Liquid Crystal Block Copolyesters. 2. Preparation and Properties of Block Copolyesters Containing Cyclohexane and Benzene Rings

Malcolm B. Polk,* Kofi B. Bota, Edmond C. Akubuiro, and Metha Phingbodhipakkiya

Department of Chemistry, Atlanta University, Atlanta, Georgia 30314.

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ABSTRACT: Poly[oxy-*trans*-1,2-cyclohexyleneoxycarbonyl-*trans*-1,2-cyclohexylenecarbonyl-*b*-oxy(2-methyl-1,3-phenylene)oxyterephthaloyl] (V), poly(oxy-*trans*-1,4-cyclohexyleneoxycarbonyl-*trans*-1,4-cyclohexylenecarbonyl-*b*-oxy-1,4-phenyleneoxyterephthaloyl) (VI), poly(oxy-*cis*-1,4-cyclohexyleneoxycarbonyl-*trans*-1,4-cyclohexylenecarbonyl-*b*-oxy-1,4-phenyleneoxyterephthaloyl) (VII), and poly[oxy-*trans*-1,4-cyclohexyleneoxycarbonyl-*trans*-1,4-cyclohexylenecarbonyl-*b*-oxy(2-methyl-1,4-phenylene)oxyterephthaloyl] (VIII) have been synthesized and characterized by infrared spectroscopy, nuclear magnetic resonance spectroscopy, differential scanning calorimetry, and viscometry. Block copolymers VI, VII, and VIII form mesomorphic solutions which depolarize plane-polarized light.

Introduction

This is the second in a series of papers which 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 cross-polarized light and therefore may be said to form liquid crystalline solutions.

The first paper in the series described the syntheses and characterizations of the following block copolyesters: I, poly[oxy(*cis,trans*)-1,4-cyclohexyleneoxycarbonyl-*trans*-1,4-cyclohexylenecarbonyl-*b*-oxy-1,4-phenyleneoxyterephthaloyl]; II, poly[oxy(*cis,trans*)-1,4-cyclohexyleneoxycarbonyl-*trans*-1,4-cyclohexylenecarbonyl-*b*-oxy(2-methyl-1,3-phenylene)oxyterephthaloyl]; III, poly[oxy-*trans*-1,2-cyclohexyleneoxycarbonyl-*trans*-1,2-cyclohexylenecarbonyl-*b*-oxy(2-methyl-1,3-phenylene)oxyisophthaloyl]; IV, poly[oxy-*cis*-1,2-cyclohexyleneoxycarbonyl-*cis*-1,2-cyclohexylenecarbonyl-*b*-oxy(2-methyl-1,3-phenylene)oxyisophthaloyl].[1] Poly[oxy(*cis,trans*)-1,4-cyclohexyleneoxycarbonyl-*trans*-1,4-cyclohexylenecarbonyl-*b*-oxy(2-methyl-1,3-phenylene)oxyterephthaloyl] was shown to form mesomorphic solutions which depolarize plane-polarized light.

Kuhfuss and co-workers[2] have prepared random copolyesters by the acidolysis of poly(ethylene terephthalate) with *p*-acetoxybenzoic acid. They found that copolyesters which contained 40–90 mol % *p*-oxybenzoyl groups formed liquid crystalline melts. McFarland and co-workers[3] have reported that replacement of *p*-oxybenzoyl groups with *m*-oxybenzoyl groups and 1,3-oxyphenyleneoxyterephthaloyl groups in the random copolyesters reduces the chain linearity to such an extent that liquid crystalline behavior disappears. While studying the properties of block copolyesters, which form liquid crystalline mesophases, we have observed a greater tolerance of the rodlike, extended-chain blocks for nonconforming blocks containing groups such as oxy(2-methyl-1,3-phenylene)oxyterephthaloyl.[1,4]

Several problems have been encountered in attempts to process these liquid crystalline polymers: (1) the relative insolubility of the polymers in organic solvents; (2) the decomposition of the polymers at the high temperatures required for processing; and (3) the low elongations-to-break of the fibers which decrease after exposure to a high temperature.

Our purpose in initiating these research efforts was to prepare liquid crystalline materials with increased solubility, lower processing temperatures, and higher levels of thermal stability. We set out to achieve these goals in a fashion somewhat different from that of other researchers in the field.[5–23] We decided to optimize the solubility, thermal, and mechanical properties of block copolyesters which contain cyclohexane and benzene rings by incorporating blocks which contained nonconforming groups into $(AB)_n$ block copolyesters which also contained extended-chain blocks.

Experimental Section

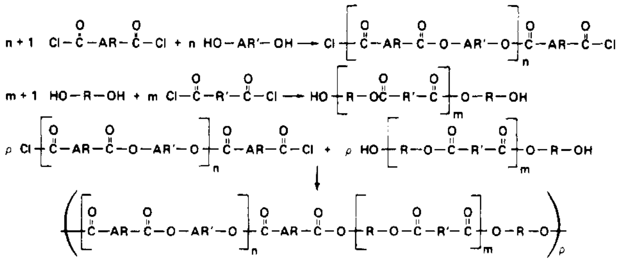
Inherent viscosities were measured at 30 °C with a Cannon-Fenske viscometer at a concentration of 0.5 g/100 mL of solvent except in those cases specified. Melting points and glass transition temperatures were determined with a differential scanning calorimeter (DuPont 990 and 1090 thermal analyzers with the DuPont 910 differential scanning calorimeter). NMR spectra were determined on deuteriochloroform solutions of the polyesters with a Bruker WH-250 spectrometer, with proton spectra taken at 250.133 MHz and carbon-13 spectra 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, *trans*-1,2-cyclohexanediol, *cis*-1,4-cyclohexanediol, hydroquinone, and methylhydroquinone were commercial products. *trans*-1,4-Cyclohexanedicarboxoyl chloride and *trans*-1,2-cyclohexanedicarboxoyl chloride were prepared according to a procedure described in the literature.[24] *trans*-1,4-Cyclohexanediol was isolated from the cis–trans 1,4-cyclohexanediol mixture according to a procedure described in the literature.[25]

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

A. Preparation of Poly[oxy-*trans*-1,2-cyclohexyleneoxycarbonyl-*trans*-1,2-cyclohexylenecarbonyl-*b*-oxy(2-methyl-1,3-phenylene)oxyterephthaloyl] (V). A 500-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 25.74 g (0.2220 mol) of *trans*-1,2-cyclohexanediol and 120 mL of dry *o*-dichlorobenzene. To the stirred solution was added 42.08 g (0.2000 mol) of *trans*-1,2-cyclohexanedicarboxoyl chloride in an atmosphere of nitrogen. The mixture was heated for 1.25 h at 115 °C, accompanied by the evolution of HCl. The mixture was then heated under reflux for 7.5 h.

A 500-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 25.0 g (0.200 mol) of 2-methylresorcinol and 180 mL of dry *o*-dichlorobenzene.

Scheme I
Synthesis of Block Copolyesters



To this stirred solution was added 46.0 g (0.2266 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 6.5 h.

After cooling, 60 mL of each of the two polyester solutions were mixed thoroughly in an atmosphere of nitrogen and heated under reflux for 1.5 h. The mixture was then heated for 8 h at 150 °C. After cooling, the polymer was precipitated by pouring the reaction mixture into 500 mL of hexane. The polymer was allowed to stand in hexane for 1 day. After washing twice with acetone, three times with deionized water, and finally with acetone, 11 g of polymer was obtained after drying in a vacuum oven for 48 h at 120 °C.

B. Preparation of Poly(oxy-*trans*-1,4-cyclohexyleneoxycarbonyl-*trans*-1,4-cyclohexylenecarbonyl-*b*-oxy-1,4-phenyleneoxyterephthaloyl) (VI). The same procedure in A was followed. For the preparation of the cycloaliphatic oligomer, 28.70 g (0.1373 mol) of *trans*-1,4-cyclohexanedicarboxoyl chloride, 17.56 g (0.1510 mol) of *trans*-1,4-cyclohexanediol, and 190 mL of dry *o*-dichlorobenzene were used. For the preparation of the aromatic oligomer, 44.70 g (0.2200 mol) of terephthaloyl chloride, 22.02 g (0.2000 mol) of hydroquinone, and 240 mL of dry *o*-dichlorobenzene were used. After 100 mL of each solution were mixed, refluxed, and heated, 17 g of VI was obtained by precipitation with acetone.

C. Preparation of Poly(oxy-*cis*-1,4-cyclohexyleneoxycarbonyl-*trans*-1,4-cyclohexylenecarbonyl-*b*-oxy-1,4-phenyleneoxyterephthaloyl) (VII). The same procedure in A was followed. For the preparation of the cycloaliphatic oligomer, 10.4 g (0.0894 mol) of *cis*-1,4-cyclohexanediol, 17.0 g (0.0813 mol) of *trans*-1,4-cyclohexanedicarboxoyl chloride, and 110 mL of dry *o*-dichlorobenzene were used. For the preparation of the aromatic oligomer 11.0 g (0.100 mol) of hydroquinone, 22.4 g (0.110 mol) of terephthaloyl chloride, and 120 mL of dry *o*-dichlorobenzene were used. After 50 mL of each solution were mixed, refluxed, and heated, 18 g of VII was obtained by precipitation with acetone.

D. Preparation of Poly[oxy-*trans*-1,4-cyclohexyleneoxycarbonyl-*trans*-1,4-cyclohexylenecarbonyl-*b*-oxy(2-methyl-1,4-phenylene)oxyterephthaloyl] (VIII). The same procedure in A was followed. For the preparation of the cycloaliphatic oligomer, 25.5 g (0.220 mol) of *trans*-1,4-cyclohexanediol, 41.8 g (0.200 mol) of *trans*-1,4-cyclohexanedicarboxoyl chloride, and 300 mL of dry *o*-dichlorobenzene were used. For the preparation of the aromatic oligomer, 24.8 g (0.200 mol) of methylhydroquinone, 44.7 g (0.220 mol) of terephthaloyl chloride, and 300 mL of dry *o*-dichlorobenzene were used. After 150 mL of each solution were mixed, refluxed, and heated, 50 g of VIII was obtained by precipitation with acetone.

Results and Discussion

Four block copolyesters were formed by the step-reaction condensation of cycloaliphatic ester oligomers capped with dihydroxy end groups and aromatic ester oligomers capped with dicarboxoyl chloride end groups (see Scheme I). The structures of the resulting block copolyesters are shown in Figure 1.

Properties of Poly[oxy-*trans*-1,2-cyclohexyleneoxycarbonyl-*trans*-1,2-cyclohexylenecarbonyl-*b*-oxy(2-methyl-1,3-phenylene)oxyterephthaloyl] (V). The inherent viscosities for poly(oxy-*trans*-1,2-cyclohexyleneoxycarbonyl-*trans*-1,2-cyclohexylenecarbonyl) and poly[oxy(2-methyl-1,3-phenylene)oxyterephthaloyl] were 0.06 and 0.44 dL/g, respectively, at 30 °C in *m*-cresol. The inherent viscosity of the corresponding block copolyester, poly[oxy-*trans*-1,2-cyclohexyleneoxycarbonyl-*trans*-1,2-cyclohexylenecarbonyl-*b*-oxy(2-methyl-1,3-phenylene)oxyterephthaloyl] was 0.27 dL/g at 30 °C in *m*-cresol.

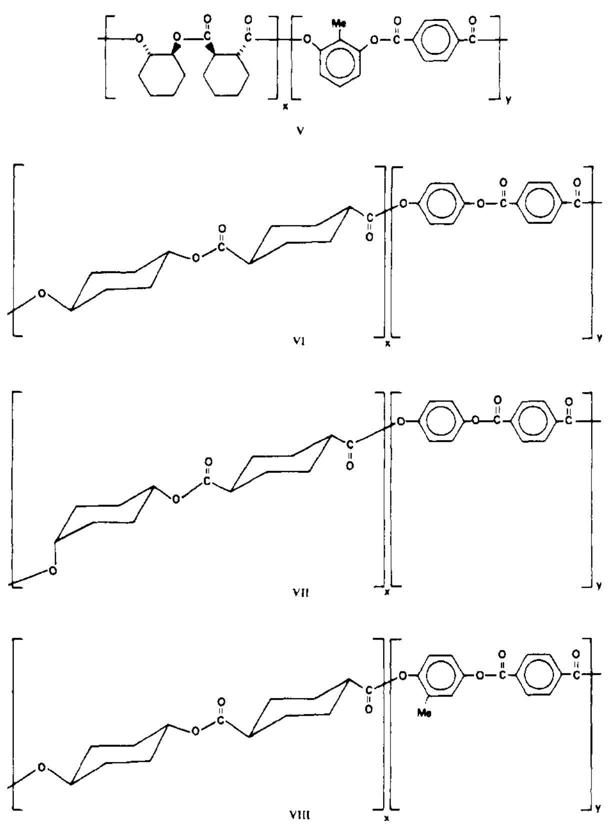


Figure 1. Block copolyesters.

Elemental analysis showed a number-average degree of polymerization of 5 for the poly(oxy-*trans*-1,2-cyclohexyleneoxycarbonyl-*trans*-1,2-cyclohexylenecarbonyl) oligomer. Anal. Calcd for $H(C_{14}H_{20}O_4)_5C_6H_{11}O_2 \cdot 2H_2O$: C, 64.59; H, 8.22. Found: C, 64.22; H, 8.13. Elemental analysis showed a number-average degree of polymerization of 17 for the poly[(2-methyl-1,3-phenylene)oxyterephthaloyl] oligomer. Anal. Calcd for $HO(C_{15}H_{10}O_4)_{17}C_8H_5O_3$: C, 70.38; H, 3.93. Found: C, 70.20; H, 4.18.

The infrared spectrum showed peaks at 3400 (O–H stretch), 2910 and 2840 (aliphatic C–H stretch), 1720 (ester C=O stretch), 1450 (aromatic nucleus), and 1250, 1070, and 1005 (C–O stretch) cm^{-1}.

The differential scanning calorimetry thermogram of poly(oxy-*trans*-1,2-cyclohexyleneoxycarbonyl-*trans*-1,2-cyclohexylenecarbonyl) showed a glass transition temperature of 68 °C. The differential scanning calorimetry thermogram of poly[oxy(2-methyl-1,3-phenylene)oxyterephthaloyl] showed a crystalline melting point of 313 °C. The differential scanning calorimetry thermogram of the corresponding block copolyester showed a melting endotherm at 320 °C.

The ^1H NMR spectrum of the block copolymer was obtained in $CDCl_3$. The ^1H chemical shifts and integrals were as follows: δ 1.26 (1.0), 1.32 (3.1), 1.74 (3.1), 1.82 (0.2), 1.85 (0.7), 1.99 (1.9), 2.15 (1.8), 2.56 (0.8), 3.74 (0.4), 4.79 (1.1), 7.20 (0.3), 7.34 (0.2), 7.36 (0.2), 8.25 (0.3), and 8.38 (1.3). The resonances at δ 1.26–4.79 represent aliphatic protons, and the resonances at δ 7.20–8.38 represent aromatic protons.

Properties of Poly(oxy-*trans*-1,4-cyclohexyleneoxycarbonyl-*trans*-1,4-cyclohexylenecarbonyl-*b*-oxy-1,4-phenyleneoxyterephthaloyl) (VI). The inherent viscosity of poly(oxy-*trans*-1,4-cyclohexyleneoxycarbonyl-*trans*-1,4-cyclohexylenecarbonyl) was 0.31 dL/g in *o*-chlorophenol at 30 °C. Poly(oxy-1,4-phenyleneoxyterephthaloyl) was insoluble in *o*-chlorophenol. An inherent viscosity of 0.43 dL/g was obtained for poly(oxy-*trans*-1,4-cyclohexyleneoxycarbonyl-*trans*-1,4-cyclohexyleneoxycarbonyl-*trans*-1,4-cyclohexylenecarbonyl-*b*-oxy-1,4-phenyleneoxyterephthaloyl) at a concentration of 0.4 g/100 mL of *o*-chlorophenol at 30 °C.

Elemental analysis showed a number-average degree of polymerization of 16 for the poly(oxy-*trans*-1,4-cyclohexyleneoxycarbonyl-*trans*-1,4-cyclohexylenecarbonyl) oligomer. Anal. Calcd for $H(C_{14}H_{20}O_4)_{16}C_6H_{11}O_2 \cdot H_2O$: C, 66.26; H, 8.02. Found: C, 66.16; H, 8.24. Elemental analysis showed a number-average degree of polymerization of 12 for the poly(oxy-1,4-phenyleneoxyterephthaloyl) oligomer. Anal. Calcd for $HO(C_{14}H_8O_4)_{12}C_8H_5O_3 \cdot H_2O$: C, 68.92; H, 3.39. Found: C, 68.72; H, 3.66.

The infrared spectrum of the block copolyester showed peaks at 3400 (O–H stretch), 2930 and 2850 (aliphatic C–H stretch), 1715 (ester C=O stretch), 1600 and 1490 (aromatic nucleus), and 1240, 1070, 1035, and 1010 (C–O stretch) cm^{-1}.

The ^1H NMR spectrum of the block copolyester was obtained in $CDCl_3$. The ^1H chemical shifts and integrals were as follows: δ 1.26 (1), 1.51 (15), 1.65 (1), 1.72 (1), 1.84 (3), 1.91 (1), 1.95 (1), 2.05 (4), 3.73 (3), 8.09 (1), and 8.11 (1). The resonances at δ 1.26–3.73 represent aliphatic protons and the resonances at δ 8.09 and 8.11 represent aromatic protons.

Methylene chloride–*o*-chlorophenol solutions of poly(oxy-*trans*-1,4-cyclohexyleneoxycarbonyl-*trans*-1,4-cyclohexylenecarbonyl-*b*-oxy-1,4-phenyleneoxyterephthaloyl) depolarized plane-polarized light when thin layers of the solutions were viewed at 504× magnification.

Properties of Poly(oxy-*cis*-1,4-cyclohexyleneoxycarbonyl-*trans*-1,4-cyclohexylenecarbonyl-*b*-oxy-1,4-phenyleneoxyterephthaloyl) (VII). The inherent viscosity of poly(oxy-*cis*-1,4-cyclohexyleneoxycarbonyl-*trans*-1,4-cyclohexylenecarbonyl) was 0.18 dL/g in *m*-cresol at 30 °C. Poly(oxy-1,4-phenyleneoxyterephthaloyl) was insoluble in *m*-cresol. An inherent viscosity of 0.44 dL/g was obtained for poly(oxy-*cis*-1,4-cyclohexyleneoxycarbonyl-*trans*-1,4-cyclohexylenecarbonyl-*b*-oxy-1,4-phenyleneoxyterephthaloyl) at a concentration of 0.4 g/100 mL of *m*-cresol at 30 °C.

The infrared spectrum of the block copolyester showed peaks at 3400 (O–H stretch), 2940 and 2860 (aliphatic C–H stretch), 1720 (ester C=O stretch), 1495 (aromatic nucleus), and 1245, 1070, 1035, and 1010 (C–O stretch) cm^{-1}.

The differential scanning calorimetry thermogram of poly(oxy-*cis*-1,4-cyclohexyleneoxycarbonyl-*trans*-1,4-cyclohexylenecarbonyl) showed a crystalline melting point of 220 °C. The transitions in the block copolyester were obscured by decomposition.

The ^1H NMR spectrum of the block copolymer was obtained in $CDCl_3$. The ^1H chemical shifts and integrals were as follows: δ 1.26 (1.1), 1.41 (3.4), 1.46 (9.5), 1.49 (3.9), 1.54 (6.6), 1.73 (16.1), 1.91 (5.4), 1.95 (3.0), 2.06 (16.8), 2.27 (7.3), 3.95 (0.3), 4.84 (7.2), 5.13 (0.7), 7.32 (0.2), 8.08 (0.3), 8.11 (0.3), 8.12 (0.1), 8.14 (0.6), and 8.20 (0.2). The resonances at δ 1.26–5.13 represent aliphatic protons and the resonances at δ 7.32–8.20 represent aromatic protons.

Methylene chloride–*o*-chlorophenol solutions of poly(oxy-*cis*-1,4-cyclohexyleneoxycarbonyl-*trans*-1,4-cyclohexylenecarbonyl-*b*-oxy-1,4-phenyleneoxyterephthaloyl) depolarized plane-polarized light when thin layers of the solutions were viewed at 504× magnification.

Figure 2. Micrograph of block copolyester VIII between crossed polarizers. 100× magnification.

Properties of Poly[oxy-*trans*-1,4-cyclohexyleneoxycarbonyl-*trans*-1,4-cyclohexylenecarbonyl-*b*-oxy(2-methyl-1,4-phenylene)oxyterephthaloyl] (VIII). The inherent viscosities of poly(oxy-*trans*-1,4-cyclohexyleneoxycarbonyl-*trans*-1,4-cyclohexylenecarbonyl) and poly[oxy(2-methyl-1,4-phenylene)oxyterephthaloyl] were 0.55 and 0.58 dL/g, respectively, in 3:1 (v/v) methylene chloride–trifluoroacetic acid at 30 °C. The inherent viscosity for the corresponding block copolyester was 0.85 dL/g in 3:1 (v/v) methylene chloride–trifluoroacetic acid at 30 °C.

Elemental analysis showed a number-average degree of polymerization of 20 for the poly(oxy-*trans*-1,4-cyclohexyleneoxycarbonyl-*trans*-1,4-cyclohexylenecarbonyl) oligomer. Anal. Calcd for $H(C_{14}H_{20}O_4)_{20}C_6H_{11}O_2$: C, 66.56; H, 7.99. Found: C, 66.38; H, 8.36. Elemental analysis showed a number-average degree of polymerization of 10 for the poly[oxy(2-methyl-1,4-phenylene)oxyterephthaloyl] oligomer. Anal. Calcd for $HO(C_{15}H_{10}O_4)_{10}C_8H_5O_3 \cdot H_2O$: C, 69.60; H, 3.96. Found: C, 69.82; H, 4.35.

The infrared spectrum showed peaks at 2940 (aliphatic C–H stretch), 1740 (ester C=O stretch), 1410 (aromatic C–H deformation), and 1250 and 1080 (C–O stretch) cm^{-1}.

The ^1H NMR spectrum of the block copolyester was obtained in $CDCl_3$. The ^1H chemical shifts and integrals were as follows: δ 1.26 (3), 1.66 (2), 1.85 (4), 2.03 (1), 2.07 (3), 2.20 (2), 2.29 (3), 2.30 (2), 4.9 (1), 5.22 (2), 6.95 (1), 7.02 (1), 7.22 (1), 7.29 (1), 8.13 (1), 8.18 (1), 8.22 (1), 8.33 (1), 8.35 (1), 8.37 (1), and 8.39 (3). The resonances at δ 1.26–5.22 represent aliphatic protons and the resonances at δ 6.95–8.39 represent aromatic protons.

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 21.5 (0.2), 27.9 (0.3), 28.2 (0.2), and 130.5 (0.4). The resonances at δ 21.5–28.2 represent aliphatic carbons. The resonance at δ 130.5 represents aromatic carbons. The resonances due to the carbonyl carbons were not observed due to the limited solubility of the block copolyester.

1,1,2,2-Tetrachloroethane–*o*-chlorophenol–phenol (60:25:15 v/v/v) solutions of poly[oxy-*trans*-1,4-cyclohexyleneoxycarbonyl-*trans*-1,4-cyclohexylenecarbonyl-*b*-oxy(2-methyl-1,4-phenylene)oxyterephthaloyl] depolarized plane-polarized light when thin layers of the solutions were viewed at 100× magnification. When the solutions were sheared by the movement of the cover slide, microdomains of oriented, extended-chain segments were observed to form on microscopic examination between crossed polarizers. This phenomenon is shown in Figure 2.

Conclusion

In summary, synthetic procedures have been developed for block copolyesters which contain cyclohexane and benzene rings. Three of these block copolyesters display mesomorphic properties in solution. In subsequent publications, the spectroscopic, mechanical, and thermal properties of these block copolyesters will be described in detail.

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References and Notes

(1) Polk, M. B.; Bota, K. B.; Akubuiro, E. C., submitted to *Ind. Eng. Chem. Prod. Res. Dev.*
(2) Jackson, W. J.; Kuhfuss, H. F. *J. Polym. Sci.* **1976**, *14*, 2043.
(3) McFarlane, F. E.; Nicely, V. A.; Davis, T. G. In *Contemp. Top. Polym. Sci.* **1977**, *2*, 115–20.
(4) Polk, M. B.; Bota, K. B.; Akubuiro, E. C. *Prepr., Div. Org. Coat. Plast., Am. Chem. Soc.* **1981**, *44*, 416.
(5) Schaefgen, J. R.; Pletcher, T. C.; Kleinschuster, J. J. Belgium Patent 828 935, 1975.
(6) Pletcher, T. C. U.S. Patent 3 991 013, 1976.
(7) Kleinschuster, J. J. U.S. Patent 3 991 014, 1976.
(8) Kleinschuster, J. J.; Pletcher, T. C. U.S. Patent 4 066 620, 1978.
(9) Calundann, G. W. U.S. Patent 4 067 852, 1978.
(10) Schaefgen, J. R. U.S. Patent 4 075 262, 1978.
(11) Calundann, G. W.; Davis, H. L.; Gorman, F. J.; Mininni, R. M. U.S. Patent 4 083 329, 1978.
(12) Schaefgen, J. R. U.S. Patent 4 118 372, 1978.
(13) Calundann, G. W. U.S. Patent 4 130 545, 1978.
(14) Jackson, W. J., Jr.; Kuhfuss, H. F. U.S. Patent 4 140 846, 1979.
(15) Morris, J. C.; Jackson, W. J., Jr. U.S. Patent 4 146 702, 1979.
(16) Jackson, W. J., Jr.; Bebeau, G. G.; Kuhfuss, H. F. U.S. Patent 4 153 779, 1979.
(17) Jackson, W. J., Jr.; Morris, J. C. U.S. Patent 4 156 070, 1979.
(18) Calundann, G. W. U.S. Patent 4 161 470, 1979.
(19) Jackson, W. J., Jr.; Morris, J. C. U.S. Patent 4 169 933, 1979.
(20) Jackson, W. J., Jr.; Morris, J. C. U.S. Patent 4 181 792, 1980.
(21) Calundann, G. W. U.S. Patent 4 184 996, 1980.
(22) Blades, H. U.S. Patent 3 767 756, 1973.
(23) Frazer, A. H. U.S. Patent 3 037 960, 1962.
(24) Doering, W. E.; Farber, M.; Sayigh, A. *J. Am. Chem. Soc.* **1952**, *74*, 4370–2.
(25) Oberg, R. C.; Pines, H.; Ipatieff, V. N. *J. Am. Chem. Soc.* **1944**, *66*, 1096.

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pH-Dependent Esterolysis by Dodecylated Poly(ethylenimine)

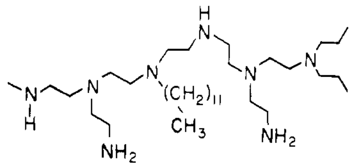
Curtis S. Lege and James A. Deyrup*

Center for Macromolecular Science, Department of Chemistry, University of Florida, Gainesville, Florida 32611. Received May 12, 1981

ABSTRACT: The esterolysis of *p*-nitrophenyl acetate (PNPA) and *p*-nitrophenyl caproate (PNPC) by partially dodecylated poly(ethylenimine) (PEI-D-NH_2-HCl) has been studied. The reactions proceed via nucleophilic attack of the pendent primary amino groups on the ester at a rate (k) which is dependent on the pH. The $pK_{a,app}$ of PEI-D-NH_2-HCl is also pH dependent. It was possible, therefore, to construct a Brønsted-type plot of log k (corrected for free amino groups) against the $pK_{a,app}$ of the polymeric amino groups for PNPA (β = 0.81). The pH dependence of PNPA esterolysis is thus accounted for by electrostatic effects on nucleophilicity. An additional pH dependence of PNPC was observed and attributed to pH effects on hydrophobic bonding.

The search for synthetic macromolecular catalysts continues and impressive developments in this area appear on a regular basis in the current literature.[1-6] At the same time many questions remain unanswered concerning the relative importance of those various factors which could contribute to catalytic activity. One such factor of particular concern relates to cooperative or bifunctional catalysis.[7] Such effects are important in many enzymatic reactions and involve the concerted interaction of two or more functional groups in the reaction with the substrate.

PEI [poly(ethylenimine)] modified by the attachment of dodecyl groups and imidazole substituents has shown remarkable esterolytic activity.[8-12] Klotz and co-workers attributed this activity to hydrophobic binding between the esters and the dodecyl groups. It occurred to us that a portion of this activity might be due to cooperative effects between the PEI backbone and the catalytically active imidazole groups. In order to address this question it became necessary to study first the esterolysis reactions of PEI substituted only by dodecyl groups. This polymer derivative (PEI-D-NH_2) contains primary amino groups



PEI - D - NH_2

but lacks heterocyclic substituents. The following paper deals with the question of cooperative catalysis in esterolyses which involve imidazole and related heterocyclic substituents. Our approach in both instances will be patterned on the work of others who have attempted to detect cooperative effects in small molecules via studies of the dependency of rate on pH.[13]

Experimental Section

Melting points and boiling points are uncorrected unless otherwise noted. Nuclear magnetic resonance spectra were recorded

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