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Influence of spacer variation on phase behaviour of liquid crystalline copolymethacrylates containing cholesteryl and *S*-(-)-4'-chloropropionyloxybiphenyl-4-yl groups

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Liquid crystalline side group copolymers containing cholesteryl and *S*-(-)-chloropropionyloxybiphenyl groups were synthesized and investigated by size exclusion chromatography, ¹H NMR spectroscopy, polarization microscopy, X-ray diffraction and differential scanning calorimetry. The spacer of the cholesteryl-containing side groups was changed by the substitution of two methylene groups by ether groups. The existence of a cholesteric phase on copolymerization of two monomers containing chiral tail groups, from which the homopolymers exhibit only smectic phases, could be observed. This cholesteric phase only exists over a narrow range of copolymer composition. The temperature dependence of the reflection wavelength for the cholesteric phase was determined. For the cholesteryl-containing homopolymer, an S_{A₂} bilayer phase was observed, whereas the *S*-(-)-chloropropionyloxybiphenyl homopolymer showed a higher ordered S_B phase below an S_{A₁} monolayer phase. The layer periodicities of the S_A phases of the copolymers depend on the composition. The substitution of two methylene groups of the spacer by ether groups led to disappearance of the cholesteric phase. Simultaneously, over a small range of copolymer composition a biphasic region was obtained.

1. Introduction

In recent years, interest in thermotropic liquid crystalline (LC) polymers forming ferroelectric smectic C* phases has increased exceptionally. The main requirement for the formation of this interesting phase is the existence of a chiral centre either in the terminal aliphatic tail or in the spacer between the mesogenic group and the spacer. However, LC polymers containing chiral groups often also exhibit a cholesteric phase. In a recent paper we have described the formation of a cholesteric phase on copolymerization of monomers whose homopolymers exhibit only smectic phases [1]. This cholesteric phase in a series of methoxybiphenyl and cholesteryl-containing copolymers exists over a broad range of copolymer composition. In another paper, the influence of chirality on the phase behaviour of copolymers containing cholesterol as the mesogenic moiety has been discussed [2]. In particular, the influence of substitution of two of the methylene groups in the spacers of the cholesteryl-containing side groups and the use of non-mesogenic 8-(methacryloyloxy)octyl (*S*-

2-chloropropionate and 8-(methacryloyloxy)octyl (*R*)-2-chloropropionate as comonomers were studied.

This paper deals with the characterization of new copolymethacrylates containing cholesteryl and *S*-(-)-chloropropionyloxybiphenyl mesogenic groups, of which the latter introduces a second chiral moiety, as well as an additional mesogenic structure into the copolymer system. Additionally, two methylene groups of the spacer of the cholesteryl-containing monomers were changed for ether groups. This substitution should lead to an increase in the flexibility of the side groups. Kossmehl *et al.* [3] have described a polymer system which contains a similar chiral group linked by a methylene spacer of different length ($n=6, 11$) and having a siloxane polymer backbone. The mesomorphic nature of the liquid crystalline phases of these polymers was found to be smectic A.

Furthermore, since we were concerned with determination of the influence of substitution in the spacer on the phase behaviour of the copolymers, a copolymer system containing only cholesteryl groups with different ratios of substituted and unsubstituted spacers was also synthesized.

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2. Experimental

2.1. Measurements

The characterization of polymers and monomers was carried out by ^1H NMR spectroscopy (Bruker, 200 MHz), IR spectroscopy (Perkin Elmer), differential scanning calorimetry (Perkin Elmer DSC 7) and size exclusion chromatography (Waters C-150), calibrated with polystyrene standards using tetrahydrofuran as solvent. The textures of the mesophases were investigated using a Mettler hot-stage FP 85 and a polarization microscope Zeiss Axioskop (Carl Zeiss).

The X-ray experiments were performed applying monochromated $\text{CuK}\alpha$ -radiation in combination with an evacuated flat-plate camera (sample–film distance 81.5 mm), or a Polaroid camera (sample–film distance 100 mm). The samples were oriented by drawing fibres from the anisotropic melt (within the liquid crystalline mesophase), as well as by a magnetic field. The results of the X-ray experiments were taken into account for the assignments of the smectic phases.

The optical investigations and measurements of birefringence were carried out using a spectrophotometer (Perkin Elmer 551) and an Abbé refractometer (Carl Zeiss).

2.2. Synthesis

2.2.1. Monomers

The monomers containing cholesteryl as the mesogenic group were synthesized according to the well known routes described by Shannon [4]. The *S*(-)-chloropropionyloxybiphenyl monomer was synthesized as follows.

(S)-2-Chloropropanoic acid (**1**). To a solution of 0.3 mol (26.7 g) of L-alanine in 750 ml of hydrochloric acid (6M), 0.4 mol (27.6 g) of sodium nitrite was added during 4 h at -5°C . The solution was stirred for 4 h at 0°C and an additional 15 h at room temperature. Sodium chloride was filtered off and the solution was shaken with 3×100 ml ether. The organic phases were dried over sodium sulphate and the ether was evaporated *in vacuo*. The 2-chloropropanoic acid was purified by distillation under reduced pressure. B.p. $100\text{--}102^\circ\text{C}/30$ mm, m.p. -11°C (lit./ -12°C). $[\alpha]_{\text{D}}^{25} = -10.19^\circ$ in water, $c = 2$ (lit. -9.1° in water, $c = 2.7$).

8-Hydroxyoctyl methacrylate (**2**). 0.1 mol (14.6 g) of 1,8-octandiol was dissolved in 50 ml of pyridine and cooled with ice (5°C). To this solution 0.05 mol (5.2 g) of methacryloyl chloride was added slowly in drops. The solution was stirred for 3 h at room temperature and then poured into a mixture of 150 ml of icewater/hydrochloric acid (pH = 2–3). After neutralization, the solution was washed with chloroform (2×100 ml). The organic phases were separated and washed with water, sodium hydrogen carbonate (10% solution in water) and water,

then dried over sodium sulphate. The chloroform was evaporated and the product purified by preparative column chromatography under pressure with ethyl acetate/hexane 1:1 (v/v) as eluent. A colourless, viscous liquid was obtained. ^1H NMR (CDCl_3): $\delta = 1.28\text{--}1.61$ (m; $6 \times \text{CH}_2$, 12 H), 1.88 (s; CH_3 , 3H), 2.10 (s; OH, 1H), 3.56 (t; CH_2 , 2H), 4.07 (t; CH_2 , 2H), 5.49–6.03 (2s; CH_2 , 2H).

4-Hydroxy-4'-(8-methacryloyloxyoctyloxy)biphenyl (**3**). 0.03 mol (6.4 g) of (**2**), 0.032 mol (8.4 g) of triphenylphosphine and 0.12 mol (22.6 g) of 4,4'-dihydroxybiphenyl were dissolved in 250 ml of tetrahydrofuran (dried over sodium) and stirred. To the solution, 0.033 mol (5.7 g) of diethyl azodicarboxylate (DEAD) was added dropwise; the solution was stirred for 2 h. Then it was carefully evaporated and the product purified by preparative column chromatography under pressure with ethyl acetate/hexane 1:4 (v/v) as eluent. A white powder was obtained. ^1H NMR (CDCl_3): $\delta = 1.27\text{--}1.62$ (m; $6 \times \text{CH}_2$, 12 H), 1.88 (s; CH_3 , 3H), 3.80–4.31 (2t; $2 \times \text{CH}_2$, 4H), 5.62–6.01 (2s; CH_2 , 2H), 6.81–7.58 (4d; CH-arom., 8H), 8.35 (s; OH, 1H).

4-(8-Methacryloyloxyoctyloxy)4'-(*S*(-)-2-chloropropionyloxy)biphenyl (**4**). 0.0157 mol (6 g) of (**3**), 0.0162 mol (1.75 g) of (**1**), 0.017 mol (3.5 g) of dicyclohexylcarbodiimide and 0.0017 mol (0.21 g) of 4-dimethylaminopyridine were dissolved in 80 ml of tetrahydrofuran (dried over sodium) and cooled with ice. The solution was stirred for 1 h at 0°C and additionally at room temperature for 4 h. The precipitate was filtered off and washed with *n*-hexane (2×15 ml). The organic solutions were combined and the product purified by preparative column chromatography under pressure with ethyl acetate/hexane 1:2 (v/v) as eluent. A white powder was obtained. ^1H NMR (CDCl_3): $\delta = 1.42\text{--}1.79$ (m; $6 \times \text{CH}_2$, CH_3 , 15H), 1.91 (s; CH_3 , 3H), 3.92–4.16 (m; $2 \times \text{CH}_2$, 4H), 4.71–4.83 (q; CH, 1H), 5.52–6.04 (2s; CH_2 , 2H), 6.90–7.68 (m; CH-arom., 8H).

2.2.2. Polymers

The polymers **P1/P2/P3** and **Co1–Co12** were synthesized by free radical polymerization in benzene for 24 h at 60°C with 2,2'-azoisobutyronitrile (AIBN, 1 mol %) as initiator. The monomers were dissolved in freshly distilled and dried benzene as 10 wt % solutions in a vial with a gas lead-through; the solution was maintained under nitrogen. At the end of the polymerization the solution was dropped into methanol; the precipitate was filtered off, dissolved in chloroform and precipitated again in methanol. The polymer was filtered off and dried *in vacuo* at 40°C for 24 h.

3. Results and discussion

The compositions determined by ^1H NMR, phase transition temperatures and molecular weights of the

synthesized homo- and co-polymers are given in tables 1–3. The average molecular weights are between 48 000 and 177 000 g mol⁻¹ (degree of polymerization from 120 to 280); therefore, there should not be any dependence of phase transition temperatures on molecular weight.

3.1. Phase behaviour

Figure 1 represents the structures of the synthesized homo- and co-polymers (**P**, **Co**). The phase behaviour of the polymers is shown in figures 2–4. The cholesteryl-containing homopolymers **P1** (described by Shannon [4]) and **P2**, as well as the new chloropropionyloxybiphenyl-containing homopolymer **P3**, exhibit only smectic mesophases. Also all the copolymers give smectic mesophases. For the copolymer **Co5**, an additional cholesteric high temperature phase was observed.

3.2. X-ray investigations

The results of X-ray diffraction experiments on **P1**, **P2** and **Co1–4** (only cholesteryl-containing mesogens) led to the conclusion of the existence of a smectic A phase (see for example figure 5(a)). The X-ray patterns of fibres consist of sharp layer reflections in the small angle region perpendicular to the fibre axis and broad crescents in the wide angle region parallel to the fibre axis. The broad halo in the wide angle region indicates a liquid-like lateral arrangement of the side groups in the layers. From the layer periodicities it can be concluded that the cholesteryl-containing side groups are arranged according to a bilayer structure with partially overlapping alkyl tails of the cholesteryl moieties. With an increasing amount of ether substitution of spacer methylene groups, the layer periodicities change

Table 1. Compositions (see figure 1), phase transition temperatures and molecular weights of the cholesteryl-containing polymers (g=glassy, S=smectic, I=isotropic).

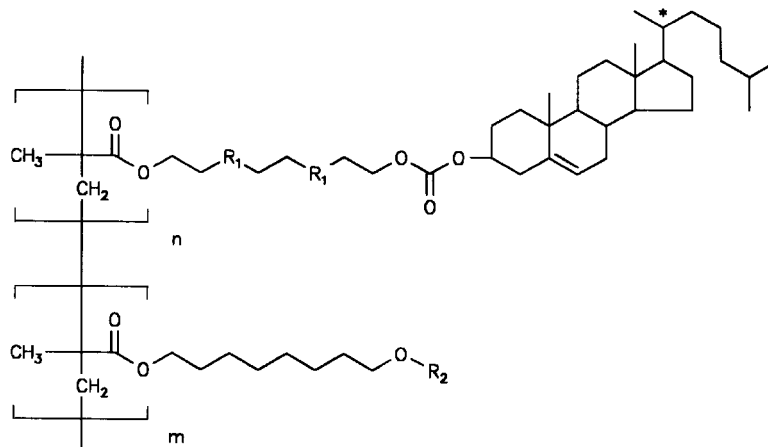
Polymer	<i>m</i> (¹ H NMR)/mol %	Phase transition temperatures/°C	Molecular weight	
			<i>M_w</i> /g mol ⁻¹	<i>M_w</i> / <i>M_n</i>
P1	100	g 39 S _{A₂} 125 I	60300	1.7
Co1	76	g 38 S _{A₂} 132 I	175000	1.9
Co2	51	g 37 S _{A₂} 143 I	57500	1.9
Co3	37	g 39 S _{A₂} 154 I	177000	2.0
Co4	17	g 41 S _{A₂} 167 I	176000	1.9
P2	0	g 41 S _{A₂} 167 I	56000	2.0

Table 2. Compositions (see figure 1), phase transition temperatures and molecular weights of the cholesteryl-chloropropionyloxybiphenyl-containing polymers with spacer modification (g=glassy, S=smectic, I=isotropic).

Polymer	<i>m</i> (¹ H NMR)/mol %	Phase transition temperatures/°C	Molecular weight	
			<i>M_w</i> /g mol ⁻¹	<i>M_w</i> / <i>M_n</i>
P1	0	g 39 S _{A₁} 125 I	60300	1.7
Co5	26	g 30 S _{A₁} 101 Ch 116 I	52900	1.8
Co6	47	g 35 S _{A₁} 122 I	50190	1.8
Co7	65	g 37 S _{A₁} 136 I	53900	2.0
Co8	84	g 58 S _{A₁} 148 I	48400	1.9
P3	100	g 85 S _B 140 S _{A₁} 169 I	101300	1.9

Table 3. Compositions (see figure 1), phase transition temperatures and molecular weights of the cholesteryl-chloropropionyloxybiphenyl-containing polymers with spacer modification (g=glassy, S=smectic, I=isotropic).

Polymer	<i>m</i> (¹ H NMR)/mol %	Phase transition temperatures/°C	Molecular weight	
			<i>M_w</i> /g mol ⁻¹	<i>M_w</i> / <i>M_n</i>
P2	0	g 41 S _{A₂} 167 I	56000	2.0
Co9	28	g 35 S _{A₁} 132 S _{A₂} 161 I	85890	1.9
Co10	50	g 32 S _{A₂} 101 S _{A₁} 127 I	94250	1.8
Co11	67	g 41 S _{A₁} 146 I	115000	1.8
Co12	85	g 58 S _{A₁} 160 I	123900	1.8
P3	100	g 85 S _B 140 S _{A₁} 169 I	101300	1.9



R ₁	R ₂	polymer
—O—		P1 (m=100) P2 (m=0) Co 1-4
—CH ₂ —		P3 (m=100) Co 5-8
—O—		Co 9-12

Figure 1. Structural representation of the samples investigated.

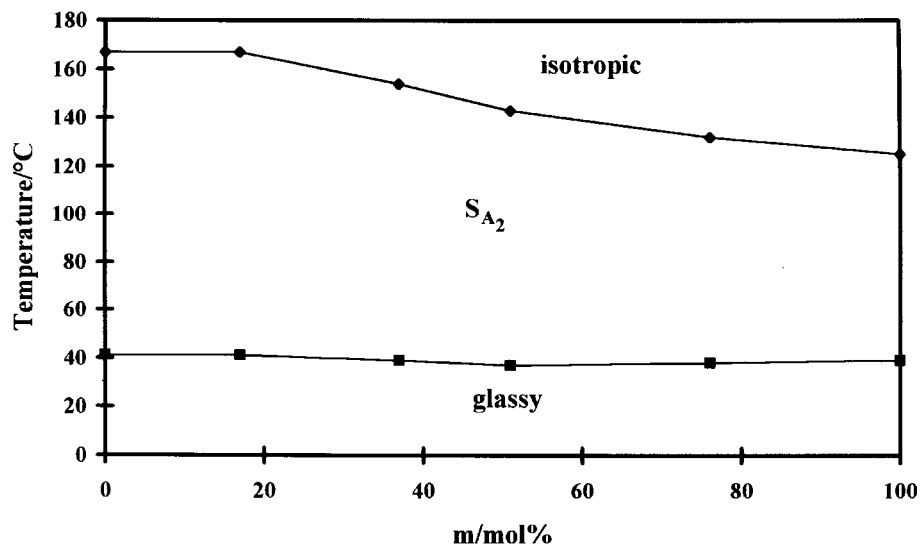


Figure 2. Phase behaviour of the homopolymers **P1** and **P2** and the cholesteryl copolymer systems **Co1-4**.

Figure 3. Phase behaviour of the cholesteryl and chloropropionyloxybiphenyl homopolymers **P1** and **P3** and the copolymer systems **Co5-8** (dotted lines: assumed phase behaviour).

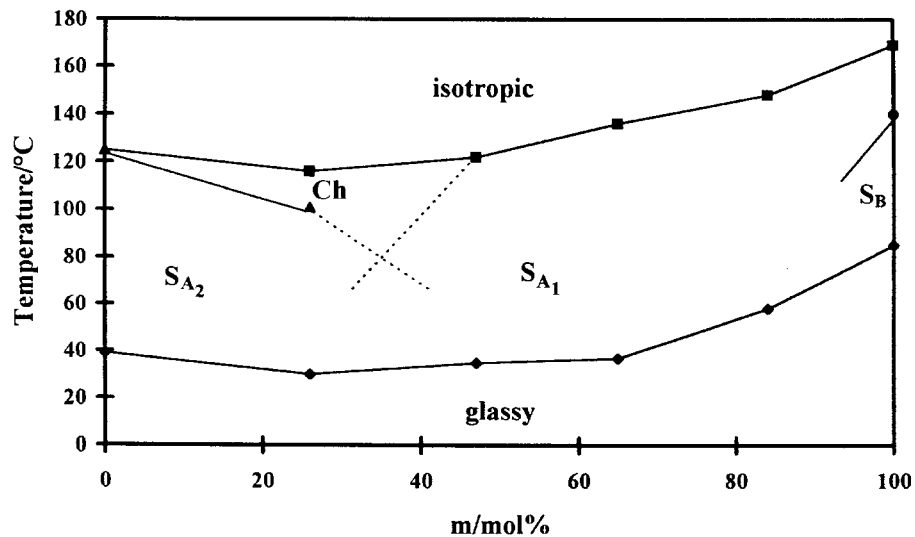


Figure 4. Phase behaviour of the cholesteryl and chloropropionyloxybiphenyl homopolymers **P2** and **P3** and the copolymer systems with spacer variation **Co9-12** (between 28 and 50 mol% biphasic region).

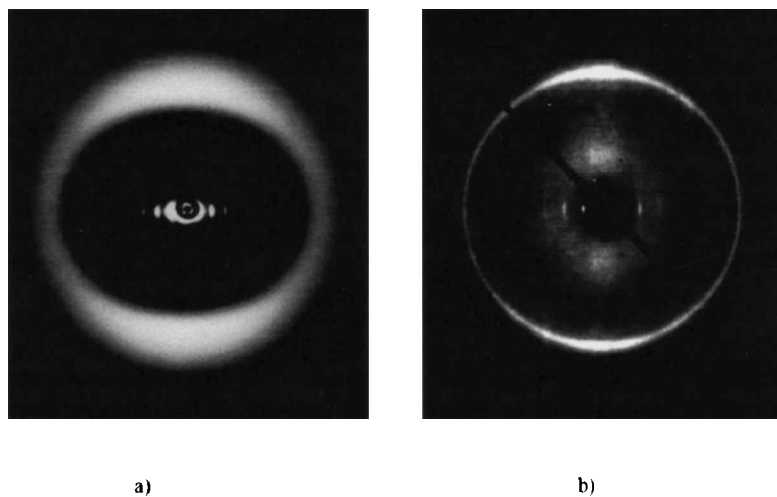
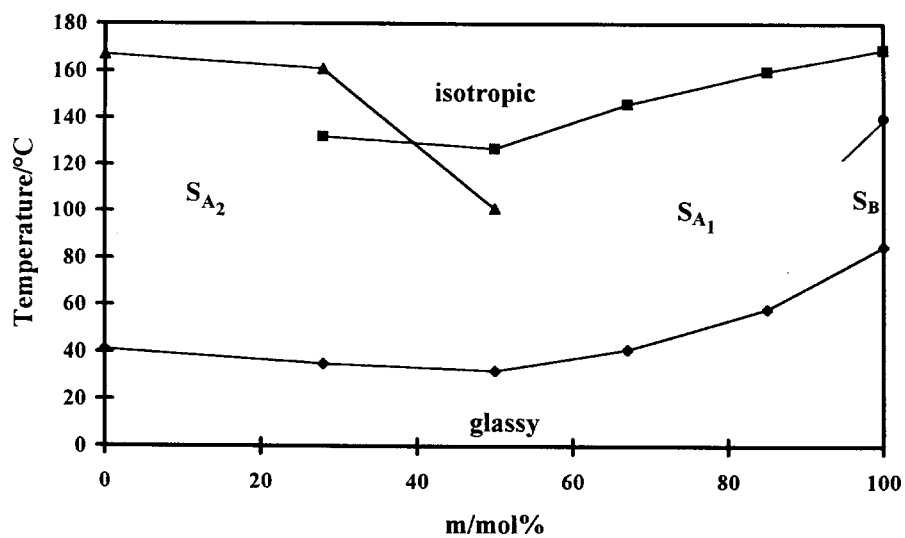


Figure 5. X-ray diffraction pattern of the homopolymers; (a) **P2** (smectic A phase, magnetically aligned, magnetic field direction horizontal) and (b) **P3** (smectic B phase, mechanically oriented, fibre axis vertical).

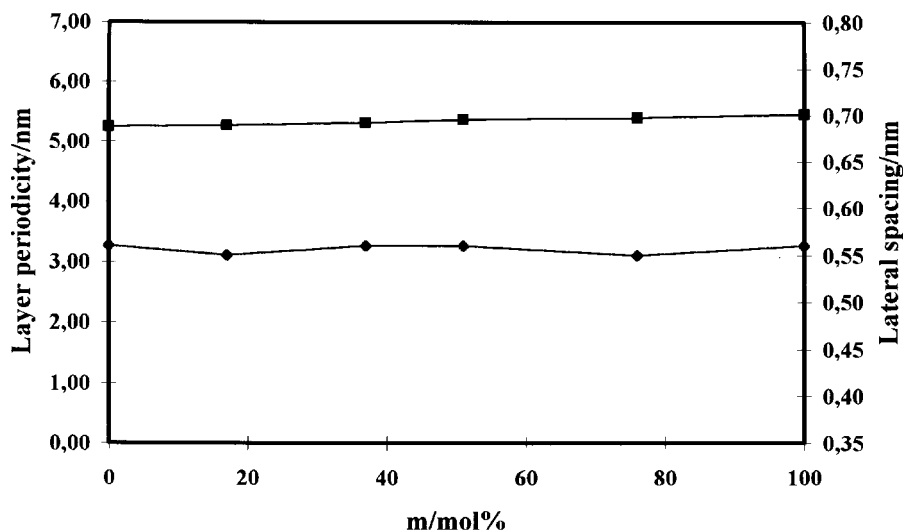
continuously from 5.46 nm (**P1**) to 5.25 nm (**P2**) (see table 4 and figure 6). This indicates a better overlapping of the more flexible side groups containing ether groups. Similar X-ray results for the unsubstituted spacer homopolymer were obtained by Shibaev [5] and Yamaguchi [6, 7].

The copolymers containing both chloropropionyloxybiphenyl and cholesteryl groups exhibit smectic A phases; the copolymer **Co5** shows additionally a cholesteric phase with a selective reflection of blue light. Below the smectic A phase, the chloropropionyloxybiphenyl homopolymer **P3** develops a low temperature smectic B phase (see figure 5(b)). In the more ordered smectic B phase, due to the hexagonal ordering within the layers, the X-ray pattern shows a sharp and intense reflection at wide angles. The side groups are arranged perpendicular to the layer plane, since the wide and small angle reflections appear perpendicular to each other. It should be mentioned that the introduction of the chiral tail group decreases the order of the biphenyl-containing side groups (E phase at low temperatures for the methoxybiphenyl homopolymer [1], and S_B phase for the chloropropionylbiphenyl homopolymer).

Table 4. Layer periodicities of the polymers **P1**, **Co1–4**, **P2** in the smectic A phases and lateral spacings of the mesogenic groups.

Polymer	m ($^1\text{H NMR}$) /mol %	Layer periodicities /nm	Lateral spacing /nm
P1	100	5.46	0.56
Co1	76	5.40	0.55
Co2	51	5.35	0.56
Co3	37	5.32	0.56
Co4	17	5.27	0.55
P2	0	5.25	0.56

Figure 6. Layer periodicities \blacksquare and lateral spacings \blacklozenge in the S_A phase of the polymers **P1**, **Co1–4**, **P2** versus amount of cholesteryl side groups containing unsubstituted spacer.



In tables 5 and 6 and in figures 7 and 8, the layer periodicities and the lateral spacings for the copolymer systems are given. In accordance with a previously investigated copolymer system [1], the layer structure is determined mainly by the chloropropionyloxybiphenyl mesogenic groups up to 50 mol% of cholesteryl terminated side groups. The side groups are arranged with a partial overlapping of the aromatic biphenyl rings and, in addition, a total overlapping of the cholesteryl-containing side groups. The small angle reflections indicate an almost constant layer periodicity (between 3.01

Table 5. Layer periodicities of the polymers **P1**, **Co5–8**, **P3** in the smectic A phases and lateral spacings of the mesogenic groups.

Polymer	m ($^1\text{H NMR}$) /mol %	Layer periodicities /nm	Lateral spacing /nm
P1	0	5.46	0.56
Co5	26	6.12	0.52
Co6	47	3.11	0.50
Co7	65	3.09	0.48
Co8	84	3.08	0.45
P3	100	3.07	0.44

Table 6. Layer periodicities of the polymers **P2**, **Co9–12**, **P3** in the smectic A phases and lateral spacings of the mesogenic groups.

Polymer	m ($^1\text{H NMR}$) /mol %	Layer periodicities /nm	Lateral spacing /nm
P2	0	5.25	0.56
Co9	28	3.06/5.35	0.48
Co10	50	3.06/5.30	0.48
Co11	67	3.03	0.46
Co12	85	3.01	0.45
P3	100	3.07	0.44

Figure 7. Layer periodicities \blacksquare (S_{A1}), \blacktriangle (S_{A2}) and lateral spacings \blacklozenge in the S_A phase of the polymers **P1**, **Co5-8**, **P3** versus amount of chloropropionyloxybiphenyl groups.

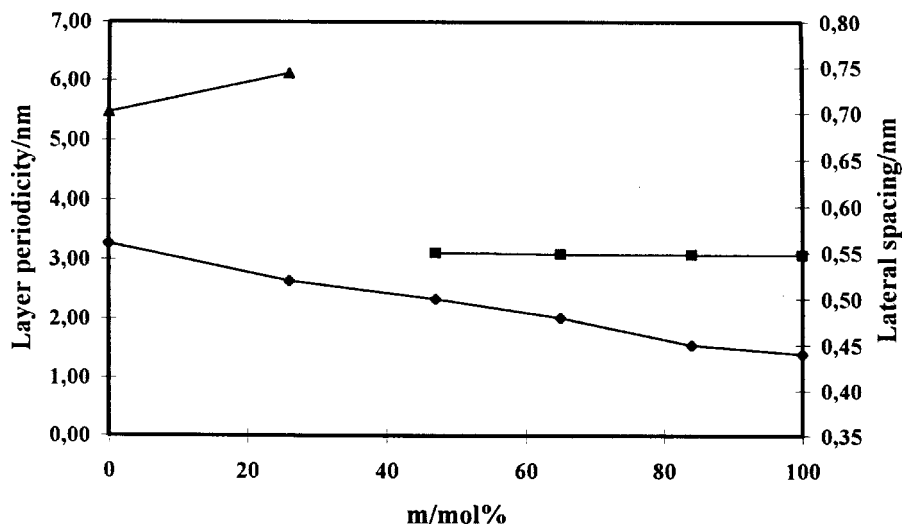
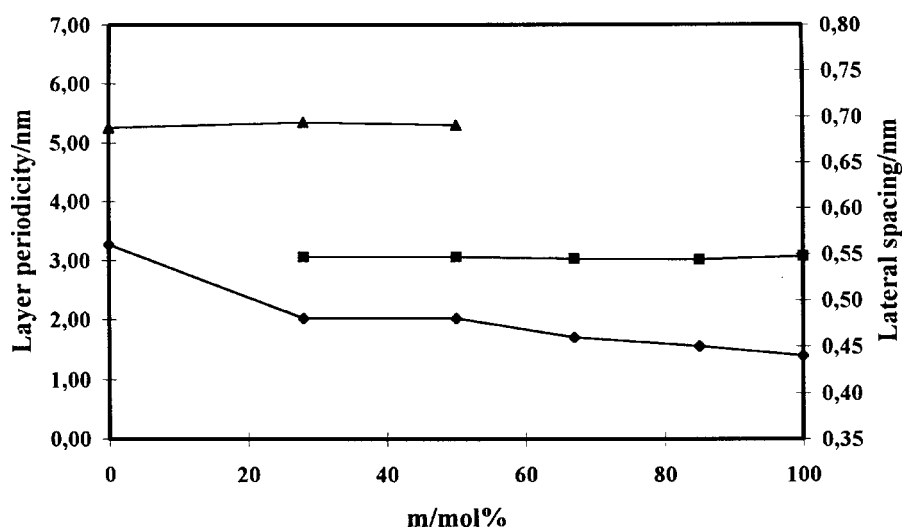


Figure 8. Layer periodicities \blacksquare (S_{A1}), \blacktriangle (S_{A2}) and lateral spacings \blacklozenge in the S_A phase of the polymers **P2**, **Co9-12**, **P3** versus amount of chloropropionyloxybiphenyl groups.



and 3.11 nm) with increasing amount of the cholesteryl moieties. More than 50 mol % of cholesteryl moieties led to a change in the arrangement of the side groups. Like the cholesteryl homopolymers **P1** and **P2**, they are packed in a bilayer structure with partial overlapping of the alkyl tails of the cholesteryl groups. Only the copolymer **Co5** with an unsubstituted spacer does not exhibit this overlapping.

3.3. Optical investigations/textures/birefringence

Figure 9 shows the optical textures of the chloropropionyloxybiphenyl homopolymer **P3** in the different smectic phases. The typical fan-like texture represents a smectic A phase. During cooling into the smectic B phase, which was established by X-ray diffraction, a sharpening of the edges of the fans, but no transition bars could be observed.

In the high temperature phase, the copolymer **Co5** shows a spontaneous reflection of light in the visible region of the electromagnetic spectrum. This indicates the appearance of a cholesteric phase. In contrast to the often described strong influence of temperature [8–13], the reflection wavelength, given in figure 10, shows only a slight temperature dependence within the cholesteric mesophase. Fast cooling into the glassy state led to a freezing in of the cholesteric helix. The copolymer has maintained the selective reflection for the two years until now.

Figure 11 displays results of the measurement of the birefringence of **Co5**. The steps in the curve indicate the phase transitions I–Ch and Ch– S_A during cooling. The transition temperatures isotropic–cholesteric and cholesteric–smectic are in good agreement with the results obtained from DSC measurements ($\Delta T = 1-2$ K).

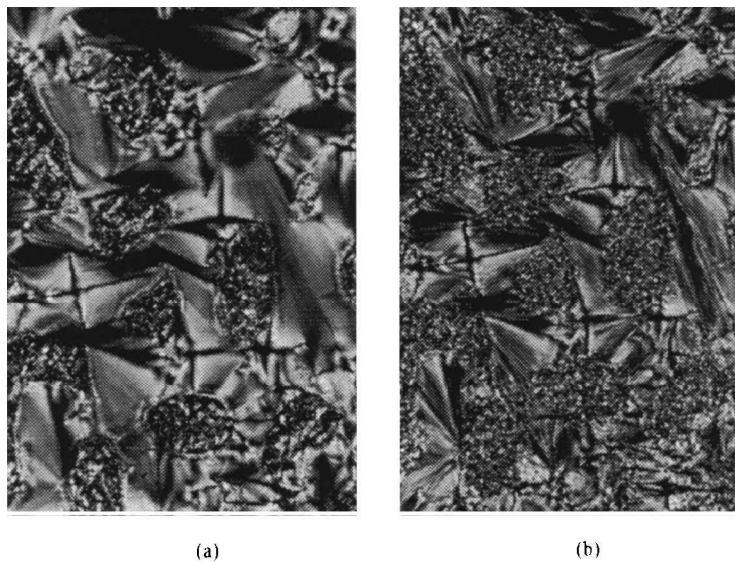


Figure 9. Textures of the chloropropionyloxybiphenyl homopolymer **P3**; (a) S_A phase at 145°C and (b) S_B phase at 125°C .

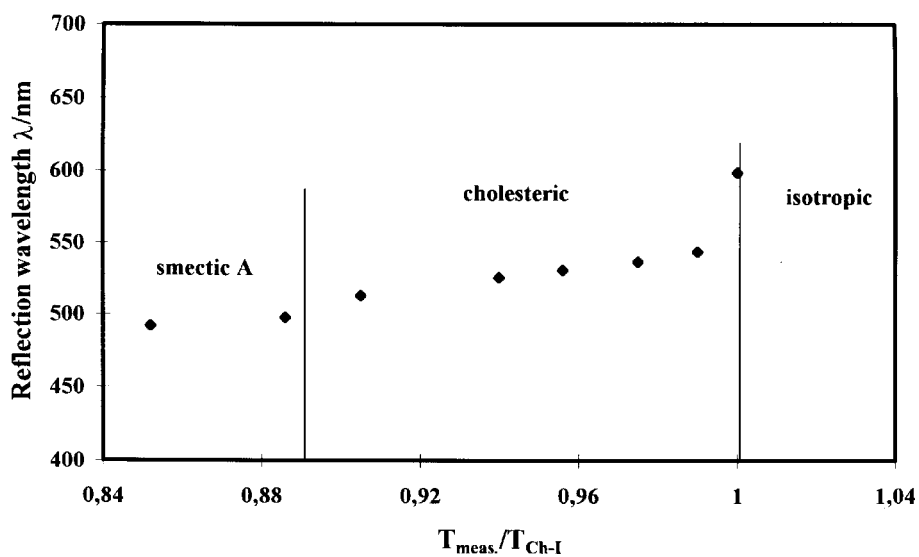


Figure 10. Temperature dependence of the reflection wavelength of copolymer **Co5** (inverse wavelength versus reduced temperature $T_{\text{meas.}}/T_{\text{Ch-I}}$).

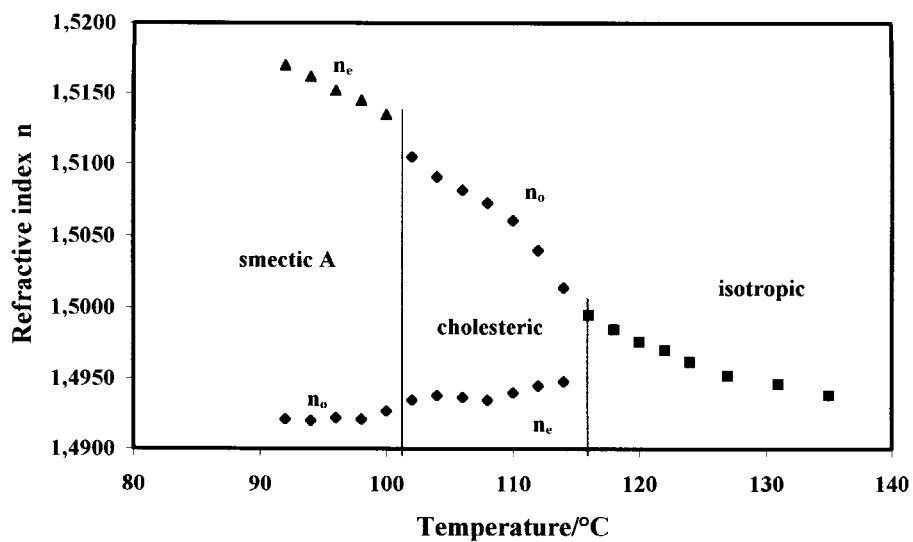


Figure 11. Temperature dependence of the refractive indices of copolymer **Co5**; n_e =extraordinary refractive index, n_o =ordinary refractive index.

4. Conclusions

The formation of a cholesteric phase by copolymerization of monomers containing two chiral moieties whose homopolymers exhibit only smectic phases has been shown. The cholesteric phase exists over only a narrow range of composition. This range is represented by a change in the packing structure of the side groups. The introduction of ether groups into the spacers leads to an increasing flexibility of these side groups and therefore to an increasing stability of the smectic A phases. In these cases, the cholesteric phase could not be obtained. The substitution of the methoxy tail group by the chiral chloropropionyl group decreases the order of the smectic low temperature phase of the homopolymer containing only biphenyl groups.

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