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Mesomorphic properties of a homologous series of chiral liquid crystals containing the α-chloroester group

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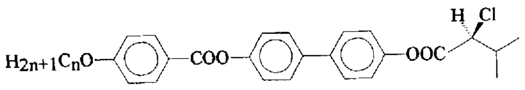
The mesomorphic properties of the N*, S_C^* and higher ordered smectic phases have been investigated for a homologous series of 4-[(*S*)-2-chlor-3-methylbutanoyloxy]-4′-(4-*n*-alkyloxybenzoyloxy)biphenyls. They have been characterized by optical texture observation, differential scanning calorimetry (DSC), small angle X-ray scattering and electro-optic measurements. The compounds exhibit a strongly twisted cholesteric phase and smectic phases with large spontaneous polarization and tilt angle values. One or two higher ordered, monotropic smectic phases were found which significantly differ in their rotational viscosity.

1. Introduction

From the beginning, the goal in ferroelectric liquid crystal research was to synthesize ferroelectric S_C^* materials with a broad temperature range which exhibit a high spontaneous polarization and a low rotational viscosity. Chiral and polar side chains derived from naturally available α-amino acids have been proved by many authors to be suitable to achieve these features [1–4].

The homologous series 4-[(*S*)-2-chlor-3-methylbutanoyloxy]-4′-(4-*n*-alkyloxybenzoyloxy)biphenyls, abbreviated as M*n*, with the general formula given below fulfils the desired properties. The phase transition data are reported in the table and the mesomorphic temperature ranges are depicted in figure 1 as a function of the number of carbon atoms in the alkoxy chain.



The synthesis of the series was first reported by Mohr *et al.* [2], but the materials were not characterized in detail. In this paper we report several properties of these compounds, namely the pitch of the cholesteric and the S_C^* phases, as well as the tilt angle, the spontaneous polarization and the rotational viscosity of the ferroelectric phases. The data are discussed with respect to phase sequence and alkoxy chain length of the homologues.

2. Experimental

The synthesis was carried out according to [2]. It is worthwhile mentioning that the compounds have been carefully purified by column chromatography using SiO_2 as stationary phase and different eluents (CH_2Cl_2, CH_2Cl_2 : *n*-hexane = 9 : 1) in order to reduce the amount of organic impurities and therefore achieve a very low electrical d.c. conductivity. Due to their purity, all the compounds exhibit very narrow two phase regions (< 0·1 K) as proven in a slow cooling process near the first order phase transition N* → S_C^*. Their d.c. conductivity was low enough to apply high electric fields (up to 50 MV m^{-1}) in the smectic phases, which was necessary for an investigation of the ferroelectric switching in the higher ordered smectic phases.

The phase transition temperatures were determined by polarizing microscopy (Olympus BH-2 microscope equipped with a Mettler FP-52 hot stage) and by differential scanning calorimetry (Perkin–Elmer DSC 7). The temperature control of the hot stage was within ± 0·1 K, and the accuracy of absolute values of the temperature was about ± 1 K. Heating and cooling rates of ± 10, ± 5 K min^{-1} and sample weights between 3 and 8 mg were chosen for the DSC measurements.

The samples were prepared in commercially available cells (E.H.C. Co. Ltd, Tokyo, polyimide coated, parallel rubbed, 10 μm cell gap) for the determination of the temperature dependence of the cholesteric pitch *P*. The

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Phase transition temperatures (°C) of the homologous series M*n*. The integer *n* denotes the number of carbon atoms in the alkoxy chain. The values in brackets refer to the molar transition enthalpies in kJ mol^{-1}.

n	I		BP		N*		S_A^*		S_C^*		S_{X2}^*		S_{X1}^*		Cr
3	●	201·3	●	200·1 (0·43)	●			110·2 (1·50)	●					104·8	●
4	●	207·7	—	207·5 (0·59)	●			120·4 (1·20)	●			(80·7 (2·03)	●)	62	●
5	●	197·5	●	197·2 (0·60)	●			128·9 (1·45)	●			(83·2 (2·19)	●)	50	●
6	●	190·8	●	189·9 (0·68)	●			138·5 (1·12)	●			(84·1 (2·54)	●)	25	●
7	●	183·6	●	182·4 (0·63)	●			142·3 (0·97)	●	(78·0 (0·50)	●	73·9 (0·50)	●)	35	●
8	●	184·6	●	183·1 (0·65)	●			146·6 (0·73)	●	(74·0 (0·92)	●	68·0 (0·23)	●)	20	●
9	●	179·9	●	178·4 (0·85)	●			153·7 (0·56)	●	(78·0 (1·17)	●	72·7 (0·34)	●)	40	●
10	●	176·7	●	174·2 (0·96)	●	158·7 (0·23)	●	157·2	●	(75·6 (1·86)	●	70·0 (0·59)	●)	50	●

$10\,\mu$m cell gap was large enough and did not affect the helical superstructure of the cholesteric phase. A defect-free, planar aligned, short pitch grandjean texture was formed and the temperature dependence of the cholesteric pitch was directly obtained from observation of distinct, discontinuous colour changes every time the number of π-twists to fit within the cell gap varied by one with temperature change [5]. Some values were confirmed using the Cano–Grandjean methods [6, 7], and the handedness of the cholesteric helix was determined by an analysis of the optical rotation dispersion. The disclination lines in the Cano experiment were difficult to observe with the naked eye because their contrast diminished by the optical activity. A blue sensitive camera (JVC, TK 1085E) was used in order to improve the observation of 20 to 30 rings.

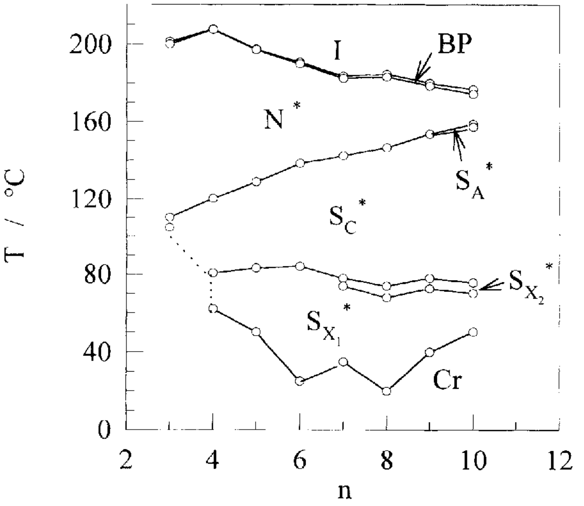

Figure 1. Transitions temperatures as a function of the number of carbon atoms *n* in the alkoxy chain. A longer terminal alkoxy chain destabilizes the chiral nematic phase and favours a smectic arrangement of the molecules.

The smectic interlayer distance d was studied by small angle X-ray scattering (Kratky compact camera, CuKα radiation, Anton Paar KG) equipped with a position sensitive counter (Fa. M. Braun). Only tilted smectic phases were found in this homologous series, except for the decyloxy-derivative (M10) which exhibits a narrow S_A^* phase of about 1°C range (see the table). Therefore, the temperature dependence of the tilt angle $\Theta(T)$ was estimated by measuring the d-values of the S_C^* phase using the calculated length of the fully extended conformation of the molecule corrected by the influence of the nematic order parameter, which is assumed to be 0·9 for the S_C^* and 1·0 for the higher ordered smectics. The accuracy of this method can directly be checked in the case of the S_A^* phase of M10: the deviation between the calculated and the measured d-values was less than 1 per cent. The pitch of the S_C^* helix was estimated from the disclination line distance in the S_C^* fan-shaped texture which was obtained by preparation of the S_C^* phase between untreated glass plates.

The triangular wave technique [8] was used to determine the temperature dependence of the spontaneous polarization with samples prepared in LC cells with a cell gap of $4\,\mu$m. A driving voltage of 3 MV m^{-1} and a frequency of 100 Hz was used for the S_C^* phase and for the higher ordered smectic phases, an electric field of $E = 10$–50 MV m^{-1} and $f = 5$–10 Hz was applied in order to achieve saturated switching.

According to a method introduced by Escher *et al.* [9], measurements of the polarization reversal current were also used to estimate the effective rotational viscosity γ_{eff}

by determination of the maximum polarization reversal current I_{max} and the corresponding electric field strength E_{m}.

$$\gamma_{\mathrm{eff}} = \gamma_{\varphi} \sin^2 \Theta = \frac{AP_{\mathrm{s}}^2 E_{\mathrm{m}}}{I_{\mathrm{max}}} \tag{1}$$

where P_{s} denotes the spontaneous polarization and A the area of the ITO electrodes.

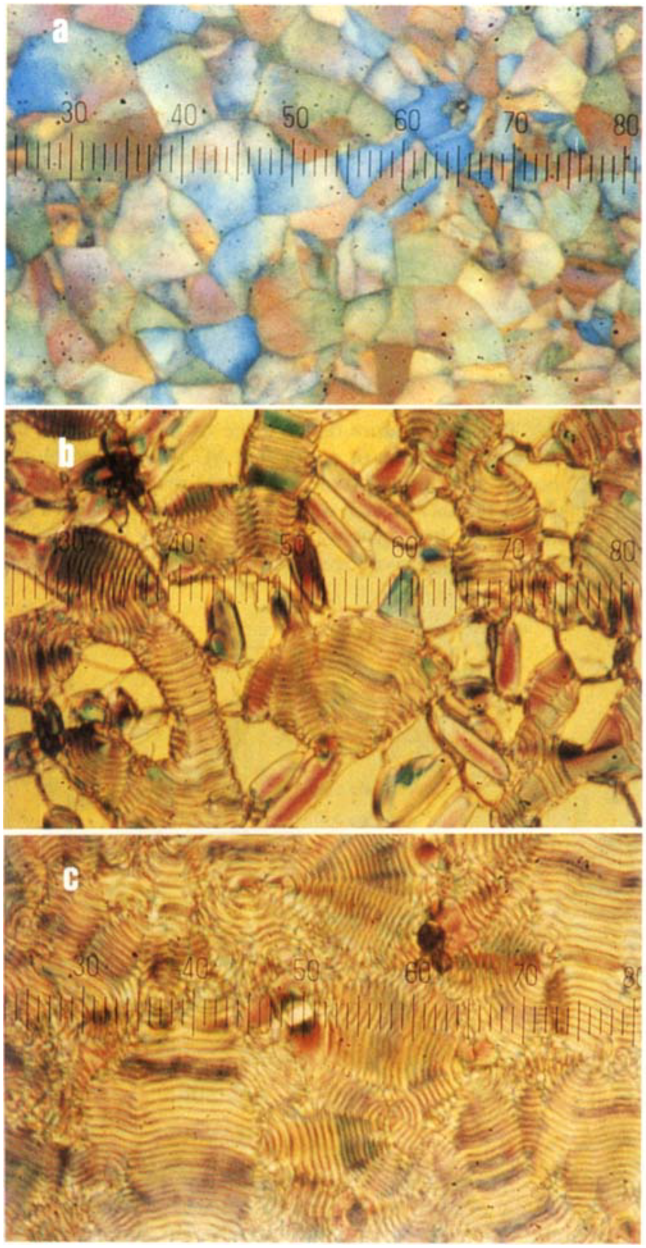

Figure 2. Typical polarizing microscopic textures of compound M7 prepared between two untreated glass plates. (10 units of scale = 60 μm). (*a*) platelet texture of the blue phase, $T = 183{\cdot}9^{\circ}\mathrm{C}$ (similar to plate 158 in [10]); (*b*) $\mathrm{N}^* \rightarrow \mathrm{S}_{\mathrm{C}}^*$ phase transition, $T = 143{\cdot}5^{\circ}\mathrm{C}$; (*c*) $\mathrm{S}_{\mathrm{C}}^*$ disclination line texture, $T = 142{\cdot}0^{\circ}\mathrm{C}$ (similar to plate 164 in [10]).

3. Results and discussion

3.1. *Characterization*

The homologous series M*n* exhibits the general phase sequence $\mathrm{I} \rightarrow \mathrm{BP} \rightarrow \mathrm{N}^* \rightarrow \mathrm{S}_{\mathrm{C}}^* \rightarrow$ higher ordered smectics (see the table). For compound M4, the blue phase is missing and for M10, a narrow $\mathrm{S}_{\mathrm{A}}^*$ phase is found additionally between the N* and the $\mathrm{S}_{\mathrm{C}}^*$ phases. The phase transition temperatures are listed in the table and are

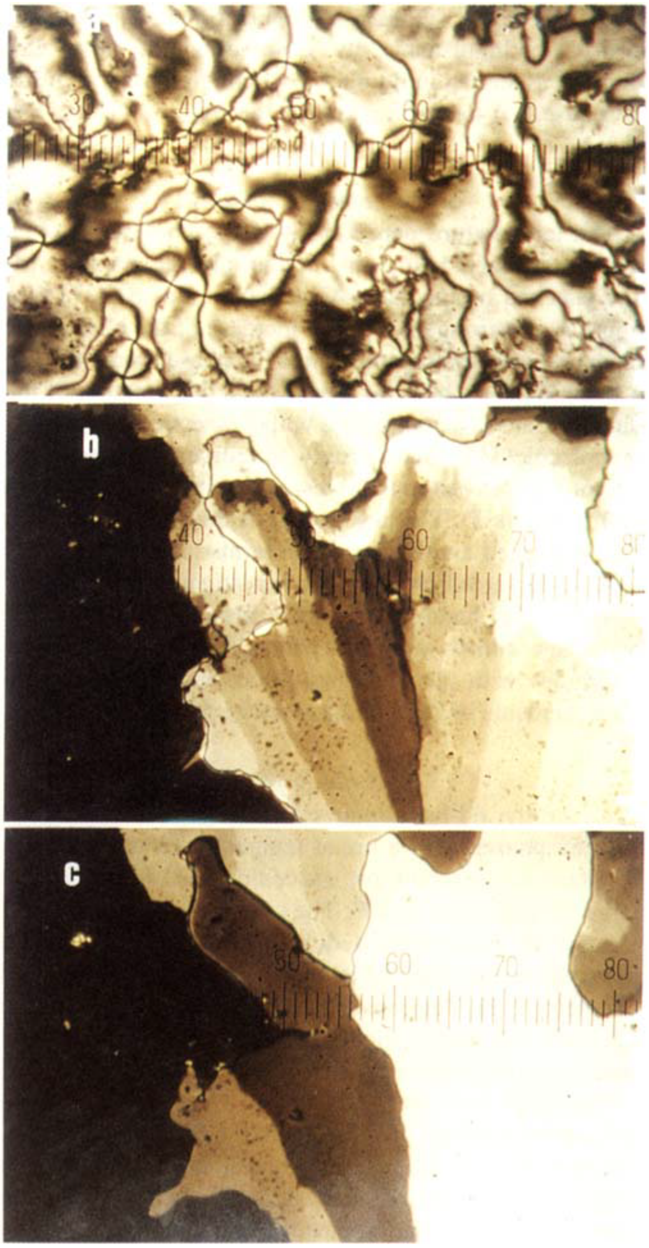

Figure 3. Typical polarizing microscopic textures of compound M7 obtained after shearing between two glass plates. (10 units of scale = 60 μm). (*a*) $\mathrm{S}_{\mathrm{C}}^*$ schlieren texture, $T = 80{\cdot}0^{\circ}\mathrm{C}$ (similar to plate 173 in [10]; (*b*) $\mathrm{S}_{\mathrm{X2}}^*$ mosaic texture, $T = 75{\cdot}0^{\circ}\mathrm{C}$; (*c*) $\mathrm{S}_{\mathrm{X1}}^*$ mosaic texture, $T = 70{\cdot}0^{\circ}\mathrm{C}$.

schematically depicted in figure 1. The DSC transitions were verified by optical texture observations. Figure 2 depicts some examples of typical textures for M7: (*a*) the platelet texture of the blue phase (BP) obtained on cooling from the isotropic liquid with the sample being prepared between two untreated glass plates, (*b*) oily-streak disclinations in the grandjean texture of the cholesteric phase (N*) directly at the N* → $\mathrm{S}_{\mathrm{C}}^{*}$ phase transition and (*c*) the broken fan shaped texture with disclination lines due to the $\mathrm{S}_{\mathrm{C}}^{*}$ helix. Textures of higher ordered phases are clearly distinguishable by observation of very thin samples as shown in figure 3: (*a*) schlieren texture of the $\mathrm{S}_{\mathrm{C}}^{*}$ phase, (*b*) mosaic texture of the $\mathrm{S}_{\mathrm{X2}}^{*}$ and (*c*) the $\mathrm{S}_{\mathrm{X1}}^{*}$ phase.

3.2. *Cholesteric phases*

The temperature dependence of the cholesteric pitch was determined using the colour change method [5] and checked by the Cano–Grandjean method [6, 7] (see figure 4). A strong divergence increase of the cholesteric pitch occurs at temperatures near the phase transition into a smectic phase, because a pure twist deformation of the director field is incompatible with a smectic arrangement of molecules [11]. Interestingly, the curves obtained for all homologues investigated intersect in one point (at about 160°C, figure 5). The description of the cholesteric pitch can be unified and expressed in terms of an equation of state valid for all homologues investigated (see inset of figure 5). The handedness of the chiral nematic structure was determined as right-handedness for all these molecules with the *S* configuration, as concluded from measurements of the optical rotatory power.

3.3. *Smectic phases*

Generally, all homologues of this series exhibit tilted smectic phases with a broad temperature range, a large spontaneous polarization exceeding $300\,\mathrm{nC\,cm^{-2}}$ and large tilt angles up to 30°. The compounds form splayed states with non-uniform director configurations when prepared in thin cells, which favour the surface stabilized geometry [12]. The mesophase properties (for example, $\mathrm{S}_{\mathrm{C}}^{*}$ pitch, tilt angle, spontaneous polarization and rotational viscosity) are reported in the following paragraphs.

The pitch p of the $\mathrm{S}_{\mathrm{C}}^{*}$ helix, which is obtained from fingerprint textures, increases with the number of methylene units $(n-1)$, with some suggestion of an odd–even effect (see figure 6), in contrast to the behaviour of the spontaneous polarization (see figure 7) and the tilt angle of the $\mathrm{S}_{\mathrm{C}}^{*}$ phase which decrease linearly with n at a fixed reduced temperature $T-T_{\mathrm{C}}$. With decreasing temperature, the tilt angle Θ jumps at the first order N* → $\mathrm{S}_{\mathrm{C}}^{*}$ phase transition to ≈ 20°. In the $\mathrm{S}_{\mathrm{C}}^{*}$ phase, the tilt angles rise continuously towards larger values of about 30° at the $\mathrm{S}_{\mathrm{C}}^{*} \rightarrow \mathrm{S}_{\mathrm{X}}^{*}$ phase transitions as depicted in figure 8.

Very high values of the spontaneous polarization P_{s} up to $300\,\mathrm{nC\,cm^{-2}}$ were observed for the $\mathrm{S}_{\mathrm{C}}^{*}$ phase and P_{s} rose discontinuously when a higher ordered smectic phase, $\mathrm{S}_{\mathrm{X1}}^{*}$ or $\mathrm{S}_{\mathrm{X2}}^{*}$, was entered (see figure 9). Assuming that the bulk

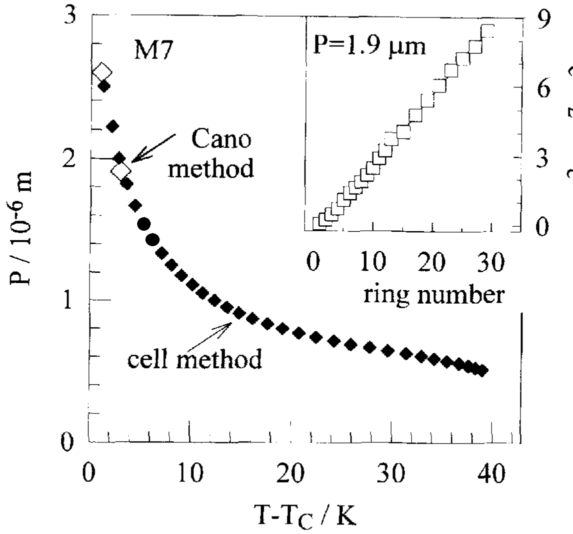

Figure 4. The temperature dependence of the pitch P of the chiral nematic phase of compound M7 determined by the Cano [6] and the cell (colour change) method [5]. In the inset, the radius r of each ring (open squares) from the Cano method is plotted against the corresponding ring number. The pitch P is derived from the slope of the straight line.

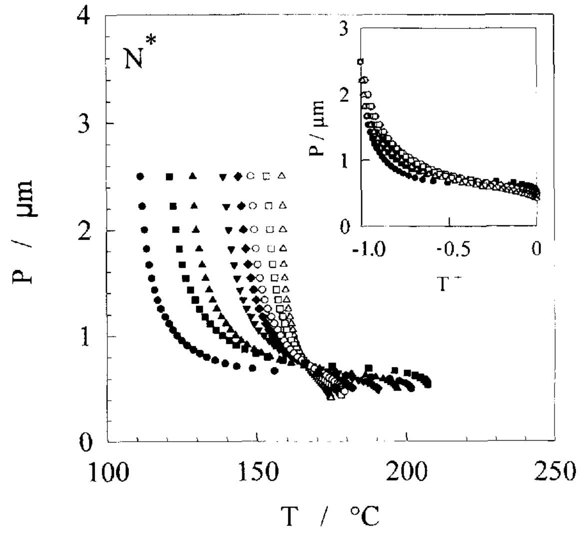

Figure 5. Temperature dependence of the cholesteric pitch $P(T)$ determined by the colour change method. Interestingly, the curves for all homologues M*n* intersect in one point ('isotwisting point') at approximately 160°C. The cholesteric pitch as a function of a reduced temperature $T^{+}=(T_{\mathrm{N}}-T)/(T_{\mathrm{C}}-T_{\mathrm{N}})$ ($T_{\mathrm{N}}, T_{\mathrm{C}}$: temperature of the N* → I and $\mathrm{S}_{\mathrm{C}}^{*} \rightarrow$ N* phase transition) is depicted in the inset. The curves resemble a situation of corresponding states. M3 (●), M4 (■), M5 (▲), M6 (▼), M7 (◆), M8 (○), M9 (□), M10 (△).

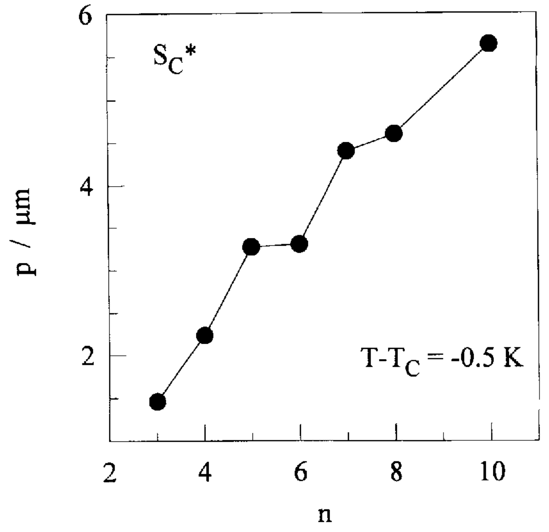

Figure 6. S_C^* pitch values p for the homologous series Mn at $T - T_C = -0.5$ K.

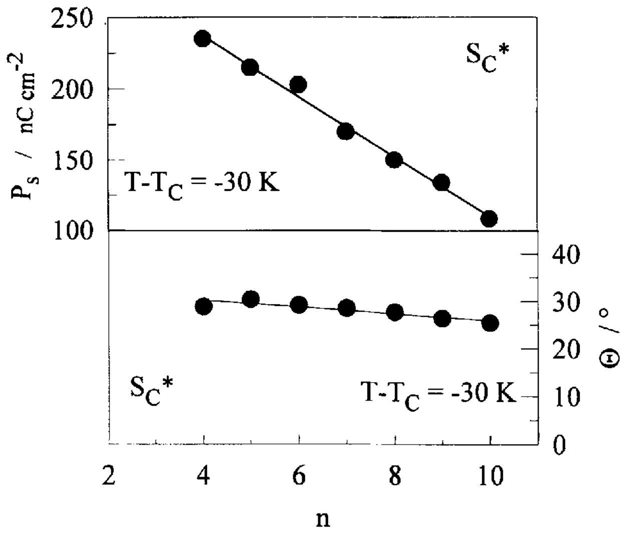

Figure 7. Spontaneous polarization P_s at $T - T_C = -30$ K in the S_C^* phase for all compounds Mn (upper part) and tilt angles Θ at the same reduced temperature (lower part).

densities of all Mn do not differ remarkably, the insertion of non-polar methylene groups decrease the volume density of the dipoles and therefore P_s (figure 7). The sign of the coupling constant P_0, $\mathbf{P}_s = P_0(\hat{\mathbf{z}} \times \hat{\mathbf{n}})$, can be obtained from electro-optic measurements: The vector of the spontaneous polarization $\mathbf{P}_s \| \mathbf{E}$, the smectic layer normal $\hat{\mathbf{z}}$ and the director $\hat{\mathbf{n}}$ form a right-handed orthogonal system, and so $P_0 > 0$ for all homologues with the S configuration.

The temperature dependence of the effective rotational viscosities γ_{eff} obtained for the S_C^* phase is depicted in figure 10; values are of the order of magnitude $\gamma_{\text{eff}} \approx 1\,\text{N s m}^{-2}$ for all homologues investigated. A decrease in γ_{eff} with increasing chain length n is observed (see figure 11).

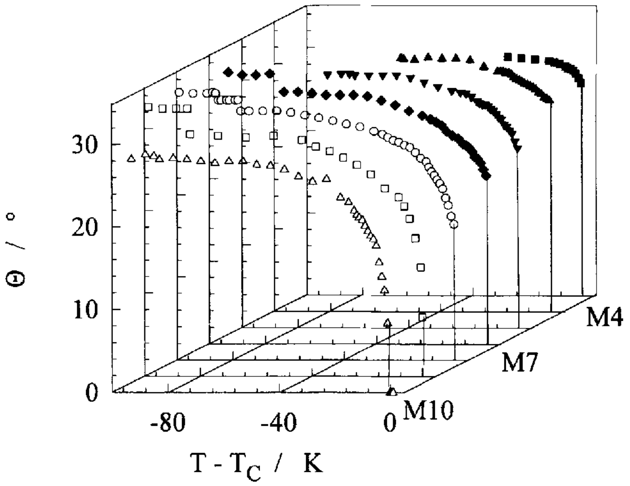

Figure 8. Director tilt angles Θ versus reduced temperature $T - T_C$. M4 (■), M5(▲), M6(▼), M7(◆), M8(○), M9(□), M10(△).

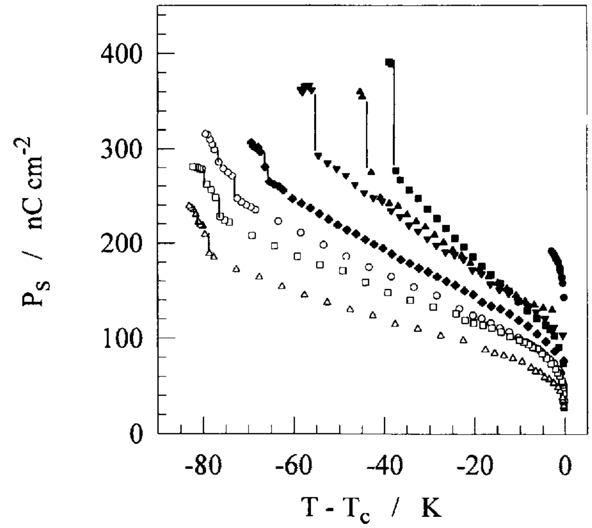

Figure 9. Temperature dependence of the spontaneous polarization $P_s(T)$. The steps marked with a solid line indicate a phase transition into a higher ordered smectic phase. The notation of the symbols is given in the legend to figure 5.

Homologues of Mn with $4 \leq n \leq 6$ exhibit an additional monotropic smectic phase (see figure 1). X-ray measurements for the S_{X1}^* phase reveal that the molecules are tilted with respect to the layer normal. Saturated switching of the spontaneous polarization can be achieved with high electric fields. Values of the rotational viscosity ($\gamma_{\text{eff}} \approx 100\,\text{N s m}^{-2}$) are at least two orders of magnitude larger than those obtained for the S_C^* phase, as shown in figure 12.

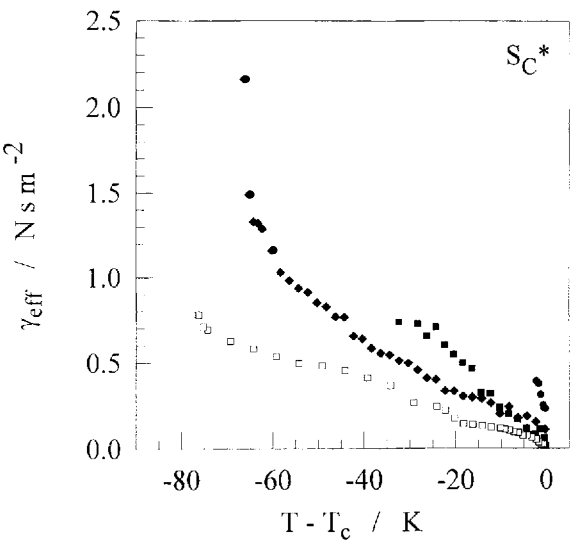

Figure 10. Effective rotational viscosities $\gamma_{eff}(T)$ measured for the S_C^* phases of some compounds M*n*: M3 (●), M4 (■), M7 (◆), M9 (□).

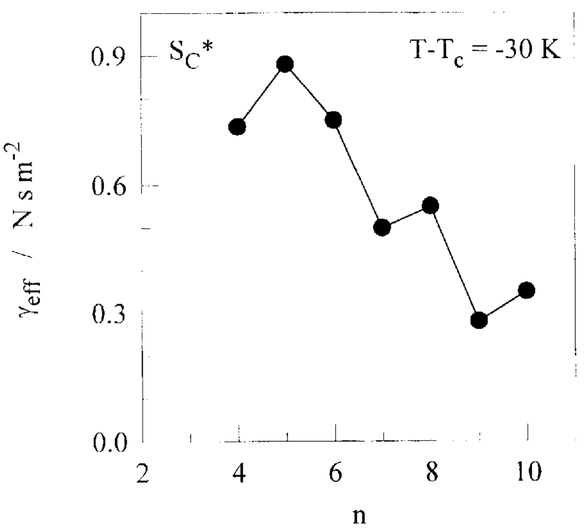

Figure 11. Effective rotational viscosity γ_{eff} for the members of the homologous series M*n* in the S_C^* phase at $T-T_C=-30$ K.

A second tilted phase named S_{X2}^* is observed between the S_{X1}^* and the S_C^* phase for homologues M*n* with $7\leqslant n\leqslant 10$. The rotational viscosities $\gamma_{eff}\approx 10\,\mathrm{N\,s\,m^{-2}}$ found for the S_{X2}^* phase lie between those obtained for the S_{X1}^* and S_C^* phases if orders of magnitude are considered (see figure 12).

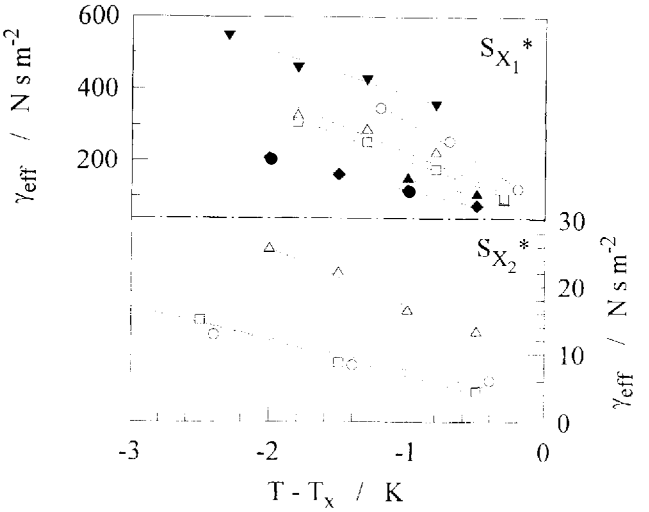

Figure 12. Temperature dependences of the effective rotational viscosity γ_{eff} in the higher ordered smectic phases: S_{X1}^* (upper part) and S_{X2}^* (lower part). M5 (▲), M6 (▼), M7 (◆), M8 (○), M9 (□), M10 (△).

There are three groups of tilted smectic phases distinguished with respect to their different intra- and inter-layer molecular ordering: fluid S_C^*, hexatic S_F^*, S_I^* and crystal G*, J*; H*, K* [10, 11]. The crystal smectics H*, K* usually exhibit large, spontaneous polarizations, but saturated ferroelectric switching is difficult to achieve, due to the long range ordering of the molecules. The increase in the effective rotational viscosities found on comparing the different ferroelectric phases suggests that the S_{X2}^* phase is hexatic in type S_F^* or S_I^* and the S_{X1}^* phase is a crystal smectic phase (G*, J*); the latter possibility is supported by the magnitude of the rotational viscosity observed. Both higher ordered smectic phases may however be hexatic in type, and this would suggest the phase sequence S_C^*, S_I^*, S_F^* with decreasing temperature.

Detailed X-ray investigations and miscibility studies are necessary to resolve this question, because no clear decision on the tilt direction (towards the apex S_I^*, J*, K* or the side S_F^*, G*, H* of the hexagonal net) and on the range of the interlayer interactions is possible from the investigations presented in this paper.

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