

**SYNTHESIS, CHARACTERIZATION AND PRODUCTION  
OF ACRYLONITRILE-VINYL ACIDS  
COPOLYMERS AND FIBRES**

*by*

**DINESH KUMAR PALIWAL**

*Thesis submitted  
in fulfilment of the requirements  
for the degree of*  
**DOCTOR OF PHILOSOPHY**

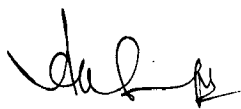


Department of Textile Technology  
**INDIAN INSTITUTE OF TECHNOLOGY, DELHI**  
NEW DELHI-110016, INDIA  
JULY, 1995

## CERTIFICATE

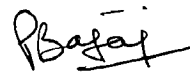
This is to certify that the thesis entitled "**SYNTHESIS, CHARACTERIZATION AND PRODUCTION OF ACRYLONITRILE - VINYL ACIDS COPOLYMERS AND FIBRES**", being submitted by Mr. Dinesh Kumar Paliwal, to the Indian Institute of Technology, Delhi, for the award of the degree of Doctor of Philosophy in the Department of Textile Technology is a record of bonafide research work carried out by him. Mr. Paliwal has worked under our guidance and supervision and has fulfilled the requirements for the submission 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.



**Prof. A.K. Gupta**

Thesis Supervisor



**Prof. (Miss) P. Bajaj**

Thesis Supervisor

New Delhi,

the 10<sup>th</sup>, July 1995.

## ACKNOWLEDGEMENTS

I express my sincerest gratitude to my research supervisors, Prof. (Miss) Pushpa Bajaj and Prof. Avdhesh Kumar Gupta for their valuable guidance and painstaking efforts. It is due to their personal attention and ceaseless promptitude that I have been able to complete this thesis.

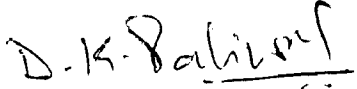
I am thankful to the University Grants Commission for awarding teacher-fellowship to undertake this research work, and to the Head, Department of Textile Technology, Indian Institute of Technology, Delhi for extending the necessary facilities.

I shall be failing in my duty, if I do not utilize this opportunity to extend my gratitude to Dr. N.D. Sharma, Dr. B.V. Rao and Staff of Sir Padampat Research Centre (SPRC), J.K. Synthetics Ltd., Kota, for providing me with the spinning facilities and all the necessary assistance. My special thanks are due to Dr. B.V. Rao for his much needed encouragement.

I wish to express my thanks to the staff of fibre production and fibre science laboratories alongwith the entire staff of the Department of Textile Technology who happily provided me all sorts of assistance at all the times. I also wish to acknowledge the debt owed to my colleagues and friends, specially, Drs. S.K. Rana, Anand Kumar, B.K. Ratnam, K. Srinivas, Sanjay Mehta, Meenakshi, Radhakrishnan, Rakesh Koul and Sh. Praveen Kumar, Sh. Sreekumar Sh. H. Bahrami and Km. Kirti Sharma, who have generously extended their help and valuable cooperation, whenever it was needed.

Sh. Sasi Kumar S.K. has typed my thesis with utmost patience, sincerety and care, for which he deserve my special thanks. I would also like to thank Sh. K.G. Padam, and Sh. N.C. Gupta for expert tracings and to Sh. Satish Kumar, Sh. D.C. Sharma, Sh. Atul Sharma and Dr. S.K. Paliwal for their encouragement and assistance.

I am indebted to my parents and family for their patience, constant encouragement, kind concern and love. To them I dedicate this thesis.

  
**Dinesh Kumar Paliwal**

	ABBREVIATIONS	i
	CODING OF THE POLYMERS AND FIBRES USED IN THIS DISSERTATION	ii
	ABSTRACT	iii
<b>CHAPTER 1.</b>	<b>INTRODUCTION AND LITERATURE SURVEY</b>	
1.1	GENERAL INTRODUCTION	1
1.2	LITERATURE REVIEW	5
1.2.1	Acrylic Fibres with Enhanced Hydrophilicity and Dyeability	5
1.2.2	Water-Absorbent Acrylic Fibres	10
1.2.3	Antistatic Soil-Release and Conductive Acrylic Fibres	11
1.2.4	Ion-Exchange Acrylic Fibres	12
1.2.5	Antimicrobial Acrylic Fibres	13
1.2.6	Flame-Resistant Acrylic Fibres	14
1.2.7	Hollow Acrylic Fibres	16
1.2.8	High Performance Acrylic Fibres	17
1.2.9	Acrylic as a Precursor to Carbon Fibres	26
1.3	OBJECTIVES OF THE PRESENT WORK	31
<b>CHAPTER 2.</b>	<b>SYNTHESIS AND CHARACTERIZATION OF ACRYLONITRILE COPOLYMERS</b>	
2.1	INTRODUCTION	33
2.2	EXPERIMENTAL	38
2.2.1	Materials	38
2.2.2	Polymerization (a)	38

2.2.3	Characterization	39
2.3	RESULTS AND DISCUSSION	40
2.3.1	Reactivity of Comonomers	40
2.3.2	Intrinsic Viscosity	45
2.3.3	FTIR Studies	46
2.3.4	NMR Studies	48
<b>CHAPTER 3.</b>	<b>THERMAL BEHAVIOUR OF ACRYLONITRILE COPOLYMERS</b>	
3.1	INTRODUCTION	54
3.2	EXPERIMENTAL	58
3.2.1	Materials	58
3.2.2	Measurements	58
3.3	RESULTS AND DISCUSSION	61
3.3.1	Melting Behaviour of Acrylonitrile Polymers	61
3.3.1.1	DSC Studies	61
3.3.1.2	High Pressure DSC Studies	65
3.3.2	Thermal Degradation of Acrylonitrile Polymers	68
3.3.2.1	Effect of Medium of Heat Treatment	68
3.3.2.2	Effect of Nature and Mole Fraction of Acidic Comonomers	71
3.3.2.3	Quantitative Analysis of Thermo-oxidative Reactions	74
3.3.2.4	DSC-FTIR Studies	77
3.3.2.5	TG-FTIR Studies	81
3.3.2.6	Exothermic Reactions Occurring during Heat Treatment of Acrylonitrile Polymers	84

**CHAPTER 4****INFLUENCE OF NATURE AND CONTENT  
OF COMONOMERS ON SPINNABILITY AND  
PROPERTIES OF ACRYLIC FIBRES**

4.1	INTRODUCTION	86
4.2	EXPERIMENTAL	90
4.2.1	Synthesis of AN Copolymers	90
4.2.2	Preparation of Spinning Dope and its Viscosity	91
4.2.3	Wet Spinning	92
4.2.4	Characterisation of Fibres	92
4.2.5	Dyeing	95
4.2.6	Scanning Electron Microscopy	97
4.3	RESULTS AND DISCUSSION	97
4.3.1	Dope Viscosity	97
4.3.2	Spinnability	100
4.3.3	Density	102
4.3.4	Mechanical Properties of the Fibres	102
4.3.4.1	Stress-strain Behaviour	102
4.3.4.2	Sonic Modulus	103
4.3.5	X-ray Studies	105
4.3.6	Boiling Water Shrinkage	108
4.3.7	Thermo-mechanical Studies	109
4.3.8	Moisture Regain	111
4.3.9	Morphology	112
4.3.10	Dyeability	112
4.3.10.1	Effect of Dye-bath Temperature	114
4.3.10.2	Effect of the Fibre Structure	114
4.3.10.3	Dye Diffusion	115

4.3.10.4	Energy of Activation	116
4.3.11	Light Fastness	117
<b>CHAPTER 5.</b>	<b>INFLUENCE OF METAL IONS ON THE STRUCTURE AND PROPERTIES OF ACRYLIC FIBRES</b>	
5.1	INTRODUCTION	118
5.2	EXPERIMENTAL	122
5.2.1	Materials	122
5.2.2	Measurements	122
5.3	RESULTS AND DISCUSSION	124
5.3.1	Chemical Transformation	124
5.3.2	WAXD Studies	127
5.3.3	Thermal Behaviour	129
5.3.3.1	DSC Studies	129
5.3.3.2	Thermogravimetric Studies	132
5.3.3.3	Thermo-mechanical Studies	134
5.3.4	Mechanical Properties	135
5.3.5	Fracture Morphology	139
<b>CHAPTER 6</b>	<b>SUMMARY AND CONCLUSIONS</b>	
6.1	SUMMARY AND CONCLUSIONS	141
6.2	SCOPE FOR FURTHER RESEARCH	147
	REFERENCES	149
<b>ANNEXURE I</b>	<b>CALCULATION OF ENERGY CHANGES DURING THERMAL DEGRADATION OF POLYACRYLO-NITRILE</b>	<b>i</b>
<b>ANNEXURE II</b>	<b>LIST OF PUBLICATIONS</b>	<b>vi</b>

\*\*\*\*\*

(d)

## ABSTRACT

Acrylonitrile (AN) was copolymerized with acrylic acid (AA), methacrylic acid (MAA) and itaconic acid (IA) by aqueous suspension polymerization at 40°C using redox initiators. The reactivity ratios for the AN-AA and AN-IA systems were calculated by the Finemann-Ross and the Kelen-Tüdős method. The influence of comonomers on the intrinsic viscosity, tacticity and number average sequence length was studied through FTIR and <sup>13</sup>C-NMR.

The thermal behaviour of the synthesized, acrylonitrile polymers was studied using DSC-FTIR, TG-FTIR and high pressure DSC techniques. Efforts were made to understand the chemistry of thermal degradation of acrylonitrile polymers having vinyl acid comonomers. Attempts have also been made to correlate the chemical reactions occurring during thermal degradation of AN copolymers in inert as well as in air atmosphere with their DSC exotherms. Influence of comonomer and heating rate were also studied on the melting behaviour of AN copolymers.

AN-copolymer with AA (10.8 wt %), MAA (10.3 wt %) and an acrylonitrile terpolymer with vinyl acetate (VAc - 7.0 wt %) and sodium methallyl sulphonate (SMAS - 0.30 wt %) having intrinsic viscosity 1.71, 1.32 and 1.14 dl g<sup>-1</sup> respectively were wet spun. Spinning was carried out on a laboratory scale wet spinning machine using dimethylacetamide : water mixture (55:45 v/v) in the coagulation bath at 30°C. Density, X-ray crystallinity and orientation, sonic modulus, moisture regain, and tensile

properties of these fibres were measured. The physico-mechanical properties of these fibres have been discussed. The dyeability of the fibres was also studied using Sandocryl Blue B-3G dye and the rate of dyeing, energy of activation for dye diffusion and light-fastness have been determined and correlated with the physico-chemical nature of the fibres.

Acrylonitrile-acrylic acid copolymer fibres were treated with sulphates of alkali metals (sodium and potassium) and transition metals (cobalt and nickel). The effect of this chemical treatment on the structure and properties of the fibres has been investigated through FTIR, X-ray, DSC and TG techniques.

\*\*\*\*\*