

Synthesis and Randomization of Well-Defined Sequence, Wholly Aromatic Copolyester/Esteramides

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SYNOPSIS

Well-defined sequence, wholly aromatic copolyester/esteramides have been synthesized by an interfacial polycondensation of a preformed triad diacid chloride monomer, di(*para*-chlorocarbonylphenyl)isophthalate, with the disodium salt of hydroquinone or of deuterated hydroquinone, or with *meta*-phenylene diamine. Carbon-13 nuclear magnetic resonance (NMR) spectroscopy provided unequivocal evidence for regularly alternating polymer structures, and coupled with statistical methods, for randomization on heating in the case of regularly alternating poly(*p*-oxybenzoate-*co-p*-phenylene isophthalate). Polymers synthesized using standard high-temperature melt-polymerization techniques were shown by statistical/carbon-13 NMR methods to have essentially random structures. Thermal properties of copolymer powders and films were found to vary with monomer sequence distribution as well as with composition. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

The variation of monomer sequence distributions in polymer backbones with the aim of optimizing polymer properties is the focus of considerable industrial research activity. A chemically ordered aliphatic aromatic liquid crystalline polymer has been reported to exhibit a distinct and narrow liquid crystalline to isotropic phase transition, in contrast to its corresponding chemically disordered structure.¹⁻³ More recently, the thermal randomization of aliphatic aromatic⁴ and wholly aromatic⁵ ordered sequence copolyesters have been investigated using carbon-13 NMR methods. Indeed, detailed microstructural investigations of wholly aromatic copolyester systems based on statistical/carbon-13 NMR methods^{6,7} have appeared.^{8,9} A wholly aromatic thermotropic liquid crystalline polyester that continues to receive much attention is the copolymer of *p*-oxybenzoate with *p*-phenylene isophthalate.¹⁰⁻¹⁴ Solid-state NMR techniques have been used to investigate molecular dynamics in bulk samples of this copolymer,^{15,16} whereas statistical

mechanics¹⁷ and molecular modeling procedures¹⁸ have been applied to single chains of the same polymer. Small-angle neutron scattering¹⁹ and NMR/IR spectroscopy²⁰ have been used to investigate transesterification kinetics in this main-chain aromatic copolyester. New synthetic procedures offering commercial processing advantages have also recently appeared.^{21,22} We report here on the synthesis and randomization of chemically ordered poly(*p*-oxybenzoate-*co-p*-phenylene isophthalate), including statistical/carbon-13 NMR structural characterization. Synthesis and thermal properties of powders and films of well-defined sequence as well as random, wholly aromatic copolyester/esteramides are also described.

EXPERIMENTAL

Reagents

Isophthaloyl dichloride from Aldrich Chemical Co. was purified by distillation under reduced pressure, followed by recrystallization from *n*-hexane. *Meta*-phenylenediamine from Aldrich Chemical Co. was purified by distillation at 1 Torr. Hydroquinone 99+%, thionyl chloride 99+%, and 1-methyl-2-pyrrolidinone 99+% anhydrous, all from Aldrich

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Chemical Co.; hexadeuterohydroquinone from Merck Co.; and *p*-hydroxybenzoic acid from Ueno Chemical Co. were used as received.

Preparation of Di(*p*-carboxyphenyl)isophthalate

In a 10 L three-neck Morton flask equipped with a nitrogen inlet and outlet, thermometer, condenser, and mechanical stirrer were placed 179.6 g (4.4 m) of sodium hydroxide, 289.8 g (2.1 m) of *p*-hydroxybenzoic acid, and 3 L of distilled water. Isophthaloyl dichloride (203 g, 1 m) was dissolved in 3 L of methylene chloride. The acid chloride solution was added to the reaction flask with fast agitation. The resulting mixture was stirred at room temperature for 1 h, and the solid disodium salt of the desired product was filtered, washed with water, and then acidified with a 10% solution of hydrochloric acid. This crude product was filtered, washed three times with distilled water and twice with hot methanol, and then dried at 100°C to obtain 300 g of di(*p*-carboxyphenyl)isophthalate (melting point 290–300°C) in 74% yield. ¹H-NMR (DMSO-*d*₆) δ 7.45–7.5 (d, 4H), 7.84–7.9 (t, 1H), 8.03–8.06 (d, 4H), 8.46–8.5 (dd, 2H), 8.8 (s, 1H), ~ 13 (Broad).

Preparation of Di(*p*-chlorocarbonylphenyl)isophthalate

In a 2 L three-neck flask equipped with a nitrogen inlet and outlet, thermometer, condenser, safety trap, scrubber containing sodium hydroxide solution, and mechanical stirrer were placed 100 g (0.246 m) of di(*p*-carboxyphenyl)isophthalate, 1500 g of thionyl chloride, and 5 mL of *N,N*-dimethylformamide. The resulting mixture was allowed to react at about 80°C for 24 h and then cooled. The white solid was filtered, washed with hexanes, and dried. The crude acid chloride was recrystallized from 5 L of toluene and dried at 100°C under reduced pressure for 16 h to obtain 77 g of di(*p*-chlorocarbonylphenyl)isophthalate (melting point 204°C) in 71% yield. The material was found to be soluble in *N*-methyl-2-pyrrolidinone, methylene chloride, dimethyl sulfoxide, and hot toluene and insoluble in hexanes and cold toluene. ¹H-NMR (DMSO-*d*₆) δ, 7.4–7.5 (d, 4H), 7.86–7.92 (t, 1H), 8.03–8.1 (d, 4H), 8.48–8.52 (dd, 2H), 8.8 (s, 1H).

Preparation of Regularly Alternating Poly(*p*-oxybenzoate-*co-p*-phenylene isophthalate)

In a 12 L three-neck Morton flask equipped with a nitrogen inlet and outlet, thermometer, condenser,

and mechanical stirrer were placed 22.15 g (0.05 m) of di(*p*-chlorocarbonylphenyl)isophthalate and 4.55 L of methylene chloride. Hydroquinone (5.5 g, 0.05 m) and sodium hydroxide (4.33 g, 0.105 m) were dissolved in 300 mL of distilled water. This solution was added to the flask, along with 50 mL of an aqueous solution containing 0.7 g of 40% benzyltrimethylammonium hydroxide in water. The resulting reaction mixture was stirred at 500 rpm at ambient temperature for 16 h. Methylene chloride was then decanted, and the solid polymer was filtered, washed twice with water, and air-dried, then washed again twice with 400 mL of acetone and with water, and dried at 100°C to obtain 17.13 g of polymer having an inherent viscosity of 0.91 dL/g (see Table I for thermal properties). FTIR (KBr) cm⁻¹ 1750, 1606, 1506, 1263, 1200, 1181, 1156, 1063, 1012, 725; ¹H NMR (TFA-*d*/CD₂Cl₂, 50/50 by weight) δ, 7.4 (s, 4H), 7.53–7.58 (d, 4H), 7.85–7.92 (t, 1H), 8.4–8.5 (d, 4H), 8.63–8.68 (dd, 2H), 9.19 (s, 1H).

Preparation of Regularly Alternating Poly(*p*-oxybenzoate-*co-p*-phenylene-*d*₄-isophthalate)

In a 12 L three-neck Morton flask equipped with a nitrogen inlet and outlet, thermometer, condenser, and mechanical stirrer were placed 22.15 g (0.05 m) of di(*p*-chlorocarbonylphenyl)isophthalate and 4.55 L of methylene chloride. Perdeuterohydroquinone (5.8 g, 0.05 m) and sodium hydroxide (4.33 g, 0.105 m) were dissolved in 300 mL of distilled water. This solution was added to the flask, along with 50 mL of an aqueous solution containing 0.7 g of 40% benzyltrimethylammonium hydroxide in water. The resulting reaction mixture was stirred at 500 rpm at ambient temperature for 5 days. Methylene chloride was then decanted, and the solid polymer was filtered, washed successively with water, 5% sodium hydroxide solution, 5% hydrochloric acid solution, water, and dried at 60°C to obtain deuterated polymer with an inherent viscosity of 0.77 dL/g (see Table I for thermal properties).

Preparation of Regularly Alternating Poly(*p*-oxybenzoate-*co-m*-phenylene isophthalamide)

In a 2 L three-neck resin flask equipped with a nitrogen inlet and outlet, thermometer, condenser, and mechanical stirrer were placed 5.4 g (0.05 m) of *m*-phenylenediamine, 4.3 g of anhydrous lithium chloride, and 216 g of *N*-methyl-2-pyrrolidinone. The resulting mixture was cooled to -15°C. Di(*p*-chlorocarbonylphenyl)isophthalate (22.15 g, 0.05 m) was added to the flask with fast agitation. The temperature of the reaction vessel was allowed to rise to

Table I Thermal Properties of Polymer Powders

Polymer Structure	Inherent Viscosity (dL/g)	T_g (°C)	T_{K-N} (°C)	T_{N-I} (°C)	T_d^{10} (°C)
<u>Poly(<i>p</i>-oxybenzoate-<i>co-p</i>-phenylene isophthalate)^a</u>					
Regular, alternating ^c	0.91	144	360, 391 (390)	465 (485)	455
Random, by heating of regular alternating	—	123	373 (320)	469 (470–483)	508
Random, from preformed triad	0.66	118	329 (320–365)	437, 471 (470)	486
Random, from three monomers	2.36	128	352 (300–360)	(495)	525
<u>Poly(<i>p</i>-oxybenzoate-<i>co-p</i>-phenylene-<i>d</i>₄-isophthalate)^b</u>					
Regular, alternating	0.77	—	346, 392 (345–399)	464 (477–491)	460
Random, from three monomers	—	123	386 (411–440)	495 (490–504)	492
<u>Poly(<i>p</i>-oxybenzoate-<i>co-m</i>-phenylene isophthalamide)^{a,d}</u>					
Regular, alternating	0.68	223		(405)	392

^a Heating rate 20°C per minute. Hot-stage microscope heating rate 20°C per minute.

^b Heating rate 10°C per minute.

^c Thermal properties measured on HFIP film (see Table II).

^d The polyesteramide had a cold crystallization temperature (T_{ccp}) of 304°C, and a DSC melting temperature (T_{mp}) of 343°C.

ambient temperature after the addition of the trimer diacid chloride. The reaction mixture was then stirred for 5 h at ambient temperature. The polymer was precipitated by adding the mixture to distilled water in a blender. The precipitated copolyesteramide was filtered, washed with water, and dried at 100°C and 0.1 Torr to obtain a polymer having an inherent viscosity of 0.68 dL/g (see Table I for thermal properties). FTIR (KBr) cm^{-1} 1750, 1656, 1606, 1550, 1494, 1487, 1425, 1300, 1200, 1150, 1063, 1013, 725; ¹H-NMR (TFA-*d*/CD₂Cl₂, 50/50 by weight) δ 7.4–7.6 (m, 8H), 7.82–7.9 (t, 1H), 8–8.2 (s + d, 6H) 8.62–8.66 (dd, 2H), 9.16 (s, 1H).

Preparation of Regularly Alternating Poly(*p*-oxybenzoate-*co-m*-phenylene isophthalamide) Films

A 7% polymer solution was made by dissolving 7 g of the regularly alternating copolyesteramide with

sequential repeat units of *p*-oxybenzamide–isophthalate–*p*-oxybenzamide–*m*-phenylene, prepared as described above, in 93 g of 1,1,1,3,3,3-hexafluoro-2-propanol at ambient temperature (about 25°C). The solution was filtered through a Millipore Teflon filter type FA 1.0 μm under 100 psi nitrogen pressure. Films of various thicknesses were cast onto glass plates at ambient temperature. The resulting transparent, clear films were soaked in distilled water to separate them from the glass. They were then dried at 100°C for 5 h in a convection oven and for an additional 16 h in a vacuum oven at 0.1 Torr and 100°C. The dried films were transparent and amorphous and ranged in thickness from 0.3 to 1 mil. Thermal characteristics of copolyesteramide film are listed in Table II. The 0.3 mil film had mechanical properties of 9.11 kpsi tensile strength, 5.7% elongation, and 395 kpsi modulus in the machine direction and 8.94 kpsi tensile strength, 4.52% elongation, and 410 kpsi modulus in the transverse direction.

Table II Thermal Properties of Polymer Films

Polymer Structure	Casting Solving	Inherent Viscosity (dL/g)	T_g (°C)	T_{ccp} (°C)	T_{K-N} (°C)	T_{N-I} (°C)	T_d^{10} (°C)
Poly(<i>p</i>-oxybenzoate-<i>co-p</i>-phenylene isophthalate)							
Regular, alternating	HFIP	0.91	144		360, 391 (390)	465 (485)	455
Random, from three monomers	HFIP	2.36	125	(160)	297 (304–345)	(480–495)	
Regular, alternating	TFA/CH ₂ Cl ₂	0.91	135	164 (170)	344, 380 (345–360)	465 (465–475)	455
Random, from preformed triad	TFA/CH ₂ Cl ₂	0.66	126	149 (160)	261, 370 (260)		471
Random, from three monomers	TFA/CH ₂ Cl ₂	2.36	133	155 (165)	271 (290–295)	(455–478)	482
Poly(<i>p</i>-oxybenzoate-<i>co-m</i>-phenylene isophthalamide)^a							
Regular, alternating	HFIP	0.68	234	297			392

^a DSC melt peak temperature (T_{mp}) 352°C.

Preparation of Random Copolyester from Preformed Triad

Random poly(*p*-oxybenzoate-*co-p*-phenylene isophthalate) with repeat units in a mol ratio of oxybenzoate monomer to comonomer of 66.66 to 33.34 was prepared by a standard polycondensation method for liquid crystalline polymers. In a 1 L three-neck flask equipped with a nitrogen inlet and outlet, thermometer, condenser, and mechanical stirrer were placed di(*p*-carboxyphenyl)isophthalate (20 g, 0.07 mol), hydroquinone diacetate (13.59 g, 0.07 mol), and potassium acetate (0.0025 g). The temperature was raised from 25 to 290°C over a period of 30 min; the mixture was then held at 290°C for 60 min, 300°C for 60 min, and then, finally, at 300°C for 30 min under reduced pressure. The resulting polymer had a viscosity of 0.66 dL/g (see Table I for thermal properties).

Preparation of Random Copolyester from Three Monomers

Random poly(*p*-oxybenzoate-*co-p*-phenylene isophthalate) with repeat units in a mol ratio of oxybenzoate monomer to comonomer of 66.66 to 33.34 was prepared by a standard polycondensation method for liquid crystalline polymers. In a 1 L three-neck flask equipped with a nitrogen inlet and

outlet, thermometer, condenser, and mechanical stirrer were placed *p*-hydroxybenzoic acid (55.20 g, 0.4 mol), isophthalic acid (33.20 g, 0.2 mol), hydroquinone diacetate (38.8 g, 0.2 mol), acetic anhydride (44.88 g, 0.44 mol), and potassium acetate (0.0096 g). The mixture was heated at 140°C for 30 min, 140–290°C for 30 min, 290°C for 30 min, 290–350°C for 30 min, 350°C for 60 min, and then, finally, at 350°C under reduced pressure for 30 min. The resulting polymer had a viscosity of 2.36 dL/g (see Table I for thermal properties).

Preparation of Random Copolyester Films

A 3% polymer solution was made by dissolving 5 g of poly(*p*-oxybenzoate-*co-p*-phenylene isophthalate), prepared as described above, in 166 g of 1,1,1,3,3,3-hexafluoro-2-propanol at ambient temperature (about 25°C). The solution was filtered through a Millipore Teflon filter type FA 1.0 μm under 100 psi nitrogen pressure. Films of various thicknesses were cast onto glass plates at ambient temperature. The resulting transparent, clear films were soaked in distilled water to separate them from the glass. They were then dried at 100°C for 5 h in a convection oven and for a further 16 h in a vacuum oven at 0.1 Torr and 100°C. The dried films were transparent and amorphous and ranged in thickness from 0.4 to 1 mil. Thermal characteristics of this

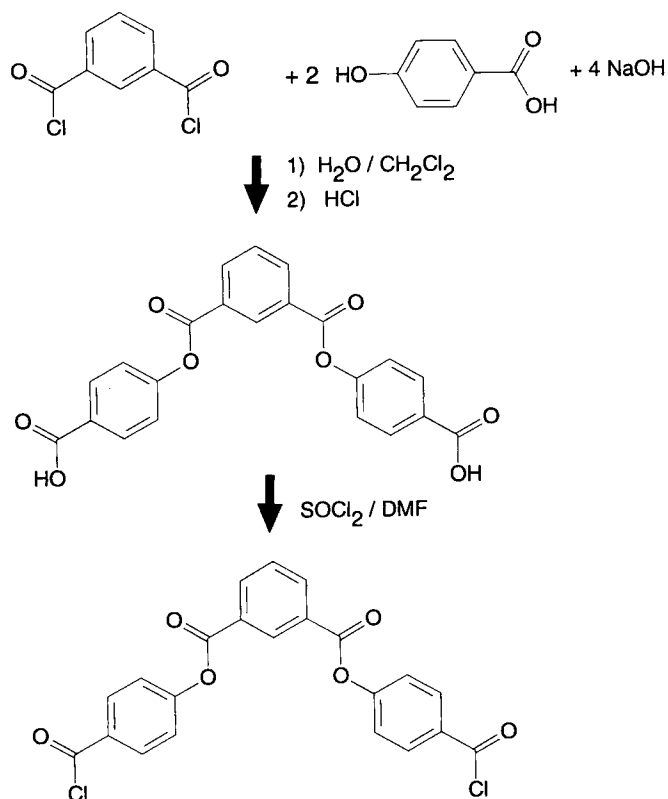


Figure 1 Reaction scheme indicating synthesis route for triad diacid and triad diacid chloride monomers.

and other copolyester films formed using similar techniques are reported in Table II. The poly(*p*-oxybenzoate-*co-p*-phenylene isophthalate) film had a dielectric constant of 3.2 at 100 kHz, a 0.03 dissipation factor, and film properties of 9.35 kpsi tensile strength, 31% elongation, and 368.4 kpsi modulus in the machine direction and 10.905 kpsi tensile strength, 22% elongation, and 396.9 kpsi modulus in the transverse direction. The film had a gas permeability of 0.061 and 0.009 barrer for oxygen and nitrogen, respectively.

Preparation of Random Deuterated Copolyester from Three Monomers

Poly(*p*-oxybenzoate-*co-p*-phenylene-*d*₄-isophthalate) with repeating units in a mol ratio of oxybenzoate monomer to comonomer of 66.66 to 33.34 was prepared by a standard polycondensation method for liquid crystalline polymers. In a 1 L three-neck flask equipped with a nitrogen inlet and outlet, thermometer, condenser, and mechanical stirrer were placed *p*-hydroxybenzoic acid (9.52 g, 0.069

mol), isophthalic acid (5.724 g, 0.0345 mol), perdeuterohydroquinone (4 g, 0.0345 mol), acetic anhydride (15.48 g, 0.152 mol), and potassium acetate (0.0017 g). The mixture was heated at 140°C for 90 min, 140–290°C for 30 min, 290°C for 30 min, 290–350°C for 30 min, 350°C for 60 min, and then, finally, at 350°C under reduced pressure for 30 min.

Carbon-13 NMR Spectroscopy

Carbon-13 NMR spectra were recorded at ~ 35°C on a Varian XL-200 NMR spectrometer operating at 50 MHz for carbon-13. Polymer samples were dissolved at ~ 8 wt % in trifluoroacetic acid-*d*: methylene chloride-*d*₂, 50 : 50 by weight for the purpose of recording NMR spectra.

Viscosity Measurements

Inherent viscosities were determined at 25°C on 0.1% solutions in 1,1,1,3,3,3-hexafluoro-2-propanol: pentafluorophenol, 50 : 50 by volume.

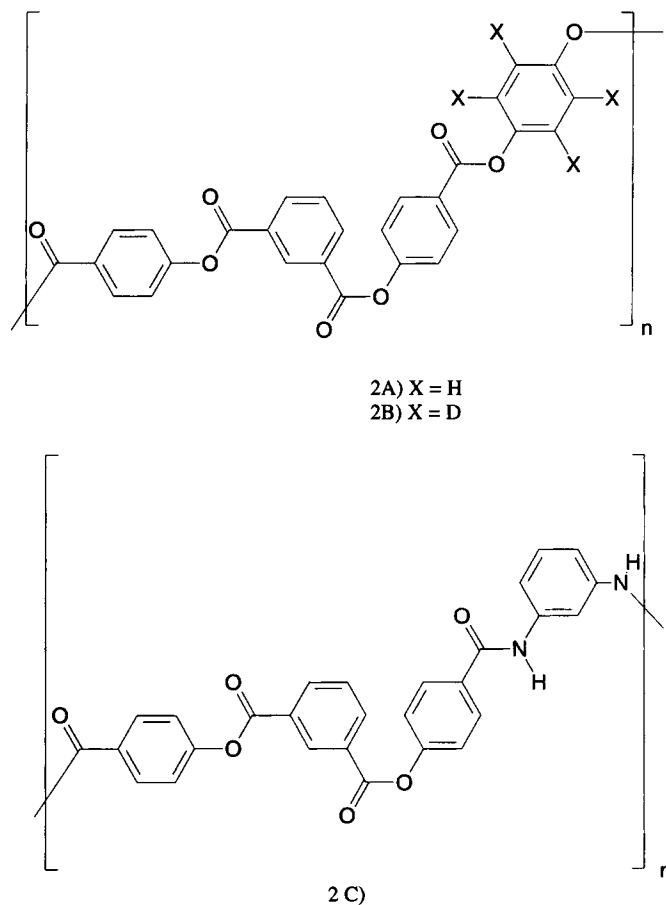


Figure 2 Structures of well-defined, regularly alternating copolyester/esteramides: (A) regularly alternating poly(*p*-oxybenzoate-*co*-*p*-phenylene isophthalate); (B) regularly alternating poly(*p*-oxybenzoate-*co*-*p*-phenylene (d_4) isophthalate); (C) regularly alternating poly(*p*-oxybenzoate-*co*-*m*-phenylene isophthalamide).

Thermal Analysis

Glass transition and liquid crystalline phase transition temperatures were determined using a Thermal Analyst 2100 computer coupled to a 910 DSC or using a Perkin-Elmer DSC-7 coupled to a Digital DEC 425C computer station. Heating rates of 20 or 10°C per minute under nitrogen were used. Thermal stabilities were evaluated by thermogravimetric analysis using a Perkin-Elmer TGA-7 run by a Digital DEC 325C computer station. A heating rate of 10°C per minute under nitrogen was employed. Melting points were determined on finely ground bulk polymers in capillaries and also by DSC at heating rates of 20°C or 10°C per minute under nitrogen.

Hot-Stage Microscopy

The morphology and liquid crystalline phases of the copolyesters and copolyesteramide were investigated using a Nikon Optiphot 2 hot-stage microscope. Co-

polymers were mounted between quartz slides and heated to 500 or 550°C at a heating rate of 20°C per minute. The heating experiments were recorded on videotape, and micrographs at 200× magnification were obtained from the videotape at selected temperatures.

Mechanical Testing

Film mechanical properties were measured at 21°C on 0.561 in.-wide films cast from polymer solutions as described above. An Instron with a load of 10 lb at a crosshead speed of 0.200 in. per minute with a gauge length of 2.000 in. was used.

RESULTS AND DISCUSSION

Synthesis of Triad Monomers

Triad diacid and triad diacid chloride monomers were synthesized according to the reaction scheme

shown in Figure 1. In the first stage, isophthaloyl chloride was allowed to react with *p*-hydroxybenzoic acid at room temperature in a mixture of water and methylene chloride in the presence of base before the solution was acidified with hydrochloric acid. Triad diacid was converted to triad diacid chloride by reaction with thionyl chloride in the presence of a catalytic amount of dimethylformamide.

Synthesis of Well-defined Sequence Copolymers

Well-defined sequence, wholly aromatic copolyester/esteramides were synthesized by interfacial polycondensation of the appropriate monomer with the preformed triad diacid chloride, di(*p*-chloro-carbonylphenyl)isophthalate. Figure 2 lists the structures of the polymers formed, as verified by carbon-13 NMR spectroscopy. In the cases of regularly alternating protonated and deuterated poly(*p*-oxybenzoate-*co-p*-phenylene isophthalate), the triad diacid chloride was reacted with the disodium salt of hydroquinone or of hydroquinone-*d*₄. The interfacial polymerization was carried out in a mixture of methylene chloride and water at room temperature. The catalyst was benzyltrimethylammonium hydroxide. Regularly alternating poly(*p*-oxybenzoate-*co-m*-phenylene isophthalamide) was synthesized by reacting the trimer diacid chloride with *meta*-phenylenediamine at -15°C in *N*-methyl-2-pyrrolidinone containing 2% LiCl. Isolated polymers were purified by repeated washing.

Random Copolymers

Random poly(*p*-oxybenzoate-*co-p*-phenylene isophthalate) was formed in three different ways: First, random poly(*p*-oxybenzoate-*co-p*-phenylene isophthalate) was formed from the regularly alternating copolyester of the same composition by heating said polymer at 375°C for 10 min. Second, the preformed triad diacid, di(*p*-carboxyphenyl)isophthalate, was reacted with hydroquinone diacetate in a melt polymerization at 300°C using potassium acetate as the catalyst. Finally, random copolyester was also formed by reacting three monomers, namely, 1 equivalent of isophthalic acid, 2 equivalents of *p*-acetoxybenzoic acid, and 1 equivalent of hydroquinone diacetate, in another standard high-temperature melt polymerization (290–350°C, KOAc catalyst). Spectroscopic evidence for random polymer structures is presented in the following section.

Statistical/Carbon-13 NMR Spectroscopic Characterization of Copolymers

Figure 3 illustrates the four bonding possibilities for the isophthalate (I) and *p*-oxybenzoate (O) carbonyls. The Bernoullian distribution for these bonding combinations is shown in Figure 4. As can clearly be read from the graph in Figure 4, all four bonding combinations are equally probable for a copolyester having 50 mol % *p*-oxybenzoate, provided Bernoullian statistics are followed. In contrast, the regularly alternating copolymers illustrated in Figure 2 have 50 mol % *p*-oxybenzoate by definition, but can embody only two of the four carbonyl bonding combinations (IO and OQ, for instance). Figure 5(a), e.g., presents the carbonyl region of a carbon-13 NMR spectrum of regularly alternating poly(*p*-oxybenzoate-*co-p*-phenylene isophthalate). As indicated in this figure, the two principal carbonyl resonances observed correspond to OQ and IO carbonyls (refer to Fig. 3 for diad designations). Similar spectra were obtained for the regular, alternating deuterated copolyester and for the regular, alternating copolyesteramide. Heating of the regularly alternating poly(*p*-oxybenzoate-*co-p*-phenylene isophthalate) at 375°C for 10 min produced a material whose carbon-13 NMR spectrum exhibited four

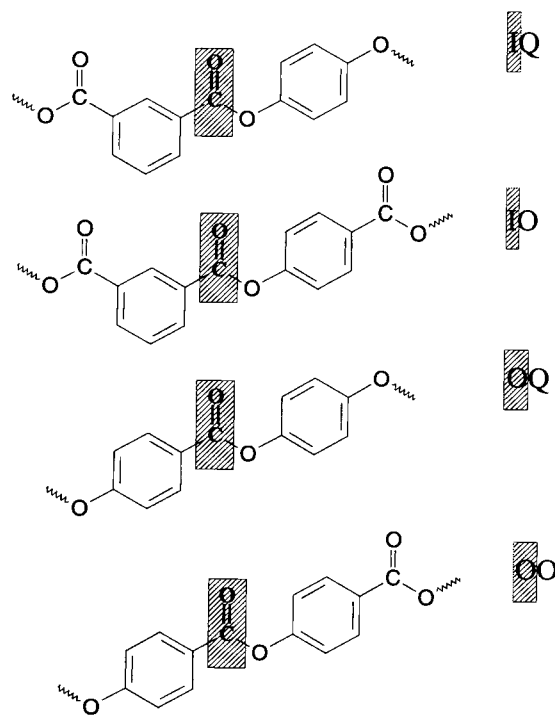


Figure 3 The two isophthalate (I) carbonyl bonding possibilities (with hydroquinone [Q] and with *p*-oxybenzoate [O]) and the two *p*-oxybenzoate (O) carbonyl bonding possibilities (likewise with [Q] and with [O]).

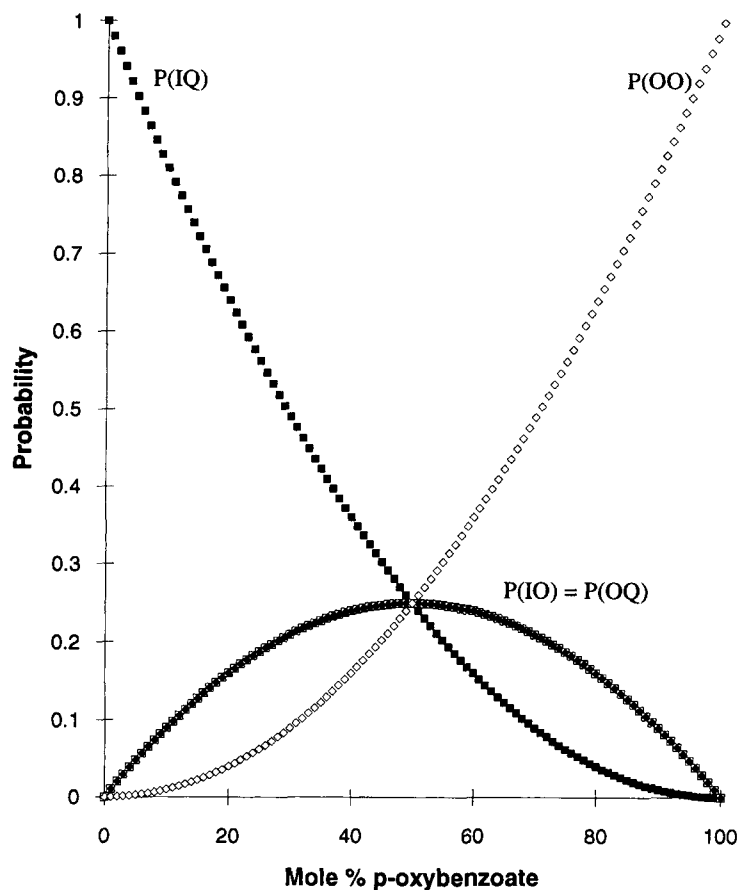


Figure 4 Bernoullian (i.e., zero-order Markovian) distribution of copolyester diad probabilities for a di-alcohol (e.g., hydroquinone), diacid (e.g., isophthalic acid), alcohol/acid (e.g., *p*-hydroxybenzoic acid) system.

carbonyl resonances of approximately equal intensity, as expected for a random copolyester [see Fig. 5(b)]. Indeed, similar, essentially random carbonyl spectra were also obtained for both melt-polymerized poly(*p*-oxybenzoate-*co-p*-phenylene isophthalate) samples [see Fig. 6(a) and (b)].

Thermal Properties of Copolymer Powders and Films

Figure 7 shows first and second heating thermograms for poly(*p*-oxybenzoate-*co-p*-phenylene isophthalate) polymers recorded at a heating rate of 20°C per minute under nitrogen. Samples were heated to 480°C (first heating), then cooled to room temperature at a rate of 10°C per minute before a second heating cycle. Endotherm peak temperatures measured from the three thermograms shown in Figure 7, as well as from a fourth poly(*p*-oxybenzoate-*co-p*-phenylene isophthalate) thermogram

not pictured, are summarized in Table I. Also listed in Table I in parentheses are transition temperatures observed during initial thermal scans using hot-stage optical microscopy at a heating rate of 20°C per minute in air. The temperature ranges listed indicate the onset and completion of phase transitions, crystal to nematic (T_{K-N}), or nematic to isotropic (T_{N-I}). Transition ranges observed optically agree reasonably well with phase transition temperatures determined by thermal analysis.

As can be seen from the data in Figure 7 and in Table I, the glass transition temperature (T_g) measured for the regular alternating polymer is somewhat higher than those observed for the random polymers. Both regular and random polymers exhibited crystal-to-nematic and nematic-to-isotropic phase transitions; the regular structure, however, exhibited two distinct crystal to nematic transitions, compared to only one (albeit somewhat broader) for the random polymers.

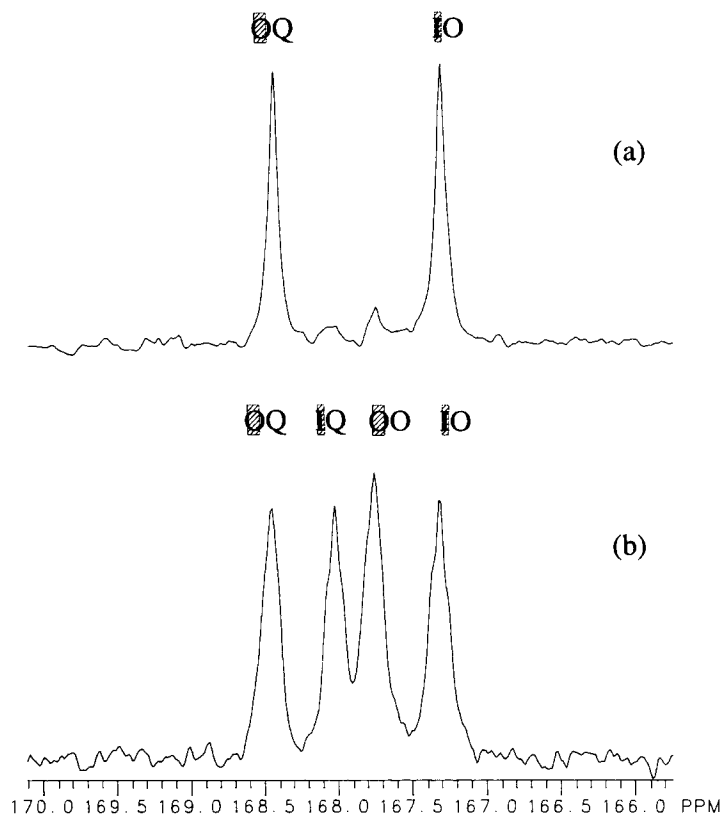


Figure 5 Carbonyl region of carbon-13 NMR spectrum of well-defined, regularly alternating poly(*p*-oxybenzoate-*co-p*-phenylene isophthalate) (a) before and (b) after heating at 375°C for 10 min.

Endotherm peak temperatures obtained from first and second heating thermograms (at 10°C per minute under nitrogen to 425°C) for poly(*p*-oxybenzoate-*co-p*-phenylene-*d*₄-isophthalate) polymers are listed in Table I. As with their protonated analogs, the regular, alternating deuterated polymer exhibits two crystal-to-nematic transitions, whereas the random deuterated polymer shows only one.

The regular, alternating copolyesteramide, poly(*p*-oxybenzoate-*co-m*-phenylene isophthalamide) had a cold crystallization temperature (T_{ccp}) of 304°C and a DSC melting peak temperature (T_{mp}) of 343°C, but did not exhibit an anisotropic mesophase. The results of thermogravimetric analyses (at 10°C per minute under nitrogen) of copolyester/esteramides are also listed in Table I. The temperature marking a 10% weight loss at the employed 10°C per minute heating rate (T_d^{10}) shows the regular, alternating copolyesters (both protonated and deuterated) to be less thermally stable than are their random counterparts.

Table II shows the transition temperatures observed for liquid crystal copolyester and copolyes-

teramide films during the initial thermal scans by DSC or using the hot-stage polarized microscope. The films were prepared by casting onto a glass plate copolyester/esteramide solutions in 1,1,1,3,3,3-hexafluoro-2-propanol or a solvent mixture of trifluoroacetic acid:methylene chloride, 50 : 50 by weight. The films resulting after evaporation of solvent were soaked in methanol and dried. The endotherm peak temperatures observed during the first heating cycle at a heating rate of 20°C per minute under nitrogen are presented in Table II. All copolyester films exhibited crystal-to-nematic (T_{K-N}) and nematic mesophase-to-isotropic (T_{N-I}) phase transitions. The regular alternating copolyesters exhibit two nematic transitions at about 345–360°C and 380–391°C, whereas the random copolyesters from three monomers exhibit only one broad nematic transition irrespective of casting solvent system, as was found for the powder samples. The random copolyesters exhibit crystal-to-nematic transitions at temperatures lower than that of the regular alternating copolyester. A major difference between copolyester film and powder thermal properties is

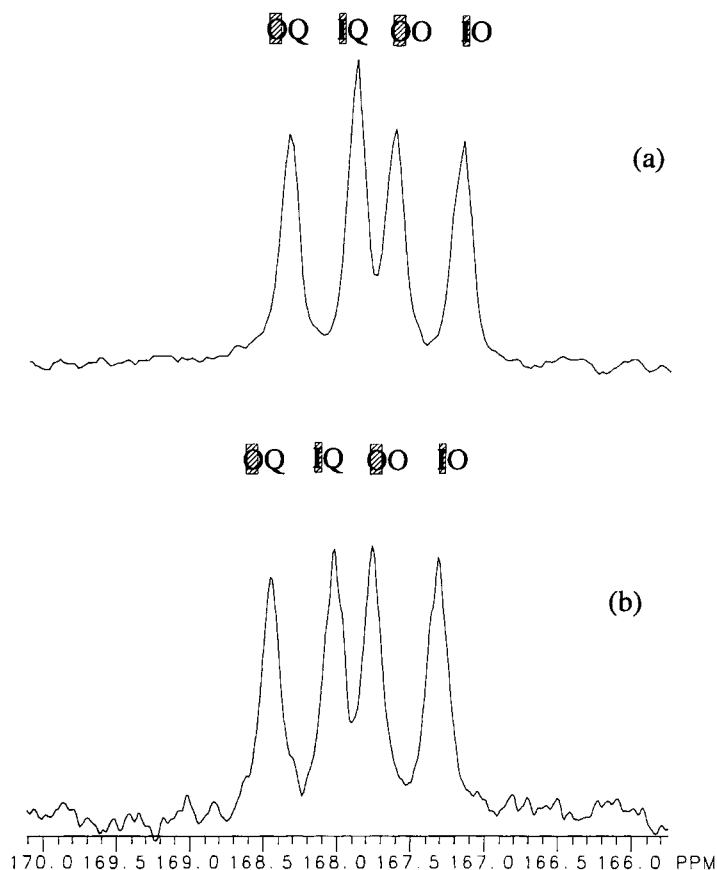


Figure 6 Carbonyl region of carbon-13 NMR spectra of poly(*p*-oxybenzoate-*co-p*-phenylene isophthalate) melt-polymerized (a) from triad diacid monomer plus hydroquinone diacetate and (b) from isophthalic acid, *p*-acetoxybenzoic acid, and hydroquinone diacetate.

the cold crystallization observed at 149–170°C for the transparent amorphous films. After cold crystallization, the film samples exhibited phase transitions similar to those found for the powder samples.

The copolyesteramide film showed a high glass transition temperature of 234°C, cold crystallized at 297°C, and became isotropic at 352°C without exhibiting an anisotropic mesophase.

CONCLUSIONS

Regular, alternating copolyester/esteramides have been synthesized by interfacial polycondensation of a preformed triad diacid chloride, di(*p*-chlorocarbonylphenyl)isophthalate, with the disodium salt of hydroquinone or of hydroquinone-*d*₄, or with methaphenylene diamine. Random copolymers could

also be formed by altering reaction conditions or by thermal treatment (i.e., processing history), as shown unequivocally by statistical/carbon-13 NMR methods. Analysis at the diad level has been presented here, but resolution at the tetrad level has already been achieved for some polymers.⁹ Thermal properties of regular, alternating protonated and deuterated copolyesters were found to be similar, but different from those of random analogs. For example, higher *T*_g's and lower decomposition temperatures were found for regular, alternating structures than for their random counterparts. Crystal-to-nematic transitions were found to be lower for films formed from random copolyesters than for the corresponding regular, alternating copolyester films, irrespective of casting solvent. Cold crystallization was observed for most transparent amorphous films. X-ray and solid-state NMR work is in progress to further elucidate structural/motional characteristics of these and related materials.

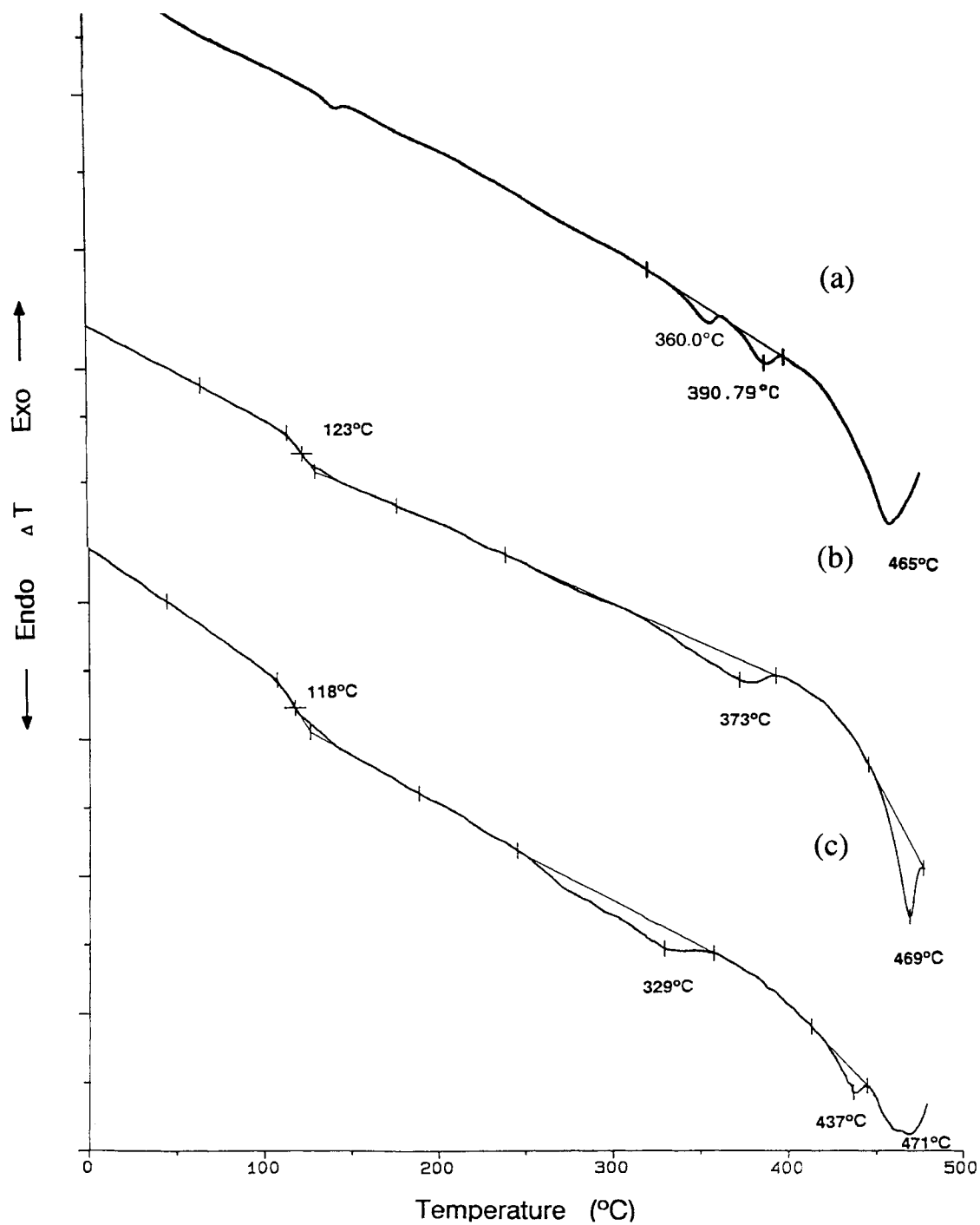


Figure 7 Thermograms (20 $^{\circ}\text{C}/\text{min}/\text{N}_2$ to 480 $^{\circ}\text{C}$) of poly(*p*-oxybenzoate-*co-p*-phenylene isophthalate) having (a) a regular, alternating structure (first heating), (b) a random structure formed by heating the regular, alternating structure (second heating), and (c) a random structure synthesized from a preformed triad (second heating).

The authors would like to thank J. Menczel for thermal analyses, T. Bruno for hot-stage microscopy, and M. Jaffe for his continued support.

REFERENCES

1. S. I. Stupp, J. S. Moore, and P. G. Martin, *Macromolecules*, **21**, 1228 (1988).
2. P. G. Martin and S. I. Stupp, *Macromolecules*, **21**, 1222 (1988).
3. J. S. Moore and S. I. Stupp, *Macromolecules*, **21**, 1217 (1988).
4. J.-I. Jin, C.-S. Kang, and J.-H. Chang, *J. Polym. Sci. A Polym. Chem. Ed.*, **31**, 259 (1993).
5. J.-I. Jin, J.-H. Chang, K. Hatada, K. Ute, and M. Hotta, *Polymer*, **33**, 1374 (1992).
6. F. P. Price, *J. Chem. Phys.*, **36**, 209 (1962).
7. J. C. Randall, *Polymer Sequence Determination—Carbon-13 NMR Method*, Academic Press, New York, 1977.
8. H. Komber, F. Böhme, D. Pospiech, and M. Rätzsch, *Makromol. Chem.*, **191**, 2684 (1990).
9. M. Borzo, E. W. Choe, M. Jaffe, J. J. Rafalko, and C. K. Saw, in *4th European Polymer Federation Symposium on Polymeric Materials*, Baden-Baden, Germany, Sept. 1992.
10. D. J. Johnson, I. Karacan, and J. G. Tomka, *Polymer*, **33**, 983 (1992).
11. D. J. Johnson, I. Karacan, and J. G. Tomka, *Polymer*, **32**, 2312 (1991).
12. D. J. Johnson, I. Karacan, and J. G. Tomka, *Polymer*, **31**, 8 (1990).
13. A. B. Erdemir, D. J. Johnson, I. Karacan, and J. G. Tomka, *Polymer*, **29**, 597 (1988).
14. A. B. Erdemir, D. J. Johnson, and J. G. Tomka, *Polymer*, **27**, 441 (1986).
15. A. Gérard, F. Lauprêtre, and L. Monnerie, *Macromolecules*, **26**, 3313 (1993).
16. R. A. Allen and I. M. Ward, *Polymer*, **33**, 5191 (1992).
17. G. C. Rutledge, *Macromolecules*, **25**, 3984 (1992).
18. S. E. Bedford, K. Yu, and A. H. Windle, *J. Chem. Soc. Faraday. Trans.*, **88**, 1765 (1992).
19. W. A. MacDonald, A. D. W. McLenaghan, G. McLean, R. W. Richards, and S. M. King, *Macromolecules*, **24**, 6164 (1991).
20. J. J. Rafalko, M. Borzo, E. W. Choe, and M. Jaffe, *Polym. Prepr.*, **34**, 770 (1993).
21. B. Gupta, G. Calundann, L. F. Charbonneau, H. C. Linstid, J. P. Shepherd, and L. C. Sawyer, *J. Appl. Polym. Sci.*, **53**, 575 (1994).
22. D. J. Blundell, W. A. Macdonald, and R. A. Chivers, *High Perform. Polym.*, **1**, 97 (1989).

Received August 11, 1993

Accepted January 10, 1994