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Polyimides from Dianhydrides and Bis-(p-Aminophenyl) Alkane Diamines. II*

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ABSTRACT

Polyimides have been synthesized from pyromellitic dianhydride, 3,3',4,4'-benzophenone tetracarboxylic dianhydride, and bis(p-aminophenyl) alkane diamines using a two-step method. All the polycondensation reactions were carried out in dimethyl acetamide under identical reaction conditions. The poly(amic acids) obtained in the first step had inherent viscosities of 0.39-0.93 and were thermally converted to polyimides. The thermal stabilities of these polyimides were measured by dynamic thermogravimetry in air. Properties of the methyl-substituted polyimides are compared with those of unsubstituted ones. The introduction of a methyl group into the polymeric chain led to a decrease in the inherent viscosity and the thermal stability.

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INTRODUCTION

A number of polyimides have been prepared [1-7] from tetracarboxylic dianhydride and diamines by the two-step polycondensation technique, i.e., ring-opening polymerization and subsequent cyclodehydration by thermal or chemical method. The excellent thermooxidative and chemical stability of the wholly aromatic polyimides is generally attributed to the structural features of the polymers, including the inert nature of the imide and aromatic groups. Attempts have been made in the past to improve solubility thermooxidative stability and processing characteristics of polyimides.

The purpose of the present investigation was to study the effect of methyl substitution on the properties of the polyimides. Thus, the present work relates to the synthesis and properties of polyimides from the following diamines with pyromellitic dianhydride (PMDA) and 3,3',4,4'-benzophenone tetracarboxylic dianhydride (BTDA).

1. 2,2-bis(4-aminophenyl) propane (PRDA)
2. 2,2-bis(4-amino-3-methylphenyl) propane (MPRDA)
3. 1,1-bis(4-aminophenyl)-1-phenylethane (PHDA)
4. 1,1-bis(4-amino-3-methylphenyl)-1-phenylethane (MPHDA)

Although the reaction of PRDA with PMDA has been reported previously, the polymer was again synthesized for this comparative study.

EXPERIMENTAL

Materials

PMDA and BTDA were purified by crystallization from dry acetic anhydride.

N,N-Dimethyl acetamide (DMAC) was dried with phosphorous pentoxide and distilled.

All the diamines were prepared in our laboratory and distilled under reduced pressure. PRDA and MPRDA were recrystallized from distilled water and aqueous ethanol, respectively. PHDA and MPHDA were recrystallized from a 1:1 mixture of benzene-petroleum ether (60-80).

Properties

NMR spectra were recorded in $CDCl_3$ on a Varian T-60 spectrophotometer with TMS as the internal standard.

IR spectra were recorded on a Pye Unicam SP-300 spectrophotometer.

Thermogravimetric analysis (TG), differential thermal analysis (DTA), and derivative thermogravimetry (DTG) were made simultaneously in air at a heating rate of 10°C/min with a Netzsch STA 409.

Inherent viscosity measurements were made with 0.5% solutions of the poly(amid acids) in DMAC at 30°C.

Synthesis of Diamines

Diamines were synthesized by reacting methyl ketones and substituted or unsubstituted aminobenzene hydrochloride with an unoccupied p-position according to a procedure derived by Ghatge and Mulik [8]. The diamines were characterized by elemental analysis and spectral data such as IR, NMR, and mass. The properties of all the diamines and the chemical shifts caused by different protons in NMR spectra are listed in Table 1. The NMR spectra of these diamines exhibit the expected chemical shifts and integrated intensities. The IR spectra of all the diamines showed the characteristic absorptions for primary amino group at 3340-3360 and 3430 cm^{-1}. The study of the mass spectra of all diamines suggests the molecular weights agree with the calculated ones.

Polymer Synthesis

Poly(Amic Acid) Synthesis

The polymerization was carried out in a nitrogen atmsophere by the addition of equimolar dianhydride to a stirred solution of diamine in DMAC at 0°C. The resulting solution was stirred for 1 h at 0 and 10-15°C. Finally, the reaction mixture was kept overnight at room temperature. The viscous poly(amic acid) solution obtained at this stage was used for film preparation.

Conversion of Poly(Amic Acid) to Polyimide

The poly(amid acid) was converted to polyimide by the thermal method.

The poly(amic acid) solution was spread uniformly on a Pyrex glass plate. The solvent was removed below 70°C in a nitrogen atmosphere. The film formed was peeled off gently and dried further under reduced pressure at room temperature. It was then cyclodehydrated in a vacuum oven at various temperatures.

RESULTS AND DISCUSSION

On comparing the viscosity (η_{inh}) (Table 2) of poly(amic acids) prepared from different diamines, it was found that the polymer obtained

TABLE 1. Properties and Proton NMR Shifts of Diamines

				Proton NMR shifts in		
No.	Diamine	mp, °C	Yield, %	Aromatic protons	Amino protons[a]	Aliphatic protons
1	PRDA	132	55	6.50 (4H,d)[b] 7.00 (4H,d)	3.43 (4H,s)[b]	1.60 (6H,s)
2	MPRDA	71	50	6.52 (2H,d) 6.93 (4H,d)	3.43 (4H,s)	1.6 (6H,s) 2.1 (6H,s)
3	PHDA	159	45	6.48 (4H,d) 6.88 (4H,d) 7.17 (5H,s)	3.50 (4H,s)	2.07 (3H,s)
4	MPHDA	152	40	6.20 (2H,d) 6.48 (4H,d) 6.87 (5H,s)	3.27 (4H,s)	2.0 (9H,s)

[a] Exchangeable with D_2O.

[b] s = singlet, d = doublet.

with 2,2-bis(4-aminophenyl) propane and PMDA or BTDA has a higher viscosity than the polymers from other diamines. This is attributed to the low basicity (due to electronic effects) and hence the low reactivity of these diamines. The presence of an ortho substituent, i.e., a methyl group (in the case of MPRDA and MPHDA), results in the formation of low molecular weight poly(amic acid) compared to the corresponding unsubstituted diamine (i.e., PRDA and PHDA). This is due to the inductive and steric effect of the methyl group, and is consistent with the results reported earlier.

Infrared Spectra

Infrared spectra of all the poly(amic acids) and polyimides showed characteristic absorption. Complete conversion to polyimide was evident from the disappearance of poly(amic acid) bands at 3200-3400 and 1650 cm^{-1} and the appearance of characteristic imide bands at 1780, 1720, 1380, and 720 cm^{-1} in all the polyimide film spectra.

Thermal Stability

In order to evaluate the effect of the diamine component on the thermal stability of polyimides, the thermooxidative degradation of polymers was studied by the TG method.

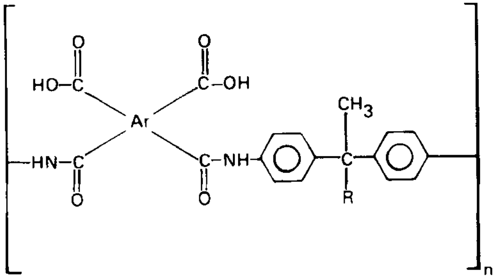
Polyimides with PMDA

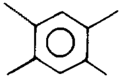
The primary thermograms for the decomposition of polypyromellitimides are given in Fig. 1. Temperature characteristics such as initial decomposition temperature (IDT), temperature for 10% weight loss (T_{10}), and temperature for maximum rate of decomposition (T_{max}) are given in Table 3.

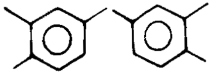
The results show that the initial decomposition temperature (taking the sharp drop in the curves as the onset of the decomposition reactions) of these polyimides varies between 390 and 415°C. A further increase in temperature causes rapid decomposition. The small weight loss at the beginning of the process (3 ± 1%) can be attributed to the removal of traces of solvent and adsorbed moisture from the polyimides.

It has been shown earlier [5-7, 9] that thermal stability of polyimides is greatly affected by the structure of the diamine. A comparison of initial decomposition temperature (IDT) of polyimides (Table 3) shows that Polyimide A (obtained from PRDA) has a higher thermal stability than the other polyimides because it contains symmetrical methyl groups in the diamine component. Substitution of a phenyl group for a methyl group at the central carbon atom connecting two aromatic rings or substitution of a methyl group ortho to the amino function in

TABLE 2. Inherent Viscosities of Poly(Amic Acids)



No.	Dianhydride	Diamine	Ar	R_1	R	η_{inh}, dL/g	Abbreviation for the corresponding polyimide
1	PMDA	PRDA		H	CH_3	0.931	A
2	"	MPRDA	"	CH_3	CH_3	0.785	B
3	"	PHDA	"	H	C_6H_5	0.634	C
4	"	MPHDA	"	CH_3	C_6H_5	0.586	D

5	BTDA	PRDA		H	CH_3	0.688	E
6	"	MPRDA	"	CH_3	CH_3	0.627	F
7	"	PHDA	"	H	C_6H_5	0.576	G
8	"	MPHDA	"	CH_3	C_6H_5	0.390	H

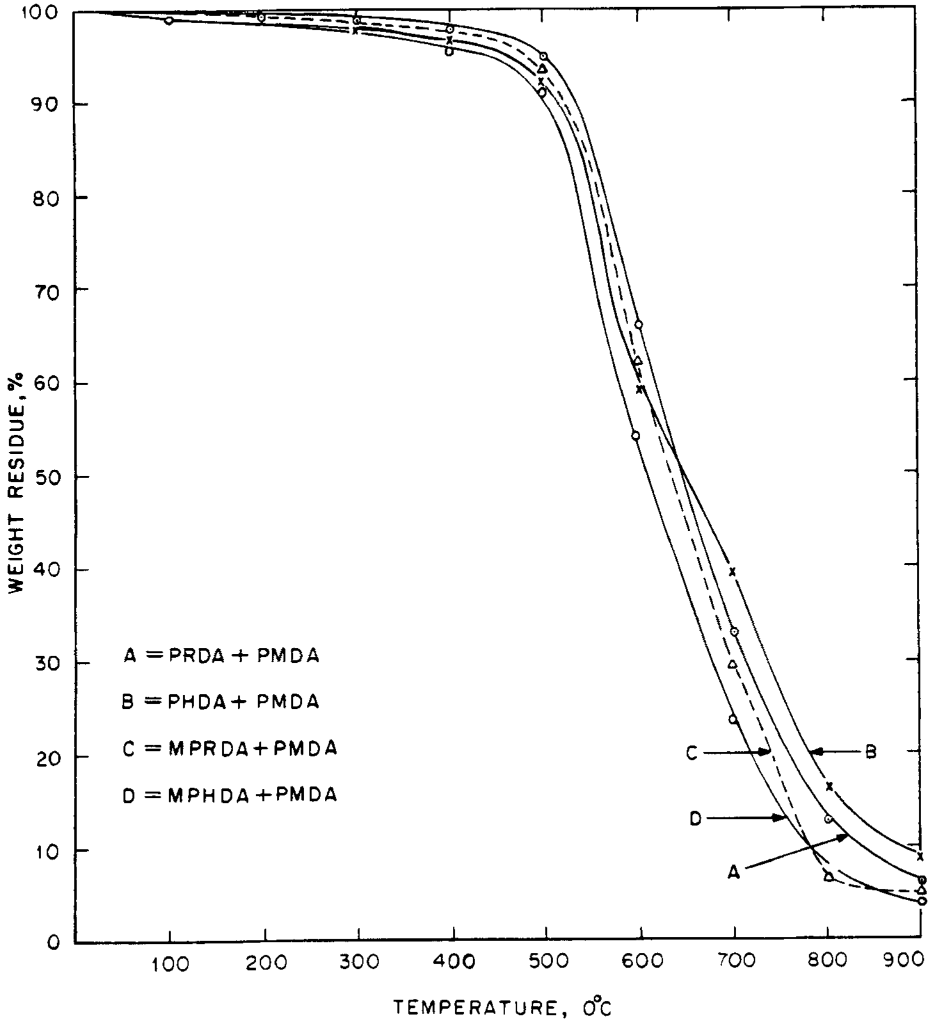


FIG. 1. TG curves in air at 10°C/min for Polyimides A, B, C, and D.

TABLE 3. Temperature Characteristics and Position of Exothermic Transition Peaks of Polyimides[a]

Polyimide	IDT, °C	T_{10}, °C	T_{max}, °C	Peak position, °C
A	415	525	600	450-720
B	410	520	590	435-730
C	405	518	600	425-715
D	400	505	585	415-735
E	405	515	595	425-735
F	400	510	590	410-730
G	395	505	595	400-730
H	390	500	580	395-725

[a] IDT = Initial decomposition temperature. T_{10} = Temperature for 10% weight loss. T_{max} = Temperature for maximum rate of decomposition.

diamine has a marked effect on the thermal stability of polyimides due to loosening of the structural symmetry and rigidity of the polymer molecule.

T_{max}, the temperature for the maximum rate of decomposition, was derived from DTG curves. The results indicate that T_{max} for the polypyromellitimides studied varies within a narrow range of temperatures (590 ± 10°C).

No endothermic transition associated with melting or glass transition was observed in the DTA curves. However, an exothermic peak was observed in all polyimides. The position of this exothermic transition is given in Table 3.

Thus, on the basis of IDT, T_{10}, and T_{max}, the thermal stability of polyimide with MPRDA (Polymer B) or MPHDA (Polymer D) is less than that of the corresponding PRDA (Polymer A) or PHDA (Polymer C), respectively.

Polyimides with BTDA

Another dianhydride of importance for the preparation of polyimides is BTDA.

As in the polypyromellitimide series, the inherent viscosity of poly(amic acid) prepared with BTDA and PRDA was higher (0.688) than those of other polymers (Table 2).

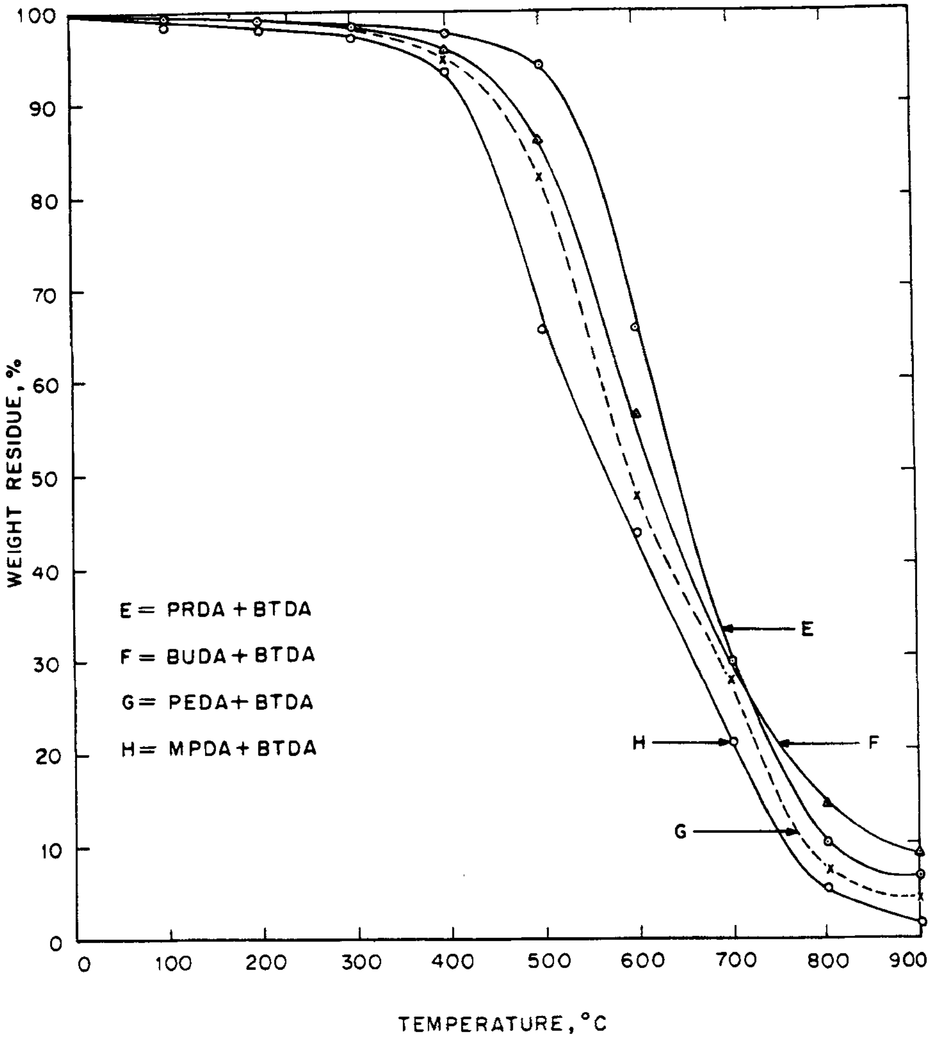


FIG. 2. TG curves in air at 10°C/min for Polyimides E, F, G, and H.

The primary thermograms for the decomposition of polyimides are given in Fig. 2. Temperature characteristics, such as IDT, T_{10}, T_{max}, and the position of the exothermic transition peak are given in Table 3. A good correlation was observed between the thermoxidative stability of polyimide and the structure of the diamine component used to obtain polyimide. Thus, among Polyimides E, F, G, and H, Polyimide E has a higher thermal stability than Polyimides F, G, and H as evidenced from Table 3.

Comparison of the thermal stabilities of Polyimides A-D with those of E-H indicates that polypyromellitimides are thermally more stable than the corresponding polyimides with BTDA.

REFERENCES

[1] V. L. Bell, L. Kilzer, E. M. Hett, and G. M. Stokes, J. Appl. Polym. Sci., 26, 3805 (1981).

[2] G. L. Brode, J. H. Kawakami, G. T. Kwiatkowski, and A. W. Bedwin, J. Polym. Sci., Polym. Chem. Ed., 12, 575 (1974).

[3] T. Ueda, M. Takahashi, S. Hishiki, and T. Imai, Ibid., 17, 2459 (1979).

[4] R. A. Dine-Hart and W. W. Wright, Makromol. Chem., 153, 237 (1972).

[5] N. D. Ghatge and G. D. Khune, Angew. Makromol. Chem., 79, 93 (1979).

[6] N. D. Ghatge and G. D. Khune, Polymer, 21, 1052 (1980).

[7] N. D. Ghatge and N. N. Maldar, Proceedings of 28th IUPAC Symposium on Macromolecules, Amherst, July 12-16, 1982, p. 302.

[8] N. D. Ghatge and U. P. Mulik, J. Polym. Sci., Polym. Chem. Ed., In Press.

[9] M. M. Koton and Yu. N. Sazanov, J. Therm. Anal., 7, 165 (1972).

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