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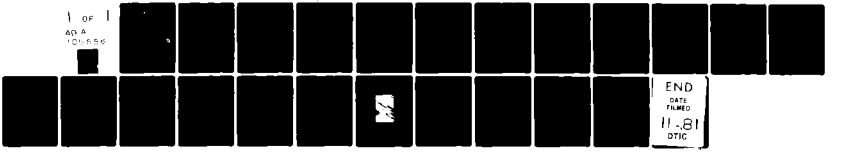

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Poly oxy-trans-1,2-cyclohexyleneoxycarbonyl-trans-1,2-cyclohexylenecarbonyl-b-oxy(2-methyl-1,3-phenylene)oxyterephthaloyl V; Poly(oxy-trans-1,4-cyclohexyleneoxycarbonyl-trans-1,4-cyclohexylenecarbonyl-b-oxy-1,4-phenyleneoxyterephthaloyl)VI; Poly(oxy-cis-1,4-cyclohexyleneoxycarbonyl-trans-1,4-cyclohexylenecarbonyl-b-oxy-1,4-phenyleneoxyterephthaloyl)VII: and Poly[oxy-trans-1,4-cycloheyleneoxycarbonyl-trans-1,4-cyclohexylenecarbonyl-b-oxy(2-methyl-1,4-phenylene)oxyterephthaloyl] VIII

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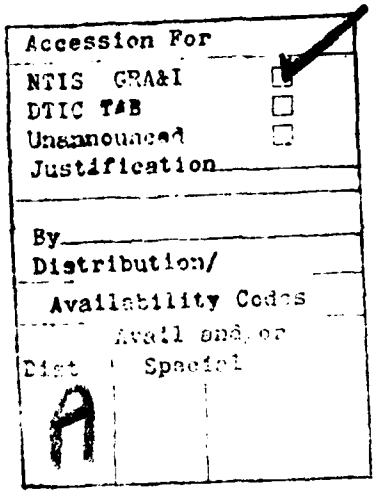

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TECHNICAL REPORT NO. 1

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

by

Malcolm B. Polk, Kofi B. Bota, Edmond C. Akubuiro

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

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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-cycloheylenecarbonyl-b-oxy(2-methyl-1,3-phenylene)oxyisophthaloyl]; and 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-cyclohexylene-oxycarbonyl-trans-1,4-cyclohexylenecarbonyl-b-oxy(2-methyl-1,3-phenylene)oxytereph-thaloyl] was shown to form mesomorphic solutions which depolarize plane-polarized light.

Kuhfuss and coworkers[2] have prepared random copolyesters by the acidolysis of poly(ethylene terephthalate) with p-acetoxybenzoic acid. They found that copolyesters which contained 40-90 mole percent para oxybenzoyl groups formed liquid crystalline melts. McFarlane and coworkers[3] have reported that replacement of para oxybenzoyl groups with meta 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 rod-like, 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 somewhat different fashion than 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/100mL 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 at 250.133MHz and carbon-13 at 62.860MHz. The chemical shifts are reported relative to tetramethylsilane. Infrared spectra were obtained on KBr discs 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. Terephaloyl chloride, trans-1,2-cyclohexanediol, cis-1,4-cyclohexanediol, hydroquinone and methylhydroquinone were commercial products. Trans-1,4-cyclohexanedicarboxylic acid chloride and trans-1,2-cyclohexanedicarboxylic acid 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-cyclohexanedicarboxylic acid chloride and trans-1,2-cyclohexanedicarboxylic acid 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 500mL 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 mole) of trans-1,2-cyclohexanediol and 120mL of dry o-dichlorobenzene. To the stirred solution was added 42.08 g (0.2000 mole) of trans-1,2-cyclohexanedicarboxylic acid chloride in an atmosphere of nitrogen. The mixture was heated for 1-1/4 hr at 115°C, accompanied by the evolution of HCl. The mixture was then heated under reflux for 7-1/2 hr.

A 500mL 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 mole) of 2-methylresorcinol and 180mL of dry o-dichlorobenzene. To this stirred solution was added 46.0 g (0.2266 mole) of terephthaloyl chloride in an atmosphere of nitrogen. The mixture was heated for 1 hr. at 120°C. The mixture was then heated under reflux for 6-1/2 hr.

After cooling, 60 ml of each of the two polyester solutions were mixed thoroughly in an atmosphere of nitrogen and heated under reflux for 1-1/2 hrs.. The mixture was then heated for 8 hrs. at 150°C. After cooling, the polymer was

precipitated by pouring the reaction mixture into 500mL 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 hrs. 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 mole) of trans-1,4-cyclohexanedicarboxylic acid chloride, 17.56 g (0.1510 mole) of trans-1,4-cyclohexanediol, and 190mL of dry o-dichlorobenzene were used. For the preparation of the aromatic oligomer, 44.70 g (0.2200 mole) of terephthaloyl chloride, 22.02 g (0.2000 mole) of hydroquinone, and 240mL of dry o-dichlorobenzene were used. After 100mL of each solution were mixed, refluxed and heated, 17 g of VI were 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 mole) of cis-1,4-cyclohexanediol, 17.0 g (0.0813 mole) of trans-1,4-cyclohexanedicarboxylic acid chloride, and 110mL of dry o-dichlorobenzene were used. For the preparation of the aromatic oligomer 11.0 g (0.100 mole) of hydroquinone, 22.4 g (0.110 mole) of terephthaloyl chloride, and 120mL of dry o-dichlorobenzene were used. After 50mL of each solution were mixed, refluxed and heated, 18 g of VII were 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 mole) of trans-1,4-cyclohexanediol, 41.8 g (0.200 mole) of trans-1,4-cyclohexanedicarboxylic acid chloride, and 300 mL of dry o-dichlorobenzene were used. For the preparation of the aromatic oligomer, 24.8 g (0.200 mole) of methylhydroquinone, 44.7 g (0.220 mole) 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 XIII were 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 dicarboxylic acid chloride end groups (see Scheme 1). 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.

Elemental analysis showed a number average degree of polymerization of five for the poly(oxy-trans-1,2-cyclohexyleneoxycarbonyl-trans-1,2-cyclohexylenecarbonyl) oligomer. Anal. Calcd for $H-(C_{14}H_{20}O_4\rightarrow_5C_6H_{11}O_2\cdot 2H_2O$: C, 64.59; H, 8.22. Found: C, 64.22; H, 8.13. Elemental analysis showed a number average degree of polymerization of seventeen for the poly[(2-methyl-1,3-phenylene)oxyterephthaloyl] oligomer. Anal. Calcd for $HO-(C_{15}H_{10}O_4\rightarrow_{17}C_8H_5O_3$: 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) ppm. The resonances at δ 1.26 - 4.79 ppm represent aliphatic protons, and the resonances at δ7.20 - 8.38 ppm 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-cyclohexylenecarbonyl-b-oxy-1,4-phenyleneoxyterephthaloyl) at a concentration of 0.4 g/100 mL o-chlorophenol at 30°C.

Elemental analysis showed a number average degree of polymerization of sixteen for the poly(oxy-trans-1,4-cyclohexyleneoxycarbonyl-trans-1,4-cyclohexylenecarbonyl) oligomer. Anal. Calcd for $H\text{-}(\text{-}C_{14}H_{20}O_4\text{-})_{16}C_6H_{11}O_2\cdot H_2O$: 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 $HO\text{-}(\text{-}C_{14}H_8O_4\text{-})_{12}C_8H_5O_3\cdot H_2O$: 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 are as follows: δ1.26 (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) ppm. The resonances at δ 1.26 - 3.73 ppm represent aliphatic protons and the resonances at δ8.09 and 8.11 ppm 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 X 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 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: δ1.26 (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) ppm. The resonances at δ 1.26 - 5.13 ppm represent aliphatic protons and the resonances at δ 7.32 - 8.20 ppm 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 X 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 twenty for the poly(oxy-trans-1,4-cyclohexyleneoxycarbonyl-trans-1,4-cyclohexylenecarbonyl) oligomer. Anal. Calcd for $H\text{-}(\text{-}C_{14}H_{20}O_4\text{-})_{\overline{20}}C_6H_{11}O_2$: C, 66.56; H, 7.99. Found: C, 66.38; H, 8.36. Elemental analysis showed a number average degree of polymerization of ten for the poly[oxy(2-methyl-1,4-phenylene)oxyterephthaloyl] oligomer. Anal. Calcd. for $HO\text{-}(\text{-}C_{15}H_{10}O_4\text{-})_{\overline{10}}C_8H_5O_3\cdot H_2O$: 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 ppm represent aliphatic protons and the resonances at δ 6.95 - 8.39 ppm 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 TMS) and integrals were as follows: 21.5 (0.2), 27.9 (0.3), 28.2 (0.2), and 130.5 (0.4) ppm. The resonances at 21.5 - 28.2 ppm represent aliphatic carbons. The resonance at 130.5 ppm

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 X 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. M. B. Polk, K. B. Bota, and E. C. Akubuiro, submitted to I & EC Product R/D.

2. W. J. Jackson and H. F. Kuhfuss, J. Polym. Sci., 14, 2043 (1976).

3. F. E. McFarlane, V. A. Nicely, and T. G. Davis in "Polyesters Exhibiting Liquid Crystal Melts", E. M. Pearce and J. R. Schaefgen, Contemporary Topics in Polymer Science, Vol. 2, Plenum Press, New York, 1977, p. 115-120.

4. M. B. Polk, K. B. Bota, and E. C. Akubuiro, Prepr. Div. Org. Coat. Plast. Am. Chem. Soc., 44, 416 (1981).

5 J. R. Schaefgen, T. C. Pletcher, and J. J. Kleinschuster, Belgium Patent 828,935 (1975).

6. T. C. Pletcher, U. S. Patent 3,991,013, (1976).

7. J. J. Kleinschuster, U. S. Patent 3,991,014 (1976).

8. J. J. Kleinschuster and T. C. Pletcher, U. S. Patent 4,066,620 (1978).

9. G. W. Calundann, U. S. Patent 4,067,852 (1978).

10. J. R. Schaefgen, U. S. Patent 4,075,262 (1978).

11. G. W. Calundann, H. L. Davis, F. J. Gorman, and R. M. Mininni, U. S. Patent 4,083,329 (1978).

12. J. R. Schaefgen, U. S. Patent 4,118,372 (1978).

13. G. W. Calundann, U. S. Patent 4,130,545 (1978).

14. W. J. Jackson, Jr. and H. F. Kuhfuss, U. S. Patent 4,140,846 (1979).

15. J. C. Morris and W. J. Jackson, U. S. Patent 4,146,702 (1979).

16. W. J. Jackson, Jr., G. G. Bebeau, and H. F. Kuhfuss, U. S. Patent 4,153,779 (1979).

17. W. J. Jackson, Jr. and J. C. Morris, U. S. Patent 4,156,070 (1979).

18. G. W. Calundann, U. S. Patent 4,161,470 (1979).

19. W. J. Jackson, Jr. and J. C. Morris, U. S. Patent 4,169,933 (1979).

20. W. J. Jackson, Jr. and J. C. Morris, U. S. Patent 4,181,792 (1980).

21. G. W. Calundann, U. S. Patent 4,184,996 (1980).

22. H. Blades, U. S. Patent 3,767,756 (1973).

23. A. H. Frazer, U. S. Patent 3,037,960 (1962).

24. W. E. Doering, M. Farber, and A. Sayigh, J. Am. Chem. Soc., 74, 4370-2 (1952).

25. R. C. Oberg, H. Pines, and V. N. Ipatieff, J. Am. Chem. Soc., 66, 1096-9 (1944).

SYNTHESIS OF BLOCK COPOLYESTERS

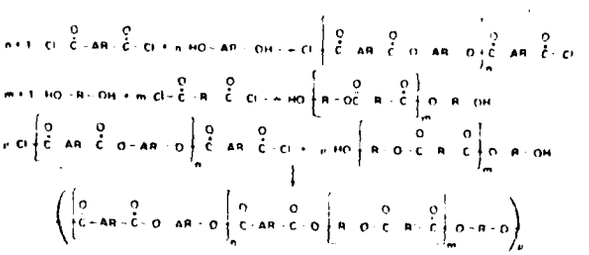
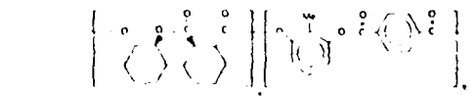
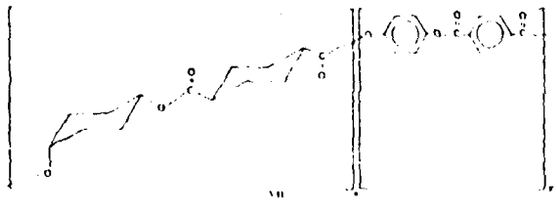


FIGURE 1
BLOCK COPOLYESTERS



VII



VIII

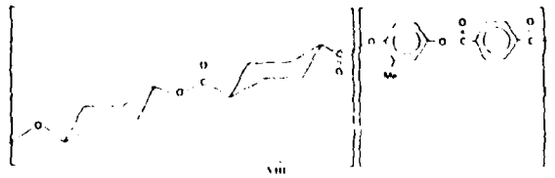


Figure 2. Micrograph of Block Copolyester VII Between Crossed Polarizers. 160X Magnification.

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