Preparation and Characterization of 3,3′,4,4′-Benzophenone Tetracarboxylic Dianhydride–Pyromellitic Diahydride Alternating Polyimides

YU YANG,* XUJIE YANG, ZHENGLIANG ZHI, LUDE LU, XIN WANG

Materials Chemistry Laboratory, Nanjing University of Science and Technology, Nanjing 210094, People's Republic of China

ABSTRACT: Four kinds of 3,3′,4,4′-benzophenone tetracarboxylic dianhydride (BTDA)–pyromelliitic dianhydride (PMDA) alternating polyimide (BTDA–PMDA API) were obtained by reacting 1 mol BTDA with 2 mol diamines to form BTDA chain-extended diamines (BTDA CED), followed by the addition of 1 mol PMDA to yield the BTDA–PMDA alternating polyamic acids (BTDA–PMDA APA), and finally by imidizing them thermally. BTDA CED were characterized by elemental analysis, infrared (IR), and ^{1}H-NMR spectroscopy. The structures of BTDA–PMDA APA and BTDA–PMDA API were investigated by IR and ^{1}H-NMR spectroscopy, and their thermal properties and interfacial tension were also studied. Furthermore, the characteristic properties of BTDA–PMDA API were compared with their corresponding homopolyimides from BTDA (BTDA HPI) and from PMDA (PMDA HPI). It was found that the alternating condensation polymerization is an effective method to modify polyimides interfacial tension with a small influence on the thermal stability. © 1997 John Wiley & Sons, Inc. J Appl Polym Sci **64:** 1585–1593, 1997

Key words: preparation; characterization; 3,3′,4,4′-benzophenone tetracarboxylic dianhydride; pyromellitic diahydride; polyimide

INTRODUCTION

Polyimides were first prepared by Bogert and Renshaw[1] in 1908, and they were then widely used and rapidly developed because of their outstanding characteristics of good tractability, high thermal stability, great mechanical stability, good water resistance, grind resistance, fire and radiation resistance, and relatively low cost. For practical purposes, much work, which may be classified into two aspects, has been done to modify the polyimides. One is to introduce such groups as amide,[2] sulfone,[3] ether,[4] among others, into the chains; our recent work in the preparation of polyimides with metals in the main chain has been reported.[5,6] The other is to react no less than two diamines with a dianhydride, or vice versa, to get alternating polyimides.[7] According to Adrova et al.,[8] cocondensed polyimides are superior to their corresponding homopolyimides in regard to mechanical and thermal properties, as well as adhesive strength with metals and glass.
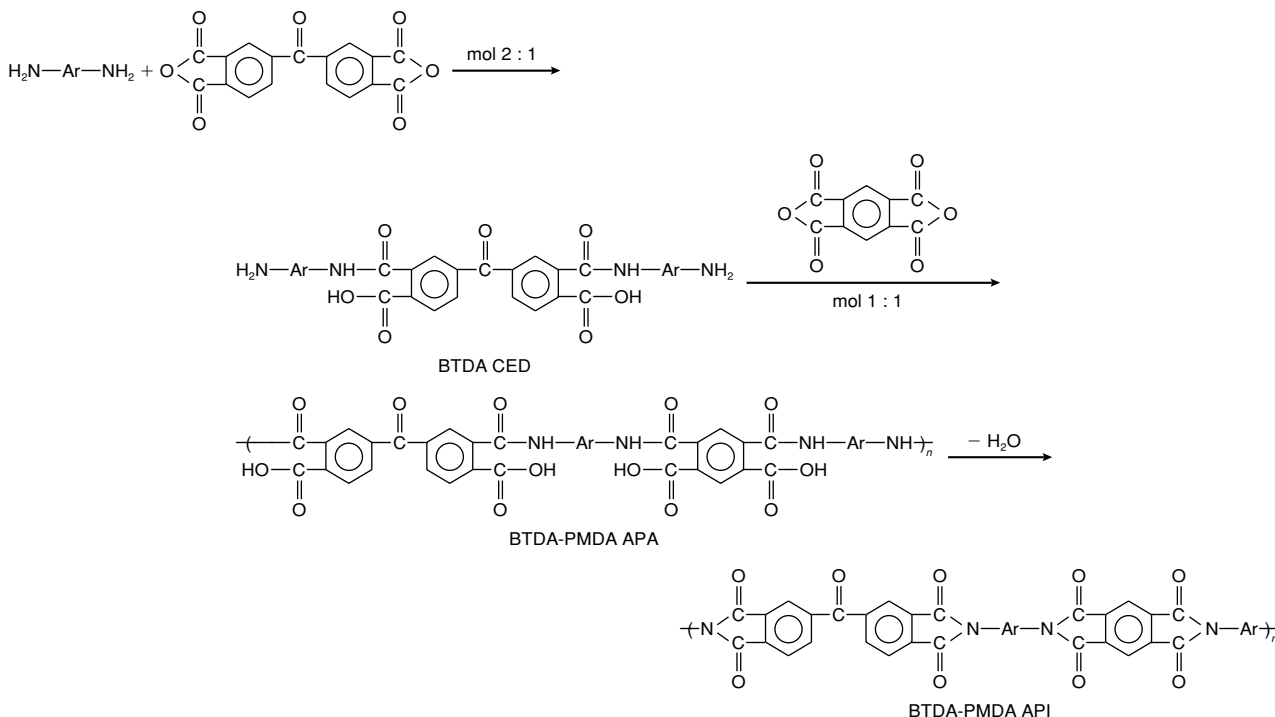
Strictly alternating copolyimides from two different dianhydrides and one aliphatic spacer prepared by the reaction of imide containing diisocyanates with different dianlydrides have been reported by Avadhani and Vernekar.[9] They found that these

H₂N—Ar—NH₂ + (dianhydride) → mol 2 : 1

BTDA CED

H₂N—Ar—NH ... NH—Ar—NH₂   → mol 1 : 1 (PMDA dianhydride)

BTDA-PMDA APA

(...)ₙ   − H₂O →

BTDA-PMDA API

Scheme 1

polyimides had very good solubility in many polar solvents, and the thermal stability was intermediate between the two sets of homopolyimides. Little information, however, is available concerning the surface energy of these kinds of polymers. In the present investigation, a series of 3,3′,4,4′-benzophenone tetracarboxylic dianhydride (BTDA)−pyromelliitic dianhydride (PMDA) alternating polyimide (BTDA−PMDA API) were synthesized and characterized; their thermal properties, interfacial tension, and infrared (IR) and ^{1}H-NMR spectra were studied and compared with their corresponding homopolyimides.

EXPERIMENTAL

Materials and Instrumentation

N,N′-dimethyl formamide (DMF), p-phenyl diamide, 4,4′-diamino dibenzene, 4,4′-diaminodiphenyl methane, and 4,4′-diaminodiphenyl ether were of analytical grade. PMDA and BTDA were the products of the Shanghai Chemical Reagents Company. IR spectra were recorded with a Shanghai 7400 IR instrument. ^{1}H-NMR spectra were measured by a Varian FT-80A Spectrometer in DMSO-d$_6$. Viscosities were determined at 25°C with a Sansei viscometer. Thermogravimetry−differential thermal analysis (TG-DTA) data were obtained by using a Beijing PCT-1 analyzer at a heating rate of 10°C min^{-1} in air. For interfacial tension, contact angles were measured with a JY-80 contact angle meter.

Synthesis of BTDA−PMDA API

Four BTDA−PMDA API were synthesized by using four diamines according to Scheme 1. Diamines may be p-phenyl diamine, 4,4′-diamino dibenzene, 4,4′-diaminodiphenyl methane, and 4,4′-diaminodiphenyl ether, being numbered by 1, 2, 3, and 4, respectively. Thus, results of the

Table I Imidization Temperatures (°C)

Sample	T1	T2	T3
BTDA−PMDA APA1	147	168	221
BTDA−PMDA APA2	130	165	213
BTDA−PMDA APA3	135	160	210
BTDA−PMDA APA4	145	165	225

T1 and T3 are the initial and end temperatures, respectively, of weight loss in the second stage of TG curve; T2 is the temperature of the second endothermic peak in DTA curve, related to the imidization.

Table II   Elemental Analysis Data of BTDA CED (Calcd) (%)

Sample	C	H	N
BTDA CED1	64.15 (64.19)	3.23 (3.26)	6.50 (6.51)
BTDA CED2	64.73 (64.77)	3.54 (3.56)	5.48 (5.53)
BTDA CED3	69.21 (69.23)	3.83 (3.85)	5.30 (5.38)
BTDA CED4	66.59 (66.67)	3.42 (3.45)	5.31 (5.36)

same kind from these four diamines can be denoted by the tail numbers, for example, BTDA CED1, BTDA–PMDA APA1, and BTDA–PMDA API1, etc.

The procedures for the synthesis were as follows. A flask equipped with a mechanical stirrer, thermometer, and addition funnel was filled with a solution containing 0.02 mol of diamine in 15 mL DMF. To the vigorously stirred solution, 0.01 mol BTDA dissolved in 25 mL DMF was added dropwise in 2 h. Stirring of the mixture lasted for 3 h more at ambient temperature, producing BTDA CED with a yield over 99%. Then, 0.0102 mol of PMDA powder was gradually added four times during 30 min to the solution with stirring. After 4 h of reaction, the resulting BTDA–PMDA APA was obtained. Viscosity was measured with ln η_γ/C to be 29.89, 32.58, 31.21, and 28.93 mL/g for BTDA–PMDA APA 1, 2, 3, and 4, respectively. The reaction solution was volatilized at room temperature for 10 h and then at 100°C *in vacuo* for 3 h; the BTDA–PMDA APA film was thus obtained. The film was heated *in vacuo* at T1, T2, and T3, originating from the TG-DTA data of BTDA–PMDA APA, as listed in Table I, for 1, 3, and 1 h, respectively, for dehydrating; and the BTDA–PMDA API film was obtained.

BTDA HPI1–4 and PMDA HPI1–4 were also synthesized. All these homopolyimic acids have visicosities between 30 and 35 mL/g in ln η_γ/C.
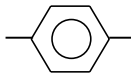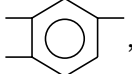
RESULTS AND DISSCUSSION

Characterization of BTDA CED

The diamines chain-extended by BTDA were characterized by IR, ^{1}H-NMR, and elemental analysis. The results of elemental analysis of BTDA CED are shown in Table II. We can see that the experimental data agreed well with the calculted values. The characteristic absorption and assignments of BTDA CED are listed in Table III.

Figure 1 shows a typical IR spectra of BTDA CED1, in which —C—OH (with O double-bonded to C) gives the absorption bands at 2900–2720 cm^{-1} (OH) and 1720 cm^{-1} (C=O); —NH—C— (with O double-bonded to C) exhibits absorption bands at 3400–3200 cm^{-1} (ν_{NH}), 1615 CM^{-1} ($\nu_{C=O}$), 1660 cm^{-1} (ν_{C-N}), and 1545 cm^{-1} (δ_{C-N}); the —NH$_2$ gives absorption bands 1620 and 3400–3200 cm^{-1}; and the phenyl ring shows the absorption bands at 1600 and 1510 cm^{-1}. The ^{1}H-NMR spectra of BTDA CED were recorded in DMSO-d_6 solution, and the results are listed in Table IV. Figure 2 presents the typical ^{1}H-NMR spectra of BTDA CED1, in which the peaks can be assigned as follows: the proton of —OH of carboxylic acid gave a singlet at a chemical shift of δ = 10.74 ppm, the protons in —NH$_2$ showed one peak at δ = 4.37 ppm (exchangeable by D$_2$O), and the peaks at δ = 7.39–6.50 ppm and δ = 8.18–7.67 ppm are associated with the protons of the two phenyl rings, i.e., (phenyl ring) and (phenyl ring), respectively.

Table III   Wavenumbers of BTDA CED (cm^{-1})

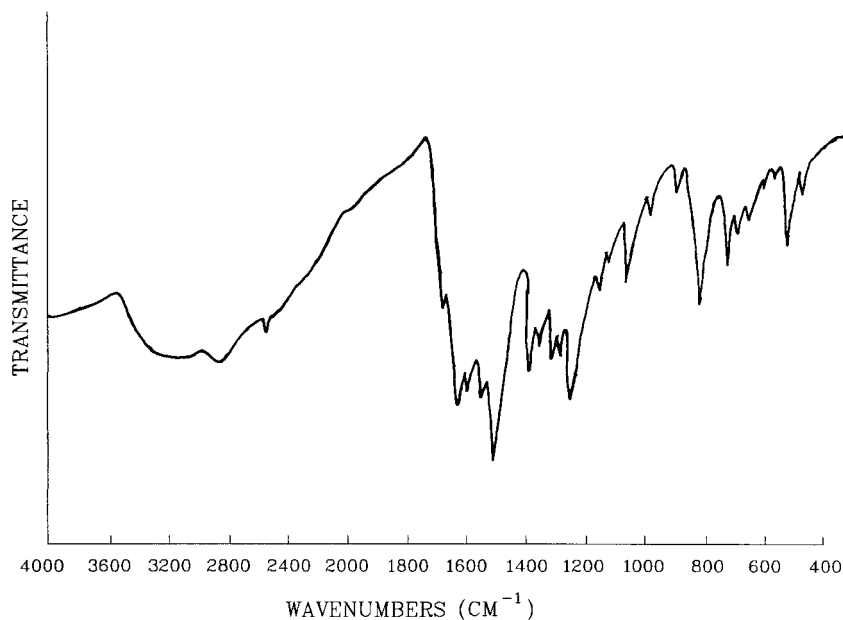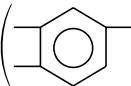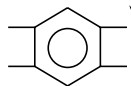| Sample	—NH$_2$	—COOH	—NH—C— (C=O)	Phenyl Ring	Other Structure
BTDA CED1	1620	1720	3400–3200, 1520	1600	
	3400–3200	2900–2720	1615, 1660	1510	
BTDA CED2	1600	1720	3400–3200, 1520	1600	
	3400–3200	2900–2720	1610, 1650	1500	
BTDA CED3	1610	1715	3400–3200, 1520	1600	
	3400–3200	2900–2720	1610, 1660	1500	
BTDA CED4	1620	1730	3400–3200, 1510	1600	1250 (—O—)
	3400–3200	2900–2720	1620, 1670	1500	

Figure 1   IR spectrum of BTDA CED1.

Based on the elemental analysis and structural characterization described above, we conclude that the BTDA CEDs have the expected structures.

Characterization of BTDA–PMDA API

As shown in Figure 3(a), the absorption bands of BTDA-PMDA APA1 at 3080–2700, 1710, 3380–3200, 1655, 1510, and 1315 cm^{-1} are attributed to the absorption of the amic acids structure. The bands at 1510 and 1410 cm^{-1} may be assigned to the phenyl ring structure. In Figure 4, the chemical shifts can be assigned as follows: 10.66

(—COOH), 7.68 (—⬡—), and 8.23–8.00

ppm (⬡ and ⬡). Also, a broad

peak appears at 4.29 ppm, which may be caused

by exchange of the proton of —NH—C— with

$$\overset{O}{\overset{\|}{\text{—NH—C—}}}$$

D$_2$O. In Figure 3(b), the characteristic bands of amic acid disappeared, while the characteristic bands of imide ring at 1780, 1720, 1360, 1120, and 710 cm^{-1} appeared. Therefore, a complete imidization was confirmed from the spectral changes.

Thermal Properties

The TG-DTA curves of BTDA–PMDA APA1 and BTDA–PMDA API1 in air are shown in Figure 5. It can be seen that the curve of BTDA–PMDA APA1 can be divided into three stages: the first stage is associated with a slight weight loss resulting from the evaporation of the remaining solvent from ambient temperature to 106.8°C, with a small endothermic peak at 64.75°C; in the second stage, the TG curve shows a second slight weight loss at 146.8–221.8°C, and another endothermic peak at 168.8°C appeared in its DTA curve, which was considered to be related to the imidization; in the third stage, the TG curve gave a great weight loss above 502.3°C, owing to degradation via oxidation; meanwhile, two exothermic peaks at 537.6 and 599.4°C appeared in its DTA curve. For BTDA–PMDA API1, degradation didn't take place until 528.7°C. It's TG curve shows a marked weight loss, and its DTA curve has two exothermic peaks at 561.0 and 599.4°C.
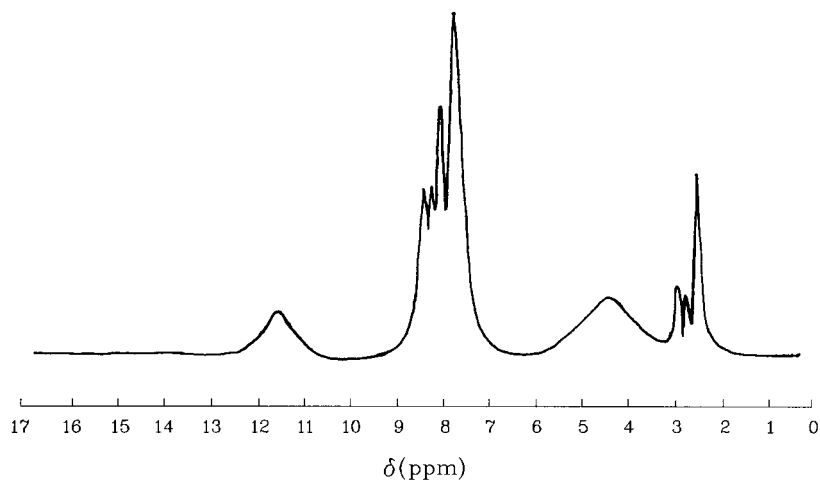
TG-DTA data of all BTDA–PMDA APA and BTDA–PMDA API are listed in Tables VIII and IX, respectively. It was found that all BTDA–PMDA APA have three-stages of thermal behaviors: evaporation of remaining solvent, thermal imidization, and thermal decomposition. And no thermal changes happened to BTDA–PMDA API before they began to undergo thermal decomposi-
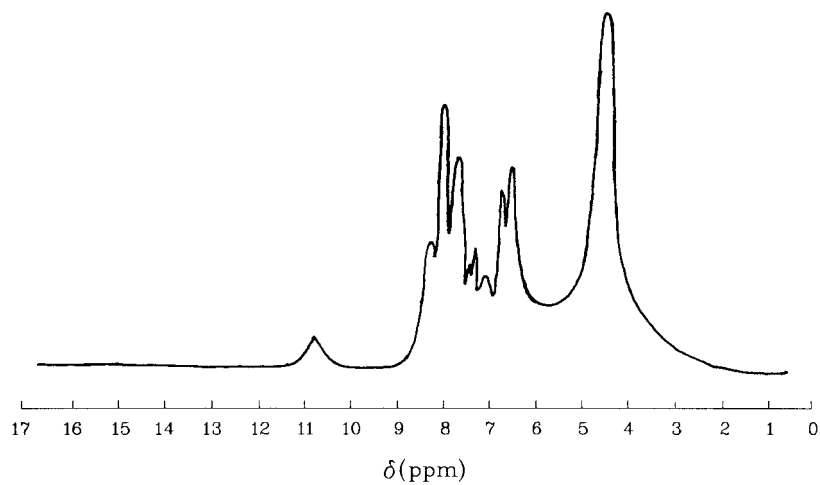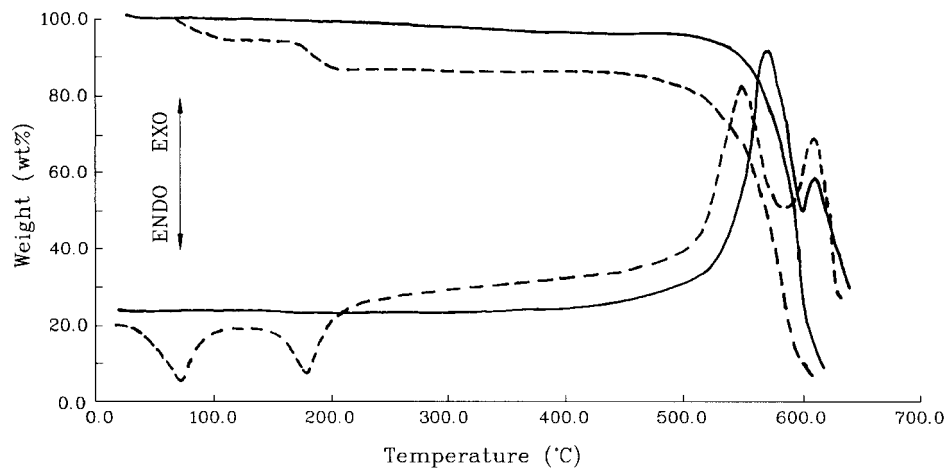
Figure 2   ¹H-NMR spectrum of BTDA CED1.
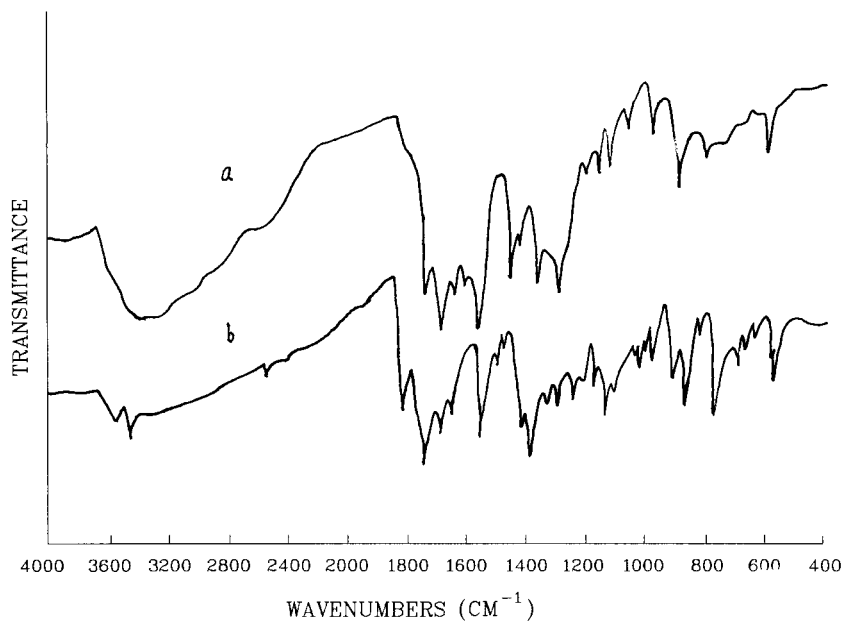
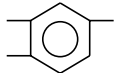**Figure 3**   IR spectrum of (a) BTDA–PMDA APA1 and (b) BTDA–PMDA API1.

Figure 4   ¹H-NMR spectrum of BTDA–PMDA APA1.

Figure 5 TG-DTA curves of BTDA–PMDA APA1 (-----) and BTDA–PMDA API1 (——).

Table IV ¹H-NMR Data of BTDA CED (ppm)

Sample	—CH$_2$	—NH$_2$/D$_2$O	⟨phenyl⟩	⟨phenyl⟩	—COOH
BTDA CED1	—	4.37	7.39–6.50	8.18–7.67	10.74
BTDA CED2	—	4.80	7.72–6.64	8.28–8.01	10.75
BTDA CED3	3.72	4.83	6.80–6.42	8.20–7.93	10.57
			7.64–7.05		
BTDA CED4	—	4.97	6.71–6.61	8.21–7.99	10.56
			7.65–6.82		
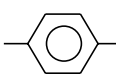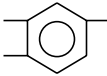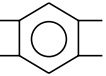
Table V Wavenumbers of BTDA–PMDA APA (cm^{-1})

Sample	—COOH	$\overset{\overset{\text{O}}{\|\|}}{\text{—NH—C—}}$	Phenyl Ring	Other Structure
BTDA–PMDA APA1	1710	3380–3200, 1655	1510, 1410	—
	3080–2700	1510, 1315		
BTDA–PMDA APA2	1710	3380–3200, 3650	1520, 1410	—
	3080–2700	1520, 1310		
BTDA–PMDA APA3	1720	3380–3200, 1630	1510, 1410	—
	3080–2700	1510, 1300		
BTDA–PMDA APA4	1710	3380–3210, 1640	1510, 1400	1220 (—O—)
	3080–2700	1540, 1300		

Table VI   Wavenumbers of BTDA–PMDA API (cm⁻¹)

Sample	$\overset{\displaystyle O}{\overset{\displaystyle\|}{}}\ \ \overset{\displaystyle O}{\overset{\displaystyle\|}{}}$ —C—NH—C—	Phenyl Ring	Other Structure
BTDA–PMDA API1	1780, 1720, 1360, 1120, 710	1510, 1360	
BTDA–PMDA API2	1770, 1720, 1360, 1120, 700	1500, 1390	
BTDA–PMDA API3	1780, 1720, 1370, 1130, 720	1500, 1370	
BTDA–PMDA API4	1780, 1725, 1380, 1120, 720	1500, 1380	1250 (—O—)

Table VII   ¹H-NMR Data of BTDA–PMDA APA (ppm)

Sample	CH₂	$\overset{\displaystyle O}{\overset{\displaystyle\|}{}}$ —NH—C—/—NH₂/D₂O	⬡ phenyl	⬢	⬢	—COOH
BTDA–PMDA APA1	—	4.29	7.68	8.23–8.00		10.66
BTDA–PMDA APA2	—	4.40	7.75–7.21	8.24–7.95		10.60
BTDA–PMDA APA3	[a]	4.07	7.61–7.20	8.24–7.92		10.65
BTDA–PMDA APA4	—	4.10	7.80–6.90	7.91–8.23		10.52

[a] Covered by the peak of $\delta = 4.07$ ppm.

Table VIII   TG–DTA Data of BTDA–PMDA APA (°C)

Sample	Volatilization Temperature		Imidization Temperature			Decomposition Temperature		
	Peak	End	Initial	Peak	End	Initial	Peak 1	Peak 2
BTDA–PMDA APA1	64.8	106.8	146.8	168.8	221.8	502.3	537.6	599.4
BTDA–PMDA APA2	52.7	94.7	131.2	165.5	212.4	505.1	540.5	567.0
BTDA–PMDA APA3	—	82.7	134.3	156.1	199.8	496.5	537.6	590.5
BTDA–PMDA APA4	52.6	88.6	143.6	143.6	162.4	521.8	531.8	550.3

All peak temperatures are from DTA, and all initial or end temperatures are from TG.

Table IX   TG–DTA Data of BTDA–PMDA API (°C)

Sample	Decomposition Temperature[a]		
	Initial	Peak 1	Peak 2
BTDA–PMDA API1	528.7	561.0	599.4
BTDA–PMDA API2	528.6	558.1	590.5
BTDA–PMDA API3	467.3	581.9	—
BTDA–PMDA API4	502.3	534.6	602.3

[a] Temperatures of peaks 1 and 2 are obtained from DTA, and initial temperature is from TG.

Table X   TG–DTA Data of BTDA HPI and PMDA HPI (°C)

Sample	Decomposition Temperature[a]	
	Initial	Peak
BTDA HPI1	543.5	578.8
BTDA HPI2	567.0	590.5
BTDA HPI3	520.0	543.5
BTDA HPI4	543.5	552.2
PMDA HPI1	531.8	567.0
PMDA HPI2	531.8	555.0
PMDA HPI3	542.0	583.0
PMDA HPI4	538.0	550.0

[a] Initial and peak temperatures are from TG and DTA curves, respectively.

Table XI   Interfacial Tension Data of BTDA–PMDA API, BTDA HPI, and PMDA HPI

Sample	Contact Angle (degree)		Interfacial Tension (dyne/cm)		
	θ_1	θ_2	γ_s^d	γ_s^p	γ_s
BTDA–PMDA API1	90.0	74.0	21.645	8.329	29.974
BTDA–PMDA API2	86.0	74.8	17.379	11.939	29.318
BTDA–PMDA API3	84.5	75.7	15.492	13.634	29.176
BTDA–PMDA API4	85.3	74.3	17.335	12.303	29.638
BTDA HPI1	85.5	72.3	19.436	11.232	30.668
BTDA HPI2	79.0	70.2	16.774	15.847	32.621
BTDA HPI3	83.0	70.3	19.440	12.437	31.877
BTDA HPI4	83.3	73.1	17.023	13.459	30.482
PMDA HPI1	82.3	72.0	17.337	13.805	31.142
PMDA HPI2	82.3	70.3	18.916	13.025	31.941
PMDA HPI3	82.0	70.7	18.323	13.460	31.783
PMDA HPI4	82.3	72.0	17.337	13.805	31.142

tion. Also, a small difference in the initial decomposition temperatures between a BTDA–PMDA APA and its corresponding BTDA–PMDA API was attributed to the different thermal imidization processes.

Table X gives the TG-DTA data of BTDA HPI and PMDA HPI. For the same diamines, the initial decomposition temperatures and the first exothermic peak temperatures of BTDA–PMDA API are found to be slightly lower than their corresponding homopolyimides (BTDA HPI or PMDA HPI).

Interfacial Tension

Interfacial tension was worked out according to the harmonic mean method,[10] as follows.

$$(1 + \cos\theta_1)\gamma_1$$
$$= 4[\gamma_1^d\gamma_s^d/(\gamma_1^d + \gamma_s^d) + \gamma_1^p\gamma_s^p/(\gamma_1^p + \gamma_s^p)]$$
$$(1 + \cos\theta_2)\gamma_2$$
$$= 4[\gamma_2^d\gamma_s^d/(\gamma_2^d + \gamma_s^d) + \gamma_2^p\gamma_s^p/(\gamma_2^p + \gamma_s^p)]$$
$$\gamma_1 = \gamma_1^d + \gamma_1^p$$
$$\gamma_2 = \gamma_2^d + \gamma_2^p$$
$$\gamma_s = \gamma_s^d + \gamma_s^p$$

where superscripts p and d are the polar component and depolar component in interfacial tension, respectively; and θ_1 and θ_2 the contact angles on the polyimide film by water and glycerin, respectively. At 25°C, $\gamma_1 = 72.8$, $\gamma_1^d = 22.6$, and $\gamma_1^p = 50.2$ dyne/cm; $\gamma_2 = 63.4$, $\gamma_2^d = 40.6$, and $\gamma_2^p = 22.8$ dyne/cm.

Interfacial tension data of BTDA–PMDA API, BTDA API, and PMDA API are listed in Table XI. For polyimides of p-phenyl diamine, the alternating polyimide had much lower γ_s^p and higher γ^d compared to the corresponding homopolyimides. As to polyimides of 4,4′-diaminodibenzene and 4,4′-diaminodiphenyl ether, the γ^p value of the homopolyimides is much higher than alternating polyimides. Much different from the above results, among polyimides of 4,4′-diaminodiphenyl methane, the γ^d value of alternating polyimide is approximately 3 dyne/cm higher than that of its corresponding homopolyimides. Furthermore, an interesting result is that all BTDA–PMDA API had interfacial tensions at 29–30 dyne/cm, being lower than those of their respective homopolyimides (≥ 30.48 dyne/cm).

According to Wu,[10] interfaces of polymers with similar chemical structure have almost the same interfacial tension. From the aforementioned, we can see that the polar component γ_s^p and depolar component γ_s^d vary with different diamines and dianhydrides, but interfacial tension γ_s changed slightly. Our study showed that alternating condensation of polymerization cannot only adjust γ_s^d and γ_s^p, but also reduce γ_s markedly; thus, it may well be an effective way to modify polyimides.

REFERENCES

1. M. T. Bogert and R. R. Renshaw, *J. Am. Chem. Soc.,* **30,** 1135 (1908).
2. G. M. Bower and L. W. Frost, *J. Polym. Sci.,* **A1,** 3135 (1963).
3. R. A. Meyers, *J. Polym. Sci.,* **A1, 7,** 2757 (1969).
4. C. V. Avadhani, P. P. Wadgaonkar, and S. P. Vernekar, *J. Polym. Sci., Polym. Chem.,* **28,** 1681 (1990).
5. W. Zeng, W. Qiu, J. Liu, X. Yang, L. Lu, and X. Wang, *Polymer,* **36,** 3761 (1995).
6. W. Qiu, Y. Yang, X. Yang, L. Lu, and X. Wang, *J. Appl. Polym. Sci.,* **59,** 1437 (1996).
7. French Pat. 1,427,126 (1966) (to Dupont Co.)
8. N. A. Adrova, M. I. Bessonov, L. A. Laius, and A. P. Rudakov, *Polyimides,* Technomic, 1970, p. 163.
9. C. V. Avadhani and S. P. Vernekar, *Polym. Bull.,* **24,** 487 (1990).
10. S. Wu, *Polymer Interface and Adhension,* Marcel Dekker, New York, 1982.