

Studies on the Synthesis and Properties of Copolyesterimide

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SYNOPSIS

A series of copolyesterimides was prepared from bisphenol A, diacid (terephthalic acid [TPA] or isophthalic acid [IPA]), and 4-carboxy-*N*-(*p* or *m*-hydroxyphenyl)phthalimide (M1 or M2) in the presence of diphenyl chlorophosphate (DPCP) and pyridine as the direct condensation agent. Copolyesterimides derived from M1 showed poorer solubility than that of M2 during polymerization; a lower M1 content should be employed to prevent precipitation of the resulting polymers. The inherent viscosities of copolyesterimides were in the range of 0.33–0.56 dL/g. Some of these copolyesterimides were completely soluble in *N*-methyl-2-pyrrolidone (NMP), *N,N*-dimethylacetamide (DMAC), dimethylformamide (DMF), and *m*-cresol. The thermal properties of copolyesterimides were examined by DSC and TGA. These copolyesterimides had glass transition temperatures in the range of 173–220°C and a 5% weight loss was observed in the range of 435–482°C. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

Aromatic polyimides have excellent high-temperature resistance, mechanical strength, and superior electrical/insulating properties. However, one of the disadvantages of polyimides is their inferior solubility in most organic solvents. This solubility problem presents a barrier in attempting to directly apply the solution processing technology for fabricating polyimide products. In most applications where polyimides are utilized, a precursor polymer (polyamic acid) is used instead of directly using the polyimide resin. After the fabricating steps, polyamic acid is then cyclized to become polyimide. The storage of polyamic acid prior to processing often causes a ponderous problem in the polyimide processing industry. This problem is aggravated by the strong corrosiveness of the polyamic acid. Furthermore, the need to dewater the final product after cyclization also adds difficulty to the polyamic acid-to-polyimide indirect solution processing approach. Therefore, soluble copolyimides such as polyesterimides and polyamideimides have been developed.

The following are the general methods used in

the synthesis of the polyesterimides: (a) polycondensation between trimellitic acid or its derivative with a diamine and a diol,^{1–4} (b) reaction between a dicarboxylic acid containing an imido group with a diol,^{4–6} (c) reaction between a dianhydride containing an ester group with a diamine,^{4,7–10} (d) pyrolytic polymerization of monomers containing preformed ester linkages,^{11,12} and (e) direct polycondensation between a dicarboxylic acid containing an imido group with a diol in the presence of a direct condensation agent.¹³ The unsatisfactory result obtained from this direct polycondensation was caused by the poor solubility of polyesterimide monomers resulting in its early precipitation within the reaction medium retarding further polymerization. These polyesterimides had relatively low inherent viscosities and formed brittle films. Thus, the solubility of monomers within the reaction media affect the properties of the copolyesterimide significantly.

This article describes a relationship between the solubility of copolyesterimides during polymerization and their monomer composition. Also, a method to synthesize high molecular weight copolyesterimide using a direct condensation method in the presence of a direct condensation agent was proposed. The thermal properties and solubilities of these copolyesterimides with different solvents were also examined.

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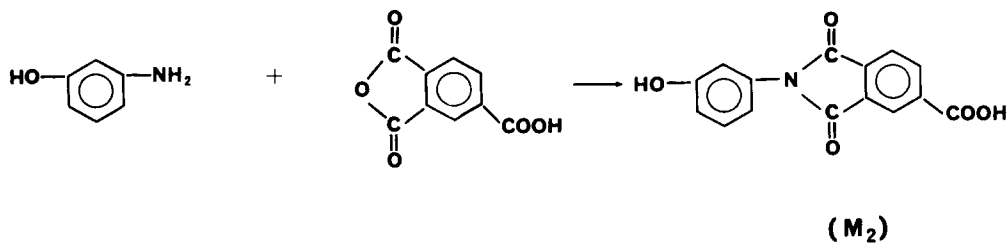
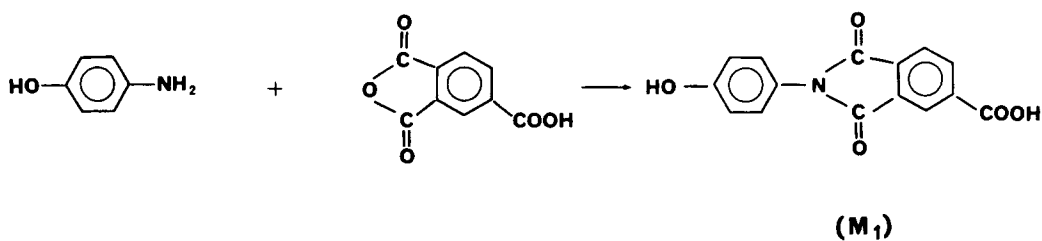
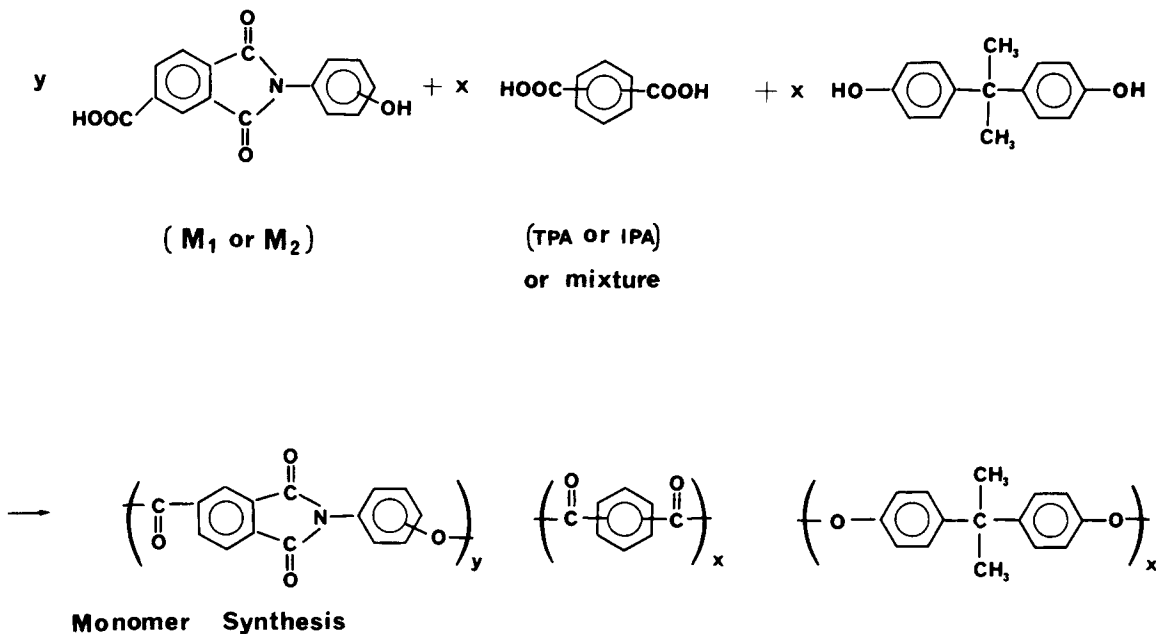
EXPERIMENT

Materials and Instrumental Measurements

Commercial trimellitic anhydride (TMA) (Janssen), *m*-aminophenol (Merck), *p*-aminophenol

(Merck), bisphenol A (Merck), isophthalic acid (IPA, Amoco), terephthalic acid (TPA, Merck), and diphenyl chlorophosphate (DPCP, Merck) were used without purification. Pyridine was purified by distillation over KOH and stored over a 4 Å molecular sieve.

Polymer Synthesis



Scheme 1

IR spectra ranging from 4000 to 600 cm^{-1} of the solid samples of the synthesized monomers were obtained by the KBr method and those of the polymers were obtained by the film method using a Jasco FTIR-7000 spectrophotometer. The inherent viscosities were measured with an Ubbelohde viscometer in *m*-cresol or *N*-methyl-2-pyrrolidone (NMP) at 25°C ($C = 0.5 \text{ g/dL}$).

DSC measurements were conducted with a DuPont 2000 instrument in Al pans at a heating rate of 20°C/min. Thermogravimetric analysis (TGA) was done using a DuPont TGA 951 instrument at a heating rate of 10°C/min under a nitrogen atmosphere.

Monomer Synthesis

4-Carboxy-*N*-(*p*-hydroxy-phenyl)phthalimide (M1)

M1 was synthesized from *p*-aminophenol and TMA according to the method reported by Kurita and Matsuda¹⁴: mp 326°C (dec).

4-Carboxy-*N*-(*m*-hydroxyphenyl)phthalimide (M2)

M2 was synthesized from *m*-aminophenol and trimellitic anhydride (TMA) according to the method reported by Dicke et al.¹⁵: mp = 302–304°C, IR

Table I Physical Properties of Polyesterimides as a Function of the Structure of the Carboxy-*N*-(*p*- or *m*-hydroxyphenyl)phthalimide (CNHP), Dicarboxylic Acid, and Bisphenol-A Employed

Code	CNHP	Dicarboxylic Acid	Bisphenol-A	Solution State	$\eta_{\text{inh}}^{\text{a}}$ (dL/g)	IR Character (cm^{-1})		
	M1	TPA/IPA						
P1	5	1.25/1.25	2.5	Ppt ^b	nd ^c			
	M1	TPA						
P2	4	3	3	Ppt	nd			
P3	3	3.5	3.5	Opaque	0.40 ^d			
P4	2	4	4	Clear	0.56	1784	1742	1378
P5	1	4.5	4.5	Clear	0.38 ^d			
	M1	IPA						
P6	5	2.5	2.5	Ppt	nd			
P7	4	3	3	Ppt	nd			
P8	3	3.5	3.5	Opaque	0.42	1783	1742	1378
P9	2	4	4	Clear	0.39	1784	1742	1380
P10	1	4.5	4.5	Clear	0.33	1783	1729	1381
	M2	TPA/IPA						
P11	6	1/1	2	Clear	0.38	1783	1731	1376
P12	5	1.25/1.25	2.5	Clear	0.47	1783	1734	1377
P13	4	1.5/1.5	3	Clear	0.52	1783	1738	1377
P14	2	2/2	4	Clear	0.47	1783	1742	1377
P15	1	2.25/2.25	4.5	Clear	0.41	1784	1742	1377
	M2	TPA						
P16	5	2.5	2.5	Clear	0.52	1783	1736	1377
	M2	IPA						
P17	5	2.5	2.5	Clear	0.37	1783	1736	1377

^a Measured in NMP at 30°C ($C: 0.5 \text{ g/dL}$).

^b ppt: Precipitation.

^c nd: Not determined.

^d Measured in *m*-cresol at 30°C ($C: 0.5 \text{ g/dL}$).

(KBr), 1777 cm^{-1} , 1671 cm^{-1} , 1388 cm^{-1} (imide C=O), 1717 cm^{-1} (ester C=O).

ANAL: Calcd for $\text{C}_{15}\text{H}_9\text{NO}_3$: C, 63.61%; H, 3.20%; N, 4.95%.

Found: C, 63.34%; H, 3.33%; N, 4.87%.

Polymer Synthesis

A solution of DPCP (13 mmol), pyridine (20 mL), and LiCl (10 mmol) was stirred at room temperature for 30 min and was then added dropwise for 10 min to a hot solution (preheated at 120°C for 5 min) containing diacid (IPA [x mmol], or TPA [x mmol], or equal parts of IPA and TPA), bisphenol A (x mmol), and 4-carboxy-*N*-(*p* or *m*-hydroxyphenyl)phthalimide (M1 or M2) (y mmol) at a ratio of $2x + y = 10$ mmol. The final solution was heated at 120°C for 3 h under stirring and was then poured into methanol to precipitate the polymer. The precipitated polymer was filtered, refluxed in boiling

methanol, filtered, and then dried at 80°C under vacuum. The routes for the synthesis of the copolyesterimides prepared are given in Scheme 1.

RESULTS AND DISCUSSION

Polymer Synthesis

A series of copolyesterimides was prepared from bisphenol A, diacid (TPA or IPA), and M1 or M2 in the presence of DPCP and pyridine as direct condensation agent. The composition of the monomer affected the state of the polymer solution significantly. Table I summarizes the results of the polymerization reaction. In the preparation of the polymer derived from M1, a lower M1 content should be employed to prevent precipitation of the resulting polymers. This is contrary to what is observed in the series of copolyesterimides (P11–P17) derived

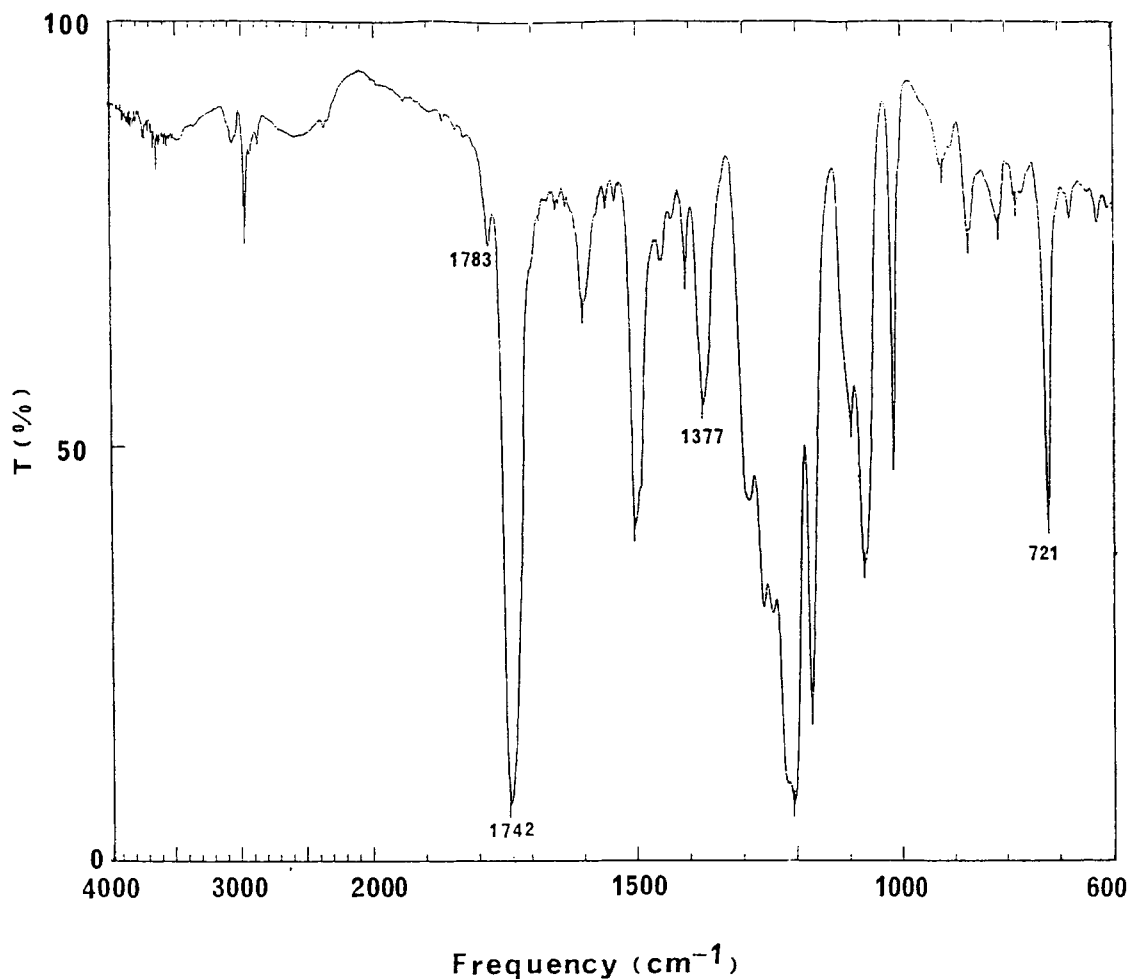


Figure 1 IR spectrum of polyesterimide (P14).

Table II Solubility of Polyester-Imide

Code	NMP	DMAC	DMF	<i>m</i> -Cresol
P1	±	±	±	±
P2	±	±	±	±
P3	±	S	S	++
P4	+	+	±	++
P5	±	±	±	++
P6	±	±	±	±
P7	±	±	±	±
P8	+	S	+	+
P9	++	++	++	++
P10	++	+	+	++
P11	++	++	++	++
P12	++	++	++	++
P13	++	++	++	++
P14	++	++	++	++
P15	++	++	++	++
P16	++	++	++	++
P17	++	++	++	++

++: soluble; +: soluble on heating; ±: partially soluble on heating; S: swelling.

from M2 where the reaction media undergoes no change in the solution state and is clear throughout the entire polymerization process. This indicates

that polyesterimides derived from M1 showed poor solubility during polymerization. The symmetric unit of M1 along the polymer main chain is attributed to cause such a difference. The inherent viscosities of these polymers, except P1, P2, P6, and P7 (those which showed precipitation during polymerizations), were in the range of 0.33–0.56 dL/g, as shown in Table I.

Chemical Structures

The IR spectra data for the copolyesterimides are shown in Table I. Typical IR spectrum curve for polyesterimide (P14) is shown in Figure 1. The presence of a cyclic imide group is indicated by the strong IR bands at 1783, 1742, and 1377 cm^{-1} and that at 1742 cm^{-1} for aryl ester and that at 721 cm^{-1} due to deformational vibration of the cyclic imide. The absorption of the ester carbonyl at 1742 cm^{-1} overlapped that of the imido carbonyl group. The results confirmed the expected structure of the copolyesterimide.

Solubility

The solubilities of these copolyesterimides in different solvents are listed in Table II. The polymers

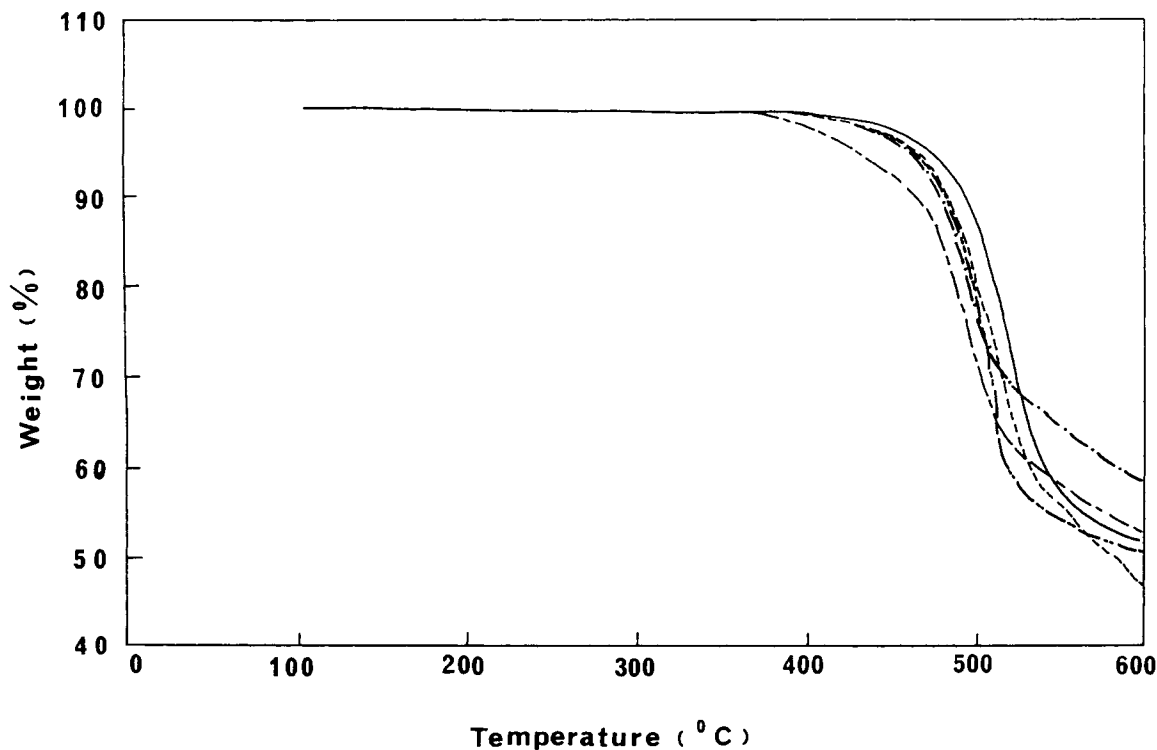


Figure 2 Thermogravimetry of polyesterimides (P6–P10).

Table III Thermal Behavior Data of Polyesterimides

Code	T_g (°C)	Temperature (°C) with the Following Weight Loss			Chart Yield at 600°C (%)
		5%	10%	20%	
P1	213	450	465	479	58
P2	nd	445	475	496	58
P3	214	444	470	486	51
P4	213	435	462	488	50
P5	198	442	466	486	47
P6	nd	453	477	493	58
P7	189	435	470	491	53
P8	184	482	498	514	52
P9	173	458	479	497	52
P10	175	457	484	502	48
P11	215	461	493	511	64
P12	213	471	496	513	56
P13	201	481	493	506	52
P14	195	459	486	503	49
P15	187	445	474	498	42
P16	220	449	473	492	59
P17	186	479	502	527	53

nd: not determined.

prepared from M2 (P11–P17) showed better solubility, and it is surmised that the existence of an asymmetric unit along the polymer main chain causes such a phenomenon. All the copolyesterimides derived from M2 were completely soluble in an amide-type solvent such as NMP, N,N-dimethylacetamide (DMAC), and dimethylformamide (DMF) and in *m*-cresol. This differs from what was reported by Eareckson¹⁶: that polyesters derived from diacid (TPA or IPA) and bisphenol A were soluble in *m*-cresol and insoluble in DMF. Copolymers formed with M1 gave a better solubility when the mol fraction of M1 was 20%. Polymer (P4) derived from TPA, M1 (20%), and bisphenol A was soluble in NMP, DMAC, and *m*-cresol. However, when the mol fraction of M1 was changed to either 30 or 10%, the copolyesterimides (P3, P5) showed poor solubility. Similar results were observed for copolyesterimides derived from IPA, M1, and bisphenol A. Polymer P9 with 20% mol fraction of M1 was soluble in NMP, DMAC, DMF, and *m*-cresol, whereas P8 and P10 with 10 and 30% mol fraction of M1, respectively, showed poorer solubility. All these indicate that copolymers formed with M1 gave better solubility only at 20% mol fraction of M1 and

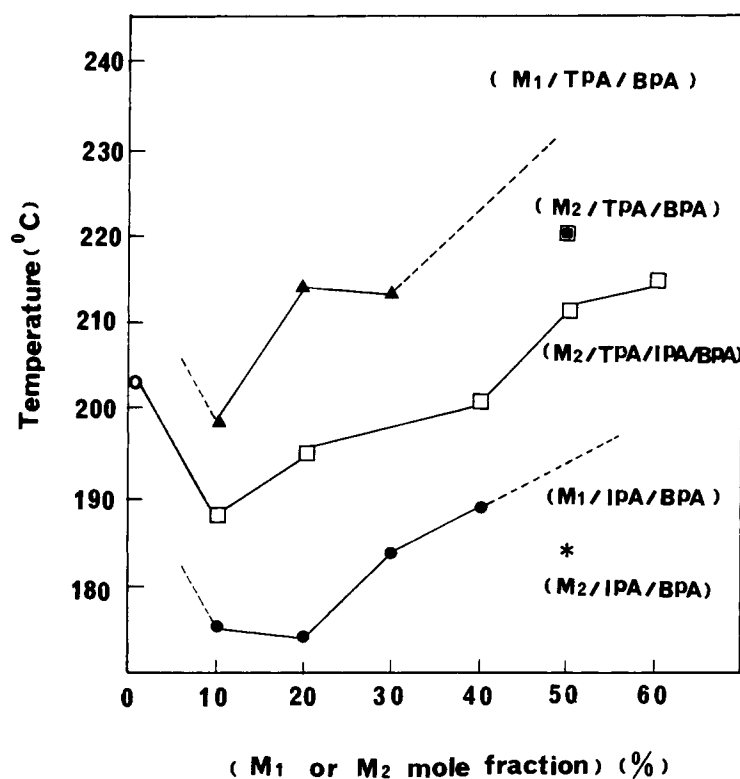


Figure 3 A relationship between T_g and mol fraction of M1 or M2 of polyesterimides: (----) prediction; (O) Ref. 16.

it is postulated that the existence of a random sequence in the copolymer main chain causes such a difference. The above results revealed that copolyesterimides formed with M1 or M2 gave better solubility than did the polyesters¹⁶ derived from TPA or IPA and bisphenol A alone.

Thermal Property

The thermal behavior of those copolyesterimides in a nitrogen atmosphere were measured using thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). Typical TGA curves are shown in Figure 2. The TGA data of these polymers and the temperatures at which 5, 10, and 20% weight losses occurred, as well as weight residues at 600°C, are given in Table III. The decomposed temperature for 5% loss of weight ranged from 435 to 482°C, which clearly indicated the beginning of significant thermal degradation. The char yield of polymers at 600°C increased as the mol fraction of M1 or M2 increased.

The glass transition temperatures (T_g) of these copolyesterimides were in the range of 173–220°C as measured by DSC. The results are shown in Figure 3 and Table III. It was found that with a small amount of M1 or M2 the T_g of the copolyesterimide decreased as compared with the homopolyester reported by Eareckson.¹⁶ However, with increase of the mol fraction of M1 or M2, the T_g increased, indicating the stiffening effect of imide units. Also, copolyesterimides derived from the M2 had relatively lower T_g than that of those derived from M1. Again, the existence of the asymmetric unit within M2 is postulated to cause such a difference. Regardless of the structure of M1 or M2, the effect of diacids on T_g of copolyesterimides are in the order TPA > TPA/IPA > IPA. This indicated that the greater chain symmetry in diacids led to higher glass transition temperature.

CONCLUSION

- (a) A series of polyesterimides with high molecular weight could be prepared from bisphenol A, diacid (terephthalic acid [TPA] or iso-

phthalic acid [IPA]), and 4-carboxy-*N*-(*p*- or *m*-hydroxyphenyl)phthalimide (M1 or M2) in the presence of diphenyl chlorophosphate (DPCP), and pyridine was used as direct condensation agent.

- (b) Polyesterimides derived from M1 showed poorer solubility than that of those derived from M2 during polymerization.
- (c) Some of these polyesterimides exhibit good solubility characteristics and moderately high thermal stability.

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