Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

Preparation and Properties of Polyimides from Diisocyanates

G. D. Khune[a][b]
[a] National Chemical Laboratory, Poona, India [b] PRRC Building, New Mexico Institute of Mining and Technology, Socorro, New Mexico, (U. S. A.)

To cite this Article Khune, G. D.(1980) 'Preparation and Properties of Polyimides from Diisocyanates', Journal of Macromolecular Science, Part A, 14: 5, 687 — 711

To link to this Article: DOI: 10.1080/00222338008066642

URL: http://dx.doi.org/10.1080/00222338008066642

J. MACROMOL. SCI.–CHEM., A14(5), pp. 687-711 (1980)

Preparation and Properties of Polyimides from Diisocyanates

G. D. KHUNE*

National Chemical Laboratory
Poona-411008, India

ABSTRACT

A series of diisocyanates was polycondensed with pyromellitic dianhydride (PMDA) and benzophenone tetracarboxylic dianhydride (BPTD) and characterized by variations in substitution at one of the hydrogen of the CH_2 connecting the two phenyl rings. All the polycondensations were carried out under the same conditions (except the final heating period) in solutions of N,N-dimethylacetamide (DMAC), dimethyl sulfoxide (DMSO), dimethyformamide (DMF), and N-methylpyrrolidone (NMP). Polymers that separated out after prolonged heating at 130°C were filtered, washed with methanol, and dried.

Nineteen different polyimides were synthesized and characterized by elemental analysis, IR spectroscopy, and viscosity measurements. Some other properties, such as solubility, and thermal stability, were also investigated. Thermogravimetric analysis (TGA), differential thermal analysis (DTA), and derivative thermogravimetry (DTG) were carried out in air at a heating rate of 9°C/min to determine thermal properties.

---

*Present address: PRRC Building, New Mexico Institute of Mining and Technology, Socorro, New Mexico 87801 (U. S. A.).

INTRODUCTION

Thermostable polymers based on recurring imide units are now being studied for two purposes: to search for new methods of synthesis and to test the thermal and thermooxidative stability of those polymers which are very promising for technical applications. Intensive developmental work in this field has been in progress for the last two decades, culminating in the preparation of various novel polyimides [1-3].

A commercially most important method for polyimide synthesis involves the reaction between diamine and dianhydride, giving an intermediate poly(amic acid) which on cyclodehydration yields polyimide. Of the other methods, one that consists of the diisocyanate-dianhydride reaction in polar solvent is simple and useful [4-7].

Reaction of dianhydride with an excess of diisocyanate yields an imide-containing polymer useful as adhesive for rubber [8, 9]. Farrissey et al. [10] have obtained polyimide foams from the reaction of benzophenone tetracarboxylic dianhydride (BPTD) and polymethylene polyphenyl isocyanate in DMSO. Isocyanate-terminated polybutadiene intermediates and polymers therefrom could be processed to give thermosetting resins [11]. Alberino [12] has described soluble polyimides from diisocyanates and BPTD.

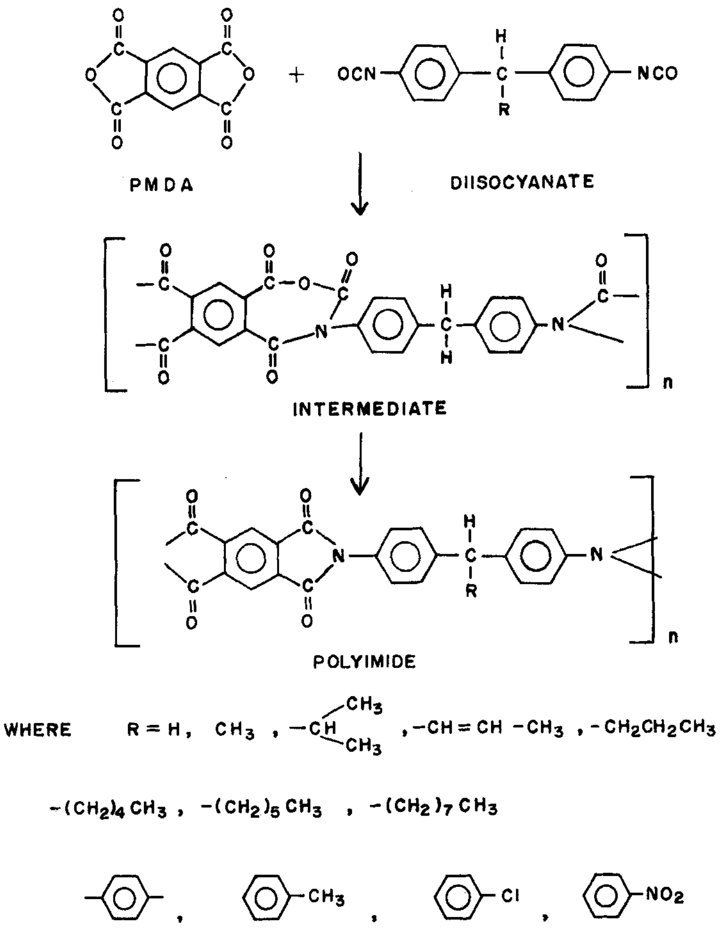
In the present investigation, polyimides from PMDA, BPTD, and various diisocyanates were prepared, and their properties were studied. In addition, bis(p-isocyanophenyl)methane (MDI) has been reacted with PMDA and BPTD to give polyimides as the end products for comparative studies. The diisocyanates used are: 4,4'-diisocyanotriphenylmethane (MTDI), 4-methyl,4',4"-diisocyanotriphenylmethane (MTMDI), 4-chloro,4',4"-diisocyano triphenylmethane (MTCDI), 4-nitro,4',4"-diisocyano triphenylmethane (MTNDI), bis(p-isocyanophenyl)1,1-ethane (BIPE), bis(p-isocyanophenyl),1,1-isobutane (BIPISO), bis(p-isocyanophenyl)1,1-butene (BIPBE), bis(p-isocyanophenyl)1,1-butane (BIPB), bis(p-isocyanophenyl)1,1-hexane (BIPHEX), bis(p-isocyanophenyl)1,1-heptane (BIPHEPT), and bis(p-isocyanophenyl)1,1-nonane (BIPNOE).

A general scheme for the polyimide synthesis is given in Eqs. (1) and (2).

EXPERIMENTAL

Materials

Pyromellitic dianhydride (PMDA) (Koch-Light Laboratories, England) was purified by sublimation under reduced pressure (0.8-1 Torr) at 205-235°C. BPTD was procured from Gulf Oil Co. in the form of yellow powder and was purified by sublimation under vacuum



(1)

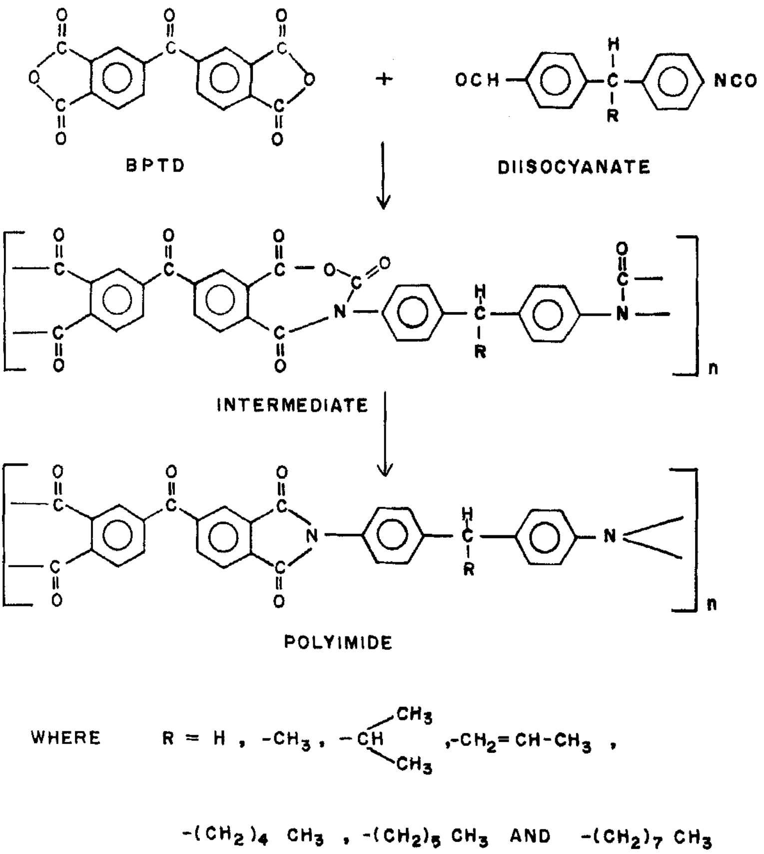
at 260-270°C/1 Torr. Before use both were vacuum dried for 2-3 hr.

DMAC, DMF, NHP, etc., all from Merck, West Germany were kept over P_2O_5 for 12 hr and then vacuum-distilled twice at 1-3 Torr.

Diisocyanates were prepared in this laboratory; they were distilled under reduced pressure and vacuum dried just before use [13]. MDI was obtained from Bayer, A. G. West Germany, and was vacuum-distilled prior to use.

Properties

Inherent viscosity measurements were made on 0.5% solutions of the polymers DMF(D) or H_2SO_4(H) at 30°C. IR spectra of the polymers



(2)

were recorded on KBr pellets by using a Perkin-Elmer spectrophotometer. TGA, DTA, and DTG were made simultaneously with a Mom Budapest derivatograph OD 102 described by Paulic et al. [14] in air at a heating rate of 9°C/min. Before determining the properties of polyimides, samples were conditioned at 100°C under reduced pressure of 10^{-5} Torr to remove entrapped solvent and adsorbed moisture, if any.

Polymerization

Diisocyanates were polycondensed with dianhydrides at both the ambient and elevated temperatures by following the general procedure described by Meyers [5]. In a typical preparation of polyimide, a dry diisocyanate (0.01 mole) was dissolved in about 30 ml of dry DMAC (or other solvents) and transferred in a 100 ml four-necked round-bottomed flask equipped with a strong magnetic stirrer, a reflux condenser, a drying tube, and a thermometer. The dianhydride was added in increments over a period of 10 min while the reaction temperature was maintained at 0°C with the help of an ice-salt mixture. The reaction mixture was slowly heated to 40°C and kept there for 2.5 hr. It was further heated to 90°C and maintained for 2 hr. A brisk CO_2 evolution was observed in MDI-dianhydride reaction at 90°C with the yellow precipitation of polyimide while in all other diisocyanate-dianhydride reactions CO_2 evolution was very much less at 90°C. The reaction temperature was further raised to 130°C, at which it was kept for 2 hr in the MDI-dianhydride reaction, whereas for all other reactions the duration of heating was 20-30 hr. In case of BIPHEX, BIPHEPT, and BIPNOE-anhydride reactions polyimides precipitated in low yields, even after prolonged heating at the boiling temperatures of the solvents. However, stoichiometric amount of CO_2 was evolved in BIPHEX, BIPHEPT, BIPNOE-dianhydride reactions when it was estimated quantitatively.

The polycondensations were repeated by making change in the solvent used; however, this same trend was noticed in all the solvents.

RESULTS AND DISCUSSION

This series of diisocyanates used for polycondensation was obtained by the phosgenation of the corresponding diamines. The diamines required in turn were synthesized by the condensation reactions of aldehydes with aniline in excellent yields.

Table 1 summarizes the preparative details and results of polymerization. The polycondensations were carried out from low (0°C) to higher (130°C) temperatures or at the boiling points of solvents used, (polar solvents such as DMAC, DMF, etc.). The time required for the MDI-dianhydride reaction to go to completion is strikingly less; the other reactions needed 10-15 times more heating at 130°C and the yields were still less.

The analysis of the dried polymer samples almost exactly corresponded to the theoretical for carbon, hydrogen, and nitrogen. This shows the perfectness of polymerization conditions and the absence of any crosslinking.

The intrinsic viscosity of the various polymers was determined in concentrated H_2SO_4 or DMF. It is obvious that a change in substitution at one of the hydrogen of the "hinge" CH_2 resulted in a decrease in $[\eta]$ of the polymer. It is important to note that the build-up of high molecular weight appears to be difficult in reactions yielding I-IV, though the diisocyanates used are more reactive than MDI. The time required for polymerization in diisocyanate PMDA or BPTD reactions was considerably more and still the polymers obtained were of lower molecular weight than those obtained in MDI-dianhydride reactions. This may be due to the change in the structure of the diisocyanate on introducing a substituted phenyl ring, thereby disturbing

TABLE 1. Reactants, Reaction Conditions, and Properties of the Polyimides Obtained

		Reaction time (hr)				Polymer isolation[a]		Inherent viscosity in conc. H_2SO_4(H) or DMF(D) (dl/g)	Elemental analysis			
No.	Reactants	At 0°C	At 40°C	At 90°C	At 130°C	Type	Yield (%)			C (%)	H (%)	N (%)
I	MTDI + PMDA	0.16	2.5	2	20	A	82-85	0.5100 (H)	Calcd:	76.59	3.85	5.95
									Found:	76.68	3.73	5.80
II	MTMDI + PMDA	0.16	2.5	2	20	A	87-90	0.5109 (H)	Calcd:	76.31	3.55	6.14
									Found:	76.20	3.49	6.00
III	MTCDI + PMDA	0.16	2.5	2	20	A	81-83	0.5318 (H)	Calcd:	71.02	3.05	5.71
									Found:	70.86	3.16	6.62
IV	MTNDI + PMDA	0.16	2.5	2	20	A	88	0.5216 (H)	Calcd:	69.46	2.99	8.38
									Found:	69.31	3.00	7.85
V	MDI + PMDA	0.16	2.5	2.	2	A	90-94	0.7001 (H)	Calcd:	72.63	3.01	7.36
									Found:	72.44	3.22	7.12
VI	BIPE + PMDA	0.16	2.5	2	20	A	82.0	0.5130 (H)	Calcd:	73.09	3.55	7.11
									Found:	73.00	3.41	6.69
VII	BIPISO + PMDA	0.16	2.5	2	20	A	66	0.4900 (H)	Calcd:	73.93	4.26	6.61
									Found:	73.81	4.04	6.43
VIII	BIPBE + PMDA	0.16	2.5	2	20	A	70	0.5010 (H)	Calcd:	74.27	3.81	6.66
									Found:	74.20	3.74	6.52
IX	BIPB + PMDA	0.16	2.5	2	20	A	68	0.5036 (H)	Calcd:	73.93	4.26	6.61
									Found:	73.68	4.10	6.21

X	BIPHEX + PMDA	0.16	2.5	2	25	A	43	0.3820 (H)	Calcd:	76.66	4.88	6.22
									Found:	76.40	4.69	6.00
XI	BIPHEPT + PMDA	0.16	2.5	2	25	A	40	0.3415 (H)	Calcd:	75.00	5.16	6.03
									Found:	74.89	5.28	6.12
XII	BIPNOE + PMDA	0.16	2.5	2	25	A	35	0.2976 (H)	Calcd:	75.61	5.69	5.69
									Found:	75.40	5.10	5.24
XIII	MDI + BPTD	0.16	2.5	2	2	A	90-92	0.6290 (H)	Calcd:	74.36	3.30	5.78
									Found:	74.15	3.00	5.25
XIV	BIPE + BPTD	0.16	2.5	2	30	B	48	0.2642 (D)	Calcd:	74.69	3.61	5.62
									Found:	74.10	3.54	5.39
XV	BIPISO + BPTD	0.16	2.5	2	30	B	45-47	0.2533 (D)	Calcd:	75.28	4.18	5.32
									Found:	75.00	4.14	5.19
XVI	BIPBE + BPTD	0.16	2.5	2	30	B	42.5	0.2805 (D)	Calcd:	75.55	3.81	5.34
									Found:	75.33	3.72	5.11
XVII	BIPHEX + BPTD	0.16	2.5	2	30	B	37.8	0.2387 (D)	Calcd:	75.81	4.68	5.05
									Found:	75.42	4.31	4.86
XVIII	BIPHEPT + BPTD	0.16	2.5	2	30	B	34.0	0.2254 (D)	Calcd:	76.05	4.92	4.92
									Found:	75.81	4.32	4.75
XIX	BIPNOE + BPTD	0.16	2.5	2	30	B	31.0	0.2189 (D)	Calcd:	76.51	5.36	4.69
									Found:	76.30	5.18	4.24

[a] Polymer isolation: (A) polyimide precipitated from solution; (B) polyimide remained in solution and was precipitated with a nonsolvent.

the symmetry of the polymer chain. As the aliphatic chain length at the "hinge" CH_2 increases, the yield as well as viscosity of the polymer decreases (polymers VII-XII and XV-XIX).

The ability of imide polymers to form stable solutions is of immense commercial and practical importance in the fabrication of these materials. In the solubility studies, it was observed that all the imide polymers were soluble in concentrated H_2SO_4, fuming nitric acid; a few of them were partially soluble in polar solvents, such as DMF and DMAC. Other solvents, viz., benzene, chloroform, alcohol, ethers, were unable to dissolve them. From Table 2, it is clear that the polyimides I-IX are not at all soluble in DMF and in other solvents while X-XII were slightly soluble. In general, these polyimides from BPTD and/or with long CH_2 chain were soluble in highly polar solvents. However, polyimide XIII was insoluble in DMF.

Meyers postulated a seven-membered ring intermediate for the diisocyanate-dianhydride reaction. In this study, IR spectra of the intermediate and that of the corresponding polymer resemble each other to a greater extent. Only the peak at 1660 cm^{-1} is intense in the spectrum of the intermediate due to the presence of additional CO group. As polyimide is being formed, CO_2 is released, and the intensity of the peak at 1660 cm^{-1} decreases. For example, polyimide IX precipitated out from the solution; the solution was filtered, and the intermediate was isolated from the filtrate by precipitation with water. As an illustration IR spectra of intermediate (Fig. 1) and of the corresponding polyimide (Fig. 2) are given. IR spectrum of polyimide II is also given in Fig. 3. They show the presence of imide bonds at 1780, 1730, 1380, and 730 cm^{-1}. A band at 1670-1660 cm^{-1} was also observed in the spectra of polyimides XIII-XIX which may be assigned to the benzophenone carbonyl group from the BPTD nucleus. The evolution of a stoichiometric amount of CO_2 and the presence of all the imide bands in IR spectra of polyimides XIII-XIX support the belief that the diisocyanate-BPTD reactions yield polyimides soluble in polar solvents. The solubility of such polymers may be due to their low molecular weights.

Figures 4-22 show TGA curves obtained for polyimides I to XIX. Table 3 summarizes the loss of weight at different temperatures for a given polymer, while Table 4 describes the temperature for zero, 10%, and maximum weight losses for corresponding polymers as calculated from TGA curves. A comparison of T_0 values of the polyimides investigated shows that the polymers with aliphatic units in the diisocyanate component exhibit lower thermal stability. Replacement of one of the hydrogens of the hinge CH_2 group by an aromatic nucleus does not increase the stability. On the contrary T_0 decreases by 5-10°C because of the disturbance to the symmetry of MDI due to the aromatic ring substitution. Koton and Sazanov [15] observed that the introduction of symmetrical substitution with respect to the central carbon atom of diaminodiphenyl methane increased the thermal stability of the polypyromellitimide as shown in Table 5.

TABLE 2. Solubility Behavior of Polyimides

Poly-imide	Solubility[a]							
	H_2SO_4	Fuming HNO_3	DMF	Benzene	$CHCl_3$	Ether	Alcohol	Acetone
I	++	++	-	-	-	-	-	-
II	++	++	-	-	-	-	-	-
III	++	++	-	-	-	-	-	-
IV	++	++	-	-	-	-	-	-
V	++	++	-	-	-	-	-	-
VI	++	++	-	-	-	-	-	-
VII	++	++	-	-	-	-	-	-
VIII	++	++	-	-	-	-	-	-
IX	++	++	±	-	-	-	-	-
X	++	++	±	-	-	-	-	-
XI	++	++	±	-	-	-	-	-
XII	++	++	±	-	-	-	-	-
XIII	++	++	-	-	-	-	-	-
XIV	++	++	+	-	-	-	-	-
XV	++	++	+	-	-	-	-	-
XVI	++	++	+	-	-	-	-	-
XVII	++	++	+	-	-	-	-	-

(continued)

TABLE 2 (continued)

Poly-imide	Solubility[a]							
	H_2SO_4	Fuming HNO_3	DMF	Benzene	$CHCl_3$	Ether	Alcohol	Acetone
XVIII	++	++	+	-	-	-	-	-
XIX	++	++	+	-	-	-	-	-

[a] Solubility: (++) = easily soluble; (+) = soluble; (±) = partially soluble; (-) = insoluble.

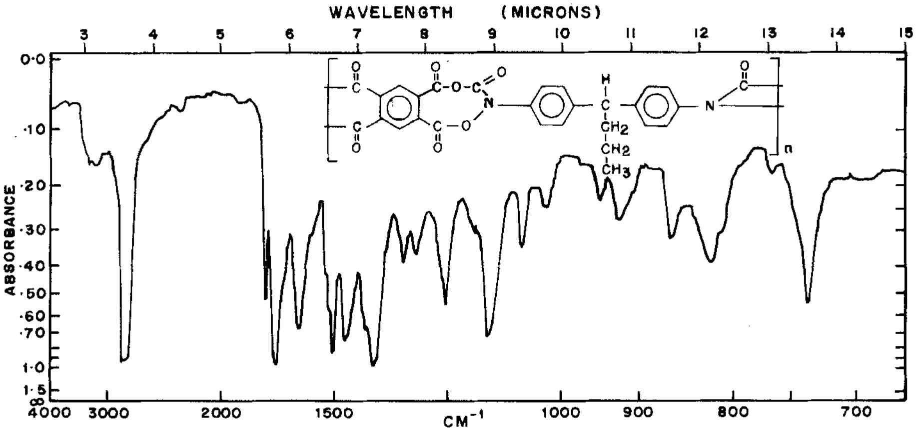


FIG. 1. IR spectrum of polyimide intermediate from BIPB-PMDA reaction.

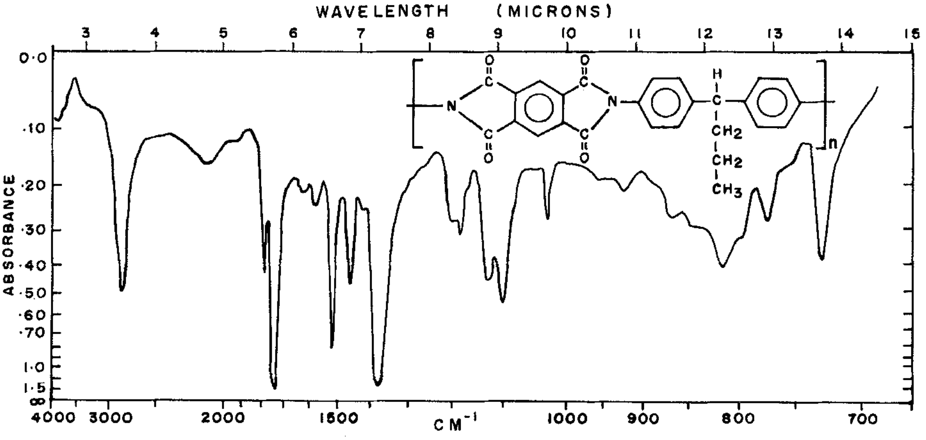


FIG. 2. IR spectrum of polyimide from BIPB and PMDA reaction.

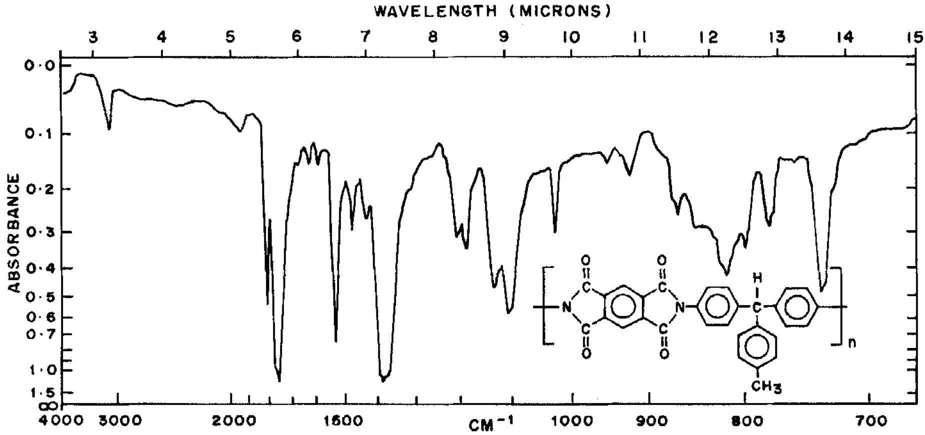


FIG. 3. IR spectrum of polyimide from MTMDI and PMDA reaction.

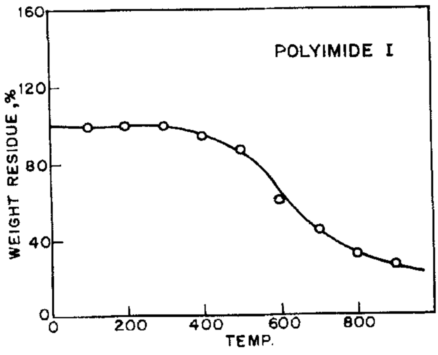


FIG. 4. TGA curve for polyimide I in air at 9°C/min.

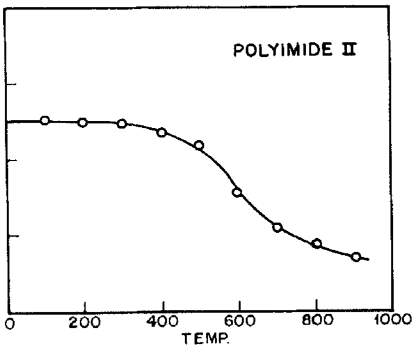


FIG. 5. TGA curve for polyimide II in air at 9°C/min.

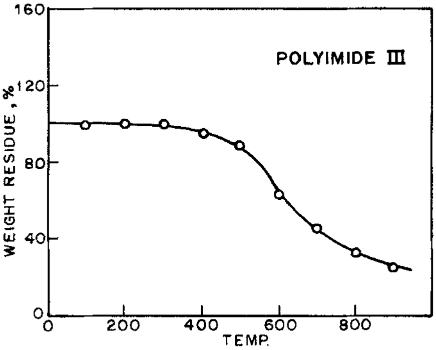


FIG. 6. TGA curve for polyimide III in air at 9°C/min.

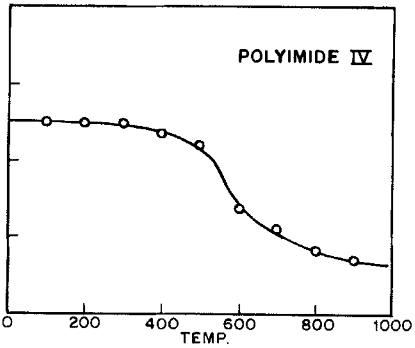


FIG. 7. TGA curve for polyimide IV in air at 9°C/min.

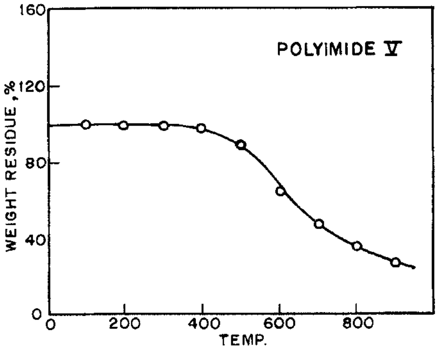


FIG. 8. TGA curve for polyimide V in air at 9°C/min.

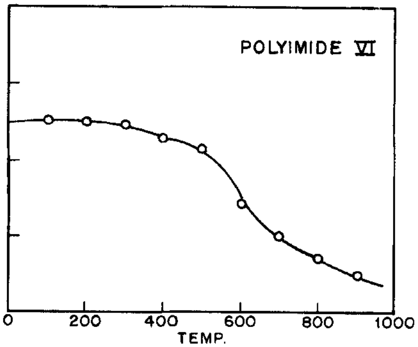


FIG. 9. TGA curve for polyimide VI in air at 9°C/min.

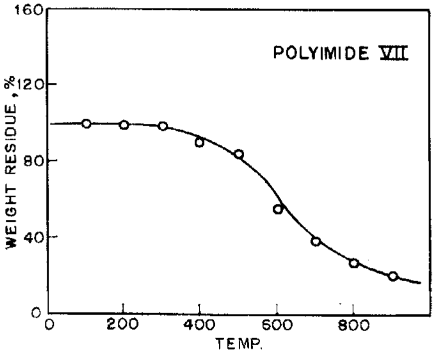


FIG. 10. TGA curve for polyimide VII in air at 9°C/min.

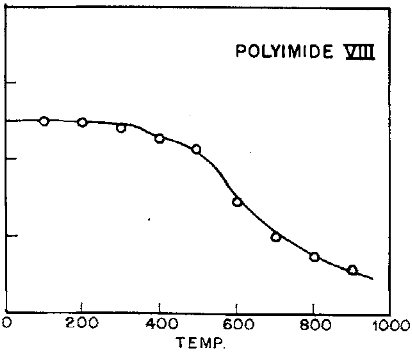


FIG. 11. TGA curve for polyimide VIII in air at 9°C/min.

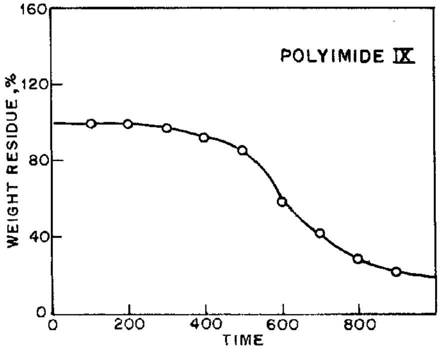


FIG. 12. TGA curve for polyimide IX in air at 9°C/min.

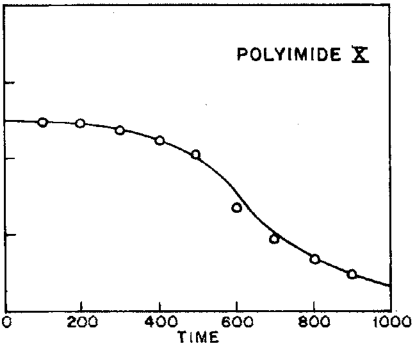


FIG. 13. TGA curve for polyimide X in air at 9°C/min.

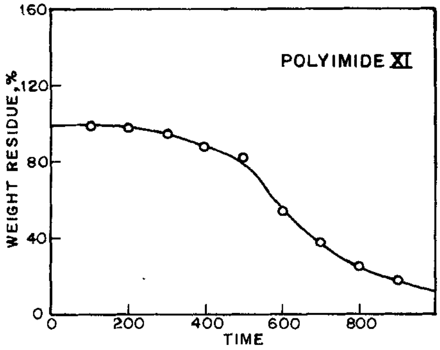


FIG. 14. TGA curve for polyimide XI in air at 9°C/min.

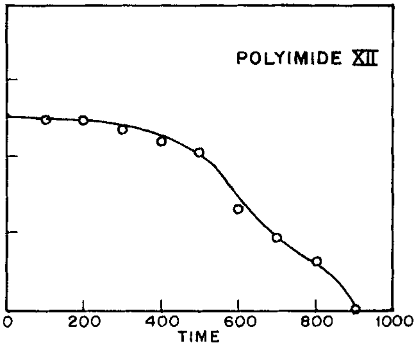


FIG. 15. TGA curve for polyimide XII in air at 9°C/min.

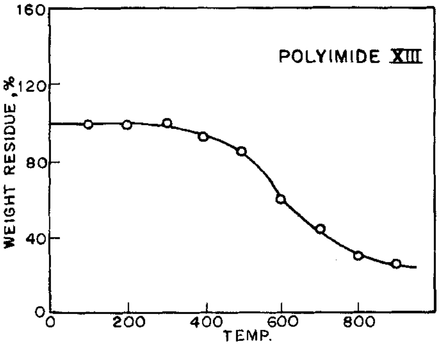


FIG. 16. TGA curve for polyimide XIII in air at 9°C/min.

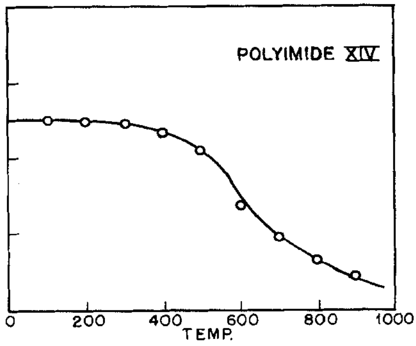


FIG. 17. TGA curve for polyimide XIV in air at 9°C/min.

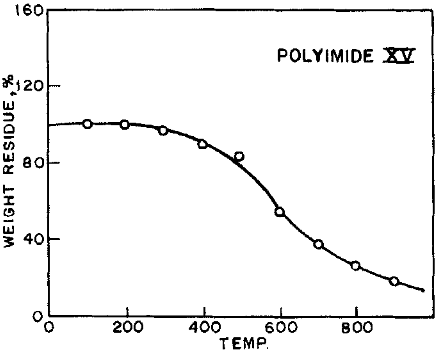


FIG. 18. TGA curve for polyimide XV in air at 9°C/min.

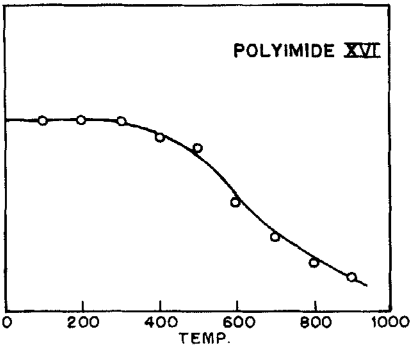


FIG. 19. TGA curve for polyimide XVI in air at 9°C/min.

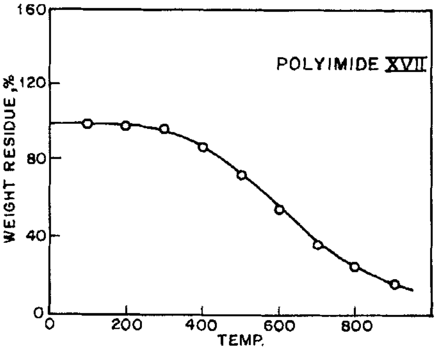


FIG. 20. TGA curve for polyimide XVII in air at 9°C/min.

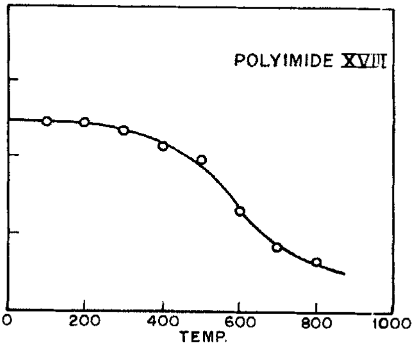


FIG. 21. TGA curve for polyimide XVIII in air at 9°C/min.

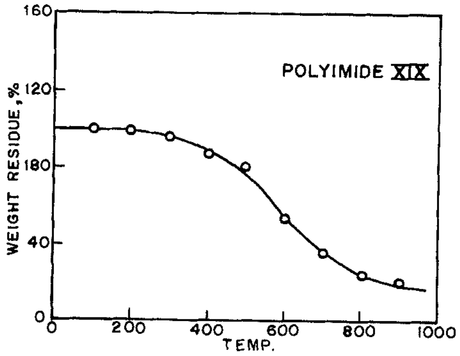


FIG. 22. TGA curve for polyimide XIX in air at 9°C/min.

A similar trend was observed in the polyimides obtained in the present study. An electron-withdrawing substituent at the para position of the third phenyl ring in case of polyimides III and IV increased T_0 by 5-10°C. Substitution of a CH_3 group at the para position of the third phenyl ring, however, did not show a change of T_0 in polyimide II. The T_0 value decreased markedly with the replacement of one of the hydrogen of the hinge CH_2 by an aliphatic group or chain. The aliphatic substitution affects the value of T_0 by 15-25°C. Unsaturation in the aliphatic chain shifts the T_0 value higher while replacement by an isomer or an increase in the chain length decreases the T_0 (polyimides VII-XII). The same trend was also observed in polyimides XIII-XIX.

T_{10}, the temperature for 10% gravimetric loss, is an important criterion for evaluating the thermal stability from TGA data in these highly heat-resistant polymers. Critical examination of the T_{10} values (Table 4) yields a correlation between the thermal stability of a polyimide and its structure. Particularly high values of T_{10} are found in those polyimides with symmetrical repeating units (polyimides V and XIII) or with an aromatic nucleus (polyimides I-IV). Introduction of longer aliphatic chain substituents into the main chain, however substantially lowered the T_{10} values.

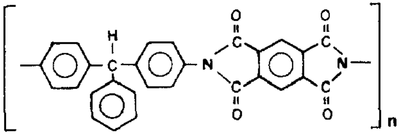
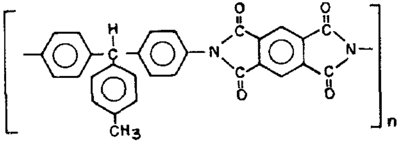
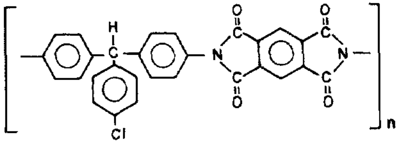
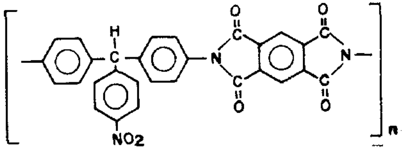
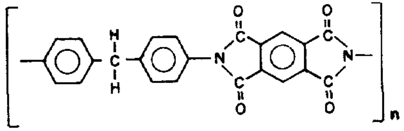
T_{max} characterizes the decomposition of the main polyimide chain of polymer, and for all the polymers T_{max} lies within a narrow range of temperature, i. e., 550 ± 25°C. However, small deviations are observed which can be assigned to the structural variations in the diisocyanate component.

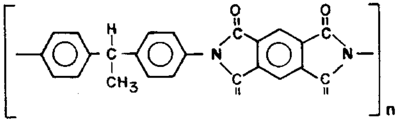
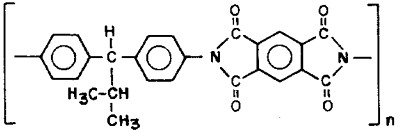
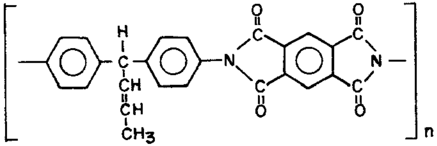
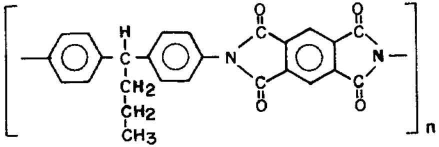
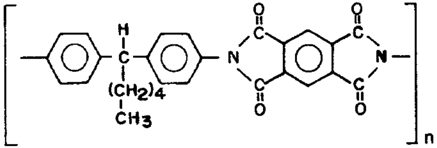
TABLE 3. Weight Loss at Different Temperatures for Polyimides

Poly-imide	Weight loss (%)								
	100°C	200°C	300°C	400°C	500°C	600°C	700°C	800°C	900°C
I	1.15	1.25	3.80	6.50	12.50	40.00	56.50	69.0	74.00
II	1.10	1.25	3.70	6.00	12.20	39.00	56.00	65.50	72.00
III	1.00	1.25	3.65	5.00	11.50	38.00	54.00	68.00	75.00
IV	1.00	1.25	3.70	5.15	12.00	38.50	55.00	69.00	73.50
V	0.35	0.60	2.25	3.00	10.15	36.00	52.00	63.00	72.00
VI	1.25	1.50	4.00	8.00	14.00	43.00	59.50	72.00	80.00
VII	1.50	2.00	5.00	10.00	15.00	45.00	61.00	73.00	80.00
VIII	1.50	1.75	4.50	9.00	14.00	42.50	60.00	70.00	77.00
IX	1.15	1.50	3.90	7.00	13.00	41.00	58.00	71.00	78.00
X	1.50	2.20	4.70	10.50	16.00	46.00	62.50	73.15	74.00
XI	1.50	2.50	4.90	11.00	17.00	46.50	61.50	74.00	76.00
XII	1.50	2.65	5.00	12.00	17.55	47.00	63.50	75.65	77.00
XIII	1.25	1.50	3.85	6.65	13.00	41.00	57.50	70.00	75.00
XIV	1.50	2.55	5.00	8.50	15.50	44.00	61.00	73.50	82.50
XV	1.50	2.70	5.50	11.00	16.50	46.50	63.00	74.50	82.00
XVI	1.50	2.60	5.00	10.50	15.00	43.50	61.50	73.00	81.00
XVII	1.50	2.75	5.60	12.00	17.50	45.00	63.50	74.00	75.00

XVIII	1.50	2.95	5.75	12.50	18.00	47.50	64.00	74.50	76.00
XIX	1.50	3.00	5.85	13.00	18.50	48.50	65.70	76.50	78.00

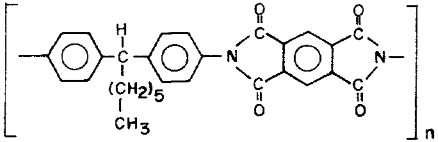
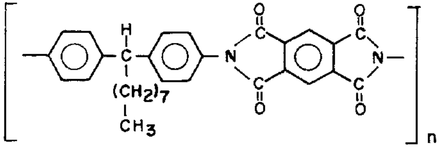
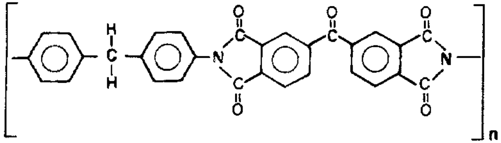
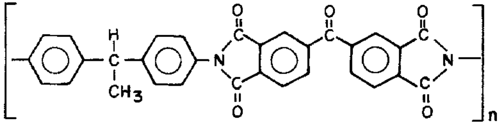
TABLE 4. T_0, T_{10}, and Temperature of Maximum Weight Loss

No.	Polyimide	T_0 (°C)	T_{10} (°C)	T_{max} (°C)	wt loss at 900°C (%)
I		365	455	565	74
II		365	450	565	72
III		375	460	560	75
IV		370	462	560	73.5
V		380	500	575	72

VI		340	440	550	80
VII		325	430	550	80
VIII		350	420	535	77
IX		320	410	530	78
X		315	405	525	74

(continued)

TABLE 4 (continued)

No.	Polyimide	T_0 (°C)	T_{10} (°C)	T_{max} (°C)	Wt loss at 900°C (%)
XI		310	400	525	76
XII		305	400	525	77
XIII		360	405	570	75
XIV		330	420	545	82.5

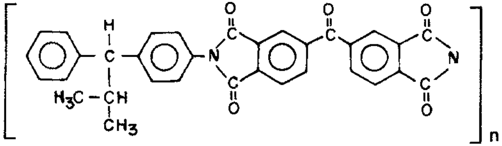
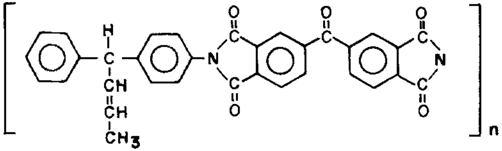
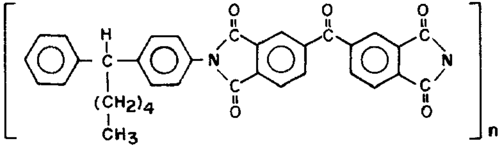
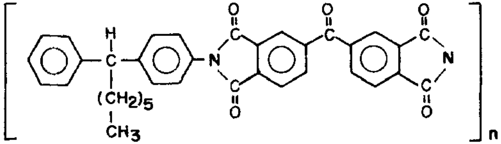
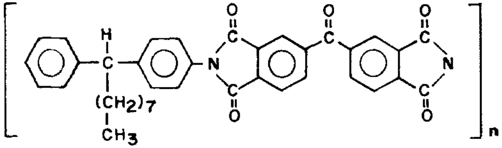
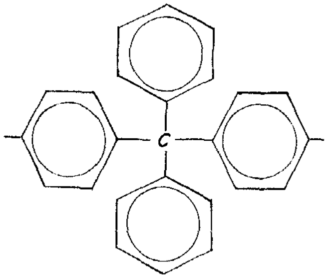
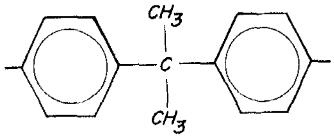
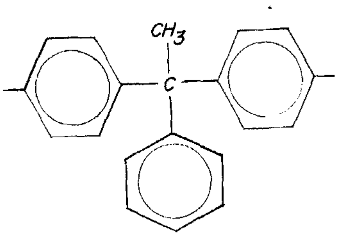
XV		320	410	535	82
XVI		340	405	520	81
XVII		305	400	520	75
XVIII		295	395	515	76
XIX		285	390	510	75

TABLE 5. Thermal Stability

Repeat unit	T_0 (°C)
	400
	360
	250

ACKNOWLEDGMENTS

The author would like to thank Dr. N. D. Ghatge, Head of the Polymer Chemistry Division, for his assistance in various phases of this work. The author also wishes to extend his appreciation to CSIR for a postdoctoral fellowship.

REFERENCES

[1] N. A. Adrova, M. I. Bessonov, L. A. Laius, and A. P. Rudakov, Polyimide, A new Class of Heat Resistant Polymers, Israel Program for Scientific Translation, 1969, pp. 13, 20, 22.

[2] C. E. Sroog, J. Polym. Sci. Macromol. Revs. Ed., 11, 161 (1976).
[3] G. M. Bower and L. W. Frost, J. Polym. Sci. A, 1, 3125 (1963).
[4] F. Kobayashi, K. Sakata, T. Mizoguchi, and P. Yamaguchi, Japan. Pats. 19,272 and 27,675 (1969); Chem. Abstr., 71, 113660 (1969); Chem. Abstr., 72, 56084 (1970).
[5] R. A. Meyers, J. Polym. Sci. A-1, 7, 2757 (1969).
[6] Y. Naya, (Tokyo Rayon Co. Ltd.), Netherlands Pat. 6,813,076 (1968); Chem. Abstr., 70, 29602d (1969).
[7] N. D. Ghatge and D. K. Dandge, Angew. Makromol. Chem., 56, 163 (1976).
[8] G. Mueller, R. Merten, W. Duenwald, and K. H. Mielke, Belg. Pat. 666,934 (1965); Chem. Abstr., 65, 3996 (1966).
[9] G. Mueller and R. Merten, U. S. Pat. 3,314,923 (1969).
[10] W. J. Farrissey, J. S. Rose, and P. S. Carleton, J. Appl. Polym. Sci., 14, 1093 (1970); Ibid., 16, 2983 (1972).
[11] W. I. Hergenrother and R. J. Ambrose, J. Polym. Sci., B12, 343 (1974).
[12] L. M. Alberino, W. J. Farrissey, Jr., and J. S. Rose, U. S. Pat. 3,768,458 (1973); Chem. Abstr., 78, 44254n (1973).
[13] N. D. Ghatge and G. D. Khune, Indian Chem. J., 9(3), 14 (1979).
[14] F. Paulik, J. Paulik, and I. Erdey, Talenta, 13, 1405 (1966).
[15] M. M. Koton and Yu. N. Sazanov, Vysokomol. Soedin., A15, 1954 (1973).

Accepted by editor May 23, 1979
Received for publication June 20, 1979