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Synthesis of a Chemically Ordered Liquid Crystal Polymer

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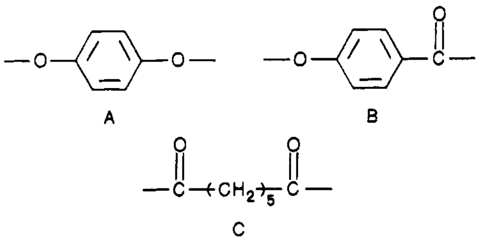
ABSTRACT: Links between chemical sequence structure in self-ordering polymers and their physics are still to be established. In order to address this problem we have proceeded to synthesize a sequentially ordered and regioregular terpolymer which exhibits liquid crystallinity. Neglecting end groups, this polymer is a constitutional isomer of a chemically random liquid crystal polymer reported previously. The synthesis of ordered–disordered chemical analogues has been difficult in the past either because of the absence of liquid crystallinity in highly regular chains or because of difficulties in developing regioregular polyesters. The mesogenic chain synthesized here contained dioxyphenyl (A), oxybenzoate (B), and pimeloate (C) structural units and was built from the condendation reaction between the symmetric monomer ABCBA and pimeloyl chloride. The structure of the regular polymer was verified by ^{13}C NMR analysis of tetrachloroethane solutions and additional characterization was carried out through DSC and dilute solution viscometry.

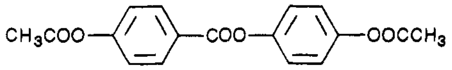
Introduction

Links between molecular structure and the physics of liquid crystal polymers are still to be established. An intriguing question is how chemical disorder along the backbone affects phase structure in the fluid state. It is also puzzling how chemically random mesomorphic chains order to form partly crystalline solids. These questions are important since many liquid crystal polymers are synthesized by transesterification reactions that lead to chemically disordered backbones. For example, Blackwell and co-workers have shown through calculated X-ray diffraction patterns that some aromatic liquid crystal polyesters can be described as chemically random.[1] Recent work from our laboratory also describes an aromatic–aliphatic polyester as random at the diad level by ^{13}C NMR analysis.[2] One possible consequence of chemical disorder is the description of the system as chain segments or chains with a flexibility distribution rather than a single persistence length. This nonuniform rigidity and chemical disorder could affect chain dynamics by controlling the density of interchain associations and entanglements. Molecular organization and phase behavior of the fluid and solid states should also be affected by chemical disorder and nonuniform rigidity.

It is in this context that we have proceeded to synthesize a chemically regular analogue to the liquid crystal polymer containing the following three structural units:



We reported earlier[2] on the synthesis of the random chain from the following two monomers:

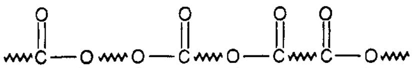


1

$HOOC\text{—}(CH_2)_5\text{—}COOH$

2

A random chain grows during this polymerization reaction for two reasons. One is that the central ester bond in 1 participates in transesterification reactions and the second is the non-symmetric nature of monomer 1 leading to an aregic chain.



We describe herein the synthesis and chemical characterization of the regular mesogen. In two following papers

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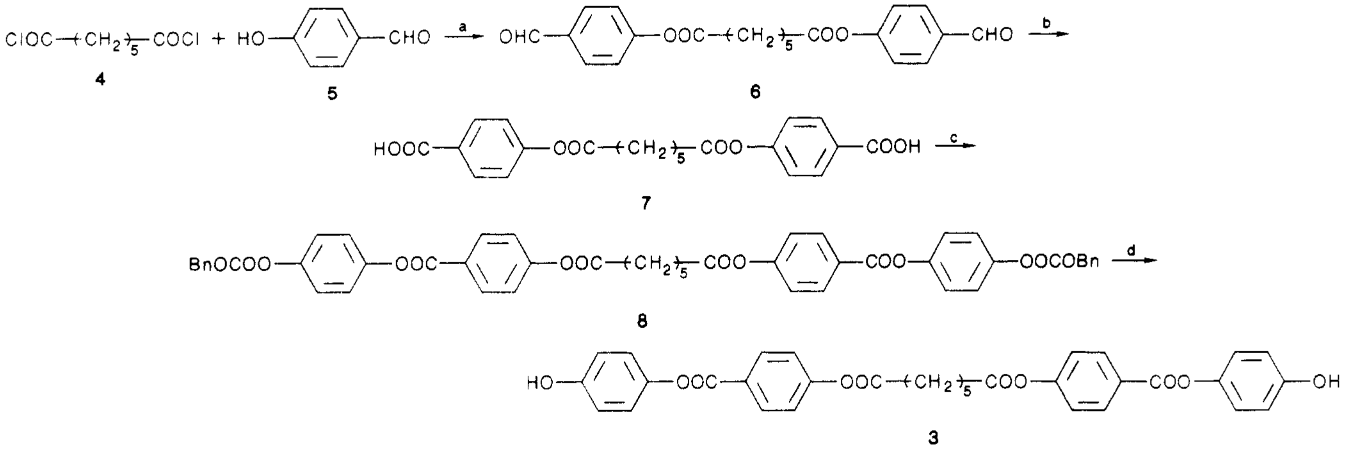
Scheme I[a]
Synthesis of the Symmetric Monomer



[a] (a) CH_2ClCH_2Cl, DMAP, pyridine, 0 °C; (b) $(n\text{-}Bu_4N)MnO_4$, pyridine, 23 °C; (c) (i) $SOCl_2$, DMF (cat), (ii) 2 equiv of BnOCOO-*p*-C_6H_4OH, CH_2ClCH_2Cl, DMAP, pyridine, 0 °C; (d) 5% Pd–C, cyclohexene, MeOH, THF.

we describe some of the contrasting physical behavior observed between the chemically ordered and chemically disordered backbones.[3]

Experimental Section

Organic solvents used in synthetic work were dried and stored over molecular sieves (Linde 4A 1/16 in pellets). Pyridine was stirred for 24 h with cerium(IV) sulfate and potassium carbonate, filtered, distilled, and stored over sieves prior to use. Thin layer chromatography (TLC) data were obtained using Merk silica gel 60 F_{254} precoated plates. ^1H NMR spectra of intermediates in the monomer synthesis were recorded at 300 MHz on a General Electric QE-300 NMR in $CDCl_3$ or Me_2SO-d_6 and referenced to an internal $SiMe_4$ standard. Chemical reactions and molecular structures associated with the synthesis of monomer 3 are shown in Scheme I.

Bis(4-formylphenyl) Pimeloate (6). In a dry three-neck, 200-mL round-bottom flask fitted with a drying tube and addition funnel was placed 16.4 g (0.135 mol) of *p*-hydroxybenzaldehyde in 130 mL of dichloroethane containing 750 mg of (dimethylamino)pyridine and 10.9 mL of pyridine. The addition funnel was charged with 10.04 mL (12.1 g, 0.062 mol) of pimeloyl chloride in 10 mL of dichloroethane. After cooling to 0 °C the pimeloyl chloride solution was added dropwise to the magnetically stirred solution of 5. Stirring was continued for 30 min at 0 °C after the addition was complete and contents were then extracted with 0.1 N HCl (2 × 150 mL) and 0.1 N NaOH (1 × 150 mL). Organic layers were dried over $MgSO_4$ and solvent evaporation left 22.0 g (96%) of crude dialdehyde. Purification was achieved by flash chromatography using silica gel eluted with methylene chloride and ethyl acetate (96:4). ^1H NMR ($CDCl_3$) δ 10.00 (s, 2 H), 7.92 (d, 4 H, J = 6.8 Hz), 7.28 (d, 4 H, J = 8.1 Hz), 2.65 (t, 4 H, J = 7.3 Hz), 1.85 (m, 4 H), 1.57 (m, 2 H).

Bis(4-carboxyphenyl) Pimeloate (7). Tetrabutylammonium permanganate,[4] 33.2 g (91.87 mmol), was dissolved in 500 mL of pyridine and stirred under nitrogen 1.5 h prior to use. To a separate three-neck, 2-L round-bottom flask fitted with a mechanical stirrer, nitrogen inlet, and addition funnel were added 17 g of dialdehyde (46.15 mmol) in 250 mL of pyridine. The addition funnel was charged with the permanganate solution which was added dropwise at room temperature over a period of 90 min. After stirring an additional 45 min the contents were poured into 3.0 L of water containing 920 mL of concentrated HCl, 1 kg of ice, and 190 g of sodium bisulfite. The solid product obtained after overnight refrigeration of the solution was recovered by vacuum filtration and washed with cold methanol. After air drying, the white powder was dried overnight in vacuo at 80 °C yielding 16.6 g (90%) of diacid 7. ^1H NMR (Me_2SO-d_6) δ 8.06 (d, 4 H, J = 8.6 Hz), 7.15 (d, 4 H, J = 8.6 Hz), 2.64 (t, 4 H, J = 7.3 Hz), 1.83 (m, 4 H), 1.56 (m, 2 H).

Bis[4-[[4-[(benzoxycarbonyl)oxy]phenoxy]carbonyl]phenyl] Pimeloate (8). Dry diacid, 16.0 g (39.96 mmol), and thionyl chloride, 40 mL, were placed in a dry 200-mL single-neck round-bottom flask. After the addition of one drop of DMF, contents were refluxed 1 h. Excess thionyl chloride was removed under vacuum leaving a brown oil which solidified upon cooling to 0 °C and was sufficiently pure to be used in the next step. To a 500-mL three-neck flask fitted with an addition funnel and nitrogen inlet was added 24.4 g (100.0 mmol) of monocarbobenzoxyhydroquinone,[5] 0.7 g (5.7 mmol) of (dimethylamino)pyridine, 8.1 mL of pyridine (100.1 mmol), and 225 mL of dichloroethane. The solution was cooled to 0 °C and the addition funnel was charged with the diacid chloride prepared above in 32 mL of dichloroethane and this mixture was added dropwise. After the addition was complete, contents were stirred 30 min at 0 °C and then diluted with 800 mL of methylene chloride. Extraction with 0.5 N HCl (2 × 400 mL) and drying over $MgSO_4$ left 35.8 g (100%) of crude 8 after solvent removal. The crude product was recrystallized from benzene–heptane. ^1H NMR ($CDCl_3$) δ 8.22 (d, 4 H, J = 9.7 Hz), 7.32 (m, 22 H), 5.28 (s, 4 H), 2.66 (t, 4 H, J = 7.3 Hz), 1.86 (m, 4 H), 1.61 (m, 2 H).

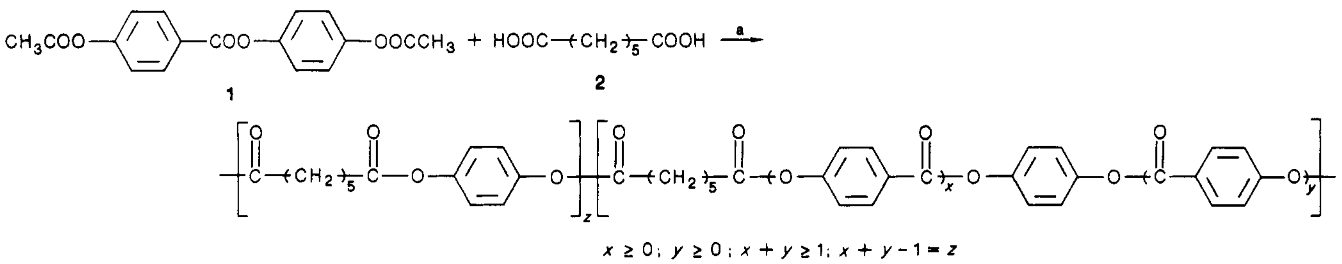
Bis[4-[(4-hydroxyphenoxy)carbonyl]phenyl] Pimeloate (3). To a three-neck, 2-L flask fitted with a nitrogen inlet and reflux condenser was added under a nitrogen blanket 9.7 g of 5% Pd–C catalyst followed by a solution of 20.0 g (23.45 mmol) of 8 in 425 mL of THF. To this suspension was added 600 mL of a 3:1 methanol–cyclohexene solution. After refluxing for 40 min, the contents were filtered to remove the catalyst, and solvent evaporation left 13.4 g (98%) of crude 3. A single recrystallization from ethanol–water left analytically pure bis phenol. ^1H NMR (Me_2SO-d_6) δ 9.50 (s, 2 H), 8.16 (d, 4 H, J = 8.6 Hz), 7.35 (d, 4 H, J = 8.6 Hz), 7.06 (d, 4 H, J = 8.8 Hz), 6.80 (d, 4 H, J = 8.8 Hz), 2.68 (t, 4 H, J = 7.2 Hz), 1.73 (m, 4 H), 1.50 (m, 2 H).

Anal. Calcd for $C_{33}H_{28}O_{10}$: C, 67.69; H, 4.83. Found: C, 67.61; H, 4.83.

Polyester. Pimeloyl chloride (Aldrich) was fractionally distilled under reduced pressure (bp 94–96 °C, 0.4 mm). Tetrachloroethane was fractionally distilled from K_2CO_3 and stored over molecular sieves 24 h prior to use. The bisphenol 3 was dried at 110 °C in vacuo for 12 h just before polymerization. Glassware was dried overnight at 120 °C, assembled hot, and cooled under dry nitrogen. Into a 100-mL, single-neck flask was weighed 580.4 mg (2.945 mmol) of pimeloyl chloride. The flask was fitted with a Claisen adapter connected to a reflux condensor with a drying tube and a nitrogen inlet which reached the flask bottom. Tetrachloroethane, 28 mL, was added to the flask along with an open weighing vial containing 1.7216 g (2.945 mmol) of the bisphenol. The flask was immersed in an oil bath preheated to 130 °C and nitrogen was bubbled through the solution for 5 h. After cooling and diluting with 20 mL of tetrachloroethane, the product was recovered by filtering the solution into 500 mL of ether. The solid was collected by vacuum filtration and dried 18 h in vacuo at 100 °C yielding 1.28 g (61%) of the polyester.

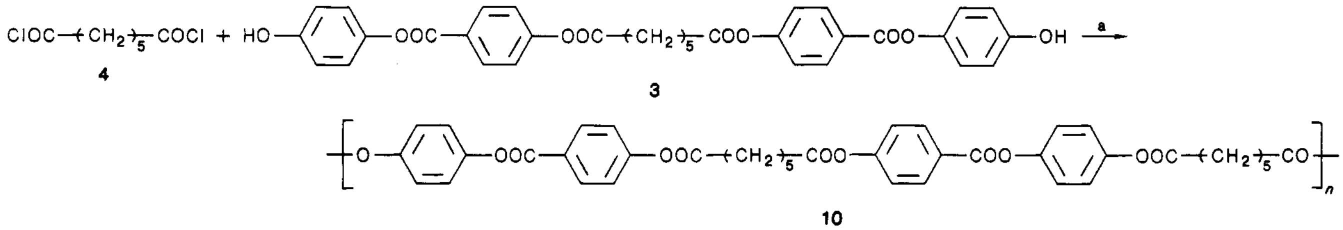
Solutions for NMR studies were prepared from tetrachloroethane-d_2 (MSD ISOTOPES). Dissolution was achieved by

Scheme II[a]
Synthesis of the Chemically Disordered Liquid Crystal Polymer



[a] (a) 200–280 °C, atm–0.5 mm.

Scheme III[a]
Synthesis of the Chemically Ordered Liquid Crystal Polymer



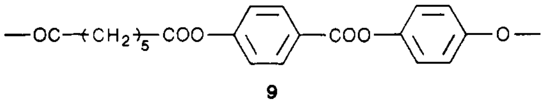
[a] (a) $CHCl_2CHCl_2$, 130 °C, 5 h.

heating the polyester and solvent at 135 °C for 60 min. Solutions of the regular polyester at concentrations less than 8% (w/w) remained homogeneous and were stable at room temperature for up to several weeks. ^{13}C NMR spectra were recorded at 75 MHz on a General Electric QE-300 spectrometer. Materials were examined as 7% (w/w) solutions at ambient temperature and referenced to the central peak of the solvent triplet (74.23 ppm versus Me_4Si). A spectral width of 20 KHz in 32K of memory and broad-band proton decoupling were employed for aquisition of a minimum of 2000 transients. Based on previously measured T1's,[2] a 90° sampling pulse and a 14-s recycle time were used to obtain quantitative ^{13}C data in the carbonyl region.

Viscosities were measured with a Ubbelohde-type viscometer at 30 ± 0.01 °C by using solutions of the polyester in tetrachloroethane which had been filtered through a 0.22-μm Millipore film. Flow times at four different concentrations were obtained with dilutions made directely in the viscometer bulb. Limiting viscosity at infinite dilution, $[\eta]$, was taken as the average value of the least-squares intercept of η_{sp}/c versus c and ln (η_r/c) versus c curves.

Results and Discussion

The synthesis of chemically regular macromolecules requires chemo- and regioselectivities during polymerization. As explained in detail below, these requirements have important implications for both monomer design as well as polymerization conditions. The specific case at hand involved the synthesis of regular polymer chains based on structural unit **9**. Structural analysis of **9** reveals the presence of three distinguishable ester groups (dioxyphenyl pimeloate, carboxyphenoxy pimeloate, and dioxyphenyl oxybenzoate) in addition to a specific orientation sequence of ester bonds. Thus, a successful synthesis of regular chains based on **9** must include chemoselective esterification as well as control over structural unit orientation.



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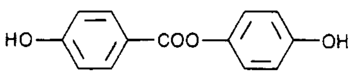
We reported earlier that the reaction shown in Scheme II leads to chemically random chains.[2] This results from the absence of chemoselectivity in the transesterification polymerization of monomer **1**. This type of control might be possible using milder polymerization conditions such as interfacial or solution methods. Krigbaum et al.[6] have reported that the diphenol shown below can be polymerized with azelaoyl chloride under conditions in which the phenyl benzoate ester group is stable. This polymerization method, however, does not control the direction of ester bonds. Therefore, structural unit placement within the polymer backbone is aregic. Ober et al.[7] have recently shown that the subtle level of randomness introduced by aregic sequences is necessary in order to observe mesophase formation. Specifically, the ordered-sequence syndioregic terpolymer containing terephthalate, oxybenzoate, and an aliphatic spacer ($-(CH_2)_{10}-$) failed to form a mesophase and melted directly from the crystalline to the isotropic state. On the other hand, its aregic analogue exhibited a mesophase over a 7 °C range.



The symmetric versus nonsymmetric nature of the monomers is naturally a critical factor in the synthesis of the perfectly regular polyester. If an a–a or b–b type monomer is nonsymmetric, the resulting chain will be aregic and thus fails to yield the desired regular mesogen. For example, the liquid crystalline polyethers reported by Percec and Shaffer based on 4,4′-dihydroxy-α-methylstilbene and an aliphatic dibromide exhibit this type of chemical disorder.[8] Polymerization of a single, nonsymmetric monomer of the a–b type can yield, of course, a perfectly regular polymer. Another way of obtaining a regular mesogen would be to polymerize two symmetric monomers of the a–a and b–b type. It is because of all the synthetic difficulties stated above that not much is known about the universal contrasts in physical behavior between chemically ordered and chemically disordered liquid crystal polymers.

The easiest way to control regioplacement of structural units is to alter monomer structure. Scheme III shows our design of a monomer that would lead to chemically regular syndioregic chains. The five-step synthetic route leading to symmetric monomer **3** is outlined in Scheme I. Esterification of two equivalents of p-hydroxybenzaldehyde with pimeloyl chloride led smoothly to the bis aldehyde **6**. Oxidation of **6** to the diacid with tetrabutylammonium

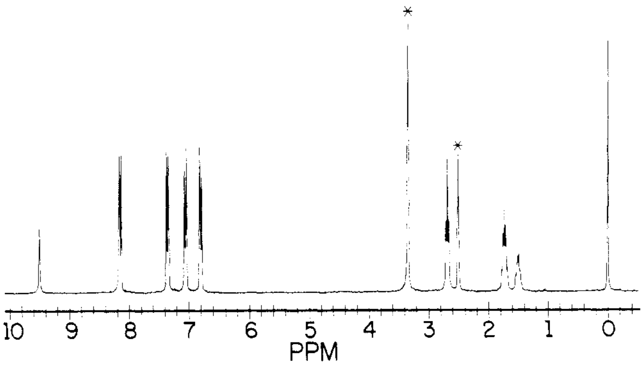


Figure 1. ^1H NMR spectrum, 300 MHz, of the symmetric monomer ABCBA recorded in $Me_2SO\text{-}d_6$ solution. Peak positions and integrated areas are given in the experimental section. Resonances marked with * are from the solvent (water and protonated Me_2SO).

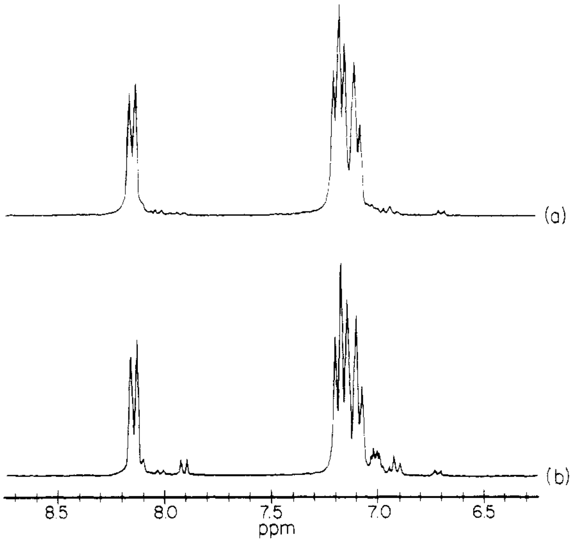


Figure 2. ^1H NMR spectra, 300 MHz, in the aromatic region of polymeric products obtained after a reaction time of 5 h at a temperature of 130 °C (a) and after a reaction time of 6 h at a temperature of 155 °C (b).

permanganate[4] followed by treatment with thionyl chloride gives the corresponding diacid chloride of 7. Further esterification with monocarbobenzoxy-protected hydroquinone[5] and subsequent deprotection by catalytic transfer hydrogenation[9] yielded the desired crystalline bisphenol 3 in overall yield of 85% for the five-step sequence. Figure 1 shows the ^1H NMR spectrum of the symmetric ABCBA monomer synthesized in this procedure.

With monomer 3 in hand, high-temperature solution polymerization according to Scheme III was attempted. Good results were obtained when the polymerization was carried out in dry tetrachloroethane at temperatures of 130 °C for periods of up to 5 h. Longer reaction times and/or high temperatures led to detectable amounts of phenyl benzoate hydrolysis products as revealed by ^1H NMR (see Figure 2). We suspect any water responsible for hydrolysis might have come from the N_2 purge used to drive off the HCl. For those materials polymerized under optimal conditions, we estimate the molar mass to be greater than 15000 on the basis of dilute solution intrinsic viscosity data and previous VPO measurements. Intrinsic viscosity in tetrachloroethane at 30 °C was found to be equal to 0.54 dL/g. Our estimate of molecular weight assumes that the Mark–Houwink constants in the regular polymer are the same as those in the random polymer. This assumption may not be strictly correct but it is simply used to estimate molar mass.

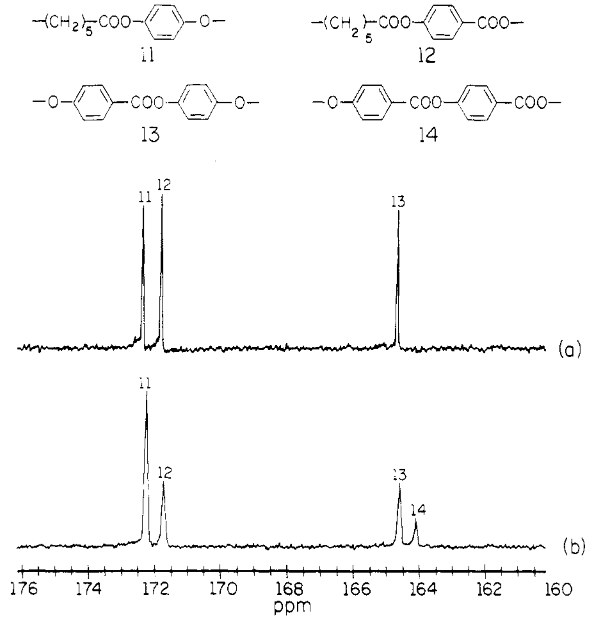


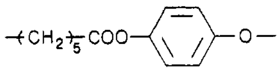
Figure 3. ^{13}C NMR spectra, 75 MHz, in the carbonyl region of the chemically ordered (a) and chemically disordered (b) polymers.

Table I
Summary of ^{13}C NMR Data

	chemical shift[a]				
polymeriztn method	diad 11	diad 12	diad 13	diad 14	$\bar{l}_{OB}$[b]
transesterificatn[c]	172.33	171.81	164.64	164.15	1.38
solution[d]	172.35	171.80	164.65		1.00

[a] Chemical shifts were recorded relative to the central peak of the tetrachloroethane-d_2 triplet (74.23 ppm versus $SiMe_4$). [b] See ref 2 for details. [c] See Scheme II. [d] See Scheme III.

We proceed now to demonstrate by ^{13}C NMR the chemical structure postulated for polymer 10 (see Scheme III). Chains having a regular chemical sequence such as that of 10 should have three unique carbonyl carbons corresponding to diads 11, 12, and 13. Each of these diads is equally probable, and therefore the three carbonyl resonances should have equal intensity. Figure 3a shows the carbonyl region of the ^{13}C spectrum for materials obtained by polymerization of 3 with pimeloyl chloride according to Scheme III. For comparison, Figure 3b shows the carbonyl region of the ^{13}C spectrum of polymer obtained by transesterification polymerization according to Scheme II. In Figure 3a, three resonance bands with nearly equal intensity are observed corresponding to the diads 11, 12, and 13 in agreement with our previous assignments[2] (see Table I). As discussed above, this spectrum is clearly indicative of chains with a regular chemical sequence. In contrast, the spectrum in Figure 3b exhibits an additional upfield peak corresponding to the oxybenzoate diad 14 (see Table I). A more quantitative probe to assess the degree of randomness can be obtained through measurement of



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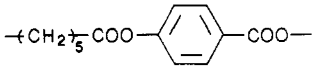

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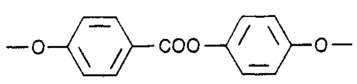

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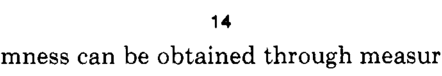

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Table II
Summary of DSC Data

seq struct	T_m, °C	$\Delta H_{k\to lc}$, cal g^{-1}	$\Delta S_{k\to lc} \times 10^3$, cal g^{-1} K^{-1}	T_i, °C
regular	203	2.73	5.7	277
random	146	2.03	4.8	*a*

[a] This transition is too broad to be observed by DSC.

oxybenzoate sequence lengths ($\bar{l}_{OB}$). As we have described previously, polymers synthesized by transesterification have $\bar{l}_{OB}$ values corresponding to random sequences at the diad level.[2] In contrast, measurement of $\bar{l}_{OB}$ from the spectrum shown in Figure 3a for the solution polymerized polymer gives an $\bar{l}_{OB}$ value of 1.0 as it must for completely regular chains. A summary of the ^{13}C NMR data obtained for these two polymers is given in Table I.

DSC data corresponding to the regular and random polymers are summarized in Table II. Both polymers undergo a well-defined solid to liquid crystal transition but only the chemically ordered chains show a sharp clearing point. Also, we find that the DSC scan remains unchanged after three heating–cooling cycles in a standard (nonhermetic) pan under nitrogen flow. As one might expect, the solid to liquid crystal transition of the regular polymer occurs at a temperature which is about 55 °C higher than that of the random polymer. Also, the enthalpy and entropy changes associated with the transition are greater for chains with a regular chemical sequence. In the following manuscript these transitions are discussed further and optical evidence is presented for the appearance of a birefringent fluid above the solid to liquid transition of the ordered polymer.

Conclusions

We have been able to synthesize a chemically ordered and regioregular terpolymer which exhibits liquid crystallinity. Neglecting end groups, this polymer is a constitutional isomer of a chemically random LCP reported previously. The postulated structure of the regular polymer was verified in this work by ^{13}C NMR analysis. The synthesis of ordered–disordered chemical analogues has been difficult in the past either because of the absence of liquid crystallinity in highly regular chains or because of difficulties in developing regioregular polyesters. The pair of macromolecules described here can be used for studies on the role of chemical sequence in the physics of self-ordering polymers.

Acknowledgment. We are grateful to the 3M Co. for support of this work. We also acknowledge Philip G. Martin of our laboratory for carrying out dilute solution viscosity measurements and obtaining DSC data. Finally, we acknowledge use of the Molecular Spectroscopy Laboratory of the School of Chemical Sciences, University of Illinois at Urbana–Champaign.

Registry No. **3**, 113380-57-7; (**3**)(**4**) (copolymer), 113380-59-9; **4**, 142-79-0; **5**, 123-08-0; **6**, 113380-54-4; **7**, 113380-55-5; **8**, 113380-56-6; **10**, 113380-58-8; 4-$PhCH_2OCO_2C_6H_4OH$, 74206-92-1.

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