Studies on the Synthesis and Properties of Soluble Homo- and Copolyester–Imide Derived from Imide–Diacid

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SYNOPSIS

A series of polyester–imides was prepared from diacid (imide–diacid [M1–M4] or a mixture of imide–diacid and terephthalic acid [TPA]) and bisphenol A in the presence of diphenyl chlorophosphate (DPCP) and pyridine as a direct condensation agent. The inherent viscosities of homo- and copolyester–imides were in the range of 0.39–0.58 dL/g. Almost all these homo- and copolyester–imides were completely soluble in N-methyl-2-pyrrolidone (NMP), N,N-dimethylacetamide (DMAC), dimethylformamide (DMF), and m-cresol. The thermal properties of homo- and copolyester–imides were examined by DSC and TGA. These copolyester–imides had glass transition temperatures in the range of 95–240°C and a 5% weight loss was observed in the range of 354–465°C. © 1995 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 solution processing technology for fabricating polyimide products. In most applications where polyimides are utilized, a precusor 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 significant 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,

copolyimides such as polyester–imides and polyamide–imides have been developed.

The general methods used in the synthesis of the polyester–imides are (a) polycondensation between trimellitic acid or its derivative with a diamine and a diol,[1–4] (b) reaction between a dicarboxylic acid containing an imide group with a diol,[4–6] (c) reaction between a dianhydride-containing 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 4-carboxy-N-(p or m-hydroxyphenyl)phthalimide, diacid, and bisphenol-A in the presence of a direct condensation agent.[13] The unsatisfactory result obtained from this direct polycondensation[13] was caused by the poor solubility of polyester–imide monomers resulting in its early precipitation within the reaction medium retarding further polymerization. These polyester–imides had relatively low inherent viscosities and formed brittle films. Also, polyester–imide synthesized from dicarboxylic acid containing an imide group with diol[4–6] had low inherent viscosity ranging from 0.09 to 0.37 dL/g. All these indicate that it is difficult to synthesize a high molecular weight polyester–imide prepared from imide–diacid

and diol. The purpose of this study was to propose a method for the synthesis of high molecular weight soluble polyester–imide derived from diacid (imide–diacid or a mixture of imide–diacid and TPA) and bisphenol-A by using the direct condensation method in the presence of direct condensation agent. The thermal properties and solubilities of these polyester–imides with different solvents are also discussed.

EXPERIMENT

Materials and Instrumental Measurements

Commercial trimellitic anhydride (TMA) (Janssen), 4,4'-diaminodiphenyl ether (Merck), 6-aminocaproic acid (Merck), bisphenol A (Merck), terephthalic acid (TPA) (Merck), p-aminobenzoic acid (Merck), m-aminobenzoic acid (Merck), and diphenylchlorophosphate (Merck) were used without purification. Pyridine was purified by distillation over KOH and stored over 4 Å molecular sieve.

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 for the polymers were obtained by the film method using a Jasco-FTIR-7000 spectrophotometer. The inherent viscosities were measured with an Ubbelohde viscometer in NMP at 25°C ($C = 0.5$ g/dL). The melting temperature of the monomers was measured by differential scanning calorimetry (DSC).

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 nitrogen atmosphere. Powder X-ray samples were taken by using a CuKα diffractometer.

Monomer Synthesis

The routes for the synthesis of monomers and polymers used in this report are given in Scheme I and Scheme II.

Preparation of Oxy-bis[N-(4-phenylene)-4'-(carboxylic acid)phthalimide] (M1)

M1 was prepared from 4,4'-diaminodiphenyl ether and trimellitic anhydride (TMA) by the procedure reported by Chang[14]; mp: 375°C (lit.[14] mp: 380–382°C).

Preparation of N-(p-carboxyphenyl)trimellitimide (M2)

To a three-necked flask equipped with a mechanical stirrer and a condenser, 400 mL DMF, m-aminobenzoic acid (0.3 mol), and trimellitic anhydride (TMA) (0.3 mol) were added. A mild exothermic reaction was noted. The mixture was heated and stirred at 120°C for 2 h. The solution was then poured into four volumes (1600 mL) of water to precipitate the compound. This was filtered, washed with water, and dried at 80°C overnight. The crude

Polymer Synthesis
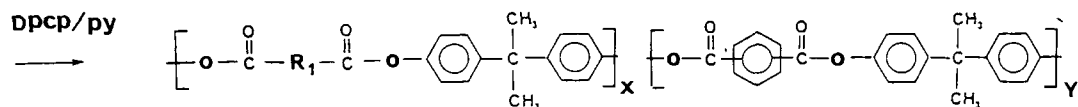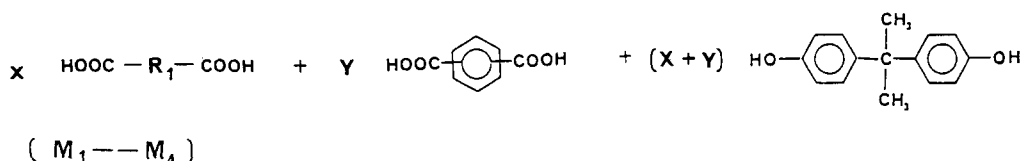
Scheme 1

Monomer Synthesis
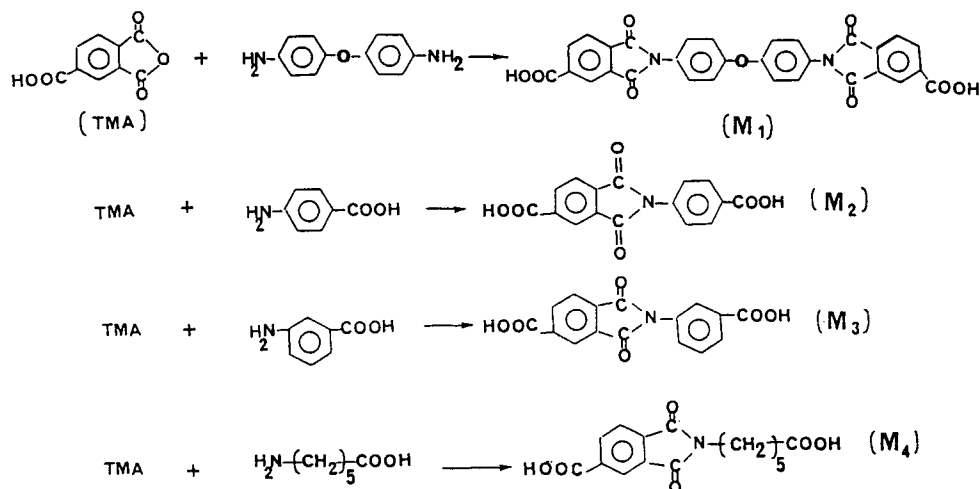
Scheme 2

product was purified by ethanol, yielding 77%. Mp
= 378–380°C (lit.[15] mp: 377–381°C), IR (KBr): 1785
cm^{-1}, 1375 cm^{-1}, (imide—C═O), and 1694 cm^{-1}
(imide C═O and ester C═O).

ANAL: Calcd for $C_{16}H_9NO_6$: C, 61.69%; H, 2.91%;
N, 4.50%.
Found: C, 61.05%; H, 3.14%; N, 4.51%.

Preparation of N-m-carboxyphenyl)trimellitimide (M3)

N-(m-Carboxyphenyl)trimellitimide (**M3**) was prepared from m-aminobenzoic acid (0.3 mol) and TMA
(0.3 mol) by the procedure described above. The
crude diacid was purified by ethanol. Yield: 77%; mp
> 400°C (lit.[15] mp: 407–408°C). IR (KBr): 1785 cm^{-1},
1375 cm^{-1} (imide—C═O), and 1694 cm^{-1} (imide
C═O and ester C═O).

ANAL: Calcd for $C_{16}H_9NO_6$: C, 61.69%; H, 2.91%;
N, 4.50%.
Found: C, 61.05%; H, 3.14%; N, 4.51%.

Preparation of N-(ω-Carboxypentylene)trillitimide (M4)

M4 was synthesized from 6-aminocaproic acid and
TMA according to the method reported by Yang
and Hsiao[16]: mp = 208°C (lit.[16] mp: 204°C), IR (KBr)
1771 and 1381 cm^{-1} (imide—C═O), 1711 cm^{-1}
(imide C═O and ester C═O).

ANAL: Calcd for $C_{15}H_{15}NO_6$: C, 59.02%; H, 4.95%;
N, 4.59%.
Found: C, 58.80%; H, 5.00%; N, 4.50%.

Polymer Synthesis (Method A)

A solution of diphenylchlorophosphate (DPCP) (13
mmol), pyridine (10 mL), and LiCl (10 mmol) was
stirred for 30 min. The diacids (5 mmol) in pyridine
(20 mL) were added to the above solution, and after
stirring for 20 min at room temperature, the mixture
was heated to 120°C and maintained for 10 min at
that temperature. Then, a solution of diol (5 mmol)
in pyridine (10 mL) was added by gravity to the hot
solution over a period of 10 min. The entire final
solution was maintained with further stirring and
heating at 120°C for 3 h. The reaction solution was
poured into methanol to precipitate the polymer.
The precipitated polymer was filtered, refluxed in
boiling methanol, then filtered and dried at 80°C
under vacuum.

Polymer Synthesis (Method B)

A solution of diphenylchlorophosphate (DPCP) (13
mmol), pyridine (20 mL), and LiCl (10 mmol) was
stirred at room temperature for 30 min and then
added dropwise for 10 min to a hot solution (preheated at 120°C for 5 min) containing N-(ω-carboxypentylene)trimellitimide (**M4**) (5 mmol) and

Table I The Properties of Polyester–Imide[a]

Code	Diacid (mol Ratio)	Diol	Reaction State	η_{inh}[b] (dL/g)	Property of Film	IR character				
P1	M1	BPA	Clear	0.40	Brittle	1782	1725	1380	725	
P2	M1/TPA (3.5/1.5)	BPA	Clear	0.50	Flexible	1782	1728	1379	723	
P3	M1/TPA (2.5/2.5)	BPA	Clear	0.58	Flexible	1782	1725	1381	723	
P4	M2	BPA	Clear	0.39	Brittle	1784	1733	1371	721	
P5	M2/TPA (2.5/2.5)	BPA	Clear	0.45	Flexible	1783	1736	1365	721	
P6	M3	BPA	Clear	0.42	Flexible	1783	1733	1373	722	
P7	M3/TPA (2.5/2.5)	BPA	Clear	0.58	Flexible	1782	1740	1380	724	
P8	M4	BPA	Clear Gel	0.45[c] 0.1	Flexible Brittle	1783	1736	1721	1364	725

[a] Diacid = diol = 5 mmol; diphenylchlorophosphate = 12 mmol; LiCl = 10 mmol; BPA = bisphenol A.
[b] Measured in NMP at 25°C.
[c] Synthesized by method B.

bisphenol A (5 mmol) in pyridine (10 mL). The final solution was heated at 120°C for 3 h under stirring and poured into methanol to precipitate the polymer. The precipitated polymer was filtered and refluxed in boiling methanol, then filtered and dried at 80°C under vacuum.

RESULTS AND DISCUSSION

Polymer Synthesis

A series of polyester–imides was prepared from diacid (imide–diacid [M1–M4] or a mixture of imide–diacid and TPA) and bisphenol-A in the presence of DPCP and pyridine as a condensation agent. The polyester–imides, except P8, were prepared by method A. As the polyester–imide P8 prepared by method A gave rise to gelation during polymerization and had relatively low inherent viscosity, method B was used for its synthesis. The inherent viscosities of these polymers were in the range of 0.39–0.58 dL/g, as shown in Table I. Most of the obtained polyester–imides exhibited flexible film when cast from NMP solution. This indicated that a high molecular weight polyester–imide was obtained by using these direct condensation methods.

The IR spectra data for the polyester–imides are shown in Table I. The strong IR bands in the ranges 1784–1782 cm^{-1} (imide symmetric carbonyl stretching), 1740–1722 cm^{-1} (asymmetric imide carbonyl and ester carbonyl stretching), 1381–1364 cm^{-1} (im-

ide ring vibration, axial stretching), and 725–721 cm^{-1} (imide ring vibration, out of plane). The absorption of the ester carbonyl, except for P8, was in the range of 1740–1722 cm^{-1}, overlapping that of the imide carbonyl group. The results confirmed the expected structure of polyester–imide.[17]

Property of Polyester–Imide

The solubilities of these polyester–imides in different solvents are listed in Table II. Most of the polyester–imides were completely soluble in NMP, DMAC, DMF and m-cresol. This differs from what was reported by Eareckson[18]: that polyesters derived from diacid (TPA or isophthalic acid [IPA]) and

Table II Solubility of Copolyester–Imide

Polymer	NMP	DMF	DMAC	m-Cresol
P1	++	++	++	+−
P2	++	++	++	++
P3	++	++	++	++
P4	++	++	++	++
P5	++	++	++	++
P6	++	++	++	++
P7	++	++	++	++
P8	++	++	++	++

++ soluble at room temperature; +− partially soluble on heating.

bisphenol-A were soluble in *m*-cresol and insoluble in DMF. The above results revealed that copolyester–imides formed with **M1–M4** gave better solubility than did the polyesters[15] derived from diacid (TPA or IPA) and bisphenol-A alone. The X-ray diagram of the polymers are shown in Figure 1. The diagram indicates that the polymers had some degree of crystallinity, whereas P3 was amorphous in nature.

The thermal behavior of those polyester–imides in a nitrogen atmosphere were measured using thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). 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 temperature for 5% loss of weight ranged from 354 to 465°C, which clearly indicated the beginning of significant thermal degradation. The glass transition temperatures (T_g) of these copolyester–imides were in the range of 95–240°C as measured by DSC. The results are shown in Table III. The T_g of the copolyester–
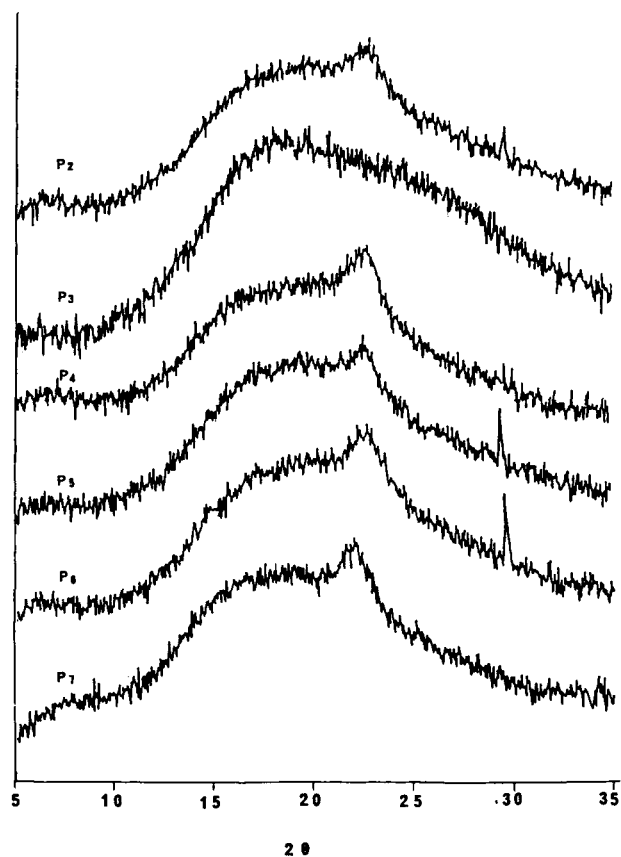

Figure 1   The X-ray diffraction diagram of copolyester–imides.

Table III   Thermal Properties of Copolyester–Imide

Polymer	T_g^a (°C)	Temperature (°C) with the Following Weight Loss[b]			Char Yield (%)
		5%	10%	20%	
P1	240	441	473	510	69
P2	214	446	496	510	64
P3	211	462	486	504	49
P4	209	434	457	480	57
P5	209	453	475	494	39
P6	224	465	488	506	48
P7	224	461	475	487	45
P8	95	354	393	416	17

[a] Measured by DSC in N2 at a heating rate 20°C/min.
[b] Measured by TGA in N2 at a heating rate 10°C/min.

imide was increased as compared with the homopolyester reported by Eareckson,[18] and this increment occurred with an increased mol fraction of imide–diacid (**M1**), indicating the stiffening effect of imide units. Similarly, the char yield of the copolyester–imides was increased with an increasing mol fraction of imide–diacid (**M1**). Among the polyester–imides, the polymers P1–P7 possess higher decomposition temperature, T_g, and char yield than those of polymer P8, due to the presence of higher aromatic segments in their backbones.

CONCLUSION

A series of polyester–imides with high molecular weight was prepared from diacid (imide–diacid [**M1–M4**] or a mixture of imide–diacid and TPA) and bisphenol-A in the presence of DPCP; pyridine was used as direct condensation agent. These copolyester–imides exhibited good solubility characteristics and moderately high thermal stability. The solubility and the T_g of the copolyester–imides were improved as compared with that of the polyester derived from diacid (TPA or IPA) and bisphenol-A.

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