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Para-Linked, Aromatic, Thermotropic Polyesters with Low Mesophase Temperatures

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ABSTRACT: The solubility, thermal, and optical properties of completely aromatic, para-linked, 2,2′-disubstituted biphenyl and substituted phenyl polyesters are reported. The results show that these moieties enhance solubility, e.g., methylene chloride and tetrachloroethane are typical solvents, and lower mesophase transition temperatures to less than 200 °C in most examples. Oriented and unoriented films of the soluble polymers are completely amorphous as evidenced by X-ray diffraction. Scattering of visible radiation by unoriented films can be attributed to voids as shown by scanning electron micrographs. Film samples which are oriented to 70–80%, measured by IR dichroism, are almost completely nonscattering and exhibit birefringence values of 0.65. These unusual properties may be attributed to a decrease in intermolecular forces caused by the trifluoromethyl-substituted phenyls and noncoplanar biphenyls.

Introduction

In recent papers[1] we described the unique optical and solution properties of 2,2′-disubstituted biphenyl polyamides for optical applications. Most of these polymers are colorless and very soluble in a variety of solvents such as tetramethylurea (TMU) and *N*-methylpyrrolidone (NMP) without LiCl. Many polymers composed of the 2,2′-bis(trifluoromethyl)biphenyl moiety are soluble in acetone or tetrahydrofuran, and one of these polymers is soluble up to 50% (w/v). Highly oriented polymer films are nonscattering, almost completely amorphous, and highly birefringent. This lack of crystallinity and unique solubility is probably due to weak intermolecular forces attributable to little or no H-bonding, random distribution of enantiomeric biphenyls, and the size and nature of the biphenyl substituents. The unusually high birefringence is a consequence of the rodlike conformation of the backbone and high electron density.

Unfortunately, none of these modified rodlike polyamides exhibit a melting point or a thermotropic liquid-crystalline transition, and consequently, oriented films can only be obtained by casting and stretching or extruding from polymer solutions. Since high molecular orientation is required for high birefringence, the orientation generated by extrusion and drawing of the extrudate must be locked-in by rapid extraction or evaporation of solvent. Although the development of this technique was partially successful, it was very difficult to obtain films exhibiting high birefringence, optical clarity, and flatness.

Because of these limitations, an investigation of rodlike polyesters was begun. The major advantage exhibited by these materials is liquid crystallinity and potential melt processability.

The first reported observations of thermotropic liquid-crystalline behavior in polymers were made by Roviello and Sirigu[2] and independently by Kuhfuss and Jackson.[3] The materials described in the latter study were copolymers of poly(ethylene terephthalate) and *p*-hydroxybenzoic acid; the solid to liquid crystal transition temperatures were in the 300–350 °C range. However, because optical devices such as polarizing beam splitters and nonabsorbing polarizers require birefringence values in excess of 0.4, it was decided to restrict the molecular structures of the polymers of this investigation to aromatic, para-linked repeat units such as poly(*p*-hydroxybenzoate) or the analogous poly(1,4-phenylene terephthalate) without flexible spacers. Unfortunately both of these polymers are highly crystalline and do not melt up to 500 °C. Subsequent developments in the field showed that the degree of crystallinity could be reduced and the crystalline to nematic transition temperatures could be lowered to the 200–400 °C range by disrupting the geometric regularity of the backbone. Three very effective molecular modifications were devised to accomplish this: a linear offset, e.g., 2,6-naphthyl,[4] lateral substituents,[5] and monomers of different length. It should be noted, however, that none of these modifications, either individually or in combination, with one possible exception,[6] completely eliminated crystallinity in rodlike polyesters.

In this report we describe the results of an investigation of the effect of 2,2′-disubstituted biphenyls and trifluoromethyl-substituted phenyls on solubility, transition temperatures, and morphology of para-linked, aromatic polyesters.

Experimental Section

Monomer Synthesis. The hydroquinones used were obtained from Aldrich Chemical Co. Hydroquinone was recrystallized from toluene. Methylhydroquinone was twice recrystallized from toluene. The diacetate of chlorohydroquinone was first prepared and purified by column chromatography before deacetylation and sublimation.

The diacid chlorides of terephthalic and 2,6-dinaphthoic acids were synthesized by standard procedures[4] and recrystallized from hexane and hexane/CH_2Cl_2, respectively, before use. The synthesis of the (trifluoromethyl)terephthalate has been described elsewhere.[7]

The 2,2′-substituted biphenyl diacid chlorides containing trifluoromethyl, bromo, and methoxy groups have also been reported previously.[1a]

1-Bromo-3,6-dioxaoctane (XXVIII). To 50 mL of 3,6-dioxa-1-octanol, 100 g triphenylphosphine, and 100 mL of CH_2Cl_2 was added 66 g of *N*-bromosuccinimide via a solid addition funnel while stirring and maintaining the reaction temperature below 25 °C. After the exothermic addition was complete, the mixture was heated to reflux and the CH_2Cl_2 was distilled off through a Vigreaux column. The pressure was then reduced to 8 mm and the product was distilled at 76–78 °C (63.7 g, 87%). ^1H NMR ($CDCl_3$) δ 1.22 (t, 3 H, CH_3), 3.40–3.90 (m, 10 H, CH_2).

Dimethyl 2,2′-Dihydroxy-4,4′-biphenyldicarboxylate (XXIX). To a stirred CH_2Cl_2 (200 mL) solution of 3.39 g (1 mmol) of 2,2′-dimethoxy-4,4′-biphenyldicarbonyl chloride (XXX) was added 10 mL of BBr_2 (in 50 mL of CH_2Cl_2) dropwise. The reaction was stirred under reflux for 16 h. Methanol was then added carefully to the flask dropwise while liberated HBr was vented to a H_2O trap. After all of the BBr_3 had reacted, the CH_2Cl_2 was distilled off while methanol was being added to maintain the volume at about 200 mL. When the distillation temperature reached 65 °C, the distillation was terminated and the volume of the reaction mixture was reduced to 100 mL by flash evaporation. After the addition of 300 mL of water the resulting white precipitate was collected by filtration. Drying under vacuum at 60 °C yielded 2.88 g (95%, mp 288–291 °C). ^1H NMR (DMSO-d_6) δ 4.00 (s, 6 H, OCH_3), 7.50 (m, 6 H, Ar), 9.70 (br, OH).

Dimethyl 2,2′-Bis(1,4,7-trioxanonyl)-4,4′-biphenyldicarboxylate (XXXI). Two grams of XXIX, 4 g of XXVIII, 10 g of K_2CO_3 (powdered), and 100 mL of acetonitrile were stirred together in a 250-mL round-bottomed flask under N_2. After the mixture was heated under reflux for 18 h, the acetonitrile was evaporated off, CH_2Cl_2 was added, and the mixture again was briefly heated to reflux. The mixture was filtered through Celite, the solids were washed with CH_2Cl_2, and the solvent was evaporated off. The resulting oil was subjected to flash chromatography on silica gel and eluted with acetone/CH_2Cl_2 (5/95 v/v). The product, an oil, was taken and hydrolyzed to the corresponding acid. ^1H NMR (CCl_4) δ 1.10 (t, 6 H, CH_3), 3.35–4.10 (m, 26 H, CH_2, $COOCH_3$), 7.18 (d, 2, Ar), 7.50 (m, 4 H, Ar); IR (neat) 1722 cm^{-1}; mass spectrum (70 eV), *m/e* 534 (M^+).

2,2′-Bis(1,4,7-trioxanonyl)-4,4′-biphenyldicarboxylic Acid (XXXII). This acid was prepared by hydrolysis of the diester XXXI in a manner similar to that previously reported for the other substituted biphenyls.[1] Yield (for two steps) 98%; mp 169–170 °C. ^1H NMR (acetone-d_6) δ 1.10 (t, 6 H, CH_3), 3.40–4.25 (m, 20 H, CH_2), 7.42 (d, 2 H, Ar), 7.70 (m, 4 H, Ar), 9.00 (br, 2 H, OH); IR (KBr) 1735 cm^{-1}; mass spectrum (70 eV), *m/e* 506 (M^+).

2,2′-Bis(1,4,7-trioxanonyl)-4,4′-biphenyldicarbonyl Chloride (XXXIII). Five grams of diacid XXXII were stirred with 10 mL of oxalyl chloride, 50 mL of CCl_4, plus 1 drop of DMF under N_2. The mixture was heated to reflux for 4 h and then the solvents were removed by distillation. The resulting yellow powder was placed in a Soxhlet and extracted with pentane which upon standing yielded 4.58 g of white crystals (mp 74–75 °C). Reextraction gave 4.42 g (82%) of product (mp 75–75.5 °C). ^1H NMR (CCl_4) δ 1.13 (t, 6 H, CH_3), 3.40–4.20 (m, 20 H, CH_2), 7.39 (d, 2 H, Ar), 7.64 (d, 2 H, Ar), 7.78 (dd, 2 H, Ar); IR (KBr) 1751 cm^{-1}; mass spectrum (70 eV), *m/e* 542 (M^+).

Anal. Calcd for $C_{26}H_{32}Cl_2O_6$: C, 57.46; H, 5.94; Cl, 13.05. Found: C, 57.72; H, 6.01; Cl, 12.61.

Dimethyl 2,2′-Di-*n*-butoxy-4,4′-biphenyldicarboxylate (XXXIV). Two grams (6.62 mmol) of XXIX and 9.07 g (66.2 mmol) of *n*-butyl bromide were added to 9.14 g (66.2 mmol) of K_2CO_3 (anhydrous) suspended in 75 mL of CH_3CN under N_2. The mixture was stirred under reflux for 6 h, cooled, and filtered through Celite. After evaporation of the solvent, the resulting oil was subjected to column chromatography on silica gel (elutant 2/1 v/v CH_2Cl_2/hexane). The product was isolated after solvent removal as a colorless oil (2.17 g; 82.7%). ^1H NMR ($CDCl_3$) δ 1.30 (m, 14 H, $(CH_2)_2CH_3$), 4.00 (s, 6 H, OCH_3), 4.10 (t, 4 H, OCH_2), 7.50 (m, 6 H, Ar).

Anal. Calcd for $C_{24}H_{30}O_6$: C, 69.55; H, 7.30. Found: C, 69.68; H, 7.57.

2,2′-Di-*n*-butoxy-4,4′-biphenyldicarboxylic Acid (XXXV). This compound was prepared in 87% yield (mp 244–246 °C) as described for other biphenyldicarboxylic acids. ^1H NMR (DMSO-d_6) δ 1.30 (m, 14 H, $(CH_2)_2CH_3$), 4.10 (t, 4 H, OCH_2), 7.50 (m, 6 H, Ar).

Anal. Calcd for $C_{22}H_{26}O_6$: C, 68.38; H, 6.78. Found: C, 68.12; H, 6.79.

2,2′-Di-*n*-butoxy-4,4′-biphenyldicarbonyl Chloride (XXXVI). The acid chloride was synthesized from the corresponding acid in $SOCl_2$. Recrystallization from pentane yielded the product as a white, crystalline solid (75%), mp 109–110 °C. ^1H NMR ($CDCl_3$) δ 1.40 (m, 14 H, $(CH_2)_2CH_3$), 4.00 (t, 4 H, OCH_2), 7.50 (m, 6 H, Ar).

Anal. Calcd for $C_{22}H_{24}Cl_2O_4$: C, 62.42; H, 5.71; Cl, 16.75. Found: C, 62.53; H, 5.78: Cl, 17.00.

Dimethyl 2,2′-Bis[(1*H*,1*H*-perfluoroheptyl)oxy]-4,4′-biphenyldicarboxylate (XXXVII). To a solution of (XXIX) (0.5 g; 1.65 mmol) and (1*H*,1*H*-perfluoroheptyl)triflate (1.67 g; 3.47 mmol) in 20 mL of acetone was added 1.14 g (8.8 mmol) of anhydrous K_2CO_3. After the mixture was stirred for 12 h under reflux, it was filtered through Celite and the solids were washed with acetone. The acetone was evaporated and the product isolated as a white solid (mp 84–86 °C) by column chromatography (silica gel, CH_2Cl_2) in 81.6% yield. ^1H NMR ($CDCl_3$) δ 4.00 (s, 6 H, OCH_3), 4.45 (t, 4 H, OCH_2), 7.65 (m, 6 H, Ar).

Anal. Calcd for $C_{30}H_{16}O_6F_{26}$: C, 37.29; H, 1.67; F, 51.11. Found: C, 37.45; H, 1.54; F, 50.66.

2,2′-Bis[(1*H*,1*H*-perfluoroheptyl)oxy]-4,4′-biphenyldicarboxylic Acid (XXXVIII). This acid was prepared by the same route used for the other acids.

Anal. Calcd for $C_{28}H_{12}O_6F_{26}$: C, 35.84; H, 1.29; F, 52.54. Found: C, 35.97; H, 1.49; F, 52.43.

2,2′-Bis[(1*H*,1*H*-perfluoroheptyl)oxy]-4,4′-biphenyldicarbonyl Chloride (XXXIX). This acid chloride was also synthesized by the route used for the other derivatives, e.g., XXXIII. The product, which melted at 97–98 °C, was recrystallized from pentane (73%).

Anal. Calcd for $C_{28}H_{10}O_4Cl_2F_{26}$: C, 34.48; H, 1.03; F, 50.65; Cl, 7.27. Found: C, 34.19; H, 1.07; F, 50.42; Cl, 7.05.

Polymer Synthesis. All of the polyesters listed in Table I were prepared via room temperature solution polymerization, the details of which have been previously reported.[8]

Polymer Characterization. Thermal analyses of the polymers were performed on a Perkin-Elmer DSC-7 and a Du Pont 1090 (TGA). Glass-transition temperatures are reported as the midpoint of devitrification and TGA temperatures as the onset of decomposition. In both cases samples were run under N_2 at a heating rate of 20 °C/min unless otherwise specified.

Thermotropic liquid-crystalline behavior was observed on a Fisher-Johns melting point apparatus (shear opalescence) and a Zeiss 9902 Pol microscope equipped with a Leitz hot stage.

Inherent viscosities were determined in a Cannon-Ubbelhode dilution viscometer at 0.5% (w/v) polymer solutions in the indicated solvent at 30 °C.

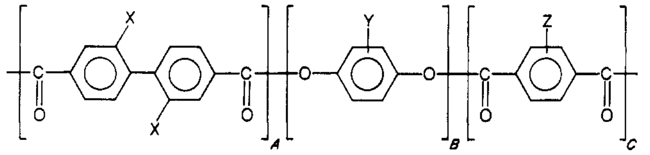
Films of these materials were formed by puddle-casting from tetrachloroethane solutions onto glass slides. After the solvent was allowed to evaporate under N_2, the films were floated off of the glass by soaking them in methanol. After they were dried under vacuum at 60 °C, the films were mounted in a unidirectional stretcher. The films were then heat stretched to varying degrees of orientation as measured by IR dichroism. Refractive indices were determined by the Brewster angle technique using a He–Ne laser (633 nm) and Becke-line analysis. Birefringences were calculated as the difference between the indices parallel and perpendicular to the stretch direction.

X-ray diffraction patterns were recorded with a D500 Siemens X-ray Powder Diffractometer and the electron micrographs were taken on a Jeol JSM-35C scanning electron microscope.

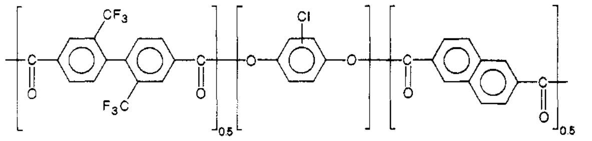
Results and Discussion

Synthesis and Solubility. The structures of the polyesters synthesized for this study and their shorthand notations are listed and defined in Table I. The polym-

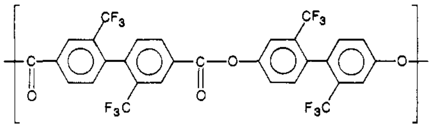
Table I
Molecular Structures of the Aromatic Polyesters



polymer designation[a]	X	A	Y	B	Z	C
I (OCH_3/CHQ)[b,c]	OCH_3	1	Cl	1		0
II (Br/CHQ)	Br	1	Cl	1		0
III (CF_3/CHQ)	CF_3	1	Cl	1		0
IV	$O(CH_2CH_2O)_2Et$	1	Cl	1		0
V (OBu/CHQ)	$O(CH_2)_3CH_3$	1	Cl	1		0
VI	$OCH_2(CF_2)_5CF_3$	1	Cl	1		0
VII ($Br_{0.5}$/CHQ/$T_{0.5}$)	Br	0.5	Cl	1	H	0.5
VIII ($Br_{0.5}$/CHQ/$TCF_{3/0.5}$)	Br	0.5	Cl	1	CF_3	0.5
IX ($Br_{0.25}$/$CF_{3/0.5}$/CHQ/$T_{0.25}$)	Br, CF_3	0.25, 0.5	Cl	1	H	0.25
X ($OCH_{3/0.25}$/$CF_{3/0.5}$/CHQ/$T_{0.25}$)	OCH_3, CF_3	0.25, 0.5	Cl	1	H	0.25
XI ($CF_{3/0.5}$/CHQ/$TCF_{3/0.5}$)	CF_3	0.5	Cl	1	CF_3	0.5
XII ($CF_{3/0.4}$/CHQ/$TCF_{3/0.6}$)	CF_3	0.4	Cl	1	CF_3	0.6
XIII ($CF_{3/0.2}$/CHQ/$TCF_{3/0.8}$)	CF_3	0.2	Cl	1	CF_3	0.8
XIV ($CF_{3/0.1}$/CHQ/$TCF_{3/0.9}$)	CF_3	0.1	Cl	1	CF_3	0.9
XV ($CF_{3/0.5}$/HQ/$TCF_{3/0.5}$)	CF_3	0.5	H	1	CF_3	0.5
XVI ($CF_{3/0.4}$/HQ/$TCF_{3/0.6}$)	CF_3	0.4	H	1	CF_3	0.6
XVII ($CF_{3/0.5}$/CHQ/$T_{0.5}$)	CF_3	0.5	Cl	1	H	0.5
XVIII	CF_3, $O(CH_2CH_2O)_2Et$	0.5, 0.5	Cl	1		0
XIX ($CF_{3/0.5}$/MHQ/$TCF_{3/0.5}$)	CF_3	0.5	CH_3	1	CF_3	0.5
XX (CF_3/CHQ/MHQ/TCF_3)	CF_3	0.5	CH_3, Cl	0.5, 0.5	CF_3	0.5
XXI (CF_3/CHQ/MHQ/T)	CF_3	0.5	CH_3, Cl	0.5, 0.5	H	0.5
XXII (TCF_3/CHQ)		0	Cl	1	CF_3	1
XXIII (TCF_3/MHQ)		0	CH_3	1	CF_3	1
XXIV (CHQ/$T_{0.5}$/$TCF_{3/0.5}$)		0	Cl	1	CF_3	0.5
XXV ($CHQ_{0.5}$/$MHQ_{0.5}$/TCF_3)		0	Cl, CH_3	0.5, 0.5	CF_3	1



XXVI



XXVII

[a] The designation is a shorthand notation for the repeat unit sequence: (biphenyl(s)/hydroquinone(s)/terephthaloyl(s). [b] The subscript indicates the molar ratio of the designated moiety in the repeat unit. If no subscript is given, it is equal to unity. [c] CHQ, chlorohydroquinone; HQ, hydroquinone; MHQ, methylhydroquinone; T, terephthaloyl; TCF_3, (trifluoromethyl)terephthaloyl.

erization reaction conditions were not optimized with respect to any of the individual polymers and monomer purity was crucial in obtaining high molecular weights. Relatively high solution viscosities were obtained for those reactions which remained homogeneous during the course of the polymerization. Those polyesters that precipitated from the reaction mixture (i.e., II, V–VII, XIV, XX–XXVI) are characterized by somewhat lower viscosities. These examples exhibit poor overall solubility which is evident from the data listed in Table II.

Of the examples with high viscosities, polyester XI ($CF_{3/0.5}$/CHQ/$TCF_{3/0.5}$), which is composed of the 2,2′-(trifluoromethyl)biphenyl diacid (CF_3), 2-(trifluoromethyl)terephthalic acid (TCF_3), and chlorohydroquinone (CHQ), was prepared several times in a number of molecular weights. One of these samples with an intrinsic viscosity of 2.74 dL/g in *s*-tetrachloroethane (TCE) has a corresponding M_n of 19600 as determined by membrane osmometry. The intrinsic viscosity, $[\eta]$, in THF was 2.64 dL/g, which is not very different from the value obtained in TCE. The insensitivity of the $[\eta]$ to solvent is consistent with rodlike behavior.[9] Currently the determination of the persistence lengths of these aromatic polyesters in various solvent systems is being carried out.

From the data in Table II, two general categories of solubility behavior can be identified. The first category contains polymers that are only soluble in *p*-chlorophenol and strong acids; this limited solubility behavior is typical of para-linked, wholly aromatic polyesters. This category can be divided into three groups on the basis of structure. The first group contains polymers composed entirely of single phenyl ring monomer units (XXII–XXV); all the members in this group exhibit some degree of crystallinity (refer to the Thermal Properties). The second group includes polymers composed of a single type of biphenyl diacid; these polymers are also semicrystalline. Examples of polymers in this group are I (with 2,2′-dimethoxy substituents), II (2,2′-dibromo), V (2,2′-dibutoxy), and VI (2,2′-$OCH_2(CF_2)_5CF_3$)—note that polymers I and VI are slightly soluble in TCE. It should also be noted that although polymers III and IV are composed of single biphenyl moieties, they are soluble in a variety of solvents and belong in the second solubility category, which is discussed below. The 2,2′-substituents in these latter polymers are trifluoromethyl (CF_3) and $O(CH_2CH_2O)_2Et$.

The only example of a polymer in the third group in this limited solubility category is composed of the solubility-enhancing, 2,2′-(trifluoromethyl)biphenyl diacid and an equimolar amount of 2,6-naphthoic diacid. The poor solubility of this polymer must be attributed to the naphthoic acid moiety.

The second solubility category is quite unique in that these polyesters—15 of the 27 examples—are soluble in a variety of nonphenolic chlorinated, ethereal, and amide solvents. It should be noted that the literature contains very few examples of liquid-crystalline polyesters which

Table II
Polyester Viscosities and Solubilities

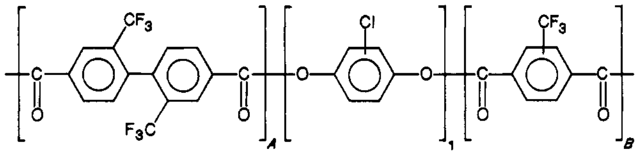
polyester	η_{inh}[a]	TCE	CH_2Cl_2	$CHCl_3$	acetone	THF	o-ClC_6H_4OH
I	1.39[b]	SS[d]	I	I	I	I	S
II	0.74[b]	I	I	I	I	I	S
III	4.80[c]	S	S	S	Sw	S	S
IV	7.4[e]	S	S	S	Sw	S	S
V	0.45[b]	I	I	I	I	I	S
VI		SS	I	I	I	I	S
VII	0.85[b]	I	I	I	I	I	S
VIII	0.70	S	S	Sw	I	I	S
IX	1.09	S	S	S	I	S	S
X	0.32	S	S	S	I	S	S
XI	2.49	S	S	S	Sw	S	S
XII	1.49	S	S	S	I	S	S
XIII	1.63	S	S	Sw	I	S	S
XIV	0.30[b]	I	I	I	I	SS	S
XV	1.92	S	S	S	Sw	S	S
XVI	0.79	S	Sw	Sw	I	I	S
XVII	1.47	S	SS	Sw	I	Sw	S
XVIII	1.29	S	S	S	I	S	S
XIX	0.68	S	S	S	SS	S	S
XX	0.63	S	S	S	I	S	S
XXI	0.73	SS	SS	SS	I	I	S
XXII	0.79[b]	I	I	I	I	I	S
XXIII	0.87[b]	I	I	I	I	I	S
XXIV	0.85[b]	I	I	I	I	I	S
XV	0.45[b]	I	I	I	I	I	S
XXVI	0.56[b]	I	I	I	I	I	SS
XXVII	1.20[c]	SS	I	I	I	S	S

[a] Inherent viscosities run at 0.5 g/dL, 30 °C in *s*-tetrachloroethane (TCE) unless indicated otherwise. [b] Viscosity solvent, 1/1 (v/v) TCE/*p*-chlorophenol. [c] Viscosity solvent, THF. [d] S, soluble; SS, slightly soluble; Sw, swells; I, insoluble. [e] Intrinsic viscosity in THF.

are soluble in these solvents and this includes most of those copolymerized with flexible spacers and nonmesogenic units. Recently, however, a series of soluble liquid-crystalline polyesters composed of alternating aromatic rigid segments and ether flexible segments has been reported.[10]

With the exception of polyester IV, which contains $-O(CH_2CH_2O)_2Et$ substituents, all of the polymers in this category contain trifluoromethyl groups in either the single phenyl or biphenyl moieties of their repeat units. The effect of the CF_3 group on solubility has been previously reported for aromatic polyamides.[1] From examples XXII–XXV it can be seen that the presence of one CF_3 group on a single phenyl ring diacid alone is not sufficient to impart good solubility. However, the addition of such a group to variously substituted biphenyl-containing polyesters does cause a marked increase in solubility. A comparison of polyester XVII with XI is indicative of this effect. Replacing the terephthalic acid component in XVII with (trifluoromethyl)terephthalate imparts solubility in $CHCl_3$. Even more dramatic is the increase in solubility of VII ($Br_{0.5}$/CHQ/$T_{0.5}$) vs. VIII ($Br_{0.5}$/CHQ/$TCF_{3/0.5}$) upon the introduction of the CF_3 group. Inspection of the solubility data for polyester XVI ($CF_{3/0.4}$/HQ/$TCF_{3/0.6}$) vs. XV ($CF_{3/0.5}$/HQ/$TCF_{3/0.5}$) in Table II reveals that just a 10 mol % increase in 2,2′-(trifluoromethyl)biphenyl (CF_3) diacid renders XV soluble in CH_2Cl_2 and $CHCl_3$. This dependence is further demonstrated in Table III for a homologous series of polymers composed of bis(trifluoromethyl)biphenyl (CF_3), (trifluoromethyl)terephthalate (TCF_3), and chlorohydroquinone (CHQ). The maximum solubility in THF falls off rapidly below 40 mol% of the biphenyl comonomer, and at 10 % percent the polyester exhibits very limited solubility in this solvent and is not even soluble in TCE. The extremely high solubility of III, XI, and XII is quite surprising, and it is of interest to note that highly concentrated, transparent solutions exhibit streaming birefringence which develops when these solutions are stressed. The solutions return to the isotropic state when the external force is removed; none of these solutions formed a detectable lyotropic phase at any concentration.

Table III
Effect of CF_3-Disubstituted Biphenyl Content on Solubility in THF



polyester	max solubility, % w/v	streaming birefringence[a]
III: $A = 1, B = 0$	53.0	+
XI: $A = 0.5, B = 0.5$	49.8	+
XII: $A = 0.4, B = 0.6$	48.5	+
XIII: $A = 0.2, B = 0.8$	11.1	−
XIV: $A = 0.1, B = 0.9$	<5.0	−
XXII: $A = 0, B = 1$	insoluble	−

[a] When these solutions were stressed and viewed between crossed polars, streaming birefringence was observed for those indicated with a (+).

It is clear from the aforementioned examples that the trifluoromethyl-substituted single phenyl moiety must be accompanied by a 2,2′-disubstituted biphenyl, preferably the bis(trifluoromethyl)biphenyl, in order to promote this unusually high solubility. The incorporation of a noncoplanar biphenyl increases the disorder along the polymer backbone thereby reducing interchain interactions, and therefore the key to enhanced solubility is the biphenyl content of the polymer.

Thermal Properties and Morphology. In general, aromatic polyesters display good resistance to thermal degradation and those listed in Table IV show typical properties. Most of these examples exhibit no appreciable weight loss up to temperatures between 450 and 500 °C. The exceptions are those polyesters that contain long-chain substituents on the 2- and 2′-positions of the biphenyl monomer units (IV, V, and VI). Most notable is the se-

Table IV
Thermal Properties

polyester	TGA,[a] °C N$_2$	TGA,[a] °C air	DSC,[b] °C T_g	DSC,[b] °C T_m	LC transitn,[c] °C
I	435	425		325	326
II	495	485		347	350[d]
III	500	485			
IV	350	185		207	210[e]
V	410	406		268	270, 310 (isotropic)
VI	420	392		265	250, 270 (isotropic)
VII	493	490		259	210
VIII	478	463	103	140 (br)	150
IX	480	463	75	137 (br)	145
X	450	430	121		140
XI	480	463	118		180
XII	465	443	110		152
XIII	470	469	95		165
XIV	465	460	87		173
XV	480	455	131		161
XVI	480	450	117		168
XVII	488	470	137		185
XVIII	395	385	80[f]	198	120, 200 (isotropic)
XIX	453	435	112		145
XX	455	445	116		144
XXI	450	435	133		143
XXII	477	460	71		127
XXIII	460	450	86		140
XXIV	490	485		165	170
XXV	430	422	68		125
XXVI	480	455	133		200
XXVII	510	485			

[a] Taken as the onset of weight loss. [b] The temperatures reported here are from the second heating cycle. T_g taken as the midpoint of devitrification and T_m as the peak temperature of the melting point endotherm. [c] Temperatures at which the solid phase transforms to a mobile nematic phase when stressed and viewed by means of a polarized light microscope. [d] Sample discoloration is observed at this temperature. [e] The sample appears partially isotropic and rubbery at this temperature probably due to some cross-linking. [f] By thermal mechanical analysis.

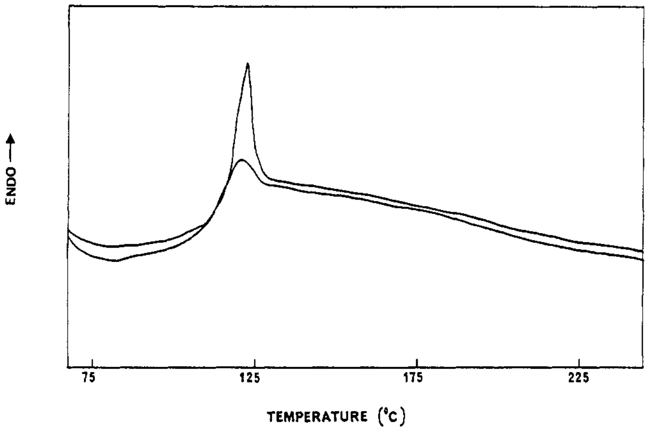


Figure 1. DSC traces for polyester XI. Second heating cycles only (20 °C/min.) Upper curve: cooled from 250 to 30 °C at 5 °C/min. Lower curve: cooled from 250 to 30 °C at 20 °C/min.

verely reduced air stability of the polyether-substituted polyester IV which begins to decompose at 185 °C. This degradation is the result of oxidation of the ether-containing side chains. Slightly diminished thermal stability has also been observed in polyester I which contains OCH_3 biphenyl substituents.

It is also evident from the data listed in the last column of Table IV that the majority of these polyesters have much lower liquid-crystalline transition temperatures than most wholly aromatic, para-linked thermotropic polyesters reported to date. Exceptions include polymers I–VI all of which are composed of a single type of 2,2′-disubstituted biphenyl diacid and chlorohydroquinone. With the exception of III, DSC scans reveal sharp, reversible first-order transitions indicating some degree of crystallinity.

Polyesters I (OCH_3/CHQ) and II (Br/CHQ) also exhibit sharp endotherms in their heating cycles; above these temperatures the polymers are transformed into nematic melts which persist up to the decomposition point. Polymer III (CF_3/CHQ) shows no detectable transitions up to 400 °C; however, a low molecular weight sample (η_{inh} = 1.0 dL/g) undergoes reversible melting at 360 °C. In analogy to I and II, polyesters IV–VI also exhibit sharp exotherms, they form narrow mesophases, and they display clearing points. The decreased stability of the mesophase and the existence of a clearing or isotropization temperature was also observed in a series of alkyl[11] and alkoxy-substituted[12] aromatic polyesters; this effect is the result of a decrease in axial ratio caused by the long-chain, lateral substituents. Unfortunately, the effect of molecular weight of polymers IV–VI on thermal transitions cannot be compared to that of other polymers of this study or to each other by means of their viscosities because their hydrodynamic behavior will be strongly influenced by the conformation of the side chains. The crystallinity of these examples persists in spite of the randomness introduced along the polymer backbone by the enantiomeric, noncoplanar biphenyls in sharp contrast to the polyamides which are completely amorphous.

In the remaining polyesters listed in Table IV, reductions in the degree of crystallinity and transition temperatures reflect the increased disorder along the backbone brought about by the presence of monomers of differing length and substitution and the atropism introduced by noncoplanar biphenyls.

All of these copolyesters exhibit shear opalescence below 200 °C with the exception of VII ($Br_{0.5}$/CHQ/$T_{0.5}$) which has a crystalline melting point at 259 °C but enters a birefringent mesophase at 210 °C. Introduction of a trifluoromethyl group into the terephthalic acid residue of VII to give VIII ($Br_{0.5}$/CHQ/$TCF_{3/0.5}$) significantly lowers the LC transition temperature and broadens the melting endotherm. An even more significant reduction occurs in the case of polyester XXII (TCF_3/CHQ), which is derived from chlorohydroquinone and (trifluoromethyl)terephthalic acid exclusive of any biphenyl comonomers. This polymer enters the fluid nematic state at 127 °C (η_{inh} = 0.79 dL/g). The influence of the trifluoromethyl group on thermal transitions is dramatically exemplified by comparing the latter polymer with an analogous polyester composed of chlorohydroquinone and terephthalic acid (η_{inh} = 0.38 dL/g) which enters the liquid-crystalline state at 340 °C.[8] The other members of this series of single ring, trifluoromethyl-containing polyesters (XXIII–XXV) also exhibit very low transition temperatures. Only one of these four polymers, e.g., XXIV, exhibits a crystalline melting point (T_m = 165 °C) and this may be due to the presence of unsubstituted terephthalic acid residues (50 mol %). Crystallinity has also been observed in halogen- and phenyl-substituted poly(*p*-phenyleneterephthalates),[5c] but most of these polymers melt at temperatures in excess of 200 °C.

In addition to the relatively low transition temperatures, another striking feature of these polyesters is that many are completely amorphous. It is postulated that the combination of lateral substituents, comonomers of different lengths, and the enantiotropic, noncoplanar biphenyls completely eliminates crystallinity by diminishing interchain interactions.

Evidence for the lack of crystallinity is obtained from DSC analysis (Figure 1) and X-ray diffraction (Figure 2).

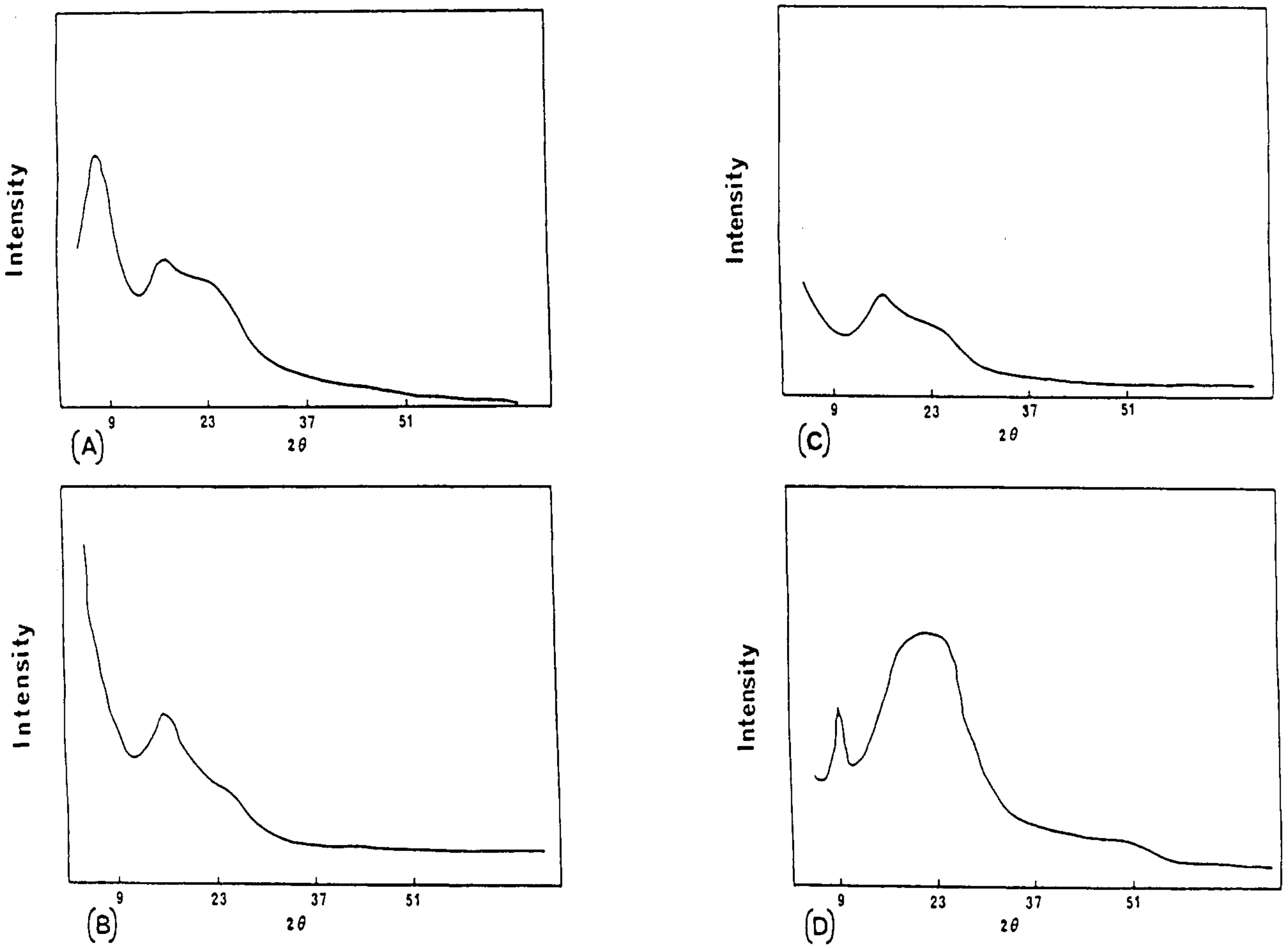


Figure 2. X-ray diffractograms of polyester films: (A) XI (unoriented); (B) XI (oriented, 60%); (C) XVII and (D) XVIII both unoriented.

The DSC analyses of the majority of the polymers synthesized for this study (X-XVII, XIX-XXII, XXV, and XXVI—polymers III and XXVII have no discernible thermal transitions) do not exhibit any first-order transitions (Figure 1). Because the crystallization rate of rigid, rodlike polyesters has been reported to be a very slow process,[13,14] several polymers from this group were annealed under a variety of conditions. In every case the results were identical—the materials do not show any tendency to crystallize even after days of annealing. When these samples are cooled at slow rates, only hysteresis is observed at the glass transition upon reheating. Figure 1 also clearly depicts the dependence of the glass transition on cooling rate for polyester XI. This type of enthalpy relaxation is typical for amorphous polymers like polystyrene[14] but is not observed for the majority of semicrystalline materials.[16] Furthermore, it is generally believed that thermotropic LC polymers could not display hysteresis due to the ordered nature of the mesophase.[17]

Further evidence for this lack of crystallinity is obtained from X-ray diffraction studies of unoriented and oriented films of various polymers (Figure 2). The X-ray patterns obtained show broad, nondescript peaks typical of amorphous, nematic materials. By mechanically stretching polymer films above the glass-transition temperature, a high degree of orientation can be obtained, but even these highly oriented samples do not exhibit a discernible increase in intermolecular correlation.

Optical Properties. In order for these polyesters to be useful for many optical applications,[18-20] they must exhibit a high degree of optical anisotropy ($\Delta n > 0.4$), and they must be nonscattering and nonabsorbing in the visible region of the spectrum. On the basis of the results obtained for aromatic polyamides, wholly aromatic, para-linked repeat units were chosen in order to maximize the birefringence. In addition, noncoplanar, 2,2′-disubstituted biphenyls were incorporated into the polyesters not only to affect morphology and processability but also because they enhance birefringence and limit inter-repeat unit conjugation.

Polyesters in general do not exhibit any absorption bands in the visible region of the spectrum, and all of the polymers of this study are white solids. The soluble members have absorption maxima in CH_2Cl_2 in the 245-nm range with little or no tailing above 310 nm. When cast from solution, polymer films scatter visible radiation to varying degrees depending on the nature of the solvent, rate of solvent evaporation, and environmental conditions; the only exception to this is polymer III (CF_3/CHQ) which forms transparent films under some solution casting conditions. These observations, coupled with the X-ray and thermal data presented previously, suggest that voids are the major cause of scattering. To help substantiate this claim, electron micrographs of cross sections of a nearly transparent, oriented film of polymer XI, which was obtained by stretching above the glass-transition temperature, were compared to those of an unoriented, translucent film (Figure 3). The results shown by the unoriented film clearly reveal a porous, cellular structure composed of a large number of irregularly shaped voids uniformly distributed throughout the entire cross section. By comparison, the oriented film shows a significant decrease in the number and sizes of voids. At present, light- and neutron-scattering investigations of polymer films and solutions have begun to help delineate the mechanism of void formation.

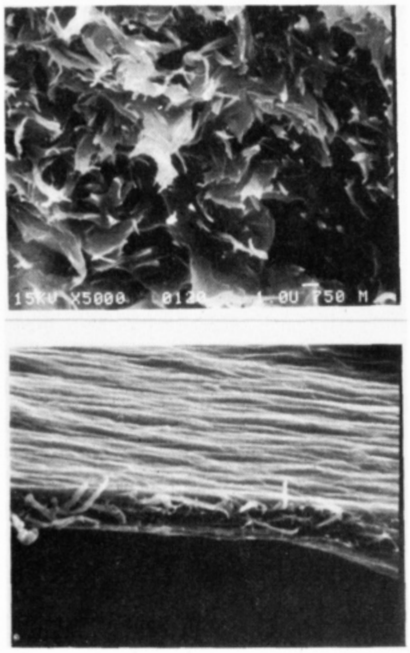


Figure 3. Scanning electron micrographs of cross sections of polyester XI. Upper: A microtomed edge of an unoriented puddle-cast film (2250 ×). Lower: A microtomed edge of an oriented sample (~40%) cut parallel to stretch direction (2250×).

It is well documented that ordered structures are formed when liquid-crystal polyesters are processed from their nematic melts. For example, highly oriented fibers and films, formed by extrusion, display enhanced mechanical properties which are strongly directionally dependent. Similarly, pronounced optical anisotropy is exhibited by the fibers and films of the thermotropic polyesters reported here; the data for the fiber samples listed in Table V were prepared by pulling fibers from the liquid-crystalline phase of the polymers. The birefringence values obtained are high considering the simple orientation process employed. A detailed comparison of the relative Δn values cannot be made due to differences in molecular structure and the absence of data related to the degree of orientation. On the other hand, the orientations of film samples of many polymers were studied in detail by means of birefringence measurements and infrared dichroism. The data for polymer XI ($CF_{3/0.5}/CHQ/TCF_{3/0.5}$), which exemplifies the results of many of these polymers, is graphically represented in Figure 4. The isotropic, solution-cast films ($n = 1.7830$) were cloudy but clarified sufficiently at about 35% orientation to allow the measurement of the parallel and perpendicular indices by the Brewster angle technique.

Table V
Fiber Birefringence

sample[a]	$n_\parallel$[b]	$n_\perp$[b]	Δn
VIII	1.790	1.564	0.226
IX	1.785	1.530	0.255
XI	1.755	1.502	0.253
XIX	1.735	1.493	0.242
XX	1.735	1.496	0.239

[a] Fibers were pulled from nematic melts at approximately 10–20 °C above the LC transition temperature. [b] Refractive indices measured by the Becke-line method.

The order parameter data plotted in Figure 4 were determined by infrared dichroism of the ester carbonyl band at 1752 cm^{-1} by using the standard equations.[21] The calculations are based on an angle of 66° between the transition moment of the carbonyl group and the chain axis. This value is somewhat different from those values recently reported for two aliphatic–aromatic copolyesters.[22] In the first of these publications,[22a] a 60° angle was used for unspecified reasons, while in the latter paper,[22b] which discusses orientation in PET fibers, an angle of 76° between the transition moment and chain axis was employed.

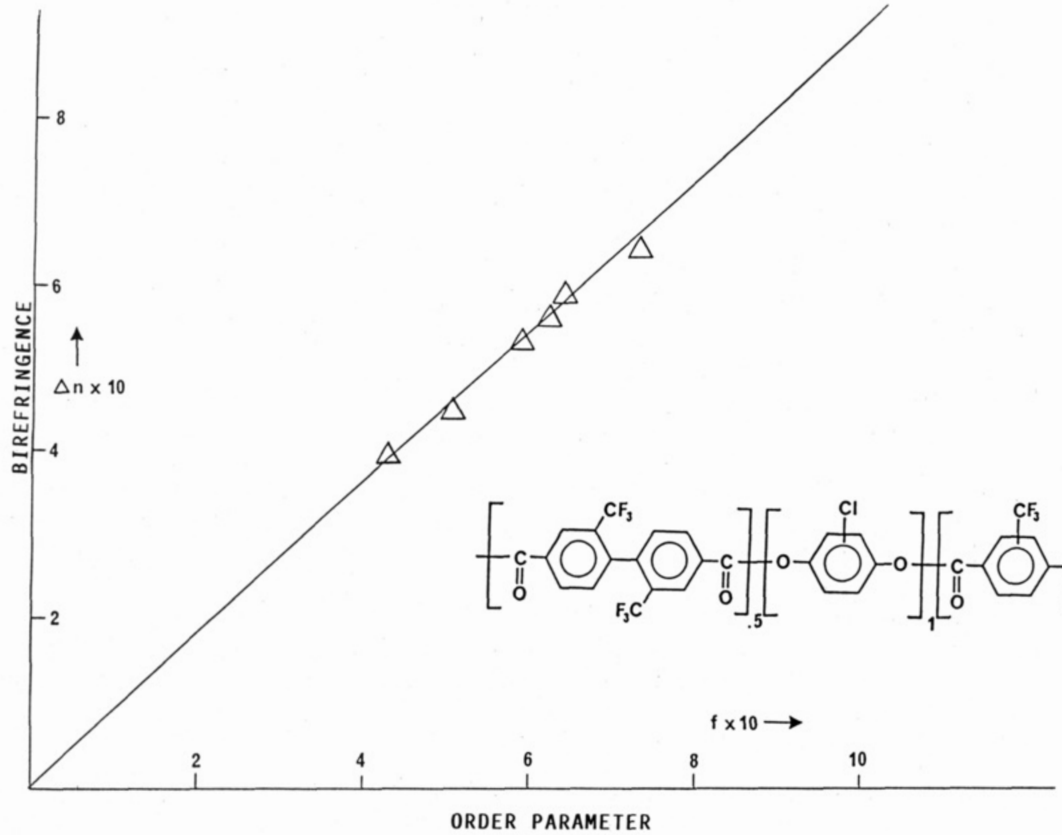
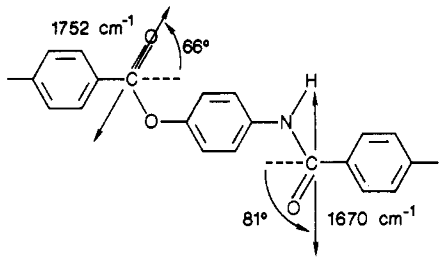


Figure 4. Plot of birefringence vs. order parameter for polyester XI.

The latter is consistent with the value reported by Brown et al.[23]

The selection of 66° is based on results obtained for a series of structurally analogous poly(ester amides) which have recently been synthesized.[24] These polymers not only have ester and amide groups in the same repeat unit, but the groups are also bonded to the same phenyl ring (a segment of which is shown below)



which makes the analysis unambiguous. When an angle of 76° was used for the carbonyl–ester transition moment in these biphenyl-based polyesters and poly(ester amides), maximum order parameters of 0.30–0.40 were obtained. These values seem anomalously low in light of the high birefringences exhibited by these samples. However, when the calculation was carried out for the poly(ester amides) by using the amide–carbonyl band (1670 cm^{-1}) and its well-established transition moment angle of 81°,[25] order parameter values of 0.70–0.80 were obtained. The amide-based order parameters were used to back-calculate the angle of the transition moment of the ester–carbonyl group; a value of 66° was obtained which was subsequently utilized for the order parameters of the polyesters reported in this study.

Reference to Figure 4 shows that the birefringence rises linearly with the order parameter, and the highest birefringence achieved by heat-stretched films is 0.65 at approximately 78% orientation. When the resulting linear relationship was extrapolated to an order parameter of one, a corresponding birefringence maximum of 0.91 was obtained. This value is lower than those obtained for wholly aromatic polyamides containing similarly substituted biphenyls,[25a] and its suggests that the aromatic polyester chain is not as rigid as that of the polyamides. We are currently pursuing this question further by comparing the persistence lengths of structurally analogous wholly aromatic, para-linked polyesters and polyamides in identical solvents.

Summary

Many examples of wholly aromatic, para-linked polyesters have been synthesized and characterized. Most of these polymers contain disubstituted biphenyls, copolymerized in various ratios with substituted and unsubstituted terephthalic acids and hydroquinones. This combination seems to effectively eliminate geometric regularity, by utilizing atropism and comonomers of different lengths, and to minimize intermolecular interactions. The latter are also affected by the size and electronic nature of the ring substituents. These molecular structures yield polymers that are completely amorphous and exhibit very high solubility, optical clarity, and unusually low transition temperatures. In general the noncoplanar biphenyls, particularly those containing 2,2′-bis(trifluoromethyl) groups, have the greatest impact on these properties.

In addition, this class of polyesters does not exhibit lyotropic behavior in any solvent even at high polymer concentrations, e.g., 50% w/v. Incomplete but precise molecular weight data coupled with birefringence measurements indicate that these polyesters have high molecular weights and rigidity. These results, in analogy to those of similarly substituted polyamides, imply that the theory of liquid crystallinity is incomplete.

Acknowledgment. We thank Mary McCann and Nancy Pickens for providing the SEM's and X-ray data. We also thank Arthur Coates for furnishing some of the thermal data.

Registry No. I (copolymer), 109977-24-4; I (SRU), 110026-23-8; II (copolymer), 109977-25-5; II (SRU), 110026-22-7; III (copolymer), 109977-26-6; III (SRU), 89800-56-6; IV (copolymer), 109977-27-7; IV (SRU), 110026-25-0; V (copolymer), 109977-28-8; V (SRU), 110026-24-9; VI (copolymer), 109977-29-9; VI (SRU), 110026-26-1; VII, 109977-30-2; VIII, 109977-31-3; IX, 109977-32-4; X, 109977-33-5; XI, 109977-34-6; XV, 109977-35-7; XVII, 109977-36-8; XVIII, 109977-38-0; XIX, 109977-39-1; XX, 109977-40-4; XXI, 109977-41-5; XXII (copolymer), 109977-42-6; XXII (SRU), 102819-40-9; XXIII (copolymer), 109977-43-7; XXIII (SRU), 110026-21-6; XXIV, 109977-44-8; XXV, 109977-45-9; XXVI, 109977-46-0; XXVII (copolymer), 109977-47-1; XXVII (SRU), 89743-42-0; XXVIII, 54550-36-6; XXIX, 109977-12-0; XXX, 86369-06-4; XXXI, 109977-13-1; XXXII, 109977-14-2; XXXIII, 109977-15-3; XXXIV, 109977-16-4; XXXV, 109977-17-5; XXXVI, 109977-18-6; XXXVII, 109977-20-0; XXXVIII, 109977-21-1; XXXIX, 109977-22-2; $HO(CH_2)_2O(CH_2)_2OEt$, 111-90-0; BuBr, 109-65-9; $F_3CSO_2OCH_2(CF_2)_5CF_3$, 109977-19-7; *N*-bromosuccinimide, 128-08-5.

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Structure and Pyrolysis of Poly(methyl methacrylate peroxide): A Thermochemical Approach

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ABSTRACT: The structure of poly(methyl methacrylate peroxide) (PMMAP) has been confirmed by using IR and NMR. The degradation of PMMAP has been studied by using differential scanning calorimetry, thermogravimetry, and pyrolysis gas chromatography. The degradation products were identified as methyl pyruvate and formaldehyde, accounting for more than 95% of the total degradation products. The measured heat of degradation of PMMAP was found to be −44 ± 2 kcal mol^{-1}. The mechanism of the primary exothermic degradation leading to the above products has been substantiated by thermochemical calculations.

Introduction

Polymeric peroxides are an important class of compounds. Since the first report of its kind in 1925 by Staudinger,[1] only a small number of polymers belonging to this class have been studied.[2-18] Of these, poly(styrene peroxide) (PSP), first reported by Bovey and Kolthoff[19] has received considerable attention.[20-29] They have been used as initiators,[30,31] in preference to conventional simple peroxides, in a search to obtain novel polymers such as comb polymers.[32] Recently, PSP has been shown to behave as a unique autocombustible polymer fuel, its combustion being controlled by degradation.[29] Poly(methyl methacrylate peroxide) (PMMAP) is another member of this class of polymers. Its formation and structure are reported along with its degradation products.[33-36] In view of their potential as initiators and, as autocombustible polymer fuels, it is of general interest to study the degradation behavior of polymeric peroxides. Hence, in the present investigation, in which a spectroscopic confirmation of the alternating copolymeric structure of PMMAP is provided, its degradation has been studied in detail and has been supplemented by thermochemical calculations.

Experimental Section

PMMAP was prepared by reacting freshly distilled methyl methacrylate (MMA) in a current of oxygen for 24 h at 50 °C in the presence of azobisisobutyronitrile initiator (0.02 M % of monomer).[33] The polymer was purified by repeated precipitation using methanol.

The IR spectrum was recorded in CCl_4 on a Perkin-Elmer Spectrophotometer, Model 597. All NMR spectra were recorded at ambient temperature in $CDCl_3$ containing tetramethylsilane. The 60-MHz ^1H NMR spectrum was recorded on a Varian T-60 spectrometer, the 270-MHz ^1H NMR spectrum on a Bruker WH270 FT NMR spectrometer, and the 25-MHz ^{13}C NMR spectrum on a JEOL FX 90Q FT NMR spectrometer.

Pyrolysis gas chromatographic (PGC) studies were carried out as described elsewhere[37] by using an OV-17 column, in the pyrolysis temperature range 150–350 °C at intervals of 50 deg. The degradation products were also identified by IR and NMR.

The thermal analysis was done using a du Pont 990 differential scanning calorimeter (DSC) at heating rates of 2, 5, 10, 20, and 50 °C/min. The sample weight was ca. 2.5 mg. The temperature axis and the measured enthalpy were calibrated by using pure indium. The thermogravimetric analysis (TGA) was done with a ULVAC SINKU-RIKO simultaneous DTA-TGA instrument at a heating rate of 10 °C/min with a sample weight of 3 mg.

Results and Discussion

The 1:1 copolymeric structure of PMMAP, shown below, was confirmed by the spectroscopic data presented in Table I. A 1:1 structure and molecular dynamics of an earlier parallel example, viz., PSP, have been studied in great detail by Cais and Bovey.[38]

$$-(O-CH_2-C(COOCH_3)CH_3-O)_n-$$

The IR spectrum (Table I) shows all absorptions characteristic of the above repeat unit of the polymer. The ^1H NMR spectrum (Figure 1a, Table I) shows signals corresponding to the CCH_3, $C(O)CH_3$, and OCH_2 protons. The ^{13}C NMR (Figure 1b,c, Table I) also shows signals corresponding to the five C atoms present in the repeat unit, with the expected off-resonance splitting patterns.

The degradation products of the polymer were analyzed by PGC. A typical pyrogram is given in Figure 2. Methyl pyruvate and formaldehyde were identified as the major products of degradation, accounting for about 95% in the temperature range 150–350 °C. Above 350 °C a greater number of peaks appeared in the pyrogram with lower retention times, probably due to secondary products. The composition of the products at the various pyrolysis temperatures was on an average 75% methyl pyruvate and 21% formaldehyde.

DSC studies revealed a highly exothermic degradation of PMMAP. A typical thermogram is given in Figure 3a. No residue was found in the pan after the degradation was over. The enthalpy of degradation, $\Delta H_d°$ calculated from the mean area under the exotherm at various heating rates, was found to be 44 ± 2 kcal mol^{-1}, after applying corrections for the heat of vaporization of methyl pyruvate and formaldehyde.

A Kissinger's plot[39] of $\ln \phi/T_m^2$ against $1/T_m$, where ϕ is the heating rate and T_m (K), the peak temperature in the DSC thermogram, is given in Figure 4. The slope of this plot gives the activation energy (E) for the process. The E value was found to be 38 ± 2 kcal mol^{-1}, which is comparable to the O–O bond dissociation energy (Table III). This, as well as the symmetry of the DSC thermo-