Symmetry and stability of polypyromellitimides

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The poly(amic acid) and polyimide films from pyromellitic dianhydride and various diamines were prepared and characterized by infrared spectroscopy, elemental analysis etc. The thermal behaviour of polyimides was studied by thermogravimetric analysis and differential thermal analysis techniques. Polyimide I was found to be thermally more stable than polyimides II to V.

INTRODUCTION

Polyimide polymers are enjoying an increasing interest in the research for thermostable materials. Thermal stability of polyimide polymer is defined by the temperature range over which they retain useful properties. To exhibit more resistance the polymer should possess certain structural requirements. These include:

(1) A high molecular weight to provide strength, toughness and flexibility, and 'general plastic properties'.

(2) A maximum of highly stable structural units and a minimum of readily oxidizable hydrogen atoms in the chain.

(3) Connecting linkages for stable chain units which can resist the effect of heat.

(4) Resistance to mechanism by which the chains can readily undergo thermal decomposition.

(5) For fabricating the polymer into useful shapes, it must exist as a soluble or formable intermediate.

(6) The polymer must exhibit technologically useful properties for a considerable time at the desired temperature.

Polyimide polymers fulfil these requirements to a great extent and, as a result, a vast amount of research has been done in this field during the last 15 years[1–5]. Sroog[6] has presented an excellent review on polyimides while Koton[7] has discussed future prospects of polyimides. Normally polyimides are prepared in two stages. First, the diamine reacts with the dianhydride at a relatively low temperature to yield a soluble poly(amic acid). This is then cast into a film, heated to 300°C to eliminate water and cyclize into a polyimide.

Studies of the aldehyde–amine condensation reactions gave us several diamines in the purest state[8]. Some of these diamines have already been polycondensed with 3,3′,4,4′-benzophenonetetra carboxylic acid dianhydride (BPTD) to obtain thin, flexible and strong polyimide films[9]. Importance of polyimide films in aerospace vehicles, electrical devices, railways and defence has further attracted our attention toward their synthesis and characterization.

In the present investigation, a few novel polyimides have been prepared by reacting diamines with pyromellitic dianhydride (PMDA) in polar solvents. A well-known diamine, bis-(4-aminophenyl) methane (MDA), has also been reacted with PMDA to produce polyimide film for comparative studies. The diamines used are:

(i) Methane, triphenyl,4-methyl,4′,4″-diamine (MTMDA)
(ii) Methane, triphenyl,4,4′-diamine (MTDA)
(iii) Methane, triphenyl,4-chloro,4′,4″-diamine (MTCDA)
(iv) Bis(4-aminophenyl)1,1-butane (BAPB)

The reaction that takes place during polyimide formation is given in *Figure* 1.

EXPERIMENTAL

Dimethyl acetamide (DMAC) (Searle, Essex, England) was kept over P_2O_5 for 36 h and distilled thrice before use.

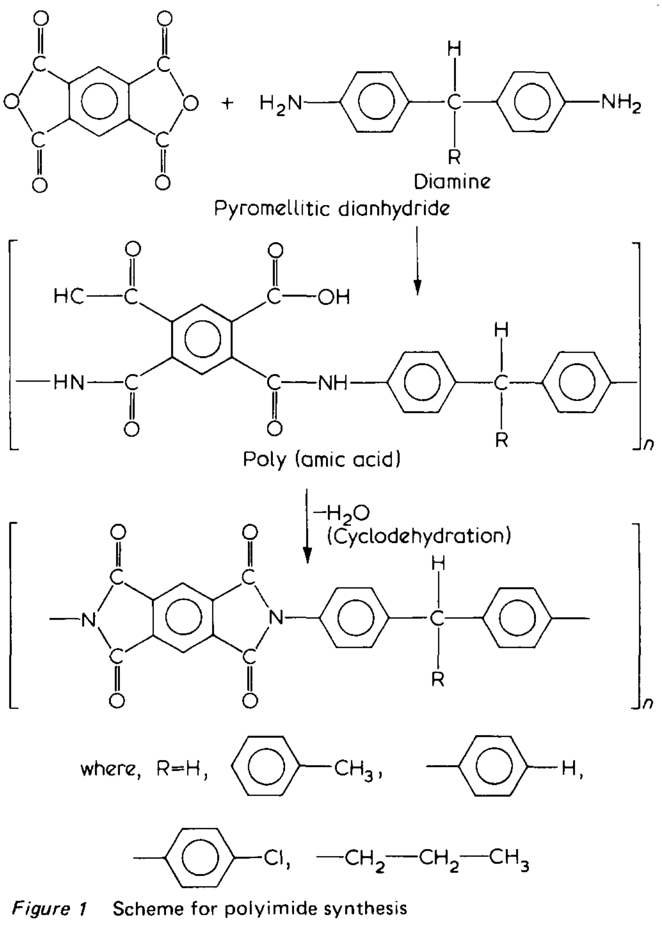

Figure 1 Scheme for polyimide synthesis

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Table 1 The reactants, reaction conditions and the elemental analysis of the products obtained.
Solvents = DMAC, DMF, DMSO & NMP
Yield = Quantitative

Polypyromellitimide	Reactants	Reaction conditions temp. °C for min.								Analysis			Reaction No.
		0	25	50–100	125–150	200	250	300		C	H	N	
I	MDA + PMDA	60	30	60	90	30	30	30	Found:	72.51	3.00	6.21	A
									Calc:	72.63	3.01	7.36	
II	MTMDA + PMDA	60	30	60	90	30	30	30	Found:	76.27	3.82	4.35	B
									Calc:	76.51	3.85	5.95	
III	MTDA + PMDA	60	30	60	90	30	30	30	Found:	76.00	3.40	6.00	C
									Calc:	76.31	3.55	6.14	
IV	MTCDA + PMDA	60	30	60	90	30	30	30	Found:	70.63	3.05	5.44	D
									Calc:	71.02	3.05	5.71	
V	BAPB + PMDA	60	30	60	90	30	30	30	Found:	73.80	4.20	6.33	E
									Calc:	73.93	4.26	6.61	

Dimethyl formamide (DMF), dimethyl sulfoxide (DMSO) and *N*-methylpyrolidone (NMP) were analytical grade reagents and further purified by distillation over P_2O_5.

Pyromellitic dianhydride (PMDA) was obtained from Koch–Light Laboratories, England, and was used without further purification.

MTMDA, MTDA, MTCDA and BAPB were prepared in this laboratory[8]. 4-MDA was obtained in the form of yellowish powder from Farbenfabriken Bayer A.G., West Germany. All the diamines were purified by distillation under reduced pressure followed by recrystallization from suitable solvent. All the reactants were perfectly vacuum dried at 30–35°C before use.

Properties

I.r. spectra were recorded on Perkin–Elmer 137 spectrometer. Thermogravimetric analysis (t.g.a.), differential thermal analysis (d.t.a.) and derivative thermo-gravimetry (d.t.g.) were made simultaneously with a Mom Budapest derivatograph OD 102 described by Paulic *et al.*[10] in air at a heating rate of 9°C min^{-1}. Before determining properties of the polyimides, all the film samples were conditioned at 100–110°C under reduced pressure of 10^{-3} mm Hg to remove the entrapped solvent and adsorbed moisture, if any. Electrical properties were determined at room temperature while u.v. spectra were recorded on Perkin Elmer 350 spectrophotometer.

Polymer synthesis

A 100 ml, three-necked, round-bottomed flask was equipped with a strong magnetic stirrer, nitrogen inlet, drying tube and thermowell. It was made perfectly dry by carefully heating it with the help of a blue burner flame, and then allowed to cool under a stream of dry nitrogen. To the flask were added 0.01 ml of diamine through a dry funnel and 45 ml dry DMAC through the same funnel simultaneously. The solution formed was stirred well and cooled to 0°C with ice-salt mixture. 0.01 mol PMDA was added over a period of 15 min through another dry funnel with vigorous stirring. Residual PMDA was washed in with 5 ml DMAC. The whole mixture was stirred for 40–60 min at 0°C and then for 1 h at 10°C. Dry nitrogen was vigorously bubbled through the solution throughout the reaction. A poly(amic acid) solution obtained at this stage was used for the film preparation. The reaction was repeated by changing the solvent only.

Poly(amic acid) films

Poly(amic acid) solutions were spread onto dry glass plates uniformly. The solvent was removed in an inert atmosphere below 70°C. The resultant colourless-to-pale-yellow films were only partly dry, and were peeled off gently from the plates after cooling.

Polyimide conversion

The poly(amic acid) films were dried at room temperature under reduced pressure to a solid level of 70–75%. The films were then slowly heated according to the heating schedules given in *Table* 1. The pale-yellow-to-yellow polyimide films obtained had good strength and flexibility.

RESULTS AND DISCUSSION

Table 1 describes the reactants used, polymerization conditions and analysis of all the polyimide polymers synthesized in the present investigation. It was observed that the addition of a dianhydride to the solution of a diamine gave a poly(amic acid) with higher molecular weight than that of the reverse addition or mixing together both the reactants. Success of the reaction wholly depended on the excellence of the drying conditions and the purity of the reactants.

All the diamines form fine yellowish solutions in DMAC (or other solvents) which turn reddish after the addition of a little quantity of PMDA. Colourless-to-pale-yellow poly(amic acid) solutions, when cast onto dry glass plates and dried partially to solid content of 70–75%, do not show any change in colour as the solvent is being removed. However, colour of the films changes to light yellow-to-fine-yellow at 125–150°C under vacuum, and it remains the same throughout the heating schedule.

Infrared spectra of poly(amic acid) films were recorded directly but such spectra did not give any useful peaks and, hence, the poly(amic acid) solutions were precipitated by water, filtered and dried to get powdered poly(amic acids). The i.r. spectra of these powdered poly(amic acids) were recorded in nujol mulls for reactions B, C, D and E respectively (*Table* 1). Poly(amic acid) spectra showed NH bands at 3200–3400 cm^{-1} and did not show any major absorption at 720–730 cm^{-1}, whereas spectra of corresponding polyimide films (polymers II–V) (*Table* 2) showed characteristic imide absor-

Table 2 Percentage weight loss at different temperatures for polypyromellitimide polymers

Temperature	Polypyromellitimide Polymers				
	I	II	III	IV	V
100	0.5	0.5	0.5	0.5	0.5
200	1.0	1.1	1.25	1.30	1.50
300	1.50	2.0	2.10	2.50	2.50
400	2.0	2.50	3.0	3.0	3.50
500	4.8	6.20	7.0	8.0	10.0
600	25.0	26.0	28.0	29.0	32.0
700	35.0	40.0	41.0	43.0	48.0
800	50.0	52.0	54.0	55.0	59.0
900	61.0	63.0	62.0	64.5	68.0

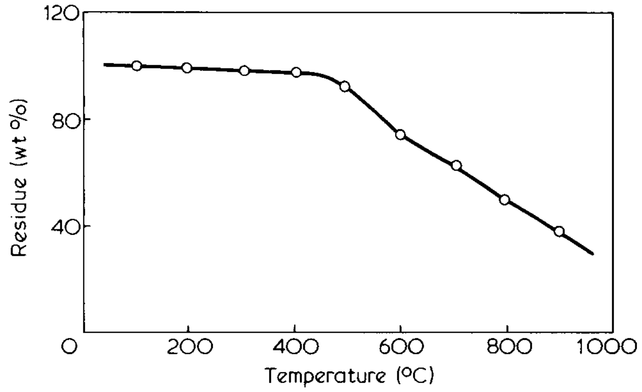


Figure 2 TGA curve in air at 9°C/min for polyimide I

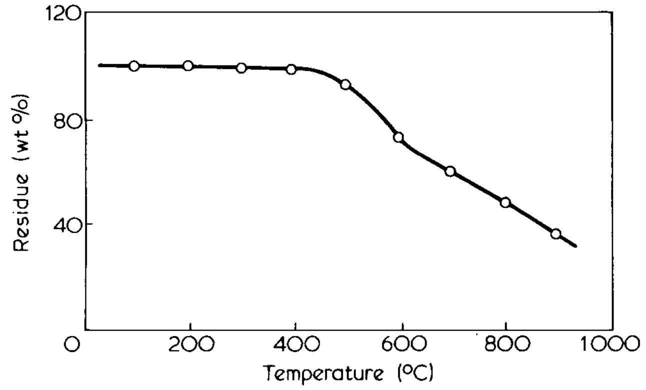


Figure 3 TGA curve in air at 9°C/min for polyimide II

ptions at 1780 cm^{-1}, and at 720–730 cm^{-1}. Complete conversion to polyimides was evident from the disappearance of characteristic NH bands at 3200–3400 cm^{-1} and appearance of characteristic imide bands at about 1780 cm^{-1}, 1730 cm^{-1}, 1380 cm^{-1} and at 730 cm^{-1} in all the polyimide film spectra. These films spectra were recorded directly without the use of solvent media or mulling agent.

U.v. spectra were also recorded. The results of analysis for carbon, hydrogen and nitrogen are given in *Table* 1. A fairly good correlation is observed between the experimental values and the calculated values for all the polyimides (I–V). However, in the case of polyimides I and II, experimental values for nitrogen are less by 1.5–2% and may be due to their higher thermal stability. Dine–Hart and Wright[11] have also faced the similar difficulty of not getting an exact elemental analysis for polyimides owing to their thermostable behaviour. This was further supported in the present studies by the weight losses in thermogravimetric analysis up to 900°C which are less than 68% (*Table* 2).

T.g.a. curves obtained for the five polyimides (I–V) are given in *Figures* 2–6, respectively. *Table* 2 summarizes loss of weights at different temperatures for a given polymer, and these were calculated from respective t.g.a. curves. It is observed that the conditioning of polymers i.e. heating at 100–110°C under reduced pressure of 0.5×10^{-3} mm Hg for 2.5 h was found to be necessary because it removes entrapped solvent and adsorbed moisture. This was clearly reflected in t.g.a. curves as they showed a remarkable increase in thermal stability after conditioning.

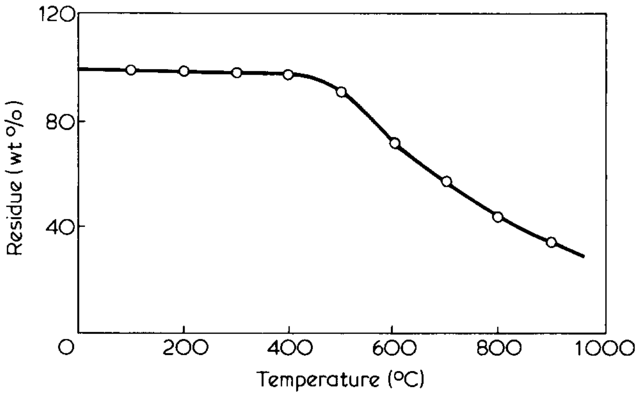


Figure 4 TGA curve in air at 9°C/min for polyimide III

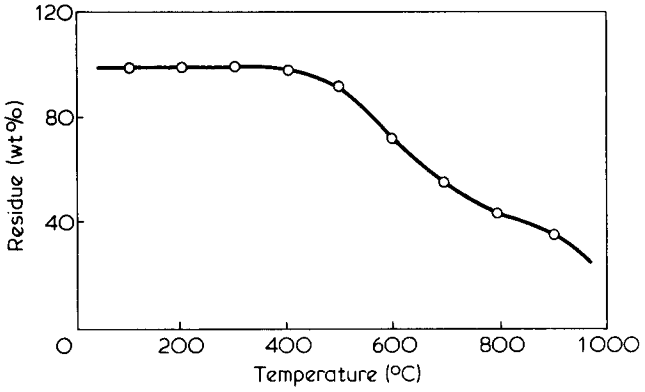


Figure 5 TGA curve in air at 9°C/min for polyimide IV

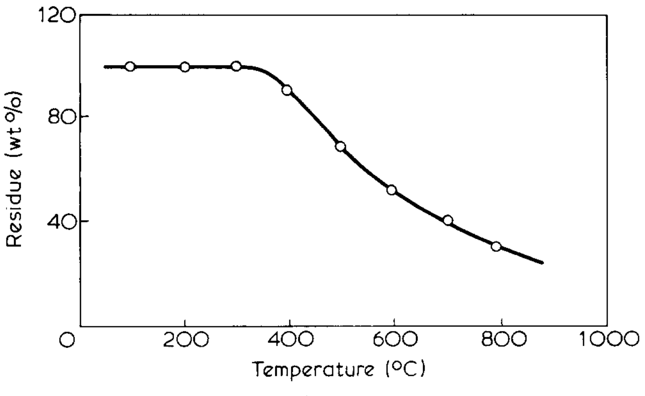
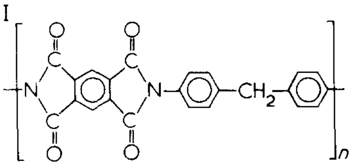
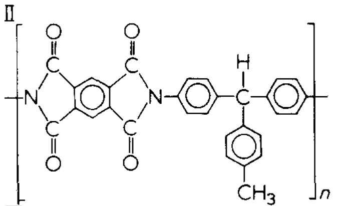
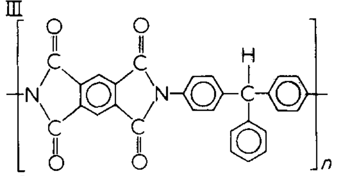
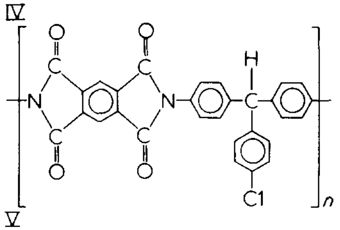
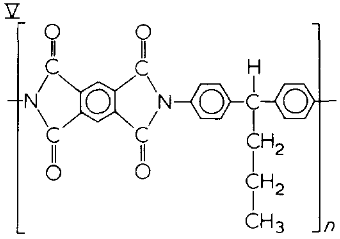
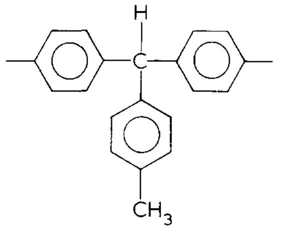
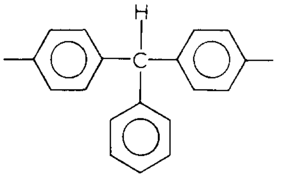
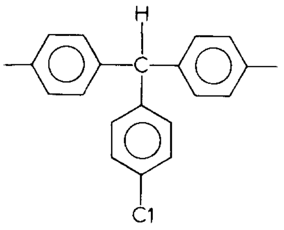
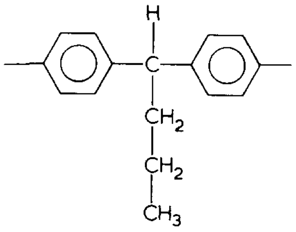


Figure 6 TGA curve in air at 9°C/min for polyimide V

Table 3 Temperature in °C for 0.10 and maximum percent weight-loss

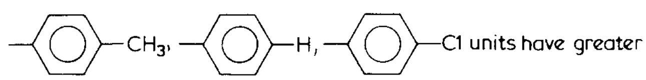
Polymer	T_0	T_{10}	$T_{max.}$	% wt. loss at 900°C
I 	430	530	740	61·0
II 	430	510	730	63·0
III 	415	515	715	62·0
IV 	405	500	710	64·5
V 	385	415	710	68·0

Amine units	T_0 °C
	430
	415
	405
	385

This group of polyimides (I–V) contains carbon atom in the diamine component connecting the two aromatic nuclei. In such cases, polymers are expected to give strong and flexible films with high resistance for thermo-oxidative degradation. The hinge groupings in polymer chains of this type are located between the phenyl rings which are in turn bound to the imide ring nitrogen by a single bond.

T_0 reflects the initial temperature up to which polymer retains its original chemical structure. Polymer weight gets stabilized at T_0, after the removal of entrapped solvent and adsorbed moisture (losses up to 2–3%), and then starts falling down due to the beginning of polymer chain breaking down process[12]. In the present investigation, polymer I seems to be more stable than the rest of the polymers (polymers II–V). This is, of course, due to the symmetrical nature of the diamine (4-MDA) used whereas, in other cases, one of the hydrogen of 'hinge' CH_2 is substituted by either *p*-substituted phenyl ring or alkyl chain. This is apparent from T_0 values obtained for polymers I–V (*Table* 3). Polymer I having symmetry in the amine unit shows a value of T_0 450°C whereas other polymers, having asymmetric amine units, are less stable. This can also be explained on the basis of the reagent reactivity i.e. –O–, CH_2-linked diamines are highly reactive whereas the presence of electron withdrawing substituents and hinges of the type –CO–, $(CF_2)_3$ etc. deactivate the diamine[11]. The presence of chlorine in MTCDA deactivates the amine partially while possibility of deactivation in MTMDA and MTDA is less. Polymer V is least stable in spite of the total absence of the effect of deactivation and may be due to the presence of alkyl chain, instead of phenyl ring at the hinge group.

T_{10} represents the 10% gravimetric weight loss, when process of weight loss due to elimination of highly volatile products are normally complete. Usually, at this stage the main polymer chain starts breaking down. Thus, more thermostable polymers have higher values of T_{10}. It is observed from *Table* 3 that the polymer having symmetric hinge, $-CH_2-$ with T_{10} value 530°C. Polymers containing:



units have greater T_{10} values whereas T_{10} value for polymer V with alkyl chain is 415°C.

T_{max} varies with a narrow range of temperatures i.e. 725 ±15°C. When T_{max} was reached, the gravimetric weight-loss of polymers is around 50%, and this indicates the decomposition stage of the imide structure of the polymer chain. The weight losses for all the polymers at 900°C are less than 68%.

Electrical properties

Table 4 shows the electrical properties of polyimide films such as volume resistivity, dielectric constant and dissipation factor (tan δ). The volume resistivity is of the

Table 4 Electrical properties of the polypyromellitimide films obtained

Polypyromelliti-mide polymer	Volume resistivity	Dielectric constant 1 Kc	Dielectric constant 10 Kc	Dissipation factor 1 Kc	Dissipation factor 10 Kc	u.v. resistance	Chemical resistance
I	2.0×10^{16}	3.12	3.10	0.0030	0.013	Good	Very good
II	1.90×10^{16}	4.60	4.59	0.0031	0.020	Good	Very good
III	1.80×10^{16}	4.61	4.58	0.0030	0.0021	Good	Very good
IV	1.20×10^{16}	6.90	6.84	0.0078	0.020	Good	Very good
V	1.75×10^{16}	3.40	3.37	0.00290	0.0160	Good	Very good

order of 10^{16} and is nearly similar for all the polymers. Higher values of dielectric constant and dissipation factor depend upon the presence of polar substituents and is true for polymer IV, where chlorine is present. These values are quite comparable to that of cellulose acetate and poly(vinyl acetate) films. The polyimide films also display good u.v. and chemical resistance. Change of solvent media from DMAC to DMF, DMSO etc. has very little or no effect on the thermal or electrical properties of the polyimide films.

CONCLUSION

Diamines and dianhydrides react in suitable polar solvents to produce polyimide films as the end-products. The thermal stability of polyimide polymer depends much upon the symmetry in the amine units, whereas polar substituents control the electrical properties. A superior quality of polyimide films result from diamine-PMDA reaction to that of diamine-BPTD reaction.[9]

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