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LIQUID CRYSTALLINE POLYMERS OF DERIVATIVES OF POLY(10,11-EPOXYUNDECANOIC) ACID, POLY(5,6-EPOXYHEXANOIC) ACID, AND POLY(10-UNDECENOIC) ACID

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LIQUID CRYSTALLINE POLYMERS OF DERIVATIVES OF POLY(10,11-EPOXYUNDECANOIC) ACID, POLY(5,6-EPOXYHEXANOIC) ACID, AND POLY(10-UNDECENOIC) ACID

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ABSTRACT

Polymeric esters and amides were prepared from the imidazolids of poly(10-undecenoic acid, poly(10,11-epoxyundecanoic acid) and, poly(5,6-epoxyhexanoic acid. They include polymeric reaction products of 4-hydroxybisphenol, 4-cyano-4’-hydroxybisphenol, 4-aminobisphenol, cholesterol, and carbazole. The reactions were carried out via the imidazolids of the polyacids and gave yields between 75% to quantitative with conversions from 60-100%. Aromatic amines gave nearly quantitative conversion; for quantative substitution with alcohols, their alkali salts should be used. The polymeric esters and amides were briefly studied for their thermal and mesogenic properties.

Key Words: Poly(10-undecanoic acid); Poly(10,11-epoxyundecanoic acid); Poly(5,6-epoxyhexanoic acid); Imidazolids; 4-Hydroxybisphenol; 4-Cyano-4’-hydroxybisphenol; 4-Aminobisphenol; Cholesterol; Carbazole; Mesogenic behavior.

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INTRODUCTION

For years, people have attemped to introduce function groups into polymeric structures [1-3]. Examples of the attempted introduction of functional groups include biologically active [4, 5], UV stabilizing groups [6, 7], electroactive, mesogenic groups [8-10] and others.

The question of the influence of the main polymer chain on the efficiency of substitution reaction certainly goes back to the study of the hydrolysis of poly (methyl methacrylate) [11]. It became clear that the reactivity of these groups significantly depended on how close they were to the polymer main chain and what reactions were involved.

Some time ago, we undertook a careful study [12-20] of the influence of the chain length between the functional group and the backbone chain. We have chosen methylene spacers and compared the more flexible poly(oxy ethylene) with the polyethylene backbone chain.

In the case of the poly(oxy ethylene) derivatives, it was found that the polymerizablity of the ω-epoxycarboxylate increased as the function of the methylene spacer length (n) increases [16] and reaches a plateau after n-3. With the polyolefin family, the polymerizablity of ω-olefin carboxylate [19] also increased, but it did not reach a plateau until one or two methylene spacer groups were added. Polymers of poly(oxy ethylene) and polyethylene esters were hydrolyzed to the corresponding ionomers and converted to the free polymeric acids. Studies were also undertaken to investigate the polyanion-polycation complex formation as a function of backbone flexibility and side chain length [21-23]. Initial work on derivatization concentrated on the reaction of 1,1'-diimidazolylcarbonyl with the free acids [24, 25].

It was the objective of this work to establish esterification and amide formation, both with aliphatic alcohols, phenols and, amino compounds using polymeric imidazolids. It was also the objective to use preferentially phenols and anilines that were known to have potential characteristics to function as mesogens or have nonlinear optical behavior. It was not our objective to prepare quantitatively substituted polymers or to study in detail the behavior of their liquid crystalline behavior.

EXPERIMENTAL

Reagents and Solvents

Poly(10-undecenoic Acid) [polyUA)] was prepared from poly(2,5-dimethylphenyl 10-undecenoate) [poly(DMPUA)] of an η =1.4 dL/g] [25], poly (5,6-epoxyhexanoic acid) [poly(EHxA)] from poly(2,5-dimethylphenyl 10-hexenoate) poly(DMPHxA) of an η =1.5 dL/g] [24] and poly(10,11-epoxyundecanoic acid) [poly(EUA)] from poly(2,5-dimethylphenyl 10,11-epoxyundecanoate) [poly((DMPEUA] of an η = 2.7 dL/g. These samples had been previously synthesized [25].

Trans-4-hydroxystilbene, carbazole, 4-aminobiphenol, N,N'-dimethylaminoethanol, Disperse red 1, Disperse orange 3 and Disperse yellow 17 were purchased from the Aldrich Chemical Co., and cholesterol from the Eastman Chemical Co., 4'-hydroxybiphenol, 4-hydroxyazobenzene were obtained from Fluka.

1,1'-Diimidazolylcarbonyl (Im_2CO) (Staab reagent) [27, 28] was provided by PPG Industries and used as received. It reacts readily with water and must be handled in a dry box.

N,N-Dimethylacetamide (DMAc) was stirred over phosphorous pentoxide for 12 hours and then fractionally distilled under reduced pressure (b.p. 58-58.5°C/10 mmHg). It was stored under purified nitrogen in a drying column filled with 4 × Linde molecular sieves.

Tetrahydrofurane (THF) was heated to reflux for 12 hours over lithium aluminum hydride, then fractionally distilled (b.p. 65°C) and stored under nitrogen.

Solvents and reagents were used as received unless the solvent had to be purified. (See above).

Measurements

General Procedures and Methods

The infrared spectra were recorded on the Perkin-Elmer Model 727 spectrophotometer. Solid samples were measured as KBr pellets and liquid samples were placed between NaCl plates. The infrared spectra of most of the polymers were measured as thin films cast directly onto a single NaCl plate from chloroform or dioxane solution. The peak assignments were made to the nearest 5 cm^{-1}.

Glass transition temperatures (T_g) and melting transitions (T_m) of the polymers were determined on a Perkin-Elmer 7 Series Thermal Analysis System at a heating rate of 20°C/minute. The instruments were calibrated against a cyclohexane standard for low temperature measurements and against an indium standard for high temperature measurements.

Melting points of low molecular weight solids were measured on a MEL-TEMP capillary melting point apparatus and are not corrected.

Microanalyses were carried out by the Microanalytical Laboratory, Office of Research Services, University of Massachusetts, Amherst, Massachusetts.

Determination of the Residual Acid in Polymers

A 500 mL volumetric flask and a 20 mL gas-tight syringe were washed, dried, and purged with nitrogen. One liter of a 25% by weight stock solution of sodium methoxide in methanol was prepared by an addition of sodium to methanol. This solution was placed in a volumetric flask; the flask was capped with a rubber septum and placed under nitrogen. A sodium methoxide solution (10.8 mL) was drawn from the container using a 20 mL gas-tight syringe and transferred into a 500 mL volumetric flask. To obtain a 0.1 N solution, the volumetric flask was filled up to the mark with purified N,N'-dimethylacetamide. A double-ended needle was used for this transfer. The 0.1 N titration solution of sodium methoxide was used immediately.

A 125 mL Erlenmeyer flask was washed, dried, capped with a 24/40 rubber stopper and purged with nitrogen. A Teflon® coated magnetic stirring bar was placed inside this flask. The compound (250 mg) to be analyzed was placed into the Erlenmeyer flask and 50 mL of anhydrous DMAc was then added to dissolve the sample.

A 50 mL titration buret was washed, dried at 150°C and cooled under nitrogen. The 0.1 N titration solution of sodium methoxide was placed in the buret and was added dropwise to the thoroughly stirred solution, which was maintained at 60°C during the titration. The end of the titration the solution changed color from dark green to blue. Thymol Blue was used as an indicator.

Determination of the Copolymer Composition

The solutions of poly(methyl 10,11-epoxyundecanoate) [Poly(MEU)], in varying concentrations in chloroform, were prepared. An IR cell for liquid samples was assembled using a 0.5 mm Teflon® spacer to guarantee a constant width of the cell for IR measurements. The absorbance of the carbonyl (C=O) peak at 1740 cm^{-1} was measured for each sample. From these measurements, calibration plots of absorbance (1740 cm^{-1}) vs. mols of C=O in the sample were made. Infrared spectra for ester-substituted copolymer samples were measured in solutions (0.5 g/dL). The carbonyl (C=O) absorbance at 1740 cm^{-1} was measured and the moles C=O present in the samples were then determined from the calibration curve and the mol% functional monomer incorporated in each copolymer was calculated.

Synthesis Procedures

Poly(Biphenyl 10,11-Epoxyundecanoate-co-10,11-epoxyundecanoic Acid) [Poly(BPhEU)]

4-Hydroxybiphenol (4-HOBPh) (3.40 g, 30 mmols) was added into the DMAc (100 mL), solution of poly(ImEU) (2 g, 9.35 mmols) which had been prepared in a 250 mL round-bottom flask. The reaction mixture was kept under nitrogen, and sodium ethoxide (10 mg) was added. The reaction mixture was stirred at 50°C for three days, poured into the methanol (1 L) and the polymer, which had precipitated as a white powder was collected and washed with methanol. The solid was dried under reduced pressure (0.01 mmHg, 12 hours). The final purification was carried out by extracting the polymer with ethanol in a Soxhlet extractor for six hours. The polymer was then dried under reduced pressure (0.01 mmHg) at room temperature for 12 hours over phosphorous pentoxide. The yield of poly(BPhEU) was 3 g (87%). Titration showed a 93% substitution.

The IR spectrum (KBr pellet) showed absorptions at 3050 cm^{-1} (C-H stretch, aromatic), 3000-2800 cm^{-1} (C-H stretch, aliphatic), 2100-1800 cm^{-1} (benzene overtones). 1740 cm^{-1} (C=O stretch, carboxylate), 1600-1500 cm^{-1} (aromatic ring doublet), 1100 cm^{-1} (stretch, ether).

Elem. Anal.: Calcd. for $-(-C_{23}H_{28}O_3-)_{0.90}-(-C_{11}H_{20}O_3-)_{0.10}-$: C, 75.21%; H, 7.74%. Found: C, 75.45%; H, 8.01%.

Poly(Biphenyl 10-Undecenoate-co-10-undecenoic Acid) [Poly(BPhU)]

4-Hydroxybiphenol (4-HOBPh) (3.40 g, 30 mmols) poly(ImU) (2 g, 10.10 mmols) in THF/DMAc (8:2) (100 mL), and sodium ethoxide (10 mg) gave 2.7 g (82%) of poly(BPhU). Titration showed a 90% substitution.

The IR spectrum (KBr pellet) showed absorptions at 3050 cm^{-1} (C-H stretch, aromatic), 3000-2800 cm^{-1} (C-H stretch, aliphatic), 2100-1800 cm^{-1} (benzene overtones), 1740 cm^{-1} (C=O stretch, carboxylate), 1600-1500 cm^{-1} (aromatic ring doublet).

Elem. Anal.: Calcd. for $-(-C_{23}H_{28}O_2-)_{0.90}-(-C_{11}H_{20}O_2-)_{0.10}-$: C, 75.36%; H, 7.71%. Found: C, 75.51%; H, 7.82%.

Poly(Biphenyl 5,6-Epoxyhexanoate-co-5,6-Epoxyhexanoic Acid) [Poly(BPhEHx)]

4-Hydroxybiphenyl (4-HOBPh) (5 g, 44 mmols) was allowed to react with poly(ImEHx) (0.86 g, 6 mmols) in DMAc (40 mL). and the mixture poured into the methanol (500 mL The yield of poly(BPhEHx) was 1.8 g (85%)). Titration showed an 80% substitution.

The IR spectrum (KBr pellet) showed absorptions at 3050 cm^{-1} (C-H stretch, aromatic), 3000-2800 cm^{-1} (C-H stretch, aliphatic), 2100-1800 cm-1 (benzene overtones), 1740 cm^{-1} (C=O stretch, carboxylate), 1600-1500 cm^{-1}(aromatic ring doublet), 1100 cm^{-1} (C-O-C stretch, ether).

Elem. Anal.: Calcd. for $-(-C_{12}H_{18}O_3-)_{0.75}-(-C_6H_{10}O_3-)_{0.25}-$: C, 70.22%; H, 6.76%. Found: C, 70.80%; H, 6.60%.

Poly(Biphenyl 10,11-Epoxyundecanoamide) [Poly(BPhEUAmd)]

4-Aminodiphenyl ($4H_2NBPh$) (7 g, 41 mmols) was reacted with poly(ImEU) (2 g, 9.35 mmols) in DMAc (100 mL). The yield of poly(BPhEUAmd) was 3.2 g (92%). Titration showed a quantitative substitution.

The IR spectrum (KBr pellet) showed absorptions at 3050 cm^{-1} (C-H stretch, aromatic), 3000-2800 cm^{-1} (C-H stretch, aliphatic), 2100-1800 cm^{-1} (benzene overtones), 1650 cm^{-1} (amide I), 1590 cm^{-1} (C-C stretch, aromatic), 1530 cm^{-1} (amide II), 1100 cm^{-1} (C-O-C stretch, ether), 820 cm^{-1} (para substituted benzene).

Elem. Anal.: Calcd. for $\text{-(-}C_{23}H_{29}NO_2\text{-)}_{0.95}\text{-(-}C_{11}H_{20}O_3\text{-)}_{0.05}\text{-}$: C, 77.99%; H, 8.22%; N, 4.10%. Found: C, 77.70%; H, 7.75%: N, 4.61%.

Poly(Biphenyl 10-Undecenoamide-co-10-Undecenoic Acid) [Poly(BPhUAmd)]

4-Aminobiphenol (4-H_2NBPh) (3.40 g, 30 mmols) was reacted with a solution of poly(ImU) (2 g, 10.10 mmols) in THF/DMAc (8:2) (100 mL). The yield of poly(BPhUAmd) was 3 g (90%). Titration showed a 95% substitution.

The IR spectrum (KBr pellet) showed absorptions at 3050 cm^{-1} (C-H stretch, aromatic), 3000-2800 cm^{-1}(C-H stretch, aliphatic), cm^{-1} (amide I), 1590 cm^{-1}(C-C stretch, aromatic), 1530 cm^{-1} (amide II), 820 cm^{-1} (*para* substituted benzene).

Elem. Anal.: Calcd. for $\text{-(-}C_{23}H_{29}NO\text{-)}_{0.95}\text{-(-}C_{11}H_{20}O_2\text{-)}_{0.05}$: C, 78.90%; H, 8.38%; N, 3.98%. Found: C, 78.90; H, 7.94%; N, 4.45%.

Poly(Biphenyl 5,6-Epoxyhexanoamide) [Poly(BphEHxAmd)]

4-Aminodiphenyl (4-H_2NBPh) (5 g, 30 mmols) was allowed to react with a solution of poly(ImEHx) (0.86 g, 6 mmols) in DMAc (40 mL).

The yield of poly(BPhEHxAmd) was 2.0 g (90%). Titration showed a quantitative substitution.

The IR spectrum (KBr pellet) showed absorptions at 3050 cm^{-1} (C-H stretch, aromatic), 3000-2800 cm^{-1}(C-H stretch, aliphatic), 21001800 cm^{-1} (benzene overtones), 1650 cm^{-1} (amide I), 1590 cm^{-1} (C-C stretch, aromatic), 1530 cm^{-1} (amide II), 1100 cm^{-1} (C-O-C stretch, ether), 820 cm^{-1} (*para* substituted benzene).

Elem. Anal.: Calcd. for $\text{-(-}C_{18}H_{19}NO_2\text{-)-}$: C, 76.57%; H, 6.76%: N, 4.98%. Found: C, 75.98%; H, 6.93%; N, 4.96%.

Poly(Azobenzene 10,11-Epoxyundecanoate-co-10,11-epoxyundecanoic Acid) [Poly(AzBEU)]

4-Hydroxyazobenzene (4-HOAzB) (10 g, 50 mmols) was added into the solution of poly(ImEU) (2 g, 9.35 mmols) prepared in DMAc (100 mL), sodium ethoxide (10 mg) was added. At the work-up an orange solid precipitated, was collected by filtration, and washed with methanol. The yield of poly(AzBEU) was: 2.44 g (70%). Titration showed a 80% substitution.

The IR spectrum showed absorptions at 3000-2800 cm^{-1} (C-H stretch, aliphatic), 1740 cm^{-1} (C=O stretch, carboxylate), 1100 cm^{-1} (C-O-C stretch, ether).

Elem. Anal.: Calcd. for $\text{-(-}C_{23}H_{28}N_2O_3\text{-)}_{0.75}\text{-(-}C_{11}H_{20}O_3\text{-)}_{0.25}\text{-}$: C, 70.54%; H, 8.17%; N, 5.15%. Found: C, 70.10%, H, 8.40%; N, 4.96%.

Poly(Azobenzene 10-Undecenoate-co-10-undecenoic Acid) [Poly(AzBU)]

4-Hydroxyazobenzene (4-HOAzB) (7 g, 35 mmols) was reacted with the solution of poly(ImU) (2 g, 10.10 mmols) in THF/DMAc (8:2) (100 mL) and sodium ethoxide (10 mg). The yield was 2.3 g (60%). Titration showed a 86% substitution.

The IR spectrum showed absorptions at 3000-2800 cm^{-1} (C-H stretch, aliphatic), 1740 cm^{-1} (C=O stretch, carboxylate). .

Elem. Anal.: Calcd. for $-(-C_{23}H_{28}N_2O_2-)_{0.80}-(-C_{11}H_{20}O_2-)_{0.20}$: C, 75.00%; H, 8.32%; N, 6.15%. Found: C, 74.65%; H, 8.50%; N, 6.29%.

Poly*(trans*-Stilbenyl 10,11-Epoxyundecanoate-co-10,11-epoxyundecanoic Acid) [Poly(StEU)]

Trans-4-hydroxystilbene (4HOSt) (7 g, 36 mmols) was allowed to react with a solution of poly(ImEU) (2 g, 9.35 mmols) in DMAc (100 mL) and sodium ethoxide (10 mg). The yield of poly(StEU) was 2.9 g (80%). Titration showed a 60% substitution.

The IR spectrum (KBr pellet) showed absorptions at 3050 cm^{-1} (C-H stretch, aromatic), 3000-2800 cm^{-1} (C-H stretch, aliphatic), 1740 cm^{-1} (C=O stretch, carboxylate), and 1100 cm^{-1} (C-O-C stretch, ether).

Elem. Anal.: Calcd. for-$(-C_{25}H_{30}O_3-)_{0.50}-(-C_{11}H_{20}O_3-)_{0.50}-$: C, 72.66%; H, 9.01%: Found: C, 72.24%; H, 9.11%..

Poly(4-Cyanobiphenyl 10,11-Epoxyundecanoate-co-10,11-epoxyundecanoic Acid) [Poly(CNBPhEU)]

4-Cyano-4'-hydroxydiphenyl (4-CNBPh) (5 g, 26 mmols) was reacted with a solution of poly(ImEU) (2 g, 9.35 mmols) in DMAc (100 mL) and sodium ethoxide (10 mg). The yield of poly(CNBphEU) was 3 g (80%) Titration showed a 85% substitution.

The IR spectrum (thin film from chloroform) showed absorptions at 3000-2800 cm^{-1} (C-H stretch, aliphatic), 2250 cm^{-1} (CN stretch), 1740 cm^{-1} (C=O stretch, carboxylate), 1600 cm^{-1} and 1500 cm^{-1} (aromatic ring doublet), 1100 cm^{-1} (C-O-C stretch, ether), 820 cm^{-1} (*para* substituted benzene).

Elem. Anal.: Calcd. for $-(-C_{24}H_{27}O_3-)_{0.80}-(-C_{11}H_{20}O_3-)_{0.20}-$: C,74.30%; H,7.74%; N, 2.97%. Found: C, 74.02; H, 8.07%; N, 2.81%.

Poly(4-Cyanobiphenyl Undecenoate-co-10-undecenoic Acid) [poly(CNBPhU)]

4-Cyano-4'-hydroxybiphenyl (4-CNBPh) (5 g, 26 mmols) was allowed to react with a solution of poly(ImU) (2 g, 10-10 mmols) in THF/DMAc (8:2) (100 mL) and sodium ethoxide (10 mg). The yield of poly(CNBphU) was 2.8 g (75%). Titration showed an 80% substitution.

The IR spectrum (thin film from chloroform) showed absorptions at 3000 cm-1 -2800 cm^{-1} (C-H stretch, aliphatic), 2250 cm^{-1} (CN stretch), 1740 cm^{-1} (C=O stretch, carboxylate).

Elem. Anal.: Calcd. for $-(-C_{24}H_{27}NO_2-)_{0.80}-(-C_{11}H_{20}O_2-)_{0.20}-$: C, 78.16%; H, 8.15%; N, 3.09%. Found: C, 77.94%; H, 8.34%; N, 2.95%.

Poly(4-Cyanobiphenyl 5,6-Epoxyhexanoate-co-5,6-epoxyhexanoic Acid) [Poly(CNBPhEHx)]

4-Cyano-4'-hydroxydiphenyl CNBPh) (5 g, 26 mmols) was reacted with a solution of poly(ImEHx) (0.86 9, 6 mmols) prepared in DMAc (40 mL). The yield of poly(CNBPhEHx) was 1.5 g (80%). Titration showed 85% substitution.

The IR spectrum (thin film from chloroform) showed absorptions at 3000-2800 cm^{-1} (C-H stretch, aliphatic), 2250 cm^{-1}(CN stretch), 1740 cm^{-1} (C=O stretch, carboxylate), 1600 cm^{-1} and 1500 cm^{-1} (aromatic ring doublet), 1100 cm^{-1} (C-O-C stretch, ether), 820 cm^{-1} (*para* substituted benzene).

Elem. Anal.: Calcd. for $-(-C_{19}H_{17}NO_3-)_{0.90}-(-C_6H_{10}O_3-)_{0.10}-$: C, 72.38%; H, 5.74%; N, 4.1 0%. Found: C, 71.85%; H, 6.14%; N, 3.83%.

Poly(Cholesteryl 10,11-Epoxyundecanoate-co-10,11-epoxyundecanoic Acid) [Poly(CholEU)]

Cholesterol (Chol) (10 g, 26 mmols) was allowed to react with solution of poly(ImEU) (2 g, 9.35 mmols) in DMAc (100 mL) and sodium ethoxide (10 mg). The yield of white poly(CholEU) was 3 g (50%). Titration showed a 70% substitution.

The IR spectrum (KBr pellet) showed absorptions at 3000 cm-1 -2800 cm^{-1} (C-H stretch, aliphatic), 1740 cm^{-1} (C=O stretch, carboxylate), 1100 cm^{-1} (C-O-C stretch, ether).

Elem. Anal.: Calcd. for $-(-C_{38}H_{65}O_3-)_{0.70}-(-C_{11}H_{20}O_3-)_{0.30}-$: C, 75.79%; H, 11.01%. Found: C, 75.43%; H, 11.28%.

Poly(Cholesteryl 10-Undecenoate-co-10-Undecenoic Acid) [Poly(CholU)]

Cholesterol (Chol) (10 g, 26 mmols) was reacted with a solution of poly(ImU) (2 g, 10.1 mmols) prepared in THF/DMAc (8:2) (1 00 mL) and sodium ethoxide (10 mg). The yield of white poly(Chol) was 3.5 g (60%). Titration showed a 70% substitution.

The IR spectrum (thin film from chloroform) showed absorptions at 3000-2800 cm^{-1} (C-H stretch, aliphatic), 1740 cm^{-1} (C=O stretch, carboxylate).

Elem. Anal.: Calcd. for -(-$C_{38}H_{65}O_2$-)$_{0.60}$-(-$C_{11}H_{20}O_2$-)$_{0.40}$-: C, 78.17%; H, 11.39%. Found: C, 78.34%; H, 10.92%.

Poly(Carbazoyl 10,11-Epoxyundecanamide-co-10,11-Epoxyundecanoic Acid) [Poly(CbEU)]

Carbazole (Cb) (7 g, 42 mrnols) was added to a solution of poly(ImEU) (2 g, 9.35 mmols) in DMAc (100 mL). The yield of white poly(CbEU) was 2.8 g (75%). Titration showed an 86% substitution.

The IR spectrum (film from chloroform) showed absorptions at 3000-2800 cm^{-1} (C-H stretch, aliphatic), 1740 cm^{-1} (C=O stretch, carboxylate).

Elem. Anal.: Calcd. for -(-$C_{23}H_{27}NO_2$-)$_{0.80}$-(-$C_{11}H_{20}O_3$-)$_{0.20}$-. C, 76.45%; H, 8.19%; N, 3.21%. Found: C, 76.10%; H, 8.50%; N, 3.50%.

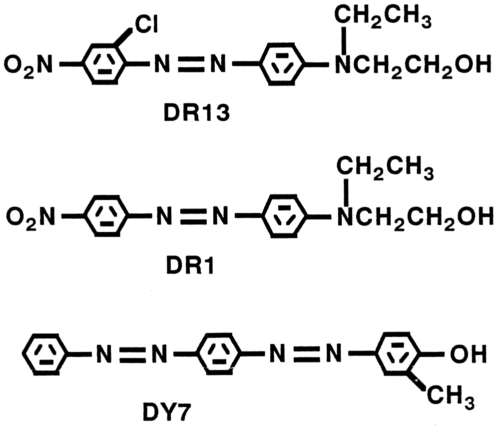
Poly(Carbazoyl 10-Undecanoamide-co-10-undecanoic Acid) [Poly(CbU)]

Carbazole (Cb) (7 g, 42 mmols) was reacted with a solution of poly(ImU) (9.84 mmols) in THF/DMAc (8:2) (100 mL). The yield of poly(CbU) was 3 g (85%) Titration showed a quantitative substitution.

The IR spectrum showed absorptions at 3000-2800 cm^{-1}(C-H stretch, aliphatic), 1740 cm^{-1} (C=O stretch, carboxylate).

Elem. Anal.: Calcd. for -(-$C_{23}H_{27}NO$-)$_{0.95}$-(-$C_{11}H_{20}O_2$-)$_{0.05}$-: C, 82.43%; H, 8.20%; N, 3.99%. Found: C, 82.52%; H, 8.31%; N, 4.13%.

In addition, reactions of poly(ImEU) with Disperse red 1 (DR1), Disperse yellow 7 (DY7) and Disperse red 13 (DR13) were carried out (Formula 1). The



Formula 1.

Table 1. Reactions from Imidazolid of Poly(10, 11-Epoxyundecanoic Acid)[a]

		Percent Substitution		Yield	
	Copolymer	El. Anal.	Titration (± 4%)	%	g
4.	Poly(DRIEU)	70	60	70	3.7
5.	Poly(DY7EU)	70	80	80	3.2
6.	Poly(DR13EU)	60	65	80	2.8

[a]Reaction conditions: three days; temperature: 50°C; solvent: Dmac; solution concentration: 2 w/v%; mol% excess of reactive compound: 200%.

results are presented in Table 1. Similar reactions of poly(ImU) with DR1, DY7 and DR13 were also carried out; the results are displayed in Table 2.

Poly(N,N'-Dimethylaminoethyl 10,11-Epoxyundecanoate [Poly(DMAEU)] 100% Substitution

Poly(EUA) (2 g, 9.84 mmols) was placed in a reaction flask with THF (100 mL) and stirred until the polymer dissolved. Im_2CO (2 g; 13 mmols) (20% excess) was added and the reaction mixture was left at room temperature (magnetic stirrer) for three hours. A mixture of THF (20 mL), DMAE (0.82 g, 1.1 mL, 1.1 mmols), and n-BuLi (12.9 mmols, 8 mL of 1.6 molar solution in n-hexane) was added to poly(ImEU). After stirring the reaction mixture for three hours, the polymer solution was poured into diethyl ether (500mL); the solid polymer was isolated in a yield of 1.8 g (70%). Titration showed quantitative substitution.

The IR spectrum (thin film) showed absorptions centered at 1740 cm^{-1} (C=O stretch, ester); 1240 cm^{-1}(C-O stretch, ethyl ester); 1080 cm^{-1} (C-O-C stretch, ether).

Table 2. Reactions from Imidazolid of Poly(10-Undecanoic Acid)[a]

		Percent Substitution		Yield	
	Copolymer	El. Anal.	Titration (± 4%)	%	g
1.	Poly(DRIU)	65	70	70	3.0
2.	Poly(DY7U)	60	70	80	3.1
3.	Poly(DR13U)	55	—	50	2.0

[a]Reaction conditions: three days; temperature: 50°C; solvent: THF:Dmac (8:2) solution concentration: 2 w/v%; mol% excess of reactive compound: 50–150%.

Poly(N,N'-Dimethylaminoethyl 10,11-Epoxundecanoate-co-10,11 Epoxyundecanoic Acid) [Poly(DMAEU-co-EUA)] 80% Substitution

From poly(EUA) (2 g, 9.84 mmols) THF (100 mL) Im_2CO (2 g; 13 mmols) (20% excess) was formed the imidazolid, and a DMAE (0.8 mL, 7.4 mmols) solution in THF (20 rnL) and n-BuLi (4.5 mL of a 1.6 molar solution in n-hexane, 7.38 mmols) was added. Thepolymer was obtained in a yield of 1.5 g (65%). Titration showed a 80% substitution.

The IR spectrum (thin film) showed absorptions centered at 3000-2800 cm^{-1} (C-H stretch, aliphatic), 1740 cm^{-1}(C=O stretch, ester); 1240 cm^{-1} (CO stretch, ethyl ester); 1100 cm^{-1} (C-O-C stretch, ether).

Poly(N,N'-Dimethylaminoethyl 10,11-Epoxundecanoate-co-10,11-epoxyundecanoic Acid) [PolyDMAEU-co-EUA)] 60% Substitution

DMAE (10 mL, 100 mmols) was added to the solution of Poly(ImEU) (2 g, 9.84 mmols) in DMAc (100 mL) and sodium ethoxide (10 mg) was also added. Yield of fhe polymer was 80% (1.9 g). Titration showed a 60% substitution.

The IR spectrum showed absorptions centered at 3000-2800 cm^{-1} (C-H stretch, aliphatic), 1740 cm^{-1} (C=O stretch, ester), 1100 cm^{-1} stretch, ether).

Elem. Anal.: Calcd. for $-(-C_{15}H_{29}NO_3-)_{0.60}-(-C_{11}H_{20}O_3-)_{0.40}-$: C, 66.24%; H, 10.45%; N, 3.09%.

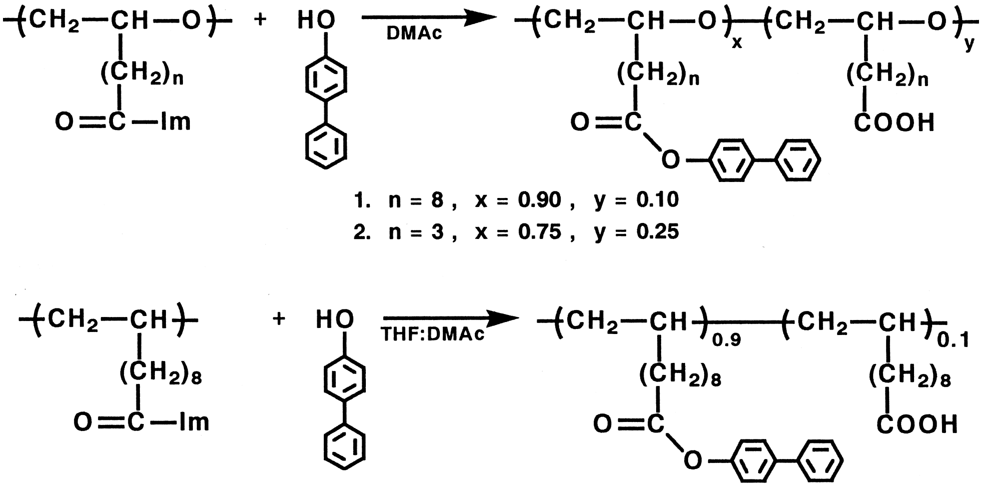
RESULTS AND DISCUSSION

Introduction of Functional Groups into Polymers

This highly versatile reaction scheme was adapted and utilized in this investigation to obtain polymeric imidazolids [28]. Poly(EUA) (n=8), poly(UA) (n=8), and poly(EHxA) (n=3) were allowed to react with 30 mol% excess of Im_2CO in DMAc at room temperature. Excess of Im_2CO insured that any residual moisture was eliminated. The reaction of polymeric acids with Im_2CO was almost instantaneous in all cases judging from the evolution of CO_2 immediately after the addition of Im_2CO to the polymer solution. Polymeric imidazolids (2% w/v solutions) were kept for immediate use in a closed system for further reactions and were not isolated.

Reactions of 4-Hydroxybiphenol [4-HOBPh] with Polymeric Imidazolids

Reactions of the imidazolids of poly(10,11-epoxyundecanoic acid) [poly(ImEU)], poly(10-undecenoic acid) [poly(ImU)] and poly(5,6-epoxyhexanoic acid) [poly(ImEHx)] were carried out with 4HOBPh. Equation 1 shows the



Equation 1. Introduction of 4-hydroxybiphenyl through imidazolid derivatives of polyacids.

general reaction scheme and the structure of the copolymers. Solutions of poly(ImEU) and poly(ImEHx) (2 w/v%) in DMAc were prepared two or three hours before the introduction of 4-HOBPh (300% excess). The solution of poly(ImU) was prepared in a mixture of THF and DMAc (8:2) due to the poor solubility of poly(UA) in DMAc.

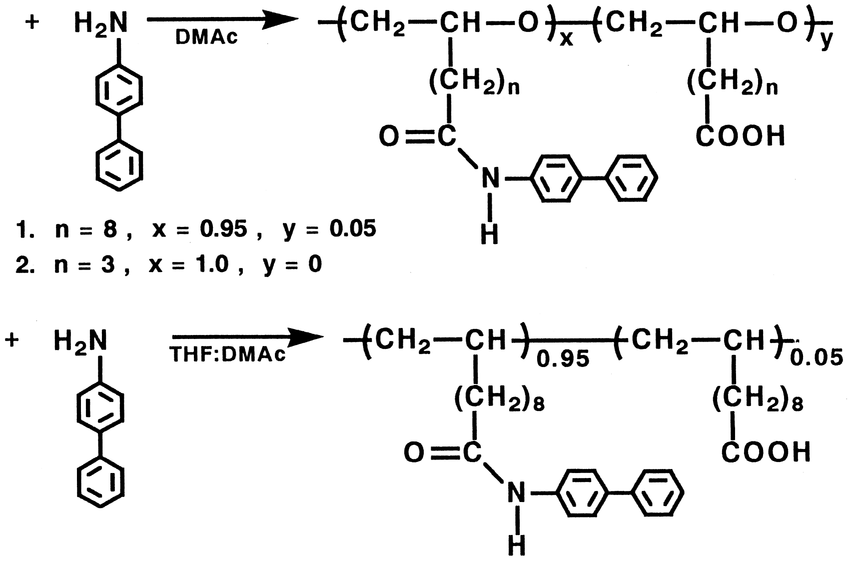
The results in Table 3 showed that substitutions of polymeric acids were achieved as confirmed by elemental analysis and titrations of the products. Copolymers were obtained with 75% to 90% substitution, based on results of the elemental analyses.

Substitution of 80% to 93% was established when the polymers were titrated. Lower substitution (75%) was obtained in the case of poly(BPhEHx). Poly(BPhEU), and poly(BPhU) were obtained in yields exceeding 80%. The infrared spectra of the copolymers showed typical features expected from such structures.

Table 3. Introduction of 4-Hydroxybiphenyl Through Imidazolid Derivatives of Polyacids[a]

Copolymer	Solvent	Time (days)	Percent Substitution El. Anal.	Percent Substitution Titration	Yield %	Methylene Spacer
1. Poly(BPhEU)	DMAc	3	90	93(±4)	90	n=8
2. Poly(BPhEHx)	DMAc	4	75	80(±4)	90	n=3
3. Poly(BPhU)	THF:DMAc (8:2)	3	90	90(±4)	80	n=8

[a] Reaction conditions: 300 mol% excess of 4-HOBPh; temperature: 50°C; solution concentration: 2 w/v%.



Equation 2. Introduction of 4-aminobiphenyl through imidazolid derivatives of polyacids.

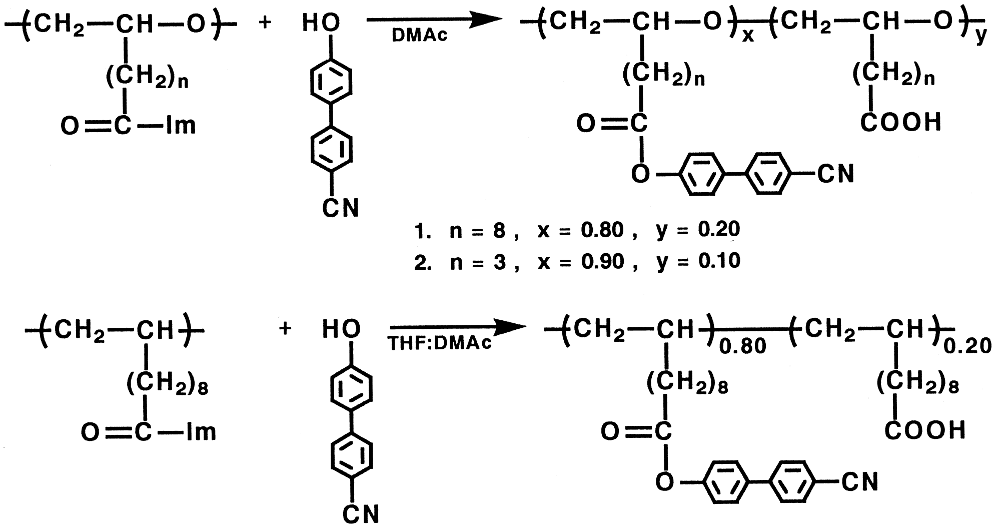
Reactions of 4-Aminobiphenol (4-H_2NBPh) with Polymeric Imidazolids

Reactions of poly(ImEU), poly(ImU), and poly(ImEHx) with 4-H_2NBph were carried out. Equation 2 shows the general reaction scheme and the structure of the copolymers. The results presented in Table 4 show that a substantial substitution of polymeric acids was achieved as confirmed by elemental analyses and titration of the products. Substitutions were also higher when compared to products of reactions of polymeric acids with 4-HOBPh described above. Polymers were obtained with 95% to 100% substitution based on results of elemental analyses and the titration of the copolymers. Poly(BPhEUAmd), poly(BPhEHxAmd) and poly(BPhUAmd), were obtained in yields exceeding 90%. The IR confirmed the nearly quantitative transformation of acid groups to the amides.

Table 4. Introduction of 4-Aminobiphenyl Through Imidazolid Derivatives of Polyacids[a]

Copolymer	Solvent	Time (days)	Percent Substitution El. Anal.	Percent Substitution Titration	Yield %	Methylene Spacer
1. Poly(BPhEUAmd)	DMAc	3	95	100(±4)	92	n=8
2. Poly(BPhEHxAmd)	DMAc	4	100	100(±4)	90	n=3
3. Poly(BPhUAmd)	THF:DMAc (8:2)	3	95	95(±4)	90	n=8

[a] Reaction conditions: 300 mol% excess of 4-H_2NBPh; temperature: 50°C; solution concentration: 2 w/v%.



Equation 3. Introduction of 4-cyano 4'-hydroxybiphenyl through imidazolid derivatives of polyacids.

Introduction of 4-Cyano-4'-hydroxybiphenyl (4-CNBPh)

Reactions of poly(ImEU), poly(ImU)], and poly(ImEHx)] with 4-CNBPh were also carried out. Equation 3 shows the general reaction scheme and the structure of the copolymers; Table 5 shows that degrees of substitution were 80% to 90% by elemental analysis and titration. The IR spectra also confirmed the composition of the polymers.

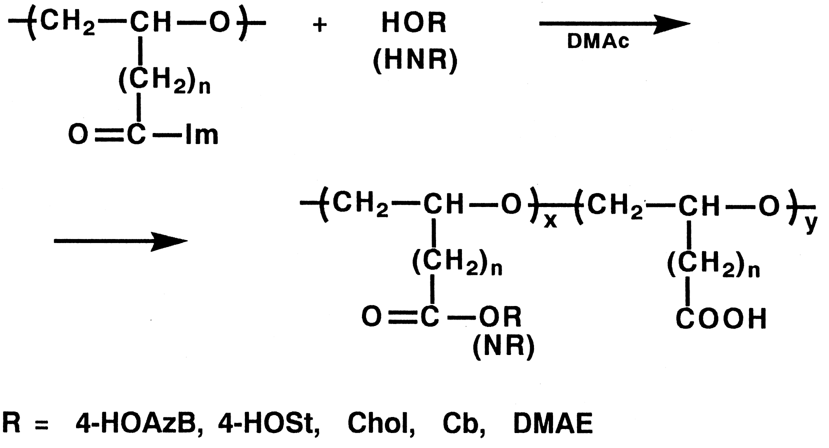
Reactions from Imidazolids of Poly(10,11-Epoxyundecenoic acid) [Poly(ImEU)]

Results of the reactions of poly(ImEU) with 4-hydroxyazobenzene (4-HOAzB), *trans* 4-hydroxystilbene (4-HOSt), cholesterol (Chol), carbazole (Cb), and N,N'-dimethylaminoethanol (DMAE) are described in Equation 4, which shows the general reaction scheme and Table 6 shows the degree of substitution of the polymeric acid groups. It was between 60 to 85% as determined by elemental

Table 5. Introduction of 4-Cyano-4'-Hydroxybiphenyl Through Imidazolid Derivatives of Polyacids[a]

Copolymer	Solvent	Time (days)	Percent Substitution El. Anal.	Percent Substitution Titration	Yield %	Methylene Spacer
1. Poly(CNBPhEU)	DMAc	3	80	85(±4)	80	n=8
2. Poly(CNBPhEHx)	DMAc	4	90	85(±4)	82	n=3
3. Poly(CNBPhU)	THF:DMAc (8:2)	3	80	80(±4)	80	n=8

[a] Reaction conditions: 150–200 mol% excess of 4-CNBPh; temperature: 50°C; solution concentration: 2 w/v%.



Equation 4. Reactions of poly(imidazolid 10,11-epoxyundecanoate).

analysis and titration. Polymers were obtained in yields ranging between 50 and 80%.

Reactions from Imidazolids of Poly(10-Undecanoic Acid) [Poly(ImU)]

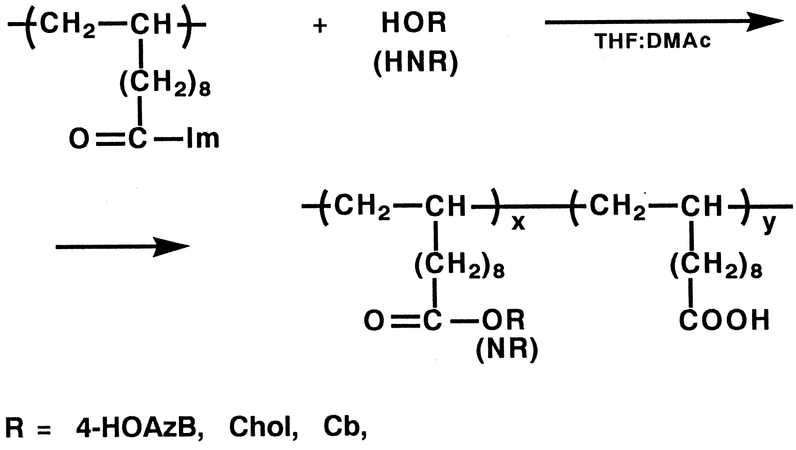
Results of the reactions of poly(ImU) with 4-HOAzB, Chol, and Cb are shown in Equation 5. Table 7 presents the degrees of substitution of the polymeric acids, which are between 60 to 95%; the polymers were obtained in yields ranging from 55 to 95%.

Poly(N,N'-dimethylaminoethyl 10,11-epoxyundecanoate [Poly(DMAEU*)* and poly(N,N'-dimethylaminoethyl 10,11-epoxyundecanoate-co-10,11-epoxyundecanoic acid) 4:1 and 3:2 were prepared from the imidazolid of poly(EUA) with the exactly needed ratio of lithium N,N'-dimethylaminoethoxide. This set of reactions was carried out to demonstrate the quantitative reaction of the polymeric imidazolid poly(ImEU) with aliphatic alkoxides. It also demonstrated the efficient preparation of polymeric tert amines.

Table 6. Reactions of Poly(Imidazolid 10,11-Epoxyundecanoate)[a]

Copolymer	Percent Substitution		Yield	
	El. Anal.	Titration (±4 %)	%	g
1. Poly(AzBEU)	75	80	70	2.44
2. Poly(StEU)	50	60	80	2.9
3. Poly(CholEU)	70	70	50	3.1
4. Poly(CbEU)	80	85	75	2.8
5. Poly(DMAEU)	—	60	70	1.5

[a] Reaction conditions: three days; temperature: 50°C; solvent: Dmac; solution concentration: 2 w/v%; mol% of reactive compound: 150–400%.



Equation 5. Reactions of poly(imidazolid 10-undecanoate).

In summary, it seems to be clear that the percent of substitution varied according to the type of molecules used for the polymer reaction. It is apparent that the highest percentage of substitution was obtained with aliphatic aromatic amines. Hydroxy-substituted biphenyls were less reactive resulting in a lower percentage of substitution. As expected, the cyano-substituted biphenyl showed the lowest degree of substitution because of the electron withdrawing cyano group in *para* position. Cholesterol, a secondary alcohol, also gave poor substitution results. Aliphatic alcohols can be used only effectively in the reaction with polymeric imidazolids when they are used as alkoxides. They can conveniently be first reacting them with butyl lithium to form the lithium alkoxide; quantitative substitution may be obtained. The length of the methylene spacer (above n-3) in the polymeric acids seem to have only a relatively small effect on the reactivity of the carboxylic acid groups.

Thermal Behavior of the Polymers

A number of mesogenic polyesters of poly(EUA), poly(EHxA) and poly(UA) were selected for the study of their thermal properties They were inves-

Table 7. Reactions of Poly(Imidazolid 10-Undecanoate)[a]

Copolymer	Percent Substitution		Yield	
	El. Anal.	Titration (±4 %)	%	g
1. Poly(AzBU)	80	86	60	2.5
2. Poly(CholU)	60	70	60	3.5
3. Poly(CbU)	95	100	85	3.0

[a] Reaction conditions: three days; temperature: 50°C; solvent: THF:Dmac (8:2) solution concentration: 2 w/v%; mol% excess of reactive compound: 150–300%.

Table 8.

Copolymer	Percent Substitution [%]	Methylene Spacer
Poly(BPhEU)	90	n=8
Poly(BPhU)	90	n=8
Poly(BPhEHx)	80	n=3
Poly(BPhEUAmd)	100	n=8
Poly(BphUAmd)	100	n=8
Poly(BPhEHxAmd)	100	n=3
Poly(CNBPhEU)	80	n=8
Poly(CNBPhU)	80	n=8
Poly(CNBPhEHx)	90	n=3
Poly(CholEU)	70	n=8
Poly(CholU)	70	n=8

tigated by DCS and observed under a polarizing microscope. Original DCS curves and photomicropraphs are recorded in Reference 28.

The data according to the percent substitution and the length of the methylene spacer groups are shown in Table 8. The thermal transition temperatures (T_g and T_m) of the copolymers were determined by DSC. The results of the DSC studies are given in Tables 9 and 10 (all samples were heated in a nitrogen atmosphere at 20ºC/min).

Table 9. Thermal Transition Temperatures of Functionally Substituted Poly(Alkylene Oxide) and Poly(ω-Olefin) Copolymers[a]

	Polymer	Tg [ºC]	Thermal Transitions [ºC] DSC	Thermal Transitions [ºC] Polarizing Microscope
1.	Poly(BPhEUAmd)	−12	Tg(-12)LC(229)l(272)	LC(198)I(255)
2.	Poly(BPhEU)	12	Tg(12)LCI(57)LCII(83)I(125)	LC(80)I(97)
3.	Poly(CNBPhEU)	27	Tg(27)LCI(54)LCII(100)I(128)	LC(50) I(95)
4.	Poly(CholEU)	−22	Tg(-22)LC(37)Chol(73)I(92)	no crystallinity found
5.	Poly(BPhUAmd)	12	Tg(12)LCI(40)LCII(74)I(280)	LC(40)I(280)
6.	Poly(BPhU)	46	Tg(46)LC(239)l(320)	LC(197)I(290)
7.	Poly(CNBPhU)	9	Tg(9)LCI(48)LCII(94)I(112)	LC(73)I(92)
8.	Poly(CholU)	−19	Tg(-19)Chol(21)I(50)	Chol(50)I(76)I(70)Chol(45)
9.	Poly(BPhEHxAmd)	49	Tg(49)LC(260)I(290)	no crystallinity found
10.	Poly(BPhEHx)	19	Tg(19)LC(64)I(94)	no crystallinity found
11.	Poly(CNBPhEHx)	44	Tg(44)LCI(67)LCII(96)I(118)	LC(104Ð105)I I(100)LC

DSC: differential scanning calorimetry

I: isotropic phase; LC: liquid crystalline phase; Chol: cholesteric phase

[a] Thin films casted from the solution on glass plates.

Table 10. Thermal Properties of Monomers and Polymers[a]

Polymer		Tg [^{0}C]	T_1 [^{0}C]	T_2 [^{0}C]	T_m [^{0}C]	(H [J/g]	(Cp [J/g-C]
1. BPhUAmd	H1	—	128	146	141.6	114.17	
	C	—	136.8	121.2		−113.9	
	H2	—	128	146.6	140.6	117.9	
2. BPhU	H1	—	21.1	55.4	47.6	84.9	
	C	—	32.2	28		−75.7	
	H2	—	20.9	52.7	44.4	76	
3. Poly(EUA)	H1		102.2	146	122	3.99	
	H2	8.2	59.4	135.6	102.5	11.9	
			153.6	199.2	192.1	6.4	0.468
After 5 D at 25	H1	9.5	62.6	140	101.8	11.0	
			145.3	198.6	184.5	4.6	0.458
	H2	7.2	63.2	131.2	97.5	7.6	
			148.5	211.2	186.4	5.2	0.481
4. Poly(BPhEUAmd)	H1	—	229.2	272	262	19.4	
	H2	−13					0.119
5. Poly(BPhEU)	H1		57.5	83.2	73	1.14	
			82.4	125	101.9	5.06	
			124.2	139.6	132.7	1.4	
Ann. At 50(2 days)	H1	12	58	93.3	74.9	10.05	0.744
	H2		48.5	85.8	66.3	4.2	
			85.2	137.2	102.8	3.8	
6. Poly(CNBPhEU)	H1		54.5	106.8	90.7	6.07	
			100.9	128.6	118.6	3.8	
	C		88	43.9	—	10.2	
			125	100	—	6.8	
	H2		103.7	131.4	116.8	4.8	
Run again	H1	28	107	133	118.9	3.5	0.551
Ann at 90(45 min)	H2	26	106.4	139.3	118.7	3.5	0.700
7. Poly(CholEU)	H1	−21	36.8	69.2	46.1	6.7	0.477
			68.6	92	79.1	5.0	
	C		58	37.6	—		
	H2	−22	58.1	89.2	72.8	5.4	0.466
Ann. At 47(2 days)	H1	−19	41.6	73.4	61.2	7.3	0.436
			72.8	89	79.6	2.7	
	C		56.3	23.8	—	−18	
	H2	−21	56.8	74.2	69.4	1.2	0.589
			73.6	91	79.3	1.2	
8. Poly(UA)	H1	54	111.2	146.6	137.2	27.8	0.719
(Q)	H2	40	109	144	137.2		
Ann. At 25(5 days)	H1	50	112.6	144	137.2	26.9	0.360
	C		100.7	69.4	87.1	−24	
	H2		107.2	146.5	136.9	23.1	
9. Poly(BPhUAmd)	H1	12	40	61.3	49.2	2.9	0.121
			61.3	74.6	67.5	1.54	
	H2		19.2	62.2	52.9		
10. Poly(BPhU)	H1	46					0.105
	H2		239.8	319.8	315.6	79.1	

Table 10. Continued

11. Poly(CNBPhU)	H1	9	48.1	94	79.6	17.9	0.04
			93.5	112.6	103	3.05	
	C		90.8	78.6	—	−5.4	
	H2		20.2	118.4	103	21.3	
12. Poly(CholU)	H1	−19	10	55.3	46.7	15.2	
			62	126.6	114.8	14.7	
	C		6.0	−27		−11.1	
	H2		21.2	50.5	38.7	12.7	0.318
13. Poly(EHxA)	H1	−2	—	—	—	—	0.241
	H2	16	—	—	—	—	0.464
5 days at 25	H1	−2	—	—	—	—	0.241
	H2	16	—	—	—	—	0.546
14. Poly(BPhEHxAmd)	H1	49	—	—	—	—	0.450
	H2						
15. Poly(BPhEHx)	H1	19	64.4	94.4	84.5	4.6	0.294
	H2	20	—	—	—		0.485
Ann. At 47(2 days)	H1	19	51.2	78.2	66.7		0.285
	H2	19	—	—	—	—	0.415
16. Poly(CNBPhEHx)	H1	50	83.2	126.5	101.6	8.6	0.432
(Q)	H2	44	83	117.3	104.1	3.0	0.493
	H3	44	78	116.8	104.2	3.5	0.537
Ann. At 50(2 days)	H1	43	67.4	96.2	83.2	2.6	0.283
			95.6	118.4	104.4	0.904	
	H2	43	82	118.6	104.2	2.07	0.331

[a]Differential Scanning Calorimetry
H: heating at 20°C/min.; C: cooling at 20°C/min.; Q: quenched at 200°C/min.
Ann.: annealed

A sample of poly(BPhEUAmd) (n=8) exhibited a T_g of -12.8°C and a liquid crystalline (LC) to an isotropic transition [T_g (-12.8)-LC(229)-I(272)]. A rearrangement of the copolymer physical structure was also taking place during the cooling of this sample, as seen on the DSC scan. When cooled, the exothermic order formation was found to be from 180-165°C and the second transition at 175°C. Observing the copolymer film under a polarizing microscope revealed that the copolymer had a LC structure up to 176°C, which changed to a second LC structure at 198°C. A LC to an isotropic (LCI) transition occurred at 260°C. Compared to poly(EUA) (according to the percent substitution and the length of methylene spacer groups =8.2°C), a 20°C lower T_g of poly(BPhEUAmd) was apparent. Results of the DSC measurements corresponded to the visual temperature changes observed under a polarizing microscope. Decomposition of the copolymer was noticed above 250°C.

A sample of poly(BPhUAmd) (n=8) showed a T_g of 12°C, a LC phase, and an isotropic phase above 280°C as determined by the DSC scan: [T_g (12)-LCI(40)-LCII(74.6)-I(280)]. The second heating revealed that two peaks which were attributed to the LC phases merged. A second LC phase appeared again when the sample was heated to 80°C and then cooled to room temperature. A melting of this polymer was observed at 220°-280°C under a polarizing microscope.

A sample of poly(BPhEHxAmd) (n=3) showed the T_g of 49°C, which is 51°C higher than the T_g of poly(EHxA), 62°C higher than a T_g of poly(BPhEUAma) and 37°C higher than a T_g of poly(BPhUAmd). The broad endothermic transition from a LC phase to an isotropic phase was recorded at 260-290°C in the first DSC heating scan. When cooled, an exotherm between 225-200°C suggested an ordering process, and a transition at 178°C was attributed to an amide bond. This transition was present in all amide derivative polymers. The second DSC heating scan showed a transition at 175°C, and a smaller endothermic transition from a LC phase to an, isotropic phase between 250-290°C.

It is noted from the data compiled in Table 11 that similar degrees of substitution were achieved for all polymers listed. This result allows direct comparison of the temperature ranges of the mesomorphism (T_i - T_g) for these polymers. As can be seen from the table the polymer with an ethylene oxide backbone chain [poly(BPhEUAmd) (n=8)] displays a larger T_i - T_g (285°C) value compared to the polymer with an ethylene backbone chain [poly(BPhUAmd) (n=8)] (T_i - T_g =268°C), which suggests that an inclination to a mesophase formation increases with an increasing backbone flexibility. Also, the polymer with a shorter length of the side chain methylene spacer group [poly(BphEHxAmd) (n=3)] displays a narrower temperature range of (T_i— T_g =241°C) as well as a higher T_g value. A higher T_g value of this polymer is attributed to a diminished "plasticizing effect" of the shorter side chain methylene spacer group. All three polymers exhibited LC mesophases. However, it is evident that the backbone flexibility and the length of the spacer group had no effect on the reactivity of carboxylic acid groups.

A number of copolymers were obtained by polymer homologous reactions in which a percentage of carboxylic acid groups remained unreacted. This however did not prevent copolymers from forming liquid crystalline phases and was con-

Table 11. Degree of Substitution, T_g and T_i of Selected Copolymers

Copolymer	Percent substitution [%]	Tg [°C]	Ti [°C]
Poly(BPhEU)	90	12	125
Poly(BPhU)	90	46	320
Poly(BPhEHx)	80	19	94
Poly(CNBPhEU)	80	27	128
Poly(CNBPhU)	80	9	112
Poly(CNBPhEHx)	90	44	118
Poly(BPhEUAmd)	100	−13	272
Poly(BPhUAmd)	100	12	280
Poly(BPhEHxAmd)	100	49	290
Poly(CholEU)	70	−22	92
Poly(CholU)	70	−19	50

sistent with available literature data. It has been shown [30] that a necessary condition for molecules having carboxylic groups to form thermotropic liquid crystals is that the COOH group be attached to a aromatic moiety. Aliphatic carboxylic acid compounds, with some exceptions, are isotropic above their melting points. In this research, it has been found that polymeric acids used in polymer homologous reactions did not form any liquid crystalline phases above their melting points and consequently, remnant carboxylic acid groups in copolymers are considered to be “diluents” of the mesogenic groups.

A sample of poly(BPhEU) (n=8) showed a broad melting endotherm (50-140°C) with multiple peaks on the first DSC heating scan. The T_g of the polymer was 12°C and two LC phases were found [T_g (12)-LCI(57)-LCII(83)-I(125)]. The first DSC cooling scan showed two distinct transitions at 95-85°C and 80-70°C. This sample was annealed at 50°C for two days and then heated again. As a result of the heat treatment, the LCI phase became prominent with transitions as follows: [T_g (12)-LCI(58)-LCII (93)-I(141)\. A sample of the polymer was analyzed under a polarizing microscope and it revealed a LC to an isotropic transition at 97°C [LC(80)-I(97)].

The sample of poly(BPhU) (n=8) showed a T_g of 46°C, a highly ordered LC structure up to 239°C, and an isotropic phase at 320°C [T_g (46)-LC(239)-I(320)], as determined by DSC scans. It also showed a broad LCI transition at 197-287°C, observed under a polarizing microscope.

Poly(BPhEHx) had a T_g of 18.6°C and displayed an endothermic peak at 88°C in the first DSC heating scan. The T_g of this copolymer was 35°C lower than the T_g of the poly(BPhEHxAmd) (n=3). The LC to isotropic transition [T_g (19)-LC(64)-I(94)] which showed on the first DSC heating scan, did not appear on the second heating scan. However, an annealed sample (at 47°C for two days) displayed again a LC order, though the isotropic phase was found at lower temperatures [T_g (19)-N(5l)-I(78)].

In Table 11, degrees of substitution, T_g glass and clearing temperatures of the copolymers, having biphenyl groups attached via carboxylate groups at the end of the methylene side chains, are displayed. The thermal behavior of poly(BPhEU) and poly(BPhU) copolymers can be directly compared because of similar degrees of substitution; the results, shown in Table 11, confirm a higher glass transition temperature for the copolymer with a stiffer ethylene backbone chain. However, the temperature range of mesomorphism was larger for the polymer with an ethylene backbone chain. Also, these copolymers displayed a different type of mesomorphic phases. The formation of a more ordered mesophase in poly(BPhU) was attributed to the decreased flexibility of the main chain in this polymer as compared to poly(BPhEU).

Poly(CNBPhEU) (n=8) had a T_g of 27°C and showed the following transitions in the first DSC heating scan: T_g (27)-LCI(54.5)-LCII(101)-I(129.6). Upon cooling, two ordering processes were observed. A LCII phase was observed at 125-100°C and the LCI phase was found at 88-43°C. The second DSC heating scan showed only an upper transition phase; annealing of the sample to 90°C for

45 minutes did not induce a LCI phase. The behavior of this copolymer in DCS experiments compliment results from the observations of the copolymer under a polarizing microscope. A LC to isotropic transition [LC(50-I(95)] appeared on both the first and second heating, and first and second cooling of the polymer sample.

The thermal transitions of poly(CNBphU) were also determined by DSC. The polymer showed a T_g of 9°C, a LC phase (LCI), a second LC phase (LCII), and an isotropic transition at 112.6°C: [T_g (9)-LCI(48)-LC II(94)-I(113)]. Upon cooling, a transition occurred from an isotropic phase to a LC phase (LCII) and then to a mixture of two phases: [I(121)-LCI(91)-LCI+LCII(25)].

Poly(CNBPhEHx) showed a T_g of 44°C, which was 34°C higher than T_g of poly(CNBPhEU-co-EUA) (n=8) and 35°C higher than T_g of poly(CNBphU-co-UA). However, as can be seen in Table 11, poly(CNBPhEHx showed a higher degree of substitution (90%) and consequently, was not compared with the corresponding copolymers having longer methylene spacer groups. Poly(CNBPhEHx) displayed a T_g of 50°C and a LC to an isotropic transition [LC(83)-I(126)] during the first DSC scan. When the polymer was quenched at 200°C and subjected to a second heating, it displayed a T_g of 44°C. Again, the LC to isotropic transition was recorded although with a narrower range of transition temperatures [LC(83)-I(117)]. Annealing of the sample at 50°C for two days increased the order in the polymer and an additional LCII phase was noticed [T_g (43)-LCI(67)-LCII (96)-I(118)] which had not appeared during the second heating of the annealed sample. Observations of this copolymer under a polarizing microscope complimented the DSC measurements. The LCI transition [LC(104-105)] was observed upon heating the copolymer sample under a polarizing microscope and the LCI transition LC(100) was registered when cooled. The decrease in the temperature of a LC to an isotropic transition was noticed at an on-going rate from poly (CNBPhEU) (n=8) to poly(CNBphU) (n=8) and to poly(CNBPhEHx) (n=3).

Poly(CholEU) (n=8) had a T_g of -22.5°C and poly(CholU) had a T_g of -19°C. The first heating scan in the DSC of poly(CholEU-co-EUA) showed two melting transitions between 40-90°C: [T_g(-22.5)-LC(36.8)-Chol(72.8)-I(92)]. The second DSC scan of this copolymer displayed transitions between 50-90°C with the peak area of the first of the two transitions slightly diminished. The cooling curve of the DSC scan showed an exothermic transition at 52°C. Further annealing of this sample at 47°C for two days increased the area of the peak corresponding to the LC-cholesteric phase transition. Poly(CholU), on the other hand, had the following transitions as shown in the DSC scan of this sample: [T_g (-19)-Chol(21.2)-I(50.5)]. Microphotographs of poly(CholU-co-UA) under a polarizing microscope and DCS curves are also shown in Reference 28.

Poly(CholEU) copolymer displays a similar degree of substitution as the poly(CholU) copolymer and the thermal properties of these two copolymers were compared in Table 11.

It is noted that the copolymer with an ethylene oxide backbone chain, poly(CholEU) (n=8), displayed a lower glass transition temperature which is attributed to an increasing backbone flexibility of the polymer. Also, a larger T_i - T_g (114°C) value for this copolymer suggests, as in the other examples, that the ease of a mesophase formation increased with increasing backbone flexibility. The increasing backbone flexibility was also responsible for the formation of a less ordered LC mesophase of poly(CholEU) (Table 9).

In addition to the thermal transitions of polymers described above, the thermal transitions of biphenyl 10-undecanoamide (BPhUAmd), biphenyl 10-undecanoate (BPhU), poly(10,11-epoxyundecanoic acid) [poly(EUA)], poly(10-undecenoic acid) [poly(UA)] and poly(5,6-epoxyhexanoic acid) [poly(EHxA)l were also determined, and the results of DSC studies are presented in Table 10.

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