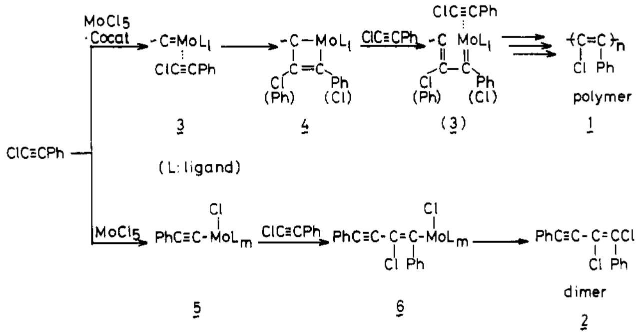
Scheme I



shown in Scheme I reasonable.

The polymerization process should involve a Mo carbene as active species: Mixtures of either WCl_6 or $MoCl_5$ with organometallics metathesize olefins[8] and polymerize cycloolefins.[9] A mechanism involving metal carbenes, which was proposed by Hêrisson and Chauvin,[10] is now generally accepted. In this analogy, in the presence of an organometallic cocatalyst and 1-chloro-2-phenylacetylene, $MoCl_5$ might be converted to monomer-coordinated Mo carbene **3**. The propagation reaction proceeds via **3** and molybdacyclobutene **4** as shown in Scheme I.[11,12]

The following dimerization mechanism seems probable: Elimination of chlorines from $MoCl_5$ by 1-chloro-2-phenylacetylene will yield a reduced Mo complex.[13] Alkynylmolybdenum **5** is formed by oxidative addition of the acetylene to the Mo complex. Then the acetylene is inserted in **5** to give alkenylmolybdenum **6**; the subsequent reductive elimination leads to dimer. If a few molecules of the acetylene are repeatedly inserted in **5**, trimer or a higher oligomer will be produced. However, the formation of a high polymer via **5**, **6**, etc. is unlikely since these species easily undergo reductive elimination. A similar mechanism has been proposed for the dimerization of monosubstituted α-hydroxyacetylenes by the Wilkinson catalyst.[14]

Acknowledgment. We acknowledge the donation of 1-chloro-2-phenylacetylene by Sanyo Chemical Industries, Ltd., Japan. Thanks are also due to Dr. Takayoshi Matsumoto for his assistance in the molecular weight measurement by the light-scattering method. Part of this work was supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science and Culture (No. 57550566).

Registry No. **2**, 88180-42-1; poly(1-chloro-2-phenylacetylene), 81953-16-4; $MoCl_5$, 10241-05-1; WCl_6, 13283-01-7; Me_4Sn, 594-27-4; Bu_4Sn, 1461-25-2; Ph_4Sn, 595-90-4; Bu_3SnCl, 1461-22-9; Bu_2SnCl_2, 683-18-1; $BuSnCl_3$, 1118-46-3; Ph_3SnCl, 639-58-7; Et_3SiH, 617-86-7; $PhMe_2SiH$, 766-77-8; $(Me_3Si)_2O$, 107-46-0; Me_3SiOBu, 1825-65-6; $PhMe_3Si$, 768-32-1; $PhEt_3Si$, 2987-77-1; Me_3SiCl, 75-77-4; Ph_2SiCl_2, 80-10-4; Ph_3Sb, 603-36-1; Ph_3Bi, 603-33-8.

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Liquid Crystal Block Copolyesters. 3. Isomerization Polymerization of Block Copolyesters Containing Cyclohexane and Benzene Rings

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Received February 22, 1983

ABSTRACT: Attempts to synthesize poly(oxy-*cis*-1,4-cyclohexyleneoxycarbonyl-*trans*-1,4-cyclohexylenecarbonyl-*b*-oxy-1,4-phenyleneoxyterephthaloyl) (VII) and poly[oxy-*cis*-1,4-cyclohexyleneoxycarbonyl-*trans*-1,4-cyclohexylenecarbonyl-*b*-oxy(2-methyl-1,3-phenylene)oxyterephthaloyl] (XI) led to the preparation of poly[oxy(*cis*,*trans*)-1,4-cyclohexyleneoxycarbonyl-*trans*-1,4-cyclohexylenecarbonyl-*b*-oxy-1,4-phenyleneoxyterephthaloyl] (I) and poly[oxy(*cis*,*trans*)-1,4-cyclohexyleneoxycarbonyl-*trans*-1,4-cyclohexylenecarbonyl-*b*-oxy(2-methyl-1,3-phenylene)oxyterephthaloyl] (II), respectively. Poly[oxy-*trans*-1,4-cyclohexyleneoxycarbonyl-*trans*-1,4-cyclohexylenecarbonyl-*b*-oxy(2-methyl-1,3-phenylene)oxyterephthaloyl] (X) was synthesized and shown to form mesomorphic solutions.

Introduction

This is the third in a series of papers that describe the synthesis and characterization of a number of block copolyesters which contain cyclohexane and benzene rings. A number of these block copolyesters in solution have been shown to rotate the plane of polarized light; e.g., they form birefringent fluid phases.

The second paper in the series described the synthesis and characterization of among other block copolyesters, what we reported as poly(oxy-*cis*-1,4-cyclohexyleneoxy-

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carbonyl-*trans*-1,4-cyclohexylenecarbonyl-*b*-oxy-1,4-phenyleneoxyterephthaloyl) (VII).[1] However, careful analysis of the ^{13}C NMR data for that block copolyester and others clearly indicates that attempts to prepare block copolyesters containing the poly(oxy-*cis*-1,4-cyclohexyleneoxycarbonyl-*trans*-1,4-cyclohexylenecarbonyl) block unit have led to the isolation of block copolyesters containing poly(oxy-*cis*-1,4-cyclohexyleneoxycarbonyl-*trans*-1,4-cyclohexylenecarbonyl) units and poly(oxy-*trans*-1,4-cyclohexyleneoxycarbonyl-*trans*-1,4-cyclohexylenecarbonyl) units along the polymer backbone.

Experimental Section

Inherent viscosities were measured at 30 °C with a Cannon–Fenske viscometer at a concentration of 0.5 g/100 mL of solvent except in those cases specified. Melting points and glass transition temperatures were determined with a differential scanning calorimeter (DuPont 990 and 1090 thermal analyzers with the DuPont 910 differential scanning calorimeter). NMR spectra were determined on deuteriochloroform solutions of the polyesters with a Bruker WH-250 spectrometer, with carbon-13 spectra taken at 62.860 MHz. The chemical shifts are reported relative to tetramethylsilane. Infrared spectra were obtained on KBr disks with a Beckman 4240 infrared spectrophotometer. Polarizing microscopy was performed on an Aus Jena Amplival Pol. D polarizing microscope. Elemental analysis was provided by Galbraith Laboratories. Terephthaloyl chloride, *cis*-1,4-cyclohexanediol, and 2-methylresorcinol were commercial products. *trans*-1,4-Cyclohexanedicarbonyl chloride was prepared according to a procedure described in the literature.[2] *trans*-1,4-Cyclohexanediol was isolated from the *cis,trans*-1,4-cyclohexanediol mixture according to a procedure described in the literature.[3]

The *o*-dichlorobenzene solvent used in the polyesterification was purified and dried by fractional distillation and stored over molecular sieves. *trans*-1,4-Cyclohexanedicarbonyl chloride was purified by distillation. Terephthaloyl chloride was purified by recrystallization from dry hexane. 2-Methylresorcinol was purified by recrystallization from deoxygenated water.

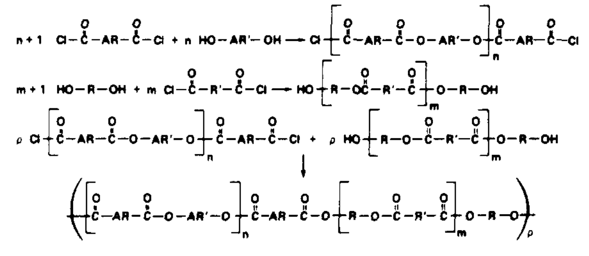
A. Preparation of Poly[oxy-*trans*-1,4-cyclohexyleneoxycarbonyl-*trans*-1,4-cyclohexylenecarbonyl-*b*-oxy(2-methyl-1,3-phenylene)oxyterephthaloyl] (X). A 1-L three-necked, round-bottom flask, equipped with a magnetic stirrer, a condenser, a nitrogen inlet, a thermometer, and a sodium hydroxide trap, was charged with 31.9 g (0.275 mol) of *trans*-1,4-cyclohexanediol and 300 mL of dry *o*-dichlorobenzene. The mixture was heated to ca. 40 °C, and to the stirred mixture was added 52.0 g (0.249 mol) of *trans*-1,4-cyclohexanedicarbonyl chloride in an atmosphere of nitrogen. The mixture was heated for 0.5 h at 120 °C, accompanied by the evolution of HCl. The mixture was then heated under reflux for 6 h. The reaction mixture was allowed to cool and stored in a desiccator overnight.

A 1-L three-necked, round-bottom flask, equipped with a magnetic stirrer, a condenser, a nitrogen inlet, a thermometer, and a sodium hydroxide trap, was charged with 55.9 g (0.276 mol) of terephthaloyl chloride and 300 mL of *o*-dichlorobenzene. The mixture was heated to ca. 40 °C, and to this stirred mixture was added 31.0 g (0.250 mol) of 2-methylresorcinol in an atmosphere of nitrogen. The mixture was heated for 1 h at 145 °C, accompanied by the evolution of HCl. The mixture was then heated under reflux for 8 h. The solution was allowed to cool and stored in a desiccator overnight.

The two separately prepared polyester solutions (200 mL each) were mixed thoroughly in an atmosphere of nitrogen and heated for 1 h at 145 °C, accompanied by the evolution of HCl. The mixture was then heated under reflux for 8 h in an atmosphere of nitrogen. After cooling, the polymer was precipitated by pouring the reaction mixture into hexane. The polymer was allowed to stand in hexane for 3 days. After washing once with acetone, twice with deionized water, once with methanol, and finally with deionized water, 53.3 g of polymer was obtained after drying in a vacuum oven for 48 h at 175 °C.

Poly(oxy-*trans*-1,4-cyclohexyleneoxycarbonyl-*trans*-1,4-cyclohexylenecarbonyl) and poly[oxy(2-methyl-1,3-phenylene)oxyterephthaloyl] homopolymers were isolated from the remaining solutions not used for block copolymerization by precipitation with acetone and hexanes, respectively. After washing and drying in the usual manner, 21.5 g of poly(oxy-*trans*-1,4-cyclohexyleneoxycarbonyl-*trans*-1,4-cyclohexylenecarbonyl) and 20.5 g of poly[oxy(2-methyl-1,3-phenylene)oxyterephthaloyl] were obtained.

Scheme I
Synthesis of Block Copolyesters



B. Attempted Preparation of Poly[oxy-*cis*-1,4-cyclohexyleneoxycarbonyl-*trans*-1,4-cyclohexylenecarbonyl-*b*-oxy(2-methyl-1,3-phenylene)oxyterephthaloyl] (XI). A 250-mL three-necked, round-bottom flask, equipped with a magnetic stirrer, a condenser, a nitrogen inlet, a thermometer, and a potassium hydroxide trap, was charged with 11.4 g (0.0983 mol) of *cis*-1,4-cyclohexanediol and 135 mL of dry *o*-dichlorobenzene. To the stirred solution was added 18.8 g (0.0900 mol) of *trans*-1,4-cyclohexanedicarbonyl chloride in an atmosphere of nitrogen. The mixture was heated for 1.5 h at 115 °C, accompanied by the evolution of HCl. The mixture was then heated under reflux for 7.5 h.

A 250-mL three-necked, round-bottom flask, equipped with a magnetic stirrer, a condenser, a nitrogen inlet, a thermometer, and a potassium hydroxide trap, was charged with 11.2 g (0.0903 mol) of 2-methylresorcinol and 135 mL of dry *o*-dichlorobenzene. To this stirred solution was added 20.1 g (0.0991 mol) of terephthaloyl chloride in an atmosphere of nitrogen. The mixture was heated for 1 h at 120 °C. The mixture was then heated under reflux for 9 h.

After cooling, 120 g of each of the two polyester solutions was mixed thoroughly in an atmosphere of nitrogen and heated for 8 h at 145 °C. After cooling, the polymer was precipitated by pouring the reaction mixture into 300 mL of acetone. The polymer was allowed to stand in acetone for 3 days. After washing twice with acetone, several times with deionized water, twice with methanol, and finally several times with deionized water, 26.5 g of polymer was obtained after drying in a vacuum oven for 4 h at 115 °C and 8 h at 175 °C.

The homopolymers were isolated from the remaining solutions not used for block copolymerization by precipitation with acetone. After washing and drying in the usual manner, 9.0 g of the cycloaliphatic homopolymer and 3.5 g of the poly[oxy(2-methyl-1,3-phenylene)oxyterephthaloyl] oligomer were obtained.

Results and Discussion

Poly[oxy-*trans*-1,4-cyclohexyleneoxycarbonyl-*trans*-1,4-cyclohexylenecarbonyl-*b*-oxy(2-methyl-1,3-phenylene)oxyterephthaloyl] (X) was prepared by the step-reaction condensation of a cycloaliphatic ester oligomer capped with dihydroxy end groups and an aromatic ester oligomer capped with dicarbonyl chloride end groups (see Scheme I). The structure of the block copolyester is shown in Figure 1.

Properties of Poly[oxy-*trans*-1,4-cyclohexyleneoxycarbonyl-*trans*-1,4-cyclohexylenecarbonyl-*b*-oxy(2-methyl-1,3-phenylene)oxyterephthaloyl] (X). The inherent viscosities for poly(oxy-*trans*-1,4-cyclohexyleneoxycarbonyl-*trans*-1,4-cyclohexylenecarbonyl) and poly[oxy(2-methyl-1,3-phenylene)oxyterephthaloyl] were 0.58 and 0.52 dL/g, respectively, at 30 °C in *o*-chlorophenol. The inherent viscosity of the corresponding block copolyester, poly[oxy-*trans*-1,4-cyclohexyleneoxycarbonyl-*trans*-1,4-cyclohexylenecarbonyl-*b*-oxy(2-methyl-1,3-phenylene)oxyterephthaloyl], was 0.74 dL/g at 30 °C in *o*-chlorophenol. Anal. Calcd for $(C_{14}H_{20}O_4)_n$-

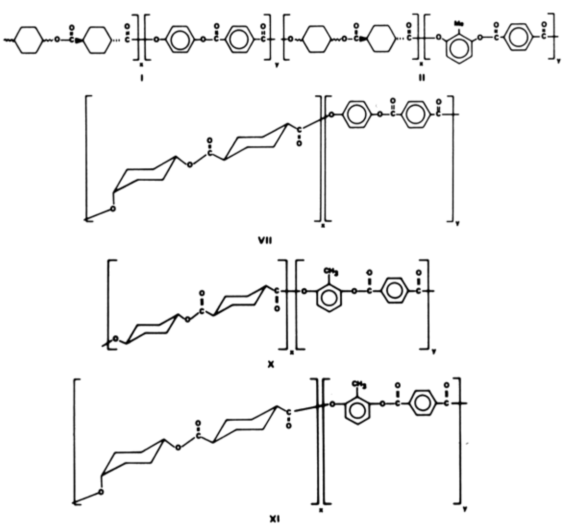


Figure 1. Structures of block copolyesters I, II, VII, X, and XI.

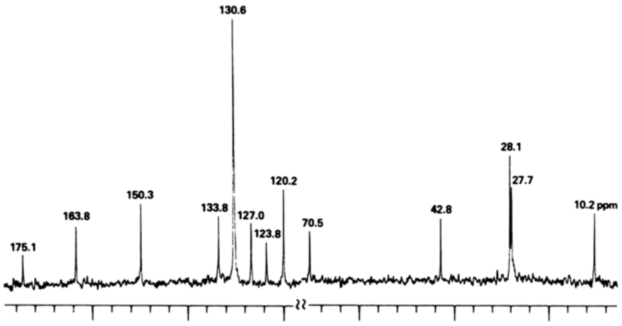


Figure 2. ^{13}C NMR spectrum of X.

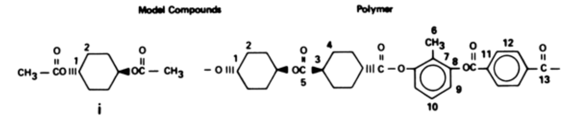
$(C_{14}H_8O_4)_n$: C, 68.29; H, 5.69. Found: C, 67.96; H, 6.30.

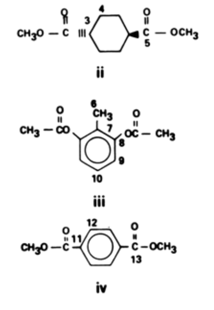
The proton-decoupled natural-abundance ^{13}C FT NMR spectrum of the block copolyester was obtained in $CDCl_3$. The ^{13}C chemical shifts (relative to Me_4Si) and integrals were as follows: δ 10.2 (0.4), 27.7 (0.9), 28.1 (1.2), 42.8 (0.5), 70.5 (0.4), 120.2 (1.0), 123.8 (0.3), 127.0 (0.6), 130.6 (3.8), 133.8 (0.6), 150.3 (0.6), 163.8 (0.5), and 175.1 (0.2). The resonances at δ 10.2–70.5 represent aliphatic carbons. The resonances at δ 120.2–150.3 represent aromatic carbons. The low-field peaks (δ 175.1 and 163.8) correspond to carbonyl carbons.

The carbon-13 spectrum of X obtained at 325 K is shown in Figure 2. Table I shows the assignments of the chemical shifts obtained for X. The model compounds used were *trans*-1,4-cyclohexanediol diacetate (i), *trans*-1,4-dimethyl cyclohexanedioate (ii),[4] 2-methylresorcinol diacetate (iii), and dimethyl terephthalate (iv).[4] *trans*-1,4-Cyclohexanediol diacetate and 2-methylresorcinol diacetate were prepared by the reaction of acetic anhydride with the corresponding diol.

The resonances at 70.5 and 27.7 ppm represent the carbons α and β to the oxygen bonded to the *trans*-cyclohexylene ring, respectively. The resonances at 42.8 and 28.1 ppm represent the carbons α and β to the carbonyl bonded to the cyclohexylene ring, respectively. The resonance at 175.1 ppm represents the carbonyl carbon of the cycloaliphatic block. The resonance at 10.2 ppm represents the methyl group carbon. The resonances at 123.8, 150.3, 120.2, and 127.0 ppm represent the carbons α to the methyl group, ortho to the methyl group, meta to the methyl group, and para to the methyl group, respectively, in the aromatic ring. The resonances at 133.8 and 130.6 ppm represent the carbons α to the carbonyl and β to the carbonyl in the terephthalate ring. The resonance at 163.8 ppm represents the carbonyl carbon of the aromatic block.

Table I
^{13}C NMR Analysis of X





ASSIGNMENTS		
CARBON	MODEL COMPOUNDS (ppm)	POLYMER (ppm)
C–1	71.7	70.5
C–2	28.2	27.7
C–3	42.6	42.8
C–4	28.3	28.1
C–5	175.5	175.1
C–6	9.8	10.2
C–7	123.5	123.8
C–8	150.2	150.3
C–9	119.8	120.2
C–10	126.5	127.0
C–11	134.0	133.8
C–12	129.6	130.6
C–13	162.9	163.8

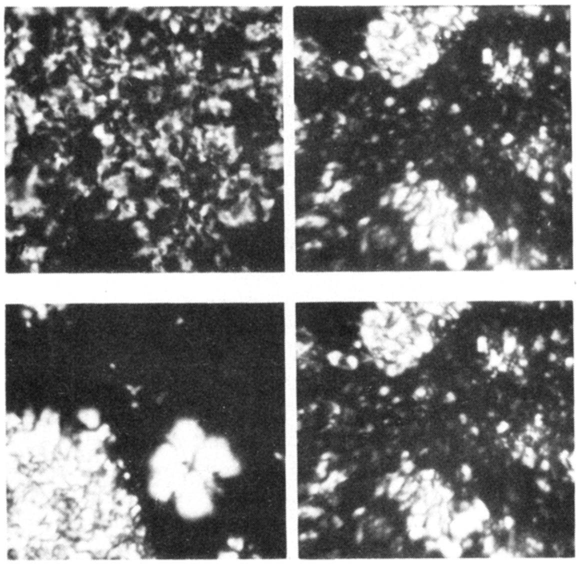


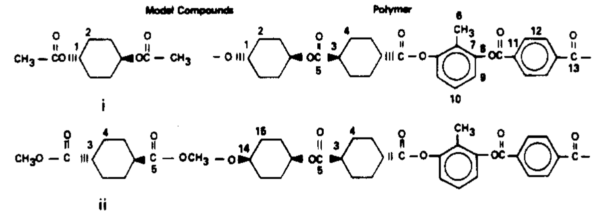
Figure 3. Micrographs of block copolyester X (25%) in *o*-chlorophenol. Magnification 158 ×.

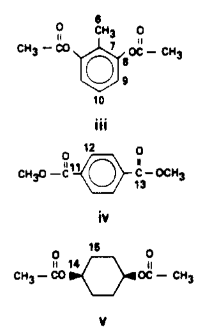
The differential scanning calorimetry thermogram of poly[oxy(2-methyl-1,3-phenylene)oxyterephthaloyl] showed a crystalline melting point of 300 °C. The differential scanning calorimetry thermograms of poly(oxy-*trans*-1,4-cyclohexyleneoxycarbonyl-*trans*-1,4-cyclohexylenecarbonyl) and the corresponding block copolyester (X) showed no transitions before decomposition.

Optical microscopy in cross-polarized light of 25% (w/w) solutions of poly[oxy-*trans*-1,4-cyclohexyleneoxycarbonyl-*trans*-1,4-cyclohexylenecarbonyl-*b*-oxy(2-methyl-1,3-phenylene)oxyterephthaloyl] (X) in *o*-chlorophenol resulted in the depolarization of plane-polarized light (Figure 3) when thin layers of the solutions were viewed at 158 × magnification. The photomicrographs of *o*-chlorophenol solutions of X resemble those of nematic–isotropic biphase systems. The photomicrographs of the birefringent phase have the appearance of the threaded schlieren texture, which is characteristic of the nematic mesophase.

Isomerization Polymerization. The attempt to prepare poly[oxy-*cis*-1,4-cyclohexyleneoxycarbonyl-*trans*-1,4-cyclohexylenecarbonyl-*b*-oxy(2-methyl-1,3-phenylene)oxyterephthaloyl] (XI) led to the preparation of poly[oxy(*cis*,*trans*)-1,4-cyclohexyleneoxycarbonyl-*trans*-1,4-cyclohexylenecarbonyl-*b*-oxy(2-methyl-1,3-phenylene)oxyterephthaloyl] (II). The structures of the

Table II
^{13}C NMR Analysis of II





ASSIGNMENTS		
CARBON	MODEL COMPOUNDS (ppm)	POLYMER (ppm)
C-1	71.7	70.6
C-2	28.2	27.7
C-3	42.6	42.8
C-4	28.3	28.1
C-5	175.5	175.0
C-6	9.8	10.2
C-7	123.5	123.8
C-8	150.2	150.3
C-9	119.8	120.2
C-10	126.5	126.8
C-11	134.0	133.9
C-12	129.6	130.6
C-13	162.9	163.8
C-14	70.1	69.8
C-15	27.4	27.4

block copolyesters are shown in Figure 1.

Properties of the Product Obtained from the Attempted Synthesis of Poly[oxy-*cis*-1,4-cyclohexyleneoxycarbonyl-*trans*-1,4-cyclohexylenecarbonyl-*b*-oxy(2-methyl-1,3-phenylene)oxyterephthaloyl]. The inherent viscosity for the aliphatic block copolyester oligomer was 0.16 dL/g at 30 °C in *o*-chlorophenol. Poly[oxy(2-methyl-1,3-phenylene)oxyterephthaloyl] was found to be too insoluble in *o*-chlorophenol, *m*-cresol, and a 3:1 (v/v) methylene chloride–trifluoroacetic acid mixture for a determination of inherent viscosity at 30 °C. The inherent viscosity of the corresponding block copolyester was 0.38 dL/g at 30 °C in *o*-chlorophenol.

The infrared spectrum showed peaks at 3440 (O—H stretch), 2930 and 2850 (aliphatic C—H stretch), 1720 (ester C═O stretch), 1450 (aromatic nucleus), and 1250, 1080, 1035, and 1005 (C—O stretch) cm^{-1}.

The proton-decoupled natural-abundance ^{13}C FT NMR spectrum of the block copolyester was obtained in $CDCl_3$. The ^{13}C chemical shifts (relative to Me_4Si) and integrals were as follows: δ 10.1 (0.4), 23.1 (0.2), 26.1 (0.2), 27.1 (0.2), 27.4 (4.8), 27.7 (5.2), 28.1 (12.2), 30.7 (0.1), 42.8 (5.1), 69.8 (2.3), 70.5 (2.7), 120.2 (0.6), 123.8 (0.2), 127.0 (0.4), 130.6 (2.3), 133.8 (0.3), 150.3 (0.3), 163.8 (0.2), 175.0 (0.6), and 175.1 (1.1). The resonances at δ 10.1–70.5 represent aliphatic carbons. The resonances at δ 120.2–150.3 represent aromatic carbons. The low-field peaks (δ 175.1, 175.0, and 163.8) correspond to carbonyl carbons.

Carbon-13 NMR Analysis. Analysis of the carbon-13 NMR spectra of the products of the attempted syntheses of block copolymers containing the oxy-*cis*-1,4-cyclohexyleneoxycarbonyl moiety indicated that the syntheses resulted instead in the preparation of block copolyesters containing the oxy(*cis,trans*)-1,4-cyclohexyleneoxycarbonyl moieties distributed along the chain.

A. Analysis of the Carbon-13 NMR Spectrum of Poly[oxy(*cis,trans*)-1,4-cyclohexyleneoxycarbonyl-*trans*-1,4-cyclohexylenecarbonyl-*b*-oxy(2-methyl-1,3-phenylene)oxyterephthaloyl] (II). The carbon-13 spectrum of II is shown in Figure 4. Table II shows the assignments of the chemical shifts obtained for II. The model compounds for II included the same four used for the analysis of the spectrum of X and *cis*-1,4-cyclohexanediol diacetate (v). *cis*-1,4-Cyclohexanediol diacetate was prepared by the reaction of *cis*-1,4-cyclohexanediol with acetic anhydride.

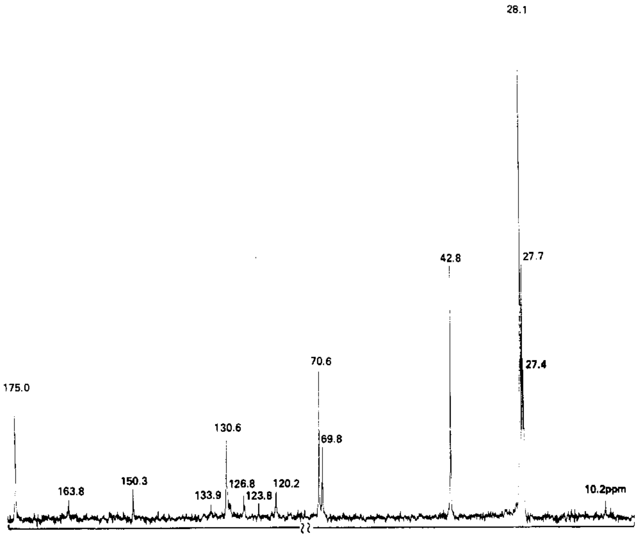


Figure 4. ^{13}C NMR spectrum of II.

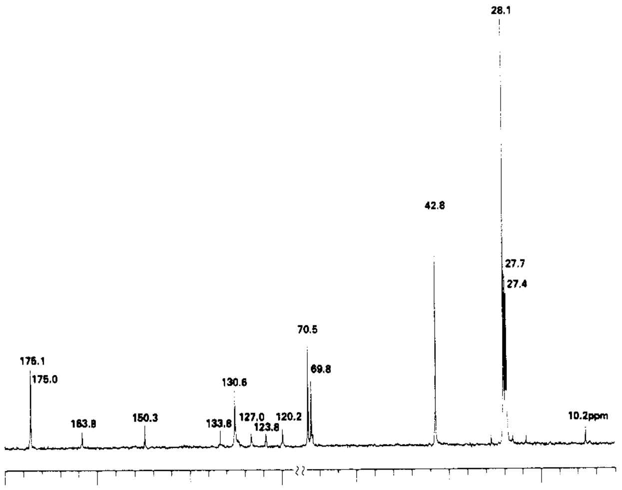


Figure 5. ^{13}C NMR spectrum of product obtained by attempted synthesis of XI.

The assignments were the same as those for X except the resonances at 69.8 and 27.4 ppm were assigned to the carbons α and β to the oxygen bonded to the *cis*-cyclohexylene ring, respectively.

B. Analysis of the Carbon-13 NMR Spectrum of the Product Obtained from the Attempted Synthesis of Poly[oxy-*cis*-1,4-cyclohexyleneoxycarbonyl-*trans*-1,4-cyclohexylenecarbonyl-*b*-oxy(2-methyl-1,3-phenylene)oxyterephthaloyl] (XI). The carbon-13 spectrum of the product of the attempted synthesis of XI is shown in Figure 5. Although the relative intensities of the peaks are different (especially in comparing the aromatic and cycloaliphatic regions) and in spite of the presence of small peaks at 23.1, 26.1, 27.1, and 30.7 ppm, which we attribute to impurities, the carbon-13 NMR spectrum is essentially the same as that of block copolyester II.

C. Analysis of the Carbon-13 NMR Spectrum of Poly[oxy(*cis,trans*)-1,4-cyclohexyleneoxycarbonyl-*trans*-1,4-cyclohexylenecarbonyl-*b*-oxy-1,4-phenyleneterephthaloyl] (I). Block copolyester I was prepared by the method described in the literature.[5] The inherent viscosity of the block copolyester was 0.48 dL/g at 30 °C in *o*-chlorophenol. The proton-decoupled natural-abundance ^{13}C FT NMR spectrum of the block copolyester was obtained in $CDCl_3$. The ^{13}C chemical shifts (relative to Me_4Si) and integrals were as follows: δ 27.4 (1.2), 27.7 (1.7), 28.1 (3.5), 42.8 (1.6), 69.8 (0.8), 70.5 (1.0),

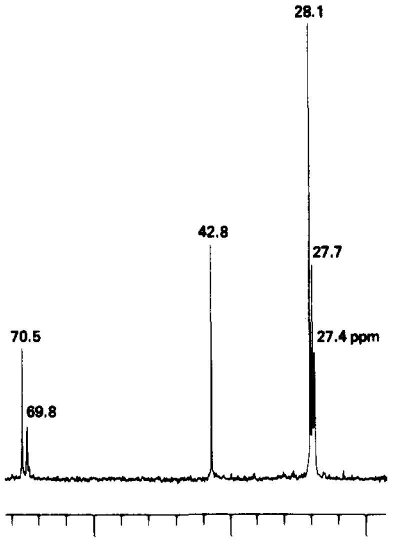


Figure 6. Aliphatic region of ^{13}C NMR spectrum of I.

Table III
Chemical Shifts for Aliphatic Regions of I, II, and VII

carbon	shift, ppm I	II	VII
C-1	70.5	70.6	70.6
C-2	27.7	27.7	27.7
C-3	42.8	42.8	42.8
C-4	28.1	28.1	28.1
C-14	69.8	69.8	69.8
C-15	27.4	27.4	27.4

133.8 (0.7), 134.4 (0.6), 134.8 (0.7), 168.7 (0.1), 175.0 (0.1), 175.1 (0.4), and 183.3 (0.3). The resonances at δ 27.4–70.5 represent aliphatic carbons. The resonances at δ 133.8–134.8 represent aromatic carbons. The low-field peaks (δ 175.1, 175.0, and 168.7) correspond to carbonyl carbons.

The aliphatic region of the carbon-13 spectrum of block copolyester I at 300 K is shown in Figure 6. Table III shows that as expected the chemical shifts for the aliphatic region of block copolyester I are the same as those for the aliphatic region of block copolyester II.

D. Analysis of the Carbon-13 NMR Spectrum of the Block Copolyester Assigned the Structure Poly(oxy-*cis*-1,4-cyclohexyleneoxycarbonyl-*trans*-1,4-cyclohexylenecarbonyl-*b*-oxy-1,4-phenyleneoxyterephthaloyl) (VII). The proton-decoupled natural-abundance ^{13}C FT NMR spectrum of block copolyester VII was obtained in $CDCl_3$. The ^{13}C chemical shifts (relative to Me_4Si) were as follows for the aliphatic region: δ 27.4 (3.6), 27.7 (3.8), 28.1 (7.8), 42.8 (3.1), 69.8 (1.6), and 70.6 (1.8). The aliphatic region of the carbon-13 spectrum of block copolyester VII is shown in Figure 7. Table III shows that the chemical shifts for the aliphatic region of block copolyester VII are the same as those for the aliphatic region of block copolyester I.

The ^{13}C NMR results demonstrate that attempts to prepare block copolyesters containing poly(oxy-*cis*-1,4-cyclohexyleneoxycarbonyl-*trans*-1,4-cyclohexylenecarbonyl) blocks resulted in the formation of poly[oxy(*cis,trans*)-1,4-cyclohexyleneoxycarbonyl-*trans*-1,4-cyclohexylenecarbonyl] blocks. In order to study this phenomenon, a ^{13}C NMR study of the monomers was initiated. *cis*-1,4-Cyclohexanediol[3] (as obtained m.p. 91 °C) and *cis*-1,4-cyclohexanediol recrystallized from acetone (m.p. 91–92 °C) were analyzed by ^{13}C NMR spectroscopy. The ^{13}C NMR spectrum showed peaks at δ 30.5 (10.7), 32.9 (5.9), 67.7 (4.3), and 69.7 (2.5). According to the literature,[6] the peaks at δ 30.5 and 32.9 (literature values were δ 31.3 and 33.9) represent the carbons β to the oxygen in the cis and trans isomers, respectively, and the peaks at δ 67.7 and 69.7 (literature values were δ 69.1 and 71.1) represent the carbons α to the oxygen in the cis and trans isomers. Therefore, the presumed *cis*-1,4-cyclohexanediol starting material was a mixture of the cis and trans isomers, with the cis isomer predominating.

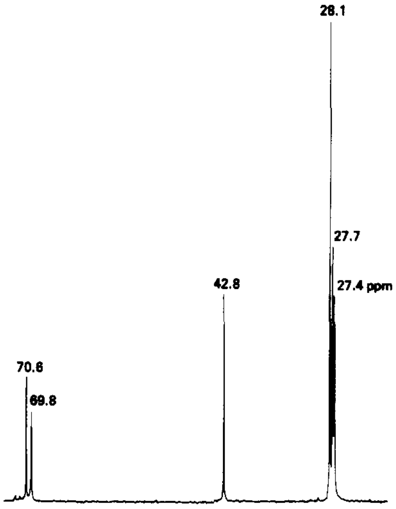


Figure 7. Aliphatic region of ^{13}C NMR spectrum of product obtained by attempted synthesis of VII.

The corresponding ^{13}C NMR resonances in block copolyester XI show that the trans configuration predominates in the polymer. The resonances and integrals corresponding to the carbons β to the oxygen in the polymer were δ 27.4 (4.8) and 27.7 (5.2) for the cis and trans isomers, respectively. The resonances and integrals corresponding to the carbons α to the oxygen in the polymer were δ 69.8 (2.3) and 70.5 (2.7) for the cis and trans isomers, respectively. Apparently, the greater thermodynamic stability of the *trans*-1,4-cyclohexane esters led to isomerization processes occurring during the polymerization of the predominantly *cis*-1,4-cyclohexanediol mixture and the resulting formation of a polymer with the predominantly *trans*-1,4-cyclohexylene configuration along the polymer backbone.

Conclusions

In summary, poly[oxy-*trans*-1,4-cyclohexyleneoxycarbonyl-*trans*-1,4-cyclohexylenecarbonyl-*b*-oxy(2-methyl-1,3-phenylene)oxyterephthaloyl] (X) was synthesized and shown to form mesomorphic solutions. Attempts to synthesize poly(oxy-*cis*-1,4-cyclohexyleneoxycarbonyl-*trans*-1,4-cyclohexylenecarbonyl-*b*-oxy-1,4-phenyleneoxyterephthaloyl) (VII) and poly[oxy-*cis*-1,4-cyclohexyleneoxycarbonyl-*trans*-1,4-cyclohexylenecarbonyl-*b*-oxy(2-methyl-1,3-phenylene)oxyterephthaloyl] (XI) led to isomerization polymerizations and the preparation of poly[oxy(*cis,trans*)-1,4-cyclohexyleneoxycarbonyl-*trans*-1,4-cyclohexylenecarbonyl-*b*-oxy-1,4-phenyleneoxyterephthaloyl] (I) and poly[oxy(*cis,trans*)-1,4-cyclohexyleneoxycarbonyl-*trans*-1,4-cyclohexylenecarbonyl-*b*-oxy(2-methyl-1,3-phenylene)oxyterephthaloyl] (II), respectively.

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Registry No. I, 88392-12-5; II, 88392-13-6; X, 88392-14-7; i, 6289-83-4; iii, 35236-42-1; (*trans*-1,4-cyclohexanediol)·(*trans*-1,4-cyclohexanedicarbonyl chloride) (copolymer), 88392-15-8; poly(oxy-*trans*-1,4-cyclohexyleneoxycarbonyl-*trans*-1,4-cyclohexylenecarbonyl), 88392-10-3; (2-methylresorcinol)·(terephthaloyl chloride) (copolymer), 88392-16-9; poly(oxy-2-methyl-1,3-phenyleneoxyterephthaloyl), 88392-11-4; (*cis*-1,4-cyclohexanediol)·(*trans*-1,4-cyclohexanedicarbonyl chloride) (copolymer), 88392-17-0; poly(oxy-*cis*,*trans*-1,4-cyclohexyleneoxycarbonyl-*trans*-1,4-cyclohexylenecarbonyl), 88424-59-3.

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Hydrolysis Polymerization of Spiro(acylpentaoxy)phosphoranes to Polyphosphates

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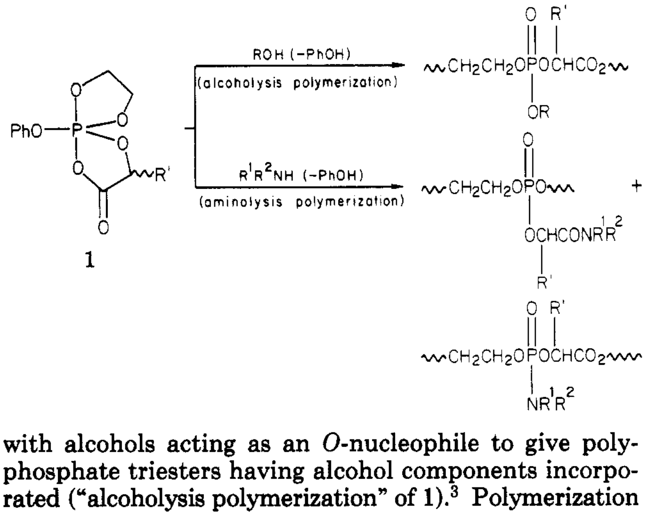
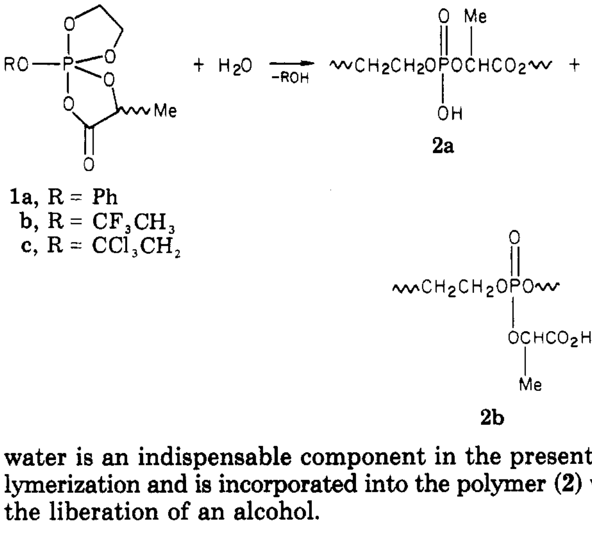
ABSTRACT: Reaction of spiro(acylpentaoxy)phosphoranes **1a–c** induced by an *O*-nucleophile of water gave polyphosphate **2** made of phosphate diester unit **2a** and phosphate triester unit **2b** ("hydrolysis polymerization" of **1**). The content of **2a** and **2b** was determined by two methods: the ^{31}P NMR method on the benzoylated polymer and the IR method on the polymer salts with triethylamine. The mechanism of the hydrolysis polymerization is outlined as follows. The reaction of **1** with water rapidly forms acyclic and cyclic phoshate triester intermediates (**7** and **8**, respectively). **7** and **8** are still reactive, and subsequent reactions between these species slowly take place to yield polyphosphate **2** via two modes of reaction: a polycondensation and a ring-opening addition polymerization.

Our recent investigations have disclosed that spiro(acyloxy)phosphoranes are quite reactive pentacovalent phosphorus species and can be used as starting monomers to give various phosphorus-containing polymers,[1] e.g., polyphosphates,[2–6] polyphosphonates,[5,7] and polyphosphinates.[6–8] All these polymerizations have been considered to proceed via phosphonium zwitterion intermediates.[1] During the course of these studies we have found that spiro(acyloxy)phosphoranes are good amphiphiles; they react with both nucleophiles and electrophiles.[9,10] Recently, we reported the reaction of spiro(acylpentaoxy)phosphoranes **1**, containing a PhO group with alcohols acting as an *O*-nucleophile to give polyphosphate triesters having alcohol components incorporated ("alcoholysis polymerization" of **1**).[3] Polymerization of **1** has also been induced by the reaction of **1** with *N*-nucleophiles of amines and ammonia to give polyphosphate derivatives possessing the amine and ammonia components, respectively ("aminolysis and ammonolysis polymerizations").[11] The present paper describes the polymerization of spiro(acylpentaoxy)phosphoranes **1a–c** induced by the reaction of **1** with an another *O-nucleophile of water*, which gives rise to polyphosphate **2** containing both open-chain phosphate diester unit **2a** and phosphate triester unit with pendant carboxylic acid group **2b** ("hydrolysis polymerization").



The present water-induced polymerization (reaction 1) is unique from the standpoint that in ionic polymerization water is normally an undesirable impurity and hence should be removed from the reaction system. In contrast, water is an indispensable component in the present polymerization and is incorporated into the polymer (**2**) with the liberation of an alcohol.



(1)

Results and Discussion

Hydrolysis Polymerization of Spiro(acylpentaoxy)phosphorane 1 Induced by Water. The polymerization of **1** with water was carried out at room temperature by using a stoichiometric or a small excess amount of water for **1**. Solvents employed were acetonitrile, chloroform,

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