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Synthesis and Characterization of Novel Side-Chain Liquid-Crystalline Polyesters

Jouni Hamara^a; Kari Liinamaa^a; Robert Jansson^a; Franciska Sundholm^a

^a Department of Polymer Chemistry, University of Helsinki, Helsinki, Finland

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SYNTHESIS AND CHARACTERIZATION OF NOVEL SIDE-CHAIN LIQUID-CRYSTALLINE POLYESTERS

JOUNI HAMARA,* KARI LIINAMAA, ROBERT JANSSON,
and FRANCISKA SUNDHOLM

Department of Polymer Chemistry
University of Helsinki
Helsinki, Finland

ABSTRACT

Novel side-chain liquid-crystalline polyesters have been synthesized by direct polyesterification of phthalic anhydride, pentaerythritol, and 4-methoxy-4'-oxybiphenyl-substituted monocarboxylic acids with different lengths of spacers. The polyesters were characterized by ¹H- and ¹³C-NMR spectroscopy, differential scanning calorimetry (DSC), gel permeation chromatography (GPC), and optical polarized light microscopy. The polymerizations reached high conversion, the number-average molecular masses were 2900–3300 g/mol, and the polydispersity indices were 4.7–12.1, respectively. The thermal properties of the polyesters varied greatly. They had one to four endothermic transitions on heating and one or two exotherms on cooling. After the first heating cycle, subsequent heating and cooling cycles on each polymer gave virtually identical DSC thermograms. Mesophases are presumed to be of the smectic type.

INTRODUCTION

Side-chain liquid-crystalline polymers (SCLCP) have been extensively studied since Finkelmann et al. first introduced polymers of this type [1]. This class of polymers has been the subject of several reviews [2–5]. The types of polymer backbones which have been employed are relatively few. The most widely used back-

bones are polyacrylates [2–4, 6], poly(methacrylates) [2, 4, 6], polysiloxanes [2, 4, 6], and poly(vinyl ethers) [7–9]. In a few cases poly(epichlorohydrins) [10] and polyoxetames [11, 12] were used. Very few papers are concerned with polyesters [13–16]. SCLCPs of these types may be homopolymers or block or random copolymers; it is characteristic of all of them that they have a relatively narrow molecular mass distribution. Thermotropic hyperbranched liquid-crystalline polymers are gaining interest as a novel class of macromolecules. Percec et al. recently published reports of polymers containing disklike mesogens and displaying a columnar hexagonal mesophase as well as dendrimeric polymers displaying a nematic mesophase [17, 18]. There are several reports of the influence of the molecular mass and the molecular mass distribution on the phase transitions of side-chain liquid-crystalline polymers. Increasing the molecular mass of a polymer increases the isotropization temperature; the higher the polydispersity, the broader is the transition temperature range [4, 8, 9, 19–23].

This paper reports our first series of experiments on the synthesis and characterization of novel side-chain liquid-crystalline polyesters containing a branched polymer backbone and a 4-methoxy-4'-oxybiphenyl group as a side-chain with varying spacer lengths. The polymerizations were performed by direct esterification at an elevated temperature of tetrafunctional pentaerythritol, bifunctional phthalic anhydride, and monofunctional mesogenic carboxylic acids. The method is widely used by the paint industry in the preparation of alkyd resins. The polymerization method used, polycondensation at an elevated temperature, creates some unavoidable side reactions. The most general side reactions in this method are etherification, ring formation, and transesterification. Due to the side reactions, the properties of the polyesters greatly vary although the composition of the starting materials and the process are maintained the same. The polyester resins are usually very polydisperse and heterogeneous materials containing monomers and oligomers with varying molecular masses and even gel particles.

Polymerization by direct polycondensation opens many possibilities for tailoring the structure and properties of the resulting polyesters by using mesogenic and nonmesogenic monomers and branching units in different proportions. The synthesis, characterization, and phase transitions of liquid-crystalline model alkyd resins are presented in this paper.

EXPERIMENTAL

Materials

4,4'-Dihydroxybiphenyl and dimethylsulfate were both from Merck. Ethyl 3-bromopropionate, ethyl 5-bromovalerate, ethyl 6-bromohexanoate, and 8-bromooctanoic acid were all from Aldrich. 11-Bromoundecanoic acid was from Sigma. Decanoic acid and phthalic anhydride were from Bie & Berntsen. Monopentaerythritol was from Perstorp Polyols. All chemicals were used as received.

Methanol (Merck) was refluxed over magnesium and freshly distilled before use.

Techniques

^1H - and ^{13}C -NMR spectra were recorded on a Varian Gemini 200-NMR spectrometer. The spectra were obtained in CDCl_3 , $(\text{CD}_3)_2\text{SO}$, or D_6 -acetone solutions

with TMS as the internal standard. The solid-state ^{13}C -NMR spectrum was obtained with a JEOL FX 200 spectrometer. A Perkin-Elmer DSC-7 differential scanning calorimeter was used to determine the melting points of the monomers and the thermal transitions of the polyesters. Heating and cooling rates were $20^\circ\text{C}/\text{min}$; indium and water were used as the calibration standards. The thermal transitions of the polymers were determined as the maxima and minima of their endothermic and exothermic peaks, respectively. The melting points of the monomers and the intermediates were read at the onset temperature. Glass transition temperatures (T_g) were read at the middle of the change in heat capacity. A Zeiss Jenapol optical polarized light microscopy (magnification 100–500 \times), equipped with a Mettler FP82 hot stage and a Mettler FP80 central processor, was used to observe the thermal transitions and to analyze the anisotropic textures. Acid numbers were determined by titration with sodium methoxide solution; phenophtalein was the indicator.

Molecular masses and molecular mass distributions were determined by gel permeation chromatography in a set-up containing the following components: Reodyne 1724 injector, Perkin-Elmer LC250 pump, SI316 and LC1100 interface, and 7700 computer. The measurements were made by using the Erma ERC 7512 refractive index detector and a set of Toyo Sodo TSK gel columns of 3000, 4000, 5000, and 9200 Å. A calibration curve was constructed with polystyrene standards. The concentration of the samples was 1% and THF was used as the eluent. Infrared spectra were recorded with a Nicolet 205 FT-IR spectrometer. The thermal stability of the monomers was tested by a Mettler M3 differential thermogravimetry and a TC10 processor with a $10^\circ\text{C}/\text{min}$ heating rate.

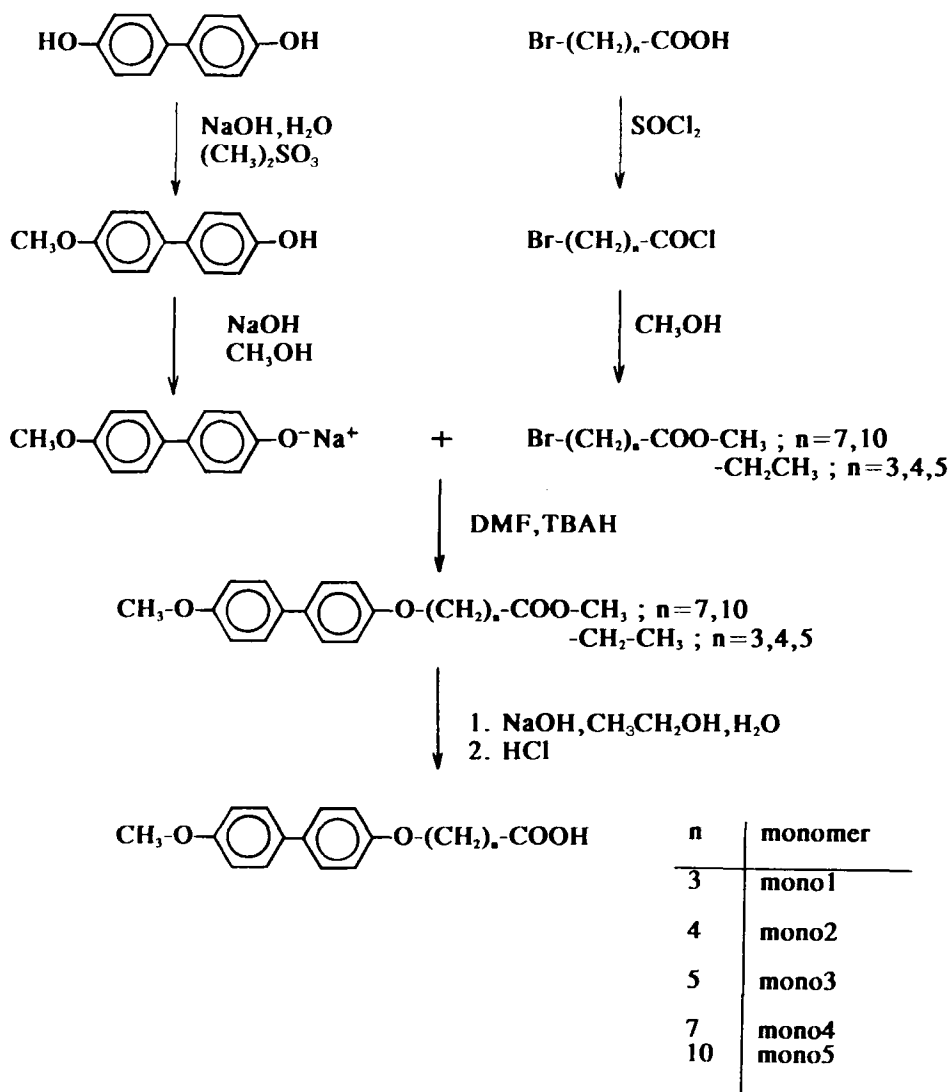
The synthetic route of the 4-methoxy-4'-oxybiphenylalkanoic acid monomers is shown in Scheme 1.

4-Methoxy-4'-hydroxybiphenyl

4-Methoxy-4'-hydroxybiphenyl was synthesized by modifying the method described by Rodriguez-Parada et al. [24]. Water (400 mL) was purged with N_2 for half an hour before adding 4,4'-dihydroxybiphenyl (100 g, 0.54 mol), NaOH (43.0 g, 1.08 mol), and $\text{Na}_2\text{S}_2\text{O}_4$ (0.8 g). Dimethylsulfate (68.0 g, 0.54 mol) was added over a period of 4 hours, and the solution was stirred until the whole reaction mixture solidified. The precipitate was filtered and washed twice with 400 mL of 10% aqueous NaOH and then with water. The solid residue was then dissolved in 3 L boiling water, and the insoluble 4,4'-dimethoxybiphenyl was separated by filtration of the hot solution. The crude product was precipitated by the addition of dilute HCl, then filtered, washed with water, and recrystallized three times from ethanol. The yield after purification was 55.0 g (51%), mp 183°C . ^1H -NMR (D_6 -acetone, TMS): 3.8 (s, 3H, $-\text{CH}_3$), 7.0, 7.5 (m, 8H, aromatic proton), 8.5 (s, 1H, $-\text{OH}$).

Methyl 8-bromooctanoate and Methyl 11-bromoundecanoate

Methyl 8-bromooctanoate and methyl 11-bromoundecanoate were prepared as described by Centore et al. [25]. 8-Bromooctanoic acid (10.0 g, 4.5 mmol) was refluxed with an excess of thionyl chloride (75 mL) until no further evolution of HCl was observed. Unreacted thionyl chloride was removed by distillation under



SCHEME 1. The synthesis of the 4-methoxy-4'-oxybiphenyl alkanoyl acid monomers.

reduced pressure, and the 8-bromooctanoyl chloride was collected. The chloride was added dropwise under a flow of nitrogen to an excess of dry methanol (150 mL). The mixture was allowed to react overnight at room temperature with constant stirring. The excess of methanol was then removed by distillation under reduced pressure, and methyl 8-bromooctanoate was collected as a distillation residue. Methyl 11-bromoundecanoate was synthesized in a similar way. The bromoesters were used without further purification by the following synthesis steps.

Ethyl-4-(4-methoxy-4'-oxybiphenyl)butyrate
Ethyl-5-(4-methoxy-4'-oxybiphenyl)valerate
Ethyl-6-(4-methoxy-4'-oxybiphenyl)hexanoate
Methyl-8-(4-methoxy-4'-oxybiphenyl)octanoate
Methyl-11-(4-methoxy-4'-oxybiphenyl)undecanoate

The esters were prepared by the method described by Pugh and Percec [26]. The general procedure used is presented by the following example: 4-methoxy-4'-hydroxybiphenyl (15.0 g, 7.5 mmol) was converted to sodium salt by a stoichiometric reaction of NaOH in methanol solution, followed by solvent evaporation and drying. The salt was used without further purification. It was dissolved in 300 mL dimethylformamide (DMF). Tetra-*n*-butylammonium hydrogensulfate (TBAH) (2.6 g, 6.0 mmol) and ethyl 4-bromobutyrate (20.0 g, 0.1 mol) were added, and the reaction mixture was stirred at 80–90°C for 5 hours. The product was precipitated in 1.5 L dilute HCl with ice, filtered, dried, and recrystallized three times from ethanol. The yield was 13.7 g (58%), mp 102°C, IR 1735 (C=O, ester). ¹H-NMR (CDCl₃, TMS): 1.3 (t, 3H, -CH₃), 2.1 (m, 2H, -CH₂-), 2.5 (t, 2H, -CH₂-COO-), 3.8 (s, 3H, -OCH₃), 4.0 (t, 2H, -O-CH₂-), 4.1 (q, 2H, -COO-CH₂-), 7.0, 7.5 (m, 8H, aromatic proton).

Ethyl-5-(4-methoxy-4'-oxybiphenyl)valerate. Yield 74%, mp 97°C, IR 1750 (C=O, ester). ¹H-NMR (CDCl₃, TMS): 1.3 (t, 3H, -CH₃), 1.9 (m, 4H, -CH₂-), 2.4 (t, 2H, -CH₂-COO-), 3.8 (s, 3H, -OCH₃), 4.0 (t, 2H, -O-CH₂-), 4.1 (q, 2H, -COO-CH₂-), 7.0, 7.5 (m, 8H, aromatic proton).

Ethyl-6-(4-methoxy-4'-oxybiphenyl)hexanoate. Yield 73%, mp 99°C, IR 1735 (C=O, ester). ¹H-NMR (CDCl₃, TMS): 1.3 (t, 3H, -CH₃), 1.6–1.9 (m, 6H, -CH₂-), 2.4 (t, 2H, -CH₂-COO-), 3.8 (s, 3H, -OCH₃), 4.0 (t, 2H, -O-CH₂-), 4.1 (q, 2H, -COO-CH₂-), 7.0, 7.5 (m, 8H, aromatic proton).

Methyl-8-(4-methoxy-4'-oxybiphenyl)octanoate. Yield 76%, mp 112°C, IR 1750 (C=O ester). ¹H-NMR (CDCl₃, TMS): 1.3–1.8 (m, 10H, -CH₂-), 2.3 (t, 2H, -CH₂-COO-), 3.6 (s, 3H, -COO-CH₃), 3.8 (s, 3H, -OCH₃), 4.0 (t, 2H, -O-CH₂-), 7.0, 7.5 (m, 8H, aromatic proton).

Methyl-11-(4-methoxy-4'-oxybiphenyl)undecanoate. Yield 78%, mp 119°C, IR 1740 (C=O, ester). ¹H-NMR (CDCl₃, TMS): 1.2–1.9 (m, 16H, -CH₂-), 2.3 (t, 2H, -CH₂-COO-), 3.7 (s, 3H, -COO-CH₃), 3.9 (s, 3H, -OCH₃), 4.0 (t, 2H, -O-CH₂-), 7.0, 7.5 (m, 8H, aromatic proton).

4-(4-Methoxy-4'-oxybiphenyl)butyric acid (mono1)
5-(4-Methoxy-4'-oxybiphenyl)valeric acid (mono2)
6-(4-Methoxy-4'-oxybiphenyl)hexanoic acid (mono3)
8-(4-Methoxy-4'-oxybiphenyl)octanoic acid (mono4)
11-(4-Methoxy-4'-oxybiphenyl)undecanoic acid (mono5)

The acids were prepared by hydrolyzing the corresponding esters for 4 hours with a 20-fold excess of sodium hydroxide in aqueous ethanol. The acids were precipitated in dilute HCl with ice, filtered, dried, and recrystallized several times from toluene.

Mono1: Yield 69%, mp 183°C, IR 3400–2400 (OH), 1700 (C=O, acid), 935 (OH, acid). ¹H-NMR (Me₂SO-D₆, TMS): 2.0 (m, 2H, –CH₂–), 2.4 (t, 2H, –CH₂–COO–), 3.8 (s, 3H, –OCH₃), 4.0 (t, 2H, –O–CH₂–), 7.0, 7.5 (m, 8H, aromatic proton), 12.2 (s, 1H, –COOH).

Mono2: Yield 62%, mp 182°C, IR 3300–2400 (OH), 1700 (C=O, acid), 925 (OH, acid). ¹H-NMR (Me₂SO-D₆, TMS): 1.7 (m, 4H, –CH₂–), 2.3 (t, 2H, –CH₂–COO–), 3.8 (s, 3H, –OCH₃), 4.0 (t, 2H, –O–CH₂–), 7.0, 7.5 (m, 8H, aromatic proton), 12.1 (s, 1H, –COOH).

Mono3: Yield 76%, mp 159°C, IR 3400–2400 (OH), 1705 (C=O, acid), 900 (OH, acid). ¹H-NMR (Me₂SO-D₆, TMS): 1.4–1.8 (m, 6H, –CH₂–), 2.3 (t, 2H, –CH₂–COO–), 3.8 (s, 3H, –OCH₃), 4.0 (t, 2H, –O–CH₂–), 7.0, 7.5 (m, 8H, aromatic proton), 12.1 (s, 1H, –COOH).

Mono4: Yield 82%, mp 147°C, IR 3300–2400 (OH), 1705 (C=O, acid), 920 (OH, acid). ¹H-NMR (Me₂SO-D₆, TMS): 1.2–1.8 (m, 10H, –CH₂–), 2.3 (t, 2H, –CH₂–COO–), 3.8 (s, 3H, –OCH₃), 4.0 (t, 2H, –O–CH₂–), 7.0, 7.5 (m, 8H, aromatic proton), 12.0 (s, 1H, –COOH).

Mono5: Yield 78%, mp 160°C, IR 2400–2400 (OH), 1710 (C=O, acid), 925 (OH, acid). ¹H-NMR (Me₂SO-D₆, TMS): 1.2–1.8 (m, 16H, –CH₂–), 2.2 (t, 2H, –CH₂–COO–), 3.8 (s, 3H, –OCH₃), 4.0 (t, 2H, –O–CH₂–), 7.0, 7.5 (m, 8H, aromatic proton), 12.0 (s, 1H, –COOH).

4-(4-Methoxy-4'-oxyphenyl)butyric acid (mono6)

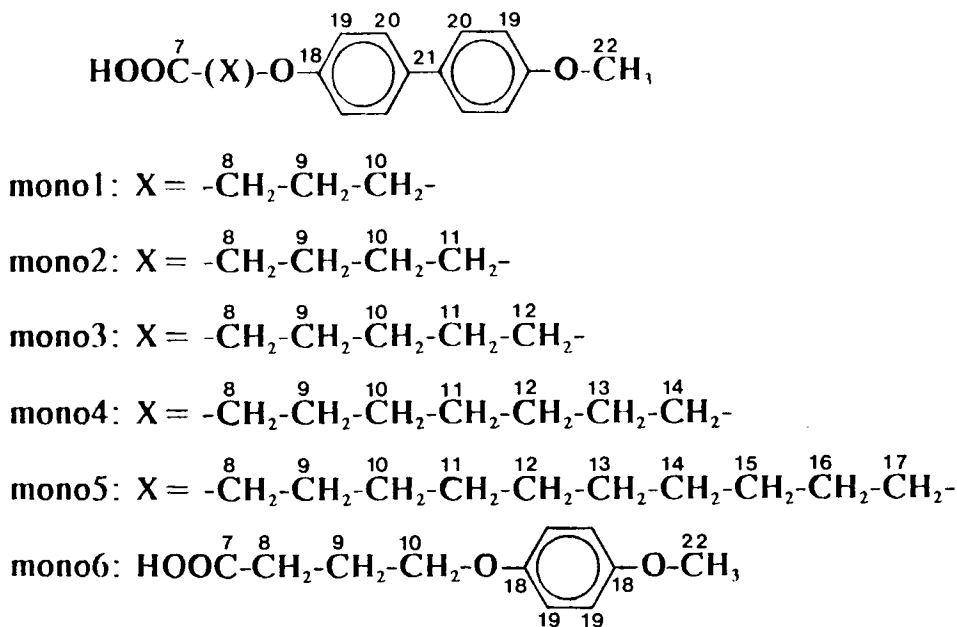
p-Methoxyphenol (20.0 g, 0.16 mol) was converted to its sodium salt by stoichiometric reaction with NaOH in methanol followed by solvent evaporation and salt drying. It was dissolved in DMF (400 mL), and a catalytic amount of TBAH (2.7 g, 8.0 mmol) was added. Ethyl-4-bromobutyrate (41.1 g, 0.21 mol) was added dropwise, and the reaction mixture was allowed to react for 5 hours at 85°C under agitation. The reaction mixture was diluted with water (500 mL) and acidified with HCl. The ester was extracted into dichloromethanol. The solvent was evaporated out and the residue was hydrolyzed in 20% NaOH aqueous ethanol. The mixture was acidified with HCl and the precipitate was filtered, dried, and recrystallized three times from toluene. The yield after purification 16 g (47%), mp 104°C, IR 3300–2300 (OH), 1720 (C=O, acid), 920 (OH, acid). ¹H-NMR (CDCl₃, TMS): 2.1 (m, 2H, –CH₂–), 2.6 (t, 2H, –CH₂–COO–), 3.8 (s, 3H, –OCH₃), 4.0 (t, 2H, –O–CH₂–), 6.9 (m, 4H, aromatic proton).

The formulas of the monomers mono1–mono6 are illustrated in Scheme 2, and the corresponding ¹³C-NMR chemical shifts are presented in Table 1.

Polymerization Procedure

The polyesters were prepared by a conventional alkyd baking method with azeotropic water removal. Formulation parameters in the polymerizations were a hydroxyl excess of 15% and an effective average functionality of 2.08. The polymerization procedure is demonstrated by the polymerization containing monomer mono1.

Mono1 (1.24 g, 4.33 mmol), phthalic anhydride (0.61 g, 4.11 mmol), and pentaerythritol (0.50 g, 3.61 mmol), were placed in a 10-mL pear-shaped reaction



SCHEME 2. Assignment of carbons in monomers mono1-mono6 for ^{13}C -NMR spectra.

flask immersed in a silicon oil heating bath with magnetic stirring. The flask was equipped with a Dean-Stark trap, a reflux condenser, and an N_2 inlet. A small amount of xylene (5 wt% of monomers) was added as azeotropic solvent. The amount of xylene was maintained by adding small amounts occasionally to replace the amount carried away by the N_2 flow. The mixture was heated under N_2 flow (~ 10 mL/min) to a bath temperature of 192°C , and the temperature was maintained for 2 hours. At this stage there was no formation of water observed, and the reaction was supposed to proceed between phthalic anhydride and pentaerythritol only. The temperature was then raised to 220°C , and the mixture was kept at this temperature for 2 hours and 20 minutes. Water formation was now observed in the trap and on the walls of the condenser. Finally, the temperature was raised to 230°C and the mixture allowed to react until the acid number reached the level of 20–25 mg KOH/g (30–60 minutes). Xylene was removed, and the polymerization was completed by lowering the pressure with an oil pump to 2 mmHg for 40 minutes. During the vacuum treatment, some (40 mg) unreacted material (mainly phthalic anhydride) sublimated into the trap. When the time had passed the bath was removed and the resin was then allowed to cool to room temperature. The yield was 2.16 g (98%). Polyesters containing the monomers mono1-mono6 or decanoic acid (mono7) were prepared in a similar manner. The polyesters containing the 4-(methoxy-4'-oxybiphenyl) alkanoyl group (poly1-poly5) as mesogenic side-chains were opaque solids. The reference polyester poly6, made from 4-(4-methoxy-4'-oxyphenoxy)butyric acid, was a transparent solid. The polyester poly 7, made from decanoic acid, was a transparent viscous liquid at room temperature.

TABLE 1. ^{13}C -NMR Chemical Shifts of the Monomers mono1–mono6. Assignments of the Carbon Atoms Are Presented in Scheme 2

| C no. | mono1 | mono2 | mono3 | mono4 | mono5 ^a | mono6 |
|-------|-------|-------|-------|-------|--------------------|-------|
| 7 | 174.0 | 174.3 | 174.4 | 174.4 | 182.1 | 179.8 |
| 8 | 30.1 | 33.3 | 33.6 | 33.6 | } | 30.6 |
| 9 | 24.2 | 28.1 | 28.5 | 28.6 | | 24.4 |
| 10 | 66.6 | 21.2 | 25.1 | 28.4 | 35.8 | 67.1 |
| 11 | — | 67.1 | 24.3 | 25.3 | 35.0 | — |
| 12 | — | — | 67.3 | 24.4 | 32.7 | — |
| 13 | — | — | — | } | 26.2 | — |
| 14 | — | — | — | | 67.4 | 24.5 |
| 15 | — | — | — | — | } | — |
| 16 | — | — | — | — | | — |
| 17 | — | — | — | — | 67.4 | — |
| 18 | 158.3 | 158.4 | 158.3 | 158.2 | 158.7 | 153.8 |
| | 157.5 | 157.6 | 157.7 | 157.7 | 158.2 | 152.9 |
| 19 | 114.7 | 114.7 | 114.7 | 114.7 | 117.8 ^b | 115.4 |
| | 114.2 | 114.2 | 114.2 | 114.2 | | 114.6 |
| 20 | 127.1 | 127.1 | 127.1 | 127.1 | 126.3 | — |
| 21 | 132.5 | 132.2 | 132.2 | 132.2 | 129.8 | — |
| 22 | 55.0 | 55.0 | 55.0 | 55.0 | 54.7 | 55.7 |

^aFrom the solid-state ^{13}C -NMR.

^bOverlapped peaks.

RESULTS AND DISCUSSION

The synthesis of the monomers, (4-methoxy-4'-oxybiphenyl) alcanoic acids (mono1–mono5), and the 4-(4-methoxy-4'-oxyphenyl)butyric acid (mono6) is a straightforward procedure, the yields are reasonable, and they were obtained in pure form. The IR, ^1H -NMR and ^{13}C -NMR spectra in all cases were consistent with the proposed structures, and no impurities could be detected in the spectra or by thin-layer chromatography.

To confirm the thermostability of the monomers, they were tested by differential thermogravimetry (DTG). The mesogenic monomers (mono1–mono5) withstand heating to 300°C without decomposition. The reference monomer mono6 started to degrade gradually above 240°C. The stability was considered to be adequate for polymerizations.

The monomers, (4-methoxy-4'-oxybiphenyl) alcanoic acids, are not liquid-crystalline as a monomeric state, and they did show only melting to isotropic liquid. This was expected from the study of C. Pugh and V. Percec. They have synthesized side-chain liquid-crystalline (smectic) poly(epichlorohydrin) and copolymers as well as poly(2,6-dimethyl-1,4-phenylene oxide) by grafting with the same mesogens as illustrated in this paper [22, 26]. It is well documented that low molecular weight potential mesogens that do not exhibit liquid-crystalline properties give rise to liquid-crystalline polymers when attached as side-chains to polymer backbones.

This is referred to as “the polymer effect” [4]. The polymerization processes were reproducible and reached high conversion according to the low acid numbers of the polyester resins (1–2 mg KOH/g). Poly1 is presented in Fig. 1 as a representative GPC trace of the polyesters. It shows a broad multimodal molecular mass distribution with minor amounts of lower oligomers. The polyesters poly1–poly5 show little variation in the number-average molecular masses (2900–3300 g/mol), and the polydispersity index (PDI) is between 4.7 and 7.3 with the exception of poly1 which has a PDI value of 12.1. The molecular masses of the reference polyesters poly6 and poly7 are also 3000–3500 g/mol, but the PDIs are much higher, 23.3–25.8. The acid numbers and the results of the GPC measurements of the prepared polyesters are collected in Table 2. The formulas of the polymers poly1–poly6 are illustrated

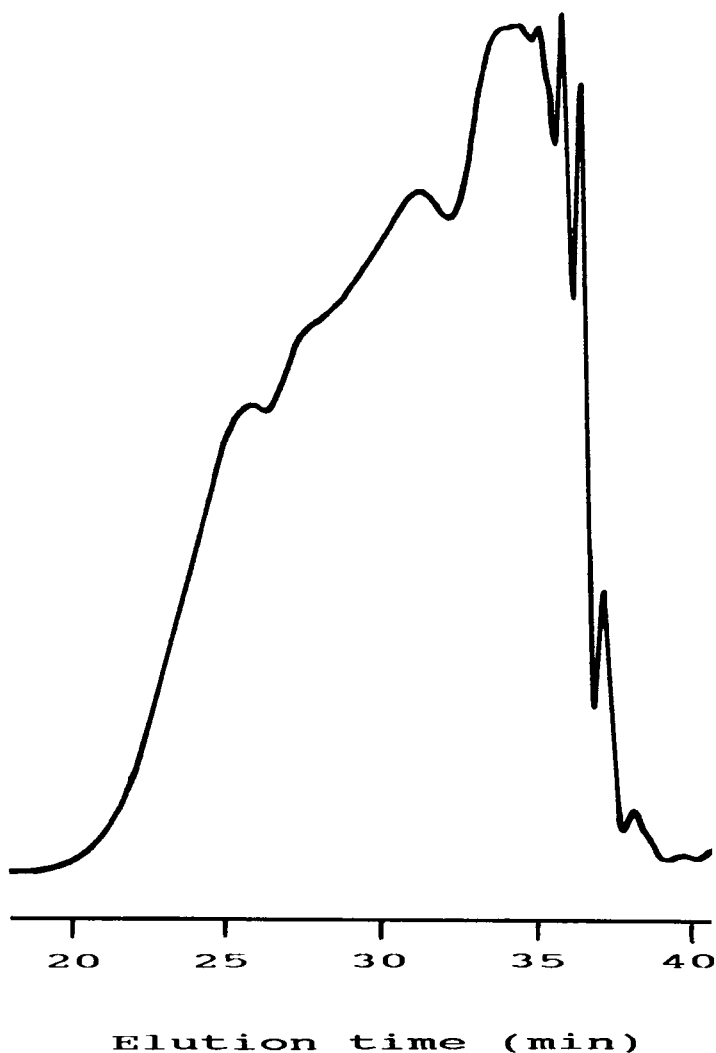


FIG. 1. The GPC trace of the polymer poly1.

TABLE 2. Characterization of the Polymers poly1–poly7

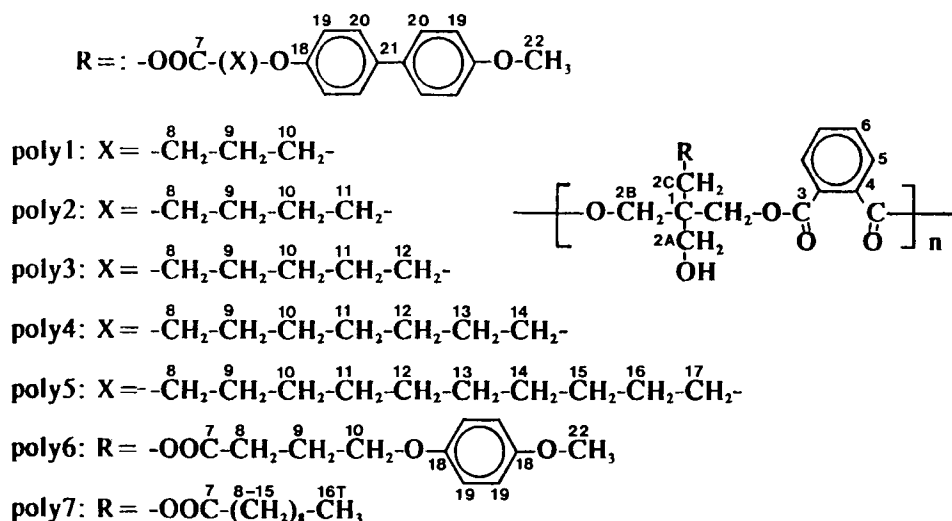
| Sample | Acid no. | GPC | | Phase transitions (°C) and corresponding enthalpy changes (J/g) | | |
|--------|----------|--------------------------------------|--------------------------------------|---|--|--|
| | | $\langle M_n \rangle \times 10^{-3}$ | $\langle M_w \rangle \times 10^{-3}$ | PDI | Heating | Cooling |
| poly1 | 1 | 3.3 | 39.5 | 12.1 | g 72 T1 107(13) i | i 92(9) T1 73 g |
| poly2 | 1 | 2.9 | 17.3 | 5.9 | g 79 T1 104 T2 113(15) ⁱ | i 91(12) T [?] 74 ^b g |
| poly3 | 1 | 3.0 | 14.2 | 4.7 | g 74 T1 100(16) i | i 88(12) T1 72 ^b g |
| poly4 | 1 | 3.2 | 19.9 | 6.3 | g 71 T1 90 T2 97(19) ⁱ | i 92 T2 82(18) ^a T1 69 ² i |
| poly5 | 1 | 3.2 | 23.4 | 7.3 | g 52 T1 74 T2 104 T3 106 T4 117 T5 124(–) i | i 102(13) T [?] 71(2) T1 49 g |
| poly6 | 2 | 3.0 | 69.4 | 23.3 | g 22 i | i 19 g |
| poly7 | 1 | 3.5 | 91.1 | 25.8 | g 1 i | i –11 g |

^aOverlapped peaks.^bEstimated, overlapped with exotherm.

in Scheme 3, and the corresponding ^{13}C -NMR chemical shifts are presented in Table 3. The NMR spectra indicate that the monomer is attached to the polymer backbone. ^1H - and ^{13}C -NMR spectra of the monomer mono3 and the corresponding polyester poly3 are presented as representative examples (Figs. 2–5). The spectra of the polyesters show the methylene group of pentaerythritol in three different chemical environments (^{13}C -NMR, 60–65 ppm; ^1H -NMR, 3.4–4.6 ppm), which indicates that both aromatic (phthalic anhydride) and aliphatic carboxylic acids (monocarboxylic acids) have esterified with the hydroxyl groups of pentaerythritol, and the excess of hydroxyl groups is maintained unreacted. The chemical shifts of the monomers are nearly unchanged in the spectra of the corresponding polyesters; only the chemical shift of the connecting carbonyl group was changed to a higher field. The spectra confirm the suggested polymer structure. The mesomorphic properties of the polyester resins were determined by means of differential scanning calorimetry and polarizing light microscopy. The molecular masses and the polydispersity of the polyester resins varied, therefore, we have to take into account the fact that the phase transitions of the resins might be affected by differences of the properties. The second heating and the first cooling scans are presented for each of the polyester resins. The heating and cooling rates were $20^\circ\text{C}/\text{min}$. The complete thermal transitions and the corresponding energy changes of all the polymers are summarized in Table 2. After the first heating cycle, subsequent heating and cooling cycles on each polymer gave virtually identical DSC thermograms.

The thermal properties of the polyester resins poly1–poly5 varied greatly. They had one to four endothermic transitions on heating and one to two exotherms on cooling.

The DSC thermograms of the polyester poly1 (Fig. 6) show the T_g and one endotherm on heating. The enthalpy change of the isotropization is 13 J/g . During cooling, after a supercooling of 15°C , a sharp exotherm with an enthalpy change of



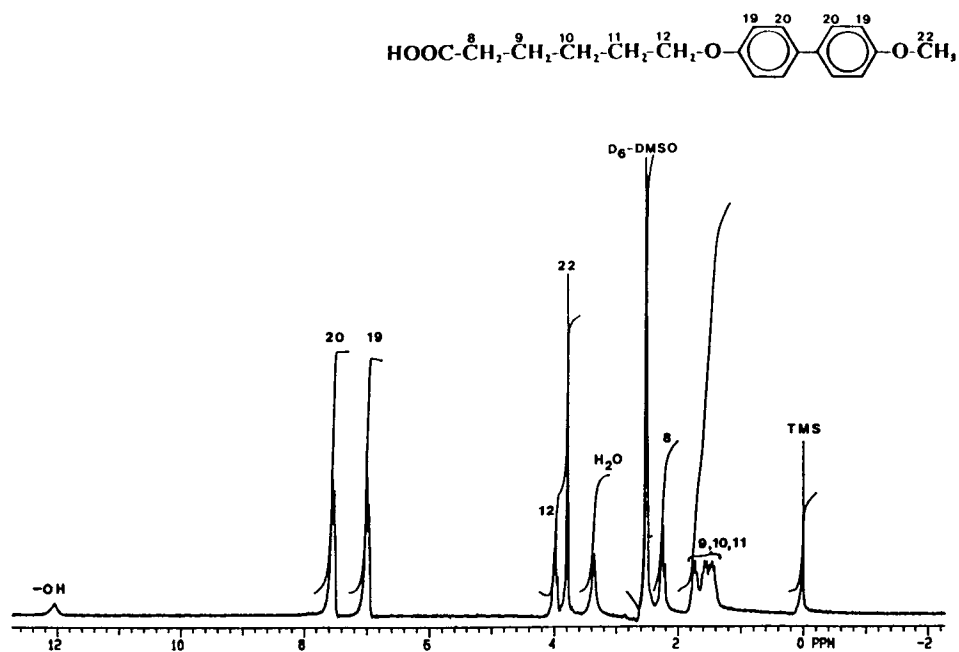
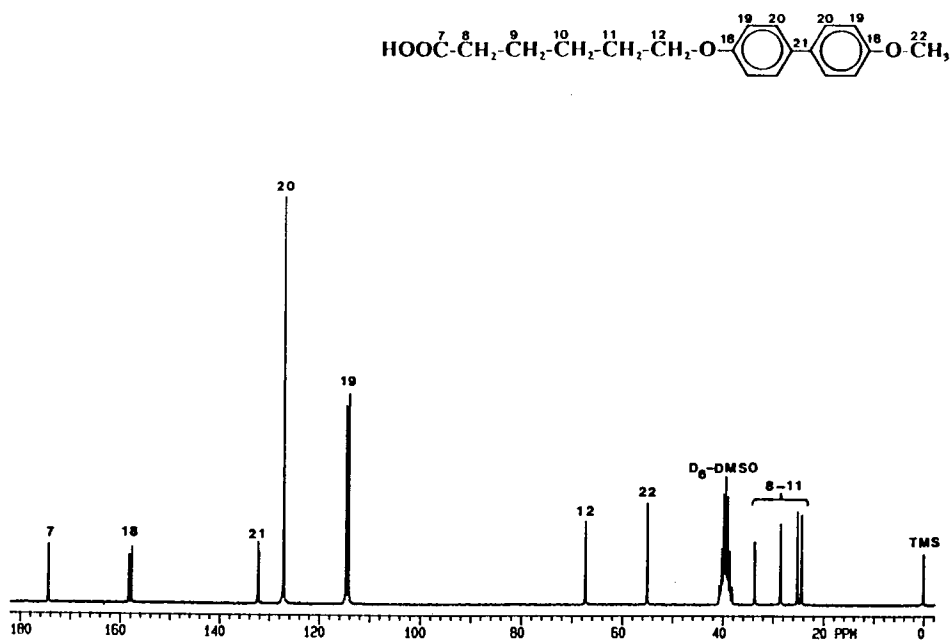
SCHEME 3. Assignment of carbons in the polymers poly1–poly7 for ^{13}C -NMR spectra.

TABLE 3. ^{13}C -NMR Chemical Shifts of the Polymers poly1–poly7. Assignments of the Carbon Atoms Are Presented in Scheme 3

| C no. | poly1 | poly2 | poly3 | poly4 | poly5 | poly6 | poly7 |
|-------|-------|-------|-------|-------|-------|-------|-------|
| 1 | 42–45 | 42–45 | 42–45 | 42–45 | 42–45 | 42–45 | 42–45 |
| 2 | 61–64 | 60–64 | 60–64 | 60–64 | 60–64 | 60–64 | 60–64 |
| 3 | 167.3 | 167.0 | 167.0 | 167.0 | 167.0 | 167.0 | 167.0 |
| 4 | 131.4 | 131.5 | 131.2 | 131.2 | 131.2 | 131.3 | 131.2 |
| 5 | 129.1 | 129.2 | 129.1 | 129.0 | 129.0 | 129.1 | 129.1 |
| 6 | 131.5 | 131.5 | 131.5 | 131.4 | 131.5 | 131.5 | 131.5 |
| 7 | 173.0 | 173.0 | 173.5 | 173.0 | 173.0 | 173.2 | 173.8 |
| 8 | 30.6 | 33.6 | 33.9 | 34.0 | | 30.6 | |
| 9 | 24.5 | 28.6 | 28.9 | 33.9 | | 24.6 | |
| 10 | 66.6 | 21.5 | 25.6 | 29.1 | | 67.2 | |
| 11 | — | 67.3 | 24.6 | 28.9 | 34.0– | — | 34.1– |
| 12 | — | — | 67.6 | 25.8 | 24.0 | — | 22.7 |
| 13 | — | — | — | 24.6 | — | — | — |
| 14 | — | — | — | 67.8 | — | — | — |
| 15 | — | — | — | — | — | — | — |
| 16 | — | — | — | — | — | — | — |
| 16T | — | — | — | — | — | — | 14.1 |
| 17 | — | — | — | — | 67.9 | — | — |
| 18 | 158.6 | 158.6 | 158.6 | 158.5 | 158.5 | 153.8 | — |
| | 157.6 | 157.9 | 158.0 | 158.0 | 158.1 | 152.8 | — |
| 19 | 114.7 | 114.7 | 114.7 | 114.6 | 114.7 | 115.4 | — |
| | 114.1 | 114.1 | 114.1 | 114.0 | 114.0 | 114.6 | — |
| 20 | 127.0 | 127.6 | 127.6 | 127.5 | 127.5 | — | — |
| 21 | 133.3 | 133.3 | 133.4 | 133.2 | 133.2 | — | — |
| 22 | 55.3 | 55.3 | 55.3 | 55.2 | 55.3 | 55.6 | — |

9 J/g occurs. The optical polarizing microscope shows the formation of a very fine grain texture which could not be identified at a magnification of $100\times$, which is the maximum magnification when heat bench is in use. The texture could be frozen in when the sample was cooled under T_g . With a magnification of $500\times$, the Schlieren texture was visible. The reference polyester, poly6 (Fig. 7), shows only with the same spacer length at T_g , indicating that a side chain of this length does not crystallize easily. The reference polyester poly7 likewise has only a glass transition (Table 2). Liquid-crystallinity usually increases the T_g of a polymer. The T_g of poly1 is higher than that of poly6, as expected.

Polyester poly2 (Fig. 6) showed a T_g at 79°C followed by a broad endotherm formed by overlapping peaks. The total enthalpy change of the endothermic peaks were 15 J/g, and on cooling the single detected exotherm had a value of 12 J/g. Again, a Schlieren texture, formed at 100°C on cooling from the isotropic phase, could be detected with $500\times$ magnification. On heating, the texture remained unchanged; only a color change occurred at 100°C and remained until the isotropization temperature was reached. On slower cooling ($5^\circ\text{C}/\text{min}$), batonnets appeared

FIG. 2. The ^1H -NMR spectrum of mono3.FIG. 3. The ^{13}C -NMR spectrum of mono3.

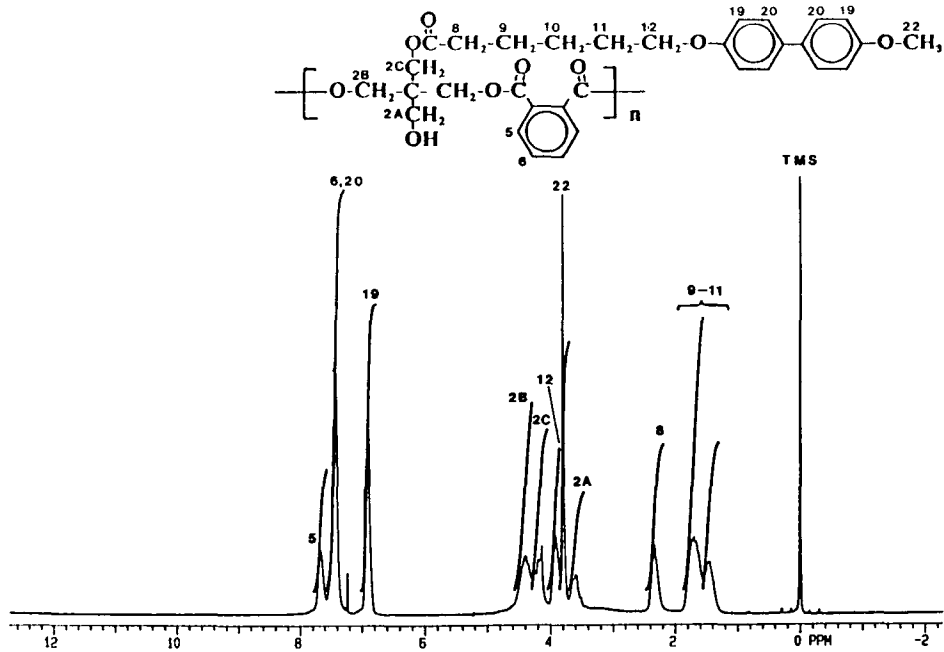


FIG. 4. The ¹H-NMR spectrum of poly3.

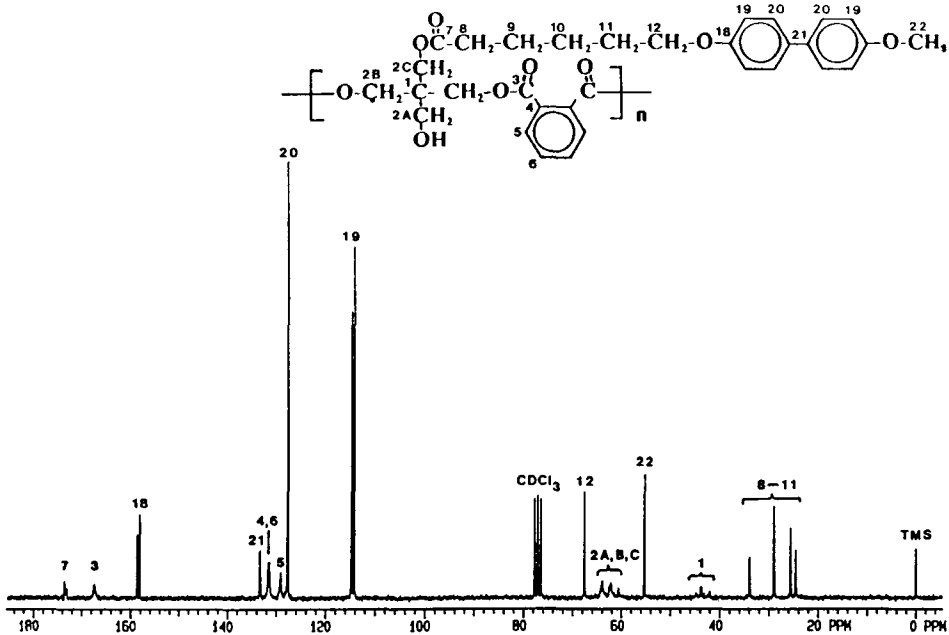


FIG. 5. The ¹³C-NMR spectrum of poly3.

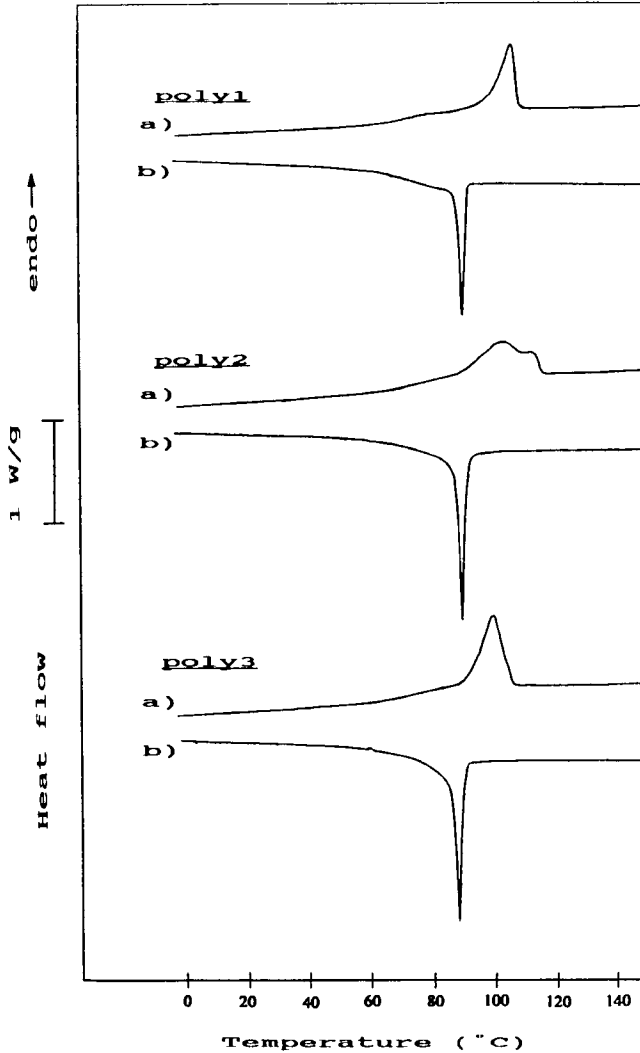


FIG. 6. The DSC thermograms of poly1-poly3. The second heating (a) and the first cooling scans (b) are presented. The heating and cooling rates were 20°C/min.

and formed focal conical domains until the Schlieren texture filled the rest of the field on further cooling.

The polyester poly3 (Fig. 6) shows a T_g (74°C) and only one phase transition, like poly1, on heating (100°C) and cooling (88°C). The transition enthalpies were 16 J/g on heating and 12 J/g on cooling. The texture formed on cooling from the isotropic state was focal conic and could be frozen in for observation with 500× magnification.

Polyester poly4 (Fig. 7) shows a T_g and two endotherms at 90 and 97°C. The cooling scan shows two exotherms, at 92°C (supercooled 5°C) and at 82°C (supercooled 8°C), respectively. The sum of the overlapped endotherms and the

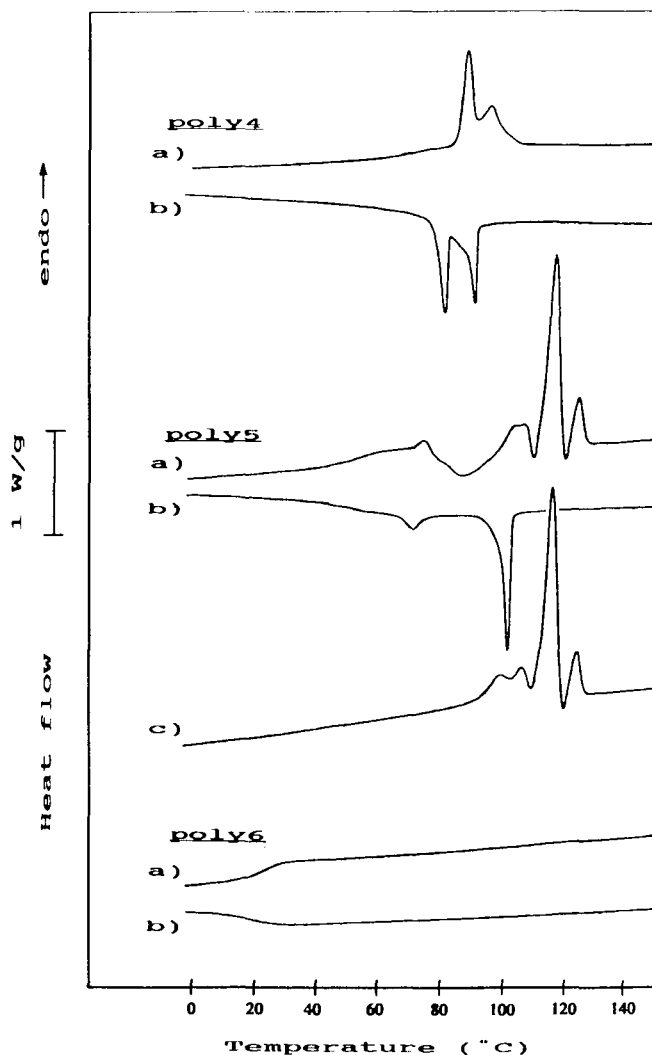


FIG. 7. The DSC thermograms of poly4–poly6. The second heating (a) and the first cooling scans (b) are presented. The heating scan of the annealed sample from poly5 (1 hour at 87°C) is presented (c). The heating and cooling rates were 20°C/min.

exotherms was 19 and 18 J/g, respectively. The texture observed in the polarizing microscope on cooling was a Schlieren texture. No change could be observed on further cooling below the second transition.

The thermal behavior of polyester poly5 (Fig. 7) was more complicated than the others. On heating, we observe T_g , followed by cold crystallization, and several melting endotherms followed by isotropization. The cooling scan shows exotherms at 102 and at 71 °C, which appears to be the crystallization of the side chain which cannot be completed so close to T_g . To verify this, the sample was annealed for 1 hour at 87°C and after this we observed from the heating scan that T_g was barely

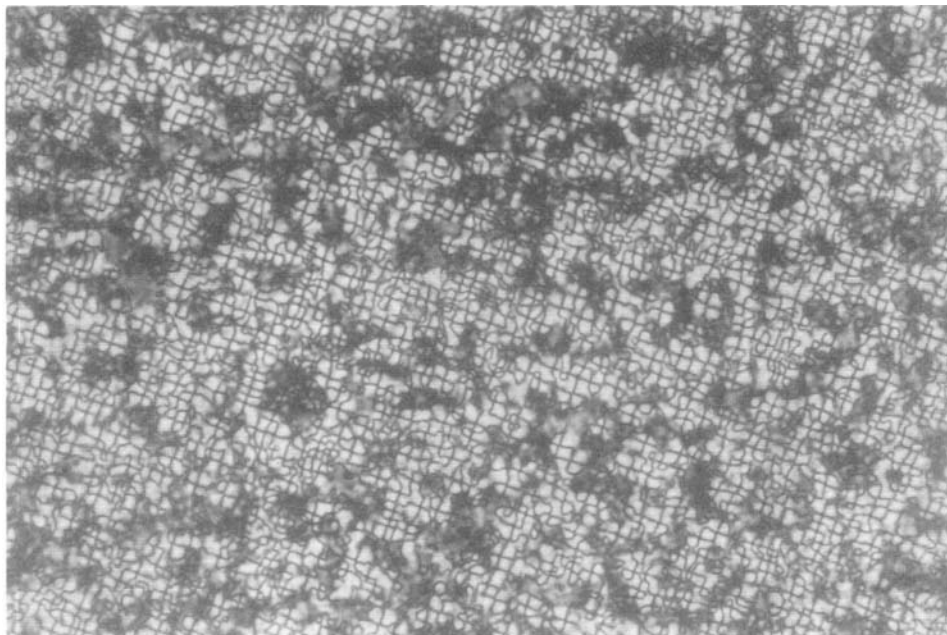


FIG. 8. Polarizing light microscope texture of poly5 annealed for 6 days at 94°C and quenched to room temperature. Magnification: 500 \times .

visible (Fig. 7), indicating increased crystallinity. The crystallization exotherm does not exist, and the endotherm at 104°C shifts to lower temperature. The microscope texture formed was a Schlieren texture at 102°C when cooling was at 20°C/min. The texture remained unchanged on further cooling. On heating, the texture changed to black and white at 107°C and then the texture darkened dramatically at 117°C. This was maintained until isotropization occurred at 128°C. Figure 8 shows the Schlieren texture formed on annealing poly5 for 6 days at 94°C.

The enthalpies of the phase transitions, the degree of supercooling, the optical polarizing microscope textures, and the high viscosities of the samples indicate that the mesophases of these polyesters are of the smectic type. It is also possible that these polymers may be biphasic systems whose behavior resembles that of phase-separated graft polymers, i.e., they exhibit a microphase-separated morphology containing main-chain and liquid-crystalline side-chain domains as in the case of some polysiloxanes [27–31]. It is difficult at this time to make many assumptions concerning the type of mesophases exhibited by these polymers, but the materials are the subject to further investigation.

CONCLUSIONS

Direct polyesterification at elevated temperature offers a method to introduce mesogenic groups to polyester resins in a simple manner. The method opens many

possibilities of tailoring the structure and thereby changing the properties of the resin by varying the molar ratio and the nature of the monomers.

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