

**SYNTHESIS OF ACRYLONITRILE / VINYL ACID/
METHYL ACRYLATE POLYMERS AND THEIR
CONVERSION TO HIGH TENACITY FIBRES.**

By

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to the



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To

My Parents

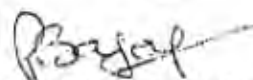
CERIFICATE

This is to certify that the thesis entitled "SYNTHESIS OF ACRYLONITRILE/ VINYL ACIDS/ METHYL ACRYLATE POLYMERS AND THEIR CONVERSION TO HIGH TENACITY FIBRES", being submitted by Mr. Sreekumar Thaliyil Veedu, to the Indian Institute of Technology, Delhi, for the award of the degree of Doctor of Philosophy in the Department of Textile Technology, is a record of bonafide research work carried out by him. Mr. Sreekumar Thaliyil Veedu has worked under our guidance and supervision and has fulfilled the requirements of the thesis.

The results presented in this thesis have not been submitted, in part or in full, to any other institute or university for the award of any degree or diploma.



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(Sreekanth Thallipati)

ABSTRACT

This dissertation deals with the synthesis, characterization and dry-jet-wet spinning of acrylonitrile (AN) polymers containing methacrylic acid (MAA), itaconic acid (IA) or methyl acrylate (MA) comonomers. Radical polymerization of acrylonitrile (AN) with methacrylic acid (MAA) and itaconic acid (IA) was carried out in a mixture of dimethyl formamide (DMF) and water at 70°C using α, α' -azobisisobutyronitrile (AIBN) as initiator using DMF/H₂O suspension polymerization. Characterization of the polymers was carried out using FTIR, CHN analysis, ¹H-NMR, ¹³C NMR, 2D- HETCOR NMR and viscometric techniques. The rate of polymerization (R_p) decreases with increase in DMF concentration in the reaction medium, viz., at 20% DMF level for AN/MAA system the R_p is 1.23 % min⁻¹ in 1hr polymerization while at 80% DMF level R_p is reduced to 0.37% min⁻¹.

Terpolymers containing AN, MA, MAA [P(AN/MA/MAA)] and AN,MA,IA [P(AN/MA/IA)] have also been prepared for the production of high tenacity acrylic fibres. The intrinsic viscosity of the polymers ranges from 0.67 to 2.90 dLg⁻¹ depending on the composition of the polymerization reaction medium. The IR absorbance ratio of the carbonyl peaks at 1734 cm⁻¹ to that of the nitrile peak at 2243 cm⁻¹ is used as a measure of the acid comonomer content in the copolymer. Using ¹³C{H} and ¹H NMR, it could be followed that at low comonomer content, the AAA sequencing predominates, while, with increasing comonomer content (4-6-mole %) AAM or AAI sequencing increases. Sequence distribution of AN is found to be random ($n_m \sim n_r \cong 2.0$).

Thermal characterization of acrylonitrile homopolymer and copolymers has been carried out using DSC, high pressure DSC and TGA. Influence of methacrylic acid (MAA 3-6 mole %) and itaconic acid (IA 2-3 mole %) on the glass transition temperature, T_g, thermo-oxidative stabilization and hydration melting of acrylonitrile copolymers has been discussed in detail. While, two T_gs are observed, near 70 and 140°C, for PAN homopolymer, copolymers with 2-3 mole % of comonomers showed another base line shift below 70°C. The copolymers showed two distinct melting peaks in the first heating cycle through high pressure DSC, but on cooling the melt exhibits a single exotherm. The melting point (T_m) of IA copolymer (158.4°C) is found to be lower than that of MAA copolymer (164°C) and PAN homopolymer (186°C). The enthalpy of fusion, ΔH_f decreases with the incorporation of comonomers, e.g.; it is the highest for PAN homopolymer (57.8 Jg⁻¹) and the lowest for P(AN/IA) copolymer (26.1 Jg⁻¹). Similarly, the entropy of fusion is also

lower for copolymers. The lower entropy of fusion (ΔS_f) of copolymers indicates that they are less mobile in the molten state.

Dry-jet-wet spinning studies of three copolymers P(AN/MAA), P(AN/MA) and P(AN/IA) having comonomer content 1.3, 1.4 and 0.7 mole % reveals that the cross-sectional shape of gel fibres undergoes a transition from kidney to oval shape and macrovoids begin to appear at higher coagulation bath temperature. However, P(AN/IA) gel fibres change from kidney shape to irregular shoe type with a gel network of interconnected polymer fibrils. F(AN/MA) fibres show higher strength (3.1 g/den) and elongation (14.6%) at 40°C coagulation bath temperature. Crystallinity does not change significantly ($\chi_c = 61-63\%$) with draw ratio, but crystal size increases from 22.9 to 43.4 Å⁰, and orientation factor 0.41 to 0.78.

Two terpolymers P(AN/MA/MAA), acid content 1.1 mol%, and P(AN/MA/IA), acid content 0.6 mole ratio, with intrinsic viscosity value $[\eta]$ ranging between 2.6-2.7 dl g⁻¹ after dry-jet-wet spinning and multi-stage drawing in boiling water and glycerol (total draw ratio 11.2) resulted in high tenacity fibres. F(AN/MA/MAA) fibres obtained after plasticized stretching in glycerol and subsequent collapsing on heater plates showed higher strength (6.44g/d), elongation-at-break (11%) and high modulus (251.9 g/d).

The main findings and general conclusions of the present work are summarized in the last chapter.

CONTENTS

	Page No.
ABSTRACT	i
ABBREVIATIONS	iii
CODING OF POLYMERS AND FIBRES	iv
CHAPTER 1 INTRODUCTION AND LITERATURE SURVEY.	
1.1 GENERAL INTRODUCTION	1
1.2 LITERATURE SURVEY	2
1.2.1 Synthesis of Acrylonitrile Based Polymers	2
1.2.1.1 Comonomers Used in Acrylic Fibre Manufacture	2
1.2.2 Methods of Polymerization	4
1.2.2.1 Solution Polymerization	4
1.2.2.2 Aqueous Suspension Polymerization	8
1.2.2.3 Solvent-Water suspension polymerization	11
1.2.3 Effect of Polymerization Techniques on the molecular structure of Acrylic Polymers	13
1.2.3.1 Chemical Configuration	13
1.2.3.2 Molecular defects during Polymerization	15
1.2.3.3 Effect of comonomers on the Physical structure of PAN	17
1.3 THERMAL BEHAVIOUR OF ACRYLONITRILE POLYMERS AND FIBRES	18
1.3.1 Effect of Comonomers on Thermal Behaviour	19
1.4 SPINNING OF ACRYLIC POLYMER-CONVERSION INTO FIBRES	21
1.4.1 Solution Spinning	21

1.4.2	Additives used in the Spinning dope	21
1.4.3	Wet Spinning	23
1.4.4	Effect of Coagulation Bath Composition and Temperature	23
1.4.5	Jet Stretch	25
1.4.6	Dry Spinning	26
1.4.7	Dry-Jet-Wet Spinning	27
1.4.8	Post-Spinning Conditions	33
1.4.9	Melt Spinning	35
1.5	OBJECTIVES OF THE PRESENT WORK	40

CHAPTER 2 SYNTHESIS AND CHARACTERIZATION OF ACRYLONITRILE/ VINYL ACIDS/ METHYL ACRYLATE POLYMERS.

2.1	INTRODUCTION	42
2.2	EXPERIMENTAL	46
2.2.1	Materials	46
2.2.2	Polymerization	46
2.2.2.1	Method I. For Reaction Rate Studies	46
2.2.2.2	Method II. For solution Spinning Studies	47
2.2.3	Intrinsic Viscosity Measurements	47
2.2.4	Acidimetric Titration	47
2.2.5	FTIR	47
2.2.6	Elemental Analysis	47
2.2.7	NMR Spectroscopy	48
2.2.7.1	Determination of Chemical Composition by NMR	48
2.2.8	X-ray Diffractometry	49

2.3	RESULTS AND DISCUSSION	50
2.3.1	Rate and Conversion	50
2.3.2	Effect of Methacrylic or Itaconic Acid Comonomer Content	51
2.3.3	Elemental Analysis	54
2.3.4	Acidimetric Titration	55
2.3.5	Intrinsic Viscosity [η]	55
2.3.6	Characterization of Acrylonitrile Polymers Using Method –II	56
2.3.7	FTIR Studies on Copolymers of Acrylonitrile	58
2.3.8	Wide Angle X-Ray Diffraction (WAXD) Studies on Copolymers of Acrylonitrile	62
2.3.9	Proton (^1H) and Carbon 13 (^{13}C) NMR Studies	63
2.3.9.1	^1H NMR	63
2.3.9.2	^{13}C NMR studies	66
2.3.9.3	2D-HETCOR	69

CHAPTER 3 THERMAL CHARACTERIZATION OF ACRYLONITRILE/ VINYL ACID COPOLYMERS

3.1	INTRODUCTION	71
3.2	EXPERIMENTAL	73
3.2.1	Material	73
3.2.2	Thermal Characterization	74
3.3	RESULTS AND DISCUSSIONS	75
3.3.1	Glass Transition Temperature	75
3.3.2	Melting behaviour of Hydrated PAN Under Autogeneous Vapour Pressure of Water.	77

3.3.2.1 Homopolymer	77
3.3.2.2 P(AN/MAA) and P(AN/IA) Copolymers	79
3.3.3 Thermo-oxidative Reactions	83
3.3.3.1 PAN homopolymer	85
3.3.3.2 Effect of Vinyl acid Comonomers	85
3.3.4 Thermo-Gravimetric Analysis (TGA)	87

CHAPTER 4 DRY-JET-WET SPINNING OF ACRYLONITRILE/ VINYL ACID COPOLYMERS

4.1 INTRODUCTION	89
4.2 EXPERIMENTAL	93
4.2.1 Materials	93
4.2.2 Dope Preparation	93
4.2.3 Brookfield Viscosity	93
4.2.4 Dry-jet-wet spinning	94
4.2.5 Wide-angle X-ray diffraction	94
4.2.6 Density measurement	96
4.2.7 FTIR	96
4.2.8 Sonic Modulus	96
4.2.9 Scanning Electron Microscopy (SEM)	97
4.2.10 Mechanical Properties	97
4.2.11 Thermo-mechanical Analysis	98

4.3	RESULTS AND DISCUSSIONS	98
4.3.1	Rheological Behaviour	98
4.3.2	Effect of Coagulation Bath Temperature	100
4.3.2.1	Diameter and Denier per Filament	100
4.3.2.2	Cross-sectional shape	102
4.3.2.3	Density	104
4.3.3	Mechanical Properties	104
4.3.3.1	Gel Fibres	104
4.3.3.2	Drawn Fibres	106
4.3.4	Wide Angle X-Ray Diffraction Studies	107
4.3.5	Sonic Modulus	109
4.3.6	Dichroic Ratio	109
4.3.7	Thermo-Mechanical Properties	110
4.3.7.1	Physical Shrinkage	111
4.3.7.2	Chemical Shrinkage	111

CHAPTER 5 PRODUCTION OF HIGH TENACITY ACRYLIC FIBRES AND CHARACTERIZATION THEREOF

5.1	INTRODUCTION	113
5.2	EXPERIMENTAL	118
5.2.1	Synthesis of Acrylonitrile Terpolymers	118
5.2.2	Dope Preparation	118
5.2.2	Spinning	119
5.2.3	Drawing and Thermosetting	119

5.3	CHARACTERIZATION	121
5.3.1	Intrinsic Viscosity	121
5.3.2	Brookfield Viscosity	121
5.3.3	Ball Fall Time	121
5.3.4	Mechanical Properties	121
5.3.5	DSC	121
5.3.6	FTIR	122
5.3.7	Thermogravimetric Analysis (TGA)	122
5.3.8	Wide-angle X-ray diffraction	122
5.3.9	Sonic Modulus	122
5.3.10	Scanning Electron Microscopy (SEM)	122
5.4	RESULTS AND DISCUSSION	123
5.4.1	Brookfield Viscosity	123
5.4.2	Ball fall Time	123
5.4.3	Structure Properties of Fibres	123
5.4.3.1	Effect of Stretching on Cross-sectional Shape	123
5.4.3.2	Effect of Stretch Ratio on Mechanical Properties	124
5.4.4	FTIR	127
5.4.5	Scanning Electron Microscopy (SEM)	129
5.4.6	Differential Scanning Calorimetry	129
5.4.7	Chemical changes during exothermic reaction	133
5.4.8	Thermogravimetric Analysis (TGA)	134
5.4.9	X-ray Diffraction Studies	137

sulfur containing end groups, derived mainly because of transfer of free radicals to bisulfite ion during polymerization, were observed using FTIR and ^{13}C NMR spectroscopic techniques.

Japan Exlan Co. [24-25] prepared an acrylonitrile copolymer with methyl acrylate having a molecular weight of $3-4 \times 10^5$. They used 900g AN, 100g MA and 10g AIBN which were added to 3000g of H_2O containing 15g of polyvinyl alcohol (PVA) at 60°C . The reaction was continued for 2h to obtain a conversion of 57.5%. The presence of PVA has been suggested to have increased the solution viscosity which decreased the radical mobility and thus resulted in higher molecular weight.

1.2.2.3 Solvent-Water suspension polymerization

In this method, approximately equivolume mixture of solvent (DMF, DMSO etc.) and water (non-solvent) is used as the reaction medium, and more water is added on the onset of precipitation. The reaction is initiated by AIBN. The presence of solvent narrows the molecular weight distribution and water reduces the overall chain transfer leading to the formation of higher molecular weight polymer. The advantages of this method are:

- High percentage conversion.
- Shorter polymerization time (1-4 hrs).
- Higher molecular weight and
- Better degree of whiteness.

Although, published literature on this method is scarce, some information is available in some patents.

A patent assigned to Mitsubishi Rayon [11] discloses the production of acrylonitrile copolymer with methacrylic acid using DMF/water suspension polymerization. Here 6 Kg of AN was copolymerized with 82g of MAA in the

CHAPTER 6 SUMMARY AND CONCLUSIONS.

6.1	SUMMARY AND CONCLUSIONS	139
6.2	SCOPE OF FUTURE RESEARCH	145
	REFERENCES	147