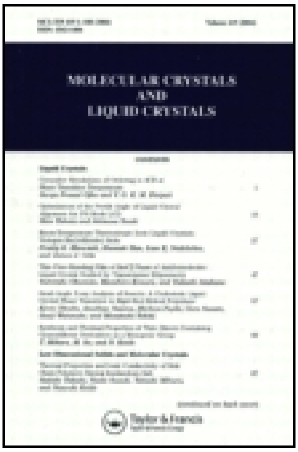

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The S_M Phase: Evidence for a New Type of Tilted Smectic Phase

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The S_M Phase: Evidence for a New Type of Tilted Smectic Phase

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X-ray and miscibility studies of the smectic phases of several 2,5-diphenylpyrimidine esters are presented. These investigations lead to the establishment of a new type of tilted smectic phase with a short range positional order within the smectic layers. The code letter *M* is proposed for this phase.

Keywords: new phase type, x-ray studies, miscibility investigations, 2,5-diphenylpyrimidines

INTRODUCTION

The classification of the liquid crystalline phases of rod-like molecules on the base of miscibility studies has led to eleven groups of smectic phases designated with latin letters *A*–*L*, with the exception of *D*.[1–5] (The code letter *L* has been suggested for the crystalline *B* phase.[3] However this designation is not commonly used.) As shown by X-ray investigations each group can be characterized by a typical arrangement of the molecules within the smectic layers. A long range positional order in connection with a long range bond orientational order has been found in the S_J, S_G, S_H, S_K, S_E and S_L phases, a short range hexagonal or pseudohexagonal positional order appears in the (hexatic) S_B, S_I and S_F phases while the long range bond orientational order is maintained, and in the S_A and S_C phases both positional as well as bond orientational order extend only over a short range. In several phases (S_C, S_I, S_F, S_J, S_G, S_H and S_K) the long molecular axis is tilted with respect to the layer normal, whereas in the S_A, S_B and S_E phases the long molecular axis and the layer normal are parallel to each other.

Since it has been found in 1975 that tilted smectic phases composed of chiral molecules can exhibit ferroelectronic properties[6] these smectic phases have been a subject of increasing interest. In recent years a lot of new chiral smectic compounds have been prepared. Some of them have been found to exhibit new types of structural order, e.g., a smectic phase with antiferroelectric properties[7] and a S_A phase with a helical order has been observed.[8]

Recently new ferroelectric liquid crystalline compounds—esters of 2-(4-hydroxyphenyl)-5-(4-alkyloxyphenyl)-pyrimidines with different 2-chlorocarboxylic acids have been synthesized.[9,10] For several of these compounds the phase sequences $S_C{}^*$-$S_M{}^*$ or $S_C{}^*$-$S_M{}^*$-$S_J{}^*$ have been found, where $S_M{}^*$ denotes a tilted smectic phase which could not be classified in the previous studies. This $S_M{}^*$ phase shows ferroelectric properties and for one compound a selective reflection has been observed, indicating a helical structure.[11]

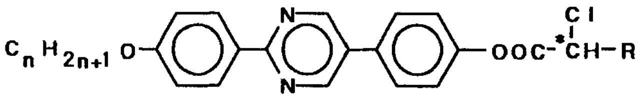
In the first part of this paper miscibility studies between different chiral compounds exhibiting the $S_M{}^*$ phase as well as X-ray investigations on the $S_M{}^*$ phases of the pure compounds are presented. It will be shown that in all cases $S_M{}^*$ denotes the same type of smectic phase and that a new type of molecular order within the smectic layers occurs in this phase. Furthermore chiral-racemic phase diagrams will be presented in order to show that the appearance of the new type of molecular order is independent on the chirality of the compounds. In the second part of the paper miscibility studies and X-ray investigations on binary systems with compounds exhibiting a S_I or S_F phase are presented. The results of these investigations show that the S_M phase is different from these phases, thus establishing a new type of smectic phase.

EXPERIMENTAL

The compounds under investigation are esters of 2-(4-hydroxyphenyl)-5-(4-alkyloxyphenyl)-pyrimidines with different chiral 2-chlorocarboxylic acids. Generally L-2-aminocarboxylic acids have been used as starting materials leading to *S*-configurated products. Additionally, two compounds with *R*-configuration have been

TABLE I

Polymorphism and transition temperatures (°C) of the investigated compounds



Comp.	Conf.	n	R	Cr °	S_5 °	S_J °	S_M °	S_C °	S_A °	I
2c-6	S	6	—C_3H_7	°106.4	(°93.4	°100.7)	°113.0	°180.2	°186.5	°
2d-6	S	6	—C_4H_9	°106.8	(°83.0	°92.1	°103.0)	°177.2	°181.6	°
2f-6	S	6	—CH_2—$CH(CH_3)_2$	°113.0	—	(°95.3	°102.0)	°154.5	—	°
2e-9	S	9	—$CH(CH_3)_2$	°127.6	—	—	(°123.0)	°173.9	°188.8	°
2e-10	S	10	—$CH(CH_3)_2$	°113.6	—	(°105.5)	°121.7	°172.5	°189.0	°
2e-11	S	11	—$CH(CH_3)_2$	°105.1	—	(°103.5)	°120.4	°168.7	°187.3	°
2e-12	S	12	—$CH(CH_3)_2$	°108.4	—	(°100.0)	°119.4	°167.1	°186.9	°
2f-6	R	6	—CH_2—$CH(CH_3)_2$	°113.3	—	(°96.3	°103.0)	°154.6	—	°
2e-10	R	10	—$CH(CH_3)_2$	°114.6	—	(°107.4)	°122.8	°172.5	°189.0	°

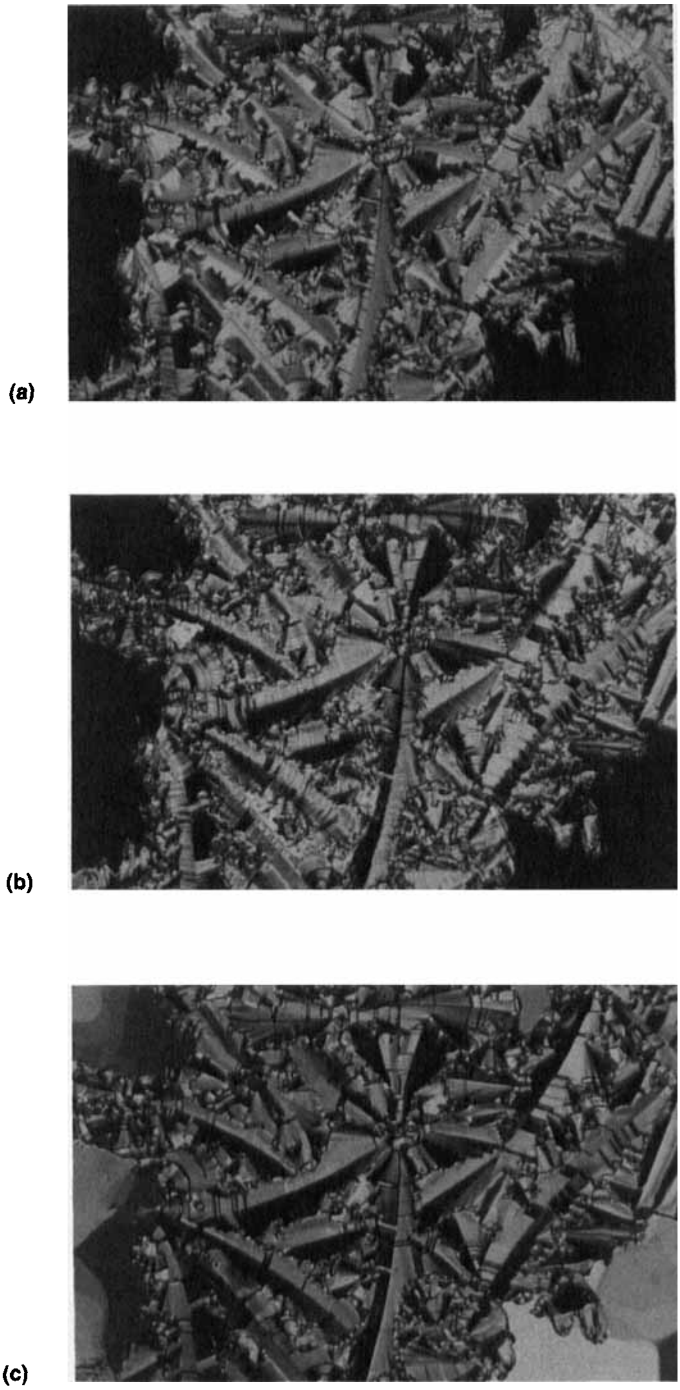


FIGURE 1 Microscopic textures of (**a**) $S_C{}^*$, (**b**) $S_M{}^*$ and (**c**) $S_I{}^*$ phase of compound **2f-6** observed on cooling from the isotropic liquid, crossed polarizers (area: 290 μm × 190 μm). See Color Plate I.

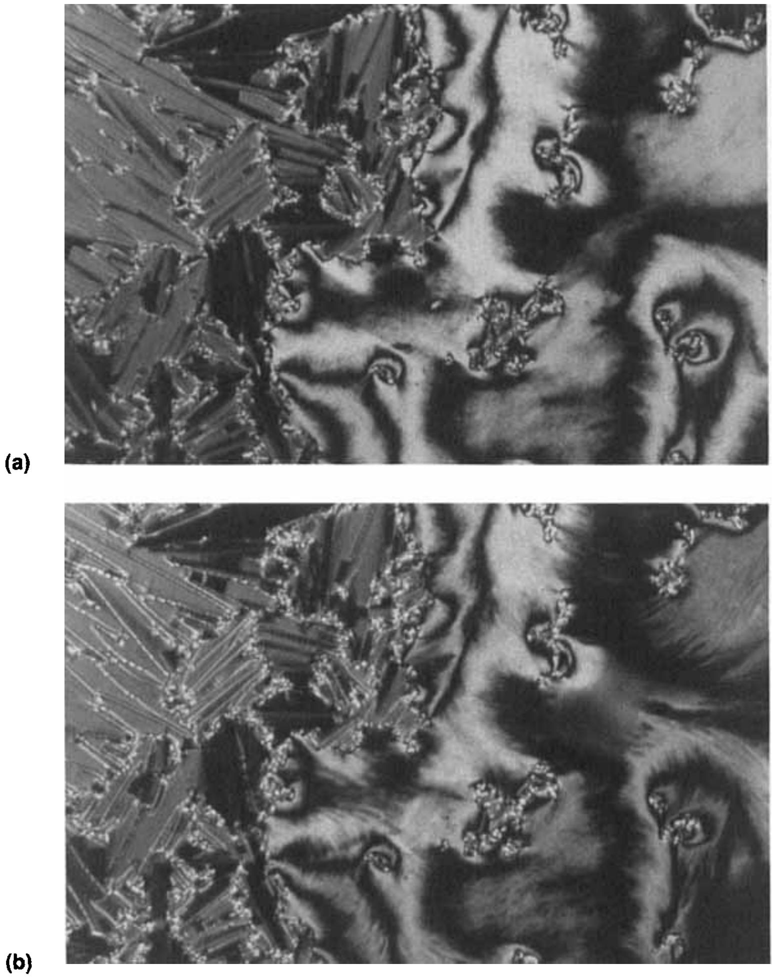


FIGURE 2 Microscopic textures of (**a**) S_C* and (**b**) S_M* phase of compound **2e-10** observed on cooling from the isotropic liquid, crossed polarizers (area: 290 μm × 190 μm). See Color Plate II.

prepared starting from the corresponding D-2-aminocarboxylic acids. All compounds have been purified by chromatography using a silica gel column and by recrystallisation until the transition temperatures remained constant.

Phase transition temperatures have been determined optically observing the textural change with a polarizing microscope as well as by DSC measurements using a Perkin Elmer DSC 7. X-ray investigations have been carried out using a Guinier film-camera and a small angle scattering equipment. With both methods nonoriented samples have been studied. Up to now, the attempt to orientate the samples by means of a magnetic field failed.

Polymorphism and phase transition temperatures of the compounds under investigation are given in Table I.

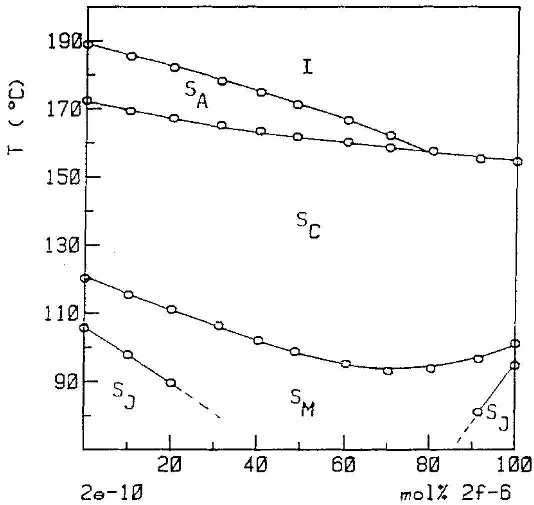


FIGURE 3 Diagram of state between compound **2e-10** and **2f-6**.

RESULTS

Optical Microscopy and Differential Scanning Calorimetry

For all compounds under investigation (Table I) a S_C^*-S_M^* transition occurs, S_M^* being the low temperature phase. The S_M^* phase exhibits either a schlieren texture or a broken focal-conic fan texture, as shown in Figures 1 and 2 for compound **2f-6** and **2e-10** respectively. On cooling the broken focal-conic fan texture of S_C^* at the transition to the S_M^* phase a slight colour change and the appearance of thin round bands are observed. The number of bands increases with decreasing temperature. At the S_M^*-S_J^* transition the number of bands which now becomes broad strongly decreases. On cooling the schlieren texture the S_C^*-S_M^* transition could only be detected in some cases where a slight colour change occurred (see Figure 2). The transition from S_M^* to S_J^* could be clearly observed by the formation of a mosaic texture in all cases.

DSC measurements have been carried out with all compounds. With the exception of the S_C^*-S_M^* transition of **2c-6, 2d-6** and **2f-6** as well as the S_M^*-S_J^* transition of **2c-6** which are only indicated by a slight change in slope of the base line, in all other cases distinct peaks are found. By extrapolating the peak areas to zero heating rate transition enthalpies ranging from 0.8 kJ/mol to 1.1 kJ/mol for the S_C^*-S_M^* and from 0.02 kJ/mol to 10.4 kJ/mol for the S_M^*-S_J^* transition are found.

Miscibility Studies Between Different Compounds Exhibiting the S_M^* Phase

For all compounds miscibility studies were performed using the contact method. As an example the phase diagram between the compounds **2e-10** and **2f-6** which has been investigated in more detail is shown in Figure 3. In all cases the S_M^* phases were found to be miscible with one another indicating that the S_M^* phases exhibited by the different compounds are identical.

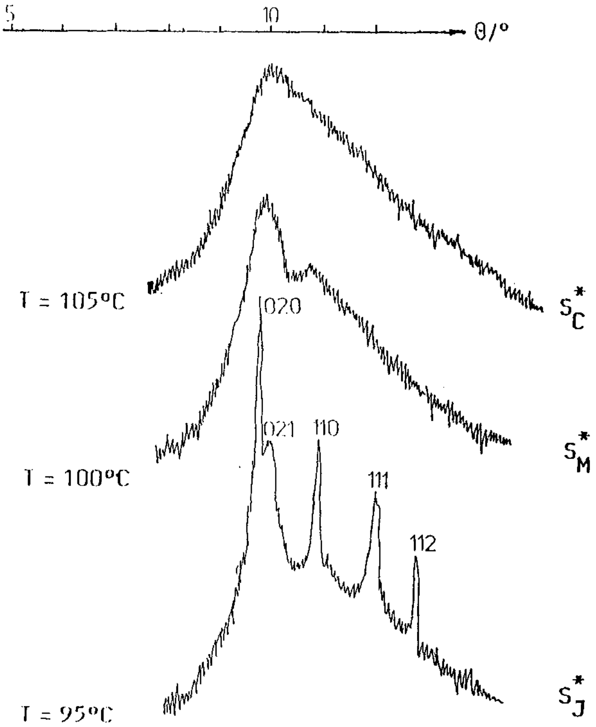


FIGURE 4 Photometer curves of the X-ray diffraction photographs of compound **2f-6**.

X-ray Investigations of the Pure Compounds

X-ray investigations of the pure compounds have been done in order to elucidate the structural peculiarities of the S_M* phase.

Figure 4 shows the photometer curves of the X-ray powder diffraction photographs (wide angle region) for the different smectic phases of compound **2f-6**. In the S_C* phase one diffuse outer scattering maximum is observed. At lower temperature the transition to the S_M* phase takes place and the diffuse scattering maximum splits into two maxima. A further decrease of the temperature leads to the S_M*-S_J* phase transition and the diffuse scattering maxima pass over into sharp reflexions in the S_J* phase. The position of the two scattering maxima in the S_M* phase at the S_M-S_J* transition temperature is nearly equal to the position of the (020) and (110) reflexion in the S_J* phase.

Compound **2e-12** has been used to study the temperature dependence of the positions and the intensities of the X-ray pattern in the S_M* phase. As shown in Figure 5 the diffuse scattering maximum of the S_C* phase also splits into two diffuse scattering maxima in the S_M* phase. With decreasing temperature the intensity of the first diffuse scattering maximum (at lower Θ values) increases and also the distance between the two maxima increases. At the S_M*-S_J* transition temperature the position of the two maxima in the S_M* phase corresponds to the position of the (020) and (110) reflexion in the S_J* phase (not shown in Figure 5).

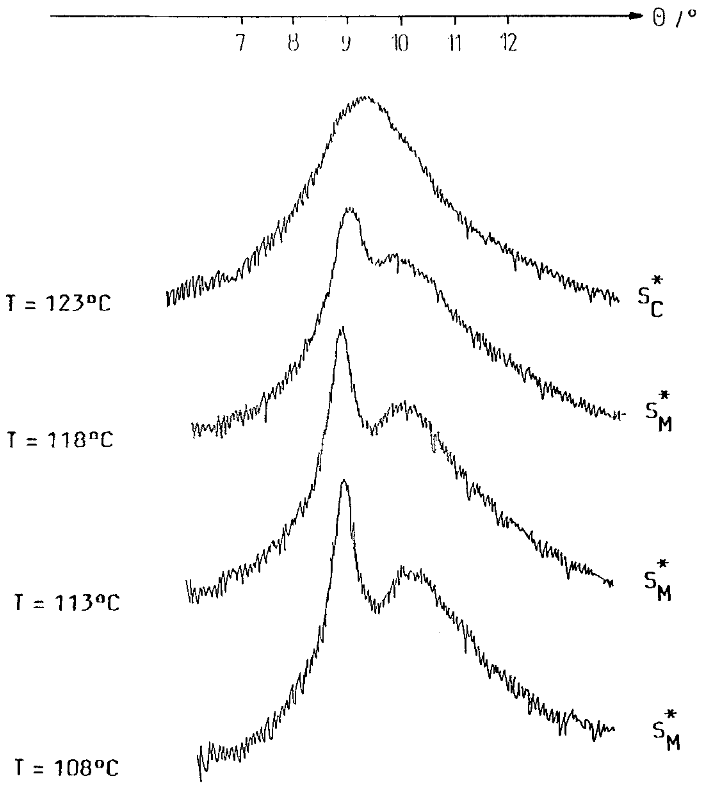


FIGURE 5 Photometer curves of the X-ray diffraction photographs of compound **2e-12**.

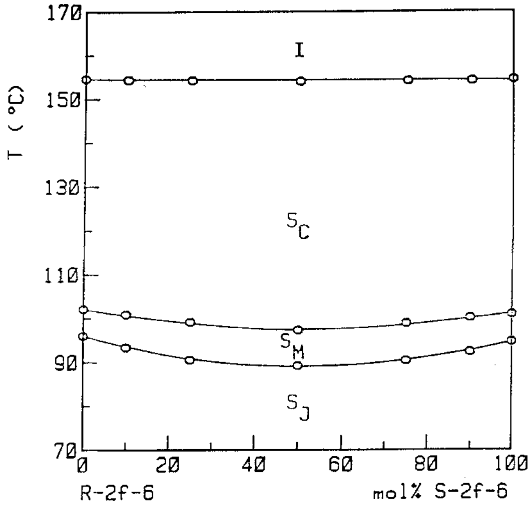


FIGURE 6 Diagram of state between the R- and the S-enantiomer of compound **2f-6**.

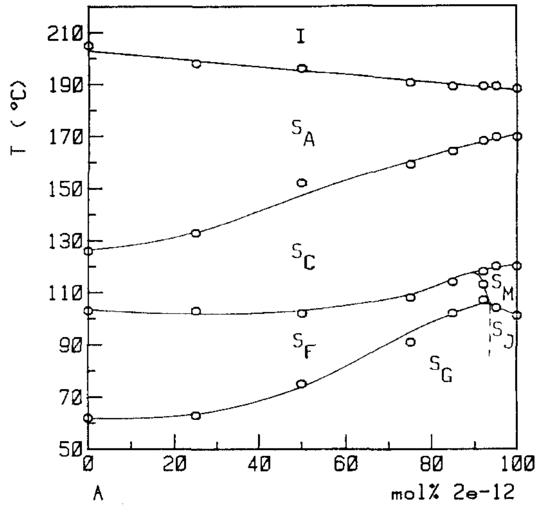


FIGURE 7 Diagram of state between compound A and compound **2e-12**.

The X-ray powder diffraction photographs of the S_M* phase of compound **2e-12** are similar to that of compound **2f-6**. In all cases two diffuse scattering maxima occur and the half width of the first diffuse scattering maximum is much lower than that of the second one. Further investigations of all other compounds exhibiting the S_M* phase have shown that the appearance of two (or even more) diffuse scattering maxima is a specific feature of the S_M* phase. Such a type of diffractogram has never been reported for any smectic phase studied so far.[2] Thus it can be concluded that a new type of molecular ordering appears in the S_M* phase.

A similar temperature evolution of positions and intensities of the scattering maxima as described before was also observed for the other compounds. Additionally, it has been found that the position of the inner ring which corresponds to the thickness of the smectic layers is independent on temperature for all investigated compounds. Tilt angles of about 30°–35° depending on the molecular structure have been calculated from that.

Chiral-Racemic Mixtures

Recently some cases are reported where optically active isomers appear to exhibit a different mesophase morphology in comparison to the racemate.[12,13] To prove whether the smectic *M** phase is only exhibited by optically active compounds for **2f-6** and **2e-10** the *R*-enantiomers have been synthesized additionally and the respective chiral racemic phase diagrams were studied. As Figure 6 shows the S_M phase exist for the total chirality range especially for the racemic mixture where the S_C-S_M and the S_M-S_J transitions are depressed by about 5K with respect to both pure enantiomers. A similar behaviour is observed for the chiral-racemic phase diagram of compound **2e-10**.

Additionally, X-ray investigations of the S_M phases of the racemic mixtures have been carried out. No differences between the X-ray powder diffraction photographs

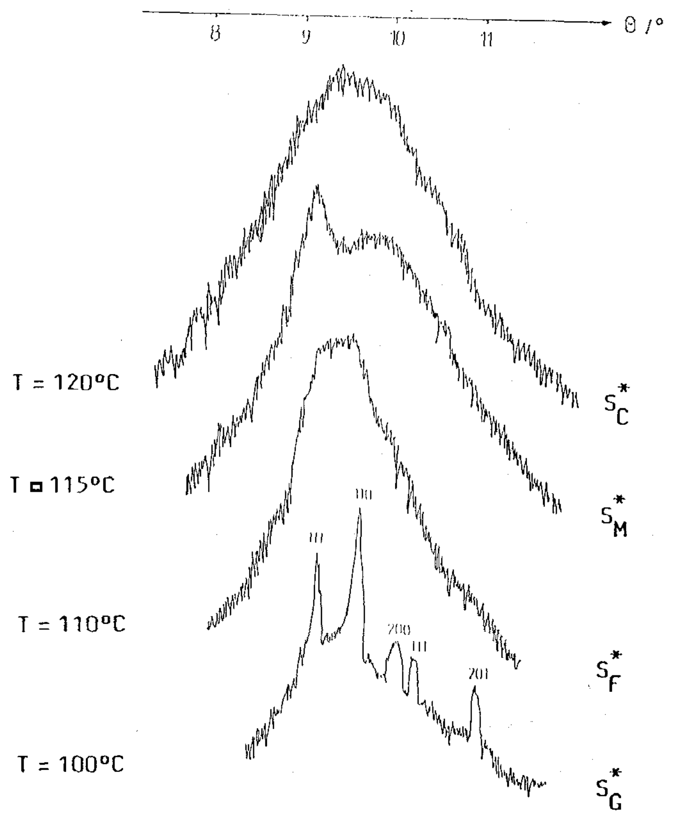
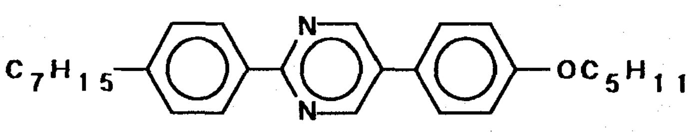


FIGURE 8 Photometer curves of the X-ray diffraction photographs of a binary mixture between 8 mol% of compound **A** and 92 mol% of compound **2e-12**.

of the pure enantiomers and the corresponding racemic mixtures were found showing that the new type of tilted smectic phase is not induced by chirality.

Binary Mixtures with Standard Compounds Exhibiting S_I or S_F Phases

The X-ray experiments carried out on the pure compounds have shown that the S_M phase is a tilted smectic phase with a short range positional order within the smectic layers, the structural order of the S_M phase being similar to that of the S_I and S_F phase. Therefore miscibility studies have been performed using the following standard S_I or S_F materials.[3,14,15]



(A)

Cr 79.5 (S_G 62) S_F 102.9 S_C 125.8 S_A 205 I

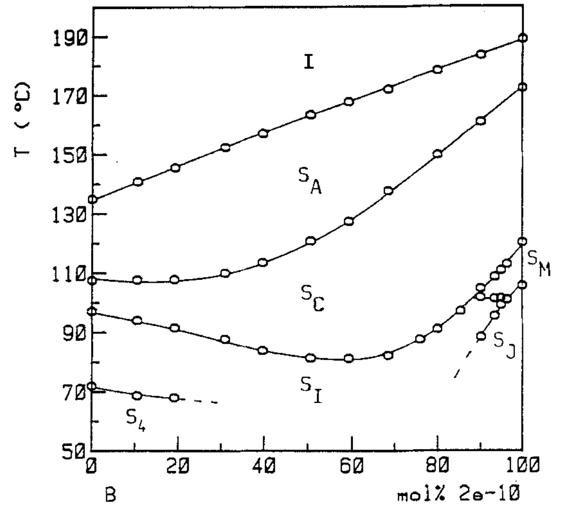
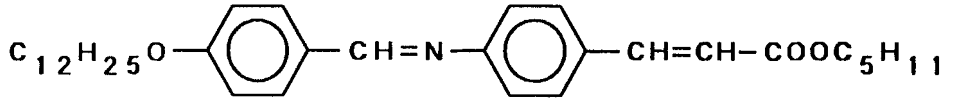


FIGURE 9 Diagram of state between compound **B** and compound **2e-10**.



(B)

Cr 73.9 (S_4 71) S_I 95.0 S_C 106.7 S_A 134.2 I

The diagram of state between the standard compound **A** and compound **2e-12** shows no miscibility between the S_M and S_F phase (Figure 7). For a small concentration range between approximately 90 and 94 mol% of compound **2e-12** a S_F-S_M transition is exhibited.

Figure 8 shows the X-ray diffractogram for the different tilted smectic phases at a concentration of 92 mol% **2e-12**. At a temperature of 120°C (S_C phase) one broad diffuse scattering maximum has been found. Decreasing the temperature to 115°C the two diffuse scattering maxima of the S_M phase can be observed. A further decrease of the temperature leads to the S_M-S_F transition. In the S_F phase again only one diffuse scattering maximum has been found. The position of this maximum is somewhere in between the positions of the two diffuse maxima of the S_M phase. Furthermore, at a temperature of 100°C the X-ray diffraction pattern of the S_G phase has been observed. These X-ray experiments give clear evidence that the appearance of the second diffuse scattering maximum in the S_M phase of the pure compounds can not be explained by pretransitional effects.

Figure 9 shows the diagram of state between compound **B** and compound **2e-10**. In a small concentration range the phase sequence S_C-S_M-S_I is observed; thus it can be concluded that the S_M phase is different from the S_I phase.

CONCLUSION

To conclude, we have found clear evidence for a new type of smectic phase, for which we propose the code letter M. The new smectic phase S_M belongs to the group of tilted smectic phases with a short range positional order. The structure could not yet be determined in detail, because attempts to obtain well oriented samples have failed so far. Presumably S_M belongs to the group of hexatic phases exhibiting long range bond orientational order. With this respect it is interesting to note that recently additional to the S_I and S_F phase two other types of tilted hexatic phases have been described theoretically.[16]

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