Macromolecules 1987, *20*, 273–281

system and are reported elsewhere.[14]

Conclusions

The experimental conditions have been determined that enable the synthesis of styrene and *n*-butyl methacrylate copolymer particles possessing different relative compositions and essentially the same size and narrow size distribution. These studies have demonstrated the importance of the polarity of the polymerization mixture during the nucleation stage in determining the ultimate size of the copolymer particles. When the solubility parameter of the starting mixture known to give the desired particle size and distribution was employed, the necessary conditions could be estimated to produce the same particle size both at different monomer concentrations and in different solvent systems. A significant drift in the reaction mixture polarity has been found to broaden the distribution of the growing particles, and this has been explained in terms of the formation of nuclei later in the reaction. If such a drift in polarity did not occur, then the distribution would remain narrow in the absence of coalescence.

Registry No. (BMA)(S) (copolymer), 25767-47-9.

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Orientation Dynamics of Main-Chain Liquid Crystal Polymers. 1. Synthesis and Characterization of the Mesogen

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ABSTRACT: We have synthesized and characterized a family of liquid crystal copolyesters for a study of orientation kinetics described in the second paper of this series. The difference among members of this homologous series of main-chain liquid crystal polymers is molecular weight. Their backbones are formed by the condensation of pimelic acid and 4-acetoxyphenyl 4-acetoxybenzoate at temperatures in the range 180–285 °C. The polymers were characterized by ^{13}C and ^{1}H high-resolution NMR, differential scanning calorimetry, vapor pressure osmometry, optical microscopy, and solution viscometry. The NMR data indicate that random terpolymers are formed during the polymerization reaction, presumably as the result of transesterification of the central ester bond in the diacetoxy monomer. The family of random liquid crystal polymers synthesized covers the molecular weight range 3900–15 800. A major endotherm is observed for all molecular weights within 3 °C of 142 °C, and optical evidence for a nematic structure is definitely observed above 185 °C. An optically visible biphasic structure is not observed below 220 °C. Calculations using a chemical model designed from experimental data predict insignificant changes in polydispersity within the molecular weight range of the polymers studied. The detailed chemical characterization is critical to our understanding of liquid crystal microstructure and dynamics. This connection is discussed in the next paper of the series.

Introduction

The type of structural chemistry associated with thermotropic, main-chain liquid crystal polymers has been well established in previous work.[1-25] In contrast, many fundamental physical properties of these materials and their relationships to molecular variables have not been extensively studied. We cite here some papers in the literature addressing this topic.[26-32] Moreover, the organization of macromolecules in the liquid crystal phase and in solids derived from anisotropic melts remains unclear. Because of their inherent anisotropy and their ability to "freeze in" field-induced orientation, these polymers may prove useful in the development of materials that exhibit special properties such as nonlinear optical behavior, piezo- and pyroelectricity, and anisotropic conductivity as well as systems with information-storage capabilities. Studies on all aspects of structure vs. properties in liquid crystal polymers will undoubtedly be useful in the molecular design of these advanced materials. This series of papers presents our findings on some physical aspects of field-induced orientation in main-chain mesogens.

Elucidating relationships between molecular variables and physical properties requires synthesis and complete characterization of a suitable material. This has therefore been the topic addressed in the first paper of the series. Detailed characterization of chemical microstructure has posed a difficult problem for many liquid crystal polymers, owing to their insolubility in common, nondegrading solvents. Thus, the usual methods of structural elucidation such as high-resolution NMR are often not feasible. Also, many liquid crystal polymers possess nonregular sequences of structural units,[18-25] and it is therefore important to characterize their chemical microstructure. For example, Ober et al.[18] were able to show through carefully designed chemistry that the thermal transition behavior of liquid crystal polymers is quite sensitive to regioregularity. In fact, this study revealed that systems with purely alternating head-to-tail/tail-to-head sequences (syndioregic) had less of a tendency to form anisotropic phases than aregic materials. It was suggested that chemical defects

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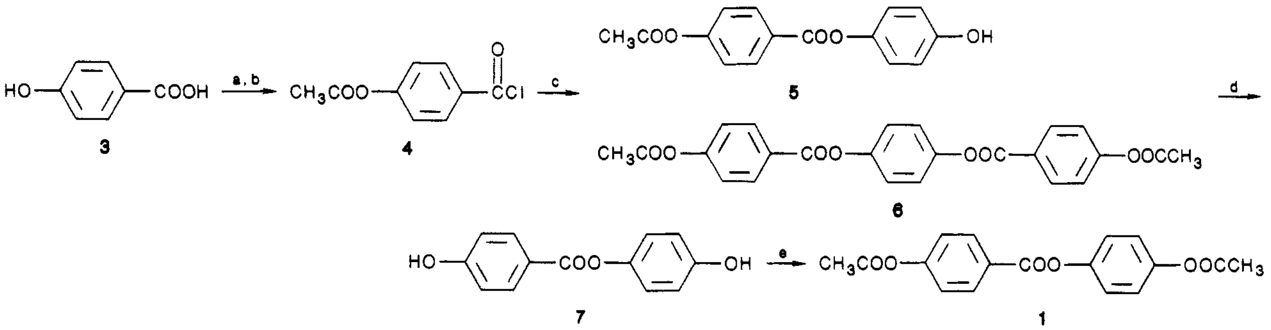
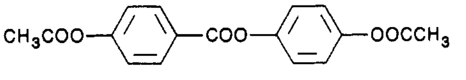
Scheme I[a]
Synthesis of the Monomer



[a] (a) NaOH, Ac_2O. (b) $SOCl_2$, DMF (catalyst). (c) 2.2 equiv of hydroquinone, pyridine, dichloroethane. (d) NaOH, sodium bisulfite. (e) Acetyl chloride, pyridine, dichloroethane, 0 °C.

introduced by the aregic microstructure lowered and broadened the melting range of the solidified material, thus permitting the formation of a liquid crystalline phase. This example clearly shows the importance of chain microstructure on liquid crystal properties. In other systems, especially those polymerized by transesterification reactions, the notion of structural unit scrambling or segregation becomes an important issue. For example, Lenz and co-workers[25] have shown through gravimetric methods that structural unit reorganization can occur in liquid crystal copolymers made from poly(ethylene terephthalate) and *p*-acetoxybenzoic acid.

One of the polymers we have selected for our studies on orientation of liquid crystal polymers is that reported by van Luyen and Strzelecki.[7] The polymer is synthesized by the reaction of the diacetoxy monomer 1 with pimelic



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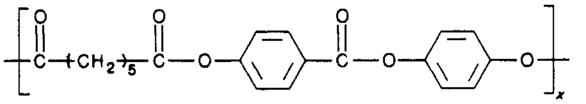
acid under transesterification conditions. The low solid-to-liquid crystal transition of 145 °C reported for this material made it a suitable polymer for experiments on orientation by high magnetic fields. However, we concluded from the literature that several details of the chain's microstructure remain unclear.[33] For example, if the central ester linkage joining the oxybenzoate ring to the dioxyphenyl ring of 1 were susceptible to transesterification, nonregular chain microstructures could evolve during polymerization. Thus, the structure of the polymer would not be accurately described by the simplified repeating unit 2. Our work on orientation required



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a series of different molecular weights and we describe in the paper how this variable was controlled. The experimental methods used for characterization include ^1H and ^{13}C high-resolution NMR, dilute solution viscometry, vapor pressure osmometry, differential scanning calorimetry, and optical microscopy.

Experimental Section

Synthesis. Organic solvents used for synthetic work were dried and stored over molecular sieves (Linde 4A $^1/_{16}$-in. pellets). Thin-layer chromatography (TLC) data were obtained with Merck silica gel 60 F_{254} precoated plates. ^1H NMR spectra of intermediates in the synthesis of the monomer and model compounds were recorded at 200 MHz on a Varian XL-200 NMR in $CDCl_3$ or Me_2SO-d_6 and referenced to a standard of Me_4Si.

Monomer. Modifications to the procedures for monomer synthesis reported by van Luyen and Strzelecki[7] are given below. Chemical reactions and molecular structures associated with synthesis of monomer 1 are shown in Scheme I.

***p*-Acetoxybenzoyl Chloride (4).** Interfacial synthesis of *p*-acetoxybenzoic acid was achieved by combining 69.1 g (0.5 mol) of *p*-hydroxybenzoic acid (3) with 200 mL of 6.25 N NaOH and 375 g of ice in a reaction blender. Acetic anhydride (85 mL (0.9 mol)) was added in one portion to the rapidly stirred mixture. After 10 min, 200 mL of 6.25 N HCl was added, and the solid product was collected by suction filtration using a sintered glass funnel. The precipitate was washed thoroughly with water and dried overnight in vacuo at 80 °C to yield 84 g (92%) of essentially pure *p*-acetoxybenzoic acid. ^1H NMR (Me_2SO-d_6) δ 8.03 (d, 2 H, J = 8.6 Hz), 7.26 (d, 2 H, J = 8.6 Hz), 2.31 (s, 3 H).

Thoroughly dried *p*-acetoxybenzoic acid (83 g (0.46 mol)) was placed in a dry 1000-mL single-neck, round-bottom flask fitted with a reflux condenser and drying tube. After 380 mL of thionyl chloride and three drops of dimethylformamide (catalyst) were added, the solution was refluxed 1.5 h. At the end of this time excess thionyl chloride was removed under vacuum, leaving a clear oil, which gave crystals of *p*-acetoxybenzoyl chloride (4) upon cooling to 0 °C. This material was used directly without further purification.

4-Hydroxyphenyl 4-Hydroxybenzoate (7). A dry 3-L three-neck, round-bottom flask was fitted with a mechanical stirrer, a 500-mL addition funnel, and a nitrogen inlet. Hydroquinone (110 g (1 mol)) was added, and the system was purged with a stream of dry nitrogen. This was followed by the addition of 750 mL of dichloroethane and 190 mL of pyridine. The addition funnel was charged with a solution of 4 in 250 mL of dichloroethane, and the solution was added dropwise with rapid stirring over a period of 2.5 h. After the addition was complete, the reaction mixture was divided into 150-mL portions and to each was added 250 mL of methylene chloride followed by extraction with 1.5 N HCl (2 × 250 mL). The aqueous layers were then extracted with methylene chloride (1 × 100 mL). All organic layers were combined and dried over magnesium sulfate. The solvent was removed, leaving 113 g of a white solid that was found to be a mixture of 5 and 6 as verified by proton NMR and TLC (85:15 benzene/ethyl acetate; R_f values: 5, 0.33; 6, 0.56). This solid was exposed to 2.5 L of 0.6 N NaOH containing 3.0 g of sodium bisulfite. The contents were vigorously stirred for 10 min at room temperature and then filtered through a Büchner funnel to remove the undissolved solid (mainly 6). The filtrate was poured onto 2 kg of ice, and 130 mL of concentrated HCl was slowly added with rapid stirring. Solid material was collected by suction filtration, giving 58 g of essentially pure 7 after drying 12 h in vacuo at 80 °C. The overall yield starting from 3 was 54.5%. ^1H NMR (Me_2SO-d_6) δ 10.43 (s, 1 H), 9.42 (s, 1 H), 7.95 (d, 2 H, J = 8.6 Hz), 6.96 (q, 4 H), 6.80 (d, 2 H, J = 8.6 Hz).

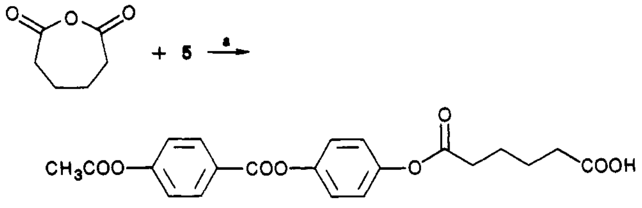
4-Acetoxyphenyl 4-Acetoxybenzoate (1). Compound 7 (44 g, (0.19 mol)) and 350 mL of 2:1 (v/v) dichloroethane–pyridine mixture were placed in a dry 2-L three-neck, round-bottom flask fitted with a mechanical stirrer, a nitrogen inlet, and an addition funnel. The addition funnel was charged with 40.7 mL (0.56 mol)

Table I
Summary of Polymerization Conditions

trial	molar ratio of pimelic acid to diacetoxy monomer (1)	reaction time,[a] h	pressure,[a,b] mm	intermediate purified	final yield after purification, %
I	1.00	1.6	atm		58.6
II	1.00	3.6	atm for 2.6 h; 50 mm for 0.5 h; 0.4 mm for 0.5 h		58.0
III	1.25	3.2 (I) 2.9 (II)	atm (I) 0.3 (II)	yes	58.2
IV	1.50	3.4 (I) 3.2 (II)	atm (I) 0.4 (II)	yes	58.2
V	1.25	3.2 (I) 3.0 (II)	atm (I) 0.2 (II)	no	84.0

[a] (I) denotes first reaction step. (II) denotes second reaction step. [b] atm denotes atmospheric pressure; all other pressures given in millimeters of mercury.

Scheme II[a]
Synthesis of the Model Compound



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[a] (a) DMAP, Et_3N, ethyl acetate.

of acetyl chloride, which was added dropwise to the solution of 7 at 0 °C over a period of 1 h. After the addition was complete the contents were stirred for 30 min at room temperature. The liquid was then divided into 100-mL portions. Methylene chloride (100 mL) was added to each of these portions, which were then extracted sequentially with 1 N HCl (2 × 200 mL), 0.1 N cold NaOH (1 × 100 mL), and water (1 × 150 mL). All aqueous layers were extracted with 50 mL of methylene chloride. The organic layers were combined and after they were dried over $MgSO_4$, the solvent was removed, leaving a tan solid. Purification was achieved by flash chromatography using silica gel eluted by methylene chloride and diethyl ether (97:3). The final product was obtained in 74% yield after a single recrystallization from ethyl acetate. ^1H NMR ($CDCl_3$) δ 8.22 (d, 2 H, J = 8.9 Hz), 7.17 (m, 6 H), 2.34 (s, 3 H), 2.31 (s, 3 H). Anal. Calcd for $C_{17}H_{14}O_6$: C, 64.96; H, 4.49. Found: C, 64.78; H, 4.47.

Model Compound. Chemical reactions and molecular structures associated with the synthesis of model compound 8 are shown in Scheme II. The mixture of intermediates 5 and 6 that resulted from monomer synthesis was used directly without purification. Adipic anhydride was synthesized according to the method reported by Hill.[34]

In a 100-mL three-neck, round-bottom flask fitted with an addition funnel and drying tube were combined 6.8 g of the mixture of 5 and 6 (thoroughly dried), 45 mL of dry ethyl acetate, 0.15 g of (dimethylamino)pyridine, and 3.6 mL of triethylamine. The addition funnel was charged with 1.9 g of adipic anhydride in 5 mL of dichloroethane. This solution was added dropwise at room temperature with rapid stirring. After the addition was complete the contents were stirred for 30 min. Ethyl acetate (250 mL) was added, and the reaction mixture was extracted with 0.8 N HCl (2 × 150). The aqueous layers were reextracted with ethyl acetate, and the organic layers were combined and dried over magnesium sulfate. 6 was removed by flash chromatography, eluting with methylene chloride and ethyl ether (85:15). The crude product of 8 was recovered by stripping the column and purified by recrystallization from benzene. Anal. Calcd for $C_{21}H_{20}O_8$: C, 62.99; H, 5.04. Found: C, 63.21; H, 5.08.

Polyester. Polymerization data on samples used in this study are summarized in Table I. Trials I and II were prepared by the procedure of van Luyen and Strzelecki[7] except that lead acetate was used as a cocatalyst instead of zinc acetate. The other trials in Table I were prepared by a two-step procedure described below. The first step was carried out in a 25-mL single-neck, pear-shaped flask fitted with a distillation head. A fine capillary tube ran down the center of the distillation head to deliver a stream of nitrogen. A condenser and graduated takeoff flask were connected to the distillation head to monitor the quantity of acetic acid removed during the polymerization. Purification of the intermediate that resulted after the first step (column 5, Table I) involved dissolution into 35 mL of tetrachloroethane followed by precipitation into a ten-volume excess of diethyl ether. Those materials not purified at the intermediate stage were transferred directly to the reaction vessel used in the second step. The second step was conducted in a 3-in.-diameter sublimation apparatus, and both reactions were heated in a sand bath. A typical procedure is described below.

Diacetoxy monomer 1 (4.71 g), pimelic acid (3.00 g (25% mole excess)), antimony trioxide (4.0 mg), and lead acetate (4.5 mg) were combined in a 25-mL flask. The pimelic acid was recrystallized from water and dried overnight in vacuo at 60 °C before use. The flask was immersed in the sand bath preheated to 180 °C, and a slow stream of dry nitrogen was bubbled through the clear melt as the temperature was raised to 280 °C over a 2-h period. After an additional 1 h of heating at this temperature, the reaction flask was cooled, and the product was purified by solution precipitation as described above. After the product was dried, it was transferred to the sublimation apparatus along with an additional 3.0 mg of antimony trioxide. The apparatus was immersed in the sand bath at 180 °C and a high vacuum was applied. The temperature of the bath was quickly raised to 285 °C and kept at this temperature for 3 h.

All polymer products were purified by solution precipitation. In the reaction described above, for example, the product was dissolved in 70 mL of hot tetrachloroethane, cooled, filtered, and precipitated into 500 mL of diethyl ether. The tan-white solid was collected by suction filtration on hardened filter paper and dried 18 h in vacuo at 100 °C.

Characterization. 1,1,2,2-Tetrachloroethane was purchased from Eastman Kodak and used without further purification. Solutions for NMR studies were prepared from tetrachloroethane-d_2 (MSD Isotopes). Dissolution was achieved by heating the polyester and solvent at 120 °C for 30–60 min. The solutions were stable at room temperature for up to several weeks.

NMR Measurements. ^1H NMR spectra of the monomer, model compound, and polymer were recorded at 200 MHz on a Varian XL-200 spectrometer. Materials were examined as 3% (w/v) solutions at 120 °C and referenced to the solvent line (5.91 ppm vs. Me_4Si). A spectral width of 2800 Hz and a 45° pulse width were used for acquisition of 64 transients on average. ^{13}C NMR spectra were recorded at 75 MHz on a General Electric QE-300 spectrometer. Materials were examined as 10–15% (w/v) solutions at ambient temperature and referenced to the central peak of the solvent triplet (74.23 ppm vs. Me_4Si). A spectral width of 20000 Hz in 32K of memory and broad-band proton decoupling were employed for acquisition of a minimum of 2000 transients. Spectra of the model compound and monomer were recorded with a 35° sampling pulse and a recycle time of 2.5 s, while spectra of the polyesters were recorded with a 90° sampling pulse and a 14-s recycle time. Quantitative measurements on the polyester spectra were made from Lorentzian interpolated peak heights.

Molecular Weight and Viscosity Measurements. Vapor pressure osmometry (VPO) molecular weight measurements were made by Arro Laboratories, Inc., using a Knauer VPO. Tetrachloroethane solutions of the polyester at 69 °C were used in these molecular weight determinations. Viscosities were measured with a Ubbelohde type viscometer at 30 ± 0.1 °C, using solutions of the polyester prepared in the same way as those for NMR studies (subsequent dilutions were made directly in the viscometer bulb). Flow times at four different concentrations were obtained for each sample. Limiting viscosity at infinite dilution, $[\eta]$, was taken as the average value of the least-squares intercept from η_{sp}/c vs. c and ln (η_r/c) vs. c curves.

Thermal and Optical Characterization. Liquid crystal textures were examined by optical microscopy between crossed polars. The instrument used was a Leitz Labrolux 12 Pol microscope equipped with a hot stage and Micristar thermal controller. Differential scanning calorimetry (DSC) analysis utilized a Du Pont 1090 instrument. During data collection samples were purged with nitrogen and heated at a rate of 10 °C/min.

Results and Discussion

Syntheses of high molecular weight polyesters by transesterification often employ conditions of stoichiometric imbalance at the start of the reaction. Successful polymerization in these cases requires a monomer in excess which is sufficiently volatile. Volatility allows removal of the excess monomer under high-vacuum and high-temperature conditions, thus driving the system to stoichiometric balance. A good example is the synthesis of poly(ethylene terephthalate) (PET).[35] The procedure reported by van Luyen and Strzelecki[7] for the synthesis of the polyester 2 involved molar equivalence of pimelic acid and 1. In our early attempts at synthesizing this polyester by their melt polymerization procedure, a white crystalline solid (2–3% by weight of the reaction contents) was always found to sublime from the reaction flask. Even when the contents were heated very slowly from 180 °C and the pressure was reduced over an extended period of time, sublimation was still observed. ^1H NMR showed the sublimate to contain both aliphatic and aromatic structures in an approximate molar ratio of 9:1. Using NMR we identified the predominant component of the sublimate to be unreacted pimelic acid. The aromatic components of the sublimate included *p*-acetoxybenzoic acid and a derivative of this compound as indicated by the characteristic ^1H NMR pattern. There appeared to be no evidence in the NMR spectrum for the presence of dioxyphenyl units in this mixture. Clearly, the loss of pimelic acid would upset the stoichiometry of the system, thus limiting the molecular weight of the product. On the basis of this information it was determined that the polymerization to high molecular weights by virtue of stoichiometric balance might be carried out successfully with an initial excess of pimelic acid. Given this excess, the high temperature and low pressure could drive the system to stoichiometric balance in much the same way as in PET synthesis.

Information on reaction conditions and stoichiometric ratios used in various polymerization trials is summarized in Table I. Trials I and II were synthesized by the procedure of van Luyen and Strzelecki except that lead acetate was used as a cocatalyst instead of zinc acetate. Also, trial I was deliberately terminated at an early point in the reaction to achieve a material with low molecular weight. Trials III–V were polymerized by using a two-step procedure and an initial excess of pimelic acid. The first step was carried out over the temperature range 180–280 °C at atmospheric pressure for a period of about 3 h. Under these conditions and with the molar ratios shown in Table I, it was found from ^1H NMR that acetoxy groups were quantitatively removed. This information is revealed in Figure 1a, which shows the aliphatic region of the ^1H NMR spectrum for the prepolymer of trial IV. Also included in this figure are spectra from an oligomeric material synthesized with an excess of the monomer (Figure 1b), the model compound 8 (Figure 1c), and the monomer (Figure 1d). Assignments can easily be made by a direct comparison of these spectra. Data for the monomer and model compound are summarized in Table II. The acetoxy bands for the monomer and model compound are observed to lie between 2.23 and 2.27 ppm. This is clearly the dominant type of end group found in the oligomer synthesized by using a slight excess of 1 (Figure 1b). From the spectrum of the model compound (Figure 1c) it can be seen that methylene protons α to the ester group are clearly resolved from methylene protons α to the carboxylic acid group. Thus, the complex series of peaks of low intensity found in the range 2.32–2.40 ppm in the spectrum of the prepolymer (Figure 1a) are likely due to protons α to carboxylic acid end groups. Furthermore, no acetoxy end groups can be detected in this spectrum. Thus, as was already mentioned, it appears that the conditions used in the first step of the polymerization are sufficient to quantitatively remove the acetoxy functional groups.

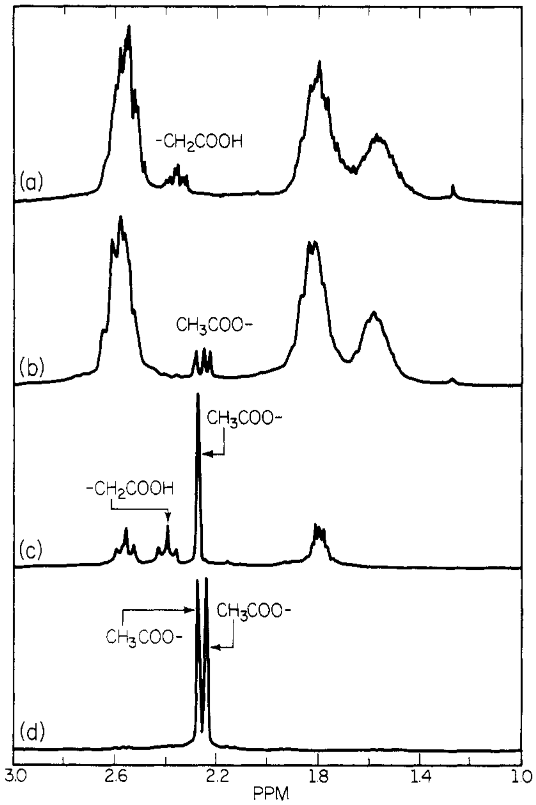
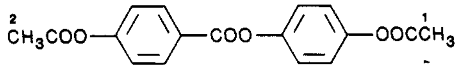
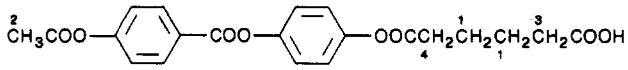


Figure 1. Aliphatic region of 200-MHz ^1H NMR spectra of (a) polyester IV at the end of the first reaction, (b) oligomeric polyester synthesized with an excess of 1, (c) model compound 8, and (d) monomer 1 in tetrachloroethane-d_2 at 120 °C.

Table II
Aliphatic ^1H NMR (200 MHz) Assignments for Monomer 1 and Model Compound 8

proton group	chem shift,[a] ppm	multiplicity[b]
		
1	2.23	s
2	2.26	s
		
1	1.79	m
2	2.27	s
3	2.39	t
4	2.56	t

[a] Chemical shifts were referenced to the solvent peak (protonated tetrachloroethane), which resonates at 5.91 ppm vs. Me_4Si. [b] s = singlet, t = triplet, m = multiplet.

Table III
Viscosity and Molecular Weight Data for Experimental Polyesters

trial	$[\eta]$,[a] dL g^{-1}	mol wt
I	0.36	3900[b]
II	0.46	6900[b]
III	0.51	8700[c]
IV	0.64	14800[c]
V	0.66	15800[c]

[a] Measured at 30 °C in *sym*-tetrachloroethane. [b] Determined by vapor pressure osmometry in *sym*-tetrachloroethane at 69 °C. [c] Estimated from viscosity data.

At the completion of the first step, two of the trials in Table I (trials III and IV) were purified by solution precipitation before the second reaction for the following reasons. First, it was though that this procedure would help remove any trace amounts of acetic acid trapped within the material. The presence of even small amounts of this condensation product could strongly inhibit formation of high molecular weight products. Second, it was thought that the purification procedure would aid in the removal of any unreacted pimelic acid. Comparison of the intrinsic viscosities for trials III and V in Table III, however, shows that purification decreased the molecular weight of the final product. The overall yield was also strongly affected.

For the second step of the polymerization, the intermediate was transferred to a flat-bottom sublimation apparatus. The larger surface area to volume ratio would be expected to aid in the removal of pimelic acid. The reaction was carried out under reduced pressure at a temperature of 280 °C for a period of 3 h (see Table I). The combined mass of sublimate from each of the two reaction steps was always greater than the theoretical excess of pimelic acid. Through ^{1}H NMR analysis it was determined that the sublimate collected from the first polymerization step was almost exclusively pimelic acid. The material that was collected from the second step contained aromatic structural units (derivatives of oxybenzoic acid) in addition to pimelic acid. Moreover, their presence (and the lack of dioxyphenyl derivatives) provides strong evidence that the central ester linkage of 1 undergoes transesterification.

On the basis of the dilute solution viscosity data (Table III), it seems apparent that those materials polymerized by the two-step procedure were higher molecular weight materials than those that resulted from the procedure of van Luyen and Strzelecki.[7] ^{1}H NMR data shown in Figure 2 reveal a large decrease in carboxylic acid end groups (α-methylene protons) after the second polymerization step. Number-average molecular weight measurements by vapor pressure osmometry were successfully carried out only on materials from the first two trials in Table I. Difficulties in preparing clear solutions of the higher molecular weight materials prevented accurate measurement of $\bar{M}_n$. For polymers obtained in the first two trials, $\bar{M}_n$ values were found to be 3900 (trial I) and 6900 (trial II), corresponding to number-average degrees of polymerization of 22 and 39, respectively. On the basis of intrinsic viscosity measurements, we believe the other three entries have even higher $\bar{M}_n$ values. We have estimated the molecular weights for these entries based on the intrinsic viscosity measurements and VPO data for trials I and II using the Mark–Houwink relation. These results are summarized in Table III.

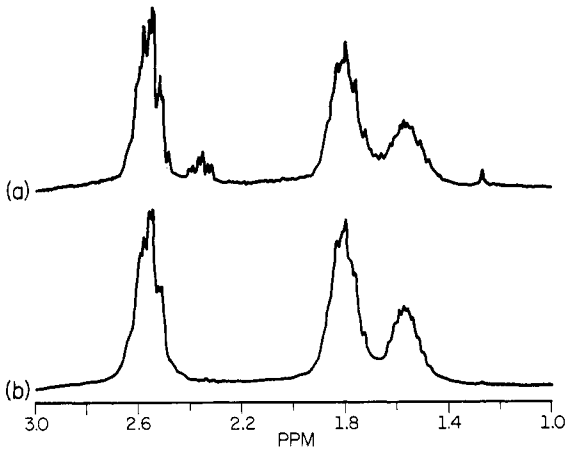
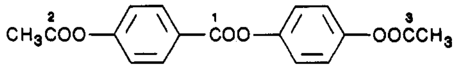
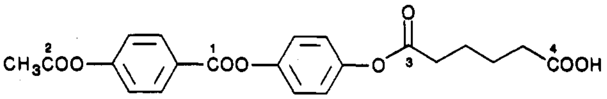


Figure 2. Aliphatic region of 200-MHz ^{1}H NMR spectra obtained in tetrachloroethane-d_2 at 120 °C of (a) polyester IV at the end of the first reaction and (b) polyester IV at the completion of the second reaction.

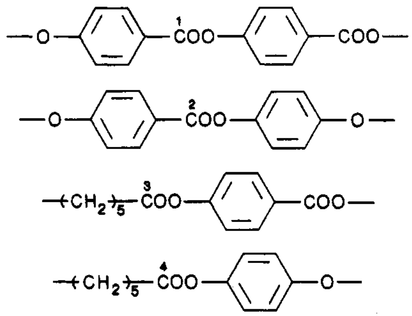
Table IV
Carbonyl ^{13}C NMR (75 MHz) Assignments for Monomer 1, Model Compound 8, and Polymer



carbon	chem shift,[a] ppm
1	164.60
2	169.26
3	169.81



carbon	chem shift,[a] ppm
1	164.69
2	169.39
3	172.18
4	179.54

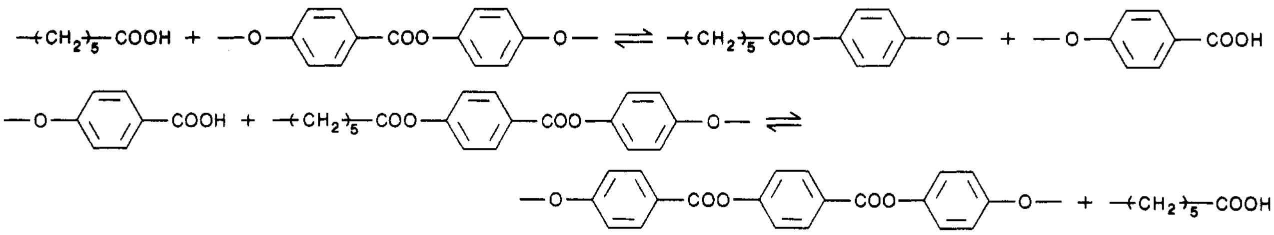


carbon	chem shift,[a] ppm	T_1, s
1	164.15	2.6
2	164.64	2.6
3	171.81	2.4
4	172.33	2.5

[a] Chemical shifts were referenced to the central peak of the tetrachloroethane-d_2 triplet (74.23 ppm vs. Me_4Si).

As mentioned earlier, oxybenzoate structural units were found to sublime from the reaction flask during the polymerization. The loss of these structural units should not, of course, have any effect on the stoichiometry of the system. However, the overall composition of the polymer should reflect this loss. The carbonyl region of the ^{13}C NMR spectrum proved useful in the examination of the structural unit compositions as well as chain microstructure. Figure 3 shows the carbonyl region in ^{13}C spectra of the polyester, the monomer, and the model compound. As described below, assignments for the various resonance peaks were made by comparison of these spectra. The assignments are summarized in Table IV. The two closely spaced peaks in the monomer's spectrum (Figure 3b) were

Scheme III
Randomizing Transesterification Reactions



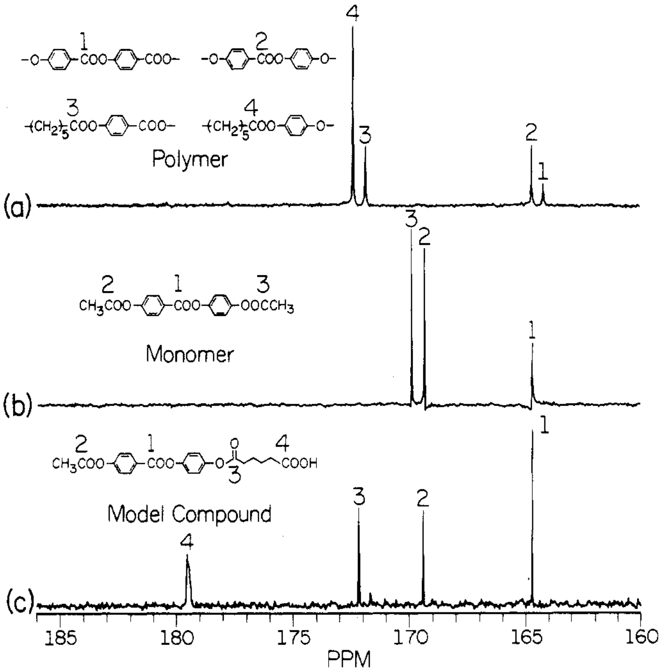


Figure 3. Carbonyl region of 75-MHz ^{13}C NMR spectra of (a) polyester V, (b) monomer 1, and (c) model compound 8 in tetrachloroethane-d_2 at 25 °C.

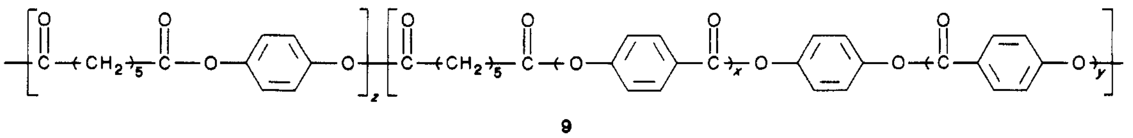
Table V
Structural Unit Composition Data and Oxybenzoate Sequence Lengths of Experimental Materials

trial	structural unit compositions P(PI)	 P(DOP)	 P(OB)	$\bar{l}_{OB}$ exptl	 calcd[a]
I	0.36	0.35	0.29	1.35	1.41
II	0.35	0.35	0.29	1.41	1.41
III	0.37	0.37	0.26	1.36	1.35
IV	0.38	0.38	0.24	1.34	1.32
V	0.37	0.37	0.26	1.34	1.35

[a] A random chemical microstructure was assumed.

assigned to the acetoxy carbonyls. The remaining peak in the spectrum was therefore assigned to the carbonyl of the ester linkage joining the two phenyl rings. This peak is also observed in the spectrum of the model compound (Figure 3c) and in that of the polyester (Figure 3a). The downfield peak observed in the spectrum of the model compound (Figure 3c) was assigned to the carbonyl of the carboxylic acid. It is clear from Figure 3 that neither type of carbonyl end group (acetoxy or carboxylic acid) can be observed in the spectrum of the polyester. This was true in all the polymeric products described in Table I. The acetoxy peak of the model compound can be assigned by comparison of its spectrum to that of the monomer. This in turn allows the assignment of the peak at 172.18 ppm to the carbonyl of the dioxyphenyl adipoate ester group. Moreover, comparison with the polyester spectrum (Figure 3a) suggests that the 172.33 ppm peak results from the dioxyphenyl pimeloate ester diad. The smaller peak at 171.81 ppm has thus been assigned to the carboxyphenoxy pimeloate ester diad. The remaining peak in the polyester spectrum occurs at 164.15 ppm, and it is assigned to an ester carbonyl joining two oxybenzoate units. The presence of the oxybenzoate diad suggested by this peak may result from the transesterification reactions shown in Scheme III. Other consequences of these reactions include the occurrence of benzoic acid end groups, the occurrence of long aromatic blocks, and an increase in the number of dioxyphenyl pimeloate ester diads at the expense of carboxyphenoxy pimeloate diads. Evidence for scrambling of structural units as implied in Scheme III is readily seen upon inspection of the polyester's ^{13}C spectrum shown in Figure 3a. For the ideal chain microstructure represented by **2**, one would expect the intensities of peaks 2, 3, and 4 to be equal. Also, peak 1, which reflects the presence of oxybenzoate diads would not be expected for the ideal microstructure. Thus, the higher intensity of peak 4 relative to peaks 3 and 2 and the appearance of peak 1 indicate that structural unit scrambling by transesterification does occur in these materials. These observations lead to the conclusion that structure **9** provides a more accurate representation of these polyesters than the ideal structure. Careful study of the generalized structure reveals that an equality between the number of dioxyphenyl oxybenzoate diads and the number of carboxyphenoxy pimeloate diads must be preserved. Experimental support of this fact is readily apparent from the ^{13}C spectrum of the polyester (Figure 3a), where it can be seen that the resonance peaks corresponding to these diads have nearly equal intensities (peaks 2 and 3).

T_1 measurements were made on the polyester and found to be nearly constant (see Table IV). On the basis of this information, a 14-s recycle time with a 90° pulse width was used to obtain quantitative ^{13}C data for all polymeric materials in Table I. On the basis of T_1's and the similarity of the immediate proton environment around the carbons analyzed, the nuclear Overhauser effect (NOE) differences among the four carbonyl resonances were assumed to be negligible. Since all diad sequences have been assigned,



9

$x \geq 0,\ y \geq 0$
$x + y \geq 1,\ z = x + y - 1$

quantitative ^{13}C analysis can provide structural unit compositions and average sequence lengths. Structural unit compositions of oxybenzoate (P(OB)), dioxyphenyl (P(DOP)), and pimeloate (P(PI)) can be calculated directly from the equations

$$P(\mathrm{OB}) = \frac{I_1 + \frac{1}{2}[I_2 + I_3]}{I_1 + I_2 + I_3 + I_4} \qquad (1)$$

$$P(\mathrm{DOP}) = \frac{\frac{1}{2}[I_2 + I_4]}{I_1 + I_2 + I_3 + I_4} \qquad (2)$$

$$P(\mathrm{PI}) = \frac{\frac{1}{2}[I_3 + I_4]}{I_1 + I_2 + I_3 + I_4} \qquad (3)$$

where I_1, I_2, I_3, and I_4 are equal to peak intensities corresponding to carbons numbered 1–4 in Table IV. Moreover, the number average sequence length of oxybenzoate units, $\bar{l}_{\mathrm{OB}}$, can be calculated as shown in eq 4. A summary of the data on all experimental materials is presented in Table V. Ideally, each of the structural units should be present in equal quantities. Thus, the loss of oxybenzoate structural units, presumably by sublimation, is clearly reflected in the data. Also, it can be seen that samples that were polymerized by the two-step reaction are more deficient in oxybenzoate than those polymerized in just one step. This is probably a consequence of longer reaction times used in the two-step procedure.

$$\bar{l}_{\mathrm{OB}} = \frac{I_1 + \frac{1}{2}[I_2 + I_3]}{\frac{1}{2}[I_2 + I_3]} \qquad (4)$$

The oxybenzoate sequence length provides an indication of the extent to which the central ester bond of 1 undergoes transesterification. If no transesterification of this bond occurred, $\bar{l}_{\mathrm{OB}}$ would have a value of unity. Experimental values of $\bar{l}_{\mathrm{OB}}$ shown in Table V are clearly greater than 1.0, suggesting that this bond does participate in transesterification reactions (Scheme III). Furthermore, the magnitude of $\bar{l}_{\mathrm{OB}}$ is sensitive to the degree of random vs. blocky character of chain microstructure. For example, a completely random system with equal fractions of each structural unit would have a sequence length of 1.5. Other calculated values of $\bar{l}_{\mathrm{OB}}$ for random microstructures at the experimentally determined compositions are shown in Table V. It is apparent by comparison of experimental and calculated sequence lengths that all of the trials have $\bar{l}_{\mathrm{OB}}$ values very near their random values. $\bar{l}_{\mathrm{OB}}$ for trial I shows the greatest deviation from random behavior, which may be the result of this trial's short reaction time. The remaining trials appear to have random chemical microstructures at the diad level, thus suggesting that all ester bonds of monomer 1 are equally susceptible to transesterification. This is somewhat surprising, as one might expect the ester group conjugated with two phenyl rings to possess added stability.

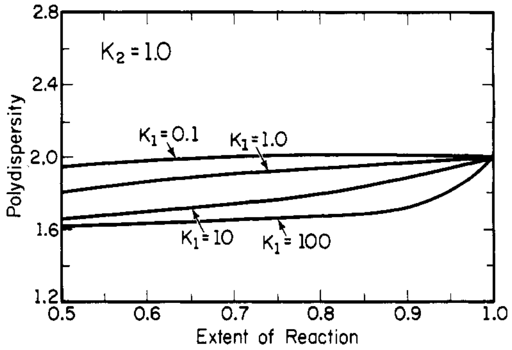
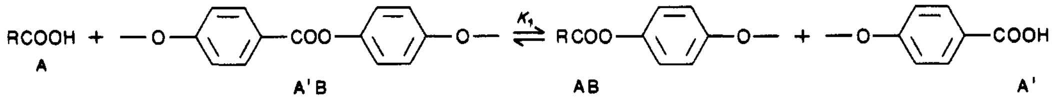
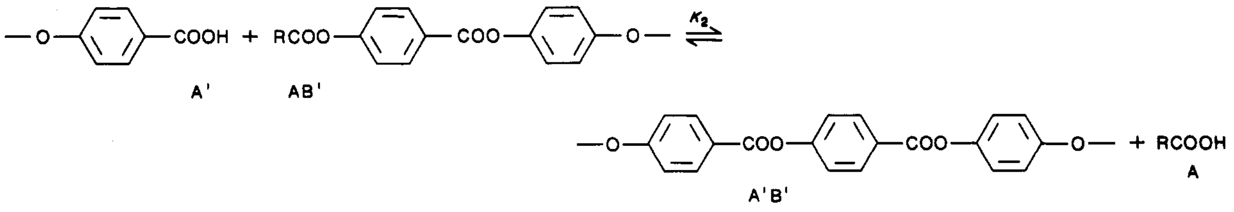


Figure 4. Calculated plot of polydispersity as a function of the extent of reaction for various assumed values of K_1 and $K_2 = 1.0$ (see text).

A general method has been described in the literature[36] to calculate average values of molecular weight and sequence lengths in linear multicomponent systems. The method is based on the recursive nature of first-order Markovian statistics and the law of total probability of expectation. The calculation involves writing first a set of recursive relations for the expected weight attached to the various monomers in terms of probabilities of reaction. The reader is referred to the original paper for a detailed explanation of the method. Being presently unable to measure polydispersity, we have adapted this method to calculate for our system the expected changes in polydispersity with increasing molecular weight. In order to make the adaptation possible, we developed a chemical model for our reactions based on experimental data. This was done because certain assumptions about the polymerization system are necessary in order to calculate reaction probability parameters. As part of the adaptation of this method to our system, we assume the polymerization to be in chemical equilibrium at all values of extent of reaction. In other words, we assume that equilibrium is established rapidly relative to the rate of condensation product removal. The equilibrium equations assumed to govern the sequence distributions and relative amounts of the various end groups are shown in eq 5 and 6, where R represents both CH_3 and $(CH_2)_5$ groups. As described in detail in the Appendix, on the basis of these equations one can write a set of mass balance and equilibrium relations from which the reaction probabilities can be calculated. The final results of the method are shown in Figure 4 as a plot of polydispersity vs. extent of reaction for various assumed values of the equilibrium constants K_1 and K_2. As expected, the polydispersity approaches a value of 2.0 in all cases as complete conversion is approached. Most importantly, however, the results also indicate that for our range of extent of reaction ($p > 0.96$), samples are not predicted to change significantly in polydispersity with increasing molecular weight. This is inferred on the basis that a value of 1 for the equilibrium constants K_1 and K_2 is easily justified (see Figure 4). The justification is based



(5)



(6)

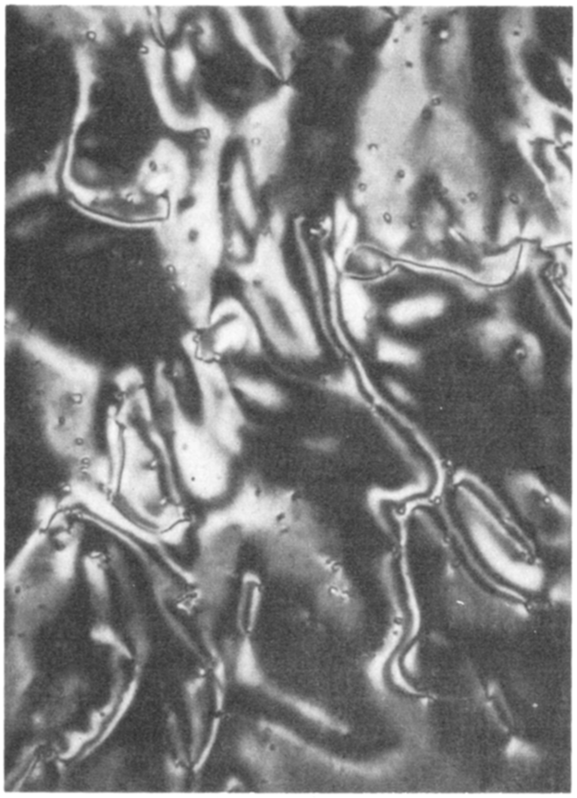


Figure 5. Optical micrograph between crossed polars of polyester V at 220 °C (192×).

not only on the fact that equilibrium constants for polyester transesterification reactions[37] typically lie in the range between 0.1 and 10 but also on our finding that K values of 1 yield calculated diad sequence lengths that match the experimental values from NMR. The issue of polydispersity as a function of molecular weight is an important one in understanding microstructure and dynamic behavior of the fluid phase. We have addressed these two issues in the second paper of the series.

Analysis of molten samples by optical microscopy between crossed polars revealed the highly birefringent fluids expected for liquid crystalline samples. A typical optical micrograph is shown in Figure 5. Microscopic analysis was carried out at temperatures in the range 25–390 °C, and schlieren patterns characteristic of a nematic phase (two brushes) were observed above 185 °C. DSC scans of all samples revealed a well-defined endotherm near 145 °C, assumed to be the solid-to-mesophase transition. Visible flow of the samples is not observed, however, below 170 °C. A characteristic DSC scan is shown in Figure 6, revealing other features in addition to the main endothermic peak. We cannot rule out the possibility of a second higher temperature endotherm at approximately 155 °C, which could indicate a liquid crystal to liquid crystal transformation or the melting of crystallites. Also, the presence of an endotherm or a secondary transition at 112 °C was noticed only in samples with the highest molecular weights. We do not know at this point what is the molecular origin of this thermal phenomenon. A well-defined endotherm for an N → I transition is not observed in DSC scans of these materials. Above 200 °C, the DSC could be interpreted as having a very broad endotherm extending to the clearing point (388 °C) as revealed by optical microscopy. However, the presumed endotherm is hardly distinguishable from the base line over the range 220–388 °C. Optical microscopy does reveal the gradual appearance of an isotropic phase above 220 °C. Thus, the polymers investigated reveal the optically visible broad isotropization range described in earlier literature[33] but only at temperatures greater than 220 °C. Below this temperature the optical micrographs only reveal the anisotropic phase. We emphasize that this point is extremely important in the interpretation of data of the second paper of this series. This paper describes the kinetics of orientation in a magnetic field and addresses the issue of "submicroscopic" molecular structure in the fluid phase of liquid crystal polymers.

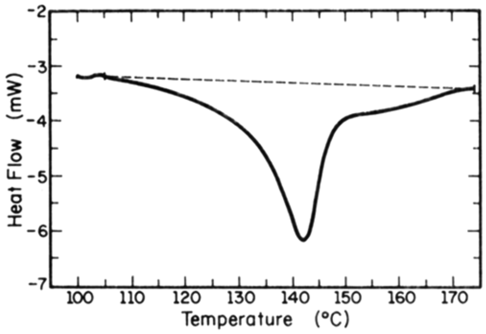


Figure 6. DSC scan of polyester II.

Conclusions

The liquid crystal polymers synthesized in this study were found to be random terpolymers resulting from transesterification reactions. These main-chain thermotropic polyesters spanned a molecular weight range from 3900 to 15800 and were found to be nematogens above 185 °C. Calculations based on our data do not predict significant changes in polydispersity within the molecular weight range involved. Generally speaking, the synthetic and characterization effort should be helpful in understanding both the microstructure and dynamics of these polymer liquid crystals. These two topics are the subject of the next paper of this series.

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Appendix

On the basis of the equilibrium reactions given in eq 5 and 6, it is possible to write the following mass balance and equilibrium relations:

$$[AB][A'] - K_1[A][A'B] = 0 \qquad (1A)$$

$$[A'B'][A] - K_2[A'][AB'] = 0 \qquad (2A)$$

$$[AB] + [AB'] + [A] = [A_0] \qquad (3A)$$

$$[A'B] + [A'B'] + [A'] = [A_0'] \qquad (4A)$$

$$[AB] + [A'B] = [B_0] \qquad (5A)$$

$$[AB'] + [A'B'] = [B_0'] \qquad (6A)$$

where [AB], [A′B], [A′B′], and [AB′] denote the diad concentrations of dioxyphenyl pimeloate (and dioxyphenyl acetate), dioxyphenyl oxybenzoate, dioxybenzoate, and carboxyphenoxy pimeloate (and carboxyphenoxy acetate), respectively. [A] denotes the concentration of aliphatic acid end groups and [A′] denotes the concentration of benzoic acid end groups. Finally, $[A_0]$ represents the total concentration of aliphatic acid groups that would result upon complete hydrolysis of all ester linkages at any given extent of reaction. Likewise, $[\mathrm{A_0'}]$, $[\mathrm{B_0}]$, and $[\mathrm{B_0'}]$ represent similar parameters for benzoic acid, hydroquinone phenol, and hydroxybenzoic acid phenol groups, respectively. The set of six nonlinear equations written above can be solved numerically for the six unknowns [AB], [A′B], [A′B′], [AB′], [A′], and [A] at some choice of the equilibrium constants K_1 and K_2 and overall stoichiometry of the system defined by $[\mathrm{A_0}]$, $[\mathrm{A_0'}]$, $[\mathrm{B_0}]$, and $[\mathrm{B_0'}]$. This allows calculation of the reaction probabilities P_{ij} used in the method of Lopez-Serrano et al.[36] The P_{ij} parameters represent the probability that group i reacts with group j. These probabilities can be written in terms of the various diad and end-group concentrations as shown below

$$P_{\mathrm{AB}} = \left[1 - \frac{[\mathrm{A}]}{[\mathrm{A_0}]}\right]\frac{[\mathrm{AB}]}{[\mathrm{AB}] + [\mathrm{AB'}]}$$

$$P_{\mathrm{BA}} = \frac{[\mathrm{AB}]}{[\mathrm{AB}] + [\mathrm{A'B}]}$$

$$P_{\mathrm{AB'}} = \left[1 - \frac{[\mathrm{A}]}{[\mathrm{A_0}]}\right]\frac{[\mathrm{AB'}]}{[\mathrm{AB}] + [\mathrm{AB'}]}$$

$$P_{\mathrm{B'A}} = \frac{[\mathrm{AB'}]}{[\mathrm{AB'}] + [\mathrm{A'B'}]}$$

$$P_{\mathrm{A'B}} = \left[1 - \frac{[\mathrm{A'}]}{[\mathrm{A_0'}]}\right]\frac{[\mathrm{A'B}]}{[\mathrm{A'B}] + [\mathrm{A'B'}]}$$

$$P_{\mathrm{BA'}} = \frac{[\mathrm{A'B}]}{[\mathrm{AB}] + [\mathrm{A'B}]}$$

$$P_{\mathrm{A'B'}} = \left[1 - \frac{[\mathrm{A'}]}{[\mathrm{A_0'}]}\right]\frac{[\mathrm{A'B'}]}{[\mathrm{A'B}] + [\mathrm{A'B'}]}$$

$$P_{\mathrm{B'A'}} = \frac{[\mathrm{A'B'}]}{[\mathrm{AB'}] + [\mathrm{A'B'}]}$$

Registry No. **2** (copolymer), 74774-70-2; **3**, 99-96-7; **4**, 27914-73-4; **5**, 74783-97-4; **6**, 79066-38-9; **7**, 28084-48-2; **8**, 105762-99-0; 4-$H_3CCO_2C_6H_4CO_2H$, 2345-34-8; H_3CCOCl, 75-36-5; acetic anhydride, 108-24-7; hydroquinone, 123-31-9; adipic anhydride, 2035-75-8.

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