

# Novel Diols Containing Ester and Amide Groups and Resulting Poly(ester amide ester)s

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**ABSTRACT:** The reaction of terephthaloyl chloride and 4-hydroxybenzoic acid resulted in terephthalyl bis(4-oxybenzoic) acid. This diester diacid was converted into its corresponding diester diacid chloride (terephthaloyl dioxydibenzoylchloride) via a reaction with thionyl chloride. Diols with preformed ester and amide groups were prepared through the reaction of terephthaloyl dioxydibenzoylchloride with 4-aminophenol and 5-amino-1-naphthol. Polycondensation reactions of the prepared diols with different ar-

omatic and aliphatic diacid chlorides afforded eight aromatic and semiaromatic poly(ester amide ester)s. The polymers were fully characterized, and their physical and thermal properties were studied. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 93: 2699–2703, 2004

**Key words:** polycondensation; polyesters; thermal properties

## INTRODUCTION

Polyarylates are high-performance engineering plastics with good thermal and mechanical properties.<sup>1,2</sup> However, they are generally difficult to process because of their limited solubility in organic solvents and their high melting and glass-transition temperatures due to their rigid structures. The addition of bulky and aliphatic units and the disruption of their symmetry are important methods of overcoming these drawbacks.<sup>3–6</sup>

Copolycondensation is one way of modifying the polymer properties. Modifying the properties of polyesters through the incorporation of hydrogen-bonded amide groups has been investigated.<sup>7–10</sup>

The materials are either random copoly(ester amide)s, in which the proportion of ester groups to amide groups can be varied through the whole range of compositions, or alternating or patterned poly(ester amide)s with regularly recurring successions of the characteristic groups in the main chain. Those of the first type are synthesized through the copolymerization of polyester-forming condensates with, for example, nylon salts or amino alcohols.<sup>11,12</sup> Those of the second type are obtained through the polyesterification of amide-containing precursors or the polyamidation of ester-containing precursors.<sup>13,14</sup>

Because of our interest in synthesizing novel aromatic diols,<sup>15,16</sup> here we describe the synthesis of novel diols containing ester and amide groups and their use in the preparation of related poly(ester amide ester)s. The structure–property relation, with respect to the addition of bulky groups, the disruption of symmetry, and the incorporation of aliphatic moieties in these polymers, was investigated. Fully aromatic polyesters showed high thermal stability, and semiaromatic ones showed improved solubility.

## EXPERIMENTAL

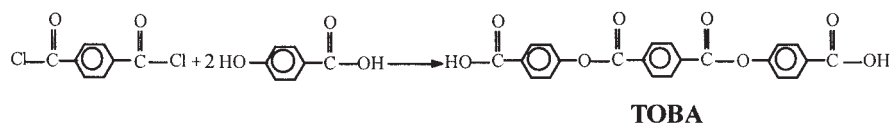
### Materials

All the chemicals were purchased from Merck or Aldrich Chemical Co. Terephthaloyl chloride (TPC) and isophthaloyl chloride (IPC) were purified by sublimation. *N*-Methyl-2-pyrrolidone (NMP), *N,N*-dimethylacetamide (DMAc), *N,N*-dimethylformamide (DMF), dimethyl sulfoxide (DMSO), and toluene were vacuum-distilled over calcium hydride.

### Instruments

IR measurements were performed on a Bruker (Ettlingen, Germany) IFS-48 Fourier transform infrared (FTIR) spectrometer. The H-NMR spectra were recorded in DMSO-*d*<sub>6</sub> solutions with a Bruker Avance DPX 250-MHz instrument. Elemental analyses were performed with a CHN-O rapid elemental analyzer (Heraeus, Wellesley, MA). Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) were performed on an STA-780 (Stanton Redcraft,

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Scheme 1 Synthesis of TOBA.

London, England). Differential thermogravimetry traces were recorded on a Polymer Lab TGA-1500 (Surrey, England). The dynamic mechanical measurements were performed on a Polymer Laboratories (Surrey, England) MK-II dynamic mechanical thermal analyzer over a temperature range of  $-100$  to  $250^{\circ}\text{C}$  at 1 Hz and at a heating rate of  $5^{\circ}\text{C}/\text{min}$ . The values of  $\tan \delta$  and the storage modulus versus the temperature were recorded for each sample. The inherent viscosities were measured with an Ubbelohde viscometer.

### Monomer synthesis

#### Synthesis of terephthalyl bis(4-oxybenzoic) acid (TOBA)

4-Hydroxybenzoic acid (23.14 g) was dissolved in 350 mL of a 0.1M aqueous solution of sodium hydroxide. After the solution was cooled to  $10^{\circ}\text{C}$ , 11.58 g of TPC dissolved in 115 mL of tetrachloroethane was added dropwise to the mixture with stirring. The reaction mixture was stirred at room temperature for 6 h. The mixture was soaked in 430 mL of 3M HCl for 14 h.

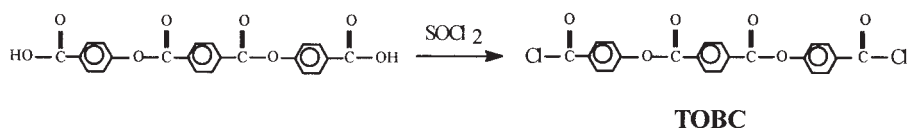
The product was obtained by filtration and washed with water, ether, and ethanol. Then, it (TOBA) was vacuum-dried at  $60^{\circ}\text{C}$  overnight.

Yield: 85%. IR (KBr,  $\nu$ ,  $\text{cm}^{-1}$ ): 3250 (O—H), 1748 ( $-\text{COOR}$ ), 1688 ( $-\text{COOH}$ ), 1425 (C=C), ca. 1285 (C—O).  $^1\text{H-NMR}$  (DMSO- $d_6$ ,  $\delta$ , ppm): 13.11 s (2H, COOH), 8.28 s (4H, aromatic), 8.14 d (4H, aromatic), 7.79 d (4H, aromatic).

#### Synthesis of terephthaloyl dioxydibenzoylchloride (TOBC)

TOBA (7.0 g) was refluxed with thionyl chloride (87.5 mL) and two drops of dry DMF for 4 h. Then, the excess thionyl chloride was removed from the mixture via distillation. The crude product was recrystallized from ether and vacuum-dried at  $50^{\circ}\text{C}$ .

Yield: 89%. IR (KBr,  $\nu$ ,  $\text{cm}^{-1}$ ): 1780 ( $-\text{COCl}$ ), 1745 ( $-\text{COOR}$ ), 1600 (C=C), 1408 (C=C), 1265 (C—O).



Scheme 2 Synthesis of TOBC.

### Synthesis of the diol (diol-AP)

4-aminophenol (0.048 mol) was dissolved in 60 mL of dry NMP. Then, the mixture was cooled to  $0^{\circ}\text{C}$ , and 5 mL of propylene oxide was added. TOBC (0.0153 mol) was added to the mixture and stirred at  $0^{\circ}\text{C}$  for 0.5 h. The mixture was further stirred for 4 h at room temperature. The product was obtained by the flask contents being poured into 300 mL of  $\text{H}_2\text{O}$ . It was then filtered and washed with methanol.

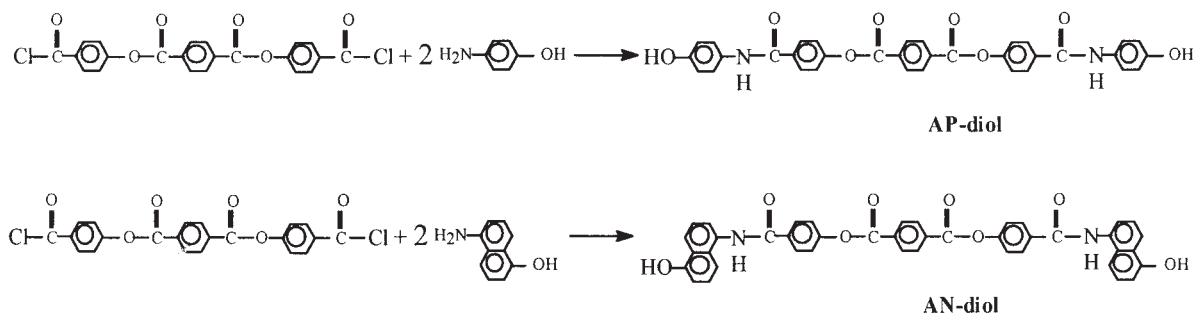
Yield: 88%. IR (KBr,  $\nu$ ,  $\text{cm}^{-1}$ ): 3320–3345 (NH, OH), 1734 ( $-\text{COOR}$ ), 1643 ( $-\text{CONH}$ ), 1250 (C—O).  $^1\text{H-NMR}$  (DMSO- $d_6$ ,  $\delta$ , ppm): 10.10 s (2H, NH), 9.22 s (2H, OH), 8.29 s (4H, aromatic), 8.15 d (4H, aromatic), 8.05 d (4H, aromatic), 7.56 d (4H, aromatic), 6.77 d (4H, aromatic).

The same procedure was performed for the preparation of (elimination of 5-amino-1-naphthol) (diol-AN). In this case, 5 amino-1-naphthol was used instead of diol-AP.

Yield: 86%. IR (KBr,  $\nu$ ,  $\text{cm}^{-1}$ ): 3198–3250 (NH, OH), 1736 ( $-\text{COOR}$ ), 1641 ( $-\text{CONH}$ ), 1263 (C—O).  $^1\text{H-NMR}$  (DMSO- $d_6$ ,  $\delta$ , ppm): 10.16 s (2H, NH), 9.40 s (2H, OH), 8.40 s (4H, aromatic), 8.15 d (4H, aromatic), 8.06 d (4H, aromatic), 7.59 d (2H, aromatic), 7.47 d (2H, aromatic), 7.36 dd (2H, aromatic), 7.16 dd (2H, aromatic), 6.94 d (2H, aromatic), 6.67 d (2H, aromatic).

### Synthesis of the poly(ester amide ester)s

A typical synthesis of the polyesters was carried out as follows. In a round-bottom flask equipped with a stirrer, a nitrogen inlet tube, an HCl outlet tube, and a condenser were placed 5 mmol of diol, 0.08 g of triethylamine hydrochloride, and 10 mL of 1,2-dichlorobenzene. The mixture was heated to  $180^{\circ}\text{C}$  under a nitrogen flow, and a solution of 5 mmol of diacid chloride in 10 mL of dichlorobenzene was added dropwise through a funnel. The mixture was heated until the evolution of HCl ceased (ca. 4 h). After cooling, the polymer was precipitated into hexane and was washed with methanol and water successively.



Scheme 3 Preparation of diols with preformed groups.

## RESULTS AND DISCUSSION

The addition of an amide structure to the backbone of polyesters and the preparation of patterned poly(ester amide)s with high thermal stabilities and modified properties were the objectives of this study. The structure–property relations of the prepared polyesters through the addition of naphthyl groups and alkyl groups and the disruption of symmetry were also investigated. In this way, for the preparation of rigid, rodlike diols with preformed ester and amide structures, the reaction of 4-hydroxybenzoic acid with TPC was achieved. Thus, the diester diacid TOBA was prepared. (Scheme 1).

For the activation of acidic groups toward nucleophilic attack, TOBA was converted into TOBC with  $\text{SOCl}_2$  and a catalytic amount of dry DMF (Scheme 2). The next step was the preparation of the diols via the reactions of TOBC with 4-aminophenol and 5-amino-1-naphthol.

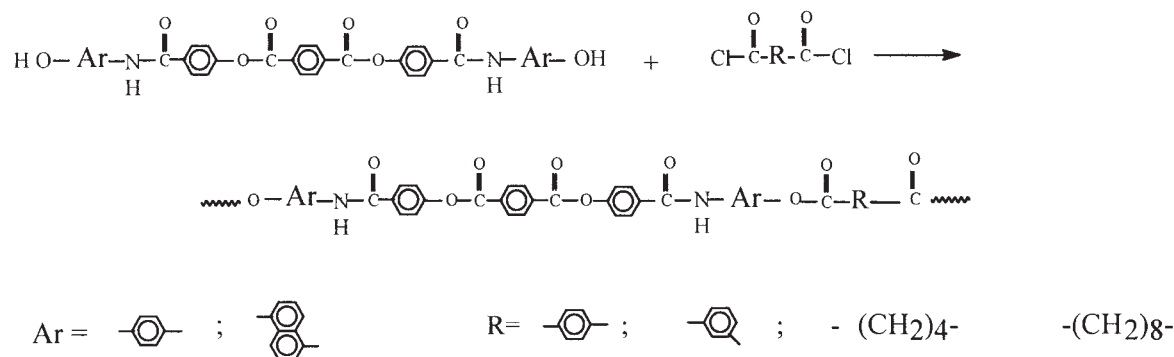
Thus, novel and rigid diols with built-in ester and amide structures were prepared with the proper reaction conditions for the nucleophilic attack of amine groups against acid chlorides (Scheme 3).

High-temperature solution polycondensation reactions of the prepared diols with aromatic and aliphatic diacid chlorides, including TPC, IPC, adipoyl chloride (AC), and sebacoyl chloride (SC), resulted in the preparation of eight different poly(ester amide ester)s

(Scheme 4). The structures of the polyesters and the yields of their reactions are tabulated in Table I.

All the polymers were characterized with FTIR and FT-NMR spectroscopy and elemental analysis. (Table II). Other methods of polyesters synthesis, including interfacial polycondensation and low-temperature solution polycondensation, produced poly(ester amide ester)s in low yields. Therefore, high-temperature solution polycondensation was the preferred method for polyester synthesis.

The inherent viscosity of the polymers, used as a measure of the molecular weight, at a concentration of  $0.5 \text{ g dL}^{-1}$  in DMAc at  $30^\circ\text{C}$  was about  $0.31\text{--}0.37 \text{ dL g}^{-1}$ , which led to a reasonable molecular weight (Table III). According to DSC and dynamic mechanical thermal analysis, fully aromatic polyesters showed glass-transition temperatures in the range of  $183\text{--}195^\circ\text{C}$ , and semiaromatic polymers showed glass-transition temperatures in the range of  $135\text{--}158^\circ\text{C}$ . The 10% weight-loss temperature and the char yield of the polyesters at  $550^\circ\text{C}$  were about  $318\text{--}349^\circ\text{C}$  and  $38\text{--}53\%$ , respectively (Table III). According to the obtained data, the prepared polyesters showed high heat resistance. Obviously, the presence of aliphatic moieties in the semiaromatic polyesters was the main reason for decreasing thermal stability in comparison with that of fully aromatic ones. This was a result of using aliphatic



Scheme 4 Preparation of poly(ester amide ester)s.

**TABLE I**  
Structure of the Poly(ester-amide-esters)

No.	Reactants	Structure of the polymer	Yield (%)
I	Diol-AP + TPC		85
II	Diol-AP + IPC		80
III	Diol-AP + AC		85
IV	Diol-AP + SC		80
V	Diol-AN + TPC		86
VI	Diol-AN + IPC		82
VII	Diol-AN + AC		95
VIII	Diol-AN + SC		92

**TABLE II**  
Characterization of the Polyesters

Polymer	IR (KBr, cm <sup>-1</sup> )	NMR (DMSO · d <sub>6</sub> , δ)	Elemental analysis					
			Calcd		Found			
			C	H	N	C	H	N
I	3325, 1732, 1643, 1610, 1539, 1400, 1252, 1201, 829	10.16 (2H, amide), 6.75–8.27 (24H, aromatic)	70.19	3.62	3.90	70.02	3.49	3.98
II	3327, 1735, 1643, 1612, 1537, 1403, 1250, 1203, 827	10.17 (2H, amide), 6.76–9.31 (24H, aromatic)	70.19	3.62	3.90	70.05	3.47	4.00
III	3323, 2929, 1740, 1643, 1610, 1535, 1400, 1252, 1165, 827	10.15 (2H, amide), 6.73–8.21 (20H, aromatic), 2.68 (4H, aliphatic), 1.60 (4H, aliphatic)	68.77	4.30	4.01	68.89	4.11	3.97
IV	3325, 2926, 1741, 1643, 1612, 1525, 1400, 1254, 1163, 824	10.13 (2H, amide), 6.74–8.20 (20H, aromatic), 2.60 (4H, aliphatic), 1.49 (4H, aliphatic), 1.27 (8H, aliphatic)	71.16	5.12	3.77	70.98	5.02	3.84
V	3252, 1740, 1641, 1599, 1528, 1406, 1259, 1221, 781	10.32 (2H, amide), 6.98–8.32 (28H, aromatic)	73.35	3.67	3.42	73.18	3.55	3.58
VI	3196, 1742, 1641, 1597, 1529, 1406, 1261, 1207, 789	10.31 (2H, amide), 6.95–9.34 (28H, aromatic)	73.35	3.67	3.42	73.15	3.86	3.27
VII	3320, 2924, 1741, 1641, 1610, 1530, 1400, 1254, 1167, 830	10.28 (2H, amide), 6.94–8.26 (24H, aromatic), 2.70 (4H, aliphatic), 1.63 (4H, aliphatic)	72.18	4.26	3.51	72.01	4.13	3.62
VIII	3331, 2928, 1740, 1644, 1603, 1531, 1406, 1262, 1165, 783	10.26 (2H, amide), 6.93–8.25 (24H, aromatic), 2.63 (4H, aliphatic), 1.52 (4H, aliphatic), 1.30 (8H, aliphatic)	73.07	4.92	3.28	72.94	5.02	3.16

TABLE III  
Thermal Analysis and Viscosity of the Polyesters

Polymer	$T_g$ (°C)	$T_0$ (°C)	$T_{10}$ (°C)	$T_{max}$ (°C)	Char yield at 550°C (%)	Inherent viscosity (dL/g)
I	195	220	349	365	52	0.37
II	190	208	344	362	45	0.33
III	158	198	338	353	41	0.34
IV	149	193	335	349	38	0.35
V	188	212	339	360	49	0.34
VI	183	201	327	359	53	0.31
VII	147	191	319	348	43	0.32
VIII	135	185	318	347	40	0.31

$T_g$  = glass-transition temperature;  $T_0$  = initial decomposition temperature;  $T_{10\%}$  = temperature for 10% weight loss;  $T_{max}$  = maximum decomposition temperature. The char yield was the weight of polymer remaining.

diacid chlorides instead of aromatic ones for the preparation of the polyesters.

From another point of view, polyesters derived from diol-AP were more-heat resistant than diol-AN derived polyesters. This was a result of the symmetry and close packing of the aminophenol unit in comparison with the bulky amino naphthol unit.

On the other hand, the incorporation of aliphatic linkages, the presence of bulky groups, and the disruption of symmetry afforded more solubility to the related polyesters. Therefore, polymer I showed maximum thermal stability and minimum solubility (ca. 0.6 g dL<sup>-1</sup> in dipolar aprotic solvents), and polymer VIII showed maximum solubility (ca. 1.3 g dL<sup>-1</sup> in dipolar aprotic solvents) and minimum thermal stability among the prepared poly(ester amide ester)s. All the polymer films that were cast from solutions were brittle.

## CONCLUSIONS

For the preparation of patterned poly(ester amide ester)s, reactions of diols containing ester and amide groups with diacid chlorides were considered. Therefore, two aromatic diols with preformed ester and amide groups were synthesized in three steps. First, a reaction of TPC with 4-hydroxybenzoic acid led to a diester diacid. In the next step, the diacid was converted into diacid chloride through a reaction with thionyl chloride. Finally, reactions of the diacid chloride with 4-aminophenol and 5-amino-1-naphthol afforded the diols. Poly(ester amide ester)s were pre-

pared through reactions of the diols with aromatic and aliphatic diacid chlorides via high-temperature solution polycondensation. The polyesters showed high thermal stability and improved solubility, and the structure-property relations of these polymers were also studied. The liquid-crystal properties of the polymers are under investigation.

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