STRUCTURE PROPERTY RELATIONSHIP IN POLYIMIDES

BY

K. R. MURTHY

DEPARTMENT OF CHEMISTRY

SUBMITTED

IN FULFILMENT OF THE REQUIREMENTS OF THE DEGREE OF

DOCTOR OF PHILOSOPHY

TO THE

INDIAN INSTITUTE OF TECHNOLOGY, DELHI

APRIL, 1984

CERTIFICATE

This is to certify that the thesis entitled " Structure property relationship in polyimides " being submitted by Mr. K.R. Murthy to the Indian Institute of Technology, Delhi for the award of the degree of Doctor of Philosophy in Chemistry, is a record of bonafide research work carried out by him. Mr. K.R. Murthy has worked under our guidance and supervision and has fulfilled the requirement for submission of this thesis which to our knowledge has reached the requisite standard.

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

I.K. Varma

(I.K. Varma)

Thesis Supervisor,
Professor of Polymer Science, Head, Centre for Materials Science and Technology, Indian Institute of Technology,
New Delhi 110 016
INDIA

D S Varma

(D.S. Varma)

Thesis Supervisor,
Professor of Fibre Science, Dean of Students, Department of Textile Technology
Indian Institute of Technology,
New Delhi 110 016
INDIA

ACKNOWLEDGEMENTS

I sincerely offer my indebtedness to Prof. (Mrs.) I.K. Varma, Professor of Polymer Science and Head, Centre for Materials Science and Technology and Prof. D.S. Varma, Professor of Fibre Science and Dean of Students, Indian Institute of Technology, Delhi for their painstaking guidance, invaluable suggestions and constant encouragement. But for their interest this work would not have reached this stage.

I am thankful to Head, Chemistry Department and Head, Textile Technology Department for providing the facilities for carrying out this work. I am grateful to Dr. A.K. Sreedhar, Director, Defence Science Centre, Delhi and Dr. B.V. Ramani, Director, DMSRDE, Kanpur for their encouragement.

I wish to thank all my colleagues and friends especially Dr. Veena Chaudhary, Dr. C.K. Geetha, Dr. Anita Tripathi, Dr. Manjeet Chaudhary and Dr. B.S. Rao for their help at various stages of this work.

I thank Mr. Rajesh Arora for the neat, fast and accurate typing of the thesis.

K. R Murthy

(K.R. MURTHY)

ABSTRACT

The thesis deals with the effect of structure on properties of polyimides which may be used as films and fibres. The aim of the present investigation was to establish structure-property relationship in copolyimides and to study the effect of introducing ether or ester groups in the polyimide backbone on thermal behaviour. To achieve this objective several polyimides having different backbone structures were synthesised.

Some of the amines employed were commercially available p-phenylene diamine (P), p-p'-diamino diphenyl ether (E), p,p'-diamino diphenyl methane (M) while others are synthesised in the laboratory by reducing the corresponding nitro compounds with hydrazine hydrate using Pd/C as a catalyst in presence of alcohol. The diamines synthesised are p-bis(aminophenoxy) benzene (aQ), m-bis(aminophenoxy) benzene (aR), 2,2-bis(aminophenoxy phenyl) propane (aB) and 4,4'-bis(aminophenyl) phenolphthalein. These were recrystallised from alcohol.

The various dianhydrides with ester linkages were prepared by condensing the diacetates of quinol, resorcinol, bisphenol and phenolphthalein with trimellitic anhydride in presence of diphenyl ether. These were precipitated with petroleum spirit and recrystallised from acetic anhydride. The dianhydrides used for preparing polyimides included pyromellitic dianhydride (P), p-phenylene bis(trimellitate) dianhydride (tQ), m-phenylene bis(trimellitate) dianhydride (tR), 2,2-bis(trimellitoxyphenyl) propane dianhydride (tB) and 4,4'-bis(trimellityl) phenolphthalein dianhydride (tP). The diamines and dianhydrides were characterised by ir, mass and NMR spectroscopy.

Polyamic acid solutions were prepared by reacting the diamines and dianhydrides in dimethyl formamide (DMF) at low temperatures. The cyclodehydration of polyamic acid precursors to polyimides was done by the use of acetic anhydride and pyridine. Three series of condensation polyimides were prepared. In series I seven polypyromellitimides were prepared by reacting pyromellitic dianhydride with M, E, aQ, aR, aB, aP and p-phenylene diamine. In series II copolyimides from PMDA and two diamines - p-p'-diamino diphenyl methane benzidine and p,p'-diamino diphenyl ether were prepared.

In series III, polyesterimides were prepared by reacting the various esterlinked dianhydrides with p,p'-diamino diphenyl ether and p,p'-diamino diphenyl methane.

Thermal cyclization of polyamic acid films in nitrogen atmosphere was also carried out in a few cases. The polyamic acids were characterised by intrinsic viscosity $[\eta]$ determination in DMF at 30°C. Higher values of $[\eta]$ were obtained in case of polyamic acids from p-phenylene diamine/benzidine.

Relative thermal stability of polyimides was evaluated by determining initial decomposition temperature (IDT), integral procedural decomposition temperature (IPDT) and temperature of maximum rate of weight loss (T_{max}). The effect of backbone flexibility on thermal behaviour was evaluated.

The effect of structure on electrical properties of polyimide films was also evaluated by thermally stimulated discharge current studies. It was concluded that dielectric relaxation in these polyimides was due to trapping of charge carriers.

Mechanical property measurements and scanning electron microscopy studies of a few polyimide fibres was carried out. Bismaleimides were synthesised by reacting the ether linked diamines with maleic anhydride in acetone. Cyclodehydration of bismaleamic acid precursor was done by refluxing with acetic anhydride and sodium acetate. These compounds were characterised by ir and DSC. The curing temperature and melting points of bisimides depended on the meta or para orientation of substituents in benzene ring.

CONTENTS