Side-Chain Liquid-Crystalline Polymers with Polystyrene Backbone

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PLEASE SCROLL DOWN FOR ARTICLE

SIDE-CHAIN LIQUID-CRYSTALLINE POLYMERS WITH POLYSTYRENE BACKBONE†

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ABSTRACT

A series of liquid-crystalline polystyrene derivatives with pendant mesogenic groups has been prepared and characterized. The side-chain is connected to the polystyrene backbone by a methyleneoxyhexyloxy spacer. The mesogenic group is a 4-alkoxy substituted biphenyl group. The length of the alkoxy end-group varied from a methoxy group to an octyloxy group. The polymers were synthesized by a radical reaction. Molar masses ($<M_n>$) varied between 17,000 and 46,000, with a molar mass distribution between 1.6 and 2.0. All the polymers were liquid-crystalline, with enantiotropic smectic phases. The polymers were characterized with polarizing microscopy, NMR spectroscopy, and calorimetry.

INTRODUCTION

There is a growing interest in liquid-crystalline polymers containing mesogens either in the side group or in the main chain. It has been demonstrated [1–4] that in the case of liquid-crystalline polymers containing mesogens as side groups, a flexible spacer has to be inserted between the polymer backbone and the side group in order to get liquid crystalline properties in the polymer. In particular, if the polymer

†Dedicated to Otto Vogl on the occasion of his 65th birthday.

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backbone is rigid or semirigid, the spacer partially decouples the mobility of the main chain from that of the mesogenic groups. Thus side-chain liquid-crystalline polymers contain three basic structural units: the polymer backbone, the flexible spacer, and the mesogenic group. In addition, the substituents of the mesogenic group are to be considered because they influence the properties of the polymer. In the case of aromatic mesogenic groups, the substituents in the *para* position should be taken into account.

Very few reports have been published on side-chain liquid-crystalline polymers with a polystyrene backbone. Percec et al. [5] presented the synthesis and characterization of *para*-substituted poly(vinyl benzyl ethers) containing biphenyl moieties connected to the polymer with oligo(oxyethylene) units or with very short spacers. Crivello et al. [6] examined the effects of various spacer lengths on the mesophase types in side-chain polymers having polystyrene and poly(α-methylstyrene) backbones with pendant azobenzene mesogenic groups. Imrie et al. [7] synthesized a copolymer with a poly(4-hydroxystyrene) backbone substituted with two different azobenzene derivatives through 1,6-dioxyhexyl spacers.
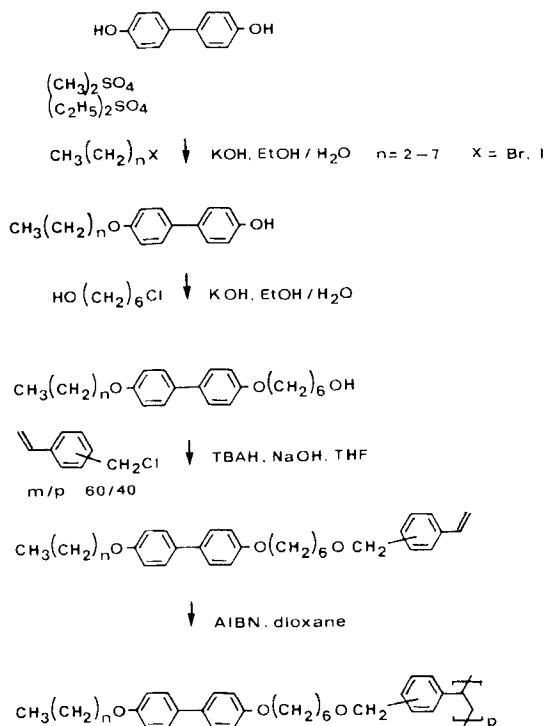
We have chosen to investigate a series of side-chain liquid-crystalline polystyrene derivatives where the mesogenic group is connected to the backbone by a hexyl oxymethylene spacer with an ether linkage. The purpose is to demonstrate the influence of the length of the alkyl end group of the mesogen on the thermal properties of the liquid-crystalline polymer. The polystyrene backbone yields polymers with relatively high glass transition temperatures which may influence their potential applications. By substituting mesogenic side groups to the polystyrene, it should also be possible to alter the viscoelastic properties of the parent polymer.

Liquid-crystalline side-chain polymers can be prepared by two general processes [8]. The liquid-crystalline side-chain polymers are usually prepared by the radical polymerization of appropriate monomers such as acrylates [9], methacrylates [1], or chloroacrylates [10]. Another synthesis route has been suggested, starting with reactive polymers which can be modified to mesogenic side-chain polymers by reaction with suitable mesogenic compounds [3]. Imrie et al. [7] used a phase transfer catalyzed reaction of 1-bromo(4-substituted azobenzene-4'-oxy)hexanes with poly(4-hydroxystyrene) to prepare liquid-crystalline polymers. Crivello et al. [6] prepared mesogenic polystyrene derivatives by a similar method. In this paper we report the syntheses and characterization of poly(vinyl benzyl ethers) substituted with 4-(6-hydroxyhexyloxy)-4'-alkoxy biphenyl groups prepared through polymerization of substituted monomers by the route indicate in Scheme 1.

EXPERIMENTAL

Materials

4,4'-Dihydroxybiphenyl, dimethyl sulfate, 1-bromohexane, 1-bromoheptane, 1-bromooctane, 2,2'-azobisisobutyronitrile (AIBN) (all from Merck), lithium aluminum hydride (Aldrich), diethyl sulfate, 1-bromopropane, 1-bromobutane, 1-bromopentane, 6-chloro-1-hexanol, tetrabutylammonium hydrogen sulfate (TBAH) (Fluka), and chloromethyl vinylbenzene (ratio of *meta/para* isomers = 60/40) (Dow) were used as received. All the reaction and polymerization solvents (tetrahy-

HO—⟨◯⟩—⟨◯⟩—OH

$\begin{pmatrix}(CH_3)_2SO_4\\(C_2H_5)_2SO_4\end{pmatrix}$

$CH_3(CH_2)_nX$ ↓ KOH, EtOH / H$_2$O   n = 2 − 7   X = Br, I

$CH_3(CH_2)_nO$—⟨◯⟩—⟨◯⟩—OH

HO$(CH_2)_6$Cl ↓ KOH, EtOH / H$_2$O

$CH_3(CH_2)_nO$—⟨◯⟩—⟨◯⟩—O$(CH_2)_6$OH

⟨◯⟩—CH$_2$Cl ↓ TBAH, NaOH, THF

m/p 60/40

$CH_3(CH_2)_nO$—⟨◯⟩—⟨◯⟩—O$(CH_2)_6$O CH$_2$—⟨◯⟩

↓ AIBN, dioxane

$CH_3(CH_2)_nO$—⟨◯⟩—⟨◯⟩—O$(CH_2)_6$O CH$_2$—⟨◯⟩$_p$

SCHEME 1.

drofuran and dioxane, from Merck) were purified and dried by conventional techniques.

Syntheses

The monomethyl and ethyl ethers of 4,4'-dihydroxybiphenyl were prepared as described by Rodriguez-Parada et al. [11]. In a typical synthesis of 4-methoxy-4'-hydroxybiphenyl, 0.054 mol 4,4'-dihydroxybiphenyl was dissolved in a solution of 0.108 mol sodium hydroxide in 40 mL water. Dimethyl sulfate (0.054 mol) was added and the reaction mixture stirred at room temperature until the mixture solidified (6 h). The precipitate was filtered and washed with 10% aqueous sodium hydroxide. It was then dissolved in boiling water and traces of starting material were separated by hot filtration. The product was precipitated with dilute hydrochloric acid, filtered, washed with water, and recrystallized from ethanol. Yield, 0.026 mol (50%); melting point, 181°C.

Monoethers with longer chains were prepared by modifying the procedure described by Zentel et al. [12]. 4,4'-Dihydroxybiphenyl (0.054 mol) was dissolved in a solution of 13.5 g potassium hydroxide in a mixture of 38 mL ethanol and 19 mL water. The mixture was gently warmed for complete dissolution, 0.054 mol bromoalkane in 19 mL ethanol was added, and the reaction mixture was refluxed

for 6 h. The color of the mixture changed from its original green to brownish. The diether formed as a by-product precipitated on cooling and was filtered off. The solution was poured into 10 mL of 2 M sodium hydroxide. On dilution with water, the 4-alkoxy-4'-hydroxybiphenyl precipitated. The product was filtered and recrystallized from ethanol which had been made slightly acidic with hydrochloric acid. Yield, 0.02 mol; 36%.

The 4-alkoxy-4'(6-hydroxyhexyl)biphenyls were prepared as described by Finkelmann et al. [2]. First, 0.0074 mol 4-alkoxy-4'-hydroxybiphenyl was dissolved in 12 mL hot ethanol. A solution of 0.0018 mol potassium hydroxide in 2.5 mL water was added. 6-Chlorohexanol (0.0081 mol) was added and the mixture was refluxed 20 h. After cooling, 15 mL water was added and the ethanol was evaporated. The precipitate was filtered off, washed with dilute potassium hydroxide solution and water, and recrystallized from ethanol. Yield, 0.0034–0.0050 mol; 46–65%.

The chloromethyl vinylbenzene was added to the substituted biphenyls by a phase transfer reaction using TBAH in tetrahydrofuran in the presence of sodium hydroxide [5]. 4-Alkoxy-4'(6-hydroxyhexyloxy)biphenyl (0.0138 mol), chloromethyl vinylbenzene (0.0151 mol), and tetrabutylammonium hydrogen sulfate (0.00276 mol) were dissolved in 150 mL tetrahydrofuran, and 7 mL of 50 wt% aqueous sodium hydroxide was added. The reaction mixture was stirred at room temperature for 22 h. Then the organic phase was separated, dried, and the solvent evaporated. The yellowish product was recrystallized from methanol. Residues of chloromethyl vinylbenzene were removed by washing with methanol. Yield, 0.0005–0.001 mol; 36–74%.

The polymerization reactions were made as described by Percec et al. [5] by a radical reaction with AIBN as the initiator. In a typical experiment, around 500 mg monomer and 10 mg AIBN were dissolved in 5 mL distilled dioxane. The reaction vessel was thoroughly purged with argon and kept at 60°C for 20 h. The polymers precipitated from the reaction mixture on cooling. The polymers were purified by solution in chloroform and precipitation with methanol twice. Yield, 160 mg; 30%.

Monomers 1M–8M and Polymers 1P–8P were characterized with IR and NMR spectroscopy. Elemental analyses were made for the polymers. The results are collected in Tables 1–5.

TABLE 1.   Elemental Analyses of Polymers 1P–8P

	C, %		H, %	
	Found	Calcd	Found	Calcd
1P $(C_{28}H_{32}O_3)_n$	80.30	80.78	7.85	7.69
2P $(C_{29}H_{35}O_3)_n$	80.61	80.93	8.04	7.91
3P $(C_{30}H_{38}O_3)_n$	80.74	81.08	8.19	8.11
4P $(C_{31}H_{41}O_3)_n$	80.86	81.22	8.44	8.30
5P $(C_{32}H_{44}O_3)_n$	80.93	81.36	8.57	8.47
6P $(C_{33}H_{47}O_3)_n$	80.99	81.48	8.90	8.64
7P $(C_{34}H_{50}O_3)_n$	81.57	81.60	8.91	8.80
8P $(C_{35}H_{53}O_3)_n$	81.38	81.71	9.06	8.95

TABLE 2. ^{1}H Chemical Shifts of Monomers 1M–8M

	1M	2M	3M	4M	5M	6M	7M	8M
ArH (m,12H)				7.5–6.9				
=CH (dd,1H)				6.75				
CH$_2$= (dd,2H)				5.75, 5.25				
CH$_2$ (s,2H)				4.5				
OCH$_2$ (s,4H)	(2H)			4.0				
CH$_3$ (s,3H)	3.85	1.4	1.05	1.0		0.95		0.9
CH$_2$O (t,2H)				3.5				
CH$_2$ (m, 8H–20H)				1.9–1.2				

Techniques

200-MHz ^{1}H- and ^{13}C-NMR spectra were recorded on a JEOL FX 200 or a Varian Gemini 2000 spectrometer. All spectra were measured in CDCl$_3$ solutions with TMS as the internal standard. IR spectra were measured on a Perkin-Elmer 457 grating or on a Nicolet 60 SX FT spectrometer. A Perkin-Elmer DSC-2B differential scanning calorimeter was used to determine the thermal transitions. Heating and cooling rates were 10 or 20°C/min, and indium was used as the calibration stan-

TABLE 3. Main IR Absorption Bands of Monomers 1M–8M[a]

Frequency	cm^{-1}	Intensity
2965	CH$_3$ asymmetric stretching	m
2936	CH$_2$ asymmetric stretching	s
2872	CH$_3$ symmetric stretching	m
2859	CH$_2$ symmetric stretching	s
1606	C—C aromatic stretching	s
1500	C—C aromatic stretching	vs
1475	C—C aromatic stretching	s
1273	Benzene ring—O stretching	vs
1250	Benzene ring—O stretching	vs
1127	C—O—C stretching	s
1036	O—C—C stretching	s
995	CH stretching in vinyl group	s
902	CH stretching in vinyl group	s
823	CH aromatic out-of-plane	vs
807	CH aromatic out-of-plane	s

[a]Bands associated with the mesogenic side chain occur at the same wavenumbers in spectra of monomers and in spectra of polymers. The main differences between the spectra of monomers and of polymers are that absorption from C—H vibrations in the vinyl group disappeared and the intensity of bands caused by CH$_2$ stretching at 2936 and 2859 cm^{-1} increased.

TABLE 4. ^{13}C-NMR Chemical Shifts of Monomers 1M–8M

		1M	2M	3M	4M	5M	6M	7M	8M
a		55.3	14.9	10.6	13.9	14.0		14.1	
b	1		63.5	69.7	68.1		68.2		
	2			22.6	31.5	28.2	29.3		
	3				19.4	29.0	25.8	29.0	29.4
	4					22.5	31.6	26.0	29.1
	5						22.6	31.8	26.1
	6							22.6	31.8
	7								22.6
c′	1	133.6				133.5			
	2					127.7			
	3	114.2				114.8			
	4	158.8		158.2		158.3			
c	1					133.4			
	2					127.7			
	3	114.2				114.8			
	4					158.3			
d	1					68.0			
	2					29.3			
	3					25.9			
	4					26.0			
	5					29.7			
	6 (m)					72.8			
	6 (p)					72.6			
e (m)						70.4			
e (p)						70.3			
f (m) 1,3						137.6–139.0 (4 signals)			
f (p) 1,4									
f (m) 2,4,6,5						125.4–128.6 (6 signals)			
f (p) 2,3,5,6									
g (m)						113.9			
g (p)						113.6			
h (m)						136.8			
h (p)						136.6			

dard. The transition temperatures were taken after the second heating and cooling cycle, from the maxima of the endo- and exothermic peaks, respectively. The glass transition temperature was read at the half height of the curve for the change in the heat capacity. A Zeiss polarizing microscope equipped with a Mettler FP 82 hot stage was used to observe the thermal transitions. Molar masses and molar mass distributions were determined with gel permeation chromatography. Number- and mass-average molar masses $<M_n>$ and $<M_w>$ were calculated by comparison with a calibration curve for polystyrene. The elemental analyses were made at Analytische Laboratorien, Gummersbach, Germany.

TABLE 5. ^{13}C-NMR Shifts of Polymers 1P–8P

		1P	2P	3P	4P	5P	6P	7P	8P
a		55.3	14.9	10.6	13.9	14.0		14.1	
b	1		63.5	69.7	67.9		68.1		
	2			22.6	31.4	28.2	29.4		
	3				19.3	29.0	25.8	29.1	29.4
	4					22.5	31.6	26.0	29.1
	5						22.6	31.8	26.1
	6							22.6	31.8
	7								22.7
c'	1	133.5				133.3			
	2					127.6			
	3	114.2				114.7			
	4	158.7	158.0	158.2		158.3			
c	1					133.3			
	2					127.6			
	3					114.8			
	4					158.2			
d	1		68.0		67.7	68.0			
	2					29.4			
	3					26.1			
	4					26.1			
	5					29.8			
	6					72.7			
e						70.4			
g,h			41						

RESULTS AND DISCUSSION

The monomers had melting points between 75 and 85°C, and none of them showed mesomorphic behavior. During heating, polymerization was observed under the microscope. The melting points of the monomers are collected in Table 6. The IR and NMR spectra of the monomers correspond to the expected structures. The IR spectra of the monomers clearly show the CH stretch of the vinyl group at 902 and 995 cm^{-1}, which are absent in the spectra of the polymers. Figures 1 and 2 show typical examples of the ^{1}H- and ^{13}C-NMR spectra of the monomers and polymers measured in solution. In the proton spectra the chemical shifts of the mesogenic group can be identified in both the polymer and the monomer. The quartet at 6.75 ppm and the doublets at 5.75 and 5.25 ppm, caused by the vinyl group protons of the monomer, are missing in the spectrum of the polymer. The data correspond very well with data published for similar structures [12, 13].

In the ^{13}C-NMR spectrum of the polymer, the chemical shifts due to the spacer, the mesogenic group, and the end group are identical with the corresponding shifts of the monomer. The absorption of the polystyrene backbone at 128 ppm (phenyl ring) is broadened below the limit of detection in the spectrum of the

TABLE 6.   Melting Points of Monomers and Molar Masses, and Molar Mass Distribution of Polymers

n	Monomer mp, °C	Monomer symbol	Polymer symbol	$<M_n>$	$<M_w>$	$<M_w>/<M_n>$
0	77	1M	1P	17,500	28,500	1.6
1	78–80	2M	2P	16,000	26,500	1.6
2	85	3M	3P	32,500	56,500	1.7
3	85	4M	4P	28,500	48,500	1.7
4	81–82	5M	5P	28,500	56,500	1.9
5	76–77	6M	6P	36,500	75,000	2.0
6	83–84	7M	7P	46,000	83,500	1.8
7	78	8M	8P	20,000	32,000	1.6

polymer. Also, the absorption of the polymer backbone methylene carbons at 41 ppm is very broad in the polymer spectrum. This is probably due to decreased mobility of the backbone caused by the large substituents [14]. The restricted motion of the backbone is also seen as a broadening of the absorption of the methylene carbon adjacent to the phenyl ring and of the first carbon in the spacer. ^{13}C-NMR chemical shifts for the polymers are collected in Table 5.

The ^{13}C-NMR spectra of the pure polymers were also measured as a function of temperature. Some typical spectra of P6 are seen in Fig. 3. Below the melting
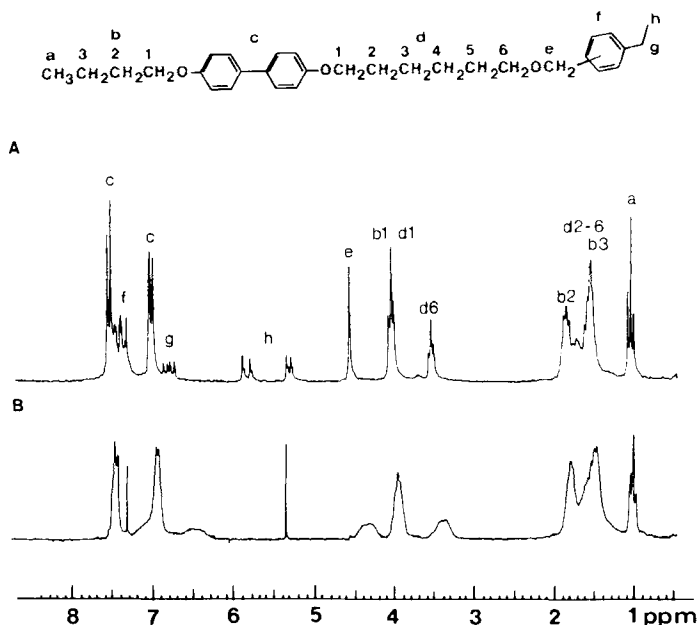

FIG. 1. ^{1}H-NMR spectra of 4M (top) and 4P in CDCl$_3$ solution. The interpretation of the spectra is indicated in the formula. The absorption at 5.3 ppm in the spectrum of 4P is due to residual water.
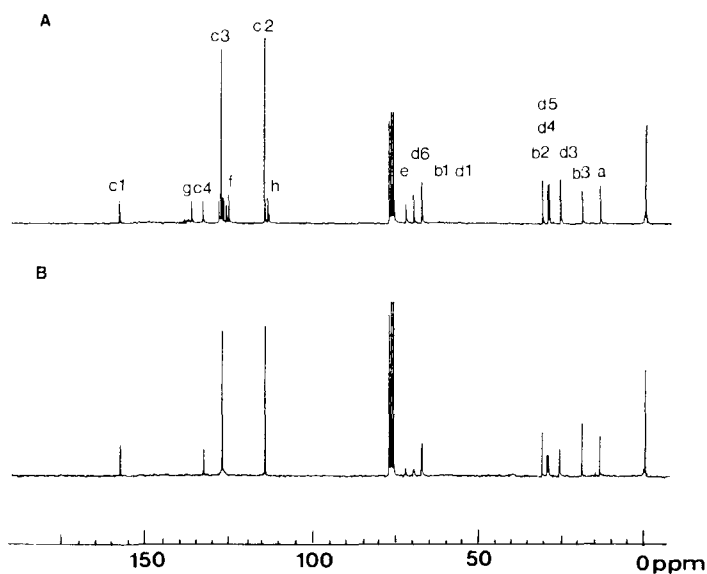
FIG. 2. ^{13}C-NMR spectra of 4M (top) and 4P in CDCl$_3$ solution. Carbon absorptions marked as in Fig. 1.

point the spectra are very poorly resolved. At temperatures exceeding the clearing point, the spectrum is very similar to the isotropic spectrum measured in solution. The absorption of the polystyrene backbone carbons is very weak or not detectable, which clearly shows that there is a considerable difference in the mobility of the polystyrene backbone and of the side chains. At temperatures at which the polymer shows smectic order, the lines in the spectra are broadened.

Table 6 summarizes the polymerization results. The radical polymerizations were performed in dioxane solution and the forming polymer precipitates during
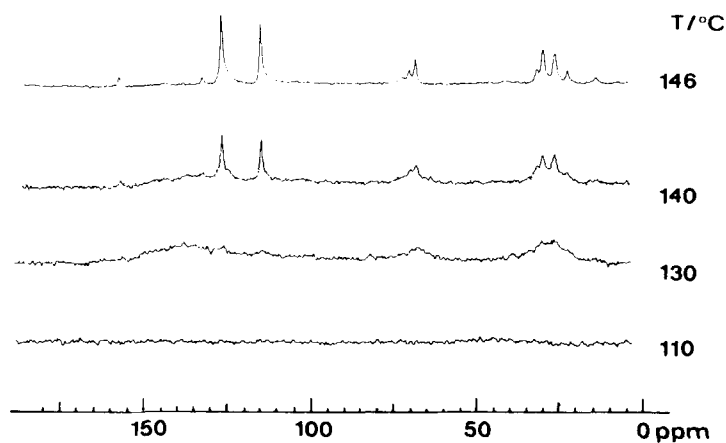

FIG. 3. ^{13}C-NMR spectra of 6P at various temperatures.

polymerization. The purification of the polymer was effectively done by a solution-precipitation cycle using chloroform–methanol as the solvent–nonsolvent pair.

The molar masses were determined by GPC relative to polystyrene standards. All the polymers show molar masses of 16,000 to 46,000 ($<M_n>$) and 26,500 to 83,500 ($<M_w>$), with molar mass distributions between 1.6 and 2.0. The lowest molar masses were measured for polymers where the amount of initiator in the polymerization mixture was 4% of the amount of monomer (1P, 2P, and 8P); higher molar masses were found for polymers which had been polymerized with 2% of initiator with respect to monomer (3P–7P). With the polymerization method used, the molar masses remain fairly low, and the resulting polymers are soluble in common organic solvents.

The spacer between the benzyl group of the polymer backbone and the mesogenic biphenyl group was chosen to be a hexyl oxymethylene chain linked with an ether linkage to the mesogenic group. The spacer thus consists of a nine atom chain. This spacer allows conformational freedom to the side-chain to stabilize mesophases of the polymers. The influence of variations in the length of the spacer will be the subject of further investigations.

The commercial mixture of *meta* and *para* isomers of vinyl benzyl chloride was used in the syntheses. The resulting polymers are thus copolymers. The possible influence of this on the transition temperatures and mesomorphic behavior will also be investigated further.

The addition of mesogenic groups to the polystyrene backbone lowers the glass transition by some 10°C. This effect probably results from increased mobility of the backbone through the influence from the large side groups. The polymers are made by radical polymerization and are therefore assumed to be atactic. The large side groups form domains with a crystal-like structure in the solid state, seen as the melting endotherm in thermograms [16].

All the polymers show enantiotropic liquid-crystalline behavior with a smectic structure of the mesophase. The thermal properties of Polymers 1P–8P are collected in Table 7. Heating thermograms of 1P–8P are collected in Fig. 4. The phase

TABLE 7.   Transition Temperatures, Enthalpies and Entropies of Transition of Polymers 1P–8P (mru = monomer repeating unit)

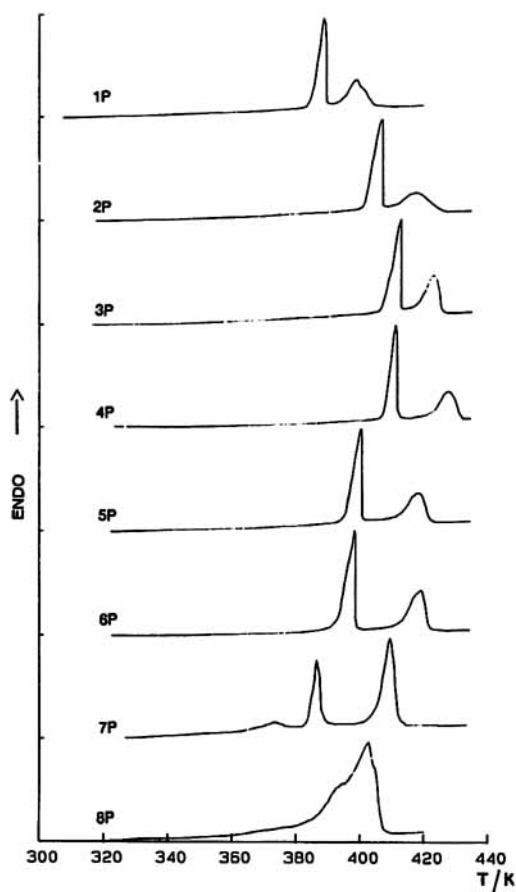|	T_m	T_i	δH_m	δH_i	δS_m	δS_i
	K		kJ/mru		kJ/mru	
1P	388	399	5.64	4.70	0.015	0.012
2P	406	418	7.33	4.55	0.018	0.011
3P	410	422	7.31	6.02	0.018	0.014
4P	411	428	8.48	7.24	0.021	0.017
5P	399	418	9.42	7.57	0.024	0.018
6P	398	419	9.01	7.12	0.023	0.017
7P	387	409	3.53	7.71	0.009	0.019
8P	. . .					

FIG. 4. DSC traces displayed by 1P-8P during the second heating scan. Heating rate: 10 K/min.

transition temperatures increase as the length of the end group increases to the butyloxy group. A similar trend of increasing transition temperatures with increasing length of the end group from methyl to butyl groups has been measured for mesomorphic polyacrylates and polymethacrylates [15]. With longer alkyl chains the transition temperatures decrease. No clear odd–even effect is observed for the polymers with respect to the length of the end group of the mesogenic group. With heptyloxy and octyloxy end groups the transitions are less clearly defined, and still longer end groups will probably inhibit the formation of liquid-crystalline phases. The thermograms from the first heating cycle show the glass transition around 70°C, but the glass transition is obscured on second and further heating cycles. The other transitions in the thermograms are reproducible, irrespective of the number of heating cycles.

The enthalpy and entropy changes of the polymers are of the order of magnitude 5–10 and 0.02 kJ/mru, respectively, at the melting temperature, and only slightly lower at the clearing temperature. Exceptions are the enthalpy and entropy

changes in 7P at the melting temperature; they are small and considerably lower than the values measured for the polymers with the shorter end groups on the mesogenic groups. However, this polymer shows weak transitions below the melting temperature, probably cold crystallizations, which explains the low values of the enthalpy and the entropy at the melting point. The energy changes at the clearing temperature are of the same order of magnitude as for 1P–6P. For Polymers 1P–7P the isotropization enthalpies and entropies are in the range expected for smectics [5, 16]. No attempt was made to calculate the energy changes for 8P because of the poorly resolved thermograms. The different thermal behaviors of 7P and 8P compared to the other polymers are probably due to a less ordered structure in the liquid-crystalline and/or in the crystalline state, where the long end groups cause strong thermal motion with liquidlike behavior and a greater mobility in the glassy state than in Polymers P1–P6.

The polymers show a rather large hysteresis of the transition temperatures. Cooling thermograms are shown in Fig. 5. This phenomenon has recently been
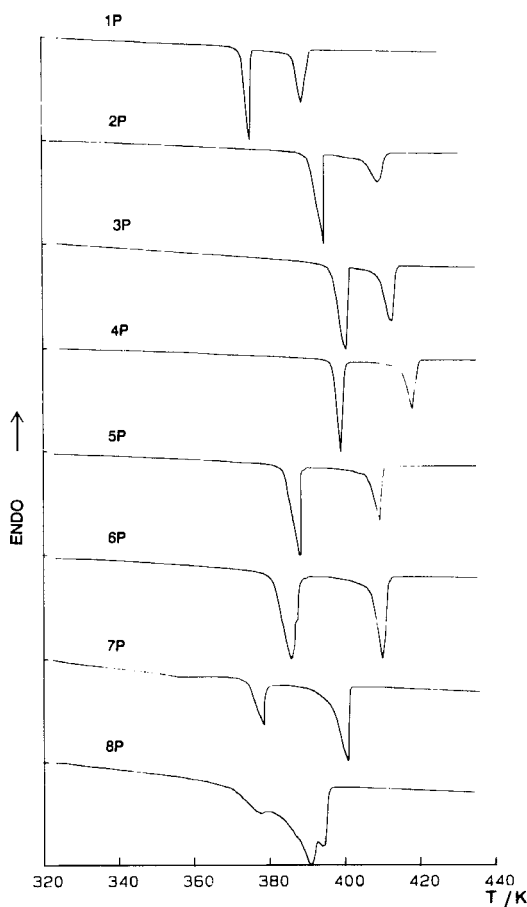

FIG. 5.   DSC traces displayed by 1P–8P during the first cooling scan. Cooling rate: 10 K/min.
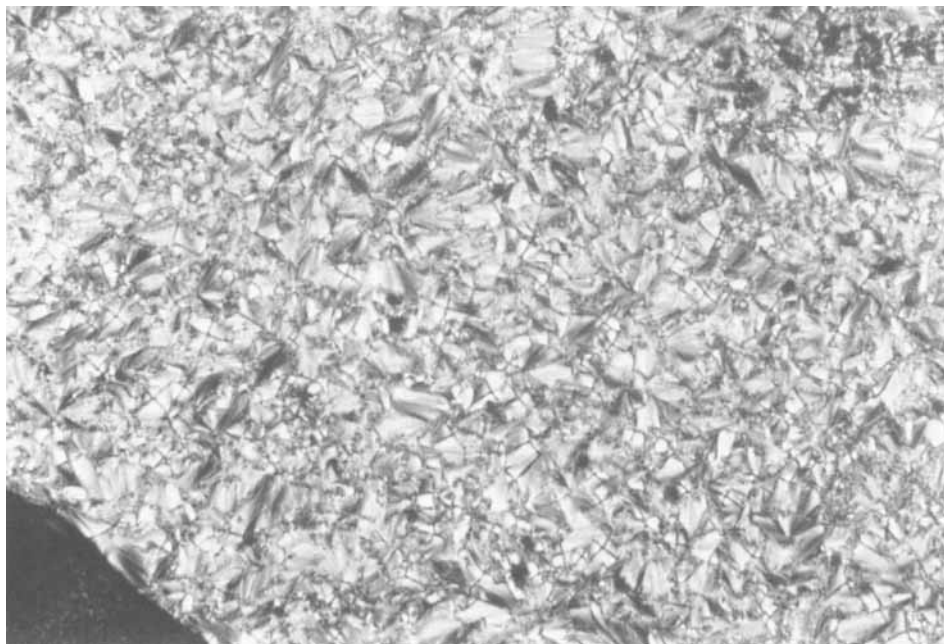
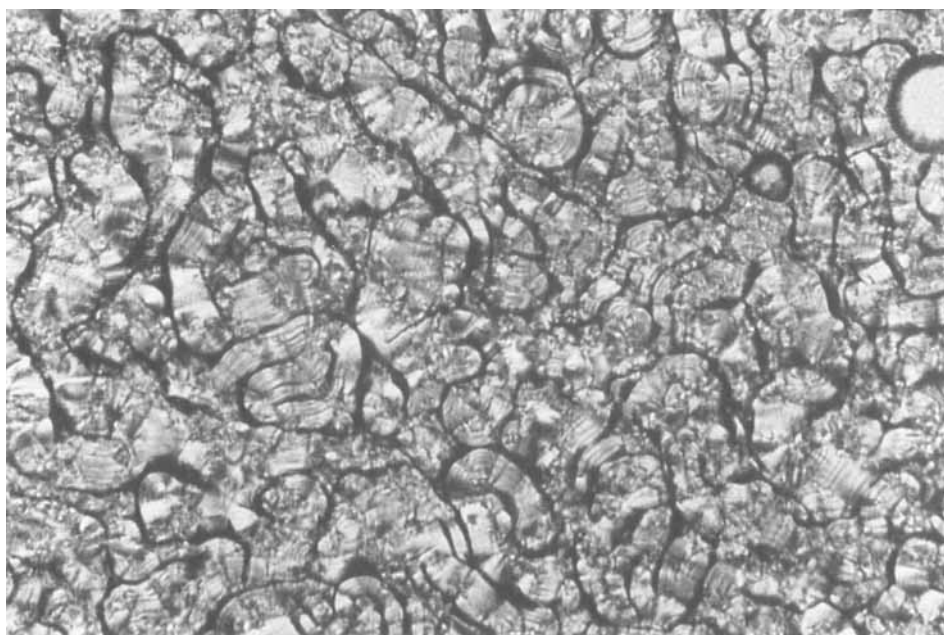FIG. 6. Optical polarized micrograph of the smectic structure of 1P at 114°C. Magnification: 100×.

FIG. 7. Optical polarized micrograph of the structure of 2P at T_m when the sample is cooled very slowly (1.25 K/min). Magnification: 200×.

interpreted as kinetic effects reflecting the presence of a low-lying glass transition [17].

The polymers were studied by optical microscopy. Some representative textures are shown in Figs. 6 and 7. They are typical of smectic structures. No trace of a nematic structure could be seen in Polymers 1P–8P. The low mobility of the polystyrene backbone [16] probably prevents the formation of a nematic structure. A high degree of order in the mesophase is to be expected for polymers based on rigid backbones [18]. We therefore conclude that 1P–8P form smectic phases. The nature of these phases will be the subject of further studies.

ACKNOWLEDGMENT

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