economical and easily synthesized type of copolymers.

Alternating copolymers are characterised by alternate arrangement of - ABABABABAB - repeat units along the polymer backbone. They are mostly obtained when equimolar quantities of the monomers are distributed in a regular alternating fashion in the chain. These types of copolymers are relatively rare, due to the requirement that pairs of monomers must have high reactivities and that special reaction conditions such as having equimolar monomer mixtures are required (Johnstone 1973).

Generally, the major incentive for synthesising random ./or alternating copolymers is to achieve homogeneous systems that display properties representing a weighted average of the two repeat units. However, the more easily prepared random copolymer closely approximate this situation and permits the attainment of averaged physical and chemical properties e.g. glass transition temperatures, mechanical properties, permeability and chemical resistance. Uniform random copolymers can display single phase morphology which may result in optical transparency in amorphous systems. This could be possible if the sequential runs present in these compositions are usually too short and 'sandwichs' between each other to induce microphase separation. However, Platzer (1970) pointed out that heterogeneity has been observed in random copolymers especially if reactivity ratios of the comonomers are far apart.

1.2.3 Block Copolymers

These are copolymers consisting of long sequences, blocks of one mer (polymer unit derived from one of the comonomers) followed by long sequence of the second mer. For example, if there arethree monomeric units A,B,and C with sequence of n unit long , m units long and p unit long respectively then

several variations can exist as illustrated below:

$\lceil A_n \rceil \lceil B_m \rceil$ .... a diblock or AB block

$\lceil A_n \rceil \lceil B_m \rceil \lceil C_p \rceil$ .... a triblock or ABC block

$\lceil A_n \rceil \lceil B_m \rceil \lceil A_p \rceil$ .... 'sandwich' triblock.

A stereoblock can be obtained if the blocks are composed of the same monomer units in different steric configuration. (Cowie 1973).

In general, block copolymers more or less resemble polyblends of the homopolymers, especially when the blocks are long. In most cases, they may have long enough homogenous chain sequence to exhibit the properties of both homopolymers rather than intermediate values. This is why block copolymers can display certain degree of incompatibility especially if the blocks are long enough to cause phase separation. However, sandwich blocks could enhance compatibility between components in the copolymer (e.g. sandwich blocks of styrene with either isoprene or butadiene produce a thermoplastic elastomer in which the polystyrene block acts as both filler and cross linking agent (Cowie 1973). Block copolymers can usually be synthesised by the use of "living polymers" and/or a polymer with an end group suitable for radical reactions.

Living polymers are polymers produced from systems in which termination is lacking. Since the termination step usually involves transfer to some species (monomer, polymer, initiator) not essential to the reaction, anionic or cationic polymerisation with carefully purified reagents may lead to systems in which termination is lacking. The resulting species, called 'living polymers' (Swarzc 1968) can be prepared for example, by polymerising styrene with sodium naphthalene to give non-terminable ends. Swarzc et al., (1956) synthesised block copolymer of

styrene - isoprene at -80°C in tetrahydrofuran using styrene (9.2g), THF (60 cm^3), sodium napthalene (3.3 x 10^{-4} mol), isoprene (3.6g). Kinetic analysis show that the polymer have an extremely narrow distribution of molecular weight and for all practically purposes be essentially monodisperse. The living polymer can be 'killed' (stopping the reaction) byaddition of a terminating agent e.g. water, at the end of the reaction. The 'living polymer' technique offers the additional advantage in that the block size can be controlled. Generally, block copolymers are thermoplastics since there are no crosslinks between the molecules.

1.2.4 Graft Copolymers

These are macromolecules consisting of polymer backbones with attached polymer branches (or appendages). There are graft copolymers of various chemical compositions either in the backbone or side chain. Considering two different monomeric units A and B, the following structures of graft copolymers can exist.

	Backbone	Side Chain	Structure
(i)	Homopolymeric	Homopolymeric	AAAAAAAAA B B B B B
(ii)	Homopolymeric	Copolymeric	AAAAAAAA B A B A B A

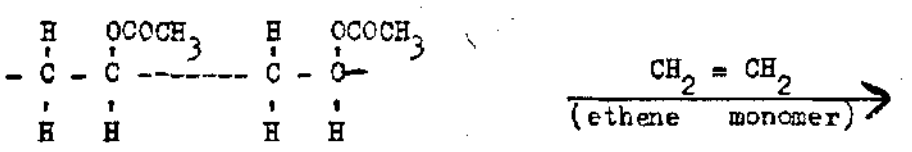
	Backbone	Side Chain	Structure
(iii)	Copolymeric	Copolymeric	AB/BAB/BAB B A B A B A
(iv)	Copolymeric	Homopolymeric	AB/BAB/B B B B B B

A graft copolymer cannot be regarded as a block copolymer because the individual polymer segments do not form a linear chain. They have a linear chain of one component from which there are side chains of different compositions. It cannot also be regarded as a branched polymer, although the major difference between them is that in a branch polymer all parts of the macromolecule are of the same chemical nature. A graft polymer is a multiphase system while a branched polymer is a single phase.

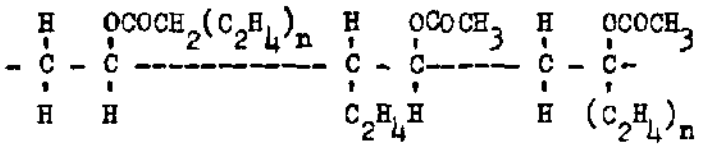
Grafting is the only method by which certain properties can be introduced permanently into a polymer without affecting its chief performance characteristics. Stannett (1970) stated that in practice, up to 15% of another polymer can be grafted without affecting the main properties of the other polymer. A good example of such graft in which the properties of the main chain remains unaffected is the grafting of 8 - 10% of polyacrylic acid onto high density polyethylene. The melting point and crystallinity of the high density polyethylene were essentially unchanged (Rieke and Hart 1969).

However, if the grafted polymer has very different properties it might affect some other properties of the base polymer e.g. in the case cited above for polyethene-graft-polyacrylic acid, the modulus and softening point of the base polymer was raised.

Grafting can be initiated by free radical mechanism where the active sites are induced on an internal monomer unit. For example, the grafting of ethylene onto polyvinyl acetate will give appreciable quantities of graft copolymer (Gaylord and Ang. 1964). This is known as transfer grafting and involves hydrogen abstraction from the main chain in the presence of another monomer which then grows from this site as a branch. For example, it has been found that chain transfer occurs on the acetoxy group of poly(vinyl acetate) to initiate the growth of any polymer (e.g. ethylene) in the graft copolymerisation of ethylene onto polyvinyl acetate.



(PVAC polymer)



PVAC - PE graft copolymer.

Chain transfer can also occur on the backbone carbon of PVAC. (Gaylord and Ang 1964). The product of such a reaction often contains homopolymers and unmodified chains in addition to the grafted product, e.g.

homopoly ethene, homopoly(vinyl acetate)and the graft PVAC - PE. Other forms of grafting include activation grafting and chemical grafting. In activation grafting, the polymer can be exposed to the source of radiation before addition of monomer (pre-irradiation technique).

An example of pre-irradiation technique of activation grafting is of polypropylene in air to yield peroxides before the introduction of acrylonitrile monomer to yield polypropylene-acrylonitrile graft copolymer (Ballantine et al; 1959). The mutual irradiation technique has been used in the graft copolymerisation of polypropylene polymer-vinyl acetate monomer mixture in the absence of air. (Ham 1964).

Chemical grafting involves redox reactions of pendant hydroxyl with metal salts such as cerium(IV) ions, Iron(III) salts or other heavy metal salts. Ceric alcohol complex has been used to produce radicals on poly(vinyl alcohol) polymeric backbone on which acrylonitrile monomer grafts. (Gaylord and Ang 1964). Excellent reviews of these techniques had been given by Ham (1964), (Gaylord and Ang 1964).

1.3 Reactivity Ratios and Copolymer Composition

The composition of any copolymer depends to a large extent on the reactivities of the monomers involved. For any two polymerisable monomers M_1, and M_2, two different types of active centres will exist and the formation of copolymer is determined by the following reactions:-

$$M_1^{\cdot} + M_1 \xrightarrow{K_{11}} M_1^{\cdot} \quad \text{- - - - -} \quad (1)$$

$$M_1^{\cdot} + M_2 \xrightarrow{K_{12}} M_2^{\cdot} \quad \text{- - - - -} \quad (2)$$

$$M_2^{\cdot} + M_1 \xrightarrow{K_{21}} M_1^{\cdot} \quad \text{- - - - -} \quad (3)$$

$$M_2^{\cdot} + M_2 \xrightarrow{K_{22}} M_2^{\cdot} \quad \text{- - - - -} \quad (4)$$

where K_{11}, K_{22} and K_{12}, K_{21} are the rate constants for self-propagation and cross propagation for M_1 and M_2 respectively.

The ratios of the rate constants K_{11}/K_{12},(r_1) and K_{22}/K_{21},(r_2) for a given radical adding to its own monomer to that for its adding the other monomer are known as relative reactivity ratios. These parameters r_1 and r_2, are very important since they characterise the copolymerisation behaviour of the two monomers. The relative reactivities of the two monomers towards the two radicals determines the type of product formed (Alfrey et al; 1952). Monomers with high reactivity ratios enter the copolymer faster than those with low values. With the relative reactivities ratios of monomers, the composition of any copolymer could be predicted.

Young and Mark (1966) have extensive compilation of reactivity ratios for different monomers. The different types of copolymerisation depend on the value of these ratios.

Copolymerisation can be classified into three main types based on whether the product of the two monomers reactivity ratios r_1r_2 is unity, less than unity or greater than unity.

1.3.1 Ideal Copolymerisation $r_1r_2 = 1$

A copolymerisation is termed ideal when r_1r_2 product is unity. Ideal copolymerisation occurs when the two types of the propagating species $M_1^\bullet$ and $M_2^\bullet$ show the same preference for adding one or the other of the two monomers. Under these conditions,

$$\frac{K_{22}}{K_{21}} = \frac{K_{12}}{K_{11}} \quad \text{or} \quad r_1 = \frac{1}{r_2}$$

and the relative rates of incorporation of the two monomers into the

copolymer are independent of the identity of the unit at the end of the chain e.g. the one involving methylmethacrylate r_1 = 10 and vinyl chloride r_2 = 0.1 at 68°C (Mark andYoung 1966). Most ionic copolymerisation (both anionic and cationic) are characterised by the ideal type of behaviour (Odian 1981).

1.3.2 Alternating Copolymerisation $r_1 = r_2 = 0$

In this case, each radical prefers to react exclusively with the other monomer. When $r_1 = r_2 = 0$ (and $r_1r_2 = 0$), the two monomers enter into the copolymer in equimolar amounts in a nonrandom, alternating arrangement along the copolymer chain. This type of copolymerisation is referred to as alternating copolymerisation. The closer the product r_1r_2 is to zero the greater is the tendency for alternating copolymer to be formed. Many radical copolymerisation show this alternating behaviour. A typical alternating radical copolymerisations show this alternating behaviour; e.g. alternating radical copolymerisation is that of styrene ($\bar{M}_1$) & diethyl fumarate (M_2) (r_1 = 0.30 and r_2 = 0.07) (Odian 1981). The behaviour of most comonomer systems lies between the two extremes of ideal and alternating copolymerisation, i.e. $0 < r_1r_2 < 1$, the reactivity ratio product lies between zero and unity. As the product r_1r_2 decreases from unity toward zero, there is increasing tendency toward alternation. Perfect alternation occurs when r_1 and r_2 are both zero. The tendency toward alternation and the tendency away from ideal behaviour increases as r_1 and r_2 become progressively less than unity.

KASHIM IBRAHIM LIBRARY
AHMADU BELLO UNIVERSITY
ZARIA, NIGERIA

1.3.3 Block Copolymerisation $r_1 > 1$, $r_2 > 1$

If both r_1 and r_2 are greater than unity (and therefore, also $r_1 r_2 > 1$), there is the tendency to form a block copolymer in which there are blocks of both monomers in the chain. This requires that each monomer tends to add selectively to its own type of radical. The extreme case of both r_1 and r_2 being much larger than unity - corresponding to the simultaneous and independent homopolymerisation of the two monomers - has not yet been observed, except in the simultaneous cationic homopolymerisation of vinyl carbazole and oxetane by Gumbs et al, (1969). In this case, intermonomer polymerisation only occurs because of r_1 and r_2 being far greater than unity.

1.4 Copolymerisation Techniques

According to Sandler and Karo (1974), copolymerisation can be carried out in bulk, solution, suspension and emulsion techniques.

1.4.1 Bulk Copolymerisation

This technique which is sometimes referred to as mass copolymerisation involves only the two monomers and the catalyst if any, which is required. It is the simplest process of copolymerisation technique with a minimum of contamination of the product.

However, bulk copolymerisation is difficult to control due to the characteristics of radical chain copolymerisation. Chain copolymerisation is highly exothermic, and with high activation energies, resulting in gel effect which makes heat dissipation difficult. Hence, mass copolymerisation of any two monomers requires careful temperature control.

The viscosity of the reaction system increases rapidly at relatively low conversion (Odian 1981) and therefore need strong and elaborate stirring equipment. The viscosity and exothermic effects make temperature control difficult.

Bulk copolymerisation is not used commercially for chain copolymerisation because of the difficulties indicated above. This technique is not extensively used for copolymerisation of vinyl monomers especially the acrylic monomers because of the difficulty of removing the product from the reactor.

1.4.2 Solution Copolymerisation

The copolymerisation which is carried out in a liquid which is a diluent for both monomers and the initiator is solution copolymerisation. Most copolymerisation (block, graft, random) are often carried out in solvents which can dissolve the monomers and the copolymer produced. Upon addition of a suitable non-solvent, the copolymer together with the respective homopolymers should be precipitated. The solvent apart from acting a diluent, also aids in the transfer of heat; produced by the copolymerisation reaction. The solvent also allows easier stirring, since the viscosity of the reaction mixture is decreased. Thermal control is much easier in solution copolymerisation compared to the bulk copolymerisation.

However, the presence of solvent may present new difficulties. Most solvents may enhance chain transfer which may lead to a decrease in the rate of the copolymerisation (Guha et al; 1964). This may go along way to affect the structure, molecular weight of the resulting

copolymer (Guha and Palit 1963). Therefore, the solvent should be chosen with appropriate consideration, so that chain transfer to solvent in minimized. The purity of the copolymer may be affected if there are difficulties in the removal of solvent.

1.4.3 Suspension Copolymerisation

In this technique, the two monomers are suspended in the aqueous phase as droplets being maintained by the suspending agent. The suspending agent (e.g. polyvinyl alcohol) is being added so that the monomer droplets will coalesce together for reaction. The copolymerisation is carried out in a reaction medium in which the copolymer product will be insoluble. The copolymerisation reaction is effected in the globule formed yielding a pearl or bead. Hence, suspension copolymerisations are often referred to as powder or granular copolymerisations, because of the forms in which the final copolymer products are obtained. There is a better heat control in the aqueous suspension medium than in the bulk technique. The suspending agents act as impurities and may give rise to products with inferior optical properties. However, the suspension method of copolymerisation is not used with monomers which are highly soluble in water or whose polymer has too high a glass transition temperature. This is because with appreciably water-soluble monomers (e.g. vinyl acetate) some of the copolymerisation reaction will take place in the solution as well as in the monomer droplets leading to low molecular weight products (Odian 1981).

Coagulation of the monomer droplets may occur at low conversions if the polymer Tg of any of the components is lower than the temperature of reaction as styrene-methyl methacrylate, vinyl chloride and vinyl acetate has been reported by Odian (1981).

1.4.4 Emulsion Copolymerisation

Emulsion copolymerisation is an important industrial technique for preparing copolymers from unsaturated monomers and yields a stable particulate dispersion of the copolymer in an aqueous medium known as latex. This latex can be used directly as an emulsion without prior separation of the copolymer from water and the other components. Such applications involves coatings, polishes, floor polishes and paints. A distinguishing feature of emulsion copolymerisation which makes it of great commercial interest is that high molar mass products are obtained without decreasing the rate of the reaction. This is because both the rate of polymerisation reaction and molar mass depends on the number of particles formed during the reaction. Other advantages includes:

(a) High rate of conversion of the comonomers to the copolymer can be attained reasonably quickly.

(b) Efficient heat transfer due to the presence of a large quantity of water (Sandler and Karo; 1974).

(c) Low viscosity of latexes at high polymer concentration and control of the copolymer composition.

However, in the emulsion copolymerisation of any two monomers, it may be difficult to remove the reaction components (surfactants and modifiers), hence application problems encountered.

The reactivities of the monomers in emulsion copolymerisation will depend on their solubilities in the aqueous medium. If the diffusion of the two monomers to the latex particles is sufficiently rapid to maintain equilibrium, the copolymerisation reactivity ratios observed for these monomers in emulsion should be practically identical with those in bulk copolymerisation. However, if one of the monomers is more water-soluble than the other, the portion of the monomer which is present in aqueous solution is not available for reaction, hence this monomer will exhibit an apparently lower copolymerisation reactivity in emulsion (Alfrey et al., 1952). The copolymerisation of styrene-methylmethacrylate in emulsion showed that the reactivity ratios were the same as obtained in bulk (i.e. reactivity for styrene $r_1 = 0.52$ and reactivity for methylmethacrylate $r_2 = 0.46$) at 60°C (Schildknecht 1952).

For normal behaviour in emulsion copolymerisation the two monomers have to exhibit the same relative reactivities that they would exhibit in homogeneous bulk or solution copolymerisation. If one of the monomers is quite water-soluble, its apparent reactivity is reduced. It is quite possible also that monomers containing long alkyl groups could also exhibit reduced apparent reactivities for a different reason, namely, the low rate of diffusion to the locus of polymerisation (Alfrey et al., 1952). Emulsion copolymerisation apart from being of industrial importance for the production of synthetic polymers normally give higher degree of polymerisation between 25 - 60°C than those in bulk or suspension (Schildknecht 1952). This technique is preferred to the bulk or solution in the case of acrylic and methacrylic ester monomers because of easy removal of the emulsion product latex unlike sticky product from these later techniques.

Also commercial emulsion copolymerisation can involve batch, semi-batch, semi continuous and continuous processes of the addition of monomer to obtain the desired reaction rate and temperature control (Cooper 1974). Molecular weight of the product is also affected by the incremental addition of the two monomers. Semi-continuous or continuous addition of initiator and chain transfer agent is employed as necessary to maintain a relatively constant initiation rate and molecular weight. For the same condition and materials for the copolymerisation in emulsion, the semi-continuous or continuous addition of monomers will lead to larger particle size than initial batch addition (Odian; 1981). Hence, it is necessary to describe these processes of emulsion copolymerisation and its application in details.

1.5 Emulsion Copolymerisation Processes

There are three basic processes which can be used for the preparation of copolymer latex by emulsion copolymerisation. These basic processes are:

(a) Batch emulsion copolymerisation

(b) Semi-continuous batch emulsion copolymerisation

(c) Continuous emulsion copolymerisation.

1.5.1 Batch Emulsion Copolymerisation

This involves the addition of the formulation components completely at the beginning of the reaction. The product of the copolymerisation reaction is removed after the desired conversion.

In a typical semi-batch emulsion copolymerisation, some of the

components may be added in parts but at separate time intervals. Emulsion copolymerisation of water insoluble monomers proceed in three stages. In the first interval, nucleation of the particles occur until micellar emulsifier droplets are depleted in the medium. The second interval is the period during which the particles are growing with constant rate of polymerisation. The third stages begin when the monomer droplets are absent and the copolymerisation is mostly that of the monomer molecules in the swollen polymer-monomer particles (Harkin; 1950), (Gardon; 1968).

1.5.2 Semi-Continuous Batch Emulsion Copolymerisation Process

This is the process in which a part of the receipe are withheld from the initial charge to the reactor and added later in a programmed manner. In more cases, the later addition may involve one of the monomers, part of the monomer charge, and sometimes other components such as water, emulsifier, initiator and transfer agents. This process is the most versatile and widely used on an industrial scale. The process can be operated under two extreme conditions, generally described as:

(a) 'Monomer flooded' which describes a state in which the monomer feeding rate (Ra) is higher than the maximum rate of polymerisation (Rp) max. (i.e. that of the equivalent batch process). In this case of 'monomer flooded' the actual rate of copolymerisation (Rp) is equal to the maximum rate of the copolymerisation (Rp) max.

(b) "Monomer Starved": If the rate of monomer addition is less than the maximum rate of the copolymerisation reaction (Rp) max, the system

is said to be operating under "monomer starved" conditions, the rate of polymerisation is approximately equal to the rate of monomer addition and the instantaneous conversion are very high, usually greater than 90%. Also monomer droplets are absent (Saleeman 1985).

Semi-continuous batch emulsion copolymerisation processes may fall into two categories (Bataille et al; 1978) namely:-

(a) Monomer addition (Madd) in which water, surfactant and part of the comonomer (usually about 10%) are charged into the reactor and initiator added to start the reaction. After a set time, the remaining comonomer is pumped into the reactor at a specified rate.

(b) Emulsion addition (Eadd): Part of the whole batch (water, surfactant, initiator, monomer) are charged into the reactor, the rest is fed gradually as monomer emulsion into the reactor at a constant rate. Both processes are very useful in copolymerisation of vinyl monomers because they give more homogeneous products.

1.5.3 Continuous Emulsion Copolymerisation

In this process, the reactants are added at a constant rate while the products (copolymer) are also being removed from the system at the same rate in the whole process. There are basically three types of continuous reactor systems:

(a) a series of continuous stirred tank reactors (CSTR'S)

(b) continuous loop reactors.

(c) continuous tubular reactors.

Tubular and loop reactors are restricted to simple formulation and also less flexible than the series CSTR's

However, they are also subject to lack of control over particle morphology. The properties of the polymer latex produced have been found to depend on the process of polymerisation or copolymerisation (Krackeler et al; 1969). The number average molar mass ($\bar{M}n$) for the polymers prepared using the batch process are higher than those of semi-continuous under monomer-starved condition. This is because there is higher monomer concentration within the growing latex particle for the batch process giving rise to a higher rate of propagation. Also another important property that depend on copolymerisation process is the particle size and its distribution. This property is very important especially when the latex is to be applied directly. Latexes obtained using the batch processes have narrow particle size distribution while those of continuous processes are broad. This should be so, because in the batch process, all particles are formed easily with the same age and size. But there is a broad distribution of residence time for individual particles in the continuous system.

Bataille et al; (1978) reported that polymers obtained by monomer addition (Madd) technique had both a narrower particle size distribution and smaller average particle than the emulsion addition (Eadd) polymer.

The comparative study of batch and monomer addtion (Madd) semi-continuous batch emulsion copolyerisation showed the dependence on rate of copolymerisation and molar mass on these techniques. (Yeliseyeva et al; 1965). The monomer addition technique gave a lower molar mass polymer with improved colloidal stability of the latex.

In an emulsion copolymerisation carried out in the batch process, the composition of the copolymer changes with time because of the differences in monomer reactivity ratios, and the presence of monomer resevoir. There will be a high proportion of the more reactive monomer in the copolymer

initially, with the final product comprising a high proportion of the less reactive monomer. The semi-continuous batch process operated under monomer-starved condition yields a copolymer of uniform composition. It was found that the relationship between the free monomer composition in the reaction mixture and the composition of the copolymer was controlled by the monomers feeding rate (Smuparek and Krska 1976). The deviation between the comonomer and the resulting copolymer becomes smaller if the feeding rate was close to the rate of polymerisation. However, the overall composition of a copolymer produced using the continuous reactor system does not change with time.

1.6 Effect of Process of Copolymerisation Rate

In any copolymerisation system, control of the rate of reaction is very important. The batch, semi-continuous batch or continuous processes of addition of the formulation should be done to obtain the desired reaction rate (Odian; 1981). In the batch process, the rate of copolymerisation is determined by the formulation used and the reaction condition. It has been pointed out that the rate of reaction is often high and can present great industrial problems with regards to removal of heat of copolymerisation (Saleeman; 1985). One motivation for using the semi-continuous batch process under monomer starved conditions is to obtain control of the rate of copolymerisation and then of heat generation. The rate of copolymerisation process is constant but may vary between different reactions in a multiple reactor system. (Saleeman; 1985). An advantage of continuous process is that they are operated under steady-state conditions with each reactor requiring a constant rate of heat removal.

1.7 Separation and Analysis of Heterogeneous Polymer Systems

Heterogeneous polymer systems (e.g. block, graft, random copolymers contaminated with homopolymers) may be separated based on differences in chemical composition and segment distribution. Before the characterisation, either the block or the graft copolymer needs to be separated from the homopolymers or random copolymers. The ease of separation depends on the ability of two liquids, one acting as a solvent and another as a non-solvent for the species to be extracted.

Those procedures which can be used to isolate a particular component from its environment include: solvent extraction, and precipitation techniques (Johnson and Cantow 1971). Some of these procedures which are described below could be adopted singly or collectively for a particular component.

1.7.1 Solvent Extraction

In this technique, the separation of the components in the heterogeneous system is based on the differences in solubility of each component in a particular liquid (solvent). The liquid which disolves a particular component is a solvent for it, and that which cannot dissolve it, is its non-solvent.

Homopolymers can be extracted from the graft or block copolymer with a solvent which does not dissolve either of the components in the copolymer mixture. Sometimes when solvent pairs are available such that each solvent dissolves only one of the components (i.e. a non-solvent for the other), then a good separation can be achieved. This is similar to the selective-elution technique employed in many analytical procedures

(Bikales 1971). Sometimes the eluting liquid consist of one component only which is a good solvent for one of the species at high temperature but becomes poor solvent at a lower temperature e.g. PEMA was found to dissolve in ethanol at temperatures above 30°C but remain insoluble at temperatures below 20°C in our laboratory. Smets and Claesen (1952) achieved the separation of grafted copolymers of poly-(methyl methacrylate)-poly(vinyl acetate) (PMMA - PVAC) from its homopolymers based on differences in solubility of the latter in hot and cold ethyl alcohol.

Solvent extraction has the advantage over other methods of separating polymer constituents (e.g. precipitation, selective elution) in that it avoids the possibility of coprecipitation. The selective-elution technique gives a good systematic separation of polymer mixtures into different components. However, one major disadvantage of solvent extraction is that if the block or graft is particularly rich in one of the homopolymers, it may dissolve partly or wholly in the solvent, the order in which solvents are used in the selective-elution technique may affect the rate of extraction or may even inhibit the elution.

1.7.2 Fractional Precipitation Technique

The separation of the component of heterogeneous polymer system is often carried out on the basis of decreasing solubility of the components with increasing molecular weight (Tompa; 1956). In a solution of homopolymers mixed with either graft or block, the progressive addition of precipitant will cause the precipitation of one of the components since there exist solubility differences between the homopolymers

and the graft or the block copolymers. This technique is very effective when a common solvent for the heterogeneous polymer system has been found (a solvent for the homopolymer, graft, block copolymers) and separate non-solvents for these components. However, one major disadvantage here is that sometimes the copolymer segments may precipitate along with either of the homopolymers. Sometimes the solvated segments of the more soluble components can retain some segments of the least soluble one in solution, (Schielbel; 1965).

1.7.3 Selective Precipitation Technique

This method can only be used when there is a solvent-precipitant system that preferentially precipitates only one of the homopolymers at each stage, the others remaining in solution. Even when excess of this particular precipitant for this homopolymer is added, the precipitation is only effected for this homopolymer in question. A mixture of polystyrene, copolymer of polystyrene-polyvinyl acetate and polyvinyl acetate was separated by dissolving the mixture first in methyl ethyl ketone-methanol (1.1) system. The addition of methanol precipitates all the homopolystyrene. The remaining mixture was extracted using methanol which removed all the homopolyvinyl acetate leaving the copolymer as precipitate (Woodward and Smets 1955).

1.8 Analytical Methods for Qualitative and Quantitative Studies of Copolymers

The qualitative studies of copolymers arise from those chemical properties or the species present in the copolymer. The melting point, Tg, the functional group analysis, density and optical properties can be studied

qualitatively. The quantitative studies help to determine the amount of copolymer formed from the component polymers. Infrared spectroscopy can be used both qualitatively and quantitively (Kossler; 1971), (Bovey; 1971). Other quantitative methods include crystallinity index, Saponification numbers, Acetyl number, Acid numbers (Brauer and Horowitz 1962).

1.8.1 Spectrophotometry

Infrared (i.r.) and nuclear magnetic resonance (n.m.r) are the two most important physical-chemical methods predominantly used in structural and analytical studies of both polymers and copolymers. The ir. can be used in structural analysis of copolymer mixture to disclose the structure by characterisation of the functional groups present and the mode of their attachment to the polymer backbone. The aim of qualitative analysis of copolymer mixtures, is to determine the presence of individual components, e.g. in the case of copolymer it is to determine the presence of individual monomer unit . The sepctrum of a mixture is additively components.

However, it is extremely difficult to distinguish between a mixture of homopolymers and a true copolymer (Kossler; 1971). In general, infra-red spectroscopy can be used for the analysis of copolymers, crystallinity index , degradation of the components in the copolymer mixture. (Koenig; 1980).

NMR studies yield qualitative and quantitative information that is most often unequivocal for copolymers. The copolymer microstructure can be studied easily by NMR as different chemical shifts can be associated with copolymer sequences. The methyl methacrylate content in acrylonitrile-

methyl methacrylate copolymer has been determined using NMR (Chujo et al., 1972). Whether applied quantitatively or qualitatively both i.r. and n.m.r. remain one of the foremost non-destructive tools for analysis of copolymers.

1.8.2 X-Ray Diffraction Methods

The physical structures of polymer mixtures can be characterised by the chain conformation, the local order and the morphology. The x-ray diffraction pattern of polymer mixtures helps to elucidate the gross morphology of the sample. The order (crystallinity) results in well defined sharp peak whereas the disorder (amorphousity) give rise to broad peaks in the diffraction material (Billemeyer; 1970); Olabisi (1979). A typical semi-crystalline polymer such as polyethylene will show sharp peaks in its x-ray pattern.

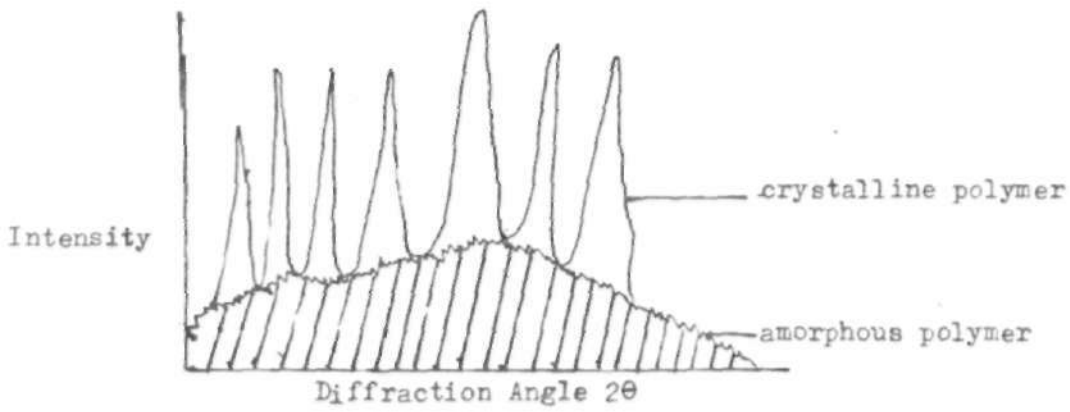


ILLUSTRATION I: X-ray Pattern Showing Amorphous and Crystalline Regions for a Typical Semi-Crystalline Polymer.

whereas an amorphous polymer, e.g. polyvinyl acetate, will show diffuse non-coherent pattern as shown in Illustration I for crystalline and amorphours polymers. If the two monomers which give a crystalline polymer and the other an amorphous polymer are copolymerised, the composition of each of these polymers in the copolymer can be determined by the X-ray method.

Melting Points

The thermal behaviour of high polymers can be assessed by the melting points. Unlike simple organic and inorganic substances, the melting point of polymers are molecular weight and structure-dependent. The influence on the thermal behaviour (e.g. melting point, glass transition temperature, softening point) of molecular weight, branching, copolymerisation, cross linking has been reported (Collins et al; 1973).

Ibiyeye (1984) reported the dependence of melting points of polyblends of polyvinyl acetate-polyethyl methacrylate on the blend composition and molecular weight ratios.

Microscopy

Microscopic methods (light microscopy, transmission electron microscopy, electron microscopy) can be used to ascertain the extent of homogeneity or heterogeneity in polymer mixtures. (Olabisi et al, 1979). Direct visual confirmation of the presence of two phases or one phase is a preliminary indication of the morphology of the mixture. A homogeneous morphology will either be attributed to the presence of only one component or total miscibility of the polymer mixture. A two phase morphology will suggest copolymer, mixture, partial or limited miscibility of the components (Olabisi et al; 1979). It is however, true that phase behaviour observed with microscopic methods may not correlate well with macrospic observation. In a copolymer, microscopic studies could give an insight to the homogeneity and compatibility of the different components in the copolymer mixture. Microscopic methods can also be used to determine not only the presence but the connectivities of the phases in the mixture (Olayemi & Yusuf 1989). Therefore, it is

useful tool in probing the different phases in a copolymeric material.

1.9 Research Aims and Objectives

Blends of PVAC and PEMA have been studied and the dependence of some mechanical properties of these blends especially of low molecular weight ratio ($\bar{M}v$)r PEMA/PVAC less than eight has been established (Olayemi and Ibiyeye; 1986). Those with wide molecular weight ratios of $5 < (Mv)r < 96$ of the same PEMA/PVAC was reported by Olayemi and Yusuf (1989). Both workers had reported superiority in properties of these blends over the homopolymers with evidence of synergistic and antagonistic behaviour.

However, industrial blending of polymers in rheometers require both high temperature and shear rates. These conditions have been reported to bring about degradation of either or both homopolymers especially if their melting temperatures are not comparable (Ibiyeye 1984).

Hence, in the case of blends of PEMA and PVAC, with wide range of temperature difference (PVAC mpt = 125°C; PEMA mpt = 276°C), meltmixing of the two polymers together at up to 276°C will lead to degradation of the low temperature component.

It is therefore necessary to seek for an alternative method of permanently incorporating the molecules of one polymer to the other by chemical bonds. One of the major alternative routes is copolymerisation of these two monomers - vinyl acetate and ethyl methacrylate which is the topic of this research.

1.10 Scope of Present Work

The main aim of the present study is aimed at copolymerising these two monomers VAC and EMA using emulsion copolymerisation techniques with

different processes batch, semi-continuous batch with a water-soluble initiator potassium persulphate ($K_2S_2O_8$) and sodium lauryl sulphate ($C_2H_{25}OSO_3Na$) emulsifier at 60°C. The properties of the products of the copolymerisation reaction are to be fully evaluated.

1.11 The Approach

The research will therefore entail:

(a) Determination of the effect of time of polymerisation on the conversion of monomer to polymer and viscosity average molecular weight ($\bar{M}v$) of the homoPVAc. and homoPEMA.

(b) Copolymerisation of EMA and VAc. in emulsion under batch, semi-batch and semi-continuous batch processes with same receipe and reaction conditions.

(c) Evolving suitable method for precipitation of product of copolymerisation using suitable non-solvent.

(d) Evaluation of the above products by means of chemical separation based on differences in solubilities of the homopolymers in known solvents.

(e) The quantitative determination of the portions of the homopolymers in the products, hence the quantity of the copolymer under each process.

(f) The qualitative study of the products and the separated components of the reactionfrom (e) above with infrared and nuclear magnetic resonance spectroscopy.

(g) Determination of the percentage ordering and crystallinity index of the samples with those of the homopolymers.

(h) Studies of the gross morphology of the products by optical microscopy.

(i) Determination of the melting points, if possible.

CHAPTER 2

2.0 LITERATURE REVIEW

2.1 General

Copolymerisation involving acrylic and methacrylic esters as the principal components have been reviewed by Luskin and Myers (1965). The mutual copolymerisation of methacrylic ester monomers (e.g. methyl methacrylate) and other monomers such as vinylacetate have been found to proceed with ease. In addition, the monomers namely: methylacrylate, n-butylacrylate, ethylacrylate and ethyl methacrylate readily copolymerise with all types of vinyl monomers (e.g. vinyl acetate, vinyl chloride, styrene). Although both the acrylic and methacrylic esters are readily incorporated to form copolymers with almost all types of monomers; the very long-chain alkyl counterparts copolymerise with difficulty (Schildknecht 1952). This behaviour of poor reactivity of long-chain alkyl esters in copolymerisation could be attributed to the steric effect. The bulkiness of the long chain alkyl monomers is suspected to be a major factor to the effect above.

The synthesis of copolymers depend on the degree of interaction of the two monomers involved. The extent of interaction between these two monomers depend on the following factors:

(i) polarity of the double bond, which is determined by the groups attached to the ethylenic double bond.

(ii) resonance stabilization of the monomer and the radicals produced.

The polarity effect is enhanced if an electron withdrawing group is attached to the double bond which will impart positive character on it. Schildknecht (1952) reported that steric hindrance, configurational effects and repulsive forces are the most important factors governing

the interaction of monomers and radicals in copolymerisation. Also, the reactivities of the monomers are affected by the type of initiators and system used e.g. whether emulsion, solution or suspension (Odian 1981). However, monomer reactivities in radical copolymerisation were believed to be little affected by experimental conditions (Odian 1981). For example, the reactivity is independent of feed composition, conversion, solvents, regulators, source of free radicals used and even the rate of polymerisation. Efforts to overcome the reluctance of monomer pairs to copolymerise have been very unsuccessful, but some progress has been made especially in activated systems (Schildknecht 1952). In the same vein, the relative ease of copolymerisation for 1:1 mixtures of acrylic and methacrylic monomers with some common monomers (e.g. acrylonitrile, styrene, vinylchloride, butadiene) have been extensively discussed (Luskin and Myers 1965).

Many polymerisation techniques such as emulsion, solution, suspension have been used in the production of copolymers. However, commercial production of acrylic copolymers is largely confined to solution and emulsion techniques (Luskin and Myers 1965). The emulsion techniques is well recognised for its convenience, speed, control of temperature, completeness of conversion and the reproducibility of product properties (Saleeman 1985).

2.2 Copolymerisation Characteristics of Vinyl acetate

Reports of copolymerisation as involving vinyl acetate and acrylic or methacrylic esters abound in literature. Also a good number of these copolymer have been patented (Schildknecht 1952), (Odian 1981). Vinyl-acetate has been known to copolymerise with acrylic esters and other

vinyl monomers - e.g. styrene,methyl methacrylate and methylacrylate. However, the reluctance of vinyl acetate to copolymerise with these other monomers have been known to industrial chemists for a good number of years (Schildknecht 1952).

Vinyl acetate copolymerisation characteristics has been extensively reviewed by Schildknecht (1952). In this review, vinyl acetate is said to be one of the least reactive monomers towards addition to growing chain in peroxide - catalysed copolymerisation with a second monomer. It was also pointed out that the addition of vinyl acetate retards the polymerisation of most other vinyl monomers. However, the degree of retardation vary from one monomer to the other. For example, at one extreme there is a marked inhibition observed with styrene - vinyl acetate whereas the retardation is reduced in peroxide-catalysed copolymerisation involving vinyl acetate with vinyl chloride or methyl methacrylate. On the other hand, vinyl acetate in the review of Schildknecht (1952), has been known to copolymerise readily with certain unsaturated compounds which do not homopolymerise readily e.g. maleic anhydride and maleic esters. It has been claimed that, to a copolymer chains having vinyl acetate at the growing end, almost all other monomers add more readily than vinyl acetate itself. The relative reactivities of some vinyl monomers when copolymerised with vinyl acetate has been reviewed (Schildknecht 1952). These vinyl monomers include methyl methacrylate methacrylonitrile, styrene, acrylonitrile, vinyl ether, methyl acrylate, isopropenyl acetate. The relative reactivities of these monomers were found to depend on the structure and functional groups.

Reactivity ratios in copolymerisation are not simply related to only rates of homopolymerisation but also depend on a number of other factors (Schildknecht 1952). These other factors include the effect of

one monomer on one another, the system (i.e. emulsion, suspension and solution), the temperature and concentration of monomers (Conn and Neher 1950). Also Ham (1964), had presented an excellent treatise on the effect of some of these factors on the copolymerisation of vinyl monomers. In copolymerisation, the most reactive monomers may be converted to radicals or macroradical chains of low reactivity or vice versa.

Although vinyl acetate has been reported to be one of the less reactive monomers in vinyl copolymerisation (Schildknecht 1952). but vinyl ethyl ether has been found to have a lower reactivity ratio (r_1 = 0.0) than vinyl acetate (r_2 = 3.0) during the copolymerisation of these two monomers. The acetate group in vinyl acetate is presumed to be more reactive than oxygen atom in the molecule of the vinyl ethyl ether (Tewari et al., 1976).

Generally, with acrylic esters and some vinyl halide monomers (e.g. vinyl chloride, vinylidene chloride), vinyl acetate copolymerises comparatively readily. Among the methacrylates, copolymerisation had been carried out mostly with the methyl methacrylate and vinyl acetate while few patents of copolymerisation of vinyl acetate with ethyl methacrylate have been reported (Schildknecht 1952). Other studies on copolymerisation involving methacrylates and vinyl acetate have also been reported in literature (Nair and Muthana 1961). This study revealed that methacrylic ester chains in n-butyl methacrylate and isobutyl methacrylate prefer to add to its own monomer than vinyl acetate. The analysis showed that the methacrylate content was more than vinyl acetate in the resulting copolymer.

KASHIM IBRAHIM LIBRARY
AHMADU BELLO UNIVERSITY
ZARIA, NIGERIA.

Several experiments carried out by Smets and Claesen (1952) confirmed that the solubilities of poly(methyl methacrylate) and poly (vinylacetate) are independent of molecular weights. They also claimed that at 20°C only poly(vinylacetate) remains in solution while poly-(methylmethacrylate) precipitates out as a solid. A modification of this method was employed in the separation of poly(ethyl methacrylate) and poly(vinylacetate) in the 'copolymerisation products' in this research as described in chapter 3.

2.3 Graft Copolymerisation of Some Vinyl Monomers with Vinyl Polymers

Studies of a number of graft copolymerisation involving a series of different monomer-polymer systems in benzene with benzoyl peroxide initiator at 70°C had been carried out by Smets and Claesen (1952). Some of these monomer-polymer pairs formed graft copolymers while others met with failure. The report is shown in table 2.1

Table 2.1: Graft Copolymerisation Involving Monomer-Polymer Pair at 70°C.

Monomer	Polymer	Whether Grafted of Not?
Vinyl acetate	Poly(methyl methacrylate)	Grafted
Vinyl acetate	Polystyrene	Not grafted
Vinyl chloride	Poly(methyl methacrylate)	Grafted
Methyl methacrylate	Poly(vinyl acetate)	Not grafted
Methyl methacrylate	Poly(vinyl chloride)	Not grafted
Styrene	Poly(methyl methacrylate)	Grafted
Methyl mathacrylate	Polystyrene	Grafted

Formation of graft copolymers have been known to be enhanced by the macroradical and the polarity difference between the monomer and the polymer. High stability of macroradical and a large polarity difference favours formation of graft copolymers while low stability and small polarity difference leads to formation of no graft but homopolymer mixtures. For example, homopolymer mixtures of poly(vinyl acetate), polystyrene were obtained from vinyl acetate - polystyrene system with benzoyl peroxide. Similar experiments with vinyl acetate - poly(methyl methacrylate) yield graft copolymer. On the other hand, the failure of the methyl methacrylate - poly(vinylacetate) system to graft was based on the fact that the degradation of poly(vinylacetate) in the presence of benzoyl peroxide being slow leading to little or no reaction in terms of grafting. However, this behaviour of poly(vinylacetate) and other methacrylate monomers (e.g. ethylmethacrylate) with other initiators such as potassium persulphate has not yet been investigated (Smets, Claesen 1952).

The degradation of vinyl polymers in the presence of initiators enhances the feasibility of grafting (Smets and Claesen 1952). The order of variation of degradation of some vinyl polymers in the presence of benzoyl peroxide at 70°C reported by Smets and Claesen (1952) follow the sequence polystyrene > poly(methylmethacrylate) > poly(vinyl acetate). This is reflected in the results from these authors in Table 2.1. Formation of graft copolymer by chain transfer mechanism is linked with the degradation of the polymer to form a macroradical. If the degradation is slow, the rate of grafting will be slow, since few macroradicals will be present for the grafting reaction. It means that the 'foreign' monomer (added monomer) will attack the few available macroradicals at the reactive sites to produce the graft copolymers. Although the

macroradicals may be present in the system, grafting will also be enhanced if the polarity difference between the macroradicals and the 'foreign' monomer is large. Hence, the quality of macroradicals present and the polarity difference between it and the 'foreign' monomer determines the extent of grafting. The more stable the macroradical is, the greater the possibility that it will be attacked by the foreign monomer to produce graft, the less stable, the less the chances for formation of graft copolymers. It is not yet very clear what factors really enhance the stability of macroradicals except that its length and molecular weight are possible factors.

Polar monomers penetrate the polymer matrix more than less polar ones. For example, acrylonitrile which is more polar than vinyl acetate has been found to penetrate starch substrate more during graft copolymerisation of both monomers onto starch matrix (Nolau 1969). However, Smets et al., (1961) reported that the polarity of the monomer used played a vital role in the degree of grafting for certain monomer - polymer system (e.g. methylmethacrylate - polystyrene) while in others (e.g. poly(methylmethacrylate) - vinyl acetate, poly(methyl methacrylate)-vinyl chloride) the role is not significant. Methyl methacrylate monomer is more penetrating than vinylacetate because the later monomer is a non-conjugated molecule. Hence methylmethacrylate penetrate poly(vinyl acetate) matrix more than vinyl acetate on the poly(methyl methacrylate) matrix. (Smets and Claesen 1952).

The effect of initiator on the degree of grafting between certain monomer - polymer by chain transfer mechanism had been reported by Smet et al., (1961). They showed that certain monomer - polymer systems (e.g. methylmethacrylate - polystyrene) could only form graft in the presence of benzoyl peroxide while only homopolymer mixtures were obtained

using azobisisobutyronitrile (AIBN) and di-tert-butyl peroxide (DTBP) initiators at 70°C. This observation could be attributed to the inferior capacity of the resonance - stabilized isobutyronitrile radical $Me_2 = \dot{C} - CN$, in comparison with the $C_6H_5^{\bullet}$ and $C_6H_5COO^{\bullet}$ radicals to engage in chain transfer reaction. The stability of these radicals follow the order $Me_2 = \dot{C} - CN > C_6H_5^{\bullet} > C_6H_5COO^{\bullet}$. Hence benzoyl peroxide can enhance grafting more than the other two initiators. However, the effect of potassium persulphate in grafting had not been reported in literature.

2.4 Emulsion Copolymerisation of Vinyl acetate with n-butylacrylate

The copolymerisation of vinyl acetate and n-butylacrylate using batch and semi-continuous batch processes have been investigated (El-Aasser and Vanderhoff 1985). The area of interest was focused on the examination of the effect of comonomer composition and the emulsion process on polymer and latex properties. The kinetics of copolymerisation was examined in detail and the copolymers fully characterised. The result clearly showed that the process had a direct influence on the polymer and the latex properties. Copolymer latex with a more uniform copolymer composition was obtained from the semi-continuous batch than from the batch process. They concluded that homogeneity in copolymer composition depends on the process of emulsion copolymerisation between these two monomers (vinyl acetate and n-butylacrylate).

2.5 Emulsion Copolymerisation of Methylmethacrylate with Vinylacetate

The emulsion copolymerisation of methyl methacrylate (MMA) and vinylacetate (VAc) has been investigated by Saleeman (1985). The investigation was aimed at determining whether poly(vinyl acetate) poly(methylmethacrylate) copolymer latex of uniform copolymer composition could be obtained using either the batch or semi-continuous batch process. The copolymers formed under these two processes were fully analysed and characterised. It was found out that semi-continuous batch process gave a copolymer of uniform composition despite the wide disparity in the comonomer reactivity ratios and water solubilities of 0.07 and 290mM for VAc and 22.0, 150mM for MMA respectively (Immergut and Brandrup 1975). Attempts to cast films from the batch copolymer latex met with failure suggesting a non-homogeneous composition of the copolymer, whereas films of good quality were formed from the semi-continuous batch copolymer latex. It could be suggested therefore that in order to obtain a copolymer of uniform composition between monomer pairs of wide disparity in reactivity ratios, the semi-continuous batch process could be employed. Although the work of Saleeman (1985) centred on the composition of the copolymers, it is also believed that the properties of the copolymers formed under the batch and semi-continuous batch processes, would definitely be different. However, the uniformity of copolymers between poly(vinyl acetate) and poly(methylmethacrylate) therefore depend on the type of emulsion copolymerisation process.

2.6 Review of Methods for Synthesis of Block and Graft Copolymers

Intensive activity in the synthesis and characterisation of block and graft copolymers is a recent development which has been reviewed by **Burlant** and Hoffman (1965). Many ingeneous methods **have** been devised over the years for the synthesis of copolymers. Some of these procedures are discussed under the following:

2.6.1 Transfer Processes and Long Lived Radical Process

The most frequently used method for the synthesis of block or graft copolymers involves a process in which the second monomer is added to an emulsion of a polymer formed by the first monomer. Sometimes the second monomer is added to a prepolymer of the first monomer before it has been completely converted. Hughes and Brown (1961) discussed the emulsion polymerising of one monomer in the presence of a preformed polymer of a different type of monomer as a two-stage polymerisation. When a monomer is polymerised in the presence of a preformed polymer emulsion, penetration of a second monomer into the polymer matrix occurs if the polymer is swollen by the monomer. There is a possibility of an outside layer rich in the polymer of the second stage monomer (i.e the added monomer) because of the new homopolymer being formed especially at high emulsifier concentration. Also Hughes and Brown (1961) had pointed out the variation in the scheduling of monomer addition in emulsion polymerisation to produce polymers with substantial alterations in chemical and physical structures. In a particular instance, monomers may be charged simultaneously into the reaction mixture which will lead to the production of a homogeneous copolymer. Again, in a related example, monomers may be charged

sequentially to produce polymers of greater heterogeneity. The 'copolymerisation products' may contain mixtures of homopolymers/or graft copolymers. There is the possibility of these products consisting of isolated regions such as concentric shells of the homopolymers. It is expected that the products obtained under these conditions should have several structural possibilities, including extremely heterogeneous random, graft or block copolymers. In most cases, evidence is always lacking for an unequivocal distinction between these several structural possibilities. The determination of such structures may indeed be a formidable task. An excellent treatise on the synthesis and characterisation of block and graft copolymers have been presented in literature (Ceresa 1965). Radical chain transfer processes have been used for the grafting of styrene, ethylacrylate and butylmethacrylate to backbones of poly(methylmethacrylate) and poly(ethylacrylate) have been reported by Gluckam et al., (1959).

2.6.2 Grafting with Preformed Initiating Sites on the Polymer Backbones

Preformed or natural polymers can be treated chemically or irradiated to form sites on the backbones which are capable of subsequent initiation of an added monomer (Woodward et al., 1954). Most of such processes involve oxidation to hydroperoxides or peroxides which are then dissociated by heating into macroradicals in the presence of monomers. Woodward et al., (1954) prepared block copolymers of polystyrene - poly(vinylacetate), polystyrene - poly(methyl methacrylate) using phthalyl peroxide - a polyperoxide in benzene at 100°C. They were able to produce block copolymers because of the initiating sites created on the polymer backbone by the peroxide radicals. Other polymeric

substrates susceptible to these procedure of peroxide initiation are polyolefins, natural and synthetic rubbers, starch, vinyl and acrylic polymers (Luskin and Myers 1965).

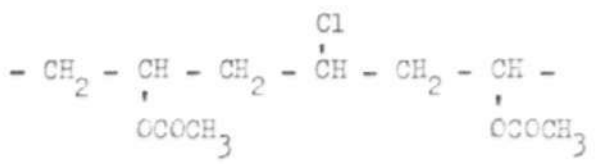
2.6.3 Photochemical Grafting

The initiation of grafting by chemical initiation by photolysis is well known. Photolysis is the absorption of electromagnetic radiation in the visible and ultraviolet region to cause rupture of chemical bonds giving rise to macroradicals in polymers. This is particularly applicable to polymers with photosensitive groups e.g. vinyl acetate with the $-C-\overset{O}{\overset{\|}{C}}-CH_3$ being photosensitive . Copolymers of methylmethacrylate and vinyl methyl ketone have been grafted on vinyl acetate unsing photochemical means (Ham 1964). In photochemical grafting, photosensitizers are employed for the photoinitiation of the whole process. Photosensitizers are molecules especially dyes, which are affected by light. A dye molecule when photoexcited abstracts a hydrogen atom from the polymer to yield a grafting site. Irradiation with photosensitizers yield grafts when it is with polymer - monomer mixture as a result of formation of free-radicals on the backbone polymer derived from the photosensitizer. Anthraquinone dyes are typical photosensitizers that have been employed in the grafting of acrylonitrile, methylmethacrylate, vinylacetate onto polymeric films such as poly(vinyl alcohol) and nylon 6,6 (Glaylord and Ang 1964).

2.6.4 Mechanical Processes

Copolymers can be produced by a mechanical process such as milling, grinding or kneading. When a mixture of two polymers is subjected to an applied shear, a mixture of block and graft copolymer are produced

(Glaylord and Ang 1964). The radicals from chain rupture can initiate polymerisation of a monomer present in the polymer being subjected to the shearing force. Crafts are also formed because chain transfer reaction can take place which lead to the location of the free radical in a non-terminal position on the polymer chain. Poly(vinyl acetate) agitated in the presence of vinyl chloride produced a block copolymer (Gaylord and Ang 1964) of the sequence



Mastication of poly(methylmethacrylate) in the presence of styrene produced block copolymers of 85% yield (Luskin and Myers 1965). Several other monomers masticated with poly(methylmethacrylate), the rates of polymerisation have been found to vary in the order of methacrylic acid methyl methacrylate> acrylonitrile > ethylacrylate > styrene > vinyl acetate (Luskin and Myers 1965). The composition and structures of these products are in most case, ill-defined.

Chapter 3

3.0 RESEARCH PROCEDURES

3.1 Homopolymerisation of Monomers

3.1.1 Ethyl Methacrylate

The ethyl methacrylate was obtained from the British Drug House Ltd. (BDH). It was stripped off its hydroquinone inhibitor by washing it repeatedly with 2% sodium hydroxide solution in a separating funnel. The organic layer which contained the monomer was washed several times with distilled water to remove traces of the alkali. The inhibitor-free monomer was dried over anhydrous sodium sulphate before distillation at 79°C under reduced pressure using water pump at a pressure of 0.15 millibar. The purity of the distillate was ascertained by treatment of a small quantity of the purified monomer with aqueous sodium hydroxide which did not produce yellow coloration in this aqueous layer. The purified monomer was stored in a brown bottle in a refrigerator until needed.

3.1.2 Vinyl acetate

Vinyl acetate(BDH) was treated in the same way as described for ethyl methacrylate in Section 3.1.1 above except that 5% sodium hydroxide solution was used in removing the hydroquinone inhibitor. The distillation temperature in this case was at 46°C and a water pressure of 0.15 millibar.

3.1.3 Initiator and Emulsifier

The initiator (potassium persulphate - $K_2S_2O_8$) and emulsifier (sodium lauryl sulphate - $C_{12}H_{25}OSO_3Na$) obtained from British Drug House (BDH) were used as received. The initiator was of analytical grade whilst the emulsifier was reagent grade.

3.1.4 Nitrogen Gas

Pure nitrogen gas was required to create an inert atmosphere for the polymerisation. To completely get rid of oxygen from the commercial nitrogen (N_2) gas supplied, the nitrogen gas was passed through Fieser solution prepared by the procedure of Fieser and Fieser (1967) to absorb the oxygen. The oxygen-free nitrogen was then passed through three other wash bottles containing calcium hydroxide to remove any trace of carbon dioxide, concentrated sulphuric acid to remove water vapour, saturated lead acetate solution to remove hydrogen sulphide impurities in the nitrogen and finally silica gel before the reaction mixture to dry the gas.

Methanol (BDH, LR), dipotassium hydrogen phosphate (BDH, AnaLAR), hexane, heptane, methyl ethylketone, ethanol, acetone, ethyl acetate, chloroform were purified by standard methods before use.

3.1.5 Polymerisation Studies of the Monomers

The polymerisation of both ethylmethacrylate (EMA) and Vinyl acetate (VAC) was independently carried out using a one litre

5-necked flask maintained at constant temperature of 60 ± 1°c in a water bath. The reaction mixture without the monomer was charged into the flask to attain the temperature of the bath. Prior to the addition of monomer, purified nitrogen was bubbled through the mixture for a period of 30 minutes. The monomer was then added via a dropper for a period of 15 seconds. Samples for the viscosity average molecular weight ($\bar{M}v$) determination were pipetted out at different time intervals of 30, 60, 90, 120, 165, 210 and 240 minutes respectively. A fixed aliquot of 25cm^3 of the mixture withdrawn during the course of the reaction was poured into ice-cold methanol for PEMA and sodium chloride solution for PVAC, recoveries respectively. After stirring, the solid which separated out was filtered, and washed thoroughly with distilled water to remove traces of water - soluble contaminants like the initiator and emulsifier. The product was dried to constant weight in a vacuum pressure oven at 40°C. The percentage conversion from the monomer was calculated for each sample. These samples were kept for the viscosity average molecular weight determination. A common receipe used for the polymerisation study is shown in table 3.1.

Table 3.1: Receipe for Polymerisation of EMA and VAc Monomers

Components	Quantity
Monomer	7.0cm^3
Potassium persulphate	0.225g
Sodium lauryl sulphate (SLS)	2.0g
Buffer solution (dipotassium hydrogen phosphate)	10.0cm^3
Distilled water	2.33cm^3

3.1.6 Viscosity Average Molecular Weight ($\bar{M}v$) Determination of PEMA and PVAc Samples

The efflux times for the polymer solutions were determined in Ubbeholde viscometer at 30 ± 0.05°C for PVAc in methanol and 35 ± 0.05°C for PEMA in ethylacetate solvents. The limiting viscosity was determined from the linear plot of $*\eta_{sp}/c$ against concentration by extrapolation to zero concentration. The viscosity average molecular weight ($\bar{M}v$) of the polymer samples were determined from the intrinsic viscosities $/\eta/$ using the Mark - Houwink - Sakurada equation $K = \bar{M}v^{a}$, (Brandrup and Immergut, 1975) The K and a constants were 31.4 x 10^{-3} cm^3 g^{-1} and 0.60 for PVAc in methanol at 30°C and 8.6 x 10^{-3} cm^3 g^{-1} and 0.72 for the PEMA - ethylacetate system at 35°C respectively. These constants were used for the calculation of ($\bar{M}v$) from the intrinsic viscosity $/\eta/$.

$*_{sp}$ = specific viscosity
c = concentration

3.2 Emulsion Copolymerisation of EMA and VAc Monomers

The copolymerisation of the two monomers - EMA and VAc was carried out at 60°C in a one - litre five - necked reaction flask immersed in a water bath. The methods of copolymerisation employed were the batch, semi-batch, semi-continous batch (semi-batch continous) and the semi-continous emulsion processes.

3.2.1 Semi-Batch Emulsion Copolymerisation

The reaction flask was charged with potassium persulphate (0.225 g) - the initiator, sodium lauryl sulphate (SLS) (2.0 g) - the emulsifier, distilled water ($170cm^3$), the buffer - dipotassium hydrogen phosphate solution ($10.0cm^3$) for one hour after the flask had attained the temperature of the bath. Stirring at a preselected suitable rate which began at the on-set of the experiment continued until the end of the experiment. To ensure an inert atmosphere, pure nitrogen gas was allowed to purge the reaction flask for thirty minutes. After allowing the contents of the flask to attain the bath temperature of 60^oC, the vinylacetate monomer ($7.0cm^3$) was then added in batch to the reactor via a dropping funnel for 15 seconds. The polymerisation of VAc was allowed to proceed for a period of 30 minutes before the addition of the ethylmethacrylate ($7.0cm^3$) in batch via a dropping funnel. The reaction was then allowed to proceed for a period of 9 hours. The above procedure was repeated but with different time intervals of 60, 120, 240, 300, 360 and 420 minutes for initial polymerisation of vinylacetate prior to addition of ethylmethacrylate into the flask. The different initial time of polymerisation of VAc prior to EMA addition and the different samples obtained are shown in table 3.2.

Table 3.2: Initial Time of Polymerisation of VAc (batch) and Time of Copolymerisation after addition of EMA (batch) in Minutes

Sample[(a)]	Initial Time of Polymerisation Of VAc prior to EMA addition in Minutes	Time of Copolymerisation After addition in EMA in Minutes	Total time of reaction in Minutes
PBB_1	30	510	540
PBB_2	60	480	540
PBB_3	120	420	540
PBB_4	240	300	540
PBB_5	300	240	540
PBB_6	360	180	540
PBB_7	420	120	540

PBB means product from batch - batch copolymerisation and numerals 1 - 7 represent the different samples with initial time of polymerisation of VAc (30, 60, 120, 240, 300, 360 and 420 minutes) prior to EMA addition.

3.2.2 Semi-batch Continous Emulsion Copolymerisation

The experiment was carried out as described in Section 3.2.1 for the semi-batch process except that the second monomer ethyl methacrylate was added at a predetermined constant rate of $7.0cm^3$ per hour into the reaction medium via a dropping funnel. This gives rise to a series of products referred to as PSB, meaning product of semi-batch continous 'copolymerisation products'. The details of the experiment is shown in table 3.3.

Table 3.3: Initial Time of Polymerisation of VAc (batch) and Time of Copolymerisation after dropping of EMA (continuous) at a fixed rate of 7.0cm^3/hour in Minutes

Sample[(a)]	Initial time of Polymerisation of VAc (batch) prior to dropping of EMA (continuous) in Minutes	Time of Copolymerisation After addition in EMA in Minutes	Total time of reaction in Minutes
PSB_1	30	510	540
PSB_2	60	480	540
PSB_3	120	420	540
PSB_4	240	300	540

PSB means semi-batch continuous copolymerisation products and numerals 1 - 4, represent the different samples with the various initial time of polymerisation of VAc (30, 60, 120, 240 minutes) prior to dropping of EMA.

3.2.3 Semi-Continuous Emulsion Copolymerisation

The experiment was performed with two variation in the manner of adding the comonomer mixture (mixture of EMA and VAc - v/v) as described below:

Monomer - Starved Addition:

The flask was charged with the potassium persulphate initiator (0.225g), sodium lauryl sulphate emulsifier (2.0g) and dipotassium hydrogen phosphate - buffer (10.0cm^3) and 10% of the comonomer mixture of EMA (7.0cm^3) and VAc (7.0cm^3) were then added to the reaction flask before the dropwise addition of the remaining 90% at a predetermined rate of 7cm^3 per hour. The 10% comonomer mixture was added 10 seconds before the 90% and the copolymerisation proceed for 9 hours. The sample was coded as PSMCM3 - meaning product from semi-continuous monomer starved reaction.

Mixed Monomer Dropping:

In this method, the comonomer mixture of EMA ($7.0cm^3$) and VAc ($7.0cm^3$) was introduced into the reaction flask at a predetermined rate of $7.0cm^3$ per hour. The sample obtained was coded PSMC - meaning product from semi-continous mixture.

3.2.4 Batch Emulsion Copolymerisation

In this method the experiment was carried out as described for the mixed monomer dropping in Section 3.2.3, except that the comonomer mixture of EMA ($7.0cm^3$) and VAc ($7.0cm^3$) was added to the reaction medium in batch at once. The product from this experiment was labelled PMMB - product from mixed monomer in batch.

A common receipe used for all the copolymerisation processes from section 3.2.1 - section 3.2.4 is shown in table 3.4.

Table 3.4: Common Receipe for Copolymerisation of ethyl methacrylate and vinyl acetate monomers

Components	Quantity
EMA Monomer	$7.0cm^3$
VAc Monomer	$7.0cm^3$
Dipotassium hydrogen phosphate - buffer	$10.cm^3$
Potassium persulphate (initiator)	0.225g
Sodium lauryl sulphate	2.0g
Distilled water	$226cm^2$

3.2.5 Preliminary Investigation of Precipitation of Copolymerisation Product using Various Non-Solvents

The product of each copolymerisation reaction was isolated from the reaction mixture by dropwise addition of the non-solvent to the mixture with vigorous stirring. The volume of non-solvent in each case was 4:1 in ratio of non-solvent to the reaction mixture. The precipitated solid was washed several times with distilled water to remove water-soluble contaminants such as the initiator ($K_2 S_2 O_8$) and emulsifier ($C_{12} H_{25} OSO_3 Na$). The solid sample was dried to constant weight in a vacuum pressure oven at 40°C. The following liquids were tried as non-solvents in order to select a suitable non-solvent for this system (poly (vinylacetate) - poly (ethyl methacrylate)): methanol, methanol/sodium chloride solution (v/v), sodium chloride solution, hexane, petroleum ether, heptane. The recovery of the 'copolymerisation product' from each non-solvent and the appearance of this product obtained from each of these non-solvent are shown in table 3.5.

Table 3.5: Recovery of same 'Copolymerisation Product' from Various Non-Solvents

Non-Solvent	Percentage Recovery	Copolymerisation Product	Appearance	Melting Point (°C)
Methanol	77.30	PP_1	white, powdery	235-236
Methanol/sodium Chloride solution (v/v)	54.57	PP_2	dull, less powdery	235-236
Sodium chloride solution	40.54	PP_3	dull, milky	235-236
Hexane	71.10	PP_4	fine, ppwdery	205-210
Petroleum ether	69.92	PP_5	dull, fine	205-210
Heptane	70.50	PP_6	fine, powdery	205-210

The removal of the 'copolymerisation product' from the sodium chloride solvent was met with difficulty as the product was 'milky' with no sharp demarcation between the precipitate and the supernatant. The other non-solvents (table 3.5) presented no difficulty as the sodium chloride solution in recovering the 'copolymerisation product' after precipitation. The percentage recovery was calculated from the formula:

Percentage conversion

$$= \frac{\text{weight of solid precipitated (g)}}{\text{volume of EMA} \times \text{*density} + \text{volume of VAc} \times \text{*density}\ (g)} \times \frac{100}{1}$$

*density of EMA = 0.917 $gmcm^{-3}$

*density of VAc = 0.934 $gmcm^{-3}$

3.3 Preliminary Investigation of the 'Copolymerisation Product' From the Various Non-Solvents

3.3.1 Solubility Test

The solubility test on all the samples (table 3.5) was carried out according to the method described by Brauer and Horowitz (1962). The powdered sample (0.1g) was placed in a test tube with the solvent (1.0cm^3) at room temperature. The test tube was shaken for every 15 minutes and the mixture observed periodically for one hour. The nature of the solution observed for each sample in the following solvent: chloroform, benzene, chlorobenzene, toluene, Acetic acid, Butanone, acetone, cyclohexanone,

methanol, ethanol. All the copolymerisation products were soluble in all the solvents except methanol and ethanol in which they were partially soluble and insoluble respectively.

Subsequent 'copolymerisation products' were recovered from the reaction mixture using hexane.

3.4 Methanol Extraction of PEMA, PVAc and Their Physical Mixtures

Woodward and Smets (1955) adopted a method in separating a graft copolymer of polystyrene - poly (vinylacetate) from the 'copolymerisation products' by dissolving the product in cold methanol to remove pure poly (vinylacetate). Similar method was used by Hayes (1953) for the extraction of poly (vinylacetate) from the copolymerisation product of poly (vinylacetate) - poly (methyl methacrylate) system. The principle adopted for the methanol extraction of the physical mixture of PVAc/PEMA was based on these two procedures.

Methanol Extraction Procedure:

A known quantity of the PEMA, PVAc homopolymers, the physical mixture of these two polymers $0.5g / 25.0cm^3$ were taken into separate conical flasks containing cold methanol. The mixture was allowed to stand for 48 hours and shaken mechanically for 3 hours. The dissolved portion was recovered from the solution by concentrating the solution of the methanol extracted portion in a weighed wash glass. The undissolved portion of the mixture (methanol-insoluble-

MIS) was removed by simply decanting the solution, washed several times with small portion of methanol. Both the methanol insoluble (MIS) and methanol soluble (MSS) were dried to constant weight in vacuum pressure oven at 40°C. Quantities of PEMA and PVAc recovered from methanol are shown in table 3.6.

Table 3.6: Methanol Extraction of PEMA and PVAc

Polymer Sample	Quantity in Methanol (g)	Quantity of Polymer Recovered (g)		Percentage Recovery [b]
		PEMA	PVAc	
PEMA	0.50	0.498	-	99.60
PEMA	0.50	0.496	-	99.20
PVAc	0.50	-	0.495	99.00
PVAc	0.50	-	0.496	99.20
PEMA/PVAc[a]	1.0/1.0	1.00	0.98	100/98.0
PEMA/PVAc	1.0/0.5	1.00	0.49	100/98.0
PEMA/PVAc	0.2/0.2	0.200	0.195	100/97.5

a = obtained by physical mixing of polymers (w/w).

b = percentage recovery

$$\text{Percentage recovery} = \frac{\text{Quantity of polymer after extraction (g)}}{\text{Quantity of polymer in methanol (g)}} \times \frac{100}{1}$$

Since methanol is a solvent for PVAc whilst at the same time a non-solvent for PEMA, the undissolved portion that is the methanol insoluble (MIS) recovered by simple decantation is the PEMA. The i.r spectra of the sample before and after the extraction confirms this fact. The dissolved portion that is the methanol soluble (MSS) which is the PVAc was recovered by

concentrating the solution in a wash glass and evaporating the solvent to dryness. Also the i.r spectrum of the sample before and after dissolution in methanol confirmed this to be PVAc.

3.4.1 Ethanol Extraction of PEMA and PVAc

The method of Smets and Claesen (1952) was modified and used in this study. Trial experiments were carried out on pure PEMA, PVAc and their physical mixtures in different proportions. This method is based on the differential solubilities of PEMA and PVAc in hot and cold ethanol. According to Smets and Claesen (1952), at a reflux temperature (80°C), the ethanol dissolve the two polymers. However, when the temperature was reduced gradually to 20°C, only PVAc remained in solution while PEMA precipitates out. They also claimed that the quantities of these two polymers recovered were independent of molecular weight.

Ethanol Extraction Procedure:

The polymer sample, the physical mixtures (0.5g) was introduced into 100cm^3 - capacity round bottomed flask containing ethanol (10cm^3). This was refluxed for 2 hours on water bath at 80°C. All the samples completely dissolved on refluxing for this period. The temperature of the flask with its content was gradually reduced to room temperature and finally to 22°C. At this temperature, a white solid precipitates out. This precipitate was collected by filteration and washed several times with small quantities of cold ethanol. The solid was dried to constant weight in a vacuum pressure oven at

KASHIM IBRAHIM LIBRARY
AHMADU BELLO UNIVERSITY

40°C. The supernatant was poured into a weighed wash glass and concentrated to dryness. The resulting solid was treated as for the precipitate above. The percentage recovery in each case was calculated using the formula below:

$$\text{Percentage recovery} = \frac{\text{weight of sample recovered (g)}}{\text{weight of sample in ethanol (g)}} \times \frac{100}{1}$$

Details of the ethanol - extraction of the PEMA and PVAc are shown in table 3.7.

Table 3.7: Ethanol Extraction of PEMA and PVAc by Refluxing for 2 hours at 80°C.

Polymer Sample	Quantity Refluxed (g)	Quantity Recovered (g)		Percentage Recovery [b]
		PEMA	PVAc	
PEMA	0.50	0.495	-	99.00
PEMA	0.20	0.195	-	98.00
PVAc	0.50	-	0.492	98.40
PVAc	0.20	-	0.195	98.00
PEMA/PVAc[a]	0.5/0.5	0.498	0.495	99.6/99.0
PEMA/PVAc	0.5/1.0	0.495	0.98	99.0/98.0
PEMA/PVAc	0.2/0.2	0.198	0.195	99.0/98.0

a = obtained by physical mixing of polymers (w/w).

b = as given in the expression above.

3.4.2 Methanol Extraction of 'Copolymerisation Products'

Based on the procedure described in Section 3.4 for the methanol extraction of PEMA, PVAc from the physical mixture, a

scheme of procedure was developed for the separation of the 'copolymerisation product' into methanol insoluble (MIS) and methanol soluble (MSS) portion.

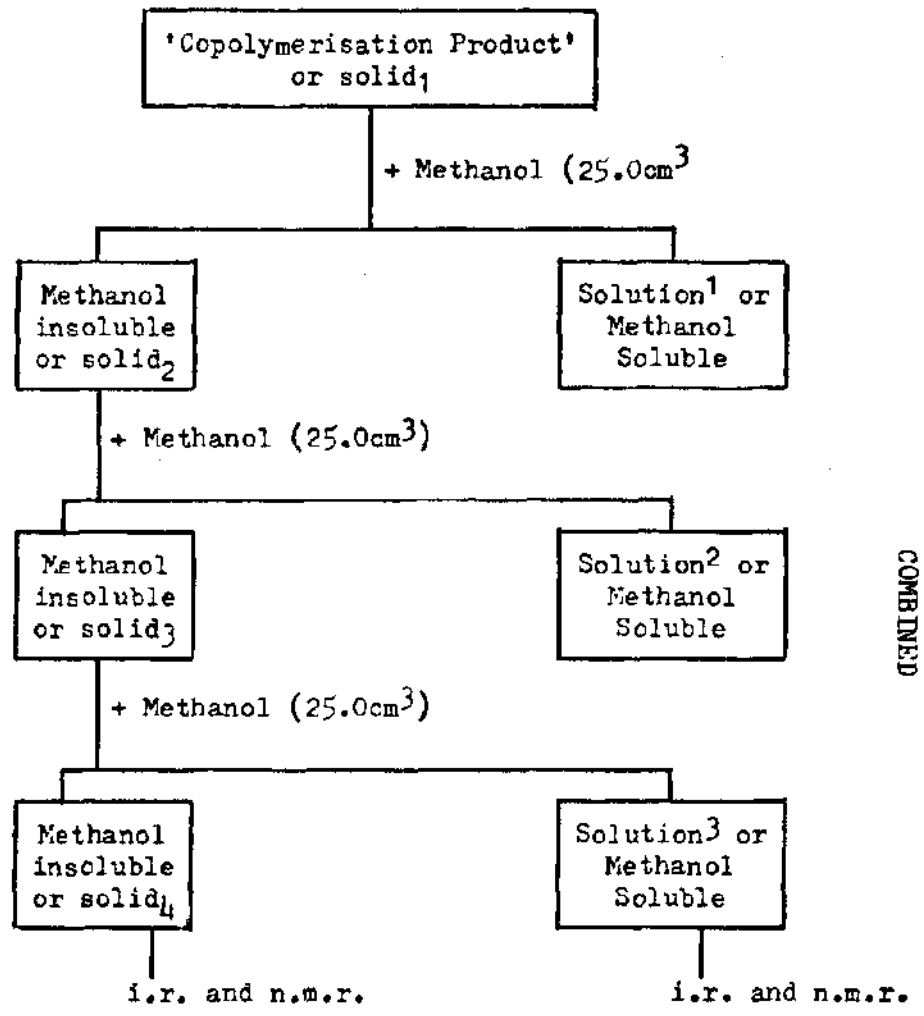


Fig. 3.1: Schematic diagram for separation of 'copolymerisation product' into Methanol insoluble (MIS) and Methanol soluble (MSS) portion.

From figure 3.1, to remove the methanol soluble (MSS) fraction from the 'copolymerisation product', a known quantity of this product (0.5g) was taken up in methanol ($25.0cm^3$) in a stoppered

conical flask. This was allowed to stand for 48 hours at room temperature and later shaken for 3 hours. The undissolved solid that is the methanol insoluble (MIS) was removed by filteration, washed several times with methanol, this procedure was repeated on this same sample for three times giving rise to $solid_2$, $solid_3$ and finally $solid_4$ with a constant weight. All the resulting solution that is solution 1 - 3 were combined together. The solvent (methanol) was evaporated to dryness in a clean weighed wash glass to obtain the methanol soluble (MSS) fraction. In all cases, the fourth extraction giving rise to $solid_4$, the final weight of the methanol insoluble (MIS) fraction showed no decrease from what it was during the previous extraction of $solid_3$. Both the methanol insoluble and methanol soluble recovered were dried to constant weight in a vacuum pressure oven at $40^{o}C$.

3.4.3 Ethanol Extraction of 'Copolymerisation Product'

The method adopted for the ethanol extraction of the physical mixtures of PEMA and PVAc (Section 3.4.1) was applied in the separation of the methanol insoluble (MIS) portion into ethanol insoluble (EIS) and ethanol soluble (ES). By refluxing the methanol insoluble portion (MIS) at $80^{o}C$ in a water bath for 2 hours, the two fractions obtained are ethanol insoluble (EIS) and ethanol soluble (ES). A schematic diagram summarising the analysis is shown in Figure 3.2 below.

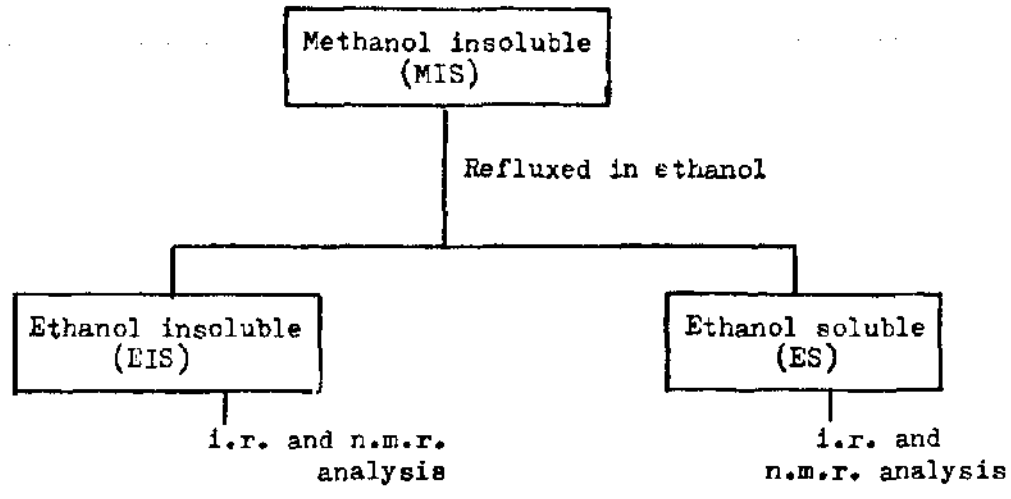


Fig. 3.2: Schematic diagram for separation of methanol insoluble (MIS) portion into ethanol insoluble (EIS) and ethanol soluble (ES).

3.5 Characterisation of Polymers

3.5.1 Melting Point Determinations

The melting points of the various samples obtained were determined using the Reinhert hot stage microscope at a minimal heating rate of 5°/min. Three determinations were carried out on each sample with the readings in a very close range.

3.5.2 Infra-red (IR) Spectroscopy

Infra-red spectra of the various samples in chloroform were recorded on Perkin-Elmer 710B IR Spectrophotometer in the Chemistry Department, Ahmadu Bello University, Zaria.

3.5.3 Nuclear Magnetic (n.m.r.) Spectroscopy

N.m.r. spectra of the samples were recorded at 60 MHZ on a Perkin-Elmer Variant T-60 NMR Spectrophotometer using solution in deuterated chloroform with tetramethylsilane (TMS) as an internal reference.

3.5.4 X-ray Analysis

The X-ray spectra of the samples were recorded on an x-ray diffractometer PW 1730/10 from the Centre for Energy Research and Training (CERT) of the Ahmadu Bello University, Zaria. The peaks in the spectra were found to be independent of the quantity of the sample introduced.

3.5.5 Optical Microscopy

Thin films (0.015 $\pm$ 0.02 cm, thick) of the samples cast from solution in chloroform were examined under an optical microscope, model LEIT 2 Ortholux 2 Pol B_4, in the Geology Department, Ahmadu Bello University, Zaria. A magnification of Sixty-three was used for all the samples. The optical micrograph of each sample was obtained from snapshots of its film, taken by means of a mounted camera. The snapshots were developed for investigation of each micrograph.

Chapter 4

4.0 RESULTS AND DISCUSSION

4.1 Emulsion Polymerisation of EMA and VAC

4.1.1 Influence of Time on Percentage Conversion of EMA, VAC to their Respective Polymers and the Viscosity Average Molecular Weight (Mv).

Figure 4.1 represents the result obtained from the kinetic study of the emulsion polymerisation of EMA and VAC, using the same volume of monomers ($7.0cm^3$), same concentration of sodium lauryl sulphate emulsifier (6.30×10^{-3} M/L), a constant initiator concentration (8.33×10^{-4} M/L) at 60°C. The plots obtained are straight lines showing a direct relationship between the percentage conversion of the monomers to their respective homopolymers with time of polymerisation. The linearity in these plots are in agreement with Harkin's (1950) prediction on the kinetics of emulsion polymerisation of VAC. and to some extent with Ibiyeye's (1984) report on emulsion polymerisation of EMA in our laboratory. Also the percentage conversion at a given time of polymerisation prior to 100% of the former increases with time for EMA-PEMA system up to 75% and 85% for VAC - PVAC system respectively. Again this result agrees with that of Ibiyeye (1984) who reported linear conversions of these two monomers to polymers from as low as 7 - 30% conversion when low emulsifier concentration was employed. It was generally observed that for a maximum time of polymerisation of 240 mins, the percentage conversion for VAC (85.2%) was higher than that for EMA (75.25%). But below 150 mins of polymerisation, the conversion of VAC to PVAC was lower than that of EMA to PEMA. This observation is in general agreement with Harkin's (1950) prediction that for insoluble and partially insoluble monomers (e.g. styrene) the

potassium persulphate initiator concentration (8.3×10^{-4} m/l) at 60°c

reaction in water is slow at first but changes to rapid with time whereas the reverse is the case with water-soluble monomers (e.g. VAC.)

Figure 4.2 and Figure 4.3 represent the pattern of relationship between the viscosity average molecular weight ($\bar{M}v$) and time of polymerisation for PEMA and PVAC respectively. The plots are linear, illustrating the increase of the viscosity average molecular weight ($\bar{M}v$) of the PEMA and PVAC respectively with time of polymerisation. The observed increase is in agreement with the reports of Ibiyeye (1984) and Olayemi and Yusuf (1989) in our laboratory both on the emulsion polymerisation of EMA and VAC with sodium lauryl sulphate concentration below the critical micelle concentration at 50°C. The following arguments explain the increase in ($\bar{M}v$) with time of polymerisation:

(i) the fact that polymer particles are large below the critical micelle concentration with increase in acceleration of the polymerisation leading to high molecular weight products (Harriot 1971).

(ii) the number average degree of polymerisation increase with time of polymerisation while rate of initiation remain almost constant (Dunn and Taylor 1965).

The above discussion therefore suggests that with the same condition of polymerisation, increasing time of reaction leads to increase in both the percentage conversion and the viscosity average molecular weight ($\bar{M}v$) for both EMA and VAC respectively.

4.1.2 Comparative Study of EMA and VAc in Emulsion Polymerisation at 60°C.

Comparing the results in Fig. 4.1, 4.2 and 4.3, the VAc polymerises faster than EMA leading to PVAc polymer with lower viscosity average

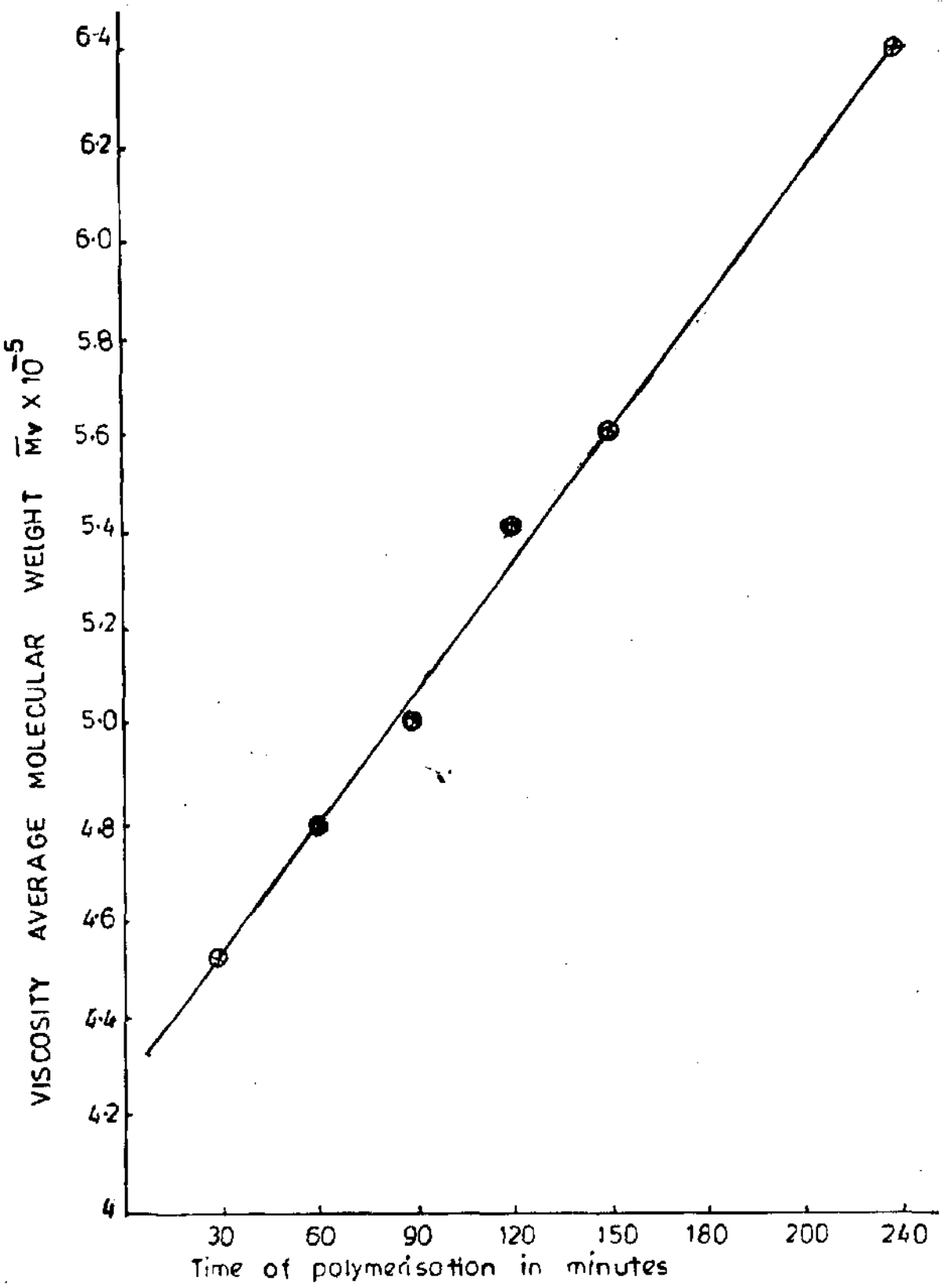


FIG. 4·2: Variation of viscosity average molecular weight and time of polymerisation for EMA (7.0cm^3) with initiator concentration of $8{\cdot}3\times10^{-4}$ m/l and Emulsifier concentration of $6{\cdot}3\times10^{-3}$ m/l at 60°c

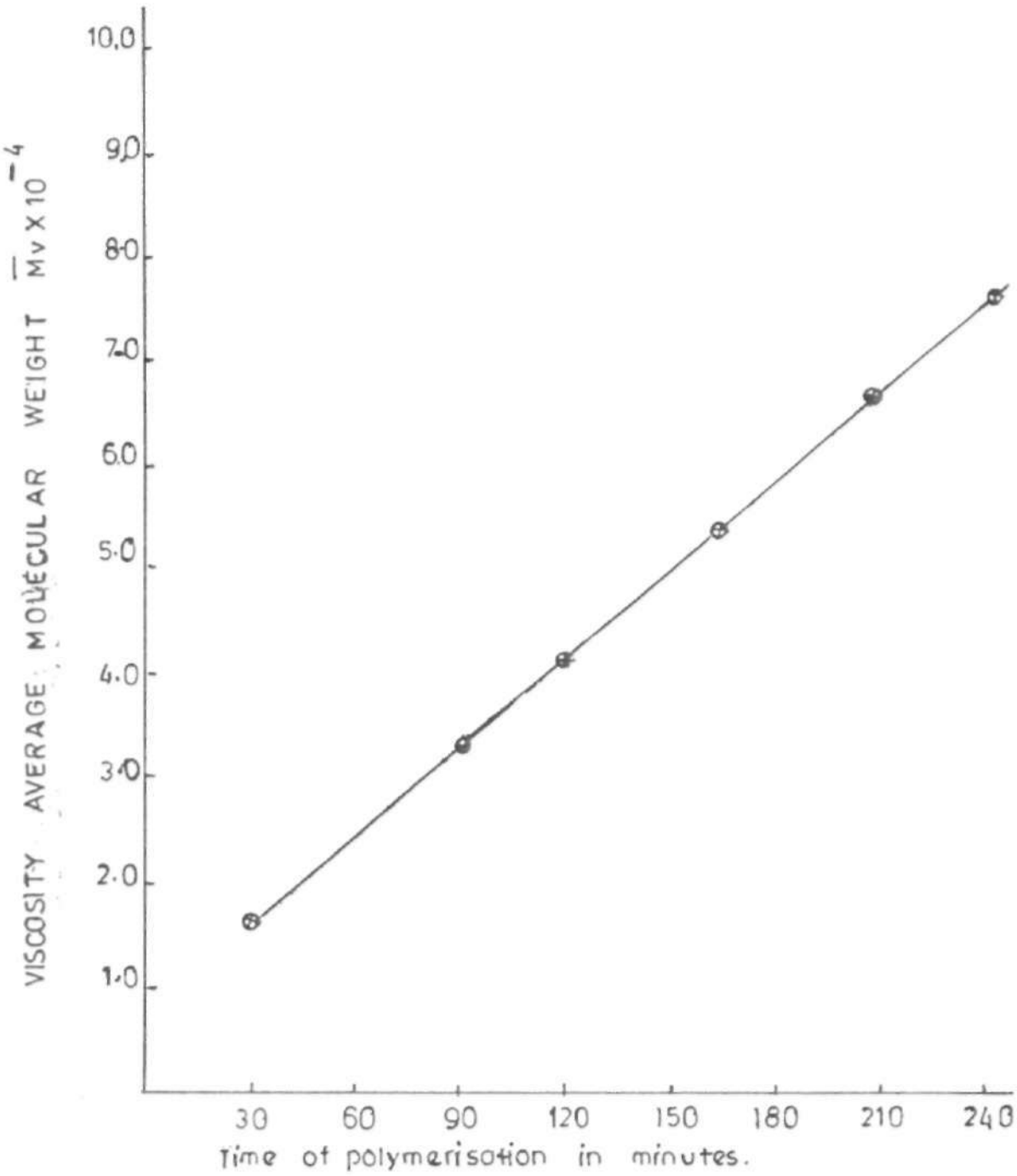


FIG. 4·3: Variation of viscosity average molecular weight and time of polymerisation for VAC ($7.0 cm^{-3}$) with initiator concentration of 8.3×10^{-4} m/l and emulsifier concentration of 6.3×10^{-3} m/l at 60°c

molecular weight ($\bar{M}v$) than PEMA polymer obtained under the same set of experimental conditions (e.g. temperature, medium) and time of polymerisation. The differences in behaviour between VAc and EMA monomers in emulsion can be explained by the fact that VAc is water soluble whereas EMA is partially water-soluble. This explains why the VAc monomer diffuses completely into the growing polymer particles very early in the reaction. This would agree with Fleischer (1975) who reported that VAc has higher water-solubility as compared to the partially water-soluble EMA. This prediction is in agreement with Pastiga's et al., (1960) study, who reported higher rates of polymerisation of VAc compared to a partially water-insoluble monomerslike styrene. Furthermore, the differences in the sizes of these two monomer molecules (VAc and EMA) could also affect the rate of polymerisation. The EMA is a bulkier molecule due to the ethyl group than the VAc with a less bulky methoxy group. Steric effect arising from the differences in sizes of these two groups has been reported to affect the rate of polymerisation (Schildknecht 1952).

4.2 Emulsion Copolymerisation of EMA and VAc. at 60°C for 9 Hours

The emulsion copolymerisation of EMA and VAc monomers carried out for all the processes as described in sections 3.2.1 - 3.2.2

4.2.1 Preliminary Investigation of the Recovery of Some Copolymerisation Product.

Samples of the same copolymerisation product of the VAc and EMA monomers were recovered from the reaction medium by precipitation using different liquids as non-solvents. The result of table 4.1 summarises the experimental conditions and the result obtained from the various

Table 4.1: Recovery of the same copolymerisation product from the reaction medium by precipitation in different non-solvents

Non-Solvent	Copolymerisation Product[a]	Percentage Recovery[b]	Appearance	Melting Point (^{o}C)
Methanol	PP_1	77.30	White, powdery	235-236
Methanol Sodium chloride (w/w)	PP_2	54.57	dull, powdery	235-236
Sodium chloride solution	PP_3	40.54	dull, powdery	235-236
Hexane	PP_4	71.10	fine, powdery	205-210
Petroleum ether	PP_5	69.92	dull, fine, powdery	205-210
Heptane	PP_6	70.50	fine, powdery	205-210

a: all copolymerisation products obtained by polymerising VAc ($7.0cm^3$) for 30 mins before addition of EMA ($7.0cm^3$), the whole reaction completed within 9 hours at $60^{o}C$

PP: = Copolymer Product

b: Percentage recovery = $\frac{\text{wt of copolymerisation product recovered (g)}}{\text{volume of EMA} \times \text{density} + \text{volume of VAc} \times \text{density}} \times 100\%$

* density of EMA = $0.917g\ cm^{-3}$

* density of VAc = $0.934gm\ cm^{-3}$

non-solvents used for the recovery of the same copolymerisation product. The percentage recovery of the copolymerisation product from the various non-solvents tried ranges from 40 - 77%. A relatively high yield (P_1 = 77.30%) was obtained from methanol as non-solvent and relatively low yield (PP_3 = 40.54%) from the sodium chloride (W/V) non-solvent. There is no clear understanding to suggest the reason for the relatively high yield from methanol and the relatively low yield from sodium chloride (w/v), except to refer to the ease of recovery of the product from the methanol and the difficulty encountered in recovering it from the later non-solvent. The yields for the hydrocarbons-hexane, petroleum ether and heptane with the copolymerisation product PP_4 = 71.10%, PP_5 = 69.92%, PP_6 = 70.50% were close to each other but higher than those obtained from methanol/sodium chloride (w/v), PP_2 = 54.57% and sodium chloride solution (w/v) PP_3 = 40.54%

The melting point ranges of the products recovered from methanol (PP_1), methanol/sodium chloride solution (v/v), (PP_2), and sodium chloride solution (PP_3) were similar -(235-236°C) while those from the hydrocarbons; hexane (PP_4), petroleum ether (PP_5), heptane (PP_6) were the same with a melting point range of 205-210°C. These results suggest the effect of non-solvent on the quality and quantity of products recovered. This effect is not yet understood.

Solubility test carried out on the copolymerisation products showed them to be soluble in chloroform, benzene, toluene, acetic acid, cyclohexanone, butanone, ethylacetate, acetone with exception of methanol and ethanol in which they were partially soluble and insoluble respectively. Also the melting point results and the infrared spectra confirm the similarities in chemical behaviour of all samples recovered from the hydrocarbons (hexane, heptane, petroleum ether).

4.3 Recovery of the Products from the Emulsion Copolymerisation of EMA, VAc Under Different Processes

All the solids were recovered by precipitation from hexane (sections 3.2.1 - 3.2.2) as non-solvent and the percentage recovery calculated based on the densities and volumes of the two monomers (VAc, EMA), according to equation 4.3.

$$\text{Percentage recovery} = \frac{\text{weight of solid precipitated (g)}}{\text{Volume of EMA (cm}^3\text{) x *density} + \text{Volume of VAc (cm}^3\text{) x +density}} \times \frac{100}{1} \quad \ldots (4.3)$$

* density of EMA = 0.917 gm cm^{-3}

\+ density of VAc = 0.934 gm cm^{-3}

The details of the experiments and percentage recovery with the initial time of polymerisation of VAc (7.0 cm^3) before additon of EMA (7.0cm^3) for the different processes are given in Appendices I and II, illustrated graphically in Fig. 4.4.

4.3.1 Effect of Initial Time of Polymerisation of VAc (7.0 cm^3) Before Addition of EMA (7.0cm^3) on Percentage Recovery

Fig. 4.4 shows the variation in percentage recovery of the copolymerisation of VAc prior to addition of a definite amount of EMA (7.0cm^3) for the batch, semi-batch, semi-continuous batch and the semi-continuous processes. The curve for the semi-continuous batch was above that for the semi-batch indicating that the percentage recovery from the former process was higher than for the later under the same set of experimental conditions (e.g. time, temperature). Similarly, the semi-continuous process gave the highest percentage recovery (91.0%) while the batch was the lowest of 58.40%, (Appendices I and II). This result is in

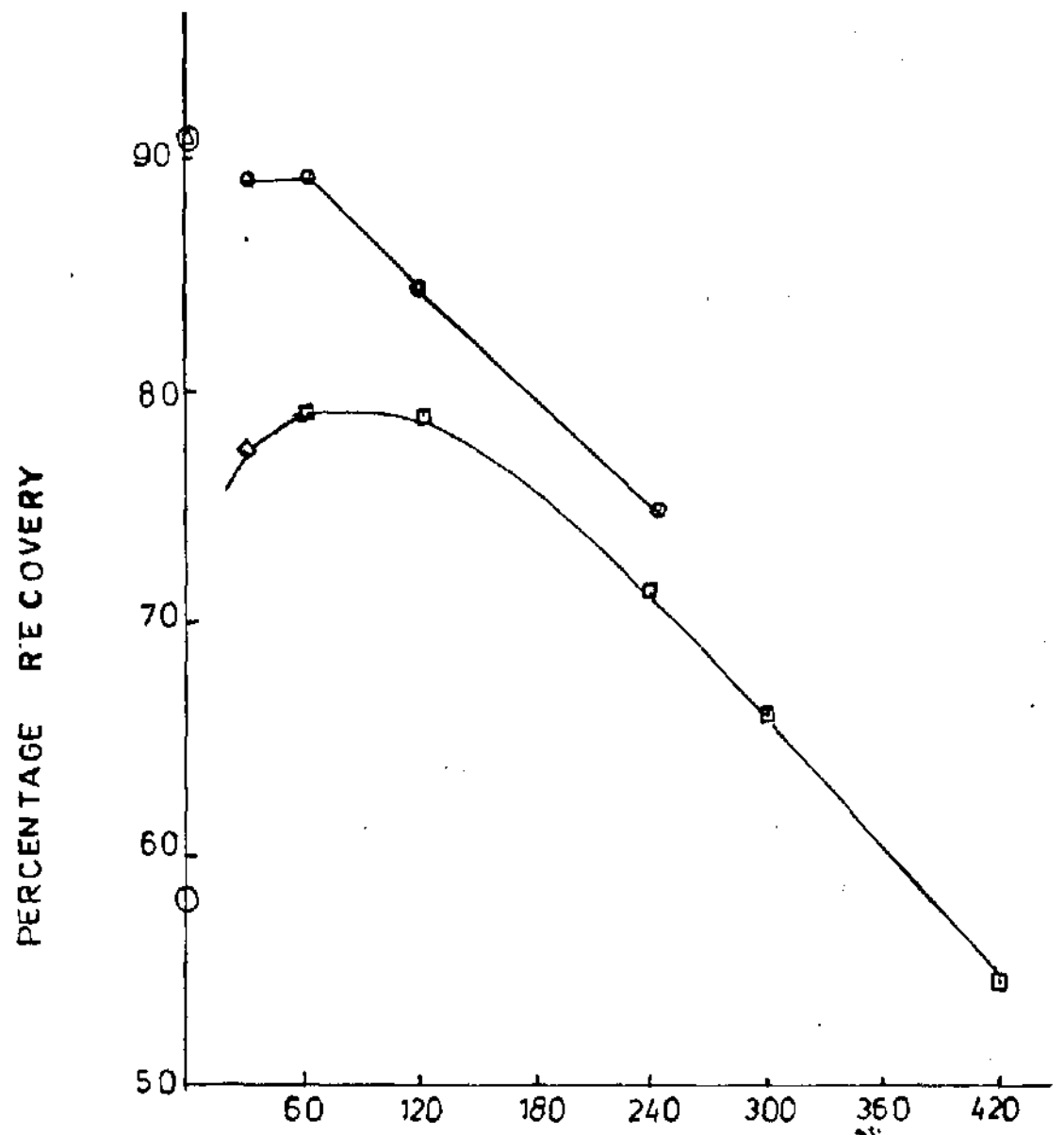


FIG 4.4: Variation of percentage recovery of copolymerisation products with initial time of polymerisation of VAC ($7.0 cm^3$) prior to addition of EMA ($7.0 cm^3$) with constant emulsifier concentration of 6.3×10^{-3} m/l, constant initiator concentration of 8.3×10^{-4} m/l for batch (○), semi-batch (□), semi batch continous (⊕) and semi-continous (△) emulsion copolymerisation at 60°C.

agreement with the report of Yeliseyeva et al; (1965) who attributed the low yield from the emulsion copolymerisation of styrene for the lack of time of growth of the polymer chains in the batch process. The general trend for this result for both the semi-batch and semi- continuous batch processes shows that the higher the initial time of polymerisation of VAc, the lower the percentage recovery, although the recovery for the initial time of polymerisation of VAc for 60 mins prior to addition of EMA is higher than that for 30 mins. In summary, these discussions suggest the fact that the time of initial polymerisation of VAc before addition of EMA is inversely proportional to the percentage recovery in both the batch and semi-batch processes. This is probably due to the reduced rate of diffusion of monomer into the PVAc matrix as time of polymerisation increases.

The semi-continuous process of polymerising 10% of comonomer mixture (v/v) priour to addition of the remaining 90% at a rate of 7.0 cm^3hr^{-1} (sample PSMCMS) gave not only the highest percentage recovery among all the processes but was at the same time higger than the recovery for the semi-continuous process of polymerising 100%, comonomer mixture (v/v) at the rate of 7.0 cm^3hr^{-1} (sample PSMC) with a recovery of 87.76% (AppendixII). This result is in agreement with the report of Snuparek and Krska (1976) on the effect of mode of monomer addition on the semi-continuous copolymerisation of styrene and butylacrylate. They claimed that the percentage recovery of the copolymersation product depend on the mode of monomer addition particularly for the semi-continuous process. In summary, the percentage recovery apart from being time-dependent for the semi-batch and semi-continuous batch processes also depend on the process of emulsion copolymerisation. The order of change being semi-continuous semi-continuous batch semi-batch batch processes. This might be altributed to the increase inhitory effects of EMA on VAc polymerisation in the semi-continuous semi continuous batch semi batch batch copolymerisation (Conn and Neher) 1950)

4.4 Solubility Studies of the Copolymerisation Products.

Solubility tests for all the samples in various solvents showed them to be soluble in chloroform, benzene, chlorobenzene, toluene, acetic acid, butanone, ethylacetate, acetone, cyclohexanone with the exception of methanol and cold ethanol in which they were partially soluble and insoluble respectively. This implies that the nature of bonds and the constituents in the 'copolymerisation products' from all processes are similar.

4.5 Analysis of Physical Mixtures of PEMA, PVAc and the Copolymerisation Products.

Preliminary solubility test on the two homopolymers (PVAc, PEMA) showsthat PVAc is soluble in methanol whilst PEMA is not. This was also found for the physical mixtures (commercial grade) of the two. The recoveries of the pure PEMA and PVAc were 99.6% and 99.0% respectively whilst the recoveries from the physical mixtures were 99% and 98% for PEMA and PVAc. Detailed results are shown in table 4.2.

With the quantitative recoveries obtained, the method was used to separate the unbound PVAc from the copolymerisation product. A similar experiment was carried out on the homopolymers and physical mixtures following the method reported by Smets and Claesen (1952). In the method, their synthesised 'copolymerisation products' were refluxed in ethanol for 2 hours at 80°C. Quantitative recoveries were obtained for the homopolymers and their physical mixture also. Detailed results are shown in table 4.3.

Table 4.2: Percentage recovery of PEMA, PVAc, Physical Mixtures by Extraction with Methanol.

Polymer (a) sample	Quantity in methanol (g)		Amount recovered (g)		Percentage recovery*	
	PEMA	PVAc	PEMA	PVAc	PEMA	PVAc
PEMA:	0.500		0.498		99.60	
	0.500		0.496		99.20	
PVAc:		0.500		0.495		99.00
		0.500		0.496		99.20
MIXTURES(b) PEMA/PVAc						
	1.00	1.00	1.00	0.98	100.00	98.00
	1.00	0.500	1.00	0.49	100.00	98.00
	0.200	0.200	0.200	0.195	100.00	98.00

(a) = commercial polymers from BDH.

(b) = obtained by physical mixing of the two homopolymers (w/w).

* = three replicate determinations.

Table 4.3: Percentage Recovery of PEMA, PVAc and Physical Mixtures from Ethanol at 80°C.

Polymer sample (a)	Quantity in methanol (g)		Amount Recovery (g)		Percentage recovery*	
	PEMA	PVAc	PEMA	PVAc	PEMA	PVAc
PEMA:	0.500		0.495		99.00	
	0.200		0.195		98.00	
PVAc:		0.500		0.492		98.40
		0.200		0.195		98.00
MIXTURES PEMA/PVAc	0.500	0.500	0.498	0.495	99.60	99.00
	0.500	1.00	0.498	0.980	99.60	99.00
	0.200	0.200	0.198	0.195	99.00	98.00

a = commercial polymer samples from BDH

* = obtained from three replicate determination.

4.6.0 Analysis of the Copolymerisation Products by Extraction.

The recovery of the unbound homopolymers from the suspected copolymer was based on the differential solubilities of the free homopolymers in methanol (unbound PVAc) and ethanol (unbound PEMA).

4.6.1 Methanol Extraction of Unbound PVAc from the Copolymerisation Product.

The details of the percentage methanol soluble (MSS) assumed to be the unbound PVAc and the methanol insoluble (MIS) extracted are illustrated in Fig. 4.5 and 4.6 respectively with Appendix III. The calculation of the percentage composition of both MSS and MIS were based on equation 4.5 and 4.6 respectively:

$$\text{Percentate Methanol Soluble} = \frac{\text{Mass of methanol soluble } (g)}{\text{Mass of copolymerisation product } (g)} \times \frac{100}{1} \quad \text{- - - - - (4.5)}$$

$$\text{Percentage Methanol insoluble} = \frac{^{*}\text{Mass of methanol insoluble } (g)}{\text{Mass of copolymerisation product } (g)} = \frac{100}{1} \quad \text{- - - - - (4.6)}$$

* The methanol insoluble is the unbound PEMA and the expected copolymer.

4.6.2 Effect of Initial Time of Polymerisation of VAc Before Addition of EMA on the MIS and MSS Composition of Copolymerisation Products

The results from Fig. 4.5 and 4.6 illustrate the variations of the percentage MIS and MSS in the copolymerisation products for the semi-batch and semi-continuous batch processes respectively. The percentage

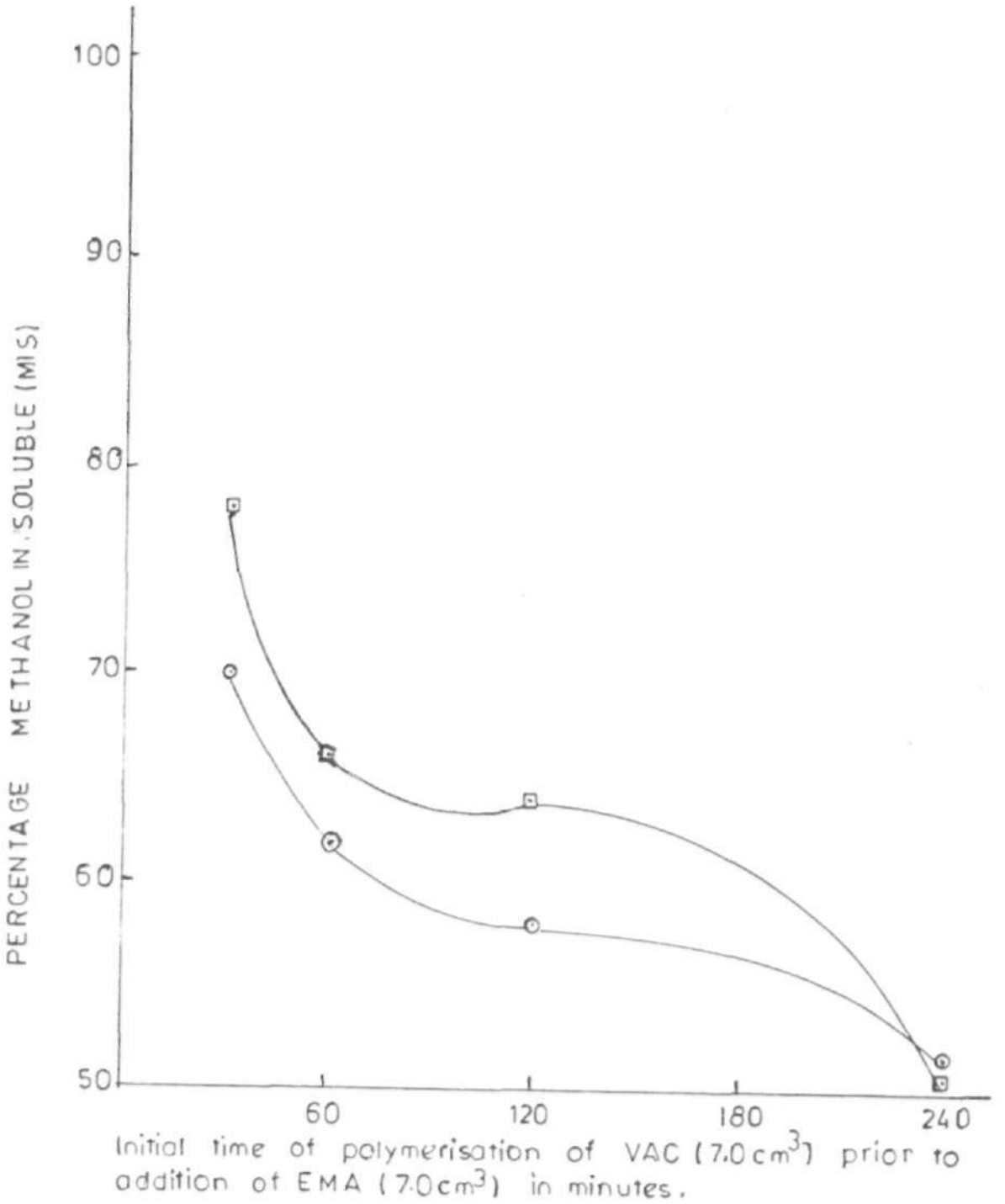


FIG. 4·5: Variation of percentage MIS with Initial time of polymerisation of VAC (7.0 cm^3) prior to addition of EMA (7.0 cm^3) for the semi-batch continous (⊡) and semi-batch (⊙) copolymerisation products.

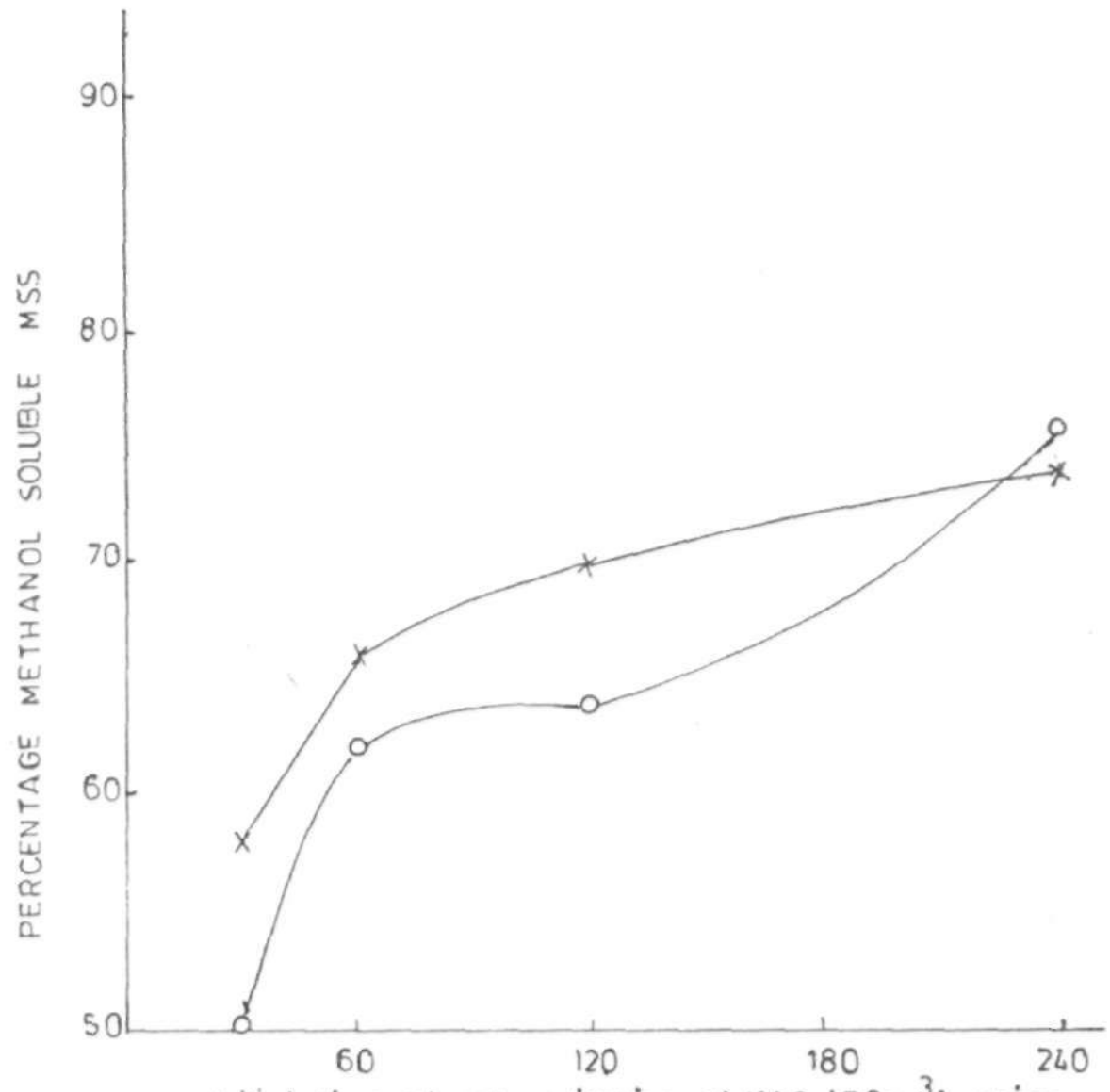


FIG.4.6: Variation of percentage MSS with initial time of polymerisation of VAC (7.0cm^3) prior to addition of EMA (7.0cm^3) for the semi-batch continous (O) and semi-batch (X) copolymerisation products.

MIS portion decreases as the initial time of polymerisation of VAc increases. The curves in Fig. 4.5 falls from its maximum value at time = 30 mins to its minimum value, time = 240 mins. This result is complementary to the previous kinetic study (section 4.11) in which the percentage recovery of the PVAc was found to increase with time of polymerisation. However, a salient characteristic of all the samples irrespective of the process obtained, is that the methanol insoluble (MIS) are greater than the corresponding methanol soluble (MSS). This is not unexpected since the MIS is supposed to be composed of the unbound PEMA and the expected copolymer. This has been confirmed by both the i.r. and n.m.r. spectra of the methanol insoluble and methanol soluble (Fig.4.14 and Fig.4.19) with bands characteristic of PEMA and PVAc respectively. The melting point studies also show that of the MIS to be higher than that of the MSS, a fact which supports the idea of MSS being unbound PVAc and the MIS - unbound PEMA and the copolymer.

4.6.3 Composition of Copolymerisation Product and the Process of Emulsion Copolymerisation

From the results in Fig. 4.5 and Fig. 4.6, the curve for the methanol insoluble (MIS) for the semi-batch continuous lie above that for the semi-batch process. This implies that the MIS for the semi-batch continuous process is higher than the semi-batch process. Also by comparing these two figures (F.g 4.5 and 4.6), it is evident that the MIS for the semi-batch and semi-batch continuous processes decrease with increasing initial time of polymerisation of VAc prior to addition of EMA while the MSS fraction increases. This variation in composition of the copolymerisation products in terms of percentage MIS and MSS is

affected by the effect of time on the conversion and the molecular weight development of both EMA and VAc during the copolymerisation. This effect on the individual monomers (EMA, VAc) have already been discussed. However, during the emulsion copolymerisation, the reactivity ratios of these two monomers have been known to be influenced by the rate of diffusion inside the growing PVAc polymer matrix (Snuparek and Krska; 1976). Hence the decrease in the composition of MIS composed of PEMA and copolymer with increase in initial time of polymerisation of VAc.

4.7.0 Ethanol Extraction of Unbound PEMA from the Copolymerisation Product

The result in table 4.4 show the percentage composition of the methanol insoluble portion of the copolymerisation products in terms of both the ethanol insoluble (EIS) and the ethanol soluble (ES portion The percentage composition of the EIS and ES were calculated based on equation 4.7 and 4.8 respectively.

$$\text{Percentage ethanol insoluble} = \frac{\text{mass of ethanol insoluble (g)}}{\text{mass of methanol insoluble (g)}} \times \frac{100}{1} \quad \text{---(4.7a)}$$

or

$$\frac{\text{Copolymerisation product (g)}}{1} \quad \frac{100}{1} \quad \text{----(4.7b)}$$

$$\text{Percentage ethanol soluble} = \frac{\text{mass of ethanol soluble (g)}}{\text{mass of methanol insoluble (g)}} \times \frac{100}{1} \quad \text{----(4.8a)}$$

or

$$\frac{\text{Mass of copolymerisation product (g)}}{1} \quad \frac{100}{1} \quad \text{---(4.8b)}$$

Generally, the percentage of EIS fractions were higher than the corresponding ES portions for all the samples. On the basis of the process of copolymerisation, the trend in the variation of the percentage ethanol soluble (ES) is semi-batch > semi-batch continous > batch while that for the ethanol insoluble is the reverse. Thus the

Table 4.4: Percentage Ethanol Insoluble and Ethanol Soluble fraction of the Methanol Insoluble (MIS) fraction of copolymerisation products determined by Ethanol Extraction.

Methanol Insoluble (MIS) of Copolymerisation Product.	[a]Percentage Ethanol Insoluble (EIS)	[a]Percentage Ethanol Soluble (ES)	[*]Percentage Copolymer in Copolymerisation Product
$MISPBB_1$	92.0 (66.0)	6.0	6.0 (4.0)
$MISPBB_2$	88.0 (54.0)	8.0	8.0 (5.0)
$MISPBB_3$	85.0 (49.0)	10.0	10.0 (6.3)
$MISPBB_4$	82.0 (43.0)	14.0	14.0 (8.0)
$MISPSB_1$	91.0 (71.0)	4.0	4.0 (3.0)
$MISPSB_3$	90.0 (58.0)	6.0	6.0 (4.0)
$MISPB_4$	84.0 (42.0)	12.0	12.0 (7.0)
MISPSCMCMS	90.0 (81.0)	6.0	6.0 (4.0)
MISPMMB	94.0 (83.0)	2.0	2.0 (1.5)

a - The values reported are averages from 3 replicate determinations.

* - The percentage Ethanol Soluble is assumed to be equal to the percentage copolymer because the unbound PEMA had been removed as Ethanol Insoluble (EIS).

( ) - Percentage of EIS, ES calculated in terms of the whole ''copolymerisation product' as:

$$\% \text{ EIS or ES} = \frac{\text{Mass of ethanol insoluble or ethanol soluble (g)}}{\text{Mass of copolymerisation product (g)}} \times 100$$

composition of the methanol insoluble (MIS) and copolymerisation product in terms of EIS and ES depend on the process of emulsion copolymerisation. The ethanol insoluble fraction would be the unbound PEMA while the ethanol soluble is the expected copolymer since the unbound PVAc have presumably been removed during the methanol extraction. This has been confirmed by the i.r. and n.m.r. spectra of these fractions (Fig. 4.14 and 4.19). Hence it can rightly be argued that the percentage copolymer depend on the process of copolymerisation. The result from the batch process (with only 2% copolymer) agrees with the report of Smets and Claesen (1952) who observed the absence of a copolymer from the copolymerisation of methylmethacrylate and vinyl acetate in benzene at 103°C using benzoyl peroxide in batch. The formation of copolymer as shown in table 4.4 for the semi-batch, semi-continuous batch is feasible due to a chain transfer process between the EMA monomer and the PVAc matrix. The chain transfer hypothesis presuposes the formation of a macroradical (from PVAc) which decomposes into smaller radicals which later adds to the 'foreign monomer' i.e. EMA (Smets and Claesen, 1952), (Gaylord and Ang 1964). The macroradical in this case is the acetate ion from the PVAc matrix polymerised 'insitu' while the 'foreign monomer' is the added EMA molecules. On the whole, the semi-batch (sample PBB_4) and the semi-continuous batch (sample PSB_4) gave 14% (8.0%) and 12% (7.0%) copolymer higher than from other samples (Table 4.4).

4.8.0 Melting Point Studies of the Copolymerisation Products, MIS and MSS Fractions

As reference, the melting points of pure PEMA and PVAc (both of commercial grades, BDH) were determined as 235-239°C and 120-125°C respectively. The melting point of their physical mixtures 50:50 PEMA/PVAC

was 190-210°C which is between the melting point values of the homopolymers. This result is in agreement with the report of Ibiyeye (1984) who observed that melting point of PEMA is lowered by the presence of PVAc, while that of PVAc is being raised by the former polymer.

The results from tables 4.5 and 4.6 show the melting points of the various copolymerisation products with the percentage composition in terms of the MIS and MSS respectively.

It could be observed that the melting point of the copolymerisation product increases as the percentage of MIS increases and decreases as the percentage of MSS i.e. PVAc increases, except for samples PBB_2, PSB_2 and PSB_3 with MIS = 62%, 66% and 64% respectively where the melting point remained within the range of 210-215°C. However, the batch sample (PMMB) had the highest melting point of 230-234°C while the semi-batch continuous samples have melting points higher than the semi-batch.

The results from tables 4.5 and 4.6 show that the melting point trend among the three components is methanol insoluble > 'copolymerisation product' > methanol soluble. Thus, the melting point of each copolymerisation product is affected by the percentage composition of either the MIS or the MSS fraction. The higher the percentage methanol insoluble (MIS) fraction, the higher the melting point of the sample and vice versa. The fact that the melting point of the methanol insoluble (MIS) > 'copolymerisation product' > methanol soluble (MSS) supports the idea earlier stated that methanol insoluble (MIS) is made up of unbound PEMA and expected copolymer while the methanol soluble (MSS) is the unbound PVAc. Also the more the initial time of polymerisation of vinyl acetate prior to addition of ethyl methacrylate, the more the poly(vinyl acetate) in the 'copolymerisation product' and the less its melting point. The fact that the melting

Table 4.5: Variation of Melting Points of Copolymerisation Products with the Percentage of Methanol Insoluble and Methanol Soluble.

Sample	Percentage Methanl Insoluble (MIS)	Percentage Methanol Soluble (MSS)	Melting Point of Copolymerisation Product (^{o}C)
Copolymerisation Product			
Semi-Batch Product			
PBB_1	70.0	28.0	225 - 230
PBB_2	62.0	36.0	210 - 215
PBB_3	58.0	40.0	209 - 215
PBB_4	52.0	44.0	190 - 195
Semi-Batch Continuous Product			
PSB_1	78.0	20.0	227 - 230
PSB_2	66.0	32.0	210 - 215
PSB_3	64.0	34.0	210 - 215
PSB_4	50.0	46.0	155 - 160
PSMCMS	80.0	14.0	227 - 230
Batch Product			
PMMB	88.0	8.0	230 - 234.

Table 4.6: Melting Point Range of Methanol Insoluble (MIS) and Methanol Soluble (MSS) from Various Copolymerisation Products.

Sample	Percentage in Copolymerisation Product	Melting Point Range (°C)
Methanol Insoluble (MIS)		
$MISPBB_1$	70.0	230 - 235
$MISPBB_2$	62.0	215 - 218
$MISPBB_3$	58.0	210 - 216
$MISPBB_4$	52.0	195 - 198
Methanol Soluble (MSS)		
$MSSPBB_1$	28.0	135 - 140
$MSSPBB_2$	36.0	125 - 128
$MSSPBB_3$	40.0	120 - 123
$MSSPBB_4$	44.0	115 - 118

points of the copolymerisation products are in between the values for PEMA = 235-239°C and PVAc = 120.125°C suggests that with copolymerisation of the vinyl acetate and ethyl methacrylate at 60°C, an optimum temperature for processing of the product can be achieved. During processing e.g. melt mixing, poly(vinyl acetate) has been found to degrade before poly(ethyl methacrylate) melts (Olayemi and Yusuf; 1989). In processing these two polymers (PEMA, PVAc), they are subjected to high temperature and high shear forces which could cause degradation, except if the forces binding their molecules are strong permanent forces e.g. covalent bonds. Covalent bonds can only be introduced into the molecules of these two polymers through a chemical reaction e.g. during copolymerisation of the monomers or if a third monomer could be synthesized from the first two monomers. Olayemi and Yusuf (1989), while conducting extensive studies on the blends of PVAc/PEMA concluded that the degradation of both the homopolymers and the blends is by chain scission. Degradation of the blends also depend strongly on blend composition and the ratio of the molecular weights $(\bar{M}v)r$ of the homopolymers. It is expected that the copolymers of these two polymers should withstand degradation effects more than the blends if formed.

4.9.0 X-ray Studies of Homopolymers, Physical Mixtures and 'Copolymerisation Products'

The X-ray spectra of all the polymer samples were printed by an automatic electronic recorder on an X-ray chart as a plot of angle (2θ from 0° - 65°) as abscissa against relative intensity as ordinate. The X-ray spectrum of the PEMA (Laboratory grade) was observed as the most crystalline with a peak at $2\theta = 43^\circ$ while that of the PVAc (Laboratory grade) as the most amorphous of all the samples. (Fig. 4.10a and 4.10b

4.10a: X-ray spectrum of PEMA (LR

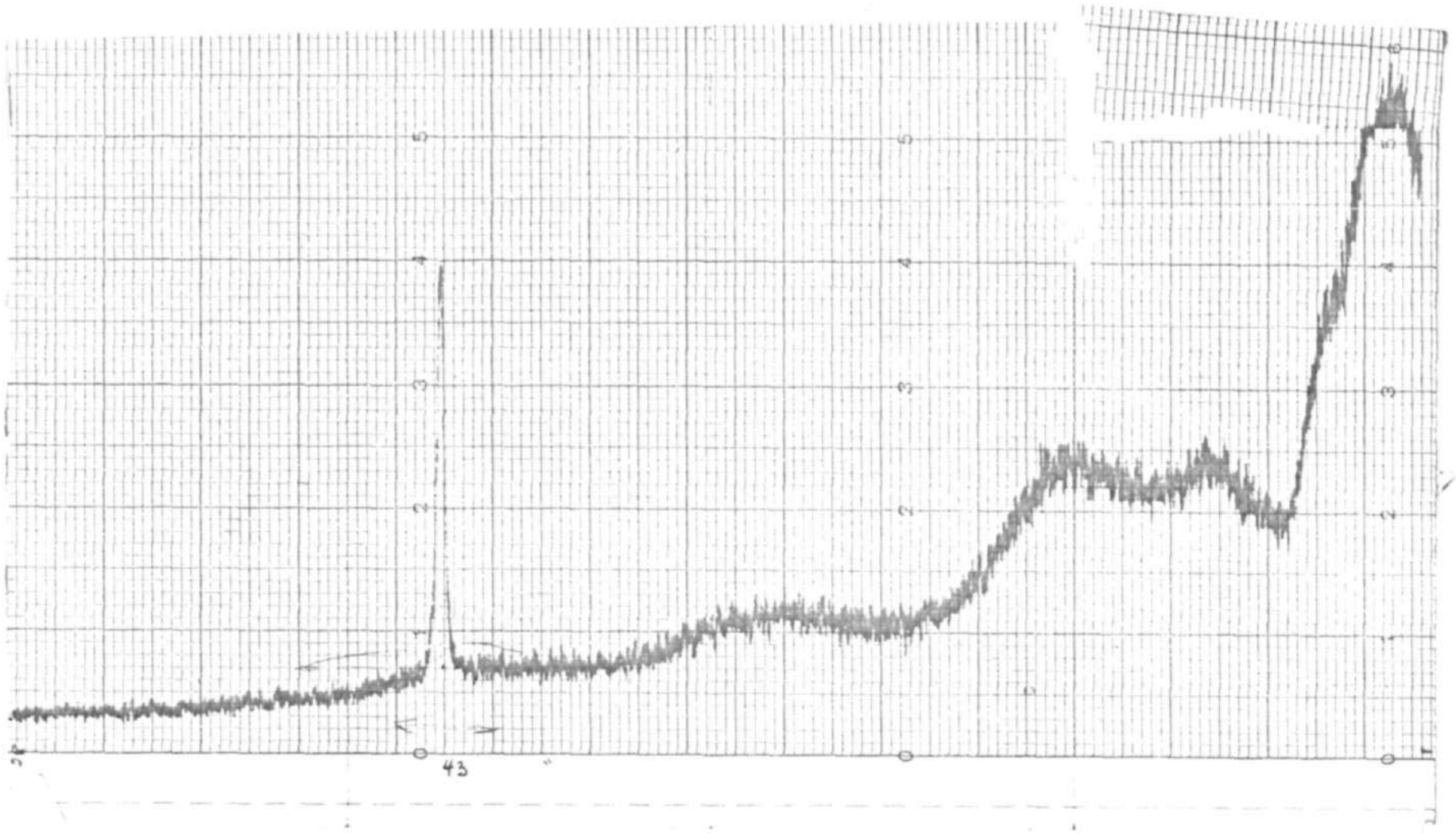
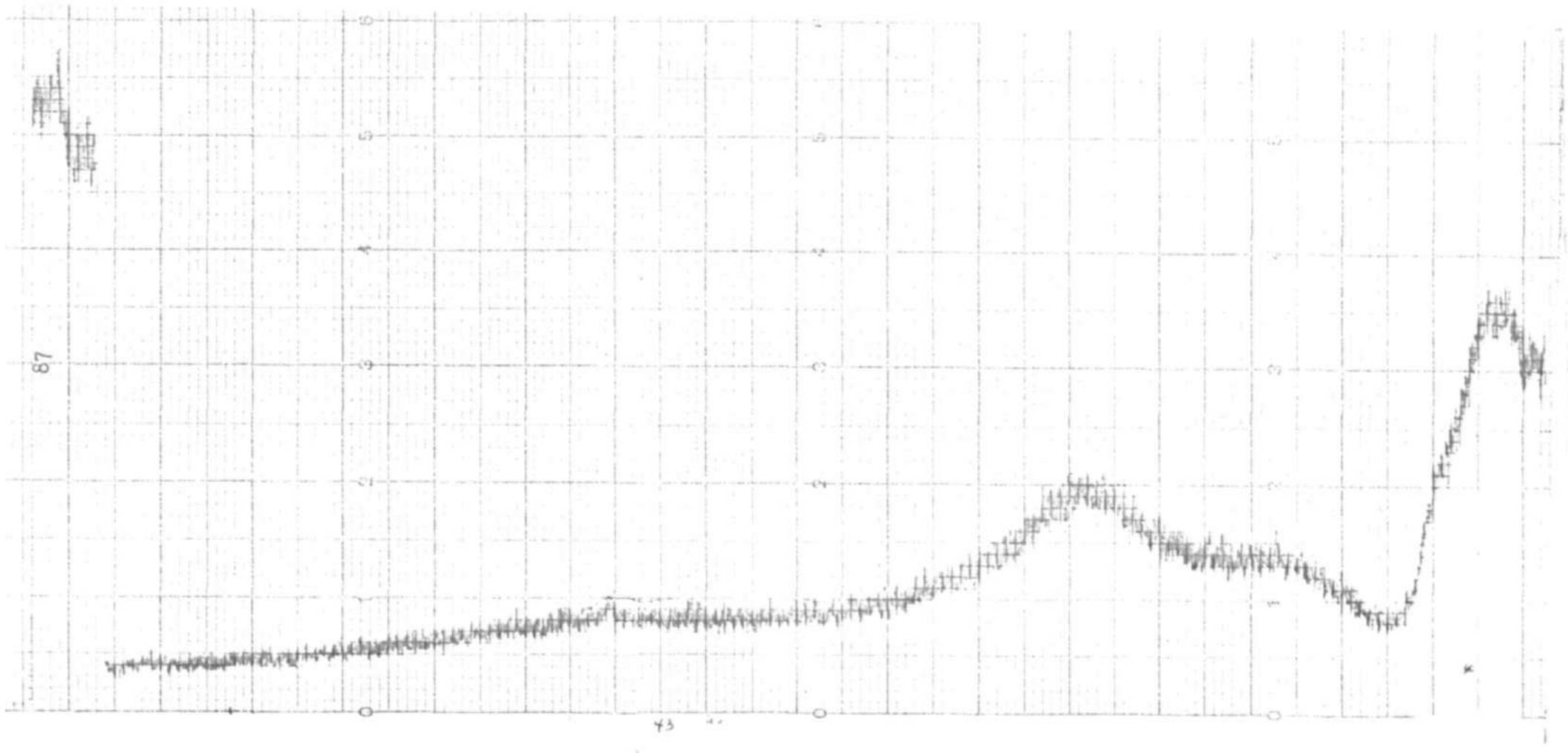


Fig. 4.10b: X-ray spectrum of PVAc (LR)



respectively. This observation implies that there is some degree of ordering of the atoms and chains in the PEMA whereas little or none exist in the PVAc. The ordering in PEMA is attributed to the bulky ethyl acetate side group which has a more steric hindrance than the methoxy group in PVAc molecule. However, x-ray patterns of polymer molecules also depend on the stereochemistry, presence of preferred orientation, tacticity and chain entanglement. (Alexander; 1969).

4.9.1 Percentage Ordering in the 'Copolymerisation Products'

All the 'copolymerisation products' were first evaluated for the degree of percentage ordering in each. Since all the samples were found to posses the characteristic peak of PEMA at $2\theta = 43^{\circ}$, the percentage ordering was calculated based on the area under these peaks using equation 4.9.

$$\text{Area under peak} = \text{Height x width at half height} \quad \text{- - - - - - (4.9)}$$

Hence, the percentage ordering was then calculated using equation 4.10

$$\text{Percentage ordering} = \frac{\text{Area under peak for sample } (m^2)}{\text{Area under peak for PEMA } (m^2)} \times \frac{100}{1} \quad \text{- - (4.10)}$$

The details of these results are given in Fig. 4.7 with Appendix IV.

The plots in Fig. 4.7 show the curve for the semi-batch continuous product lying above that for the semi-batch products. This implies that the percentage ordering in the semi-batch continuous products were higher than those of the corresponding semi-batch products. There was no ordering at all for the batch copolymerised sample PEMB with zero percentage ordering (Appendix IV). Copolymerisation products from the semi - batch continuous process were more ordered in the arrangement of atoms and chains

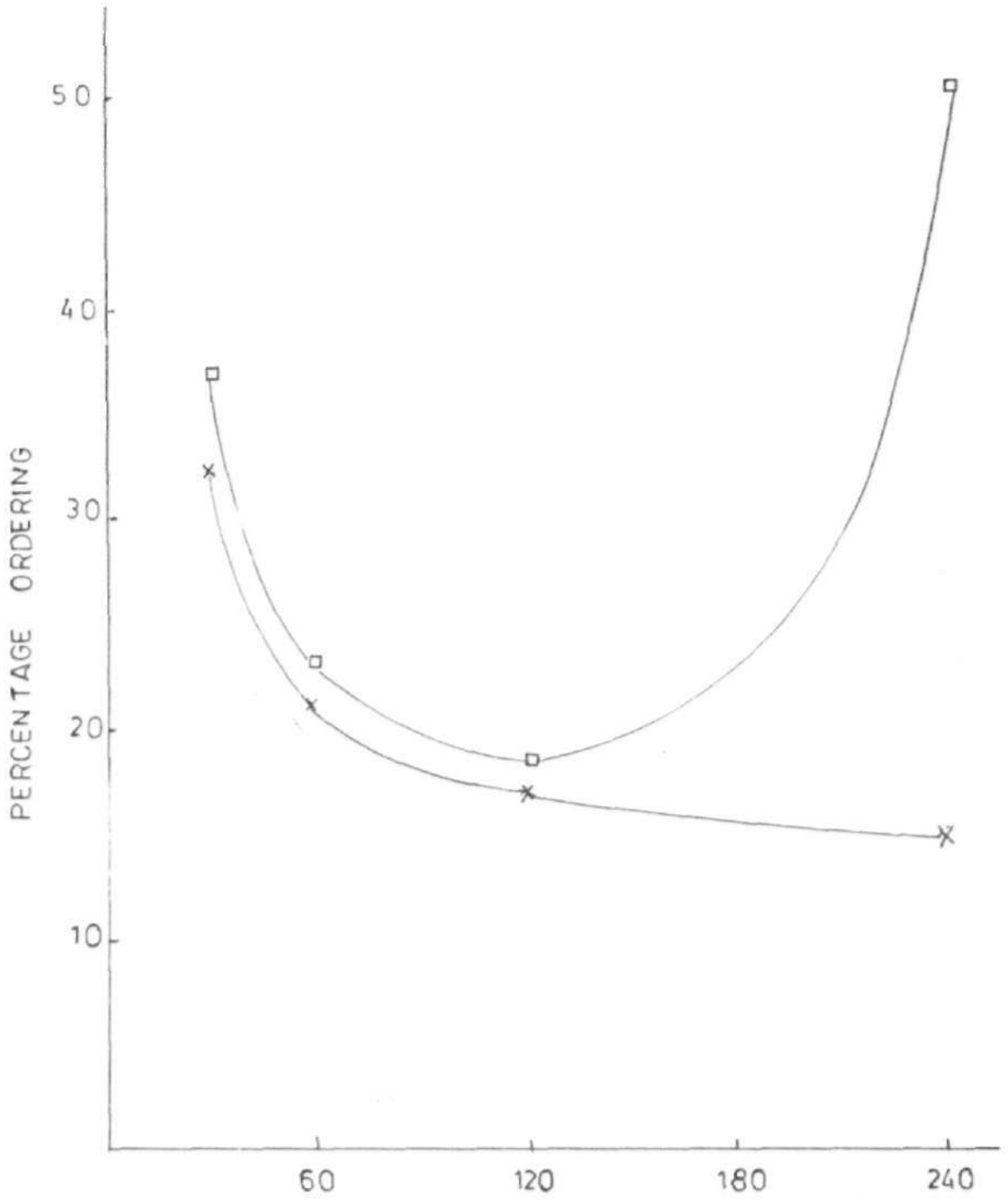


FIG. 4.7: Variation of percentage ordering with time of polymerisation of VAC prior to addition of EMA for the semi-batch (X) and semi-batch continous (□) copolymerisation products.

in the products more than the other processes.

4.9.2 Percentage Ordering and Initial Time of Polymerisation of VAc Before Addition of EMA

Comparing the two curves in Fig. 4.7 the percentage ordering was found to decrease with increase in initial time of polymerisation of VAc. prior to EMA addition. This is not unexpected since with increase in time, more PVAc is formed leading to an overall decreasing order as PVAc in wholly amorphous with an ordering of zero. However, the semi-batch continuous product obtained with the initial time of VAc polymerisation for 240 minutes (PSB_4) was found to have highest value of percentage ordering (50.82%), next to 100% of the pure PEMA. These results also suggest that the phenomenon of ordering in the copolymerisation products, does not depend on the quantity of the PEMA, but is connected with other factors such as arrangements of atoms, tacticity and overall stereochemistry (Alexander; 1969).

4.9.3 Comparative Studies of Percentage Ordering for Physical Mixtures and Copolymerisation Products

A calibration curve showing the relationship between the percentage ordering in the physical mixtures of PEMA/PVAc with the percentage of PEMA in the mixture (commercial grade polymers) has been shown in (Appendix V). The percentage ordering in the physical mixtures decrease with increase in the percentage PVAc in the sample. However, at 20% PVAc in the mixture, the percentage ordering of the physical mixture, (PEMA/PVAc) was drastically reduced to as low as 11.0%.

This observation suggests that the presence of PVAc in the mixtures leads to a reduction of the ordering while the PEMA enhances ordering.

Table 4.7: Comparison of Percentage Ordering from calibration Curve

Sample	* Percentage PEMA	From Calibration Curve	Percentage Ordering From Experimental
PBB_1	(66.0)	11.0	32.0
PBB_3	(54.0)	10.0	17.0
PBB_4	(43.0)	9.0	15.0
PSB_1	(71.0)	12.0	37.0
PSB_3	(58.0)	11.0	19.0
PSB_4	(42.0)	9.8	51.0

* Percentage PEMA is the same as percentage EIS in terms of copolymerisation product in table 4.4.

Also, the result from table 4.7 show the percentage ordering from the calibration curve to be lower than those obtained from the experimental determinations. The discrepancies between these two results suggest that there are interacting forces in the 'copolymerisation products' which are absent in the physical mixtures of the commercial polymers. This feature also buttresses the evidence that these 'copolymerisation products' are not physical mixtures but may consist of other components with stronger bonds between the molecules of PEMA and PVAc (e.g. covalent bonds) not present in their physical mixtures.

4.10 Crystallinity Index from Differential Intensity Measurement

The crystallinity index is a ratio of the crystalline content to both the crystalline and amorphous contents of the sample (Young 1981). The crystallinity indices of all the samples were calculated with the modified form of the equation by Alexander (1969) for the determination of crystallinity indices for cotton cellulose as given in equation 4.11

$$C_i = \frac{\sum_{2\theta = 38^\circ}^{2\theta = 45^\circ} Is - IPAc}{\sum_{2\theta = 38^\circ}^{2\theta = 45^\circ} IPEMA - IPVAc} \quad \text{---------- (4.11)}$$

C_i = crystallinity index

Is = intensity for the copolymerisation product.

IPEMA = intensity for the pure PEMA

IPVAc = intensity for the pure PVAc.

The crystallinity indices of all the copolymerisation products were below that of the pure PEMA (C_i = 1.0) while most of them have C_i above that of PVAc (C_i' = 0) Appendix VI.

However, the batch sample PMMB was found to have a crystallinity index (C_i' = -0.07) which was below that of the pure PVAc. This implies that the arrangement of the atoms and their packing in the unit cells for this sample is more irregular than in the pure PVAc. Statton (1963) obtained some samples of poly(ethylene terephthalate) with negative crystallinity index C_i which was due to the higher content of amorphous portion relative to the crystalline portion.

4.11 Effect of Initial Time of Polymerisation of VAc on Crystallinity Index

Figure 4.9 shows the variation of crystallinity index (C_i.) of the copolymerisation products with time of VAc polymerisation for the semi-batch and semi-batch continuous processes respectively. The two curves in the plots are characteristically a 'U' shaped with a minimum value of crystallinity index (C_i = 0.025) at time = 120 minutes for the semi-batch a minimum crystallinity index (C_i = 0.10) for the semi-batch continuous sample. The maximum values of crystallinity indices were obtained for the semi-batch at time = 30 minutes (Ci = 0.45) and for the semi-batch continuous product at time of 240 minutes (Ci = 0.72) respectively.

Generally, the crystallinity indices for the semi-batch continuous products were higher than those for the semi-batch products. This suggest variations in the chains of the PEMA or PVAc being grafted onto one another in these copolymerisation products. Apart from this fact, the semi-batch continuous process gave rise to products with more ordered

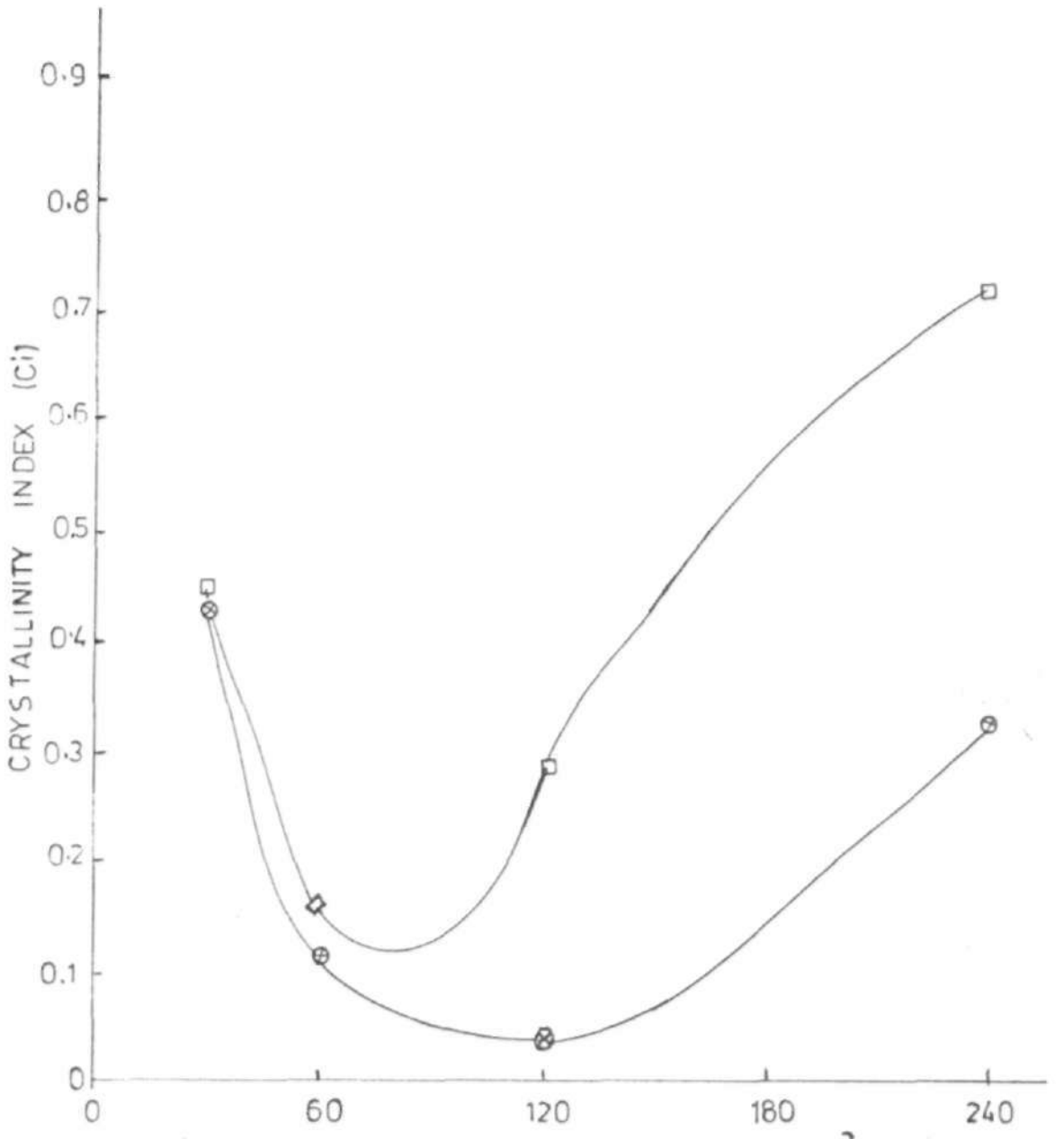


FIG. 4.9: Variation of crystallinity index (Ci) with Initial time of polymerisation of VAC prior to EMA addition for semi-batch continous (□) and semi-batch (⊗) copolymerisation products.

chain arrangement than the semi-batch. From these discussions, the process of copolymerisation (batch, semi-batch, semi-batch continuous) affects the structures in the products which in turn affect the crystallinity. The degree of crystallinity is important industrially as it affects the mechanical properties, swelling, dye absorption and general chemical activities of the polymer.

4.12 Infrared Spectroscopy Studies of Monomers Homopolymers and Copolymerisation Products

A detailed summary of the important infrared bands for the EMA (Fig.4.11a), VAc (Fig.4.11b), PEMA (Fig.4.12a), PVAc (Fig. 4.12b), physical mixture of PEMA/PVAc (Fig. 4.13a), copolymerisation product (Fig. 4.13b) with the various fractions (Fig. 4.14a - 4.15b) have been shown (Appendix VII).

The disappearance of the bands between 1620-1660 cm^{-1} due to the vinyl stretch ($-C=CH_2$) in the monomers from the spectra of the polymers confirm the fact that polymerisation has taken place to a high degree. A critical study of Fig.4.11a,4.11b,4.12a and 4.12b show other observeable differences which involve the shifting of the band at 1320 cm^{-1} due to the C - O - C stretch in VAc to 1380 cm^{-1} in the PVAc polymer. This suggest that the increase in molecular weight in the polymer might cause shifts of some bands to higher frequencies. Also the band at 1140-1180 cm^{-1} due to CH- bend in the two polymers (Fig. 4.12a and 4.12b) were absent in the spectra of both monomers (Fig. 4.11a 4.11b). The band between 1720 - 1740 cm^{-1} due to the C = O stretch in carbonyl compounds is common to both polymers and monomers. This is an evidence that polymerisation does not affect the functional groups but is through the vinylic bond. Comparing Fig. 4.12a and 4.12b for the i.r.

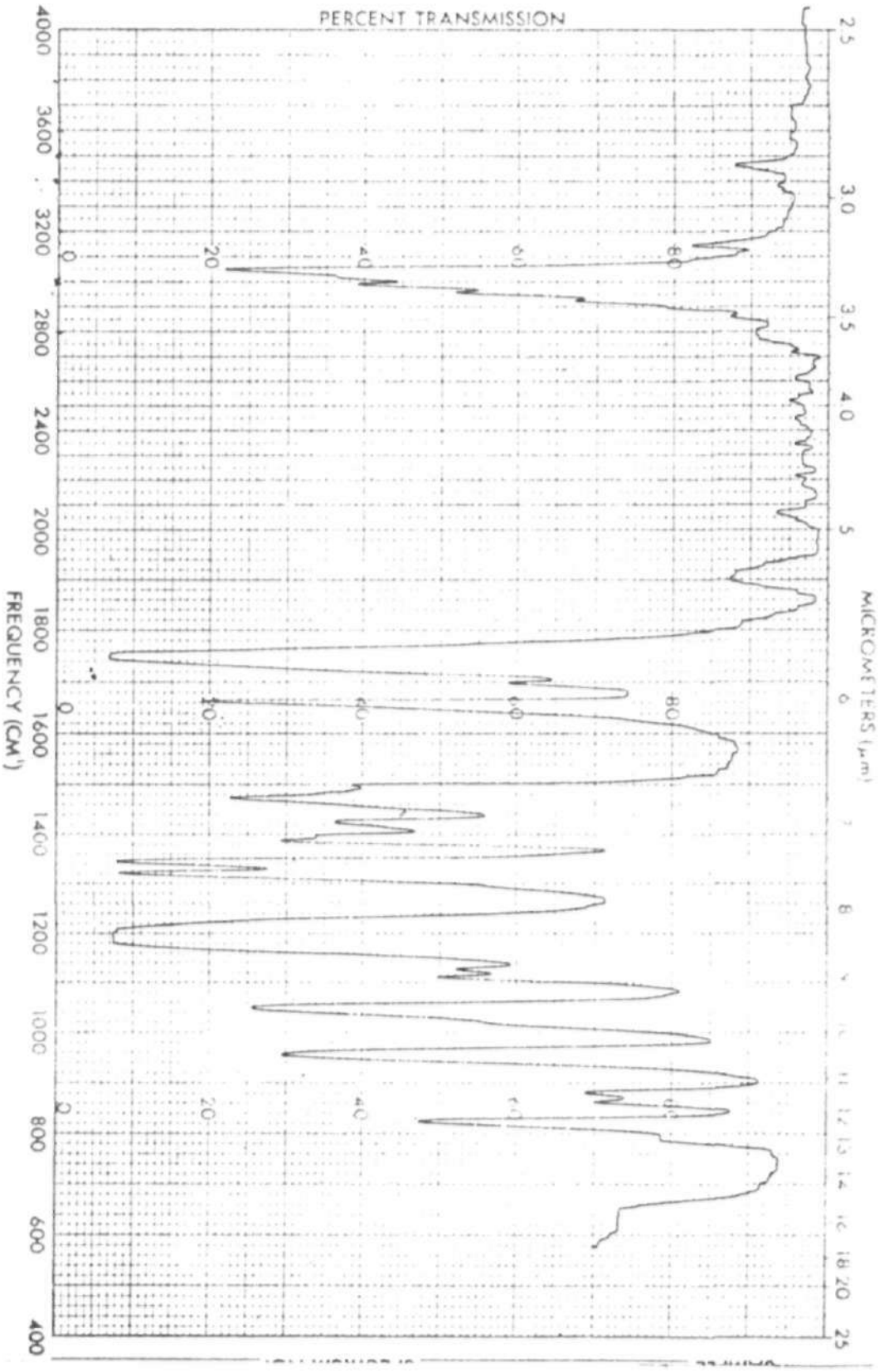


Fig. 4.11a: I.R. spectrum of EMA monomer

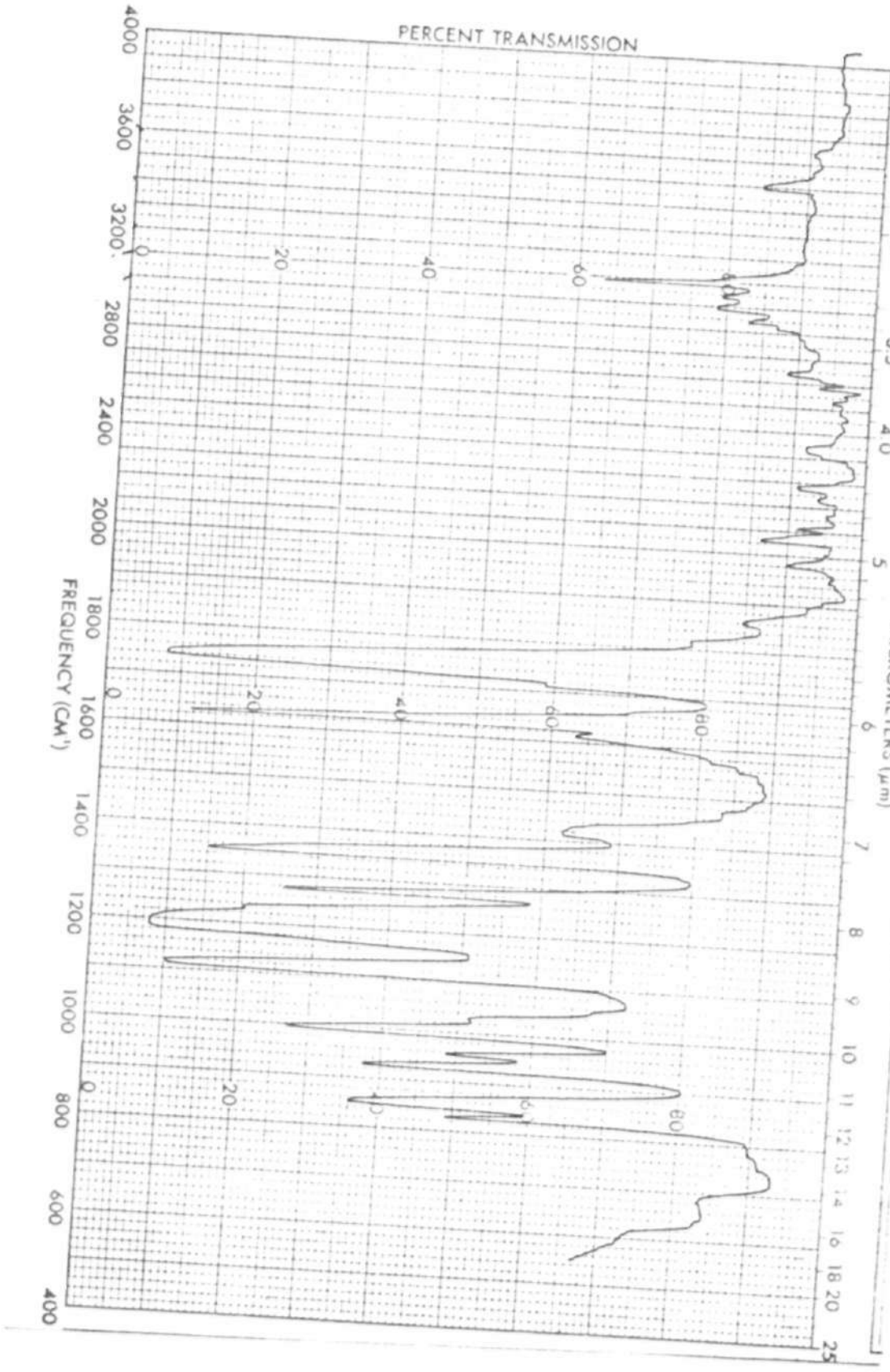
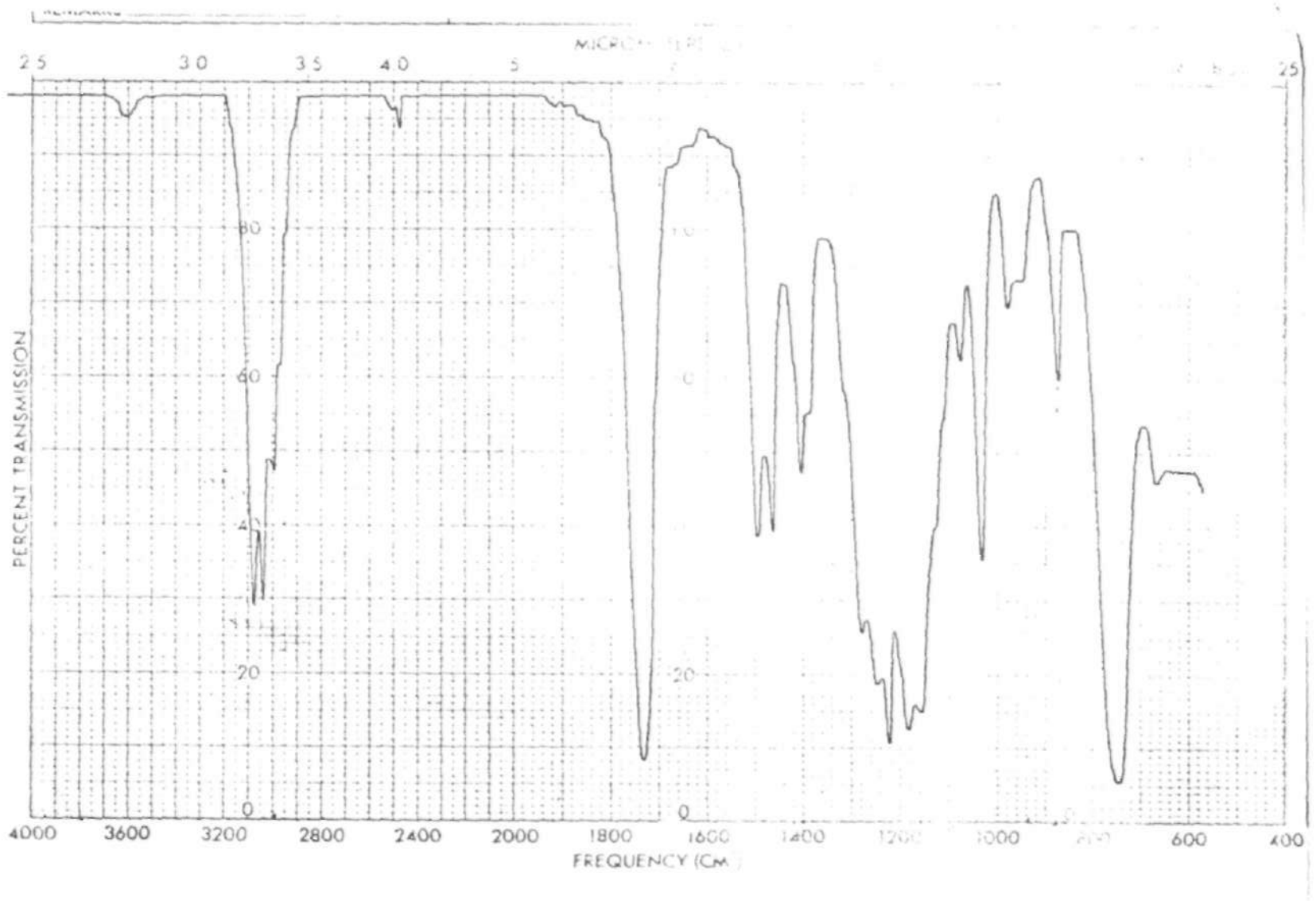


Fig. 4.11b: I.R. spectrum of VAc monomer

Fig. 4.12a: I.R. spectrum of Pure PEMA



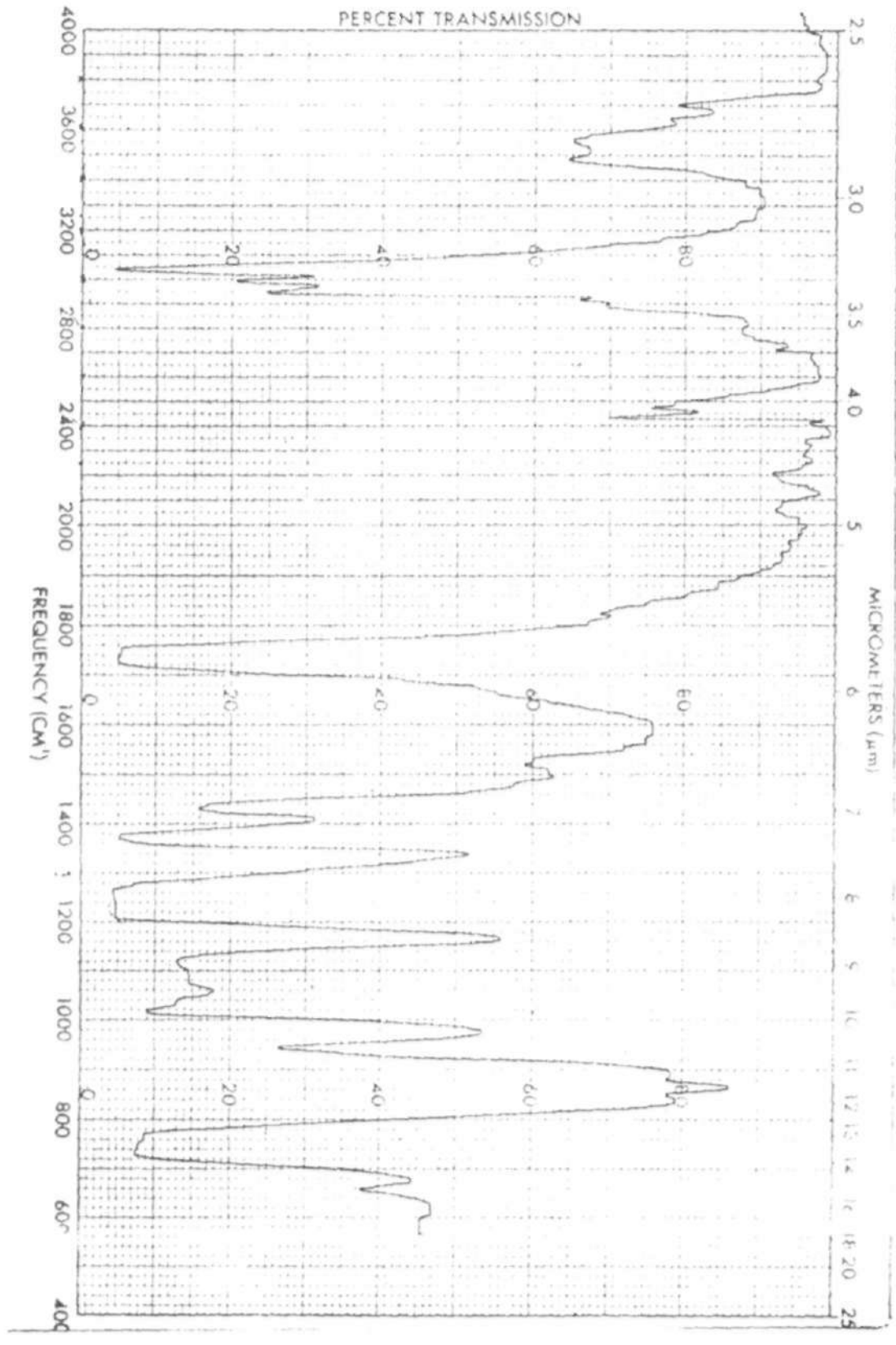


Fig. 4.12b: I.R. spectrum of Pure PVAc

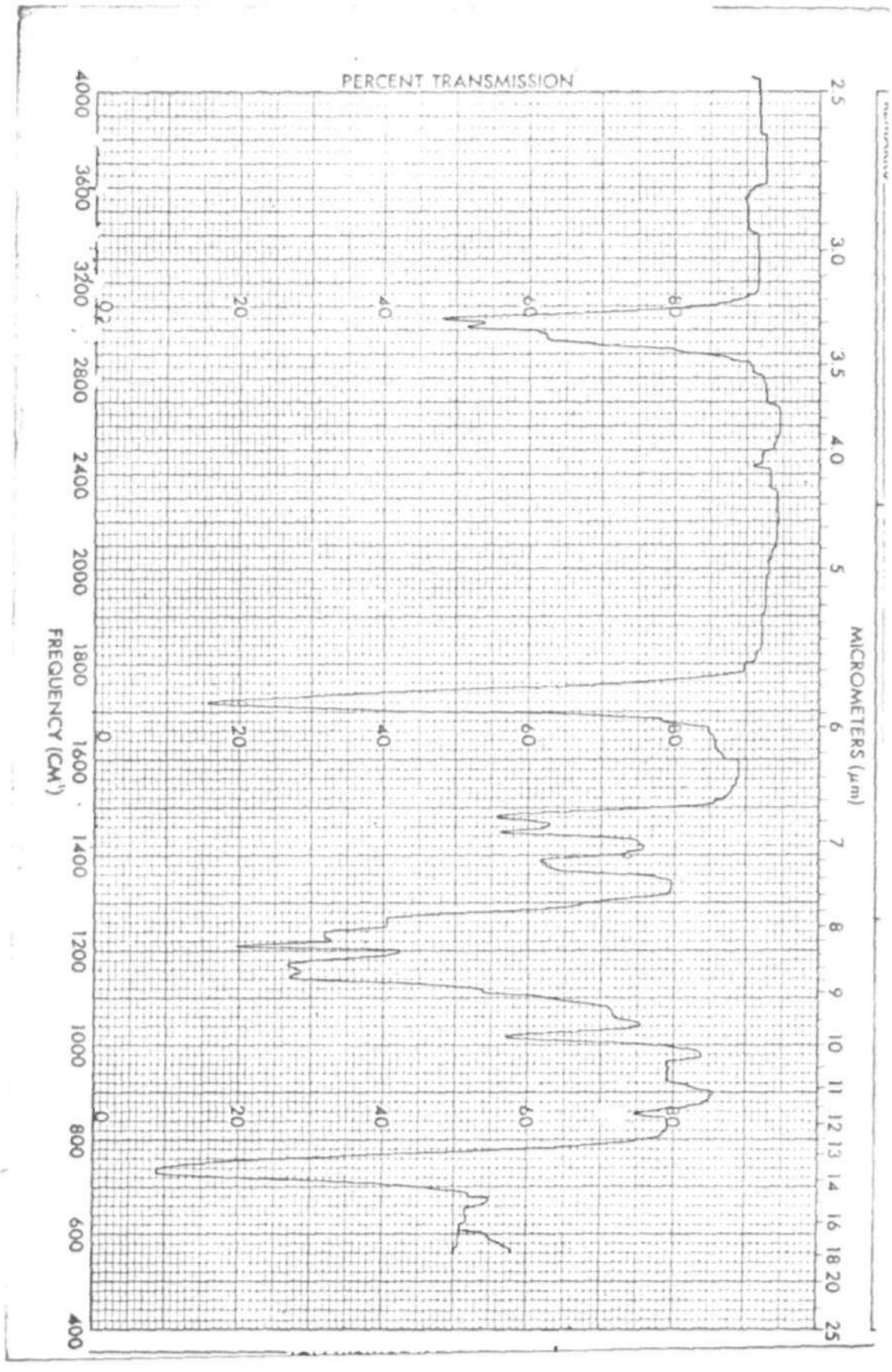


Fig. 13a: I.R. spectrum of mixture of PEMA/PVAc

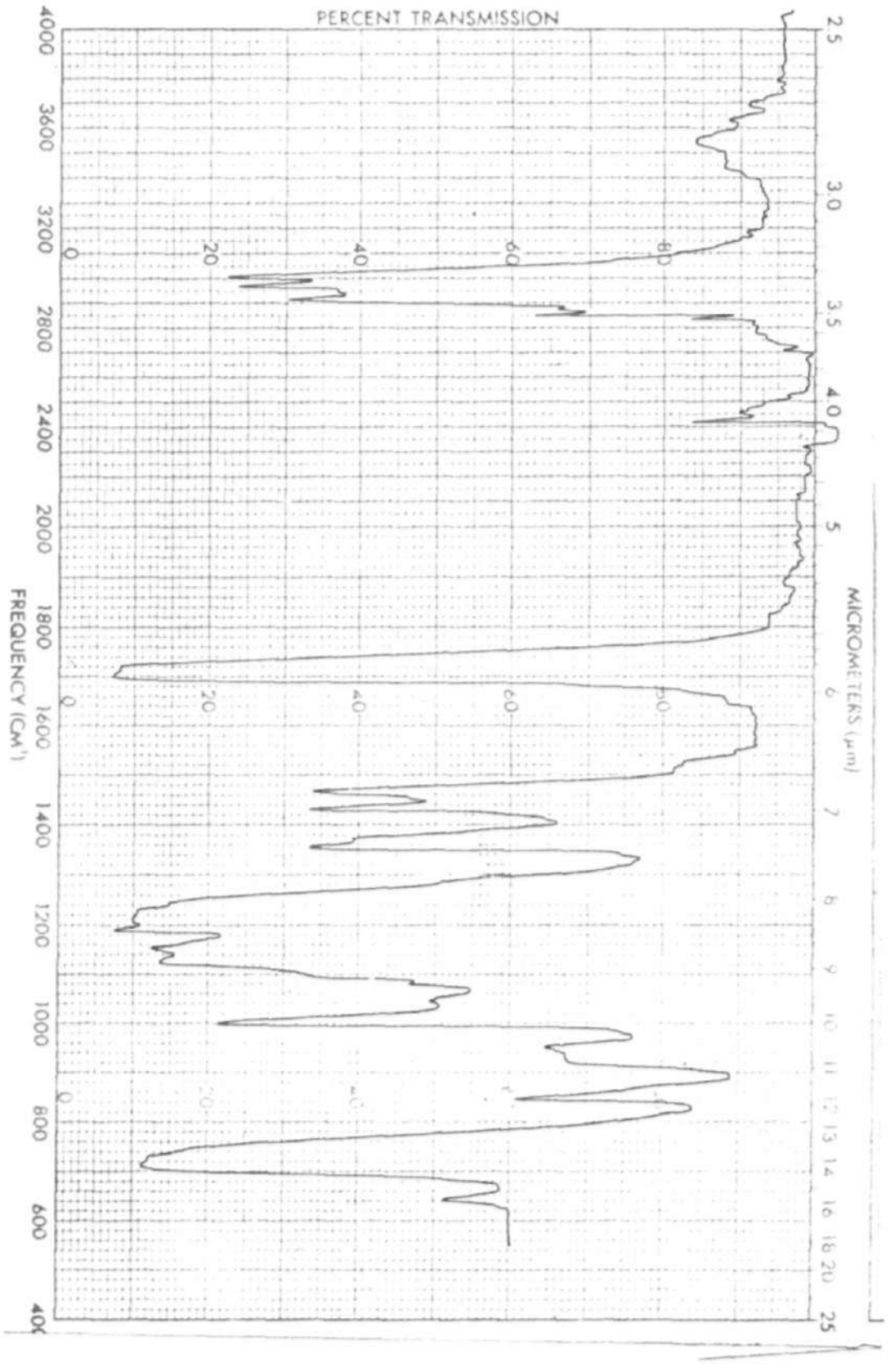


Fig. 4.13b: I.R. spectrum of a typical copolymerisation product

KASHIM IBRAHIM LIBRARY
AHMADU BELLO UNIVERSITY
ZARIA, NIGERIA.

312577

of PEMA and PVAc respectively, a broad band at 3500 cm^{-1} due to the CH_3-stretch was observed in PVAc but found weak in PEMA while the band at 1360 cm^{-1} due to C - O - C stretch in PVAc was completely absent in PEMA. The bands between 840-860 cm^{-1}, 1140-1180 cm^{-1} were present in PEMA but completely absent in PVAc. The presence of bands between 1360-1380 cm^{-1} with the absence of the one between 840-860 cm^{-1} with the broad band at 3500 cm^{-1} are characteristic of PVAc (Fig. 4.12b) while the splitting of the band between 1480-1500 cm^{-1} and 920-960 cm^{-1} characterise only PEMA (Fig. 4.12a). Fig. 4.13a for the i.r. of the physical mixture (PEMA/PVAc) show that more bands are split in this spectrum (e.g. band between 1460-1480 cm^{-1}, 1140-1180 cm^{-1}) than in the homopolymers (Fig.4.12a and 4.12b).

4.12.1 Analysis of Infrared Spectroscopy Studies of Copolymerisation Products

Fig. 4.13b is a typical i.r. spectrum of the 'copolymerisation product' and the detailed analysis of all the spectra (Appendix VII) show that these spectra are identical for the batch, semi-batch and the semi-batch continuous products. The bands at 1420 cm^{-1} in PVAc spectrum (Fig. 4.12b) was shifted to 1440-1480 cm^{-1} while the one between 1480-1500 cm^{-1} in pure PEMA spectra (Fig. 4.12a) was also found at 1440-1480 cm^{-1} in the spectra of the copolymerisations product but were completely absent in the spectra of the mixture . The fact that the sharp band between 1200-1260 cm^{-1} due to $-CH_2 - CH_2 -$ interaction in the physical mixture and homopolymers becoming broad in the spectra of copolymerisation product and the absence of the band between 1620-1660 cm^{-1} due to $- C = CH_2$ stretch suggest the formation of a covalent bond. The quantitative analysis

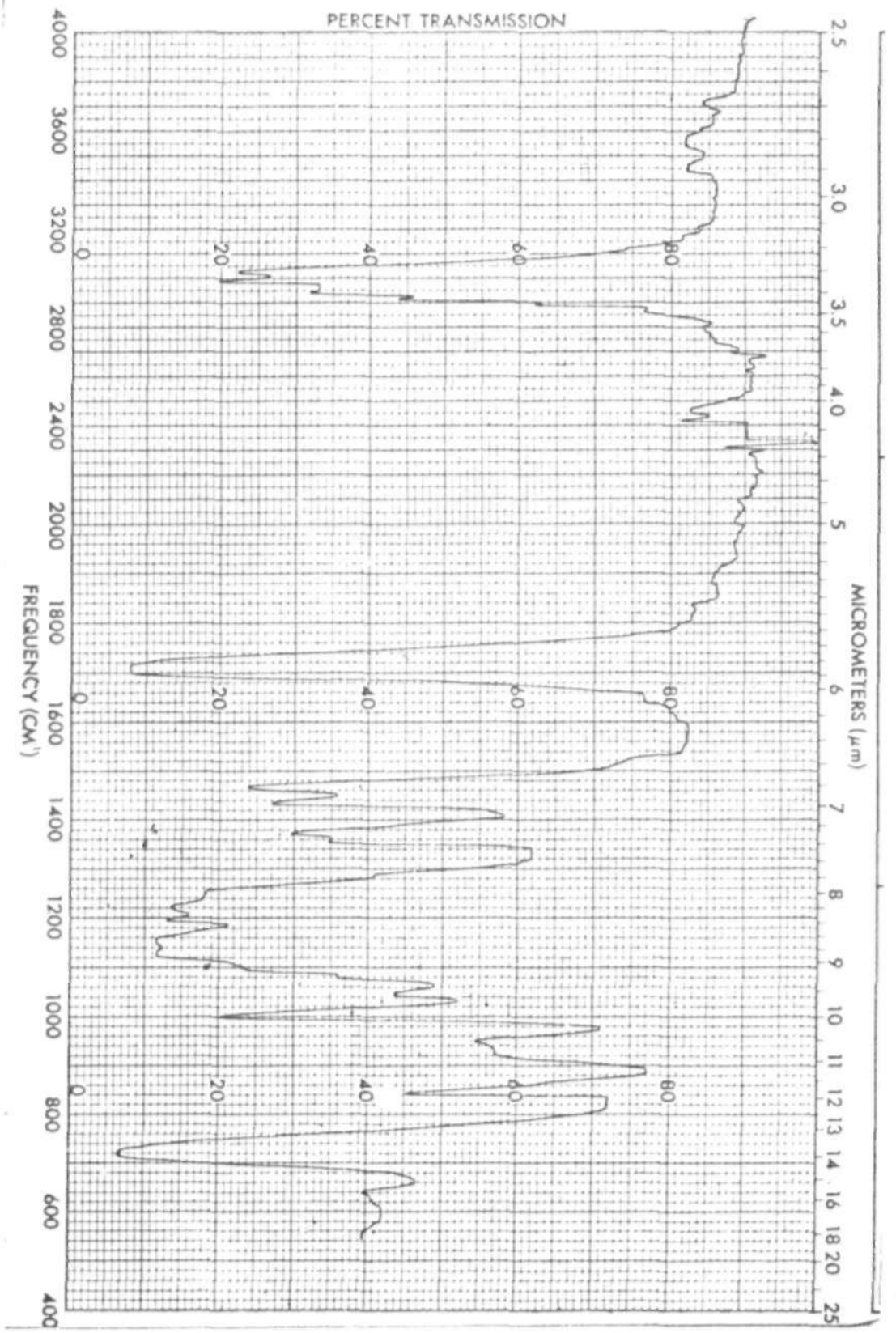
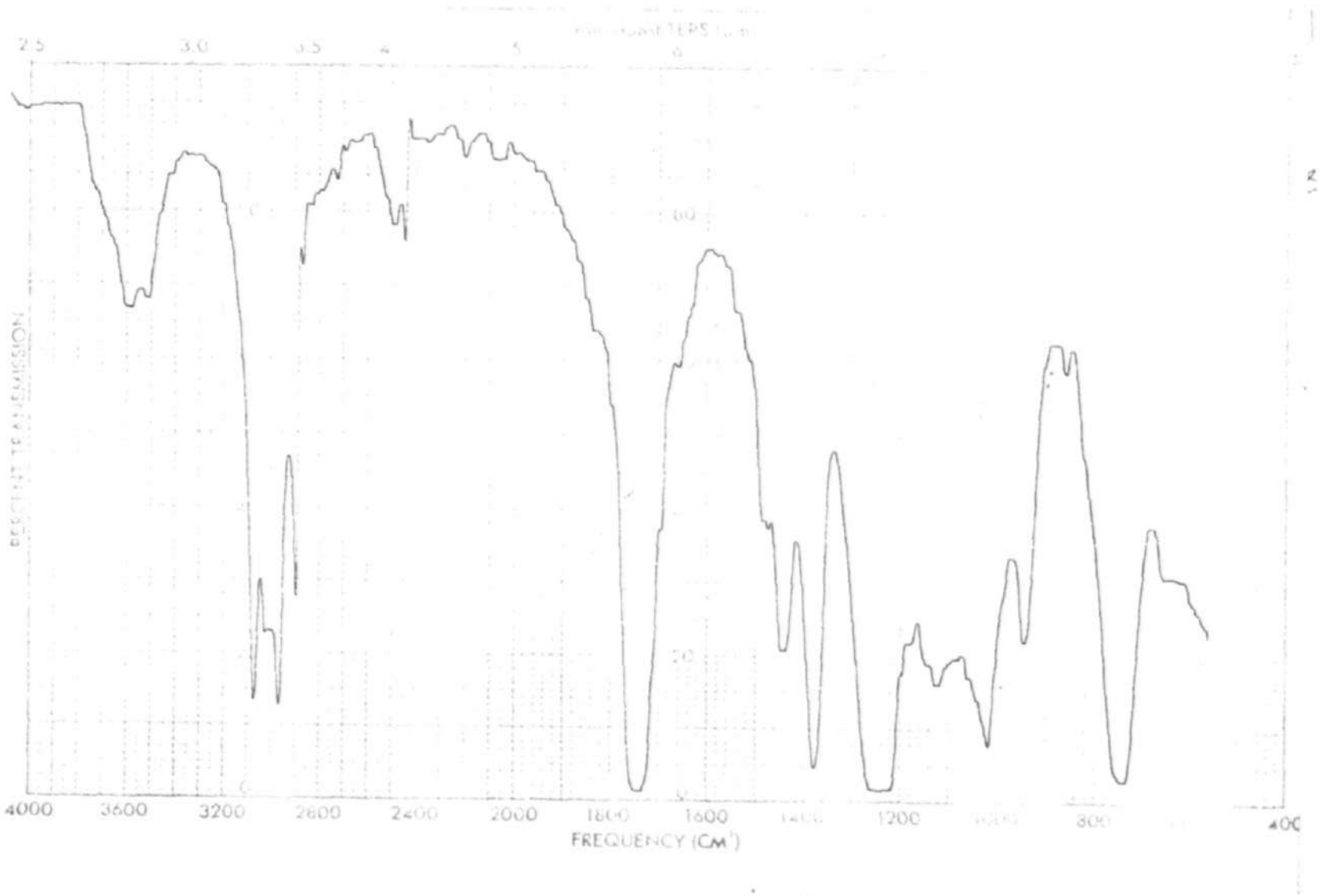


Fig. 4.14a: I.R. spectrum of a typical methanol insoluble

Fig. 4.14b: I.R. spectrum of a typical methanol soluble



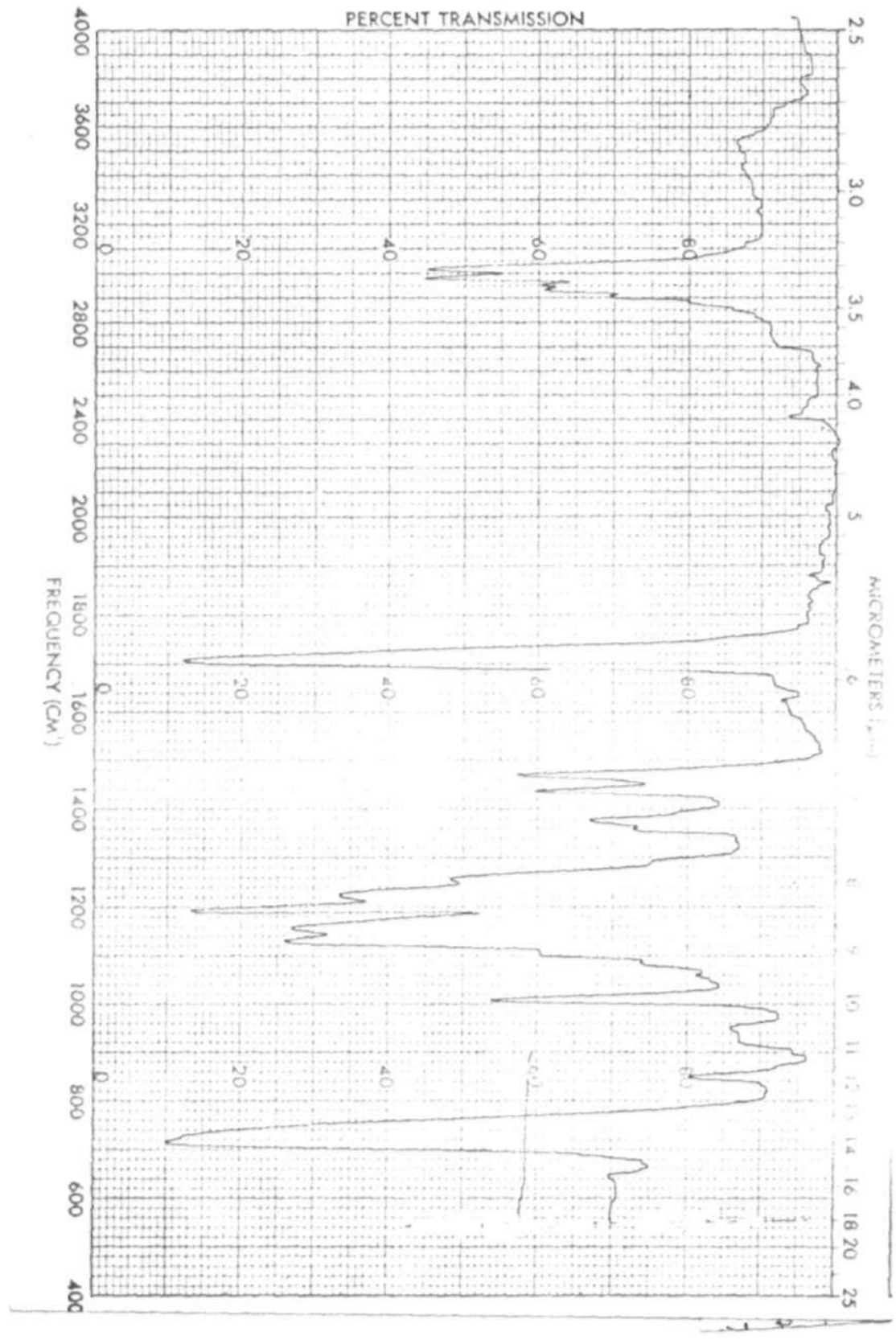


Fig. 4.15a: I.R. spectrum of a typical ethanol insoluble

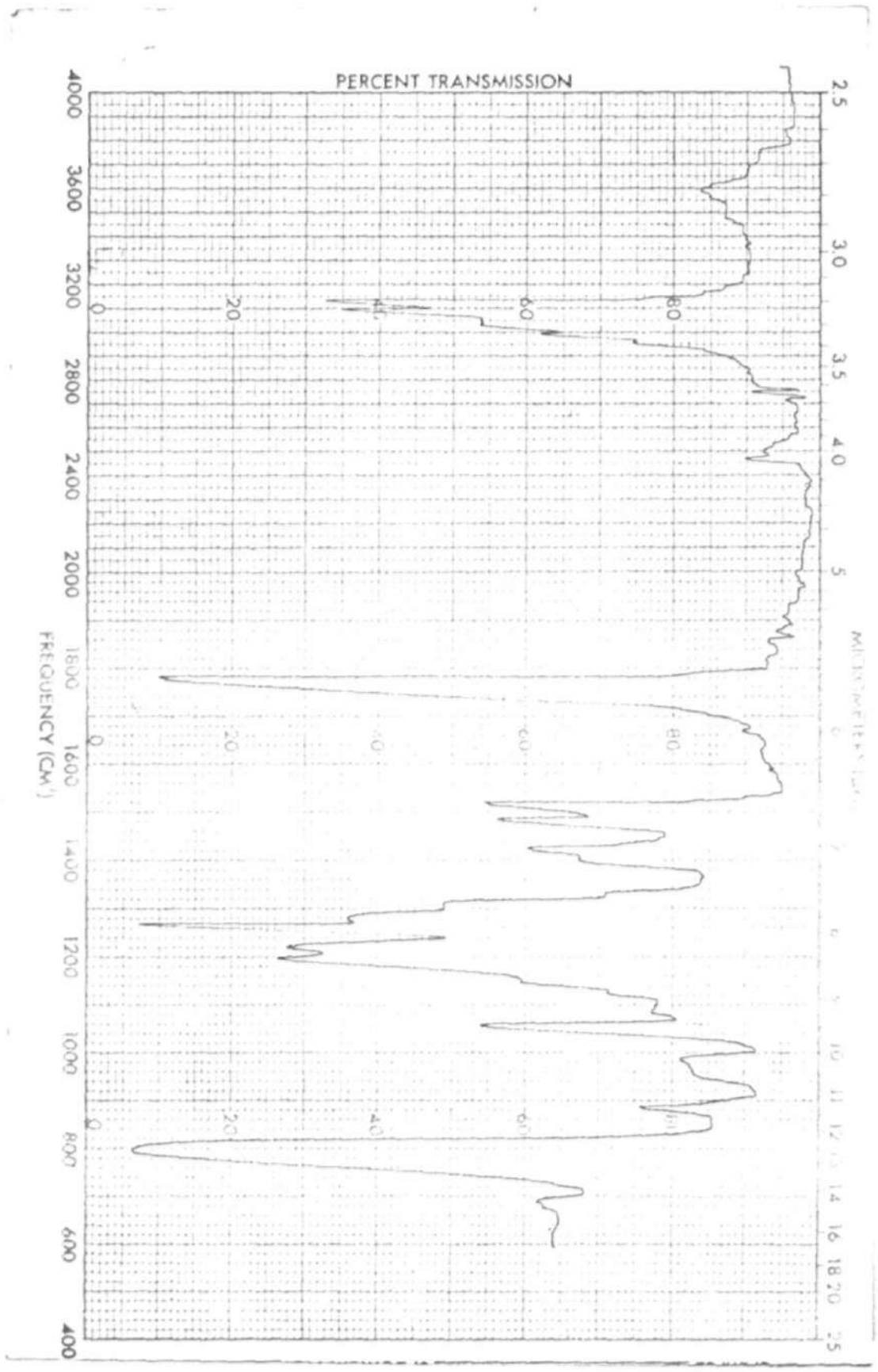


Fig. 15b: I.R. spectrum of a typical ethanol soluble

(section 4.60-4.70) of the copolymerisation product had established the presenc of three components namely the unbound PVAc (MSS), the unbound PEMA (EIS) and the third one as ethanol soluble - the expected copolymer. Also the i.r. spectrum of the ethanol soluble (ES) in Fig. 4.15b showed it to be different from that of the unbound PEMA (Fig. 4.15a) and the unbound PVAc (Fig. 4.14b). Thus the i.r. spectroscopy studies had established the presence of a copolymer in the 'copolymerisation product' apart from the unbound PVAc and unbound PEMA.

4.12.2 Analysis of I.R. Spectroscopy Studies of Various Fractions of the Copolymerisation Products

The copolymerisation products were separated according to the scheme in Fig. 4.21. The i.r. and n.m.r. of these fractions were studied.

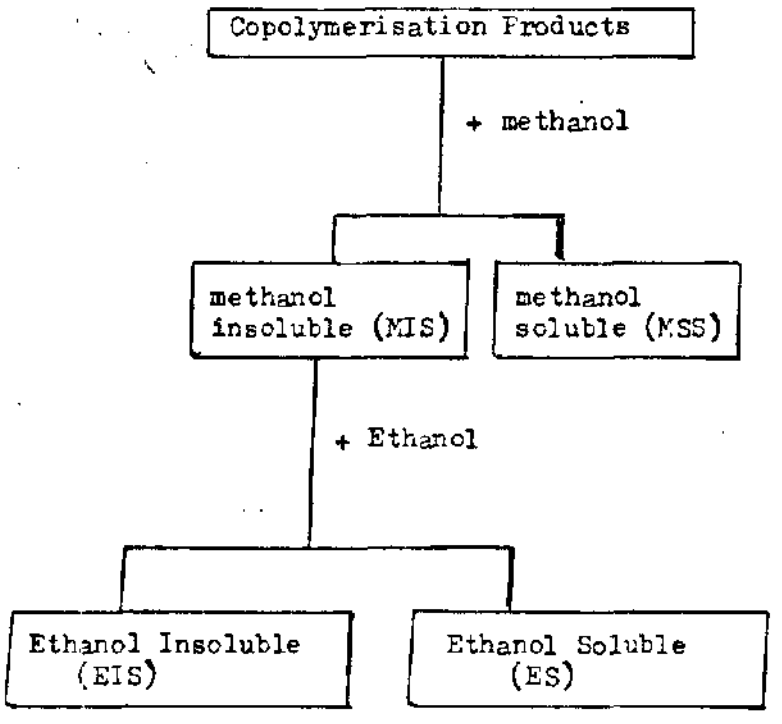


Fig. 4.21: Schematic diagram for the separation of copolymerisation products.

Comparing Figures 4.13b and Fig. 4.14a, typical spectra for the copolymerisation products and methanol insoluble (MIS) fractions, showed the bands between 1440-1480 cm^{-1}, 1360-1380 cm^{-1} and 1200-1260 cm^{-1} are splitted in the MIS whereas these bands are single in the copolymerisation products. This suggest that the methanol insoluble (MIS) fraction comprises of more than one component. Solubility test, melting point and x-ray studies had earlier confirmed the fact that the methanol insoluble (MIS) is composed of the unbound PEMA and the expected copolymer.

However, the spectra of the methanol soluble (MSS) fraction (Fig. 4.14a) closely resemble that of the pure PVAc spectrum (Fig. 4.12b). All the bands (at 1480-1500 cm^{-1}, 1140-1180 cm^{-1} and 840-860 cm^{-1}) missing from the spectrum of the PVAc were also absent in those for the MSS fractions. This implies that methanol was efficient in removing all the unbound PVAc from the copolymerisation products.

The spectra of all the ethanol insoluble (EIS) fraction (Fig. 4.15a) closely resemble that of the pure PEMA (Fig. 4.12a) while being different from those of PVAc and MSS fraction respectively. For example, the bands between 1400-1500 cm^{-1}, 1200-1260 cm^{-1} and 1140-1180 cm^{-1} were found split in the spectra of PEMA and EIS fraction respectively. This is an evidence that ethanol had extracted the unbound PEMA from the methanol insoluble (MIS) fractions leaving one other fraction - the ethanol soluble (ES).

The spectra of the ethanol soluble (ES) fractions (Fig. 4.15b) while resembling those of the copolymerisation products show presence of bands characteristic of both PEMA and PVAc respectively. The fact that the band at 1360 cm^{-1} with a weak band at 2450 cm^{-1} and the split bands between 1480-1500 cm^{-1}, 1140-1180 cm^{-1} and 840-860 cm^{-1} which are characteristic bands in PVAc and PEMA respectively suggest the formation of a covalent bond in the ethanol soluble (ES) fraction. Also the disappearance of the

bands between 1620-1660 cm^{-1} and the broad band between 1200-1260 cm^{-1} in the spectrum of the ES (Fig. 4.15b) confirms the formation of a copolymer.

4.13 Nuclear Magnetic Resonance Studies of Monomers, Polymers, Mixtures and Copolymerisation Products

A detail analysis of the n.m.r. peaks from the spectra of the monomers, polymers, mixtures and copolymerisation products with the various fractions have been presented in Appendix VIII.

In the spectrum of ethyl methacrylate (EMA) monomer (Fig. 4.16a), four distinct peaks are observed whereas three peaks are found in the spectrum of vinyl acetate (VAc) monomer (Fig. 4.16b). The absence of the peaks at 4.0 - 4.5 δ due to the vinylic ($-C=CH_2$) proton in both monomers from the n.m.r. spectra of PEMA (Fig. 4.17a) and that of PVAc (Fig.4.17b) is attributed to the fact that during polymerisation, the vinylic chain disappears in the polymers.

The nuclear magnetic resonance of PEMA (Fig. 17a) shows four peaks while that of PVAc (Fig. 4.17b) showsthree peaks which are singlets. Comparison of n.m.r. spectra of PVAc and PEMA with standard n.m.r. spectra of PVAc reported by Bovey et al., (1963), Ritchey and Knoll (1966) show PVAc to be wholly amorphous while the PEMA is syndiotactic. The x-ray studies had confirmed PVAc to be wholly amorphous while some degree of ordering had been reported for PEMA.

4.13.1 Analysis of the N.M.R. Spectra of the Physical Mixtures and Copolymerisation Products.

Fig. 4.18b with the details in Appendix VIIIshow fewer peaks for the copolymerisation products than in the homopolymers (Fig. 4.17a and 4.17b)

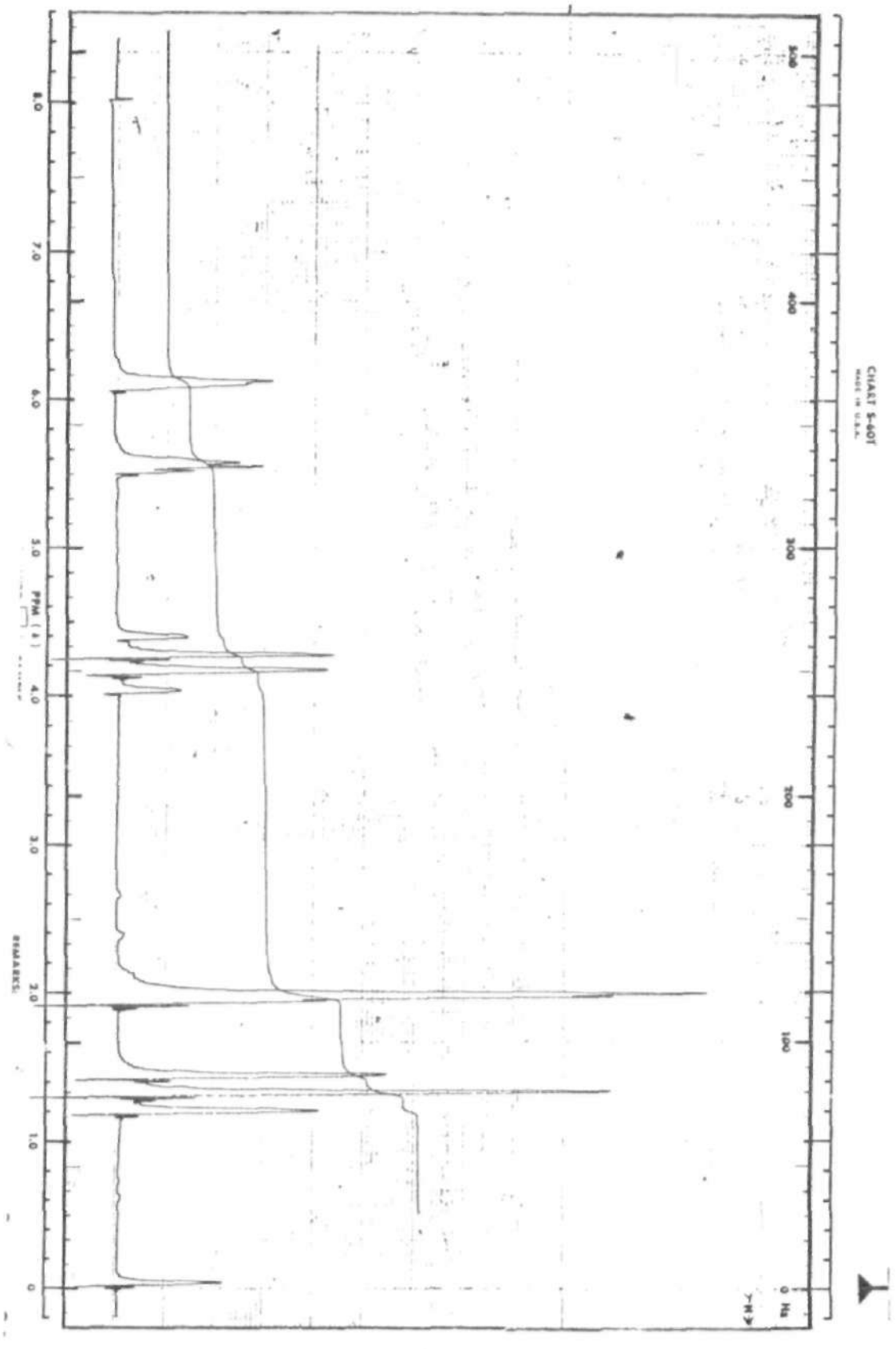


Fig. 4.16a: N.M.R. spectrum of EMA monomer

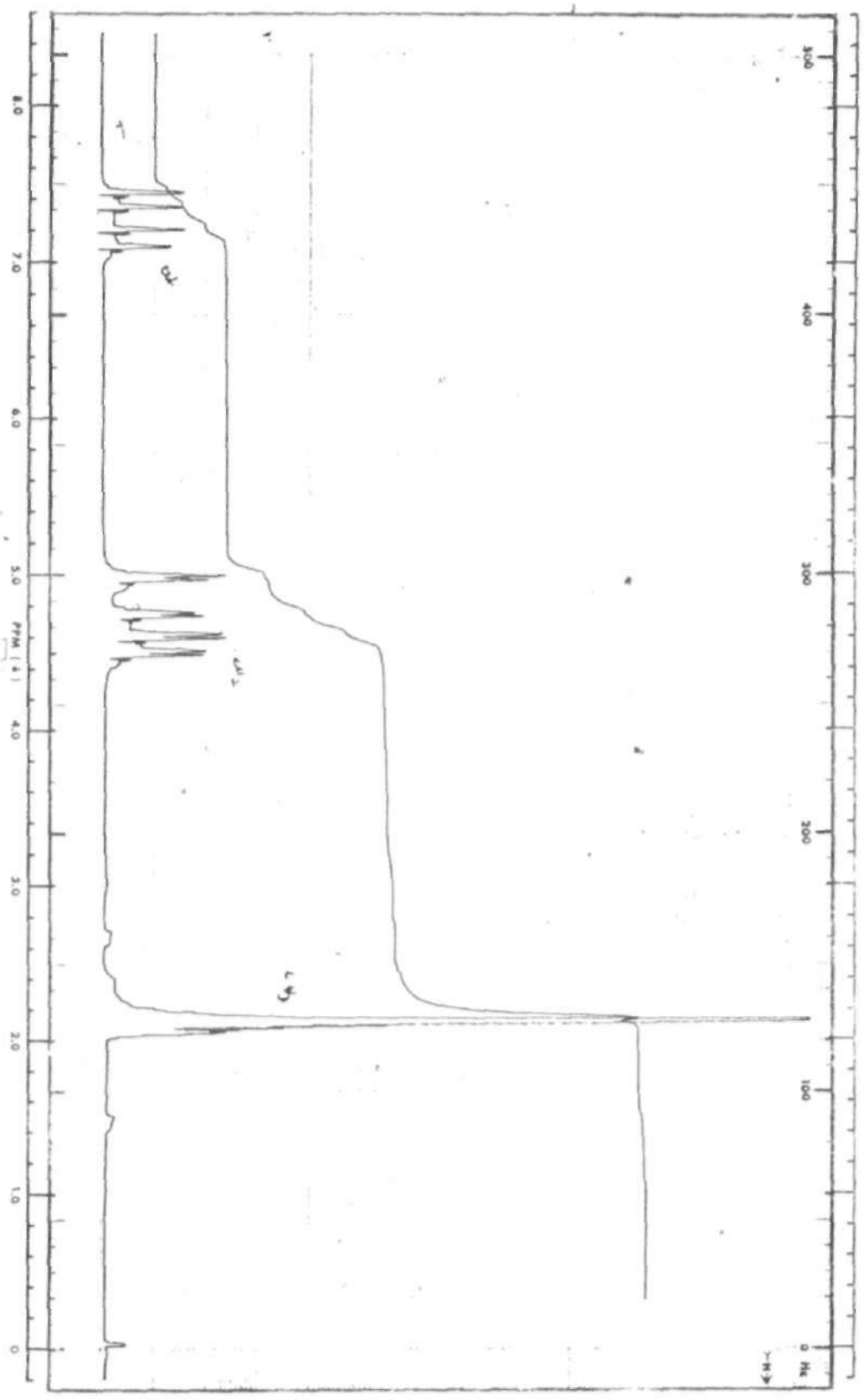


Fig. 4.16b: N.M.R. spectrum of VAc monomer

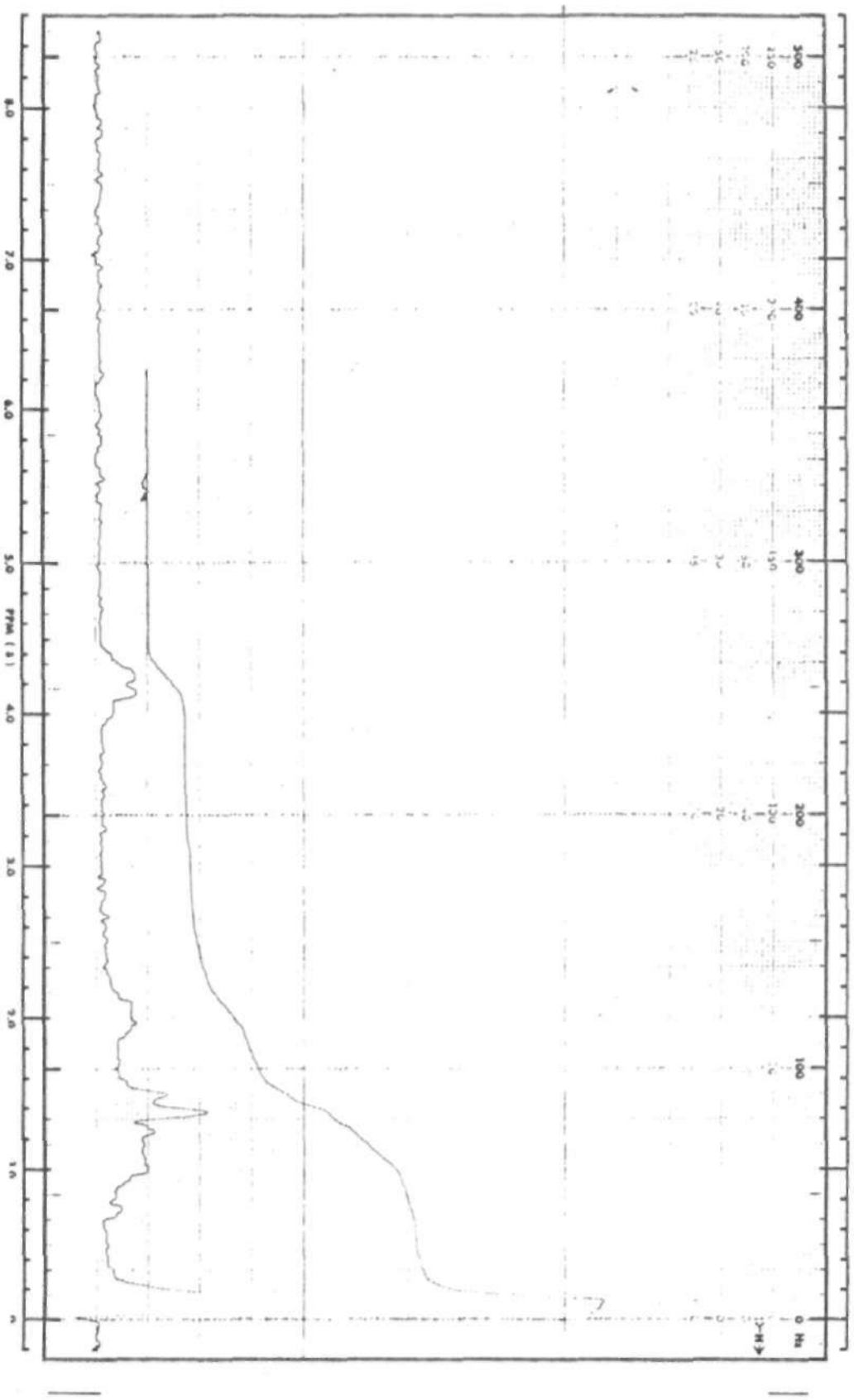


Fig. 4.17a: N.M.R. spectrum of pure PEA

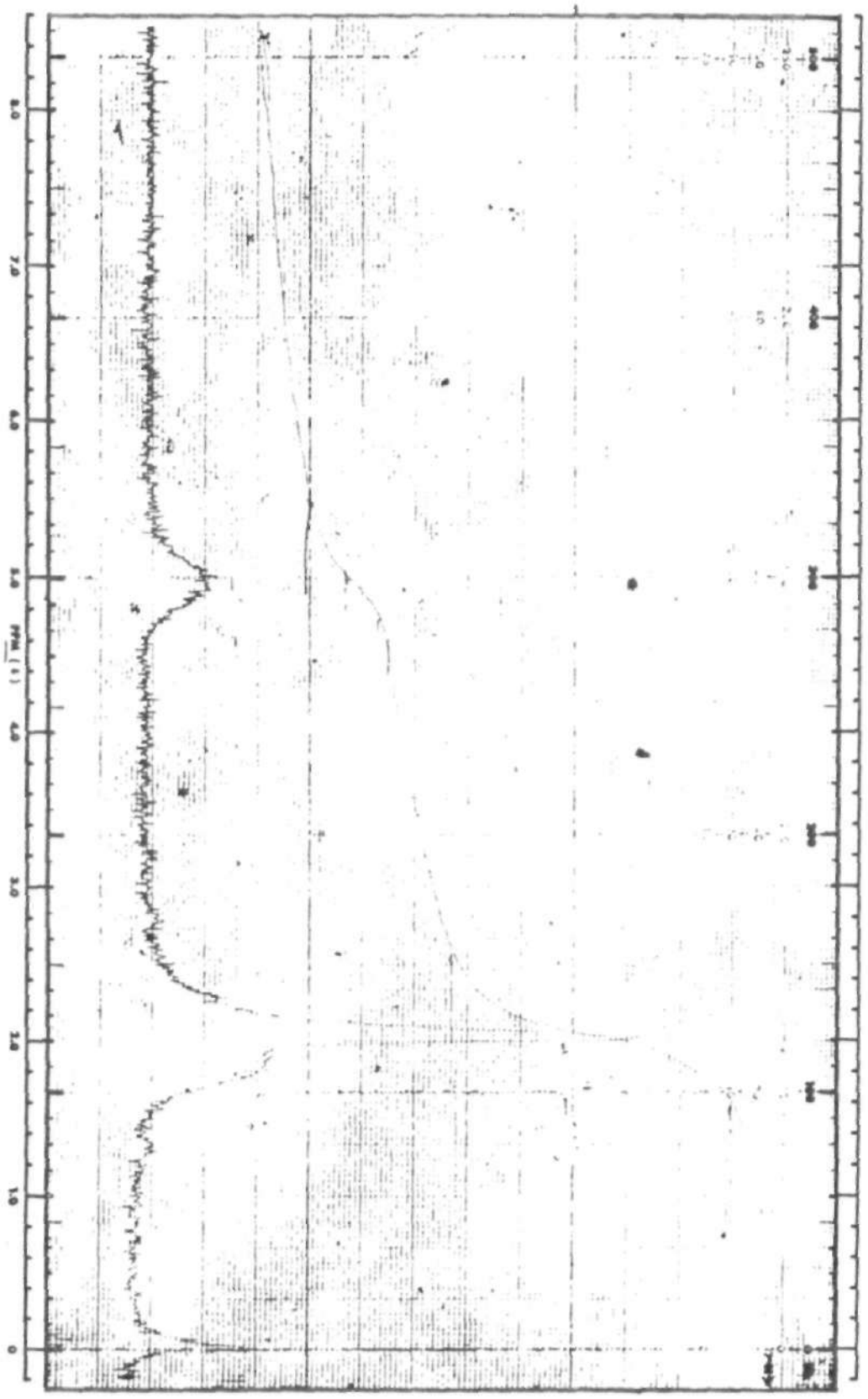


Fig. 4.17b: N.M.R. spectrum of Pure PVAc

and their physical mixture. This implies that there is hindrance of coupling of the protons in the copolymerisation products, which is a strong evidence for the phenomenon of copolymerisation process (Hummel 1974). For example, the peak at 2.0 - 2.1 δ due to the ester proton is more reduced in the 'copolymerisation products' than the physical mixture or homopolymer. Another evidence of copolymerisation with the formation of a covalent bond is the disappearance of the peak at 4.8 - 5.2 δ found in the spectra of monomers due to the methylene ($-CH_2$) proton from that of the copolymerisation product (Fig. 4.16a 4.16b and 4.18b). This has already been inferred by the i.r. studies of these samples and the quantitative analysis (section 4.6 and 4.7).

4.13.2 Analysis of the N.M.R. Spectroscopy of Fractions of the Copolymerisation Products

Figure 4.19a which is a typical spectrum of methanol insoluble (MIS) fraction shows a triplet peak at 1.0 - 1.5 δ not well-resolved as in those for the corresponding copolymerisation products (Fig. 14. 18b). With other peaks (singlet at 0.7 - 0.9 δ , doublet at 4.2 - 4.4 δ , singlet at 1.8 - 2.0 δ and singlet at 2.0 - 2.3 δ), the presence of both PEMA and PVAc in the MIS fraction can be inferred.

On the contrary, the spectra of all the MSS fractions (e.g. Fig.4.19b) were similar to that of the pure PVAc (Fig. 4.17b) with all the peaks at different positions being only singlets. This implies that methanol had extracted probably only the unbound PVAc from the copolymerisation product. Similar evidence had earlier been observed during the i.r. studies.

It is note worthy that the spectra of all the ethanol insoluble (EIS) fraction (e.g. Fig. 4.20a) were similar to that of pure PEMA (Fig. 4.17a) with all the characteristics shown in Appendix VIII.

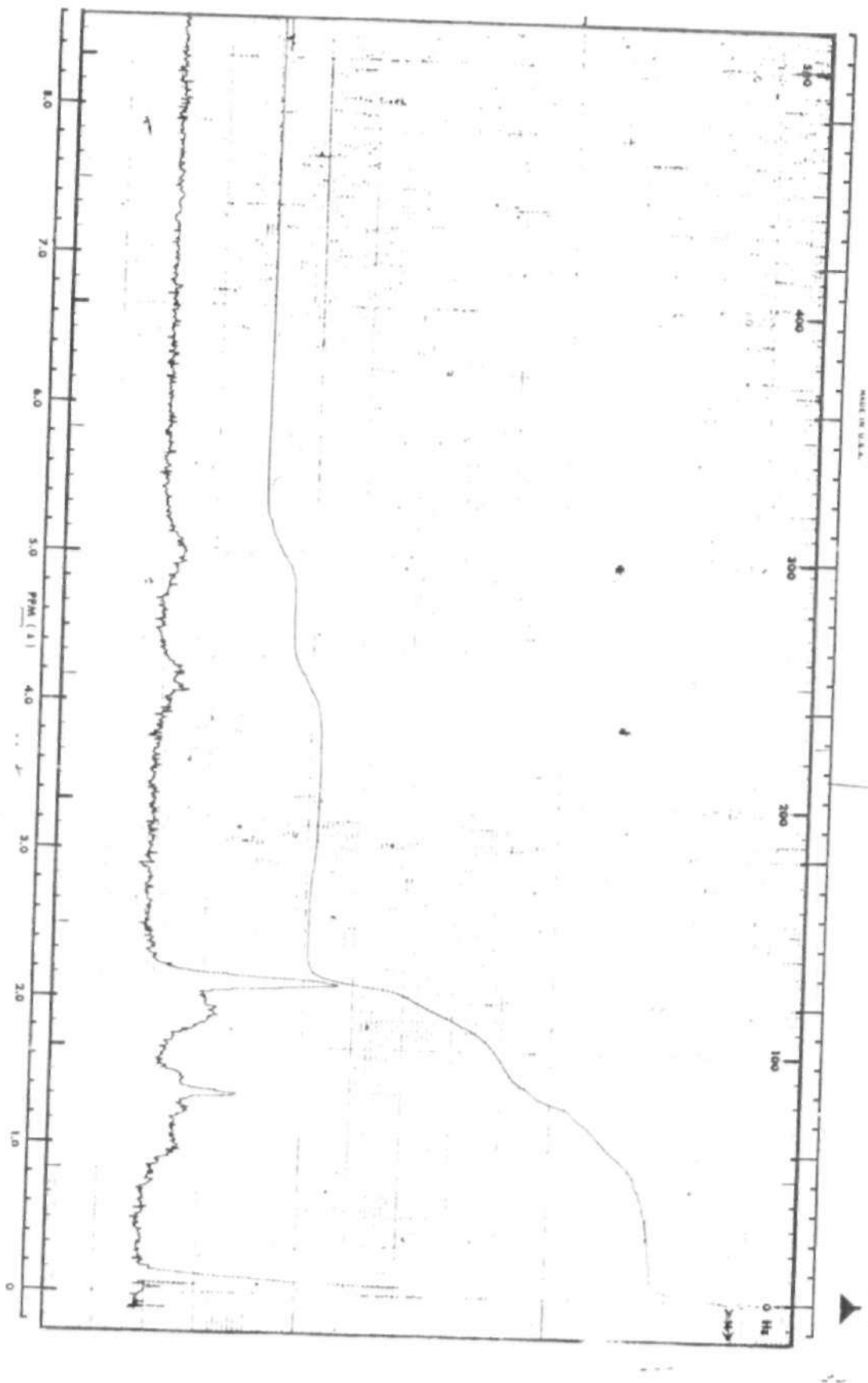


Fig. 4.18a: N.M.R. spectrum of mixture of PEMA/PVAc

Fig. 4.18a: N.M.R. spectrum of a typical copolymerisation product.

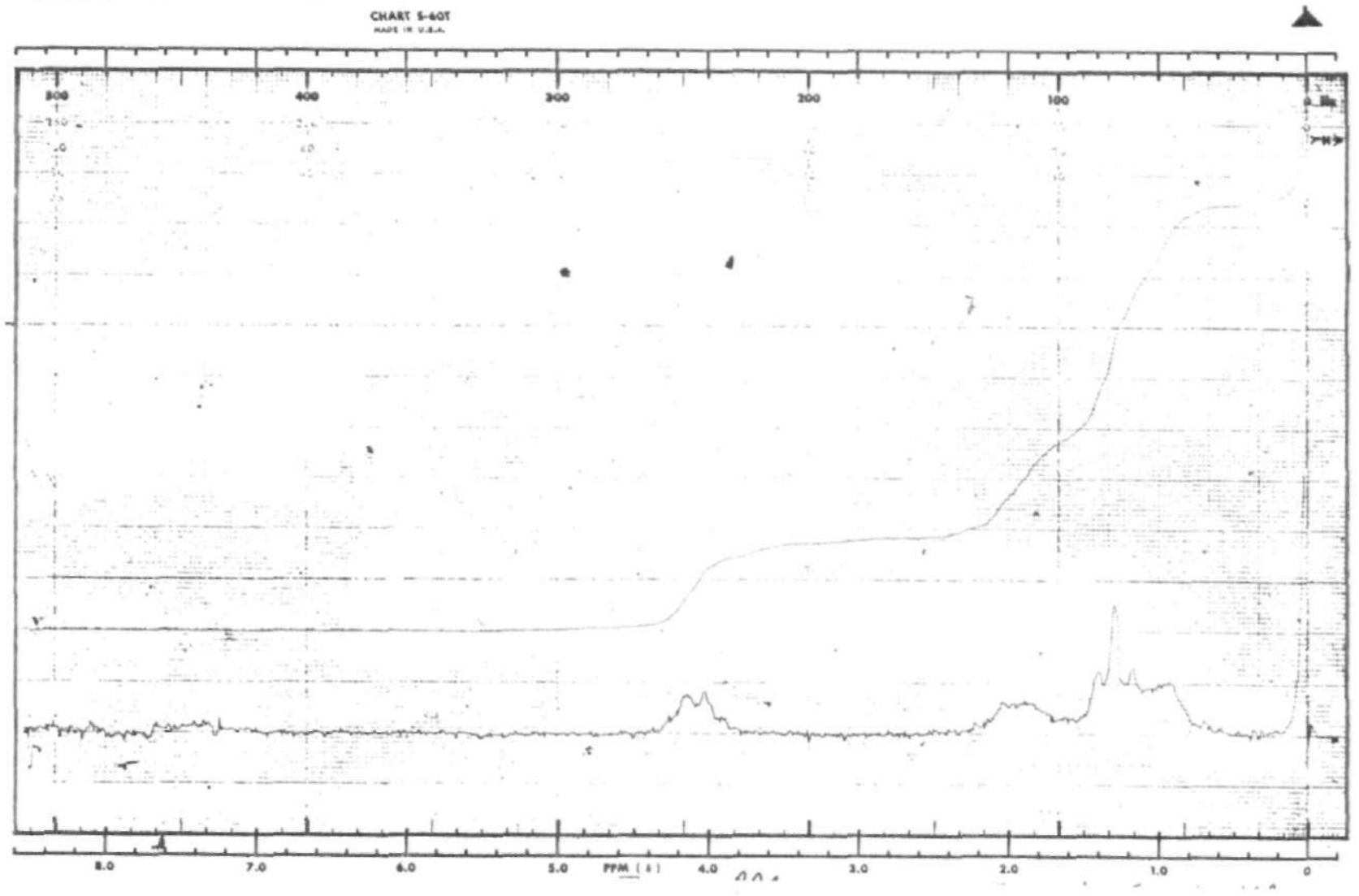
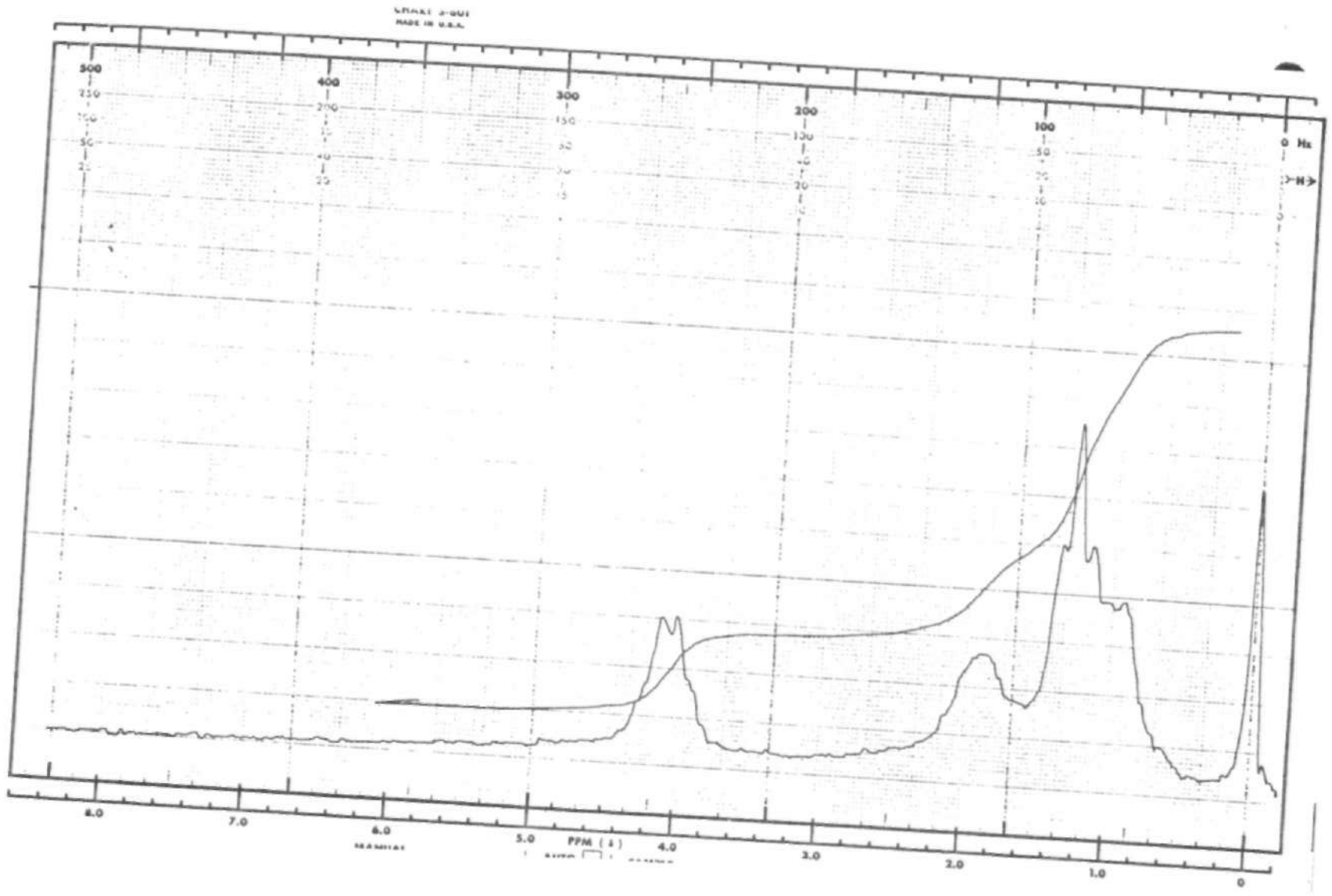


Fig. 4.19a: N.M.R. spectrum of a typical methanol insoluble



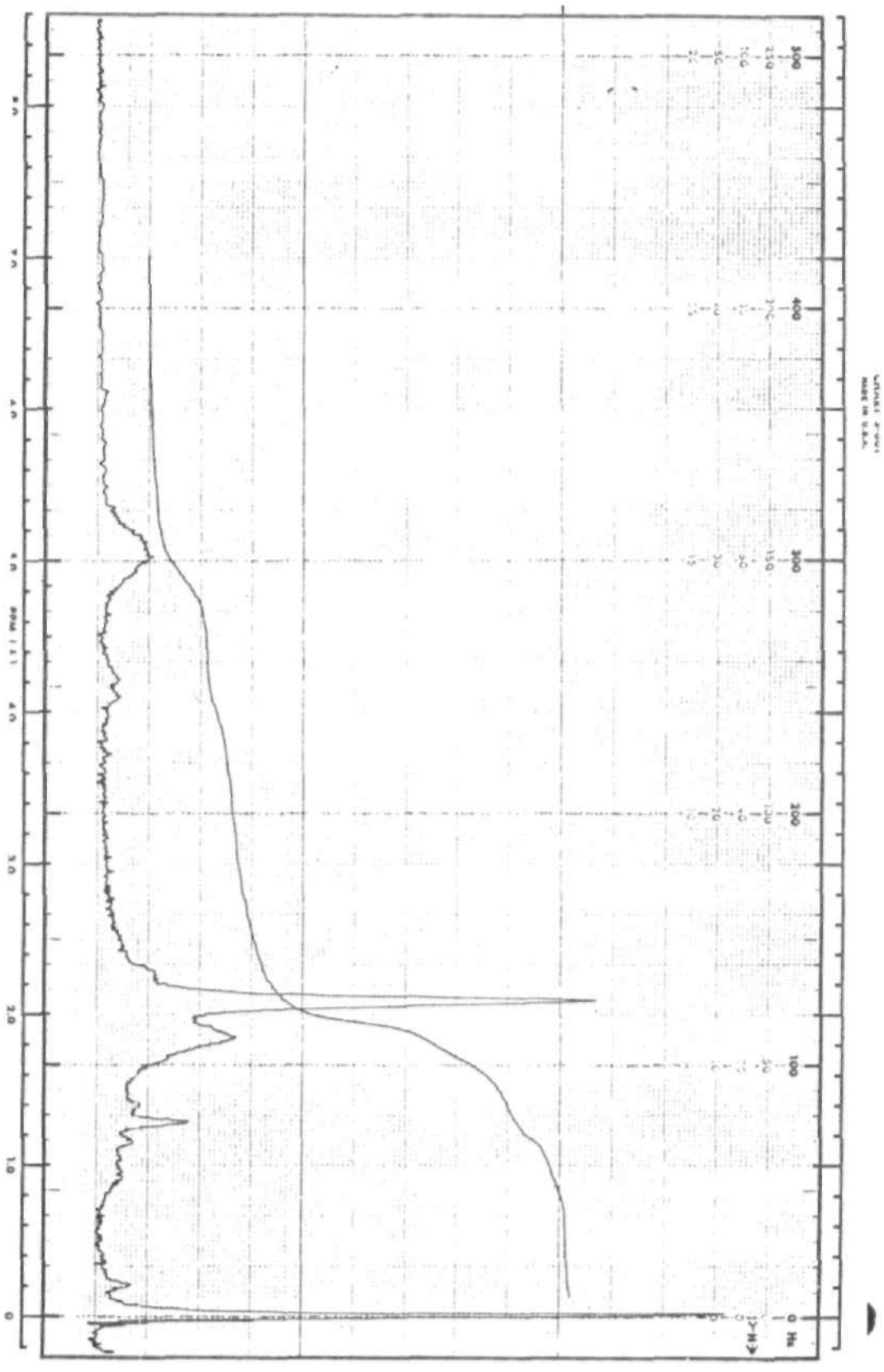


Fig. 4.19b: N.M.R. spectrum of a typical methanol soluble

Fig. 4.20a: N.M.R. spectrum of a typical ethanol insoluble

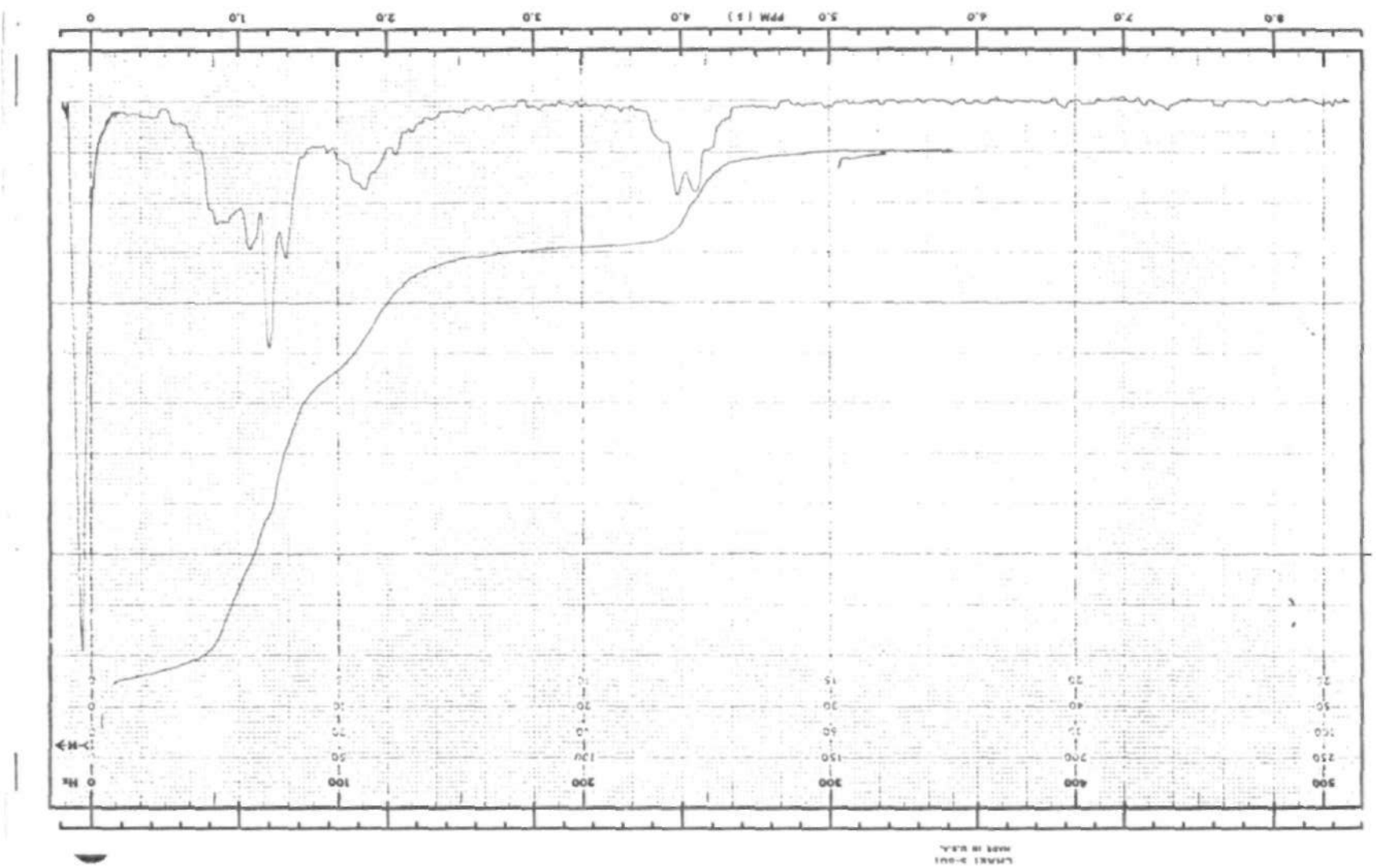
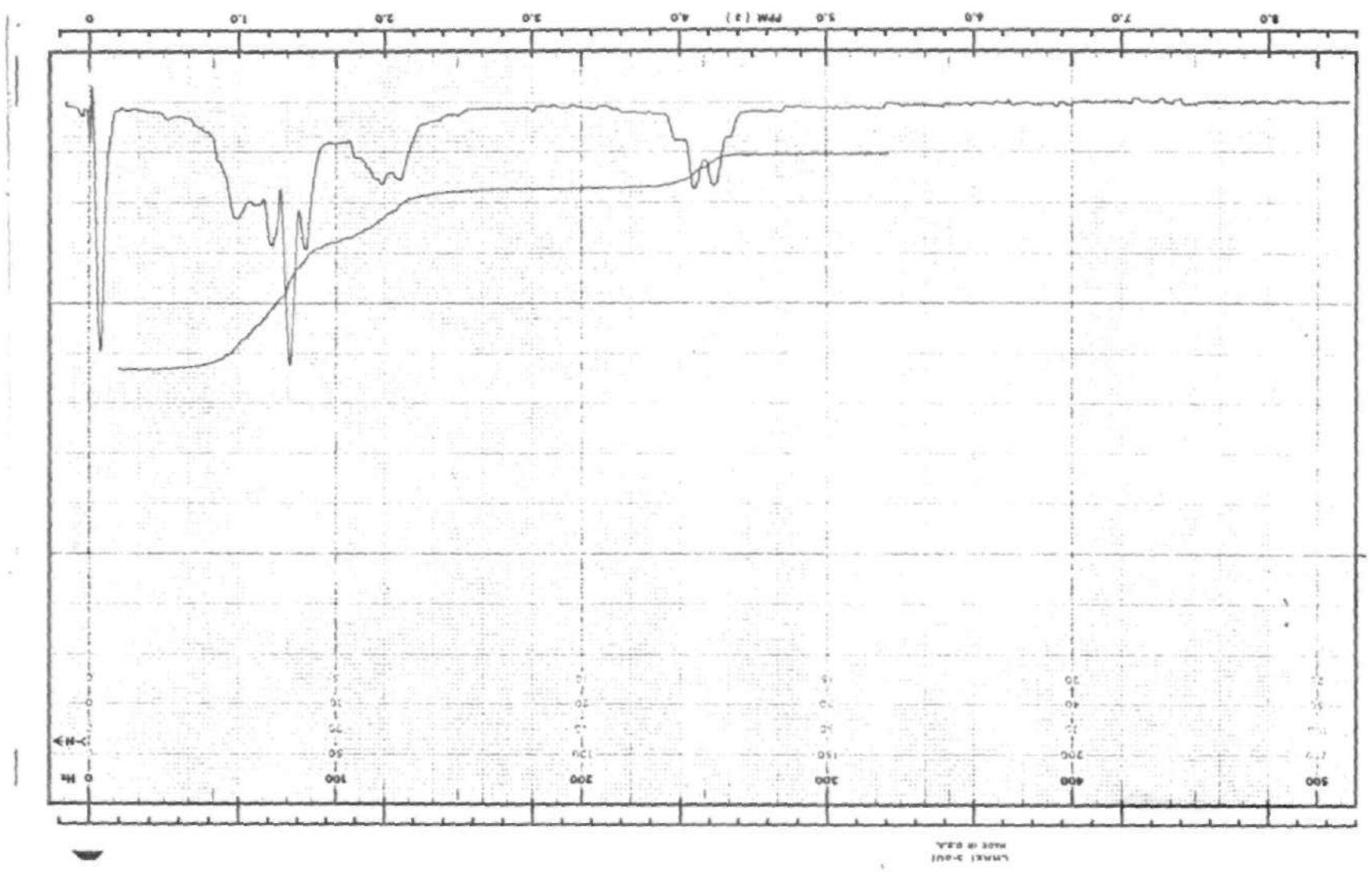
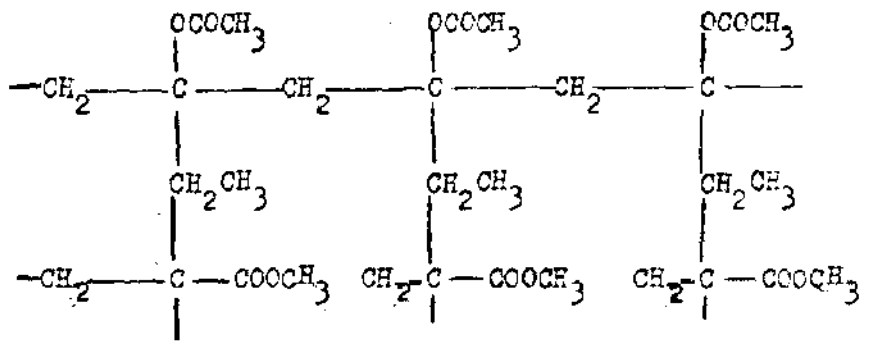


Fig. 4.20b: N.M.R. spectrum of a typical ethanol soluble

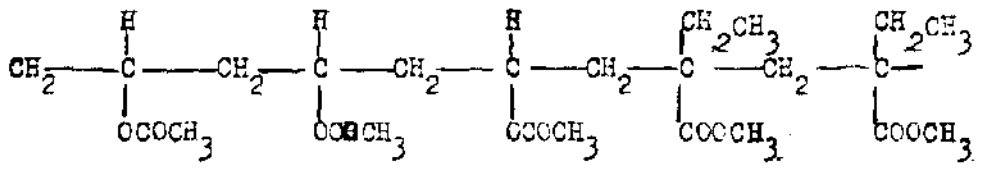


Also the spectra of all the ethanol soluble (ES) fractions (Fig. 4.20b) closely resemble those of the corresponding copolymerisation products (Fig. 4.18b). The formation of acovalent bond through the methylene ($-CH_2-$) proton of the PVAc, PEMA polymer backbones is inferred from the spectra of the ES fraction because of the presence of the doublet at 4.1 - 4.3 δ not found in the spectra of the homopolymers and their physical mixtures. Hence a model of the expected copolymer between the PEMA and PVAc through the ($-CH_2-$) of the backbone of these two polymers is being proposed from the i.r. studies and also confirmed by the n.m.r. studies.

Two proposed structures of such copolymers are shown below:



A random copolymer comprising of long segment of PVAc with short chains of PEMA



PVAc block PEMA block

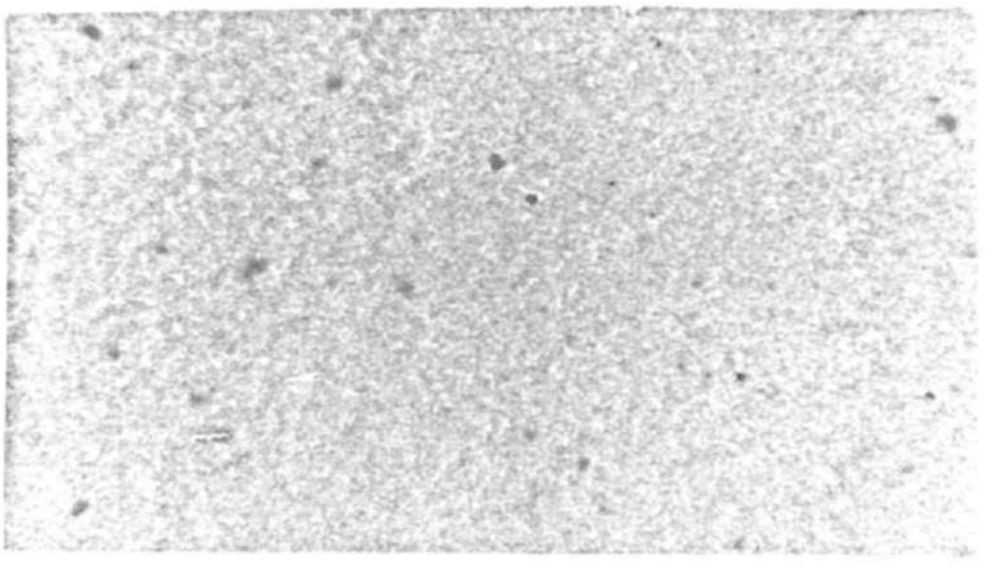
A block copolymer of PVAc - PEMA.

4.14 Optical Microscopy

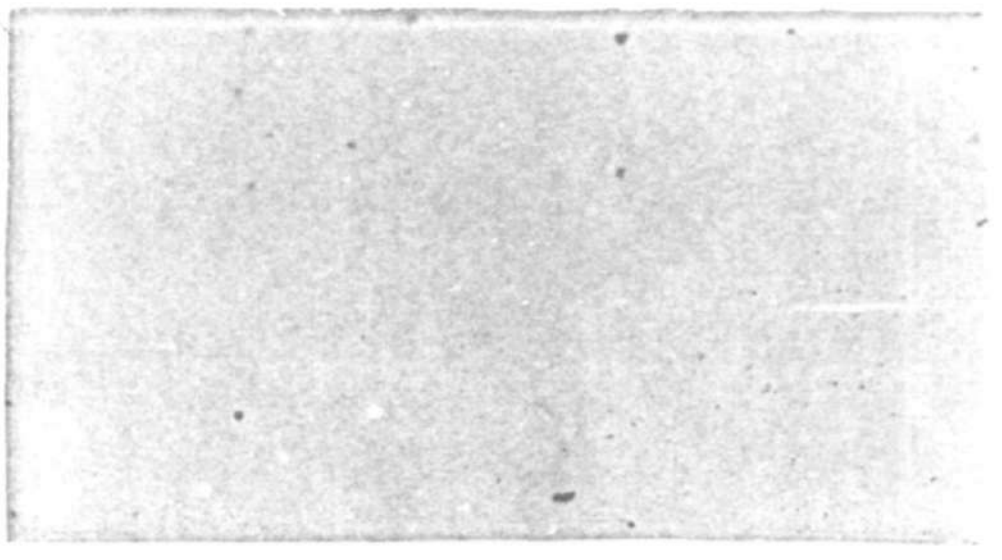
All the optical micrographs of the samples - homopolymers (PEMA, PVAc), the copolymerisation products with the various fractions (MIS, MSS, EIS, ES) were taken from thin films of thickness 0.015 ± 0.02 cm. The micrographs of the PEMA ($\bar{M}v = 5.19 \times 10^5$) and PVAc ($\bar{M}v = 5.1 \times 10^4$) appeared characteristically homogeneous in morphology (Plates I and II). The homogeneity in the morphologies of these two homopolymers had earlier been reported in our laboratory (Olayemi and Yusuf 1989). On the other hand the optical micrographs of the copolymerisation products show varying degrees of phase contrast as illustrated by samples PBB_1, PSB_1, PBB_2, PSB_2, PBB_4, PSB_4 in plates III, IV, V, VI, VII, VIII respectively. Further examination of these micrographs show that the degree of phase contrast (heterogeneity) in the semi-batch continuous product is more pronounced than in the corresponding semi-batch products. For example the phase contrastin the micrograph of sample PSB_2 (plate VI) is more pronounced than in the corresponding semi-batch sample PBB_2 (Plate V). Similar examples are observed between plates III and IV for PBB_1, PSB_1 respectively, Plates VII and VIII for PBB_4, PSB_4 respectively. This result agrees with a similar report by Saleeman (1985) who reported differences in particle size and particle size distribution for the semi-batch and semi-batch continuous copolymerisation products of vinylacetate and methylmethacrylate.

4.14.1 Comparative Studies of the Optical Micrograph of the Various Fractions of Copolymerisation Products

The optical micrographs of the various fractions of the copolymerisation products namely methanol insoluble (MIS), methanol soluble (MSS), ethanol inscluble (EIS) and ethanol soluble (ES) as represented in

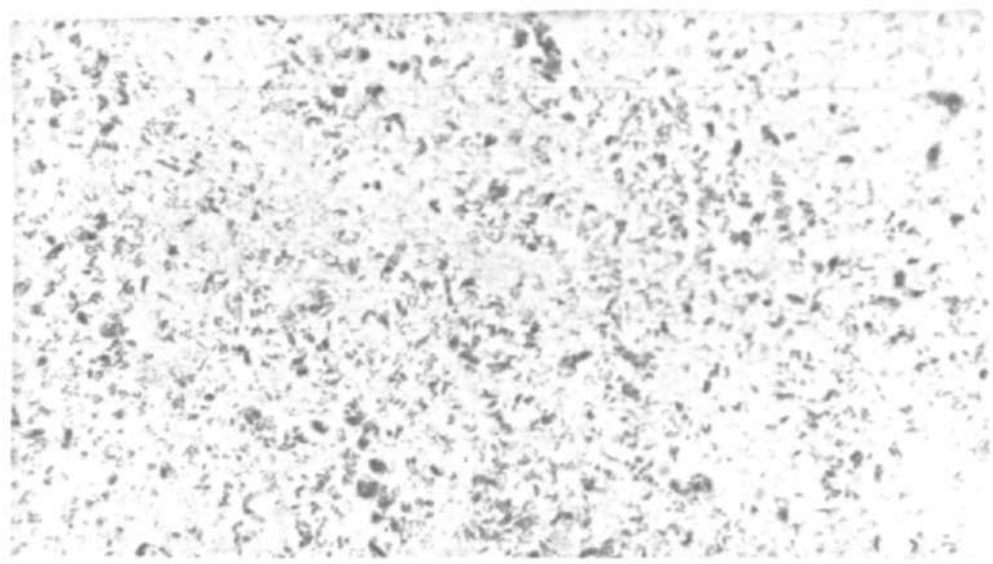


* PLATE I: 100% PEMA (LR)

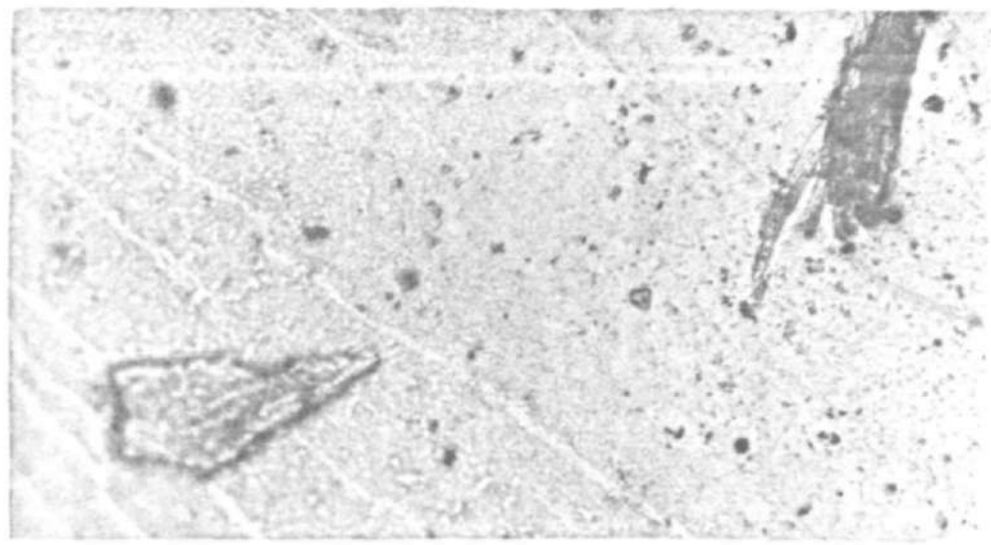


* PLATE II: 100% IVAC (LR)

* MAGNIFICATION OF 63

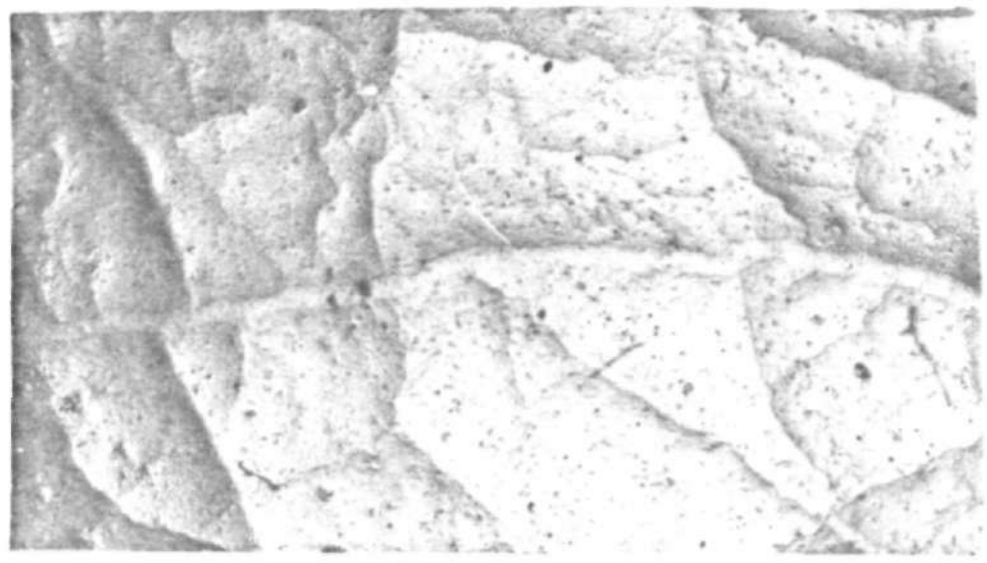


* PLATE III: PLB_1: 66% MIC, 28% MSS, 4% ES
COPOLYMERISATION PRODUCT

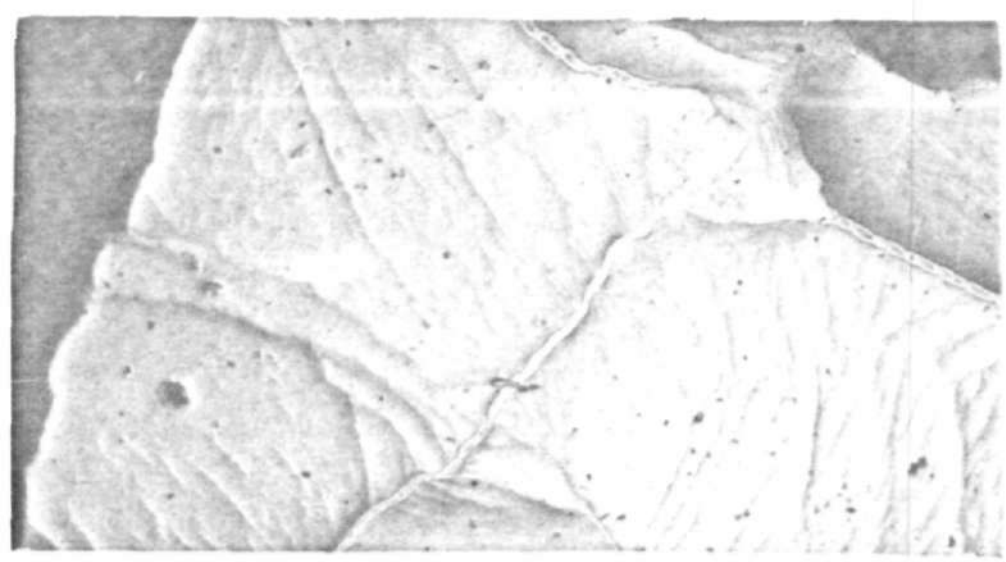


* PLATE IV: PSB_1: 71% MIS, 20% MSS, 3% ES
COPOLYMERISATION PRODUCT

* MAGNIFICATION OF 63

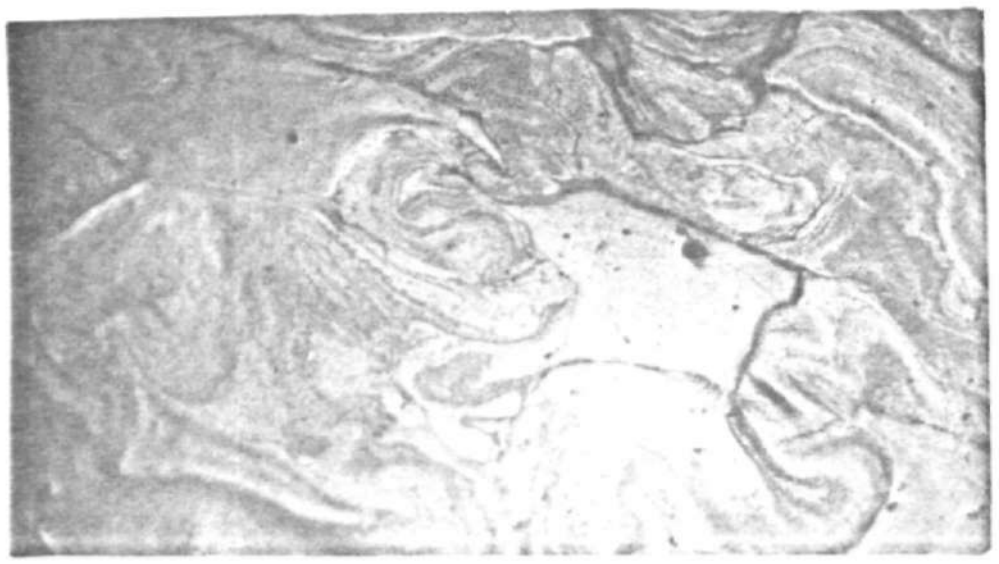


* PLATE V: PBE_2: 54% EIS, 36% ESS, 5% ES
COPOLYMERISATION PRODUCT

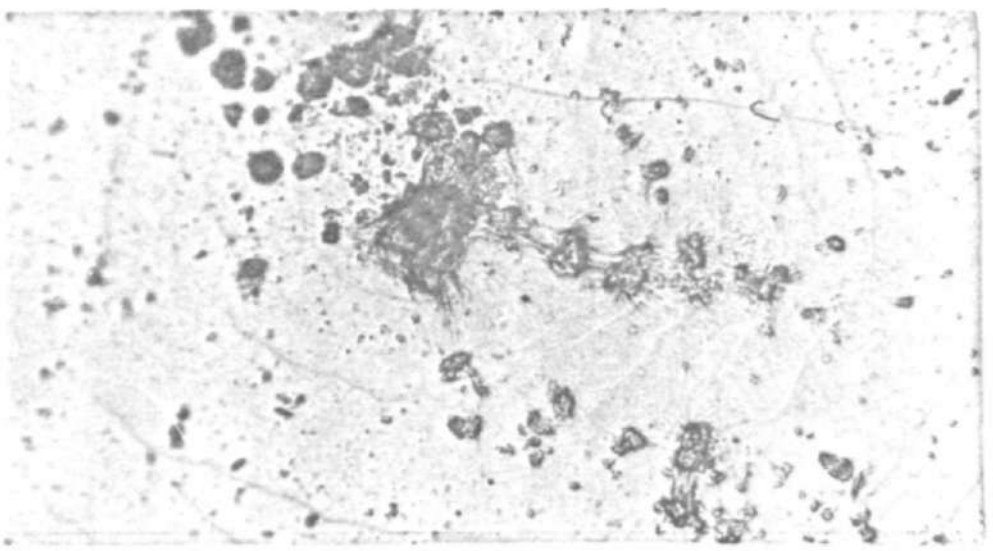


* PLATE VI: PSE_2: 58% EIS, 32% ESS, 6% ES
COPOLYMERISATION PRODUCT

* MAGNIFICATION OF 63



* PLATE VII: PEB_4: 43% EIS, 44% MSS, 8% ES
COPOLYMERISATION PRODUCT



* PLATE VIII: PSB_4: 42% EIS, 46% MSS, 7% ES
COPOLYMERISATION PRODUCT

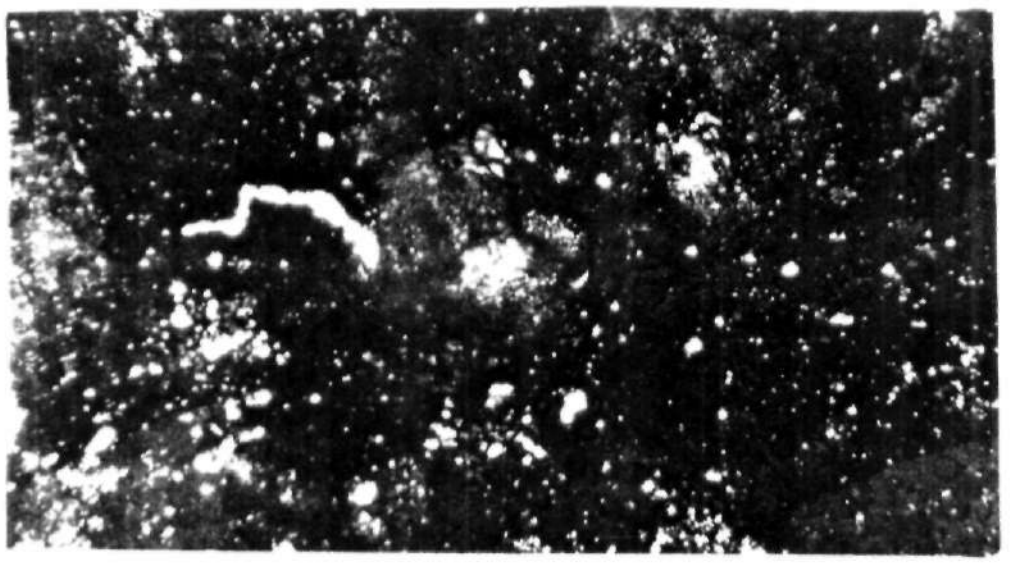
* MAGNIFICATION OF 63

Plates IXA, IXB and IXC show the heterogeneous morphologies of the methanol insoluble fractions (MIS). Also there are variations in the particle sizes within the morphologies of the various MIS fractions. These particle sizes are seen to increase with increase with the initial time of polymerisation of VAc prior to addition of EMA. For example, the particle sizes in MIS of sample PSB_4 (plate IXC) are larger than in MIS of sample PBB_1 (plate IXA). Again the particle sizes for the MIS of the semi-batch continuous copolymerisation products were larger than those from semi-batch products - (plates IXB and IXC).

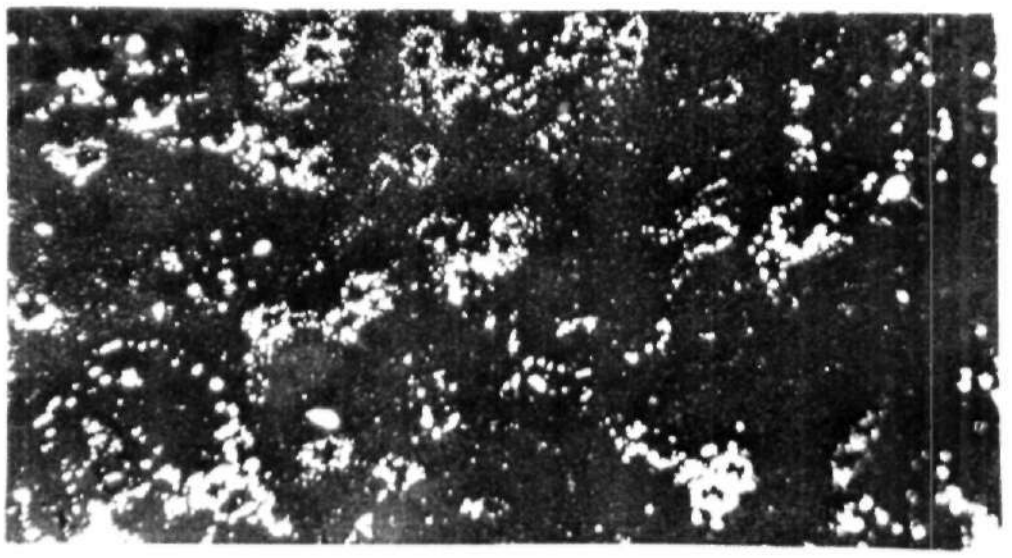
Plates XA - XC show the similarity in the morphologies of the methanol soluble (MSS) of the copolymerisation products as being heterogeneous in nature. There is also variation in the particle sizes depending on the initial time of polymerisation of VAc prior to EMA addition and the process of emulsion copolymerisation. Semi-batch continuous sample of copolymerisation products have larger particle sizes than the corresponding MSS of batch products. At the same time, the particle sizes for samples obtained at longer initial time of polymerisation of VAc prior to EMA addition are larger than those from shorter times of reaction. (Plates XA and XC).

The morphologies for the ethanol insoluble fractions as observed from plates XIA and XIB are wholly homogeneous similar to that of PEMA homopolymer (plate I). The i.r. and n.m.r. had established the fact that the EIS is presumably the unbound PEMA.

Finally, the morphologies of the ethanol soluble (ES) which is the expected copolymer as observed in plates XIIA - XIIB are characteristically heterogeneous. This implies that the ES which is the expected copolymer of the PEMA and PVAc shows phase contrast. The presence of two components (PEMA, PVAc) in the ES fractions has been confirmed by both the i.r. and n.m.r. spectrocopies. On the whole the differences in phase

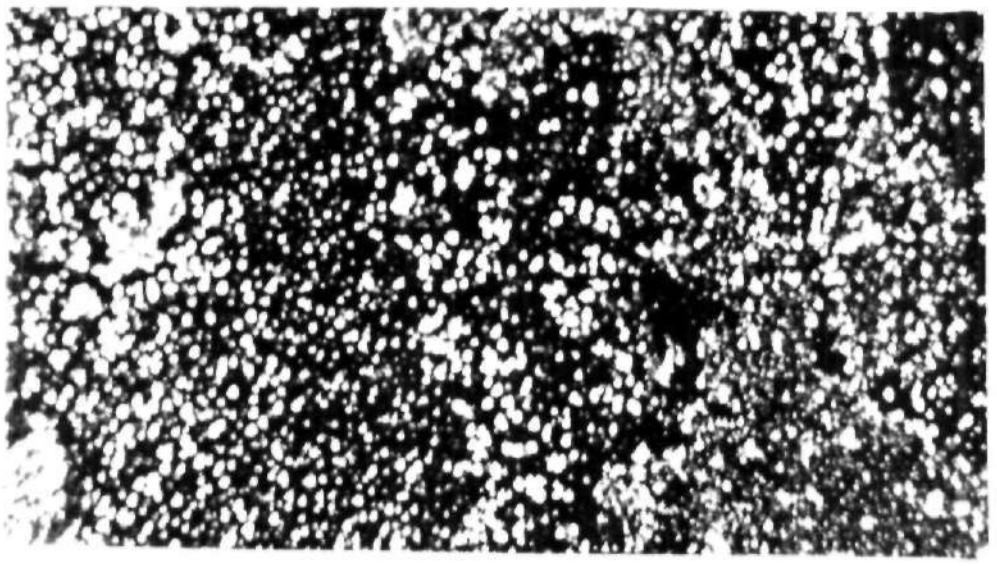


IXA: IBF_4 METHANOL IN

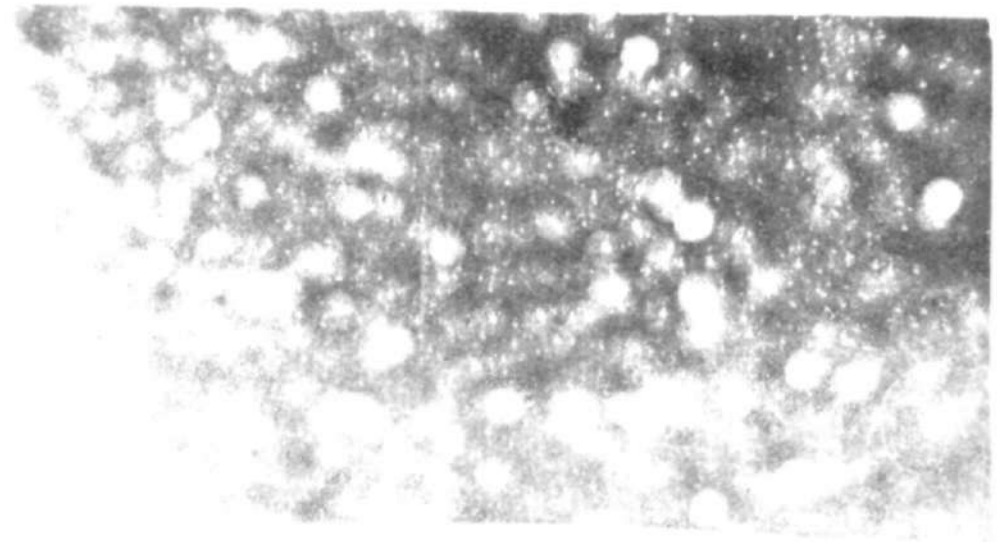


IXB: IBF_2 METHANOL INSOLUBLE

* MAGNIFICATION OF 63

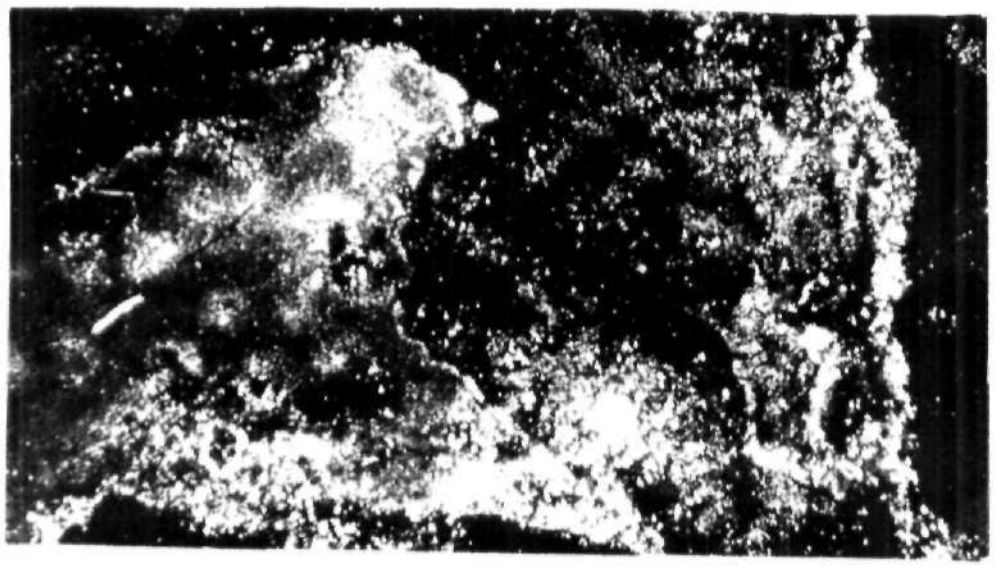


* PLATE IXC: PSB_4 METHANOL INSOLUBLE

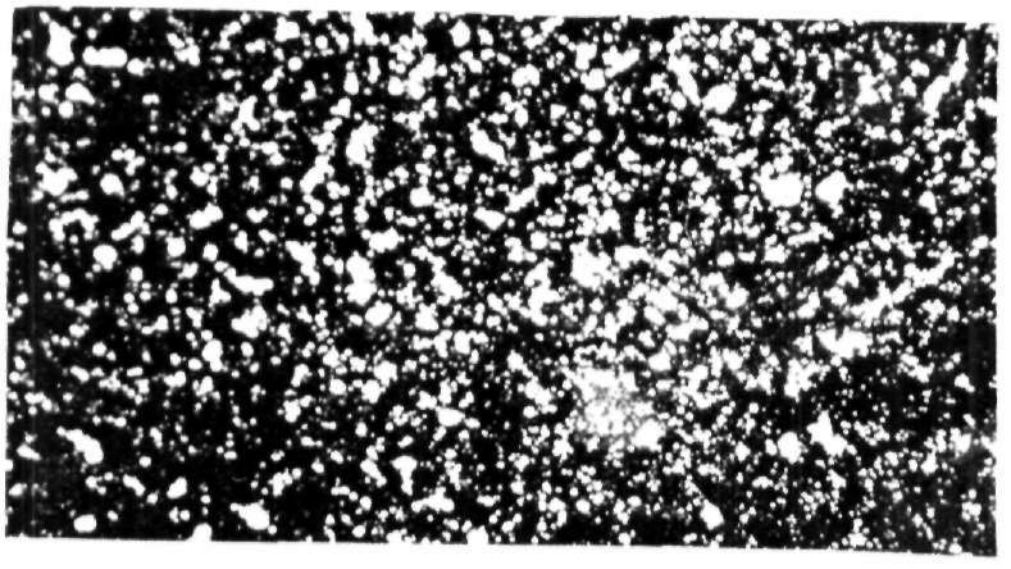


* PLATE XA: PSB_1 METHANOL SOLUBLE

* MAGNIFICATION OF 63

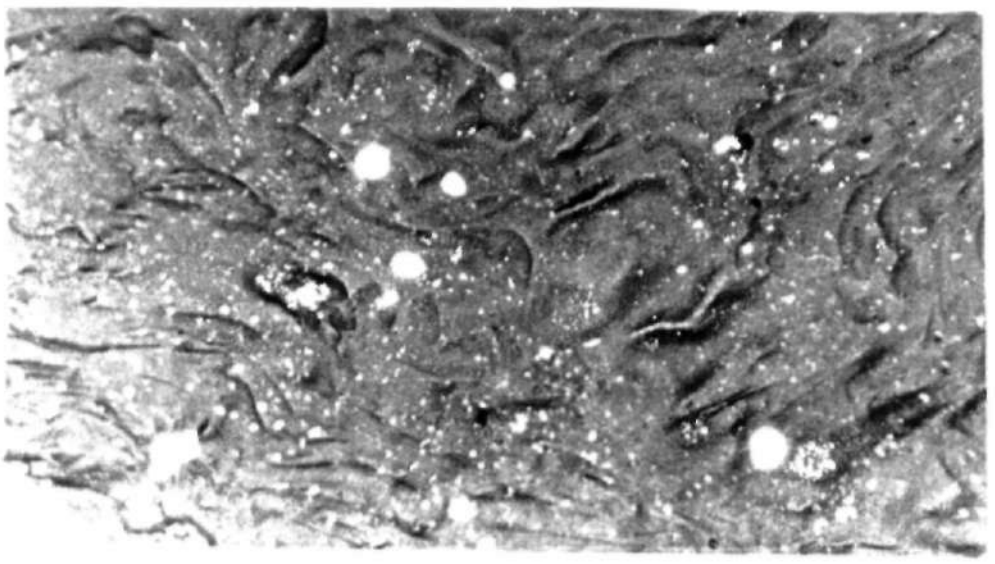


* PLATE XB: FSB_2 METHANOL SOLUBLE FRACTION

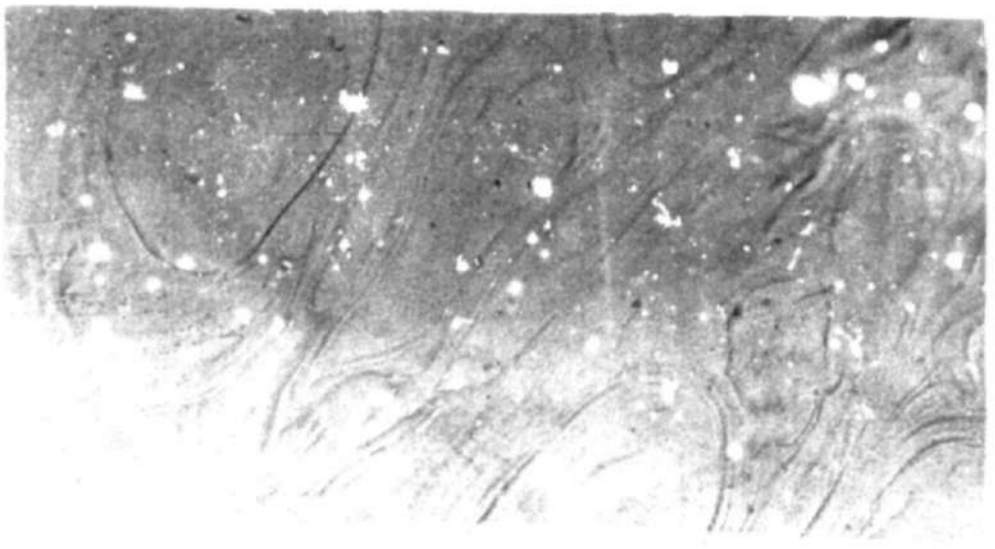


* PLATE XC: PSB_4 METHANOL SOLUBLE FRACTION

* MAGNIFICATION OF 63

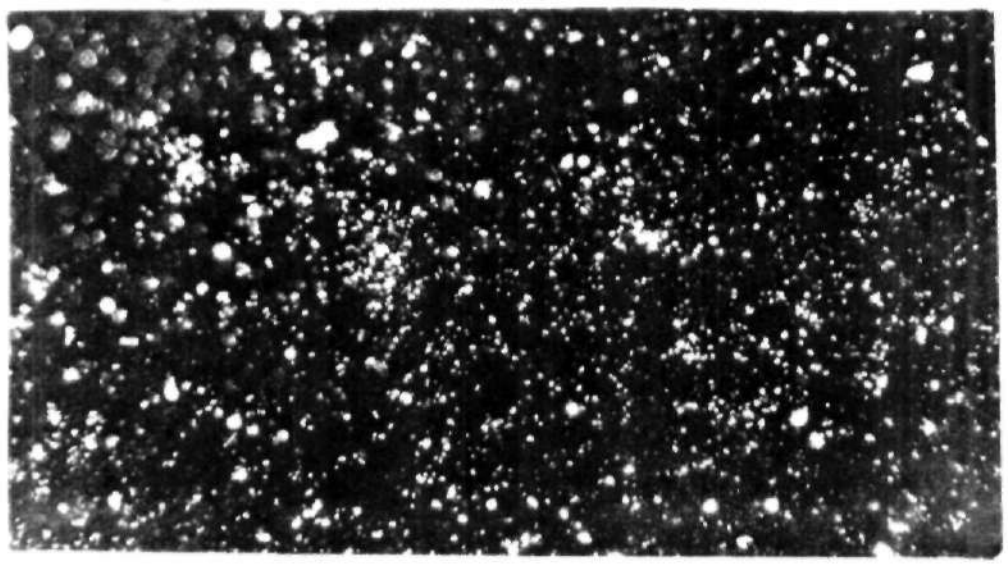


* PLATE XIA: PBB_2 ETHANOL INSOLUBLE

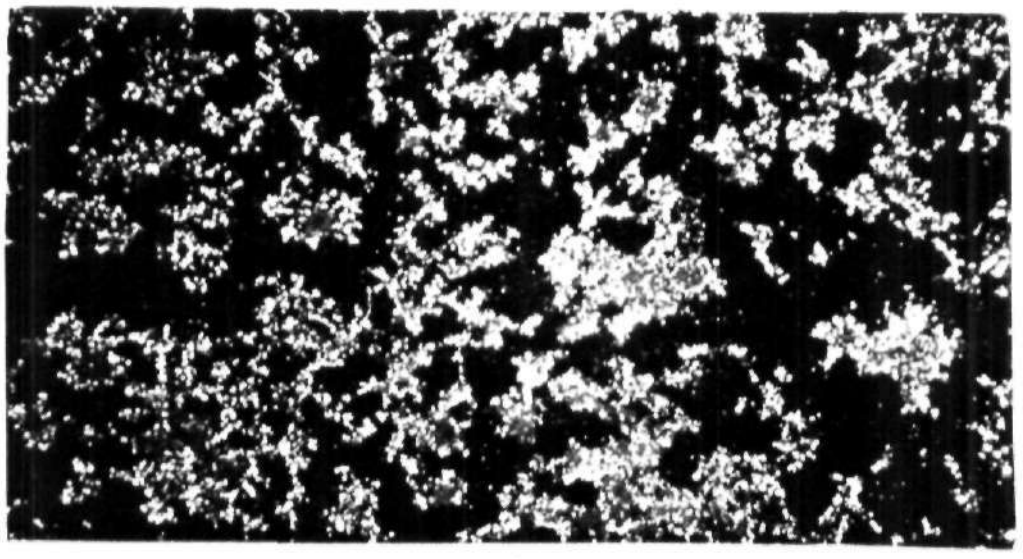


* PLATE XIB: PBB_4 ETHANOL INSOLUBLE

* MAGNIFICATION OF 63



* PLATE XIIA: PBE_2 ETHANOL SOLUBLE



* PLATE XIIB: PSB_2 ETHANOL SOLUBLE

* MAGNIFICATION OF 63

contrast in the morphologies suggest that percentage composition and molecular weight affect the compatibility of polymer-polymer systems (Olayemi and Yusuf 1989).

CHAPTER 5

5.0 SUMMARY AND CONCLUSION

5.1 SUMMARY

Preliminary investigation of the behaviour of EMA and VAc monomers in emulsion polymerisation with some concentration of sodium laury sulphate (SLS) emulsifier (6.3×10^{-3} M/L) and a constant concentration of potassium persulphate initiator (8.33×10^{-4} M/L) at 60°C have indicated that:

(i) The percentage conversion of the monomers to the homopolymers and the viscosity average molecular weight ($\bar{M}v$) of the homopolymers obtained increase with increase in time of polymerisation. However, the viscosity average molecular weight of the PEMA obtained under the same polymerisation conditions and time were higher than that of the corresponding PVAc.

(ii) The conversion of the monomer to homopolymer for the VAc - PVAc system was initially faster than that of EMA to PEMA. The reverse was the case at longer period of polymerisation under the condition investigated.

(iii) Emulsion copolymerisation of these two monomers was studied under the batch, semi-batch, semi-batch continuous and semi-continuous processes at 60°C for 9 hours:

(a) Percentage recovery (yield) was found to change in the order of semi-continuous > semi-batch continuous > semi-batch > batch.

(b) The percentage recovery for both the semi-batch and the semi-batch continuous was found to decrease with increase in the time for initial polymerisation of VAc prior to addition of EMA.

(c) All the copolymerisation products obtained show partial solubility in methanol while completely insoluble in cold ethanol. Hence the removal of the unbound PEMA and the unbound PVAc from these products was based on their differential solubilities in methanol and hot ethanol. On this basis,

each sample was separated into four different components - methanol insoluble (MIS), methanol soluble (MSS), ethanol insoluble (EIS) and ethanol soluble (ES).

(d) Melting point studies of fraction from copolymerisation products show the methanol insoluble (230-235°C melting point) > copolymerisation product (225-230°C mpt.) > methanol soluble (135-140°C melting point) for sample PBB_1. This trend of change in melting point was found for all other samples studied.

(e) X-ray studies show PEMA to have a peak at $2\theta = 43^{\circ}$ indicating some degree of ordering while PVAc was wholly amorphous as there was no peak in its x-ray spectrum. The copolymerisation products of the EMA, VAc monomers show peaks at $2\theta - 43^{\circ}$ except the batch sample PMMB with no peak at all in its x-ray spectrum. The percentage ordering and crystallinity indices were calculated for each sample from their x-ray spectra. The semi-batch continuous sample of PSB_4 was more ordered and more crystalline (percentage ordering = 50.82%, $C_i = 0.72$) which was next in order to the pure PEMA (percentage ordering = 100%, $C_i = 1.00$) with the highest degree of ordering and crystallinity index. However, the batch sample PMMB was the most disordered (percentage ordering = 0.0%, ($C_i = -0.07$) as the pure PVAc (percentage ordering 0.0% and $C_i = 0.0$).

The results from calibration curve of physical mixtures of PEMA/PVAc confirms the fact that the crystallinity indices for these physical mixtures were lower than those of the synthesised copolymerisation products from emulsion copolymerisation of EMA and VAc. These indices depend on method of synthesis of the samples and the initial time of polymerisation of VAc. prior to addition of EMA as in the studies reported here.

Generally, crystallinity indices varied as semi-batch continuous > semi-batch > batch.

(f) Both the i.r. and n.m.r. studies of the 'copolymerisation products' and their separated fractions (unbound PEMA unbound PVAc and the expected copolymer) suggest presence of a new bond between the methylene ($-CH_2-CH_2-$) groups in both PEMA and PVAc along the polymer backbones.

The i.r. band at 1620-1660 cm^{-1} due to the vinyl group ($-C-CH_2$) and the n.m.r. spectra with the peak at 4.1 - 4.3 δ due to the ($-C-CH_2-$) group confirmed the existence of this new bond in the copolymer formed. Thus a model of a random and possibly a block copolymer had bean proposed in the text (section 4.13.2).

(g) Finally, the optical microscopy has established the heterogeneity in the copolymerisation products. An evidence that they are mixtures of unbound PVAc, PEMA and the expected copolymer. The semi-batch continuous samples were more homogeneous than the corresponding semi-batch products. The optical micrographs of the MSS were similar to that of pure PVAc while that of EIS were similar to that of pure PEMA.

5.2 CONCLUSION

From these results, it has been established that EMA formed PEMA polymer with higher viscosity average molecular weight ($\bar{M}v$) than VAc. The fact that VAc is more soluble in water than the EMA which is partially soluble has been attributed to these differences of the two monomers in emulsion polymerisation. The rate of polymerisation of VAc being initially faster than that of EMA, and the reverse being the case at longer periods of polymerisation is in accordance with Harkin's (1950) prediction on differences in polymerisation between a water-water-soluble monomer-VAc and a partially water soluble-styrene.

The semi-batch continuous emulsion copolymerisation process give the highest percentage recovery of the 'copolymerisation product' among all the processes under investigation.

Also the quantitative analysis has indicated the presence of four fractions namely methanol insoluble (MIS), methanol soluble (MSS), ethanol insoluble (EIS) and ethanol soluble (ES) from all the 'copolymerisation products' studied.

The degree of ordering and crystallinity indices of these synthesised 'copolymerisation products' depend on the method of synthesis. The semi-batch continuous give products that are the most crystalline while the batch gave products that are the most amorphous. Homo PVAc produced in this study is wholly amorphous while the homo PEMA produced in the same study has some elements of crystallinity. The formation of a copolymer by the copolymerisation of these two monomers (EMA, VAc) in emulsion at 60°C for 9 hours has been suggested from the i.r. and n.m.r. studies. The formation of this copolymer was found to increase with increasing initial time of polymerisation of VAc prior to addition of EMA and also gave the highest for the semi-batch continuous process while the batch synthesised sample (PEMB) contain very small quantity of copolymer (e.g. the semi-continuous batch sample PSE_4 with percentage copolymer of 12% while the batch sample PEMB had the lowest 2.0%).

REFERENCES

Adeniyi, J.B. (1986). Environmental Determination and Stabilization of Polymers Part I. The Chemistry of Stabilization of ABS by Butyl Hydroxylbenzyl Thioglycolate and Tinuvin P: Journal of Polymer Material 3: 1-25

Alexander, L.E. (1969). X-ray diffraction Methods in Polymer Science. 2nd Ed. Wiley Interscience, N.Y.

Alfrey, T. (Jr.), Bohrer, J.J. and Mark, H. (1952). Copolymerisation. Interscience, N.Y.

Ballantine, D.S., Glines, A., Aldler, G. and Metz, D.J. (1959). Graft Copolymerisation by Pre-Irradiation Technique. Journal of Polymer Science 34: 419 - 433.

Bikales, N.M. (1971). Characterisation of Polymers. John Wiley and Sons Inc., N.Y.

Billimeyer, F.W. (Jr.) (1970). A textbook of Polymer Science, 2nd Ed. Wiley-Interscience - a Division of John Wiley and Sons Inc., N.Y., P.328.

Brandrup, J. and Immergut, E.H. (1975). Polymer Handbook, 2nd Ed. A Wiley Interscience, N.Y., PP. V-51, V-55.

Brauer, G.M. and Horowitz, E. (1962). Systematic Procedures. In: Kline, G.M. (Ed.) Analytical Chemistry of Polymers Part III. Identification Procedures and Chemical Analysis. High Polymers Vol. 12. Interscience Publishers - a division of John Wiley and Sons Inc., N.Y., PP. 1-134.

Bovey, F.A. (1971). Nuclear Magnetic Resonance In: Bikales, N.M. (Ed.) Characterisation of Polymers. Encyclopedia Reprints. John Wiley and Sons Inc., N.Y., PP.149 - 189.

Bovey, F.A., Anderson, E.W. and Douglas, D.C. (1963). Polymer NMR Spectroscopy X. The use of H^1 - H^1 Spin Decoupling in the Elucidation of Polymer Structure. Journal of Chemical Physics 39 1116 - 1119.

Burlant, W.J. and Hofmann, A.S. (1964). Block and Graft Copolymers. In: Luskin, L.S. and Myers, R. (Eds.) Acrylic Ester Polymerisation. Encyclopedia of Polymer Science and Technology Vol. I. Interscience Publications - a division of John Wiley and Sons Inc., N.Y., PP. 280 - 283.

Ceresa, R.J. (1965). Block and Graft Copolymers. In: Luskin, L.S. and Myers, R. (Eds.) Acrylic Ester Polymerisation. Encyclopedia of Polymer Science and Technology Vol.I. Interscience Publishers - a division of John Wiley and Sons Inc. N.Y., PP. 270 - 282.

Chujo, R; Ubara, H. and Nishioka, A. (1980). Nuclear Resonance Spectroscopy of Polymer Chains In: Koenig, J.L. (Ed.), Microstructure of Polymer Chains. A wiley-Interscience Publication. John Wiley and Sons Inc., N.Y., PP.217-266.

Collins, E.A., Bares, J. and Billimeyer, F.W. (Jr.) (1973). Experiments in Polymer Science. John Wiley and Sons Inc. N.Y., PP. 120 - 127.

Conn, W.R. and Neher, H.T. (1950). Inhibitory Effect on Acrylonitrile on Polymerisation of Vinyl Acetate. Journal of Polymer Science, 5:355-367.

Cooper, W. (1985). Emulsion Polymerisation In: Saleeman, A. A. (Ed.) Emulsion Copolymerisation of Vinyl Acetate and Methylmethacrylate. Unpublished MSc. Thesis, Institute of Technology Manchester, U.K., PP. 9 - 13.

Cowie, J.M.G. (1973). Polymers: Chemistry and Physics of Modern Materials. Billings, London, PP. 3, 4.

Dunn, A.S. and Taylor, P.A. (1965). The Polymerisation of Vinyl Acetate in Aqueous Solution Initiated by Potassium Persulphate at 60 C. Macromolecular Chemistry 83: 116 - 207

El-Aesser, M. and Vanderhoff, J.W. (1985). Emulsion Polymerisation of Vinyl Acetate In: Saleeman, A.A. (Ed.), Emulsion Copolymerisation of Vinyl Acetate and Methylmethacrylate. Unpublished MSc. Thesis, Institute of Technology, Manchester, U.K., P.16.

Fieser, F.L. and Fieser, M. (1967). Reagents for Organic Synthesis. John Wiley and Sons Inc., N.Y., P.393.

Fleischer, D. (1975). Physical Properties of Monomers. In: Brandrup, J. and Immergut, E.H. (Eds.), Polymer Handbook. Interscience Division of John Wiley and Sons Inc., N.Y., PP. V11-39.

French, D.M. (1958). Mechanism of Vinyl Acetate Emulsion Polymerisation. Journal of Polymer Science 32:395-411.

Gardon, J.L. (1968). Emulsion Polymerisation, Recalculation and Extension of the Smith-Ewart Theory. Journal of Polymer Science, A-1 6:623-641.

Gaylord, N.G. and Ang, A.S. (1964). Graft Copolymerisation In: Fette, E.M. (Ed.), Chemical Reaction of Polymers; High Polymers 19, Interscience, PP. 831 - 856.

Gluckam, M.S., Kempt, M.J., O'Brian, J.L. and Fox, T.G. (1959). Graft Copolymers from Polymers Having Pendant Mercaptan Groups II. Synthesis and Characterisation. Journal of Polymer Science, 37:411-423.

Guha, T., Biswas, M., Konar, R.S. and Palit, S.R. (1964). Role of Organic Diluent in Sol-Phase Polymerisation. Journal of Polymer Science, 2:1471-1479.

Guha, T. and Palit, S.R. (1963). Study of the Rate of Heterogeneous Polymerisation of MethylAcrylate in Aqueous Solution. Journal of Polymer Science, Part A-1:877-893.

Gumbs, R., Penczak, S., Jagur, J. and Swarc, M. Simultaneous homopolymerisation in Vinylcarbazole and Oxetane. Macromolecules, 2:77-82.

Ham, G.E. (1967). Vinyl Polymerisation Vol. I Part I. Marcel Dekker Publishing Co. Inc., N.Y., P.25.

Ham, G.E. (1964). Copolymerisation. Interscience Publishers, a division of John Wiley and Sons, N.Y., P.376.

Harkins, W.D. (1950). General Theory of Mechanism of Emulsion Polymerisation II. Journal of Polymer Science, 5(2): 217 - 251.

Hayes, R.A. (1953). Polymeric Chains Transfer Reactions. Polymerisation of Some Vinyl Monomers in the Presence of Vinyl Polymers. Journal of Polymer Science 11:531-537.

Harriot, P. (1971). Kinetics of Vinyl Acetate Emulsion Polymerisation. Journal of Polymer Science Part A-1 9:1153-1163.

Huggins, M.L. and Herman, J.J. (1952). Report on Nomenclature in the Field of Macromolecules. International Union of Pure and Applied Chemistry. Journal of Polymer Science 8:257-277

Hughes, L.J. and Brown, G.L. (1961). Heterogeneous Polymer System I. Journal of Applied Polymer Science, 5(17): 580-588.

Hummel, D.O. (1974). Polymer Spectroscopy - Monographs in Modern Chemistry 6 Verlag Chemie W. Germany, P.116.

Ibiyeye, M.K. (1984). Some Studies on the blends of poly(vinyl Acetate) and poly(ethylmethacrylate). Unpublished MSc. Thesis, A.B.U., Zaria.

Johnson, J.F. and Cantow, M.J.R. (1971). Fractionation. In: Bikales, N.M. (Ed.), Characterisation of Polymers. Encyclopedia Reprints, John Wiley and Sons Inc., N.Y. PP. 23-52.

Johnstone, N.W. (1973). Polymer Preparation. John Wiley and Sons Inc., N.Y., PP. 1-46.

Koenig, J.L. (1980). Chemical Microstructure of Polymer Chains A Wile - Interscience Publication, N.Y., PP 1-217.

Kossler, I. (1971). Infrared - Absorption spectroscopy. In: Bikales , N.M. (Ed.) Characterisation of Polymers. Encyclopedia Reprints. John Wiley and Sons Inc., N.Y.

Krackeler, J.J. and Naidus, H. (1969). Particle Size and Molecular Weight Distribution of Various Polystyrene Emulsion. Journal of Polymer Science C-27; 207-235.

Luskin, L.S. and Myers, R. (1965). Acrylic Ester Polymerisation In: Mark, H. and Gaylord, N.G. (Eds.) Encyclopedia of Polymer Science and Technology Vol. 8. John Wiley and Sons, N.Y.

Molau, G.E. (1969). Colloidal Properties of Block and Graft Copolymers - Polymer Reprints, 10(2): 512 - 700.

Nair, A.S. and Muthana, M.S. (1961). Studies on the Polymerisation of Methacrylic Esters Part III. Copolymerisation of n-Butylmethacylate with Vinyl Acetate and Acrylonitrile Macromolecular Chemistry 47:138.- 147

Odian, G. (1981). Principles of Polymerisation, 2nd Ed., A Wile Interscience Publication, John Wiley and Sons Inc., N.Y.

Olabisi, C., Robeson, L.M. and Shaw, M.T. (1979). Polymer-Polymer Miscibility Acada Press., N.Y.

Olayemi, J.Y. and Ibiyeye, M.K. (1986). Blends of Poly(vinyl acetate) and poly(ethylmethacrylate). Some Mechanical Properties. Journal of Applied Polymer Science, 31: 237 - 248.

Olayemi, J.Y. and Yusuf, A.K. (1989), Further Experimental Evidences of the Compatibility of Poly(vinyl Acetate) with Poly(ethyl methacrylate) and its dependence on ratio of the molecular of the two homopolymers. Journal of Applied Polymer Science 38: (20 pages) in the Press.

Pastiga, R., Litt, M. and Starnett, V. (1960). The Emulsion Polymerisation of Vinyl Acetate Part I. Journal of Physical Chemistry, 60: 801 - 804.

Platzer, N.A. (1970). Multicomponent Polymer Systems Symposium In: American Chem. Soc. Advance in Chemistry Series 99 Washington D.C.; PP. III-XIV.

Rieke, J.K., Hart, G.M. and Kennedy, C.C. (1963). Properties of Polyethylene - Acrylic Acid Graft Copolymers. Journal of Polymer Science Part C1-3: 117-131.

Ritchey, W.M. and Knoll, P.J. (1966). Concerning N.M.R. Line Ordering and Multiplicity Owing to Tactic Structures in Polymers. Journal of Polymer Science Part B; Polymer Letters 4: 853 - 860.

Saleeman, A.A. (1985). Emulsion Copolymerisation of Vinyl Acetate and Methylmethacrylate. Unpublished MSc. Thesis Institute of Technology, University of Manchester, U.K.

Sandler, S.R. and Karo, W. (1974). Polymer Synthesis. Acada Press Inc., N.Y. 29(1); PP. 290 - 295.

Schiebel, E.G. (1965). Extraction. In: Mark, H.F., McKetta, Othemer, D.F. and Standen, A. Encyclopedia of Chemical Technology Vol. 8, Interscience Publishers, John Wiley and Sons Inc., N.Y., PP. 719 - 775.

Schildknecht, C.E. (1952). Vinyl and Related Polymers, J. Wiley and Sons Inc., New York.

Smets, G. and Claesen, H. (1952). Graft Copolymerisation (In French) Journal of Polymer Science 8: 290 - 294.

Smets, G. and Woodward, A.E. (1954). A New Method for Preparation of Block Copolymers, Journal of Polymer Science 14: 125-127.

Smets, G., Roovers, J. and Van Humbeek, W. (1961). Influence of the Initiator on the Grafting of Polyvinyl Polymers. Journal of Appl. Polym. Sci. 5(14): 149 - 152.

Snuparek, J. (Jr.) and Krcka, F. (1976). Semi-Continuous Emulsion Copolymerisation of Styrene and Butyl Acrylate. Journal of Applied Polymer Science 20: PP. 1753 - 1764.

Stannett, V. (1970). Some Recent Advances in Pure and Applied Aspect of Graft Copolymers. Journal of Macromolecular Science Chemistry A4(5): 1171 - 1191.

Statton, W.C. (1963). An X-ray Crystallinity Index Method with Application to Poly(ethylene terephthalate). Journal of Applied Polymer Science 7: 803 - 812.

APPENDIX I: Percentage recovery of copolymerisation products using batch and semi-batch processes of emulsion copolymerisation at 60°C for 9 hours.

Description of Process	Initial time of Polymerisation of VAc before EMA	Copolymerisation product code [a]	Percentage recovery [b]
i. Batch Process:			
VAc ($7.0cm^3$) and EMA ($7.0cm^3$) mixed and polymerised for 9 hours	0	PMMB	58.40
ii. Semi-Batch Process:			
VAc ($7.0cm^3$) polymerised for 30 mins before addition of EMA ($7.0cm^3$) in batch for 9hrs	30 mins	PBB_1	77.30
VAc ($7.0cm^3$) polymerised for 60 mins before addition of EMA ($7.0cm^3$) in batch for 9hrs.	60 mins	PBB_2	79.31
VAc ($7.0cm^3$) polymerised for 120 mins before addition of EMA ($7.0cm^3$) in batch for 9hrs.	120 mins	PBB_3	78.89
VAc ($7.0cm^3$) polymerised for 240 mins before addition of EMA ($7.0cm^3$) in batch for 9hrs.	240 mins	PBB_4	71.09
VAc ($7.0cm^3$) polymerised for 300 mins before addition of EMA ($7.0cm^3$) in batch for 9hrs.	300 mins	PBB_5	65.50
VAc ($7.0cm^3$) polymerised for 360 mins before addition of EMA ($7.0cm^3$) in batch for 9hrs.	360 mins	PBB_6	61.54
VAc ($7.0cm^3$) polymerised for 420 mins before addition of EMA ($7.0cm^3$) in batch for 9hrs.	420 mins	PBB_7	54.92

APPENDIX I (Contd.)

a = all the copolymerisation products were recovered by precipitation from hexane.

b = average of triplicate determination for each sample.

APPENDIX II: Percentage recovery of copolymerisation products using semi-batch continuous and semi-continuous processes of emulsion copolymerisation at 60°C for 9 hrs.

Description of Process	Initial time of polymerisation of VAc before EMA.	Copolymerisation product code	% Recovery[a]
i. Semi-batch continuous process.			
VAc ($7.0cm^3$) polymerised in batch for 30 mins before dropping of EMA ($7.0cm^3$) at a rate of $7.0cm^3 hr^{-1}$	30 mins	PSB_1	88.90
VAc ($7.0cm^3$) polymerised in batch for 60 mins before dropping EMA ($7.0cm^3$) at a rate of $7.0cm^3hr^{-1}$	60 mins	PSB_2	89.00
VAc ($7.0cm^3$) polymerised in batch for 120 mins before dropping EMA ($7.0cm^3$) at a rate of $7.0cm^3hr^{-1}$	120 mins	PSB_3	83.49
VAc ($7.0cm^3$) polymerised in batch for 240 mins before dropping EMA ($7.0cm^3$) at a rate of $7.0cm^3hr^{-1}$	240 mins	PSB_4	74.97
ii. Semi-continuous Process			
Equal volumes ($7.0cm^3$) of both VAc and EMA mixed, the mixture polymerised by dropping at a rate of $7.0cm^3hr^{-1}$	0	PSMC	87.76
Equal volume ($7.0cm^3$) of both VAc and EMA mixed, 10% of mixture polymersied in batch for 10 mins, 90% of mixture dropped at a rate of $7.0cm^3hr^{-1}$	10 mins	PSMCMS	91.00

a - average of triplicate determinations for each sample.

APPENDIX III Methanol Extraction of the Copolymerisation Products Showing the Percentage Methanol Insoluble (MIS) and Percentage Methanol Soluble (MSS).

Copolymerisation Product	Mass (g)	Mass of MIS (g)	Mass of MSS (g)	Percentage MIS	Percentage MSS
Batch Process					
PMMB	0.50	0.44	0.04	88.0	8.0
Semi-Batch Process					
PBB_1	0.50	0.35	0.14	70.0	28.0
PBB_2	0.50	0.31	0.18	62.0	36.0
PBB_3	0.50	0.29	0.20	58.0	40.0
PBB_4	0.50	0.26	0.22	52.0	44.0
Semi-Batch Continuous Process					
PSB_1	0.5	0.39	0.10	78.0	20.0
PSB_2	0.5	0.33	0.16	66.0	32.0
PSB_3	0.5	0.32	0.17	64.0	34.0
PSB_4	0.5	0.25	0.23	50.0	46.0

APPENDIX IV : Result from X-ray spectra of polymers and copolymerisation products at $2\theta = 43^{\circ}$

Sample	Source/ Method Preparation	Time of VAc ($7.0cm^3$) Polymerisation prior to addition of EMA ($7.0cm^3$) in minutes	Area Under Peak $10^{-5}m^2$	Percentage ordering at 2θ-43°
PEMA	Lab. Grade	-	26.07	100.00
PEMA	Commercial Grade	-	7.59	29.11
PVAc	Commercial Grade	-	0.00	0.00
PVAc	Lab. Grade	-	0.00	0.00
Mixture of PVAc/PEMA	20 PEMA/80 PVAc	-	4.00	15.34
Copolymerisation Products				
Batch				
PMMB	Mixture of VAc ($7.0cm^3$) and EMA ($7.0cm^3$) copolymerised in batch for 9hrs at $60^{\circ}C$	0	0.0	0.00
Semi-batch				
PBB_1	VAc ($7.0cm^3$) polymerised in batch for 30 mins prior to addition of EMA ($7.0cm^3$) in batch for 9hrs at $60^{\circ}C$	30	8.25	31.65
PBB_2	VAc ($7.0cm^3$) polymerised in batch for 60 mins prior to addition of EMA ($7.0cm^3$) in batch for 9hrs at $60^{\circ}C$	60	5.4	20.71

APPENDIX IV (Contd.)

Sample	Source/Method Preparation	Time of VAc ($7.0cm^3$) Polymerisation prior to addition of EMA ($7.0cm^3$) in minutes	Area Under Peak $10^{-5}m^2$	Percentage at 2θ-43°
PBE_3	VAc ($7.0cm^3$) polymerised in batch for 120 mins. prior to addition of EMA ($7.0cm^3$) in batch for 9hrs. at $60^\circ C$	120	4.5	17.30
PBE_4	VAc ($7.0cm^3$) polymerised in batch for 240 mins prior to addition of EMA ($7.0cm^3$) in batch for 9hrs at $60^\circ C$	240	3.75	15.40
Semi-batch continuous				
PSB_1	VAc ($7.0cm^3$) polymerised in batch before dropping EMA ($7.0cm^3$) at a rate of $7.0cm^3hr^{-1}$	30	9.6	36.92
PSB_2	VAc ($7.0cm^3$) polymerised in batch before dropping EMA ($7.0cm^3$) at a rate of 7 $7.0cm^3hr^{-1}$	60	6.0	23.10
PSB_3	VAc ($7.0cm^3$) polymerised in batch before dropping EMA ($7.0cm^3$) at a rate of $7.0cm^3hr^{-1}$	120	4.8	18.46
PSB_4	VAc ($7.0cm^3$) polymerised in batch before dropping EMA ($7.0cm^3$) at a rate of $7.0cm^3hr^{-1}$	240	13.25	50.82

APPENDIX V

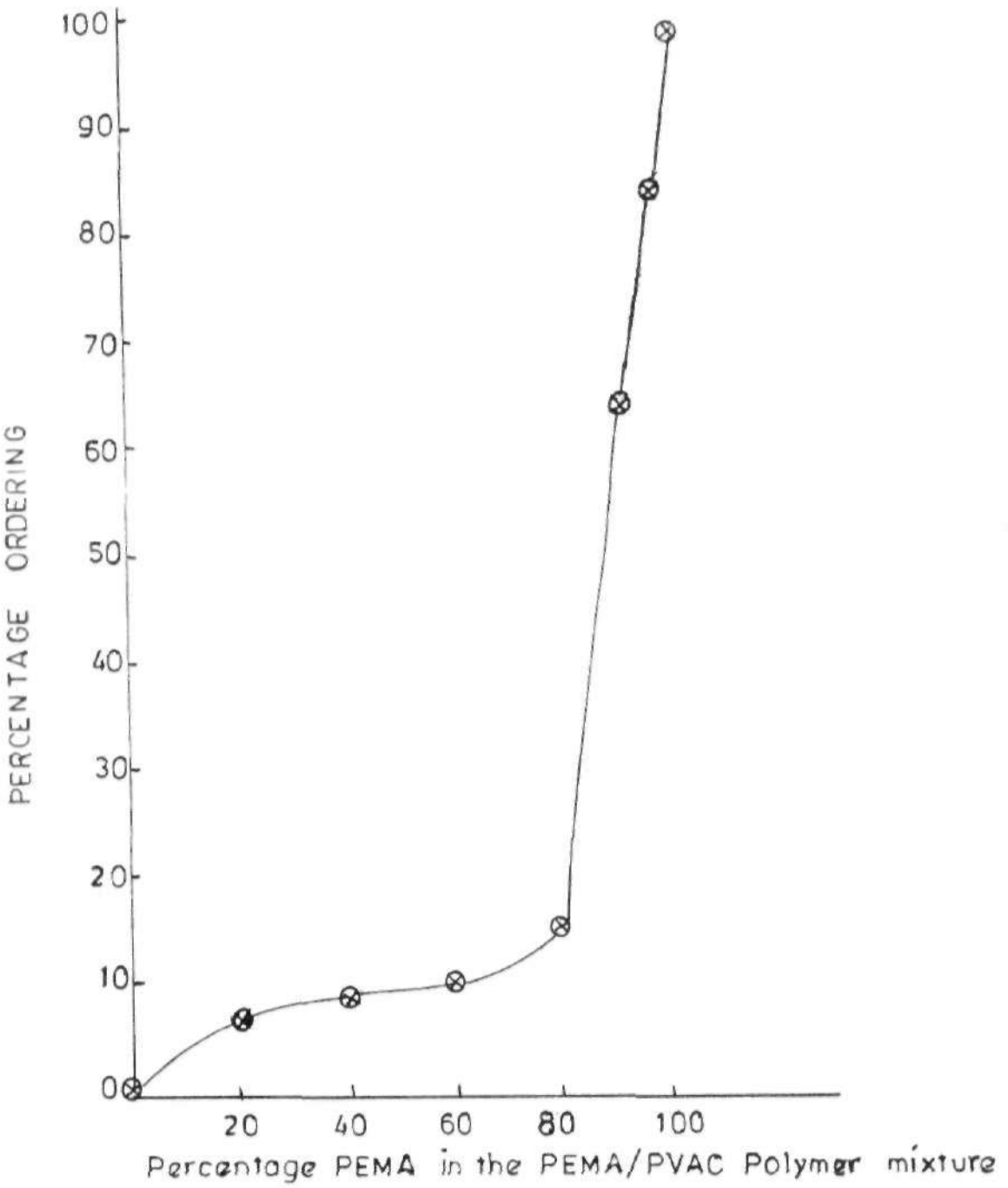


FIG. 4·8 Calibration curve for variation in percentage ordering with percentage PEMA in PEMA/PVAC mixture.

APPENDIX VI : Crystallinity Indices or degree of crystallinity of samples.

Sample	Time of VAc ($7.0cm^3$) polymerisation before EMA	*Is(cm)	*Is-IPVAc (cm)	Crystallinity indices
PEMA	-	8.40	8.40	1.00
PVAc	-	0.00	0.00	0.00
Semi-batch samples				
PBB_1	30 mins	3.3	1.6	0.45
PBB_2	60 "	1.6	0.9	0.12
PBB_3	120 "	0.9	0.2	0.03
PBB_4	240 "	3.10	2.4	0.32
Semi-continucus batch				
PSB_1	30 "	3.9	3.2	0.43
PSB_2	60 "	1.9	1.2	0.16
PSB_3	120 "	2.8	2.1	.28
PSB_4	240 "	5.3	4.6	0.72
PSMCMS	-	0.95	0.25	0.13
PMMB	-	0.5	-0.2	-0.07

* Is = Intensity for the sample

IPVAc = intensity for the pure PVAc.

APPENDIX **VII** **Important Band** Frequencies in (cm^{-1}) from Infrared Spectra of Samples.

Sample	3500	3050	2450	1740–1720	1660–1620	1480–1440	1460–1440	1380–1360	1260–1200	1180–1140	1140–1120	1080–1040	1040–1000	960–920	860–840
1. Ethyl methacrylate	P(w)	P(s)	P(w)	P(s)	P(s)		P(s)	Ps) at 1320	P(s)		P(m)	P(s)	P(m)	P(s)	P(m) split
2. Vinyl acetate	P(w)	P(m)	P(w)	P(s)	P(s)		P(m) at 1420	P(s)	P(s) at 1280		P(s)		P(m)	P(s) split	P(m)
3 PEMA	P(w)	P(s)	P(vw)	P(s)			P(m) split at 1480–1500		P(s) split	P(s)		P(w)	P(s)	P(w) split	P(m)
4 PVAc.	P(b)	P(s)	P(m) split	P(s)			P(m)	P(s)	P(s)		P(s)	P(w)	P(s)	P(s)	
5* Mixture PEMA/PVAc.	P(b)	P(s)	P(w)	P(s)		P(m) split btn 1480–1460		P(m)	P(s)	P(s) split		P(w) at 1020		P(w)	P(w)

APPENDIX VII (Contd.)

Samples	3500	3050	2450	1740–1720	1660–1620	1480–1440	1460–1440	1380–1360	1260–1200	1180–1140	1140–1120	1080–1040	1040–1000	960–920	860–840
Copolymerisation Products															
Semi-Batch Products:															
6. PBB_1	P(w)	P(s)	P(m)	P(s)		P(m) split		P(s)	P(b)	P(s) split	P(s)		P(m)	P(m)	P(m)
7 PBB_2	P(w)	P(s)	P(w)	P(s)		P(m) split		P(s)	P(b)	P(s) split	P(s) at 1120		P(m)	P(m)	P(m)
8 PBB_3	P(w)	P(s)	P(m)	P(s)		P(s) split		P(s)	P(b)	P(s)	P(s)		P(m)	P(m)	P(m)
9 PBB_4	P(w)	P(s)	P(w)	P(s)		P(s) split		P(s)	P(b)	P(s)	P(s)		P(s)	P(m)	P(m)
10 PSMCMS	P(w)	P(s)	P(w)	P(s)		P(s) split		P(w)	P(s)	P(s)			P(w)		
Semi-Batch Continuous															
PSB_1	P(w)	P(s)	P(w)	P(s)		P(s) split		P(s)	P(s)	P(s)	P(s)		P(m)	P(w)	P(w)
PSB_2	P(w)	P(s)	P(w)	P(s)		P(s)		P(s)	P(s)	P(s)	P(s)		P(s)	P(m)	P(m)
PSB_3	P(w)	P(s)	P(w)	P(s)		P(s) split at 1440–1440		P(s)	P(s)		P(s) at 1120–1160		P(s)	P(m)	P(m)
PSB_4	P(w)	P(s)	P(w)	P(s)		P(s) split		P(s)	P(s)	P(m) split			P(s)	P(w)	P(w)
Batch:															
PMMB	P(w)	P(s)	P(w)	P(s)		P(s) split		P(s) at1400	P(s)	P(s) split		P(s)		P(w)	P(w)

APPENDIX VII (Contd.)

Sample	3500	3050	2450	1740–1720	1660–1620	1480–1440	1460–1440	1380–1360	1260–1200	1180–1140	1140–1120	1080–1040	1040–1000	960–920	860–840
Methanol Insoluble (MIS):													P(s)	P(w)	P(w)
MIS of PBB_1	P(w)	P(s)	P(w)	P(s)		P(s) split		P(s) at 1400	P(s) split	P(s) split					
MIS of PBB_2	P(w)	P(s)	P(w)	P(s)		P(s) split		P(s) at 1400	P(s) split	P(s)		P(w)	P(s)	P(m)	P(w)
MIS of PBB_3	P(w)	P(s)	P(w)	P(s)		P(s) split		P(s) at 1400	P(s) split	P(s)		P(w)	P(s)	P(m)	P(w)
MIS of PBB_4	P(w)	P(s)	P(w)	P(s)		P(s) split		P(s) at 1380	P(s) split		P(s) at 1160–1120	P(w)	P(s)	P(m) split	P(m)
MIS of PSB_1	P(w)	P(s)	P(w)	P(s)		P(s) split		P(s) at 1380	P(s) split	P(s)	P(s)	P(w)	P(s)	P(m)	P(m)
MIS of PSB_2	P(w)	P(s)	P(w)	P(s)		P(s) split		P(s) at 1380	P(s) split	P(s)	P(s)	P(w)	P(s)	P(m) split	P(m)
MIS of PSB_4	P(w)	P(s)	P(m)	P(s)		P(s) split		P(s) at 1400	P(s) split	P(s) split	P(s)	P(w)	P(s)	P(m) split	P(m)

APPENDIX VII (Contd.)

Samples	3500	3050	2450	1740-1720	1660-1620	1500-1480	1460-1420	1380-1360	1260-1200	1180-1140	1140-1120	1080-1040	1040-1000	960-920	960-840
Methanol Soluble (MSS):															
MSS of PBB_1	P(b)	P(s)	P(m)	P(s)			P(m)	P(s)	P(s)		P(w)		P(s)	P(m)	
MSS of PBB_2	P(b)	P(s)	P(m)	P(s)			P(m)	P(s)	P(s)		P(w)		P(s)	P(m)	
MSS of PBB_4	P(b)	P(s)	P(m)	P(s)			P(m)	P(s)	P(s)		P(w)		P(s)	P(m)	
MSS of PSB_1	P(b)	P(s)	P(m)	P(s)			P(m)	P(s)	P(s)		P(w)		P(s)	P(m)	
MSS of PSB_3	P(b)	P(s)	P(m)	P(s)			P(m)	P(s)	P(s)		P(w)		P(s)	P(m)	
MSS of PSB_4	P(b)	P(s)	P(m)	P(s)			P(m)	P(s)	P(s)		P(w)		P(s)	P(m)	
Ethanol Soluble (ES):															
ES of PBB_1	P(w)	P(s)	P(vw)	P(s)		P(m) split	P(m)		P(s)	P(s) split			P(s)	P(w)	P(w)
ES of PBB_2	P(w)	P(s)	P(vw)	P(s)		P(m) split	P(m) at 1400		P(s)	P(s) split			P(s)	P(w)	P(w)
ES of PBB_4	P(w)	P(s)	P(vw)	P(s)		P(m) split	P(m) at 1380		P(s)	P(s) split			P(s)	P(w)	P(w)
ES of PSB_3	P(w)	P(s)	P(vw)	P(s)		P(m) split	P(m) at 1400		P(s)	P(s) split			P(s)	P(w)	P(w)
ES of PSB_4	P(w)	P(s)	P(vw)	P(s)		P(m) split	P(m) at 1400		P(s)	P(s)			P(m)	P(vw)	P(vw)

APPENDIX VII (Contd.)

Samples	3500	3050	2450	1740–1720	1660–1620	1500–1480	1460–1420	1380–1360	1260–1200	1180–1140	1140–1120	1080–1040	1040–1000	960–920	860–840
Ethanol Insoluble (EIS):															
EIS of PBB_2	P(w)	(s)		P(s)		P(m) split at 1440–1460		P(s) at 1380	P(s) split	P(s) split			P(s)	P(w)	P(w)
EIS of PBB_3	P(w)	P(s)	P(vw)	P(s)		P(m) split at 1440–1480		P(s) at 1400	P(s) split	P(s) split			P(s)	P(m)	P(m)
EIS of PSB_4	P(w)	P(s)	P(w)	P(s)		P(m) split		P(s) at 1380	P(s)	P(s)			P(s)	P(m)	P(m)
EIS of PBB_4	P(w)	P(s)	P(w)	P(s)		P(m) split		P(s) at 1380	P(s)	P(s)			P(s)	P(m)	P(m)

P = present (b) = broad (vw) = very weak

(w) = weak (m) = medium split = band splitted at the frequency range.

(s) = strong

APPENDIX VIII Important N.M.R. Peaks in (δ) from N.M.R. Spectra of Monomers, Polymer Samples.

Sample	Nature of Peak	Position of Peak on the Spectra (δ)
Monomers:		
Ethylmethacrylate (EMA)	Triplet	1.2 - 1.5
	Singlet	1.9 - 2.2
	quart	4.0 - 4.5
	Singlet (two)	5.6 - 6.2
Vinyl Acetate (VAc)	singlet	2.0 - 2.3
	quart	4.6 - 5.2
	quartet	7.1 - 7.6
Homopolymers:		
Polyvinyl Acetate (PVAc)	singlet*	1.8 - 2.0
	singlet	2.0 - 2.3
	singlet (broad)	4.8 - 5.2
Polyethylmethacrylate (PEMA)	singlet*	0.7 - 0.9
	triplet	1.2 - 1.5
	singlet (broad)	1.9 - 2.1
	doublet	4.2 - 4.4
Mixture of PEMA/PVAc	triplet*	1.2 - 1.5
	singlet*	1.8 - 2.0
	singlet	2.0 - 2.3
	doublet*	4.1 - 4.3
	singlet (broad)*	4.8 - 5.2

APPENDIX VIII (Contd.)

Sample	Nature of Peak	Position of Peak on Spectra (δ)
Copolymerisation Products		
PBB_1	triplet	1.2 - 1.4
	singlet	2.0 - 2.1
	doublet	4.0 - 4.3
PBB_3	triplet	1.2 - 1.4
	singlet	2.0 - 2.3
	doublet	4.0 - 4.3
PBB_4	singlet*	0.9 - 1.10
	trilet	1.2 - 1.5
	singlet*	2.0 - 2.2
	doublet	4.0 - 4.3
PSB_1	singlet*	0.9 - 1.0
	triplet	1.2 - 1.4
	singlet	2.0 - 2.2
	doublet	4.0 - 4.3
PSB_2	singlet	0.9 - 1.0
	triplet	1.1 - 1.4
	singlet*	2.0 - 2.2
	doublet	4.0 - 4.3
PSB_4	singlet	1.0 - 1.2
	triplet	1.2 - 1.5
	singlet*	2.0 - 2.1
	doublet	4.0 - 4.3

* = the peak is diminished.

APPENDIX VIII (Contd.)

Sample	Nature of Peak	Position of Peak on Spectra (δ)
Methanol Insoluble (MIS):		
MIS of PBB_2	triplet+	1.0 - 1.5
	singlet (broad)	1.8 - 2.2
	doublet	4.0 - 4.5
MIS of PBB_3	triplet +	1.0 - 1.4
	singlet (broad)	1.8 - 2.1
	doublet	4.0 - 4.3
MIS of PBB_4	triplet+	1.0 - 1.4
	singlet (broad)	1.8 - 2.2
	doublet	4.0 - 4.5
MIS of PSB_1	triplet+	2.0 - 1.5
	singlet (broad)	1.8 - 2.2
	doublet	4.0 - 4.5
Methanol Soluble (MSS)		
MSS of PBB_2	singlet	1.2 - 1.5
	singlet	2.0 - 2.3
	singlet (broad)	4.8 - 5.2
MSS of PBB_4	singlet	1.2 - 1.5
	singlet	1.6 - 2.0
	singlet (broad)	4.8 - 5.2
MSS of PSB_4	singlet	1.2 - 1.5
	singlet	1.6 - 2.0
	singlet	2.0 - 2.3
	singlet (broad)	4.8 - 5.2

+ - the peak not well resolved

APPENDIX VIII (Contd.)

Sample	Nature of Peak	Position of Peak on Spectra (δ)
Ethanol Insoluble (EIS):		
EIS of PBB_1	singlet	0.9 - 1.0
	triplet	1.0 - 1.4
	singlet (broad)	1.9 - 2.0
	doublet	4.1 - 4.3
EIS of PBB_4	singlet	0.9 - 1.0
	triplet	1.0 - 1.4
	singlet (broad)	1.9 - 2.0
	doublet	3.9 - 4.2
EIS of PSB_4	singlet	0.9 - 1.0
	triplet	1.0 - 1.4
	singlet (Broad)	1.6 - 2.0
	doublet	3.9 - 4.2
Ethanol Soluble (ES):		
ES of PBB_1	singlet	0.9 - 1.0
	triplet	1.2 - 1.4
	singlet	1.9 - 2.1
	doublet	4.1 - 4.3
ES of PSB_1	singlet	1.0 - 1.1
	triplet	1.2 - 1.5
	singlet (broad)	2.0 - 2.2
	doublet	4.1 - 4.3
ES of PBB_4	singlet	1.0 - 1.1
	triplet	1.2 - 1.5
	singlet (broad)	2.0 - 2.3
	doublet	4.0 - 4.3
ES of PSB_4	singlet	1.0 - 1.1
	triplet	1.2 - 1.5
	singlet (broad)	2.0 - 2.3
	doublet	4.1 - 4.3

KASHIM IBRAHIM LIBRARY
AHMADU BELLO UNIVERSITY
ZARIA, NIGERIA.