Phase behaviour of copolymers containing cholesterol and 4-methoxybiphenyl as mesogenic groups

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Phase behaviour of copolymers containing cholesterol and 4-methoxybiphenyl as mesogenic groups

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Liquid crystalline side group copolymers containing cholesterol and methoxybiphenyl were synthesized and investigated by size exclusion chromatography, ^{1}H NMR, polarization microscopy, X-ray diffraction, differential scanning calorimetry and additionally by measuring the birefringence and the optical reflection of the cholesteric phase. This cholesteric phase could be obtained by copolymerization of two monomers whose homopolymers exhibit only smectic phases. The cholesteric phase exists over a broad range of copolymer composition. For the cholesterol containing homopolymer an S_{A2} bilayer phase was observed, whereas the methoxybiphenyl homopolymer shows a highly ordered E phase below an S_{A1} monolayer phase. The layer periods of the S_A phases of the copolymers depend on the composition. By measuring the birefringence the order parameter in the cholesteric phase could be determined.

1. Introduction

The cholesteric phase of liquid crystalline polymers represents one of the most interesting liquid crystalline phases because of its unique optical properties such as the selective reflection of circularly polarized light. The polymerization of cholesteric monomers leads only to the formation of smectic polymers. The principles for obtaining cholesteric phases in polymers were given by Finkelmann and Rehage [1]. The copolymerization of nematogenic and chiral comonomers or the mixture of nematic polymers with chiral polymers or monomers can be applied to obtain cholesteric polymers. The formation of this interesting phase by copolymerization of two different comonomers, whose homopolymers exhibit only smectic phases, has not yet been described. Thus our aim was to investigate the phase behaviour of a series of copolymers consisting of two common monomers. Figure 1 gives the structure of the polymers synthesized.

The cholesterol containing homopolymer **P1**, described by Shannon [2], as well as the homopolymer containing methoxybiphenyl **P2**, described by Finkelmann et al. [3] and Hahn et al. [4], exhibit smectic phases. Especial attention was required for the determination of the phase behaviour of the methoxybiphenyl homopolymer. Both authors obtained two phases, but no glass transition was observed. Finkelmann et al. [3] explained
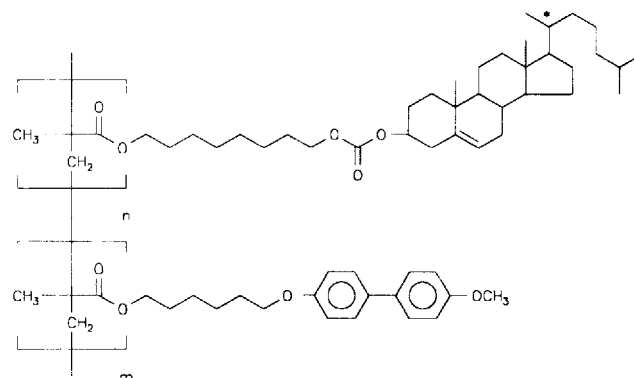
Figure 1. Structural representation of the polymers investigated.

the low temperature transition by the melting of crystalline side group domains or by a transition involving a low temperature smectic phase, whereas Hahn et al. [4] described this phase as probably crystalline or partially crystalline.

Optical investigations had shown a fan shaped texture typical for the smectic phases, but in X-ray studies the authors did not find any sharp reflections in the small angle region. These results did not show agreement for the assignment of the high temperature phase and were interpreted by Hahn et al. [4] in terms of the occurrence of smectic layers not stacked in a way which gives rise to a periodic structure.

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Table 1.   Compositions, phase transition temperatures and molecular weights of the polymers investigated.

Polymer	m [^{1}H NMR] /mol %	Phase transition temperatures/°C							Molecular weight M_w/g mol^{-1}	M_w/M_n
P1	0	g	39	S_{A2}			125	I	60300	1·7
Co1	24	g	36	S_{A2}	106	Ch	117	I	74200	1·8
Co2	48	g	42	S_{A1}	83	Ch	108	I	94500	2·0
Co3	64	g	48	S_{A1}	95	Ch	112	I	120000	1·8
Co4	85	g	57	S_{A1}	118	Ch	123	I	137000	2·2
P2	100	E	119	S_{A1}			136	I	19500	1·8

Recently, Yamada *et al.* [5] found an X-ray pattern for the high temperature phase typical for an S_A phase, but only the second order layer reflection was observed. For the low temperature phase of this anionically polymerized biphenyl containing homopolymer, in addition to three orders of layer reflections in the low angle region, these authors found several sharp reflections in the wide angle range. They assigned this phase as crystalline, but the structure was understood to be of the layer type rather than of three dimensional order.

Duran *et al.* [6–8] have described a similar polymer which contains oligo (ethylene oxide) units in the spacer. The mesomorphic structure of the low temperature phase of this polymer was stated to be an E phase.
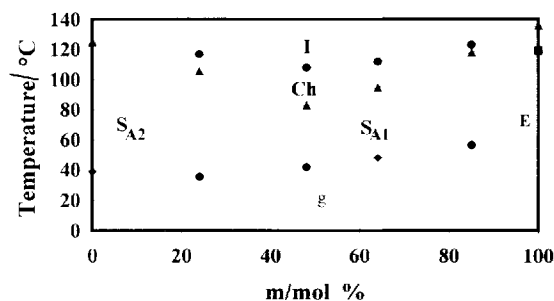
2.   Experimental

2.1. *Measurements*

The characterization of monomers and polymers was carried out by ^{1}H NMR spectroscopy (Bruker, 200 MHz), IR spectroscopy (Perkin Elmer), differential scanning calorimetry (Perkin Elmer DSC 7, scanning rate 10 K min^{-1}) and size exclusion chromatography (Waters C-150), calibrated with polystyrene standards and using tetrahydrofuran as solvent. The textures of the mesophases were investigated using a Mettler hot-stage FP 85 and a polarizing Zeiss Axioskop microscope (Carl Zeiss). The X-ray experiments were performed using

Figure 2.   Phase behaviour of the copolymer system investigated (---- assumed continuation of curves).
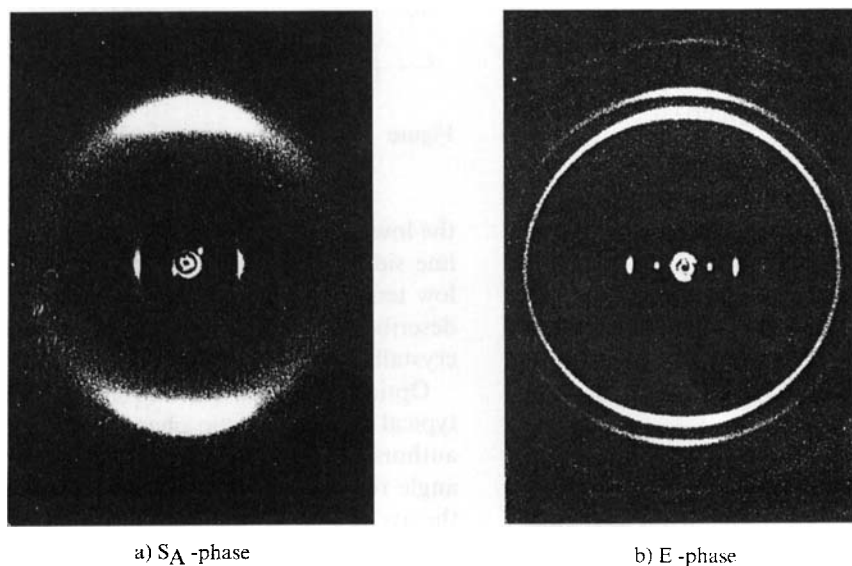

a) S_A -phase

b) E -phase

Figure 3.   X-ray diffraction pattern of the methoxybiphenyl homopolymer **P2** oriented in a magnetic field (field direction horizontal): (*a*) smectic A phase; (*b*) E phase.

Table 2. Layer periods of the polymers and lateral spacings of the mesogenic groups in the smectic A phases.

Polymer	m[^{1}H NMR] /mol %	Layer periods/ nm	Lateral spacing/ nm
P1	0	5·5	0·56
Co1	24	6·7	0·58
Co2	48	3·4	0·55
Co3	64	3·1	0·52
Co4	85	2·9	0·49
P2	100	2·6	0·46

monochromated CuK$_\alpha$ radiation in combination with an evacuated flat-plate camera at distances of 81·5 mm and 84 mm from the sample. The samples were oriented by drawing fibres from the anisotropic melt (within the smectic region). For the biphenyl containing homopolymer **P2**, samples oriented in a magnetic field (2·4 T) were additionally investigated. The results of the X-ray experiments are taken into account in 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

The monomers were synthesized according to the well known routes described by Shannon [2] and Finkelmann *et al.* [3].

The polymers were synthesized by free radical polymerization in solution 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 head-space vial. The solutions were held under nitrogen. At the end of the polymerization, the solution was dripped into methanol, the precipitate was filtered off, redissolved in chloroform
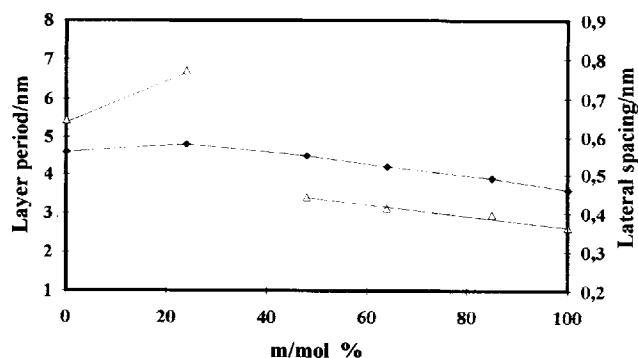

d = 2.65 nm
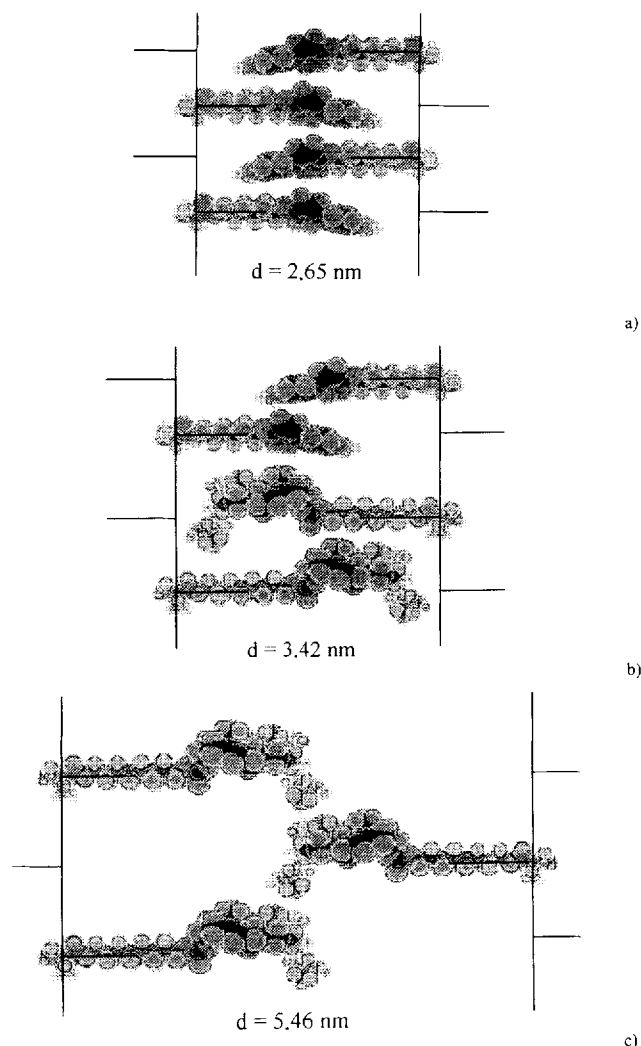
a)

d = 3.42 nm

b)

d = 5.46 nm

c)

Figure 5. Schematic representation of the arrangement of the side groups in the S$_A$ phases: (*a*) biphenyl homopolymer **P2**; (*b*) copolymer **Co2**; (*c*) cholesterol homopolymer **P1**. (Note that due to the linkage of the cholesterol moiety to the spacer and due to the chirality of the tail group, the shape of that side group is not flat.)

Figure 4. Layer periods -△- and lateral spacings -◆- in the S$_A$ phases of the polymers versus amount of methoxybiphenyl.

and precipitated in methanol again. The polymer was then filtered off and dried in vacuo at 40°C for 24 h.

3. Results and discussion

3.1. Phase behaviour

The compositions determined by ^{1}H NMR, phase transition temperatures and molecular weights of the synthesized homo- and copolymers are given in table 1. With the exception of the methoxybiphenyl homopolymer, the average molecular weights were between 60000 and 140000 gmol^{-1} (degree of polymerization from 150 to 200), therefore there should not exist any
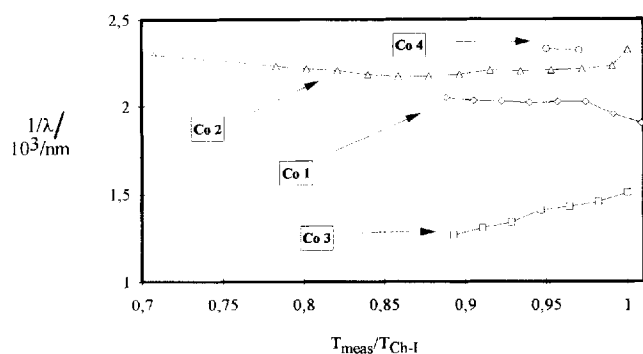
Figure 6.   Temperature dependence of the reflection wavelength of copolymers **Co1-Co4** (inverse wavelength versus reduced temperature T_{meas}/T_{Ch-I}).

Figure 8.   Temperature dependence of the birefringence Δn of copolymers **Co1-Co4** ($T_{red} = T_{meas} - T_{Ch\ I}$).

dependence of phase transition temperatures on molecular weight.

The phase behaviour of the polymers is shown in figure 2. The cholesterol containing homopolymer **P1**, as well as the methoxybiphenyl homopolymer **P2** exhibit

Figure 7.   Temperature dependence of the refractive indices n_e and n_o of samples **Co1-Co4** (for a better comparison, the same temperature range from 80–130°C is displayed in each case).

Figure 9.   Log-log plot of $(n_e^2 - n_o^2)/(\bar{n}^2 - 1)$ for the copolymers **Co1-Co4** versus $1 - T_{meas}/T_{Ch\ I}$.
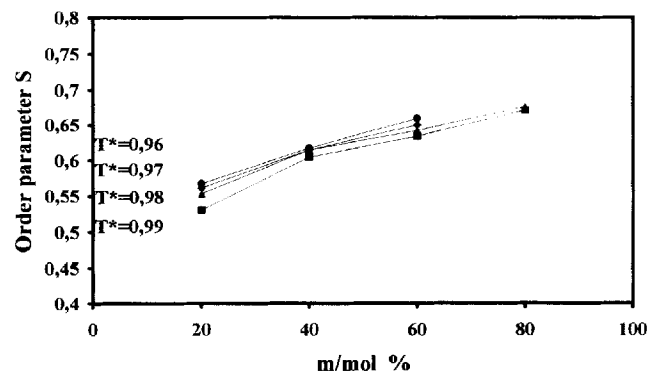
Figure 10.   Order parameter S of the cholesteric phase versus concentration of methoxybiphenyl containing side groups in the copolymers for different temperatures $T^* = T_{meas}/T_{Ch\ I}$.

Table 3. Phase transition enthalpies of the polymers: [a] S_A-I; [b] E-S_A; [c] not calculated, broad DSC peak.

Polymer	ΔH/kj·mol^{-1}	
	S_A-Ch	Ch-I
P1	2·20[a]	—
Co1	1·58	0·28
Co2	0·81	0·66
Co3	[c]	1·48
Co4	0·41	1·63
P2	5·45[b] 2·65[a]	—

Figure 11. Order parameter S in the cholesteric phase versus the phase transition enthalpies for the transition cholesteric-isotropic.

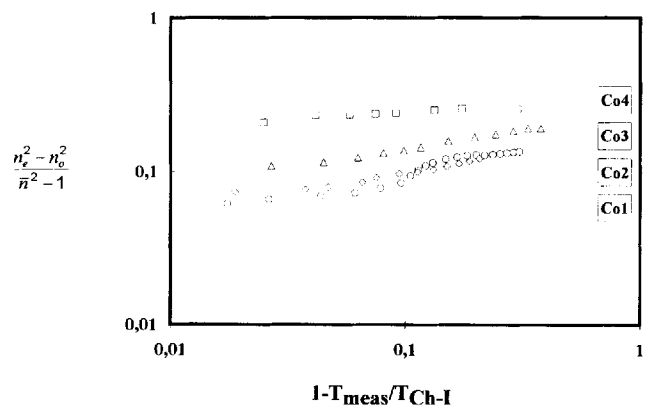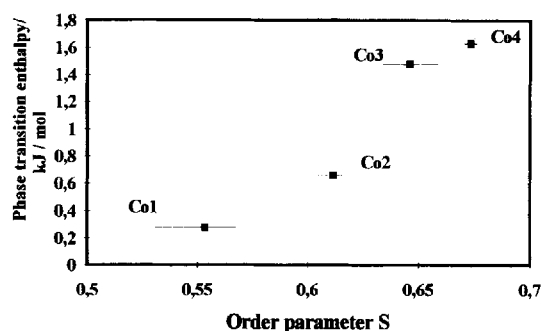only smectic phases, whereas for the copolymers additional cholesteric phases were observed. A maximum in the temperature range of the cholesteric phase was found at a ratio of 1:1 for the two comonomers.

The X-ray diffraction experiments led to the conclusion that the smectic phases were A in type. Additionally the methoxybiphenyl homopolymer **P2** has a highly ordered E phase at lower temperatures. At one time this phase was referred to as smectic E, but is now known to be a three-dimensionally ordered, but soft crystal phase called simply an E phase. In figure 3 the diffraction patterns of **P2** in the smectic A and E phases are shown. In the smectic A phase the broad halo in the wide angle region indicates a liquid like lateral arrangement of the side groups in the layers. The absence of the first order layer reflection, which can be explained by the existence of a glide plane, may be the reason why Hahn *et al.* [4] did not observe any layer reflections corresponding to the full length of the side group unit.

The X-ray pattern for the S_A phase reported by Yamada *et al.* [5] shows the same periodicities of the layers and the lateral arrangement of the mesogenic side groups as those reported in table 2. The X-ray pattern of

the low temperature phase of **P2**, figure 3 (*b*), consists of three sharp reflections at 2·51 nm (relative intensity: medium), 1·26 nm (strong) and 0·84 nm (very weak), indicating three orders of the layer reflections. Since the reflections occur parallel to the magnetic field direction and the periodicity of 2·51 nm corresponds to the calculated length of the side groups in an all-*trans*-conformation, we assume a monolayer arrangement. In accordance with [5], the strong intensity 2nd order layer reflection gives rise to two maxima in the electron density per layer period, which can be explained by a segregation of the backbone and mesogenic side groups. Perpendicular to the layer reflections and typical for an E phase, three sharp reflections in the wide angle region at 0·450 nm (very strong), 0·400 nm (strong) and 0·328 nm (weak) can be observed. Indexing these reflections with (1 1 0), (2 0 0) and (2 1 0) according to an orthorhombic structure, the biphenyl side groups are arranged in a two-dimensional lattice with $a = 0·800$ nm, $b = 0·544$ nm and with a periodicity in the c-direction of 2·51 nm. Using the calculated parameters of a, b and c, the (2 1 0) reflection could be calculated as 0·322 nm (measured: 0·328 nm). Similar results were obtained by Yamada *et al.* [5] ($a = 0·804$ nm, $b = 0·545$ nm and $c = 2·58$ nm). In addition to the reflections we observed, in [5] three more very weak reflections of the $(hk0)$ type were reported. This my be explained by a difference in the backbone configuration (80% syndiotacticity was reported for the anionically polymerized sample **P2** in [5]).

In table 2 and in figure 4, the layer periods and the lateral spacings for the smectic A phases of the copolymer system are given. For polymers with more than 50 mol % of methoxybiphenyl containing side groups, only S_A monolayer phases were observed (see figure 5 (*a*) for homopolymer **P2**). The small angle reflections indicate decreasing layer periods with increasing amount of methoxybiphenyl moieties. For such samples with a relatively high concentration of cholesterol moieties, the layer period is determined by a total overlapping of the cholesterol containing side groups (allowing the biphenyl containing side groups to overlap partially). A schematic arrangement of the side groups for **Co2** is given in figure 5 (*b*).

Polymers **P1** and **Co1** form smectic A bilayer phases. For **Co1**, the side groups are packed without any overlapping of the alkyl tails of the cholesterol, whereas the cholesterol containing homopolymer **P1** exhibits a partial overlapping; for the schematic arrangement of the side groups, see figure 5 (*c*). Similar results for the homopolymer were obtained by Shibaev *et al.* [9] and Yamaguchi *et al.* [10, 11]. However, it may also be possible that the alkyl spacers are not in an all-*trans*-conformation. In this case a small number of methoxybiphenyl mesogenic groups should increase the amount of all-*trans*-

conformation, increasing the layer period, as observed for **Col**.

3.2. *Selective reflection of light*

In the high temperature phase, the copolymers **Col–Co4** show a spontaneous reflection of light in the visible region of the electromagnetic spectrum. This indicates the existence of the cholesteric phase. The reflection wavelengths, obtained from transmission spectra, are often found to depend on the composition of copolymers [12] and on temperature [13–18]. But in our polymers, only copolymer **Co3** shows a significant dependence of the reflection wavelength on temperature. With decreasing temperature, the wavelength is shifted to the near infrared region, as shown in figure 6. This dependence could be explained by the flexibility of the side groups reaching a maximum in this range of composition of the copolymers. The helix seems to be more flexible, and **Co3** also exhibits a broad temperature range of the cholesteric phase. The cholesteric–smectic transition of **Co3** was very broad and not clearly determined using DSC. However, investigation of the birefringence of this copolymer led to a determination of the transition temperature. Fast cooling into the glassy state, led to a freezing in the cholesteric arrangement. The copolymers particularly exhibited their selective reflection over many months (up to now, one year).

3.3. *Birefringence*

The measurement of the birefringence of polymers in their liquid crystalline phases is one method of determining the order parameter of the mesogenic groups [19].

The long range orientational order of the nematic polymer can be described by equation (1):

$$S = \tfrac{3}{2}(\overline{\cos^2\Theta} - \tfrac{1}{3}) \qquad (1)$$

where S represents the order paramter and Θ the angle between the long axis of the mesogenic groups and the director of the nematic phase. Using the modified Lorentz–Lorenz equation which describes the relation between the molecular polarizabilities $\alpha_\perp$ and $\alpha_\parallel$ and the mean refractive index n_i, and transforming the refractive indices of the cholesteric phase into the nematic equivalents [20] according to equations (2 *a*) and (2 *b*),

$$n_{o,n} = n_{e,ch} \qquad (2\,a)$$

$$n_{c,n} = (2n_{o,ch} - n_{c,ch}^2)^{1/2} \qquad (2\,b)$$

the order parameter S can be calculated by

$$S = \left(\frac{n_c^2 - n_o^2}{\bar{n}^2 - 1}\right)^A \qquad (3)$$

with n_e the extraordinary refractive index, n_o the ordinary refractive index, $\bar{n}^2 = \tfrac{1}{3}(n_e^2 + 2n_0^2)$, A a scaling factor.

The results of the measurements of the extraordinary and the ordinary refractive indices are shown in figure 7. In figure 8, the dependence of the birefringence $\Delta n = n_e - n_o$ of copolymers **Col–Co4** on the temperature is displayed. The steps in the curves of both figures indicate the phase transitions S_A–Ch. The scaling factor A was determined from a log–log plot of the expression in parentheses of equation (3) versus $1 - T_{meas}/T_{Ch-I}$ (see figure 9) according to the method which was described by Haller *et al.* [21]. In the low temperature region, this expression appears to be proportional to $1 - T_{meas}/T_{Ch-I}$. To obtain the scaling factor A the curves in figure 9 must be extrapolated to $T{\rightarrow}0K$.

In figure 10, the order parameter S, calculated according to equation (3), is plotted against the concentration of methoxybiphenyl containing side groups in the copolymers. It is shown that an increasing amount of methoxybiphenyl groups leads to an increase in the order in the cholesteric phase of the copolymers. The higher ordering of the cholesteric state of those copolymers containing more methoxybiphenyl side groups can also be concluded from the values of the cholesteric–isotropic phase transition enthalpies (see table 3). With increasing amount of biphenyl moieties in the copolymers, the enthalpy for the isotropic–cholesteric transition increases, whereas the enthalpy for the transition to the smectic A phase decreases. The correlation between order parameter for the cholesteric phase and enthalpy for the cholesteric–isotropic phase transition is shown in figure 11.

4. Conclusions

The phase behaviour of the methoxybiphenyl homopolymer, as well as those of the synthesized copolymers were determined by different methods. The methoxybiphenyl homopolymer shows a highly ordered E phase at low temperatures and a high temperature S_{A1} monolayer phase, whereas for the cholesterol containing homopolymer a S_{A2} bilayer phase was observed.

For the first time, copolymers with a cholesteric phase, resulting from comonomers whose homopolymers exhibit only smectic phases, were observed. Additionally, all copolymers exhibit S_A phases with layer periods depending on the composition. Measurement of the birefringence of the copolymers in their cholesteric phases has shown an increasing order parameter with increasing concentration of methoxybiphenyl moieties.

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