

# Synthesis and Characterization of Novel Polyesterimides

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**ABSTRACT:** A series of soluble novel polyesterimides was synthesized from diamines [a mixture of 2,2-bis(4-(4-aminophenoxy)phenyl)propane (BAPP) with amine-terminated polysiloxane (ATPS) in various mole ratios] and the ester-group-containing dianhydrides. The ester group containing dianhydrides in turn was synthesized by the transesterification reaction of trimellitic anhydride (TMA) with diacetate ester of hydroquinone (HQ), 4,4'-dihydroxyphenyl (BP), 1,6-hexanediol, or ethylene glycol. The resulted polyesterimides were characterized by using Fourier-transform infrared spectroscopy, inherent viscosity, solubility, differential scanning calorimetry (DSC), and thermogravimetric analysis (TGA). The polyesterimides of BP and HQ had relatively high glass transition temperatures in the range of

214.7–227.2 and 195.7–210.5°C, respectively. The glass transitions decreased rather slowly with the increase in polysiloxane content. Thermal stability and the weight-loss behavior of polyesterimides were studied by TGA. All polyesterimides of BP and HQ (BPI and HQI) showed no significant weight loss below 500°C in a N<sub>2</sub> environment, and the decomposition temperatures ( $T_{d5\%}$ ) of BPI and HQI were >520°C. Most polyesterimides were soluble in polar aprotic solvents and *m*-cresol. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 94: 730–738, 2004

**Key words:** glass transition; thermal properties; polysiloxane

## INTRODUCTION

Polyimides are an attractive class of polymers because of their unusual thermal and oxidative stability, high mechanical strength, and, especially, for their good insulation properties with low dielectric constant. However, wholly aromatic polyimides are usually intractable and lack the properties essential for successful fabrication into useful form and suffer from processing problems due to their high glass transition temperature and poor solubility in organic solvents. Polyamideimides and polyesterimides were developed to improve solubility and avoid voids from water evolution during imidization. The conventional method used, in the synthesis of the polyesterimides, involves polycondensation between trimellitic acid chloride with a diamine and adiol.<sup>1–3</sup> The problem is aggravated by the strong corrosiveness of hydrogen chloride. The direct polycondensation route avoids using moisture-sensitive acid chlorides and provides significant advantages in manufacturing operations compared with conventional methods. Several methods used in the synthesis of polyesterimides via the polycondensation process were reported.<sup>4–7</sup> The unsatisfactory results reported from some polyconden-

sation processes were caused by the poor solubility of oligomers resulting in early precipitation from the reaction medium, which prevented further polymerization and resulted in a low inherent viscosity and brittle polymer.<sup>4,7</sup> Aromatic polyamideimides (PAIs) and polyesterimides (PEIs) are useful high-performance materials that exhibit better processing characteristics when compared with polyimides of analogous structures and have been extensively investigated by many authors.<sup>8–22</sup> The modification of polyimides with amine-terminated polysiloxane (ATPS) has developed high-performance heat-resistant polymers, which can be applied in advanced microelectronics, aerospace, and printed circuit industries.<sup>23–28</sup> Many of these polysiloxane-containing systems are soluble in aprotic polar solvents because of the decreased intermolecular interaction in the presence of linear flexible Si—O chains. Additionally, the siloxane particles (a few micrometers in size) uniformly dispersed in the matrix did not significantly sacrifice the thermal stability of the resulted polyimides. Therefore, for this study, a new class of polyesterimides containing siloxane was synthesized and their properties were explored.

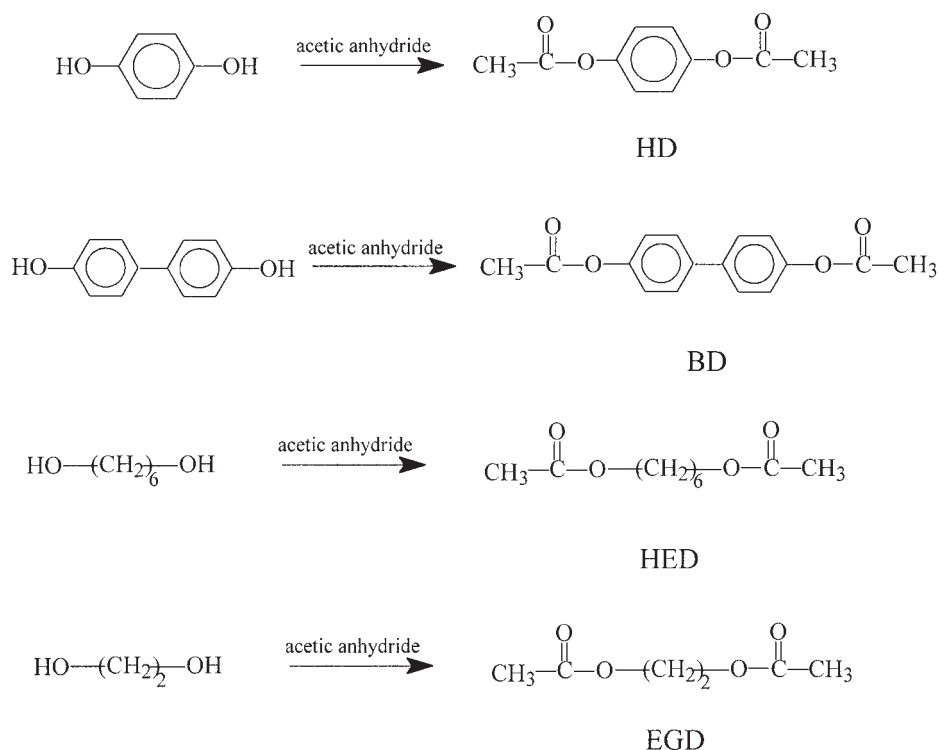
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## EXPERIMENTAL

### Materials

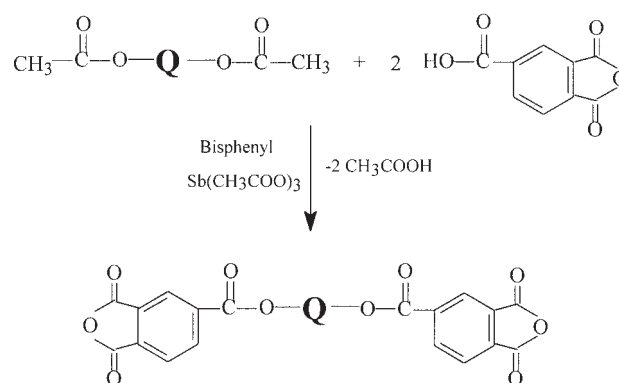
All reagents were reagent grade or were purified by standard methods before use. 2,2'-bis(4-(4-aminophenoxy)phenyl)propane (BAPP) from Chris; trimellitic



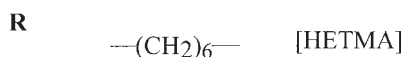
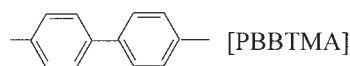
Scheme 1 Synthesis of diacetates.

anhydride (TMA) from Aldrich (St. Louis, MO); hydroquinone from Panreac (Meyzieu, France); 4,4'-dihydroxyphenyl from Grand (Aboboda, Portugal); and 1,6-hexanediol and ethylene glycol from Acros (Pittsburgh, PA) were used as received. Amine-terminated polysiloxane (ATPS; equivalent weight of amine group = 450) was purchased from Shin-Etsu (Tokyo, Japan). *N*-methyl-2-pyrrolidone (NMP; Tedia, Houston, TX), *N,N*-dimethylformamide (DMF; Fisher, Houston, TX), *N,N*-dimethylacetamide (DMAc; Tedia), dimethyl sulfoxide (DMSO; Panreac), tetrahydrofuran (THF; Tedia), cyclohexanone (Acros), and chloroform (Acros) were used as solvent for solubility studies without purification. Antimony(III) acetate was used as catalyst. For synthesis of the carboxyl-

terminated diimides and for the determination of inherent viscosities of polymers, NMP was dehydrated with  $\text{CaH}_2$  before use.



Q : Ar



Scheme 2 Synthesis of dianhydrides.

TABLE I  
Elemental Analysis and Melting Point of Diacetates

Monomer	Formula	$M_w$	Anal.	C%	H%	$T_m$ (°C)
HD <sup>a</sup>	$\text{C}_{10}\text{H}_{10}\text{O}_4$	194	Calcd.	61.86	5.15	122–124
			Found	61.74	5.19	[121–123] <sup>d</sup>
BD <sup>b</sup>	$\text{C}_{16}\text{H}_{14}\text{O}_4$	270	Calcd.	71.10	5.19	162–165
			Found	70.95	5.19	[164] <sup>e</sup>
HED <sup>c</sup>	$\text{C}_{10}\text{H}_{18}\text{O}_4$	203	Calcd.	59.41	8.91	—
			Found	59.30	8.80	

<sup>a</sup> HD: *p*-Dimethyl hydroquinone diacetate.

<sup>b</sup> BD: 4,4'-Dimethyl biphenyl diacetate.

<sup>c</sup> HED: 1,6-Dimethyl diacetate.

<sup>d</sup> Lit. CAS 1205-91-0.

<sup>e</sup> Lit. CAS 32604-29-8.

**TABLE II**  
Elemental Analysis and Melting Point of Dianhydrides

Monomer	Formula	$M_w$	Anal.	C%	H%	$T_m$ (°C)
PPBTMA <sup>a</sup>	C <sub>24</sub> H <sub>10</sub> O <sub>10</sub>	458	Calcd. Found	62.90 62.58	2.18 2.38	271–273 [274] <sup>e</sup>
PBBTMA <sup>b</sup>	C <sub>30</sub> H <sub>18</sub> O <sub>10</sub>	538	Calcd. Found	67.42 67.44	2.62 2.71	303–305 [298–301] <sup>f</sup>
HETMA <sup>c</sup>	C <sub>24</sub> H <sub>18</sub> O <sub>10</sub>	466	Calcd. Found	61.80 61.75	3.86 3.80	158–160
EGTMA <sup>d</sup>	C <sub>24</sub> H <sub>10</sub> O <sub>10</sub>	410	Calcd. Found	58.50 58.45	2.44 2.43	167–169

<sup>a</sup> PPBTMA: *p*-phenylene bis(trimellitic monoester anhydride).

<sup>b</sup> PBBTMA: *p*-biphenyl bis(trimellitic monoester anhydride).

<sup>c</sup> HETMA: 1,6-hexyl trimellitic monoester anhydride.

<sup>d</sup> EGTMA: 1,2-ethyl trimellitic monoester anhydride.

<sup>e</sup> The referenced melting point of PPBTMA (data from ref. 1).

<sup>f</sup> The referenced melting point of PBBTMA (data from ref. 1).

## Measurements

<sup>1</sup>H-NMR spectra were determined by using a Bruker Avance-600 spectrometer using DMSO-*d*<sub>6</sub> as a solvent. Elemental analyses were carried out with a Heraeus CHN-Rapid elemental analyzer. Fourier transform infrared (FTIR) spectra were recorded on a Nicolet Magna-550 spectrometer with KBr pellets or using 10- to 15- $\mu$ m film. Spectra in the optical range of 400–4000  $\text{cm}^{-1}$  were obtained by averaging 32 scans at a resolution of 4  $\text{cm}^{-1}$ . The inherent viscosities of the polyesterimides in concentrated NMP solutions (concentration: 0.2–0.4 g/dL) were measured at 30°C with a Ubbelohde viscometer. Differential scanning calorimeter (DSC; Perkin-Elmer DSC-7) measurements were used in this work: samples of ~5–10 mg in weight were sealed in hermetic aluminum pans and scanned in the calorimeter with a heating rate of 10°C/min in the range of 50–340°C under N<sub>2</sub> atmosphere and the glass transition temperature ( $T_g$ ) values were taken as the change of the specific heat in the heat flow curves. Thermogravimetric analyses (TGA) were performed on a Perkin-Elmer TGA-7 thermal analyzer by using a heating rate of 20°C/min in N<sub>2</sub> at a purge pressure of 25 psi within the temperature range of 100–800°C.

## Monomers synthesis

Synthesis of diacetates of HQ, BP, HD

To a 1-L reaction vessel equipped with a temperature controller, overhead stirrer, and a reflux condenser were added 110 g (1 mol) hydroquinone (HQ) and 306 g (3 mol) acetic anhydride. The mixture was first heated slowly to 50°C to dissolve hydroquinone and then reacted for 2 h while the temperature was increased to 130°C. The reaction was assumed to be

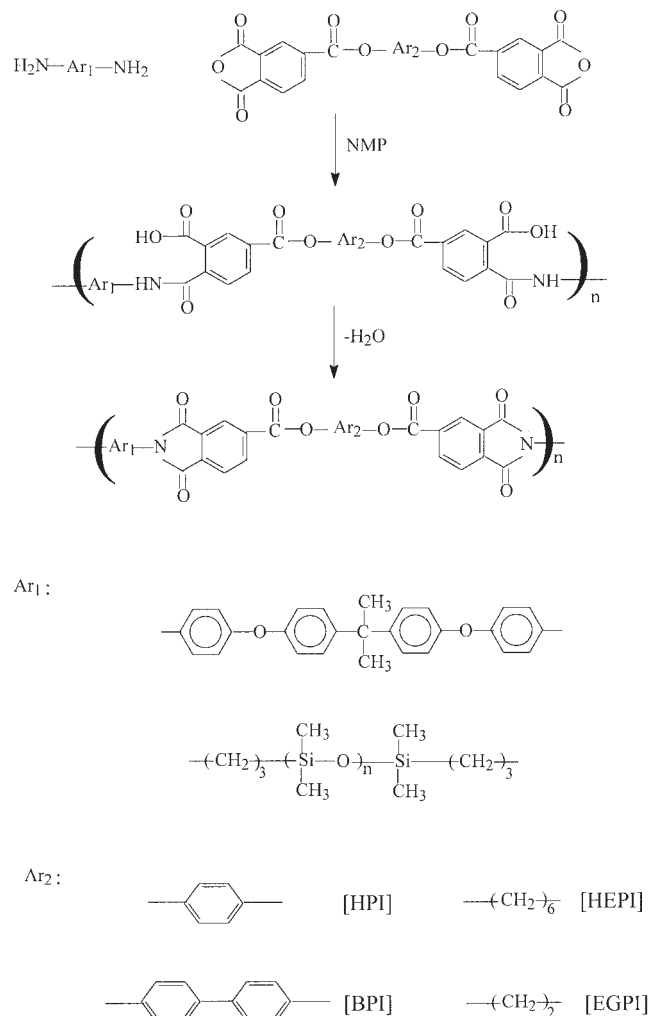
complete when hydroquinone was consumed as determined by GC analysis. Excess acetic acid and acetic anhydride were distilled under vacuum and the product was precipitated with deionized water. The product was washed several times with water and then dried under vacuum to give hydroquinone diacetate (HD).

Yield: 99%; melting point (mp): 122–124°C. The reaction is shown in Scheme 1. The shift and splitting pattern of <sup>1</sup>H-NMR spectrum was  $\delta = 2.25$  (6H, —CH<sub>3</sub>),  $\delta = 7.14$  (4H, Ph—H). Anal. Calcd. for C<sub>10</sub>H<sub>10</sub>O<sub>4</sub>: C, 61.86; H, 5.15; O, 32.99. Found: C, 61.74; H, 5.19; O, 33.07. EIMS,  $m/z$ : 194 (32. M<sup>+</sup>).

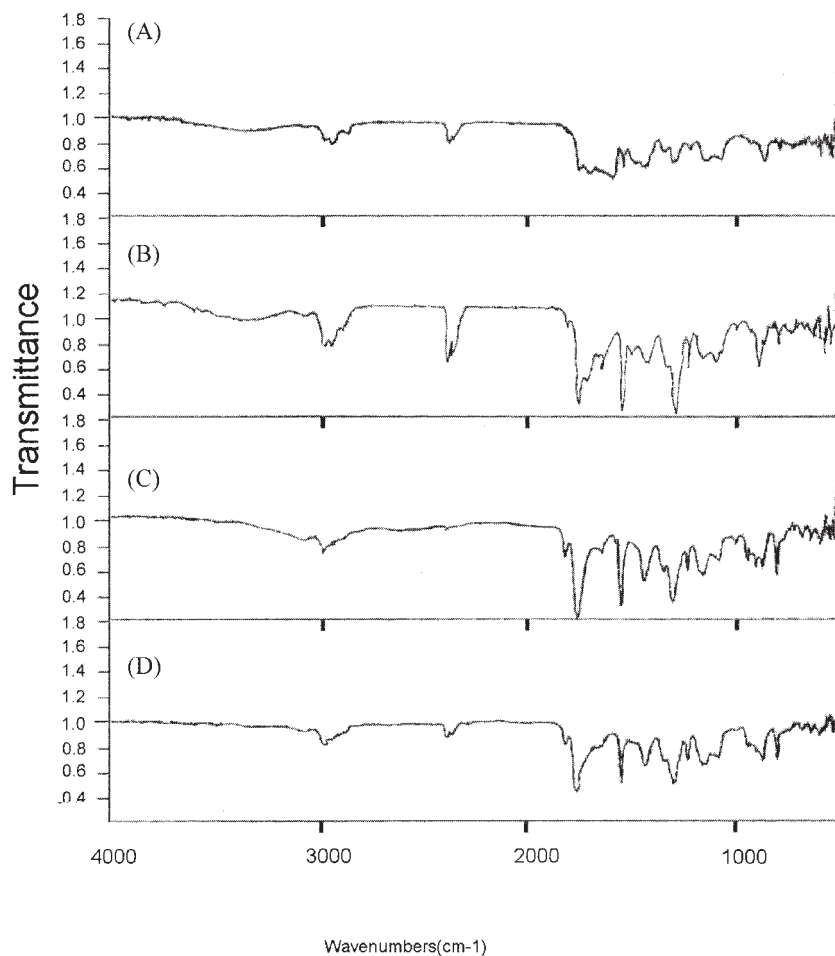
Other diacetates of biphenol (BP) and 1,6-hexanediol were synthesized in an analogous manner. The reactions are also shown in Scheme I. Their melting point and elemental analyses are shown in Table I. The products are designated as HD, BD, and HED.

## Synthesis of dianhydride—PPBTMA, PBBTMA, HETMA

Into a reactor equipped with a stirrer, a reflux condenser, a thermometer, a Dean–Stark water separator,



**Scheme 3** Synthesis of polyesterimides.



**Figure 1** IR spectra of 20 mol % siloxane containing polyesterimides: (A) HPI; (B) BPI; (C) HEPI; (D) EGPI.

and a nitrogen inlet were charged 38.8 g (0.2 mol) of HD, 76.8 g (0.4 mol) of trimellitic anhydride, 100 g BP as solvent and  $6 \times 10^{-6}$  mol of antimony(III) acetate as catalyst. The mixture was heated to 280°C and maintained at that temperature for 3 h under a nitrogen atmosphere to distill acetic acid. The reaction mixture was then cooled to 100°C and poured into toluene, and the precipitate was isolated by filtration. The product was recrystallized from toluene/DMF to give *p*-phenylene bis(trimellitic monoester anhydride) (PPBTMA).

Yield: 98%; mp: 271–273°C. The reaction is shown in Scheme 2. The shift and splitting pattern of  $^1\text{H-NMR}$  spectrum is  $\delta = 7.85\text{--}8.65$  (6H, —Ph—H),  $\delta = 7.52$  (4H, Ph—H). Anal. Calcd. for  $\text{C}_{24}\text{H}_{10}\text{O}_{10}$ : C, 62.90; H, 2.18; O, 34.92. Found: C, 62.58; H, 2.38; O, 35.04. Other dianhydrides are synthesized in an analogous manner. The reactions are also shown in Scheme 2.

Their melting point and elemental analyses are shown in Table II. The products of *p*-phenylene bis(trimellitic monoester anhydride), *p*-biphenyl bis(trimellitic monoester anhydride), and 1,6-hexane trimellitic monoester anhydride were designated as PPBTMA, PBBTMA, and HETMA.

#### Synthesis of dianhydride—EGTMA

Into a reactor equipped with a stirrer, a reflux condenser, a thermometer, a Dean–Stark water separator, and a nitrogen inlet were charged 62 g (1 mol) of ethylene glycol and 306 g (3mol) of acetic anhydride. The mixture was cooled to 5–10°C and maintained at that temperature for 12 h to obtain ethylene glycol diacetate (EGD). Because EGD was soluble in water, it was reacted further without isolation. To the EGD in the reactor was charged 2 mol of trimellitic anhydride, 100 g biphenyl as solvent, and  $3 \times 10^{-5}$  mol of antimony(III) acetate as catalyst. The mixture was heated to 280°C and maintained at that temperature for 8 h under a nitrogen atmosphere. The reaction mixture was cooled to 100°C and poured into toluene, and the precipitate was isolated by filtration. The product was recrystallized from toluene/DMF to give ethylene glycol bistrimellitic dianhydride (EGTMA).

Yield: 98%; mp: 167–169°C. The reaction is shown in Scheme 2. The shift and splitting pattern of  $^1\text{H-NMR}$  spectrum is  $\delta = 4.726$  (4H, —CH<sub>2</sub>),  $\delta = 8.19\text{--}8.47$  (6H, Ph—H). Anal. Calcd. for  $\text{C}_{20}\text{H}_{10}\text{O}_{10}$ : C, 58.50; H, 2.44; O, 39.02. Found: C, 58.45; H, 2.43; O, 39.12.

**TABLE III**  
**Thermal Properties and Intrinsic Viscosities (IV) of PEIs**

Sample symbol	Si-content (mol %)	Sample weight (g)	IV (dl/g)	$T_g$ (°C)
HPI	0	0.0439	0.94	210.5
	5	0.0442	0.91	206.8
	10	0.0506	0.88	203.9
	15	0.0496	0.84	197.6
	20	0.0494	0.81	195.7
BPI	0	0.0377	2.20	227.2
	5	0.0386	2.13	220.3
	10	0.0367	1.92	216.8
	15	0.0395	1.56	216.0
	20	0.0382	1.12	214.7
HEPI	0	0.0495	0.63	177.8
	5	0.0484	0.59	152.0
	10	0.0467	0.58	136.2
	15	0.0476	0.55	102.9
	20	0.0495	0.51	100.5
EGPI	0	0.0386	0.67	180.2
	5	0.0303	0.62	175.2
	10	0.0397	0.61	170.4
	15	0.0383	0.55	154.9
	20	0.0360	0.55	154.5

<sup>a</sup> HPI: Polyesterimide was prepared with raw material of PPBTMA.

<sup>b</sup> BPI: Polyesterimide was prepared with raw material of PBBTMA.

<sup>c</sup> HEPI: Polyesterimide was prepared with raw material of HETMA.

<sup>d</sup> EGPI: Polyesterimide was prepared with raw material of EGTMA.

#### Preparation of polymers containing polysiloxane

Into a reactor equipped with a stirrer, a reflux condenser, a thermometer, a Dean-Stark water separator, and a nitrogen inlet were charged 0.02 mol of diamine (various mole ratios of BAPP and ATPS) by using NMP as solvent. The mixture was cooled to 5–10°C and 0.02 mol of PPBTMA was added. The mixture was maintained at that temperature for 12 h to obtain polyamic acid (PAA). The solution of PAA was coated onto a glass plate to form a thin film and dried at 60°C for 12 h in a forced air oven. The film on glass was then converted to the polyesterimide by heating in an air oven at 100, 150, 200, and 250°C each for 1 h, respectively. The film was cooled to room temperature and stripped from the plate by soaking in water and then drying to give polyesterimide of HPI. The reactions are shown in Scheme 3. Polyesterimide analysis by FTIR (Fig. 1) is as follows.

IR (KBr or 10–15  $\mu\text{m}$  film)  $\text{cm}^{-1}$ : 1650–1718, 1730–1775 (imide ring), 1000–1100 (Si—O—Si), 750–850 (Si—CH<sub>3</sub>), 3100–3750 (Ph—H), 1720 (C=O). The polyesterimides from PBBTMA, HETMA, and EGTMA were synthesized in the same manner and designated as BPI, HEPI, and EGPI, respectively.

## RESULTS AND DISCUSSION

### Monomer synthesis

Aromatic TMA-bearing dianhydride PPBTMA, PBBTMA, and aliphatic TMA-bearing dianhydride

HETMA, and EGTMA were synthesized in high yield via the transesterification reaction between trimellitic anhydride and various diacetates, according to Scheme 2. Although the diacetate of EG was not isolated because of its high solubility in water; it was successfully converted to EGTMA in excellent yield. The structures of PPBTMA, PBBTMA, HETMA, and EGTMA were confirmed by elemental analysis and mass spectroscopy.

### Polyesterimides formation

The TMA-bearing dianhydrides were converted to the corresponding polyesterimides by condensation with mixed diamines (BAPP and diaminopolysiloxane) in almost quantitative yield. The inherent viscosities of resulted polyesterimides, HPI, BPI, HEPI, and EGPI series, ranged from 0.81 to 0.94, 1.12 to 2.20, 0.51 to 0.63, and 0.55 to 0.67 dL/g, respectively.

### Intrinsic viscosity determination and $T_g$

Intrinsic viscosities of polyesterimides were measured using the Ubbelohde viscometer. The advantage of using this viscometer is that the measurement is inde-

**TABLE IV**  
**Thermal Properties and Isothermal Oxidation Test of PEIs**

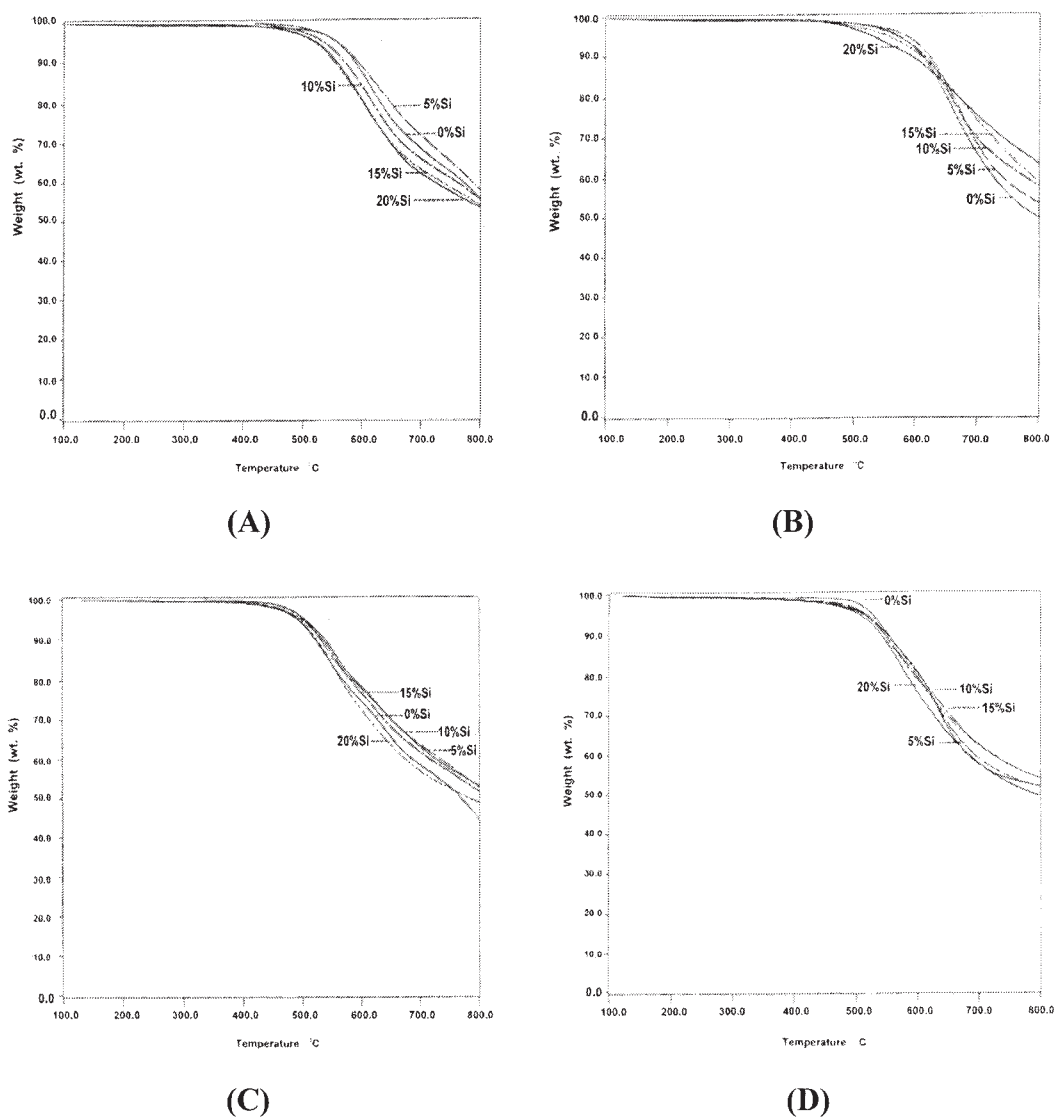
Sample symbol	Siloxane content (mol %)	$T_d^{5\%}$ (°C)	Char yield at 800°C	Weight retention 400°C 150 min
HPI <sup>a</sup>	0	558.4	55.5	95.4
	5	560.2	57.7	94.6
	10	535.4	55.2	91.5
	15	522.0	53.8	91.0
	20	519.4	53.2	89.8
BPI <sup>b</sup>	0	576.2	49.7	98.8
	5	588.1	53.0	98.7
	10	574.0	57.4	97.8
	15	559.1	58.5	97.3
	20	533.5	63.1	96.3
HEPI <sup>c</sup>	0	492.4	44.6	91.0
	5	497.8	52.6	90.9
	10	505.2	53.0	90.6
	15	502.4	51.6	90.5
	20	493.5	48.7	89.8
EGPI <sup>d</sup>	0	526.0	51.4	92.8
	5	514.8	51.6	91.9
	10	514.6	53.4	90.4
	15	510.9	53.4	90.2
	20	504.4	49.8	89.3

<sup>a</sup> HPI: Polyesterimide was prepared with raw material of PPBTMA.

<sup>b</sup> BPI: Polyesterimide was prepared with raw material of PBBTMA.

<sup>c</sup> HEPI: Polyesterimide was prepared with raw material of HETMA.

<sup>d</sup> EGPI: Polyesterimide was prepared with raw material of EGTMA.

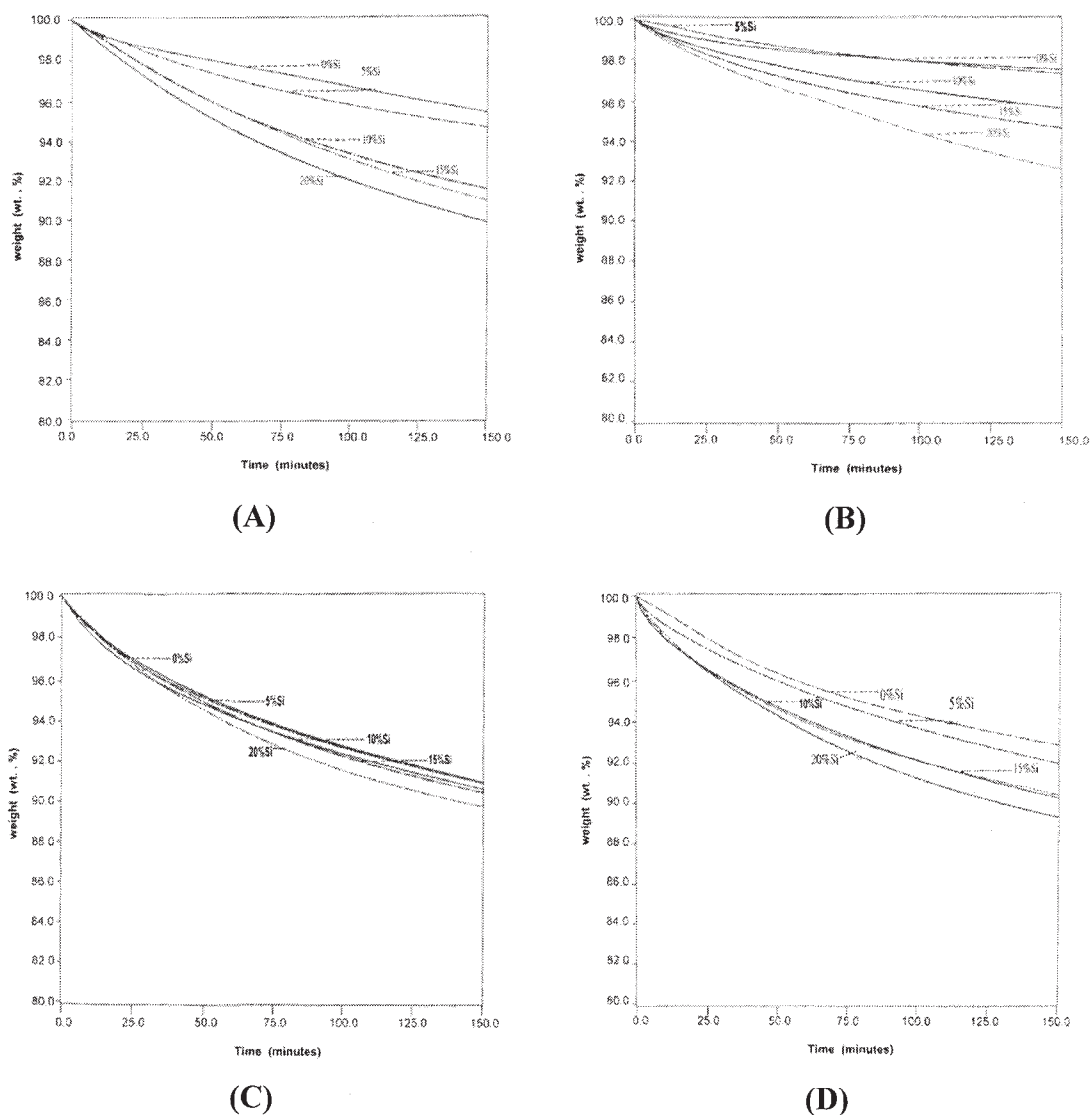


**Figure 2** TGA thermograms of polyesterimides in  $N_2$ : (A) HPI; (B) BPI; (C) HEPI; (D) EGPI.

pendent of the amount of solution in the viscometer and viscosity can easily be calculated by the Ram Mohan Rao equation.<sup>29</sup> The polymer sample (0.06 g) was accurately weighed (0.001 g) and dissolved in 25 mL of NMP. The solution was maintained at 120°C for 20–25 min to achieve a complete solution of the polymer in the solvent. The solution was then cooled to room temperature and filtered through a 0.45- $\mu$ m disposable membrane filter (cellulose acetate). By using the viscometer at 30°C, the intrinsic viscosity was calculated from the relative viscosity by means of the Ram Mohan Rao equation. The intrinsic viscosities of polyesterimides were determined and the results are summarized in Table III. The polyesterimides were obtained in almost quantitative yield with inherent viscosities of 0.51–2.20 dL/g. The solubility of the polymer solution affects the inherent viscosity of the resulting polyesterimides significantly.<sup>18</sup> The molecular weight of polyesterimides, HEPI and EGPI, ob-

tained from linearly aliphatic structure with hexyl and ethyl groups was lower. This might be attributed to their low nucleophilicity.

The  $T_g$  is a very important parameter of a polymer because the  $T_g$  establishes the service environment for the materials usage. In most applications, the polyimide is used at a temperature well below  $T_g$ . Identifying mechanisms responsible for  $T_g$  changes and being able to predict  $T_g$  depression are critical for material applications and engineering design.<sup>30</sup> Thermal behavior of the  $T_g$  of the polyesterimides was evaluated by means of DSC traces: endotherms or exotherms were completely lacking, reflecting their amorphous nature. The result indicated that without siloxane incorporation (control) BPI had higher  $T_g$  (227°C) than that of HPI (210°C), HEPI (177°C), and EGPI (180°C). It should be noted that the  $T_g$  of polyesterimides of BPI and HEI slightly decreased with the increase in siloxane content, whereas  $T_g$  of HEPI and EGPI decreased dramat-



**Figure 3** TGA isothermal thermograms of polyesterimides in  $N_2$  at  $400^\circ\text{C}$  15 min: (A) HPI; (B) BPI; (C) HEPI; (D) EGPI.

ically with the increase in siloxane content. The results indicated that the simple additivity of component contribution to  $T_g$  would fail with this system and the toughening effect dominated the system.<sup>31,32</sup> The  $T_g$  itself varies widely with structure and other thermodynamic parameters, such as molecular weight, intermolecular force, chain motion, and chain stiffness.<sup>33</sup> The transition corresponds to the major  $T_g$  of the polyesterimide above which significant chain motion and chain stiffness takes place. A major difference between aromatic structure motion (BPI, HEP) and aliphatic structure motion (HEPI, EGPI) is the flexibility imparted to the polymer. Aliphatic structure acts to absorb energy much better than the equivalent aromatic structure in the face of impact blows. On the other hand, an aromatic structure usually behaves as a rigid state in the polyesterimides system to increase the polymer's  $T_g$  as well as to affect mechanical properties.<sup>34</sup> The  $T_g$ 's of all these polyesterimides are listed in Table III.

### Thermal properties for polyesterimide

TGA is the most favored technique for rapid evaluation in determining and ranking the thermal stability and thermal degradation behavior of various polymers. TGA results for various polyesterimides with or without siloxane units under nitrogen are shown in Table IV and Figure 2. The results indicate that most of these polyesterimides have a  $T_{d5\%}$  of over  $500^\circ\text{C}$ . The thermal stabilities, based on  $T_{d5\%}$ , are BPI > HPI > EGPI > HEPI. The same trend was observed by the isothermal oxidation test as shown in Table IV and Figure 3. The 5% degradation temperatures of the polyesterimides decreased with the increase in Si content, while char yield increased. The linear structure of polysiloxane and the methyl group may contribute to the reduction in the thermal stability. Furthermore, the high free volume of polysiloxane might have resulted in lower molecular interaction and reduced the thermal stability. The increase in char yield is mainly from

TABLE V  
Solubility Test of Polyester-imides<sup>m</sup>

Si(mol %)	Solvent							
	NMP	DMAc	DMF	DMSO	m-cresol	Cyclohexanone	THF	H <sub>2</sub> SO <sub>4</sub>
HPI								
0	+–	+–	+–	+–	+	+–	–	++
5	+	+	+	+	+	+–	–	++
10	+	+	+	+	+	+–	–	++
15	+	+	+	+	+	+–	–	++
20	+	+	+	+	+	+–	–	++
BPI								
0	+–	+–	+	+	+	+–	–	++
5	+–	+–	+	+	+	+–	–	++
10	+–	+–	+	+	+	+–	–	++
15	+	+	+	+	+	+–	–	++
20	+	+	+	+	+	+–	–	++
HEPI								
0	++	++	++	++	+	+–	+–	++
5	++	++	++	++	+	+–	+–	++
10	++	++	++	++	+	+–	+–	++
15	++	++	++	++	+	+–	+–	++
20	++	++	++	++	+	+–	+–	++
EGPI								
0	+–	+–	+–	+–	+–	+–	+–	++
5	+	+	+	+	+–	+–	+–	++
10	+	+	+	+	+–	+–	+–	++
15	+	+	+	+	+–	+–	+–	++
20	+	+	+	+	+–	+–	+–	++

(++) soluble at room temperature, (+) soluble in hot solvent, (+–) swelled or slightly soluble in hot solvent, (–) insoluble in hot solvent.

<sup>m</sup> measured at a concentration of 0.5 g/dL.

<sup>a</sup> HPI: Polyesterimide was prepared with raw material of PPBTMA.

<sup>b</sup> BPI: Polyesterimide was prepared with raw material of PPBTMA.

<sup>c</sup> HEPI: Polyesterimide was prepared with raw material of HETMA.

<sup>d</sup> EGPI: Polyesterimide was prepared with raw material of EGTMA.

the formation of silica layers that retard oxidation of the char<sup>35,36</sup> during siloxane degradation.

### Solubility of polyesterimides

The solubility behaviors of polyesterimides are shown in Table V. The solubility increased with the increase in siloxane content in the polyesterimides, possibly due to the decreased intermolecular interaction in the presence of the linear flexible Si—O chain. In addition, the —OH and —COO— group in polyesterimide also contribute to the increased interaction with polar solvents. However, they exhibit somewhat limited solubility in common solvent, such as THF.

Table V shows the qualitative solubility of the polyesterimides in various solvents. The results indicate that the solubilities are in the order: HEPI > EGPI > HPI > BPI. BPI and HPI in general are less soluble than HEPI and EGPI; this may be attributed to their higher molecular weight and higher molecular interactive force because of the presence of rigid structure.

### CONCLUSION

For all polyesterimides synthesized, the solubility increased with the flexibility of the main chain and the

content of polysiloxane unit. The decomposition temperatures ( $T_{d5\%}$ ) of HPI and BPI are >500°C, and  $T_g$ 's decrease rather slowly with the increase in polysiloxane content. Overall, the HPI series with 5% polysiloxane exhibits not only good solubility but also excellent thermal stability.

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