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Thermotropic Polyesters Based on *trans*-1,4-Cyclohexane Dicarboxylate Mesogens and Flexible Spacer Groups

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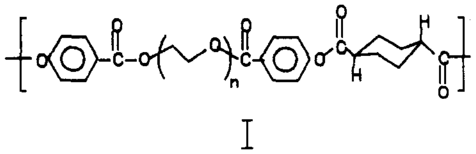
ABSTRACT: The synthesis and properties of a series of thermotropic polyesters based on *trans*-1,4-cyclohexanedicarbonyl chloride and α,ω-oligo(oxyethylene) bis(4-hydroxybenzoate)s are described. They are soluble in halogenated solvents and have low crystalline melting points when compared to thermotropic polyesters with all aromatic mesogenic cores and oxyethylene spacers. Under suitable conditions, molecular weights greater than number average of 25 000 g/mol were achieved. Differential scanning calorimetry and X-ray diffraction showed that the melt-quenched polyesters were noncrystalline. The effects of molecular weight and number of oxyethylenes in the spacer group on mesophase thermal transitions are described. Polarizing microscopy gave evidence of two mesophase types, smectic and nematic, for most of the polyesters. X-ray scattering from the smectic layers was only weakly observed, especially compared to smectic polyesters with all aromatic mesogenic groups. The nematic melts were easily aligned by mechanical drawing. The temperature dependence of the order parameter (S) was measured by infrared spectroscopy. At room temperature S was 0.3–0.4 and decreased irreversibly at temperatures near the smectic–nematic transition. Copolymerization was found to alter the stability of the smectic and nematic states in an unpredictable manner and can provide noncrystalline material with an extended mesophase range.

Introduction

We have been interested in developing low melting thermotropic polyesters for liquid crystal coating systems. Several approaches to lower the melting points of thermotropic polyesters, including the use of flexible spacers, lateral substituents within the mesogen, bent and crankshaft monomers, and copolymerization, have been the topic of reviews.[1–3] Melting points ranging from 120 to 300 °C have been achieved with these approaches. Polyesters with even lower melting points and high solubility characteristics were desired for our applications.

In low molecular weight liquid crystals, cyclohexyl moieties have been used to replace aromatic rings in mesogens to both lower the crystal melting point and increase the breadth of the nematic phase.[4] In polymers, cyclohexyl moieties have also been used in the formation of rigid main-chain polymers,[5–8] block copolyesters,[9] and semiflexible polyesters containing mesogens and flexible spacers.[10,11] In semiflexible polymers, *trans*-1,4-cyclohexanediol and *trans*-1,4-cyclohexane diacid have been used in mesogens together with methylene spacers to give polyesters with enhanced solubility and low crystal melting points.



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We describe here the synthesis and characterization of new thermotropic polyesters (I) with mesogenic cores comprising a *trans*-1,4-cyclohexane diester of 4-hydroxybenzoate and oligo-oxyethylene flexible spacers. These polyesters have low melting points and high solubility in halogenated solvents. They exhibit two distinct mesophases and their transition temperatures show a significant molecular weight dependence.

Experimental Section

The polyesters were prepared according to Scheme I. Dimethyl *trans*-1,4-cyclohexanedicarboxylate was a sample obtained from Eastman Kodak Chemicals. Samples of 2-chloroethyl ether and 1,2-bis(2-chloroethoxy)ethane were purchased from the Aldrich Chemical Co. and Eastman Kodak Chemicals, respectively. The higher oligomers, 1,1′-oxybis[2-(2-chloroethoxy)ethane] and 1,14-dichloro-3,6,9,12-tetraoxatetradecane, were prepared from the corresponding diols by treatment with thionyl chloride and pyridine.[12]

***trans*-1,4-Cyclohexanedicarboxylic Acid.** To dimethyl *trans*-1,4-cyclohexanedicarboxylate (97 g, 0.5 mol) in water–methanol (1:1, 200 mL) was added potassium hydroxide (66 g, 1 mol) in water (300 mL) over 0.5 h at reflux. The mixture was stirred 5 min after the addition was complete and poured, while hot, into a mixture of ice and 6 N hydrochloric acid (180 mL). The white solid was dried overnight under vacuum to give the trans diacid (86 g, 95% yield): mp 312 °C (lit.[6] mp 312–313 °C); ^{13}C NMR (MeOH-d_4) 29.3, 43.6, 179.3 ppm. No peaks due to the cis diacid were evident.

***trans*-1,4-Cyclohexanedicarboxylic Acid Chloride.** A suspension of *trans*-1,4-cyclohexanedicarboxylic acid (34.6 g, 0.2 mol) in 100 mL of toluene was heated to reflux with a Dean-Stark apparatus for 15 min to remove residual water. After the solution was cooled to room temperature, 0.25 mL of dimethylformamide was added, followed by the dropwise addition of thionyl chloride (36 mL, 59.5 g, 0.5 mol) with heating to give an even evolution of gas. After the addition was completed, the mixture was heated to reflux for 0.5 h. Extended heating of the toluene thionyl chloride solution resulted in isomerization of the trans diacid chloride to the cis derivative. Excess thionyl chloride and toluene were distilled at 15 mmHg to give a pale yellow solid. The solid was distilled on a Kugelrohr apparatus, bp 110–125 °C (0.3 mmHg), to give 39.0 g (93%) of the diacid chloride: mp 65–68.5 °C (lit.[6] mp 68–69 °C); ^{1}H NMR (CDCl$_3$/(Me)$_4$Si) 1.4–1.8 (m, 4 H), 2.1–2.4 (m, 4 H), 2.6–2.9 ppm (m, 2 H); ^{13}C NMR 27.7, 53.6, 176.0 ppm; IR (CHCl$_3$) 1790, 1720 cm^{-1}.

Diphenol 1a. A solution of *p*-hydroxybenzoic acid (151.8 g, 1.1 mol) in dimethylformamide (330 mL) was heated to 90 °C with mechanical stirring in a 1-L three-neck flask. Potassium hydroxide (66 g, 85% KOH, 1.0 mol) was added in 8–10 portions over 5 min causing a vigorous exotherm, the temperature rising to 130 °C. The mixture was stirred for 5 min, followed by addition of 2-chloroethyl ether (37.75 g, 0.25 mol) all at once.

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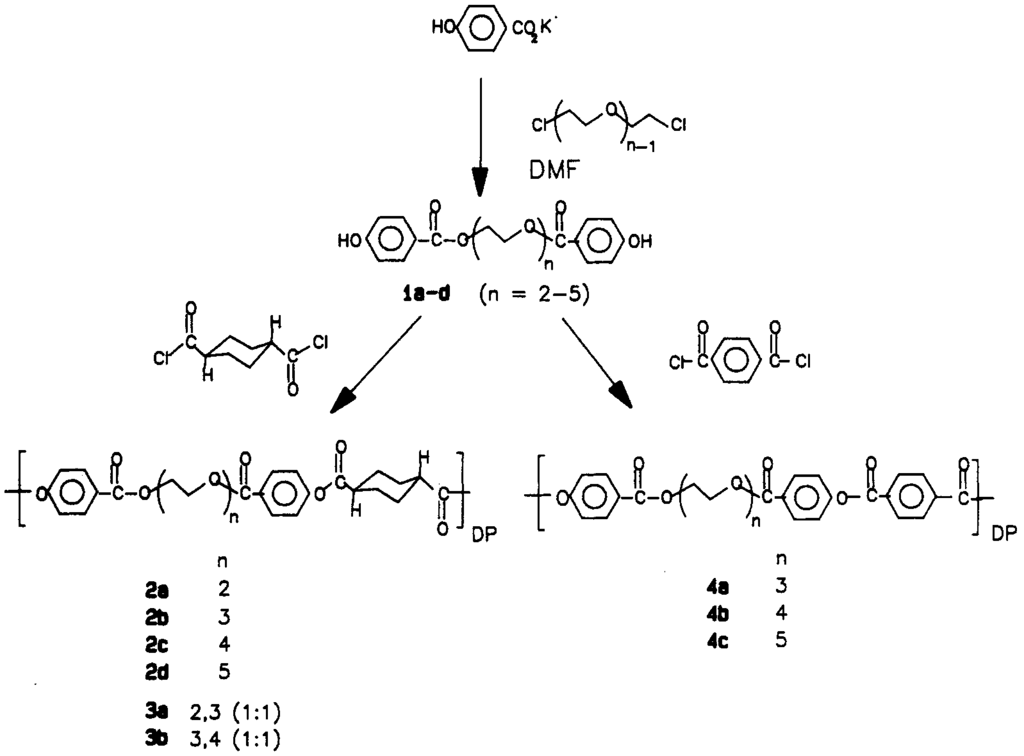
Scheme I



1a–d (n = 2–5)

	n
2a	2
2b	3
2c	4
2d	5
3a	2,3 (1:1)
3b	3,4 (1:1)

	n
4a	3
4b	4
4c	5

The mixture was heated at 120–125 °C for 5.5 h. After being cooled to room temperature, the mixture was washed twice with a total of 1-L of ether–dichloromethane (4:1). The extract was washed twice with 100-mL portions of cold saturated sodium hydrogen carbonate–1 N sodium carbonate (1:1), was washed one time with brine solution, and was dried magnesium sulfate. Concentration at reduced pressure gave a solid (74.0 g) that was recrystallized twice from ethyl acetate–dichloromethane (1:1.5, 425 mL) to give a white solid (43.0 g, 49.5%), mp 134–135.5 °C. Analytical sample prepared from the same solvent: mp 137–138.5 °C (lit.[13] mp 154 °C): ^{1}H NMR ($CDCl_3$ + 5% DMSO-d_6) 7.9 (d, 4 H), 6.85 (d and br s, 6 H), 4.40 (d of d, 4 H), 3.80 ppm (d of d, 4 H); IR (KBr) 3300, 1705, 1680, 1610, 1592 cm^{-1}. Anal. Calcd for $C_{18}H_{18}O_7$: C, 62.42; H, 5.24. Found: C, 62.25; H, 5.33.

Diphenol 1b. Treatment of 1,2-bis(2-chloroethoxy)ethane (46.7 g, 0.25 mol) with *p*-hydroxybenzoic acid as described for **1a** gave a white solid (79.9 g) after concentration of the extract. The solid was worked with hot toluene (400 mL) on a steam bath, cooled to room temperature, and filtered. The process was repeated with toluene–methanol (10:1, 330 mL) to give diphenol **1b**: 36.8 g, 38%; mp 140.5–142.5 °C. Analytical sample prepared from toluene–methanol (10:1): mp 141–143 °C (lit.[13] mp 139 °C): ^{1}H NMR ($CDCl_3$ + 5% DMSO-d_6) 3.7 (s, 4 H), 3.80 (d d, 4 H), 4.36 (d of d, 4 H), 6.85 (d, 4 H), 7.9 ppm (d, 4 H); ^{13}C NMR 63.4, 69.1, 70.5, 115.2, 120.9, 131.6, 161.9, 166.2 ppm; IR (KBr) 3380, 3240, 1708, 1611, 1597 cm^{-1}. Anal. Calcd for $C_{20}H_{22}O_8$: C, 61.53; H, 5.68. Found: C, 61.99; H, 5.71.

Diphenol 1c. Treatment of 1,1′-oxybis[2-(2-chloroethoxy)ethane] (57.75 g, 0.25 mol) with *p*-hydroxybenzoic acid as described for **1a** gave a yellow oil (89.8 g) after concentration of the extract. Chromatography of the oil on silica gel with hexane–ethyl acetate (1:2) gave 61.2 g of colorless oil that was recrystallized from ether to give a white solid (50.6 g, 46.7%), mp 59–61 °C. This material had 0.5 equiv of ether tightly bound to it that was removed by drying at 0.1 mmHg at about 60 °C. Analytical sample prepared from ether: mp 61–64 °C; ^{1}H NMR ($CDCl_3$ + 5% DMSO-d_6) 7.9 (d, 4 H), 7.5 (br s, 2 H) 6.85 (d, 4 H), 4.4 (d of d, 4 H), 3.8 (d of d, 4 H), 3.18 ppm (s, 8 H); ^{13}C NMR 166.5, 161.7, 131.8, 121.1, 115.3, 70.6, 69.2, 63.6 ppm; IR ($CHCl_3$) 3340, 1710, 1611, 1595, 1515 cm^{-1}. Anal. Calcd for $C_{22}H_{26}O_9$: C, 60.82; H, 6.03. Found: C, 61.21; H, 6.27.

Diphenol 1d. Treatment of 1,14-dichloro-3,6,9,12-tetraoxatetradecane (68.8 g, 0.25 mol) with *p*-hydroxybenzoic acid as described for **1a** gave an orange oil (103.3 g) after concentration of the extract. Chromatography of the oil on silica gel with hexane–ethyl acetate (1:2) gave 69.8 g of pale yellow oil that was crystallized from ether–dichloromethane (20:1) to give a white solid (54.8 g, 46%): mp 63.5–66.0 °C; ^{1}H NMR ($CDCl_3$ + 5% DMSO-d_6) 8.1 (br s, 2 H), 7.9 (d, 4 H), 6.85 (d, 4 H), 4.4 (d of d, 4 H), 3.8 (d of d, 4 H), 3.65 ppm (2 s, 12 H); ^{13}C NMR 166.6, 161.6, 131.8, 121.3, 115.3, 70.5, 69.3, 63.7 ppm; IR ($CHCl_3$) 3310, 1710, 1611, 1595, 1517 cm^{-1}. Anal. Calcd for $C_{24}H_{30}O_{10}$: C, 60.24; H, 6.32. Found: C, 59.98; H, 6.24.

Polyesters. The liquid crystalline polyesters were prepared by condensation of diphenols (1) with *trans*-1,4-cyclohexane diacid chloride in 1:1 mixtures of pyridine–dichloroethane or pyridine–tetrahydrofuran solution. The flexible spacer group within the diphenol monomer was varied between two and five ethylene oxide moieties. The ratio of diphenol to diacid chloride was varied from 1.2 to 1 to provide a series of molecular weight ranges. Polyesters of greatest molecular weight were prepared in pyridine–trichlorobenzene solvent with extended periods of heating.

Copolyesters **3a,b** containing two flexible spacer groups were prepared by condensation of the acid chloride with a 1:1 ratio of diphenols.

Polyesters **4a–c** were prepared by the condensation of diphenols **1b–d** with terephthaloyl acid chloride using pyridine–1,2-dichloroethane as solvent. A ratio of 11:10 diphenol to acid chloride was used and the polymer precipitated from the hot solution shortly after the addition of the acid chloride.

Typical Example. To a solution of diphenol **1b** (9.35 g, 24 mmol) in anhydrous pyridine (16 mL) was added a solution of *trans*-1,4-cyclohexanedicarbonyl chloride (4.18 g, 20 mmol) in 1,2-dichloroethane (16 mL) all at once at room temperature. The mixture was heated to reflux for 0.5 h followed by distillation of most of the 1,2-dichloroethane under reduced pressure. The remaining molten mass was worked with warm water four times and once with methanol. The white granular solid was dried at 50 °C at 15 mmHg overnight to provide polyester **2b** (10.8 g, 90%).

Methods. Intrinsic viscosities of selected polyesters were measured at 30 °C in 1,2-dichloroethane. Number-average molecular weights of **2a–d** and **3a,b** were measured by proton nuclear magnetic resonance (NMR) analysis of the phenol end groups using a JEOL 90-MHz instrument. The aromatic protons adjacent to the phenolic hydroxyl group appeared as clearly defined doublets at about 6.8 ppm, upfield from the rest of the aromatic protons. The polyesters based on cyclohexane carboxylic acid chloride were readily soluble in halogenated solvents at room temperature. Gel permeation chromatography (GPC) was used to qualitatively measure the molecular weight dispersities for members of the **2a** and **2b** series. Chloroform was used as eluant and narrow molecular weight polystyrenes as molecular weight calibrants. The number-average molecular weights measured by GPC and by NMR end-group analysis were within 10%.

Differential scanning calorimetry (DSC) measurements were carried out on a Perkin-Elmer DSC4 instrument equipped with a data station. A scan rate of 10 K/min was used with samples of mass 5–10 mg. All experiments were conducted by using a nitrogen atmosphere and scanning base-line subtraction. The maximum in the peak position was taken as the transition temperature. Mesophase ranges were measured with a Leitz optical microscope using a Mettler FP2 and FP52 temperature control. A nitrogen purge was used in most measurements because the polyesters degrade in air at temperatures above 150 °C. Mesophase–mesophase transitions were readily observed under crossed polarizers by the change in texture. Isotropic transition temperatures were identified with the disappearance of birefringence.

For the X-ray measurements, three types of instrument were used. A Philips diffractometer was used to record the wide-angle X-ray scattering (WAXS) pattern in the reflection mode for both crystalline and quenched unoriented polyesters films. Oriented films were prepared by shearing the mesophase melt and quenching to room temperature. Diffraction patterns for these films were recorded onto a flat plate camera with pinhole collimation. Exposure times of up to 8 h were used. Both oriented and unoriented specimens were examined at room temperature by using a Rigaku-Denki low-angle diffraction apparatus with photographic detection. In all cases Cu Kα radiation was used. Polarized infrared spectra were recorded on a Digilab FTS-10 spectrometer at a resolution of four wavenumbers and with the coaddition of one hundred scans.

The polyester films were aligned on polished sodium chloride plates by shearing the mesophase in the nematic state and cooling to ambient with a blast of compressed air. A high-efficiency polarizer was used, and the draw direction of the films was parallel to the polarizer.

Results and Discussion

Synthesis. Liquid crystalline polyesters comprising *trans*-1,4-cyclohexane diesters of 4-hydroxybenzoate and oligo-oxyethylene flexible spacers were prepared by condensation of diphenols **1a–d** with trans-1,4-cyclohexane diacid chloride as outlined in Scheme I. Similar polyesters containing the terephthaloyl moiety in place of the *trans*-1,4-cyclohexane moiety were prepared for comparison purposes. These polyesters have previously been studied by Lenz[14,15] and more recently by Jedlinski and co-workers.[13]

Two of the requisite diphenols,**1a,b**, have previously been reported by Jedlinski.[13] However, we found a very convenient alternative method to prepare the diphenols **1a–d** that is noteworthy. Treatment of the bis(chloroethyl) ethers derived from diethylene glycol, and higher analogues with potassium 4-hydroxybenzoate gave rapid displacement of chloride to provide the diphenols **1a–d** in good yield. In our experience 4-hydroxybenzoate prepared in situ from 85% potassium hydroxide gave significantly higher reaction rates and better yields than when anhydrous potassium 4-hydroxybenzoate in dry dimethylformamide was used. Diphenols **1a** and **1b** could be purified by recrystallization.

Diphenols **1c** and **1d** were more readily purified by preparative chromatography. Yields ranged from 38 to 49%.

Table I
Molecular Weight Data for Polymers 2a–d and 3a,b

polymer	$\bar{M}_n$(NMR)	DP	$\bar{M}_n$(GPC)	$\bar{M}_w/\bar{M}_n$	IV
2a	6000	12	9770	2.6	
2a	11960	25	13670	2.2	0.24
2a	25000	52	30900	2.2	0.45
2b	3400	6	6230	2.2	0.15
2b	5200	10	7300	2.5	0.26
2b	19560	37	25934	2.1	0.5
2c	3600	6			
2c	9900	17			
2c	25000	44			
2d	4000	7			
2d	7200	12			
3a	4000	8			
3a	10000	20			
3b	5200	9			

Molecular Weight. The molecular weights of the liquid crystalline polyesters listed in Table I were determined by solution NMR analysis and, in selected cases, solution viscosity measurements and GPC. The number-average degree of polymerization (DP) was calculated from the number-average molecular weight determined by NMR. The NMR method is limited to molecular weight determinations below 20 000 g/mol. The uncorrected GPC values for the average molecular weights should be considered on relative basis within a series of polyesters. The apparent polydispersities of the polyesters **2a–d** are similar.

Texture Studies. All the polyesters formed turbid melts. Representative optical textures observed in the liquid crystal state of **2b** ($n = 3$, DP = 10) are shown in Figure 1. In general at the crystal–melt transition (T_m), a viscous fluid forms with a nondescript texture (Figure 1i). Further heating results in an obvious decrease in viscosity at one point to give a clearly defined nematic texture (Figure 1ii). This is tentatively assigned to a smectic–nematic transition (T_{sn}). After annealing or the application of mechanical shear, a homogeneous texture usually forms, indicating a well-aligned nematic texture. At the isotropic point there is a rapid and very uniform loss of birefringence with a very narrow biphasic region. Polyesters **2d** ($n = 5$) are the exception. They do not exhibit a clearly defined nematic phase and show a broad biphasic region on heating to the isotropic point.

Upon cooling from the isotropic melt most of the polyesters form nematic homogeneous textures with large domains. A phase transition occurs on further cooling and over a period of minutes to an hour a fanlike smectic texture usually forms (Figure 1iii,iv) on rubbed glass slides. In some preparations a typical nematic–smectic domain texture forms (Figure 1v).[16] Both textures have been observed within one preparation. The latter texture seems to prevail with higher molecular weight polymers on untreated glass.

Thus, optical microscopy observations clearly support the existence of two liquid crystal phases: a high-temperature nematic phase and a lower temperature smectic phase spanning the whole range of molecular weights for polyesters **2a–c**. Polyester **2d** appears to exhibit only one liquid crystal phase, probably a smectic phase, judging from the batonnets that form upon cooling the isotropic melt.

This phase behavior is similar to that described by Lenz et al., for the series of polyesters containing a terephthaloyl moiety in the mesogenic core and oligo-oxyethylene spacer.[14,15] Polyesters containing two to four oxyethylene units showed two liquid crystal phases. Polyesters containing five and seven oxyethylene units showed only a smectic mesophase and those containing six oxyethylene units exhibited both nematic and smectic phases.

Thermal Transitions. The properties of the homopolymers **2a–d** and **3a,b** are listed in Table II. In most cases the transition temperatures determined by DSC correspond well with those measured by hot-stage

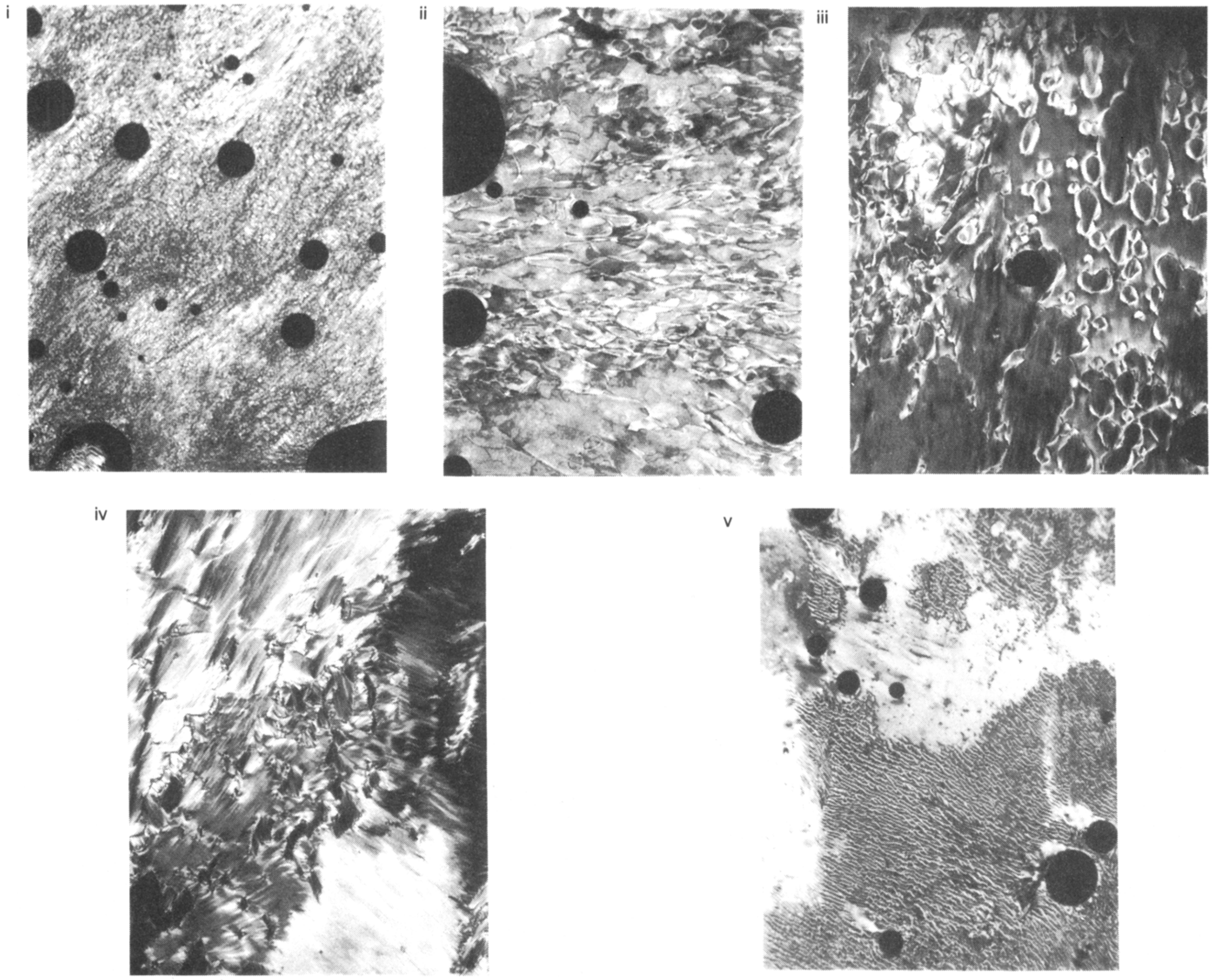


Figure 1. Photomicrographs of a sample of **2b** (DP = 10). Heating from ambient: (i) taken at 120 °C, close to the melting point; (ii) taken at 130 °C. Cooling from isotropic: (iii) taken at 120 °C after annealing for 2 min; (iv) taken at 115 °C after annealing for 10 min; (v) taken at 122 °C after annealing for 10 min (magnification 150×).

Table II
Thermal and Microscopy Data[a] for Polyesters 2a–d and 3a,b

polymer	DP	T_g, °C	T_m, °C	T_{sn}, °C	T_i, °C	ΔH_m, kJ/mol	ΔH_{sn}, J/mol	ΔH_i, J/mol
2a	12	32	111 (115)	124 (125)	190 (193)	10.2	1130	100
2a	25	36	122 (121)	168 (169)	223 (226)	9.7	2020	179
2a	52	53	135 (132)	180 (184)	241 (234)	12.9	2625	200
2b	6	5	119 (118)	109 (104)	153 (160)	15.4	45	440
2b	10	15	122 (121)	128 (131)	180 (181)	14.8	45	660
2b	37	16	123 (124)	160 (160)	201 (200)	14.9	90	880
2c	6	−4	61	91	110	6.2	380	70
2c	17	−3	62	132 (134)	149 (150)	7.4	550	335
2c	44	3	62	149 (149)	163 (163)	10.0	760	405
2d	7	−12	51		58 (66)	9.3		770
2d	12	−11	52		90 (92)	9.9		1670
3a	8	19	73 (75)	90 (93)	171 (170)	7.2	40	210
3a	20	21	90	109	194	4.2	105	465
3b	9	4	80 (85)	137 (136)	166 (169)	8.5	390	410

[a] Data in parentheses determined by hot-stage microscopy.

optical microscopy.

Figure 2 shows DSC curves for as-polymerized samples of **2a** (n = 2, DP = 25) and **2b** (n = 3, DP = 37). The multiple-peaked crystal melting can be attributed to the presence of different size crystallites with melt recrystallization evident in **2b** (DP = 37) with a well-defined exotherm at 100 °C (Figure 2ii).

The polyesters **2a,b,d** crystallize slowly from the supercooled mesomorphic melt phase when annealed between 30 to 50 °C. For example, the half-life of the crystallization process was 20 h for polyester **2b** (n = 3, DP = 10) crystallized at 39 °C. Polyester **2c** (n = 4) did not show any crystallinity after annealing for several days at 30 °C. Both crystalline melting points and enthalpies of fusion for the homopolyesters are lowered with increasing flexible spacer length.

A second DSC scan of the quenched mesomorphic melt was useful in detecting monotropic mesophase transi-

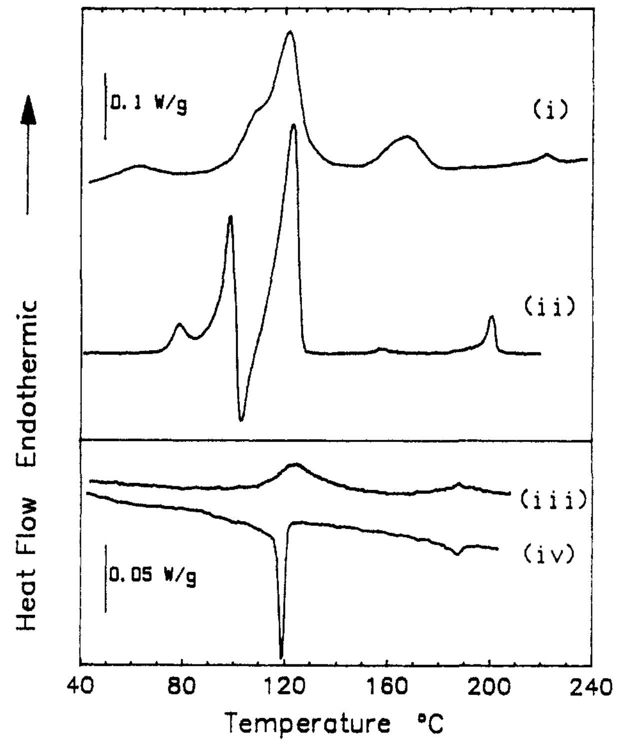


Figure 2. DSC thermograms in the heating cycle for (i) as polymerized sample of **2a** (n = 2, DP = 25) and (ii) **2b** (n = 3, DP = 37). Thermograms of quenched **2a** (DP = 12): (iii) heating cycle; (iv) cooling cycle from 210 °C (scan rate = 10 K/min).

Table III
Mesophase Layer Spacing from X-ray Diffraction (d) and Calculated Monomer Repeat Length (L) for Quenched Polyesters 4a,b

	d, nm	L, nm	
		T_2	T_2G
4b	2.9 (strong)	3.1	2.5
4c	3.2 (strong)	3.4	2.7

tions as shown in Figure 2iii and for the determination of the glass-transition temperature. The glass transitions (T_g) of the polyesters decrease with increasing length of the flexible spacer and increase with molecular weight for a given homopolymer.

For polymers **2a–c**, two endothermic mesophase transitions were detected. They exhibit a smectic mesophase (assigned by observation of the textures on a polarized light microscope) and a nematic phase. The DSC exotherms are also better defined in the cool cycle (e.g. Figure 2iv). Only a small degree of undercooling was observed. The enthalpies obtained on heating and cooling are the same within experimental error. Figure 3 shows the effect of molecular weight on the mesophase transitions of series **2b**. The endotherms are broader for the lower molecular weights and this is a consequence of the polydispersity of the polyesters.

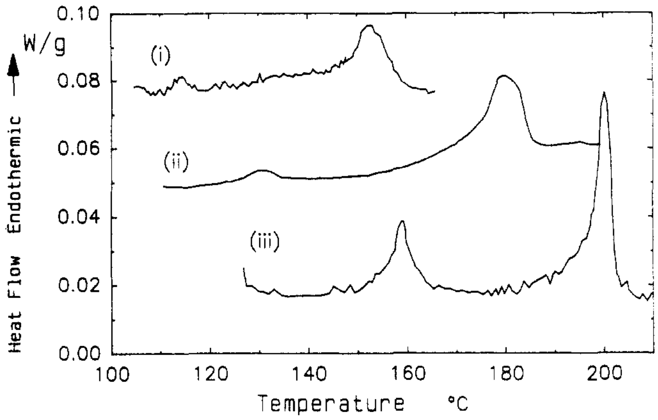


Figure 3. DSC thermograms of the supercooled mesophase melt of polyester series **2b**: (i) DP = 6; (ii) DP = 10; (iii) DP = 37 (heating rate = 10 K/min).

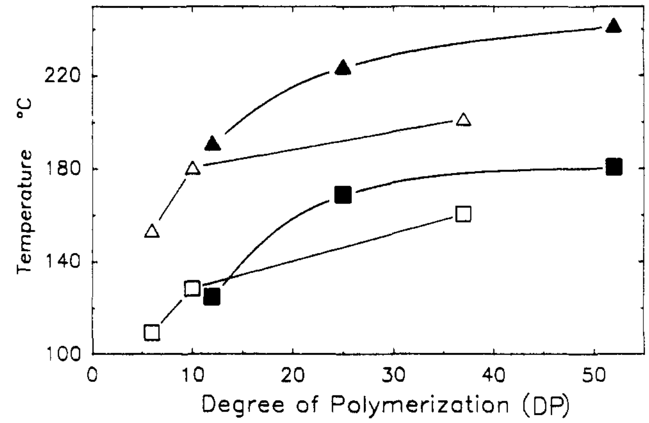


Figure 4. Effect of degree of polymerization on mesophase transitions of series **2a** (closed symbols) and series **2b** (open symbols). DSC transition temperatures: smectic–nematic (squares); nematic–isotropic (triangles).

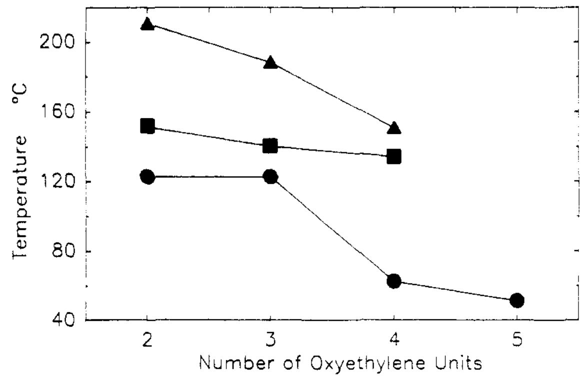


Figure 5. Interpolated DSC transition temperatures as a function of the oxyethylene spacer units (data were interpolated to DP = 20): crystal–smectic (●); smectic–nematic (■); nematic–isotropic (▲).

The smectic–nematic and nematic–isotropic transition temperatures increase with increasing number-average degree of polymerization as shown in Figure 4. At the same time, the enthalpies of the transitions also increase substantially, indicating increased ordering because of cooperative segmental interactions. This behavior has previously been documented for other nematic homopolymers.[17] A comparison of thermodynamic properties of polyesters with different spacer lengths should be made at the same molecular weight. Data were interpolated to a constant number-average degree of polymerization of 20. The interpolated mesophase transition temperatures are plotted in Figure 5. It is predicted that **2d** (n = 5) should not exhibit a thermodynamically stable nematic phase. This is supported by optical microscopy for which a smectic phase was observed. The interpolated mesophase transition entropies and enthalpies are plotted in Figures 6 and 7, respectively. As in the case of other thermotropic polymers there is an odd–even effect in the thermodynamic values.[17] The flexible spacers must participate in the ordering process by affecting the orientational correlation of the rigid group although we cannot deduce the conformational state of the spacer groups in the mesophases from this data alone.

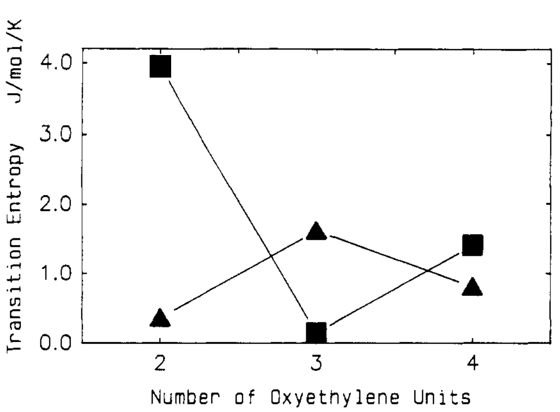


Figure 6. Interpolated transition entropies as a function of the oxyethylene units in flexible spacer: smectic–nematic (■); nematic–isotropic (▲).

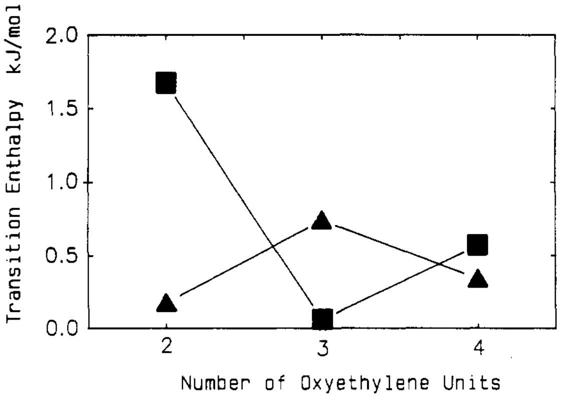


Figure 7. Interpolated transition enthalpies as a function of the oxyethylene units in flexible spacer: smectic–nematic (■); nematic–isotropic (▲).

Table IV
Transitions[a] and Thermodynamic Properties of Polyesters 4a–c

polym	T_g, °C	T_m, °C	T_i, °C	ΔH_m, kJ/mol	ΔH_i, kJ/mol
4a	43	209 (195)	283 (220–270[b])	21.8	5.66
4b	25	148 (145)	221 (217–239)	19.6	4.14
4c	14	138 (141)	164 (162–182)	10.9	2.94

[a] Data in parentheses determined by hot-stage microscopy. [b] Upper temperature limit of the hot stage.

The copolyesters **3a** and **3b** have low crystallinities. They did not crystallize from the supercooled mesophase melt even after annealing at 35 °C for 1 week. The mesophase transition ranges of the copolyesters are modified by the appropriate mixing of diphenols during copolymerization. Most notable, T_m for **3a** (n = 2, 3, DP = 8) is only 73 °C yet exhibits a nematic phase from 90 to 171 °C. However, for **3b** (n = 3, 4) the nematic mesophase range only spanned 29 deg.

The thermal properties of the polyesters based on terephthaloyl acid chloride (**4a–c**) are listed in Table IV. The presence of an all-aromatic mesogenic core results in higher melting points and crystallinities. The melting range of the mesophase to isotropic state is broader than observed for series **2a,b**, and only one endotherm was discernible. Thus, only one mesophase is evident by DSC. The disappearance of birefringence under polarized light is over a wide temperature range. For **4a** (n = 3), a smectic–isotropic biphase develops above 220 °C, with the birefringent regions gradually dissipating as the isotropic point is approached. Cooling of the isotropic fluid results in formation of smectic A batonnets and eventually a fanlike texture. For **4b** (n = 4) at 217 °C an apparent triphasic region consisting of isotropic, smectic, and nematic phases was observed. Cooling from the isotropic gives a smectic A texture in isotropic fluid; on further cooling a triphase was evident with nematic droplets visible.

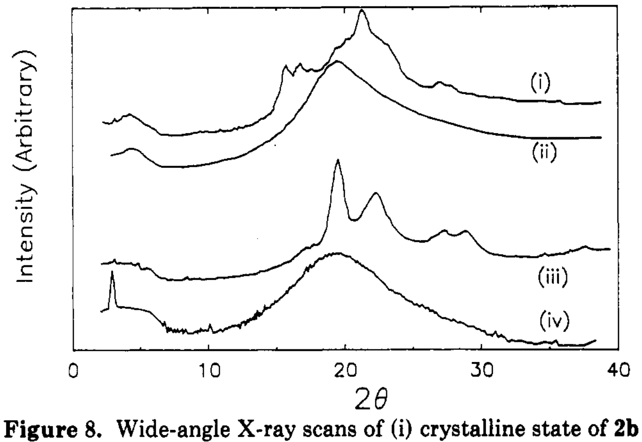


Figure 8. Wide-angle X-ray scans of (i) crystalline state of **2b** (n = 3, DP = 10); (ii) supercooled mesophase of **2b** (DP = 10) recorded at 25 °C; (iii) crystalline state of **4b** (n = 4); (iv) smectic mesophase of **4b** recorded at 160 °C.

The crystal melting points of **4a** and **4b** are 29 and 27 deg higher, respectively, than the corresponding polyesters reported by Lenz.[14] The differences in properties could arise from different synthetic pathways to the polymers resulting in different end groups and molecular weights. Our endotherms corresponded well with those reported by Jedlinski, who used a similar synthetic route.[13]

X-ray Diffraction. The X-ray scattering curves from unoriented polyester **2b** (n = 3, DP = 10) in the crystalline and supercooled (unaligned) mesomorphic state are shown in Figure 8i,ii. The melt-quenched polyesters are all noncrystalline and display a broad diffuse halo at 2θ = 19.7°, indicating an average interchain intermolecular spacing of 0.4 nm. Instrumental artifacts associated with the WAXS reflection technique led to difficulty in interpretation of data below a scattering angle of 2θ = 5°. No definitive diffraction peaks associated with the monomer repeat length were observed for **2a–d** for both the crystalline and supercooled mesomorphic state. A similar observation was made from the small-angle X-ray scattering studies. Very weak diffraction was only observed for **2a** and corresponded to a layer spacing of about 2.1 nm. Since the X-ray experiments were carried out at 25 °C, the quenched polyesters all should be smectic according to the optical microscopy studies.

For the oriented samples of polyesters **2a–d** diffraction arcs equatorial to the mechanical draw direction were observed by using the flat plate technique. The lack of meridional scatter indicates a nonparallel alignment of chains.

Two-dimensional smectic phases usually give a sharp inner ring and diffuse halo. Such discrete X-ray scattering from the smectic layer spacing has been reported for main-chain thermotropic polyesters with azoxybenzene mesogens and oxyethylene spacers.[18] It is useful to compare the results for **2a–d** with the X-ray scattering reported for polyesters with either the same mesogenic unit or flexible spacer group.

Replacement of the cyclohexyl group with a terephthaloyl group results in polyesters **4a–c** with smectic textures under the optical microscope. X-ray diffraction studies of these polyesters have not been reported in the literature. The X-ray diffraction of the crystalline state of **4a–c** does not show any discrete scatter in the region

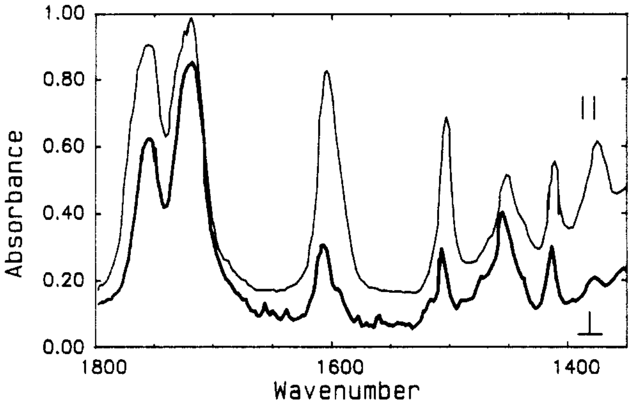


Figure 9. FT-IR spectra of polyester **2b** (DP = 10) oriented by mechanical shear and recorded at 25 °C: (||) electric polarization vector parallel to draw direction; (⊥) electric polarization vector perpendicular to draw direction.

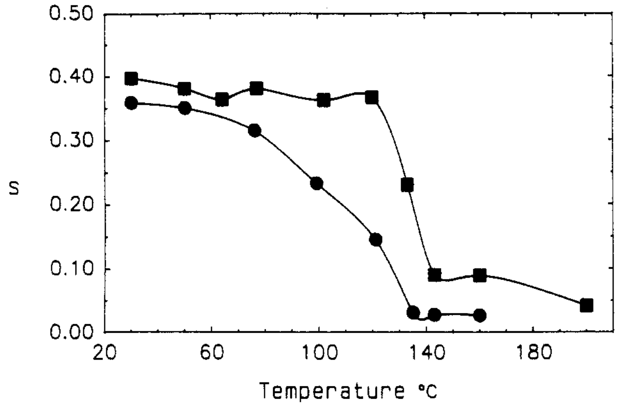


Figure 10. Order parameter as a function of temperature for **2b**: DP = 10 (●) and DP = 37 (■).

expected for the monomer repeat unit. The diffraction curve for crystalline **4b** is shown in Figure 8iii. The crystallinity is reduced by rapid cooling of the polymer melt by quenching in an ice–water bath. For quenched polymers **4b,c**, diffraction peaks corresponding to the smectic layer thickness were readily observed. X-ray scattering was also recorded at 160 °C for **4b** in the smectic state and a layer spacing of 2.9 nm was calculated from the low-angle diffraction peak (Figure 8iv). Results are given in Table III together with the calculated monomer repeat unit length (*L*). This was calculated assuming an extended conformation for the mesogenic core and either an all-trans (T_2) or a helical (T_2G) conformation for the oxyethylene spacer. Steric packing considerations for mesophase formation would favor the most extended structure, and the measured layer spacings are more consistent with the all-trans conformation. Diffraction from smectic layers was also readily observed for a thermotropic polyester based on the condensation of *trans*-1,4-cyclohexanedicarbonyl chloride and 1,10-decamethylene bis(4-hydroxybenzoate).[19]

Thus, the nematiclike X-ray diffraction for the low melting mesophase of **2a–c** is inconsistent with the well-defined smectic structures observed by optical microscopy. The combination of a distorted mesogenic core and flexible oxyethylene spacers probably results in a polymer conformation that deviates significantly from the fully extended state in the mesophase.

Order Parameter. Samples of polyester **2b** with different molecular weights were heated into the nematic state and aligned by mechanical shearing and then quenched to room temperature.

The long-range orientational order parameter, *S*, was estimated by infrared dichroism for the aromatic mesogenic unit in the polyesters. An aromatic ring vibration (1610 cm^{-1}) was chosen because this band is well isolated (Figure 9) and the transition moment is nearly parallel to the major axis of the molecule. The transition moment of this vibration was calculated for a model compound, methyl (4-acetyloxy)benzoate, using the MOPAC computer program to generate the force constants.[20]

The dichroic ratio in the x–y plane of the film (R_{xy}) is the ratio of the area of the absorbances with radiation recorded parallel and then perpendicular to the mechanical draw direction. In all cases, R_{xy} was greater than 1, indicating that the long axis of the mesogen was aligned with the mechanical draw direction and is in agreement with the X-ray diffraction results. The order parameter of the aromatic mesogen was calculated by using equations that have been applied to low molecular weight liquid crystals:

$$S = \frac{(R_{xy} - 1)}{(R_{xy} + 2)}$$

The value of *S* was found to vary with the draw-down technique. For the polyester **2b** (DP = 37) the highest value of *S*, measured at 30 °C, is 0.55, with 0.3–0.4 being typical for all the polyesters. The molecular weight of the polyester did not affect the extent of orientation, which reflects the ease in which the low-viscosity mesogenic state can be oriented by shear, increasing their utility for practical coating applications.

Measurements were also made on **2b** (DP = 10 and 37) as a function of temperature (Figure 10). The order parameter was observed to decrease rapidly above 120 °C for the higher molecular weight, while the decrease in *S* was over a broader temperature range for the lower molecular weight polyester. This effect is a reorientation phenomenon because of the low melt viscosity in the nematic state. On cooling the sample from 140 °C to ambient, the order parameter retains the reduced value measured at the higher temperature. The polyesters should therefore be cooled as rapidly as possible to retain their alignment.

All the polyesters are easily aligned in the nematic state without the use of strong electric or magnetic fields, increasing their utility for practical coating applications.

Conclusions

The new series of polyesters described in this work all exhibited mesomorphic properties. They have low crystal melting points, broad mesophase ranges, and high solubilities in halogenated solvents. The mesophases were identified by using optical microscopy and exhibited well-defined textures and little or no biphasic regions near the transition points. The increase in the transition temperatures with molecular weight is also consistent with a liquid crystal state. The weak or in most cases undetectable discrete X-ray diffraction expected from the layer structure of the smectic state indicates a poor degree of molecular alignment within the smectic planes. Order parameter measurements indicate that significant alignment of the mesophase is observed from these polyesters after mechanical shearing. The low melting points, broad mesomorphic temperature ranges, and facile alignment make these polyesters valuable for liquid crystal coating systems.

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Registry No. 2a (copolymer), 126035-73-2; **2a** (SRU), 126035-82-3; **2b** (copolymer), 126035-74-3; **2b** (SRU), 126035-83-4; **2c** (copolymer), 126035-75-4; **2c** (SRU), 126035-84-5; **2d** (copolymer), 126035-77-6; **2d** (SRU), 126035-85-6; **3a**, 126035-78-7; **3b**, 126035-79-8; **4a** (copolymer), 105709-24-8; **4a** (SRU), 84329-77-1; **4b** (copolymer), 126035-80-1; **4b** (SRU), 84329-76-0; **4c** (copolymer), 126035-81-2; **4c** (SRU), 116695-92-2.

Monte Carlo Simulations of Ultrathin Polymer Blend Films: Influence of Interaction Strength on Segregation and Shape of Coils

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ABSTRACT: The influence of the interaction strength on segregation and anisotropy of individual polymer coils is studied by Monte Carlo simulations of chains on a square lattice for a homopolymer blend, a random copolymer/homopolymer blend, and a pure random-copolymer melt. These simulations show that in a two-dimensional blend an increase in interaction strength causes anisotropic swelling of polymer coils. The anisotropic swelling is less pronounced for the random copolymer/homopolymer blend where intramolecular repulsion also induces internal reorganization of the polymer coils. For realistic values of the interaction parameter segregation of individual coils remains a dominant feature. Therefore, in ultrathin polymer blend films a characteristic microdomain morphology may be present even if both components are *miscible*.

Introduction

Two-dimensional polymer blends were investigated as a starting point for a more detailed study of the influence of the strength and type of interactions on polymer conformations and phase behavior in thin polymer films. Although truly two-dimensional polymer systems probably do not exist, the present study is directed to those properties that are believed to be of relevance for real polymer monolayers as well. Support for the existence of two-dimensionally coiled conformations was given by M. Watanabe et al.[1] They produced Langmuir–Blodgett films of poly(vinyl alkylals) consisting of hydrophilic main chains spread over the air/water interface with the hydrophobic side chains approximately normal to the interface. All observations indicated that the main chains had two-dimensional coiled conformations. From the limiting area results they concluded that the two-dimensional coiled main chains were packed very closely. Monolayers of mixtures of polymers at the water/air interface were already considered by Gabrielli and co-workers.[2,3] A typical example is given by mixtures of poly(methyl methacrylate) and poly(propyl methacrylate). These polymers were shown to be miscible, and the miscibility was ascribed to the interaction between the hydrophobic chains that were almost parallel to the air/water interface.

In the common bulk situation the driving forces for polymer miscibility can be divided into two principal classes: intramolecular repulsion and specific interactions. The intramolecular repulsion effect is characteristic for many blends involving random copolymers[4,5] but is also suggested to be of importance for blends of homopolymers such as poly(vinyl chloride) with aliphatic polyesters[6] or polyamide blends.[7] A clear example of specific intermolecular interactions is sulfonated polystyrene with poly(4-vinylpyridine).[8] Both classes will be considered and compared in the present study.

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