STUDIES ON THE CHARACTERIZATION OF LIQUID CRYSTALLINE POLYESTERS

by

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CENTRE FOR MATERIALS SCIENCE AND TECHNOLOGY

A thesis submitted
in fulfilment of the requirements of the degree of

DOCTOR OF PHILOSOPHY

to the

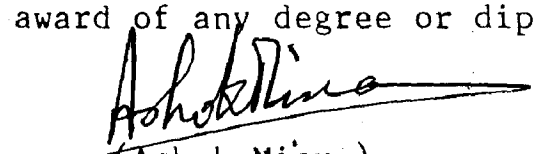
INDIAN INSTITUTE OF TECHNOLOGY, DELHI

MAY, 1986

CERTIFICATE

This is to certify that the thesis entitled "Studies on the Characterization of Liquid crystalline polyesters." being submitted by Mr. Subrata Kumar Bhattacharya, to the Indian Institute of Technology, Delhi, for the award of Doctor of Philosophy in the Centre for Materials Science and Technology is a record of bonafide research work carried out by him. Mr. Subrata Kumar Bhattacharya worked under my guidance and supervision and has fulfilled the requirements for the submission of the thesis.

The results contained in this thesis have not been submitted, in part or in full, to any other University or Institute for the award of any degree or diploma.



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ACKNOWLEDGEMENT

I wish to express my sincere thanks to Dr. Ashok Misra, Assistant Professor, Centre for Materials Science and Technology (CMST), Indian Institute of Technology, Delhi for his constant encouragement, dynamic guidance and kind help which motivated me to do this work.

I am thankful to Prof. R.W. Lenz and Prof. R.S. Stein of University of Massachusetts, U.S.A. for providing laboratory facilities and for valuable discussions and suggestions about my work.

I am thankful to Prof.(Mrs.) I.K. Verma, Head,CMST and Prof.(Miss) P.Bajaj, Former Head, Textile Technology Department, Indian Institute of Technology, Delhi for providing laboratory facilities and for their encouragements. I am also thankful to Dr.B.L.Deopura, Assistant Professor, Textile Technology Department for valuable discussions and kind help.

Thanks are due to Dr.O.Deex of Monsanto Chemical Company, U.S.A. for providing polymer samples and for valuable discussions. Thanks are also due to Dr.W.J. Jackson of Eastman Kodak Company, U.S.A. for providing polymer samples.

I wish to acknowledge the National Science Foundation (U.S.A) for providing the funding for this research work. I am in particular thankful to Mr.K.R.Subramanium, NSF representative, U.S. Embassy, New Delhi for arranging my travel abroad and his encouragement.

I thank Mr.Swapan Dhara, Mr.Debaprasad Mitra, Mr.Ramshankar Halder, Dr.Sarvesh Sharma, Mr.Ashok Tendolkar, Mr.Kashi Bhowmick (I.I.T Delhi), and Dr.S.N.Garg & Ms.Paula Hahn (University of Massachusetts) and all other colleagues for their help and co-operation. The valuable help from the technical staff is also gratefully acknowledged.

Lastly, I could not have carried out this work without constant support from my wife Ruma; no amount of thanks is adequate for her contribution. She also helped me in correcting the proof and in various other ways which I like to acknowledge.

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DEDICATED

TO MY PARENTS

ABSTRACT

Liquid Crystalline (LC) polymers are relatively recent additions to the family of polymers. They exhibit anisotropy in the liquid state which may be a melt above the melting temperature or a solution at some critical concentrations. This anisotropy is attributed to orientation which can be preserved in the processed state. On account of this, LC polymers exhibit a range of useful and interesting properties. Among the LC polymers, the LC polyester are the most prominent due to their ease of synthesis and good properties. Some work has been done on the morphology and structure-property relationships of these polymers but much work has to be done in order to understand these systems properly. This thesis primarily deals with the structure-property studies on selected polyester/copolyester LC systems. Some work on synthesis of copolyesters was also carried out.

Morphological and rheological studies are reported for a commerical thermotropic LC polyester. Small angle light scattering (SALS) studies were carried out as a function of temperature using H_V and V_V polarization with photographic as well as photometric techniques. No scattering was observed from a thin film cast from a dilute solution of the polymer in a highly volatile solvent. When the film was heated, scattering was observed above glass transition temperature of the polyester. The scattering was found to be azimuthally dependent with V_V intensities being much higher than the

corresponding H_V intensities. The size of the morphological features were calculated and were found out not to change significantly with temperature ranging from glass transition temperature to solid-nematic transition temperature of the polymer. The X-ray diffraction patterns of solution cast polymer was representative of an amorphous structure. Solution cast films annealed under various conditions (all above the T_g of the polymer) contained crystalline and amorphous structure. The maximum apparent crystallinity for annealed samples was of the order of 30%. In rheological studies using capillary and cone & plate rheometer, rapid fall in melt viscosity with shear rate, negative die swelling and pseudoplastic melt behaviour were observed. In another experiment the storage modulous of the polyster was found to decrease with temperature and increase with frequency.

The phase transition kinetics studies were carried out for an experimental LC polyster during its transition from the isotropic melt state to the nematic state. The amount of heat evolved in the process was found to be both temperature dependent as well as time dependent. The Avrami exponent value for such a transition was found to be below one signifying one dimentional growth associated with the transition. Concept of "degree of liquid crystallinity" has been illustrated in this context.

The partially compatible blends of a commercial LC polyster with polyethylene terephthalate (PET) were studied

for mechanical and morphological properties. The DSC data show some evidence of nucleation of PET by the LC copolyster. The SALS photographic results show the presence of some rod-like scattering entities in the blend systems above the melting temperature of PET. These entities are believed to be responsible for nucleation of PET. X-ray diffraction studies show that the LC copolyester not only nucleates PET but also takes part in the development of structures and superstructures. The as-spun fibres from the blend show the presence of orientation and crystallinity in X-ray studies. The orientation is believed to be responsible for higher strength of blend fibres compared to pure PET fibres as observed in mechanical property studies.

Copolyesters of terephthalic acid, chlorohydroquinone and hydroquinone/bisphenol-A of various compositions have been synthesized by solution polymerization and their transition temperatures and thermal stability have been studied. The effect of chain assymetry on LC state stability and transition temperatures were observed.

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