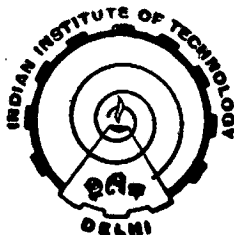


**STRUCTURE - PROPERTY RELATIONSHIP  
IN  
POLYIMIDE FILMS**

by  
**SNEH SAXENA**

*THESIS SUBMITTED  
IN FULFILMENT OF THE REQUIREMENTS OF  
THE DEGREE OF  
DOCTOR OF PHILOSOPHY*



**Centre for Materials Science & Technology  
INDIAN INSTITUTE OF TECHNOLOGY, DELHI  
AUGUST, 1988**

CERTIFICATE

This is to certify that the thesis entitled "STRUCTURE-PROPERTY RELATIONSHIP IN POLYIMIDE FILMS" being submitted by Mrs. Sneh Saxena to the Indian Institute of Technology, Delhi, for the award of degree of Doctor of Philosophy is a record of bonafide research work carried out by her. Mrs. Sneh Saxena has worked under our guidance and supervision and has fulfilled the requirements for the submission of this thesis which to our knowledge has reached the requisite standard.

The results contained in this 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*

Prof. (Mrs.) I.K. Varma  
Centre for Materials Sci. & Tech.,  
Indian Institute of Technology,  
Hauz Khas, New Delhi-16.

*D S V*

Prof. D.S. Varma  
Dept. of Textiles Tech.,  
Indian Institute of Tech.,  
Hauz Khas, New Delhi-16.

## ACKNOWLEDGEMENTS

I would like to express my deep sense of gratitude and indebtedness to my supervisors Prof. (Mrs.) I.K. Varma and Prof. D.S. Varma for their valuable guidance, constant encouragement and generous cooperation, without which this work would not have been possible.

I am thankful to Dr.(Mrs.) Anita Tripathi for helping me in carrying out the electrical measurements. I am also grateful to the teaching and non teaching staff of the Centre for Materials Science and Technology for their help and cooperation.

I acknowledge all my friends for providing extensive help at various stages of my work.

I also thank Mr. Surinder, Mr. L.C. Sharma and Mr. Durga Singh for their help in taking thermograms and IR spectra. I am also thankful to Akhilesh and Sarita Sharma for helping me in typing this thesis. Thanks are also due to Mr. Saraswat and Mr. B.B. Arora for drawing the figures.

The authorities of I.I.T. Delhi and CSIR are acknowledged for the financial assistance provided for carrying out this work.

Finally I express my thanks to my husband, Dr. Anil, who constantly encouraged me and showed immense patience through out my research work. My thanks are also due to my son Amoor and my sister Seema. I acknowledge the immense contribution, love and affection of my parents, parents-in-law and all well-wishers.

  
(SNEH SAXENA)

## ABSTRACT

Aromatic polyimides, especially films, possess a unique combination of properties. They exhibit high thermal stability with good mechanical and electrical performance over a wide temperature range. The potential application areas of these polymers can be further extended by structural modifications.

One of the research goals in the present work was to study the effect of structural modifications on the properties of polyimide films. New phosphorus containing polypyromellitimides with pendant maleimido groups were synthesised and effect of maleimido groups on thermal behaviour of polyimides was investigated. Incorporation of metallic salts on properties of polyimides films was also studied.

Several copolyimides were prepared by reacting pyromellitic dianhydride (PMDA) with 4,4'-diaminodiphenyl ether (DADPE) and 3-maleamido-acid-phenyl-3',3''-diaminodiphenyl phosphine oxide (TAP-MA).

TAP-MA was prepared in two different solvents i.e. acetone and N,N-dimethylformamide (DMF). It was possible to isolate the intermediate TAP-MA from acetone solution. Further reaction of TAP-MA with PMDA and DADPE was carried out in DMF. This method has been designated as two step

method. The intermediate could not be isolated, when this reaction was carried out in DMF. Therefore, in this case PMDA and DADPE were added to the same reaction flask containing DMF solution of TAP-MA. This method has been designated as single pot method. Cyclodehydration of the copoly(amide-acid)s obtained from single pot method was done using sodium acetate and acetic anhydride, while pyridine: acetic anhydride: toluene solution (1:1:1) was used for copoly(amide-acid)s prepared by two step method. Alternately, the DMF solution of copoly(amide-acid)s (two step method) was spread on glass plates and the polymer film thus obtained was thermally cyclodehydrated by heating for 1 h each at 100 and 200°C and 0.5 h at 250°C. Polypyromellitimides based on DADPE or TAP-MA have been designated as E and P respectively.

For the copolyimides preparation, 0.01 mole of DADPE was used and the molar concentration of TAP-MA was varied as 0.001 ( $PE_{10}$ ), 0.002 ( $PE_5$ ), 0.003 ( $PE_{3.3}$ ), 0.005 ( $PE_2$ ) and 0.0075 moles ( $PE_{1.3}$ ).

Characterisation of TAP and TAP-MA was done by IR,  $^1H$ -NMR spectroscopy and amine estimation. Absorption bands due to  $P=O$  ( $1180\text{ cm}^{-1}$ ),  $P-C_6H_5$  ( $1432\text{ cm}^{-1}$ ) and amino groups ( $3224-3384\text{ cm}^{-1}$ ) were observed in the IR spectrum of TAP. In TAP-MA, presence of maleamide-acid was confirmed by appearance of  $1710\text{ cm}^{-1}$  due to  $\nu_{C=O}$  in addition to the

other absorption bands mentioned above. Protons due to amino and amido groups were observed in the  $^1\text{H}$ -NMR spectrum of TAP-MA.

A decrease in intrinsic viscosity of copoly(amide-acid)s in DMF was observed with an increase in TAP-MA content in the backbone.

Absorption bands due to imide group were observed at 1780, 1720, 1120 and 730  $\text{cm}^{-1}$  in polyimides. The relative intensities of these absorption bands depended on the molar concentration of the two diamines (DADPE, TAP-MA). Presence of residual amide-acid in the polyimide samples was indicated on the basis of elemental analysis.

Amongst the various polyimide samples, P, was having maximum solubility of 38% in DMF.

An exothermic transition was observed in the DSC scans of polyimides (single pot method) in the temperature range of 72-202°C. The temperature of completion of exotherm was 67°C higher (i.e. ~267°C) in polyimides obtained by two step method. An increase in  $\Delta H$  value was observed as the maleimido content was increased in the samples. The  $\Delta H$  values varied linearly with composition for polyimides prepared by single pot method. These  $\Delta H$  values were lower than those obtained by two step method using chemical cyclodehydration. The  $\Delta H$  values of PI

obtained by thermal cyclodehydration were lowest. This may be due to partial polymerisation of maleimido groups during thermal treatment (250°C for 30 min).

A two step decomposition was observed in the TG traces of uncured polyimides while in polyimides cured at  $220 \pm 5^\circ\text{C}$  for 4 h, major decomposition was observed above 456°C. The weight loss observed in the temperature range of 160-275°C may be due to cyclodehydration of residual poly(amide-acid) and the main degradation of the polymer occurred above 500°C. Char yield at 800°C increased after curing and also with the increase in phosphorus content in the copolyimides.

Effect of metal halides on the properties of two polyimide films based on DADPE and PMDA or BTDA were investigated. 10% w/w of metallic halides ( $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$  and  $\text{CoCl}_2$ ) were added to the poly(amide-acid) solution in DMF. These solutions were spread on the glass plate by a doctor's blade. Cyclodehydration of the films was done by heating the films in nitrogen atmosphere for 1 h each at 100, 200 and 250°C. The polyimides have been designated as E and BT-E (for PMDA-DADPE and BTDA-DADPE).

Intrinsic viscosity was found to be 2.0 dL/g (E) and 0.69 dL/g (BT-E). Characteristics peaks due to imido group (1780, 1720, 1125 and  $730 \text{ cm}^{-1}$ ) were observed in the

IR spectra of the films. No additional band was observed in doped PI suggesting thereby the absence of interaction between PI and metal ions. Elemental analysis indicated presence of residual amide-acid in doped films. Metal analysis indicated partial loss of metal during the cyclodehydration reaction. Density of polyimide films increased upon doping.

In polyimide films E and BT-E, insignificant weight loss (~1%) was observed in the temperature range of 250-385°C. However in presence of dopants, the weight loss in temperature range of 200-425°C was considerably higher (3.1 - 7.7%). The increase in the weight loss in this temperature range may be due to either (a) loss of residual solvent (DMF) from the film or (b) cyclisation of residual amide-acid. In order to understand the contribution of these two reactions, DSC scans of the doped PI films were recorded. An exothermic transition was observed in the temperature range of 276-370°C. The existence of exotherm indicated the possibility of cyclodehydration reaction which was confirmed by mass spectroscopy studies. These results indicate that dopants influence the cyclodehydration reaction of poly(amide-acid). Major weight loss was observed above 475°C in doped PI films. This may be due to decomposition of the polyimide. A decrease in char yield was observed on doping with metal salts.

Presence of metallic salts in PI films resulted in a decrease in percentage elongation, tensile strength and tensile modulus.

Variation of current (I) as a function of voltage was determined in the temperature range of 50-150°C for E and 40-200°C for BT-E films. A sublinear/ohmic behaviour was observed in undoped PI films while incorporation of metallic ions resulted in a non-ohmic behaviour. Conduction mechanism was deduced from  $\log I$  versus  $V^{\frac{1}{2}}$  plots. Linear dependence was indicative of either Richardson-Schottky or Poole-Frenkel type of mechanism of conduction in undoped PI films. The  $\beta_{RS}$  values (Schottky's coefficient) were calculated from the slopes of the lines and were found to be twice the theoretical values at high temperature and field. This suggests the possibility of Poole-Frenkel type of mechanism at high temperature and field. At low temperature and field, however, the charge mobility was very low and hence a sublinear behaviour was observed.

In doped PI films, the slope values were twice at high field and low temperature but were 4-5 times the theoretical  $\beta$  values at high temperature. The mechanism of conduction might be a combination of ionic and electronic type. Activation energy for conduction was also calculated for all the films. Activation energy was in the range of 1.4 to 5.4 kcal/mole at lower temperatures and 10.2 - 23.2 kcal/mole at temperatures above 120°C.

Dielectric characteristics (  $\epsilon$  and  $\tan \delta$  ) as a function of frequency and temperature were also investigated. Increase in frequency resulted in a decrease in dielectric constant and loss values. Temperature dependence of  $\epsilon$  and  $\tan \delta$  at a fixed frequency of  $10^5$  Hz was also studied. Dielectric constant increased with addition of dopants.  $\tan \delta$  was maximum for highest frequency at low temperature while minimum for highest frequency at high temperature.

## CONTENTS

Page No.

CHAPTER I	: INTRODUCTION AND LITERATURE SURVEY	1
CHAPTER II	: POLYPYROMELLITIMIDES HAVING PENDANT MALEIMIDO GROUPS: SYNTHESIS AND CHARACTERISATION	38
	Introduction Experimental Characterisation Results and Discussion	
CHAPTER III	: POLYIMIDE FILMS CONTAINING METALLIC SALTS: PREPARATION & CHARACTERISATION	87
	Introduction Experimental Results and Discussion	
CHAPTET IV	: POLYIMIDE FILMS CONTAINING METALLIC SALTS:THERMAL & MECHANICAL PROPERTIES	100
	Introduction Experimental Results and Discussion	
CHAPTER V	: POLYIMIDE FILMS CONTAINING METALLIC SALTS: ELECTRICAL PROPERTIES	114
	Introduction Experimental Results and Discussion	
CHAPTER VI	: SUMMARY AND CONCLUSIONS	164
	SUGGESTIONS FOR FUTURE WORK	181
	REFERENCES	182
	BIODATA	
	PAPERS PUBLISHED AND PRESENTED	