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Liquid-Crystalline Polymers. 12. Polyesters with either Alternating or Random Orientation of Mesogenic Units

Christopher Ober and Robert W. Lenz*

Materials Research Laboratory, Chemical Engineering Department, University of Massachusetts, Amherst, Massachusetts 01003

Giancarlo Galli and Emo Chiellini

Istituto Chimica Organica Industriale, Università di Pisa, 56100 Pisa, Italy.
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ABSTRACT: A new synthetic route was used to prepare polymers containing either random or alternating sequences of the mesogenic dyad $-O-CO-C_6H_4-O-CO-C_6H_4-CO-O-$. The polymer with random head–tail orientations of the oxybenzoate units in the dyad was thermotropic, but the liquid-crystal phase existed over a much narrower temperature range when compared to that for the polymer with related triad mesogenic units. Surprisingly, the compositionally identical polymer with an exactly alternating head–tail arrangement of mesogenic units in successive dyads did not form a mesophase. Hence, the randomness of mesogenic group orientations in the main chain can be very important in determining mesophase formation and properties.

Introduction

Main-chain thermotropic polymers generally contain mesogenic units consisting of structures with two or more aromatic or cycloaliphatic rings, and these units may or may not be connected by flexible spacers.[1,2] Both the molecular structure of the components and the manner in which they are assembled can have a great effect on the thermal properties of these polymers, as demonstrated by Blumstein and co-workers using azoxy mesogenic groups.[3] In fact, changes of type and even of direction of their connecting bonds alter the geometry and the polarizability of the mesogenic units and ultimately the liquid-crystal properties.

Most synthetic routes result in polymers with a well-defined arrangement of the mesogenic units in the main chain,[2-5] but an outstanding exception to this is the series of thermotropic copolyesters, obtained by melt-phase transesterification, containing several different types of mesogens with a terephthaloyl unit and one or more *p*-oxybenzoyl units.[6-8] Recently we reported[9] on the synthesis of new liquid-crystalline polymers containing regularly "alternating" head-to-tail, tail-to-head aromatic ester dyads with one terephthaloyl, T, and one *p*-oxybenzoyl, O, unit, structure I in Figure 1.

As a part of these studies, polymers were also prepared that contained the aromatic dyad oriented along the polymer chain in a "random" fashion, structure II in Figure 1. These polymers can be considered to be random copolymers of head-to-tail and tail-to-head ester units as indicated in Figure 1. Decamethylenediol and triethylene glycol were chosen as flexible spacers, which were known to be able to yield, under appropriate conditions, smectic-like polyesters.[9,10] As a comparison a polymer sample containing decamethylenediol and the mesogneic dyad with an "alternating" orientation was obtained by the procedure previously reported.[9]

Experimental Section

Benzyl 4-(Carbobenzoxy)phenyl Terephthalate (5). Reflux of 12.3 g (0.048 mol) of **2** in 40 mL (0.37 mol) of $SOCl_2$ was carried out for 1 h in the presence of a catalytic amount of DMF. The $SOCl_2$ was removed, and the white crystalline acid choloride (**3**) was ready for use.

To a solution of 15 g (66 mmol) of **4** in 200 mL of dry pyridine was added 15.5 g (48 mmol) of **3**. The mixture was heated at 60 °C for 4 h, stirred at ambient temperature for 2 days, and poured into 600 mL of 2 N HCl. The precipitate (**5**) was filtered, dried, and crystallized in 95% ethanol: yield 65%; mp 98–100 °C; IR (KBr) 3060 (weak), 1740, 1720, 1710, 1605, 1500, 1450, 1410, 1380, 1370, 1260, 1205, 1160, 1105, 1065, 1015, 760, 730, 715, 695 cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.40–8.05 (m, 3, terephthalate and 2,6-oxybenzoate), 7.65–720 (m, 6, aromatic benzyl and 3,5-oxybenzoate), 5.39 and 5.37 (2 s, 2, CH_2). Anal. Calcd for $C_{29}H_{22}O_6$: C, 74.7; H, 4.7. Found: C, 74.4; H, 4.8.

4-Carboxyphenyl Hydrogen Terephthalate (6). Benzyl-blocked diacid **5** (10 g (0.021 mol)) was dissolved in 150 mL of CF_3COOH, 5 mL of a 33% solution of HBr in CH_3COOH was added, and the mixture was allowed to stir for 4 h. A precipitate formed after about 15 min, and stirring became more difficult. The reaction was stopped by addition of acetone, and the product was filtered, washed with acetone, dried under vacuum, and then crystallized from a 5:1 CH_3COOH/water mixture:[10] yield 79%; dec. >310 °C; IR (KBr) 2900 (very broad), 1745, 1690, 1500, 1425, 1270, 1205, 1165, 1070, 1020, 760, 720 cm^{-1}; ^1H NMR (Me_2SO-d_6) δ 8.45–7.90 (m, 3, terephthalate and 2,6-oxybenzoate), 7.36 (d, 1, 3,5-oxybenzoate). Anal. Calcd for $C_{15}H_{10}O_6$: C, 62.9; H, 3.6. Found: C, 63.2; H, 3.9.

Polymer Preparation and Characterization. Preparation of the diacid chlorides and soltuion polymerization were carried out according to earlier procedures.[9] Viscosity measurements were performed in 1,2-dichloroethane solution at 25 °C by using a Desreux-Bischoff dilution viscometer. Calorimetric analyses were carried out on a Perkin-Elmer DSC-2 apparatus at a heating and cooling rate of 10 °C/min. Indium standards were used for temperature calibration. Thermal-optical analysis (TOA) measurements were made with an American Optical Microstar polarizing microscope, suitably equipped with a Mettler FP5 programmable heating stage and a photometer.

Results and Discussion

The synthetic route leading to the mono(4-carboxyphenyl) ester of terephthalic acid (**6**), a mesogenic structure capable of yielding thermotropic polyesters, is outlined in Scheme I. It is of interest to note that in this reaction sequence, neither **6** nor any of the intermediates have liquid-crystalline properties.

Polymers with randomly oriented mesogenic groups were prepared in 1,2-dichloroethane solution at 60 °C by reacting the diacid **6**, after quantitative in situ conversion to the diacid chloride, with the appropiate diol. The polymeric products were obtained in good yields and were characterized by low molecular weights, as suggested by the values of the intrinsic viscosity, but precise values of molecular weight are not known. The IR and NMR spectra exhibit the expected signals of both reacted monomeric units to substantiate the formation of aryl alkyl polyesters.

In the present case the mesogenic dyads, OT and TO, are "randomly" oriented in the polymer chain, while in the earlier system constitutional regularity was provided by

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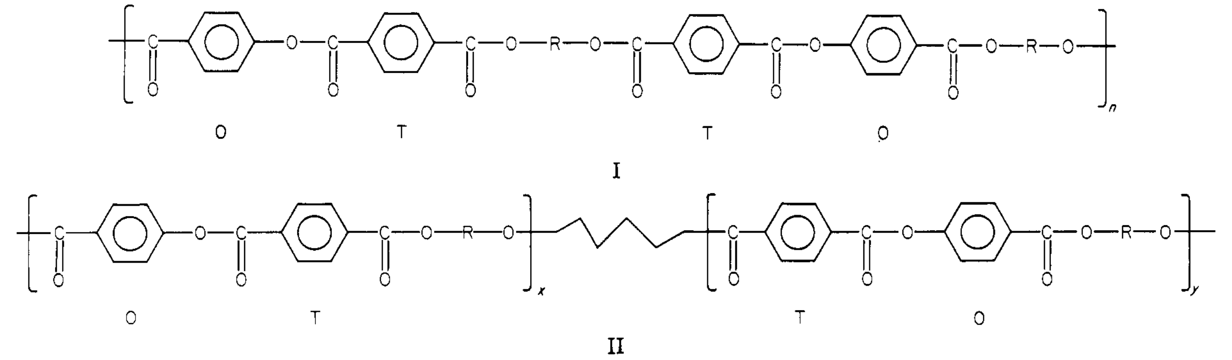


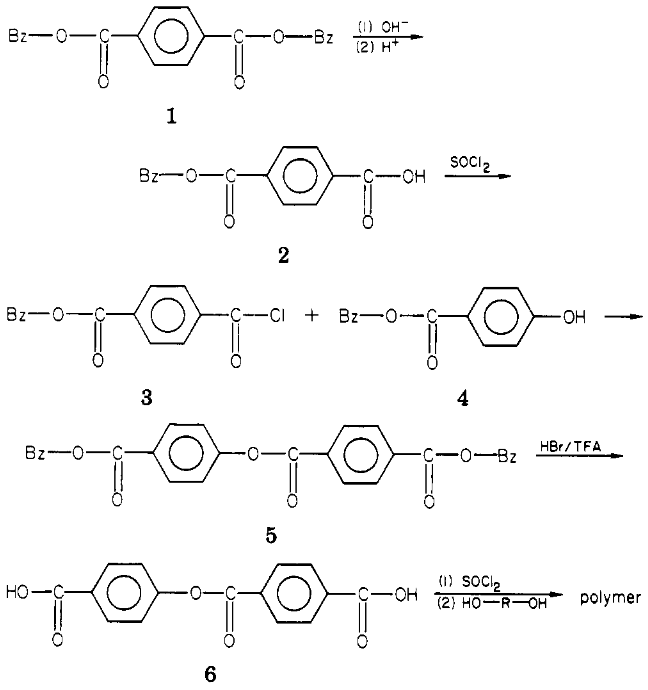
Figure 1. Structure of polymers containing alternating and random orientation of head-to-tail ester dyad units. Structure I, homopolymer with alternating head–tail ester dyads, $-[\mathrm{OTTO}]_n-$. Structure II, polymer with random head–tail orientation of ester dyads, $-[\mathrm{OT}]_x-\sim\sim-[\mathrm{TO}]_y-$.

Table I
Synthesis and Properties of Polyesters Containing Mesogenic Aromatic Dyads

				polymeric product				
polymer	polymer structure	dyad sense[a]	diol[b] monomer	yield, %	diol content,[c] mol %	$[\eta]$,[d] dL/g	T_m,[e] °C	T_i,[e] °C
1	II	R	$H(OCH_2CH_2)_3OH$	46.0	48	0.09	63	86[f]
2	II	R	$HO(CH_2)_{10}OH$	98.7	47	0.17	140	133[g]
3	I	A	$HO(CH_2)_{10}OH$	41.7	52	0.11	140	h

[a] R = random sequences, A = alternating tail-to-tail, head-to-head sequences. [b] Molar ratio diol/diacid = 1:1 in the starting mixture. [c] Determined by NMR. [d] In DCE at 25 °C. [e] Temperature at end of the DSC endothermic peak; see Figures 2 and 3. [f] Optically determined. [g] Observed only on cooling from the melt. [h] No mesophase observed.

Scheme I



their strictly "alternating" arrangement (Figure 1, structures II and I, respectively) of the mesogenic ester dyads in a head-to-head, tail-to-tail sense. At least three mesogenic dyads are needed in the chain to differentiate between the dyad types.

In Table I are summarized some data on the polymerization and properties of the polymers under investigation. The polymer based on triethylene glycol (polymer 1, Table I) was found to have liquid-crystalline properties on analysis by combined thermal and optical analyses. However, the temperature range of existence of the mesophase was very narrow in both the heating and cooling cycles and could not be very accurately determined by DSC, but it was observed by microscopy. The results for polymer 1 of Table I show important differences in the thermal behavior in comparison to those of the previous series of polymers containing three aromatic ester units and the same glycol ether as a spacer.[10] The present polymer composed of only two consecutive aromatic units had a much lower melting point, and the thermal stability of the mesophase was greatly reduced.

Polymer 3 in Table I, containing the mesogenic dyads interconnected by a decamethylene spacer and oriented in an alternating fashion in the main chain, structure I, did not exhibit any thermotropic mesophase. The DSC thermograms of this sample had only a structured and highly endothermic melting transition showing two endothermic peaks (Figure 2, $\Delta H_m = 9.3$ kcal/mol, $\Delta S_m = 24$ cal/(mol K)). Both of these endotherms are melting transitions, and the absence of a mesophase is consistent with our previous report on the same polymer series,[9] for which the mesophase stability significantly decreased on increasing the polymethyl length from $n = 2$ to $n = 6$. The introduction of the longer spacer, $n = 10$, completely prevented the mesophase behavior of the alternating dyad polymer.

Quite surprisingly, polymer 2, the nonordered or random polymer containing the same type of mesogenic dyad and spacer, structure II, did show a mesophase. This difference in behavior is attributable to a lowering and broadening of the melting range due to the effect of the random orientation of the mesogenic dyad (in a head-to-tail sense) along the main chain in polymer 2 as contrasted to the regular orientation in polymer 3. The clearing transition for polymer 2 may be assigned to the weak shoulder on the high-temperature side of the melting curve in both the DSC and TOA thermograms at about 150 °C in Figure 3. However, during the heating cycle on the hot stage of the polarizing microscope, the mesophase could not be observed because melting and clearing occur simultaneously. During the cooling cycle the exothermic transition from the isotropic liquid to the liquid-crystalline state was well

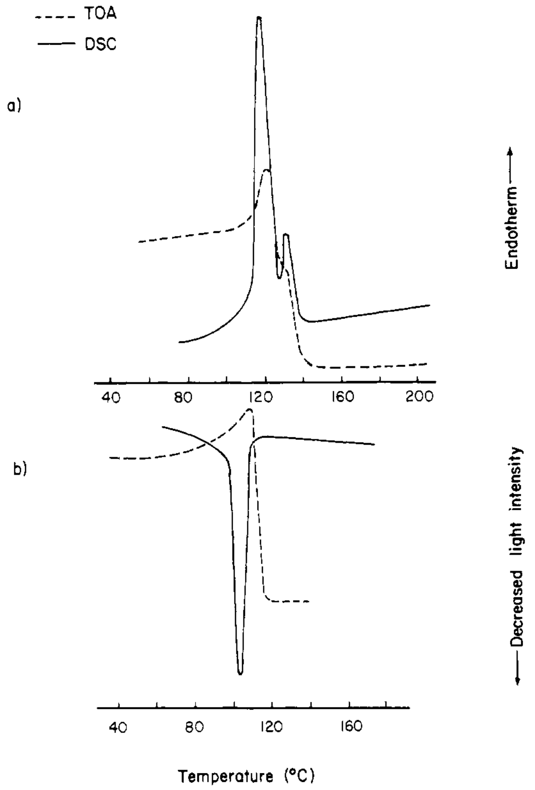


Figure 2. Differential scanning calorimetry (DSC) and thermal-optical analysis (TOA) of the alternating dyad polymer with the decamethylene spacer, polymer 3: (a) heating cycle; (b) cooling cycle.

resolved in the DSC thermogram; see Figure 3. The measured thermodynamic parameters are ΔH_m = 1.9 kcal/mol, ΔS_m = 5.3 cal/(mol K), ΔH_i = 1.1 kcal/mol, and ΔS_i = 2.9 cal/(mol K). Polymer 2, therefore, exhibited monotropism; that is, the mesophase was stable only when obtained by cooling from the isotropic melt, but mesophase formation was not achieved on melting from the crystalline state. It should be pointed out that the previously reported dyad polymer with the hexamethylene spacer was also found to be monotropic.[9] Such behavior is rather unusual for thermotropic main-chain polymers.[2]

The polymers with decamethylene spacers were prepared by different synthetic methods, which might cause some structural differences. Both their ^{13}C and ^{1}H NMR spectra showed essentially identical compositions for both routes, but end groups due to oxybenzoate residues were present in the polymer containing the alternating dyad. While this end unit may have some effect on thermal properties, experience with triad polymers prepared in two different ways showed that the synthetic route chosen had very limited control over the formation of a mesophase by the polymers and so probably was not a factor here.[9]

The effect of molecular weight on the transition temperatures of liquid-crystalline polymers is well documented, and it has been shown that above a critical chain length both the melting and clearing temperatures reach a plateau value.[3,12,13] The disappearance of the mesophase at low molecular weights does not take place even for a degree of polymerization as low as 5, although transition temperatures are depressed. These observations support the conclusion that the differences between the polymers with alternating and random dyads are, in fact, due to structural differences and not a result of low molecular weights. The results, therefore, can be attributed to the importance of the arrangement of the mesogenic unit on mesophase behavior.

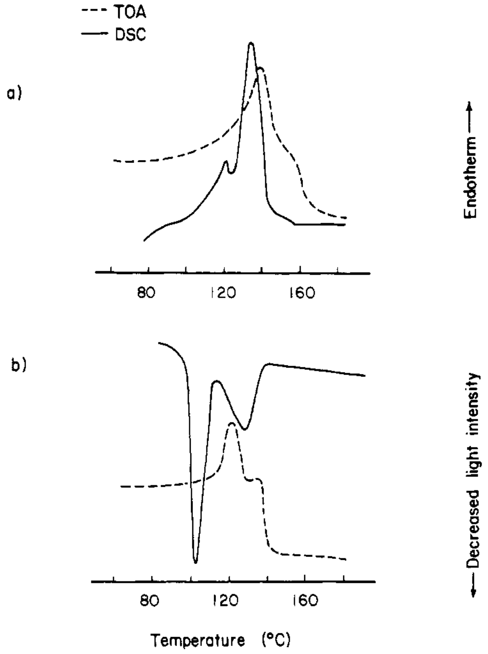


Figure 3. Differential scanning calorimetry (DSC) and thermal-optical analysis (TOA) spectra of the polyester containing aromatic mesogenic dyads randomly oriented, polymer 2: (a) heating cycle; (b) cooling cycle.

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Registry No. 3, 67852-95-3; 4, 94-18-8; 5, 85763-41-3; 6, 85763-38-8; 6-H(OCH_2CH_2)$_3$OH copolymer, 85763-39-9; 6-HO-(CH_2)$_{10}$OH copolymer, 85763-40-2.

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