Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Liquid Crystalline 2-[4-(2-chloroalkanoyloxy)-phenyl -5-(4-n-hexyloxyphenyl)-pyrimidines-New Ferroelectric Compounds Exhibiting Interesting Polymorphism

G. Heppke [a], D. Lötzsch [a], N. K. Sharma [a b], D. Demus [c d], S. Diele [c], K. Jahn [c] & M. Neundorf [c]

[a] Iwan-N.-Stranski-Institut, Technische Universität Berlin, Sekr. ER 11, Str. des 17. Juni 135, 10623, Berlin, Germany

[b] Department of Chemistry, University of Jammu, Jammu Tawi, 180 004, India

[c] Sektion Chemie, Martin-Luther-Universität, 06108, Halle-Wittenberg, Germany

[d] Chisso Corporation, Research Center, 5-1 Goi Kaigan, Ichihara-shi, Chiba-ken, 290, Japan

Version of record first published: 24 Sep 2006.

To cite this article: G. Heppke , D. Lötzsch , N. K. Sharma , D. Demus , S. Diele , K. Jahn & M. Neundorf (1994): Liquid Crystalline 2-[4-(2-chloroalkanoyloxy)-phenyl -5-(4-n-hexyloxyphenyl)-pyrimidines-New Ferroelectric Compounds Exhibiting Interesting Polymorphism, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 241:1, 275-288

To link to this article: http://dx.doi.org/10.1080/10587259408029764

Mol. Cryst. Liq. Cryst., 1994, Vol. 241, pp. 275–288
Reprints available directly from the publisher
Photocopying permitted by license only

Printed in the United States of America

Liquid Crystalline 2-[4-(2-Chloroalkanoyloxy)-phenyl]-5-(4-*n*-hexyloxyphenyl)-pyrimidines—New Ferroelectric Compounds Exhibiting Interesting Polymorphism†

G. HEPPKE, D. LÖTZSCH and N. K. SHARMA‡

Iwan-N.-Stranski-Institut, Technische Universität Berlin, Sekr. ER 11, Str. des 17. Juni 135, 10623 Berlin, Germany

and

D. DEMUS,§ S. DIELE, K. JAHN and M. NEUNDORF

Sektion Chemie, Martin-Luther-Universität, 06108 Halle-Wittenberg, Germany

(Received January 27, 1993)

Seven chiral 2-[4-(2-chloroalkanoyloxy)-phenyl]-5-(4-*n*-hexyloxyphenyl)-pyrimidines were synthesized and their liquid crystalline as well as their ferroelectric properties investigated. The new compounds possess a rich variety of polymorphism including six different smectic phase types. On the basis of X-ray investigations and miscibility studies these smectic modifications were classified as SmA, SmC*, SmJ*, SmG*, SmH* and SmM'* whereby SmM'* denotes a smectic phase which presumably is identical to the recently discovered SmM* phase. In the second part of this paper the ferroelectric properties of the 2-[4-(2-chloroalkanoyloxy)-phenyl]-5-(4-*n*-hexyloxyphenyl)-pyrimidines were investigated. High values of spontaneous polarization (up to about 400 nC/cm^2) were established for the SmC* and SmM'* phases of these compounds as well as in one case also for the SmJ* phase.

Keywords: 2,5-diphenylpyrimidines, ferroelectric liquid crystals, X-ray, miscibility studies, SmM phase

INTRODUCTION

Since the discovery of ferroelectricity in chiral tilted smectic phases[1] such materials have been a subject of increasing interest from both fundamental as well as practical points of view. During the past fifteen years the liquid crystalline as well as fer-

†Presented in part at the 13th Int. Liq. Cryst. Conf., Vancouver, 1990.

‡On leave of absence from the Department of Chemistry, University of Jammu, Jammu Tawi-180 004, India.

§Present address: Chisso Corporation, Research Center, 5-1 Goi Kaigan, Ichihara-shi Chiba-ken 290, Japan.

roelectric properties of a lot of new chiral smectic compounds have been studied. These investigations not only have led to many efforts in the development of fast switching ferroelectric display devices[2] but also to the discovery of new types of structural order, e.g. smectic phases with antiferroelectric properties[3] and a SmA phase with a helical order.[4]

Recently, new ferroelectric liquid crystals, esters of 2-(4-hydroxyphenyl)-5-(4-*n*-alkyloxyphenyl)-pyrimidines with different 2-chlorocarboxylic acids, have been prepared.[5,6] For several of these compounds the phase sequence SmJ*—SmM*—SmC* has been found, where SmM* denotes a new type of ferroelectric tilted smectic phase.[7]

In this paper synthesis, polymorphy and ferroelectric properties of 2-[4-(2-chloroalkanoyloxy)-phenyl]-5-(4-*n*-hexyloxyphenyl)-pyrimidines are presented. The structure of these compounds is very similar to the structure of the 2,5-diphenylpyrimidine derivatives for which the occurrence of the SmM* phase has been established; only the positions of the chiral and the non-chiral side chain are exchanged. It will be shown by X-ray investigations and miscibility studies that the new compounds possess a rich variety of polymorphism including a smectic modification (denoted as SmM'*) which is presumably identical to the SmM* phase. Moreover, high values of spontaneous polarization (up to about 400 nC/cm^2) are established for the SmC*, SmM'* and in the case of one compound also for the SmJ* phase.

SYNTHESIS

Chiral starting materials for the synthesis of the 2-[4-(2-chloroalkanoyloxy)-phenyl]-5-(4-*n*-hexyloxyphenyl)-pyrimidines (**4a** to **4g**) were the *L*-amino acids alanine (**a**), 2-amino butanoic acid (**b**), norvaline (**c**), norleucine (**d**), valine (**e**), leucine (**f**) and isoleucine (**g**). According to Reference 8 the *L*-amino acids were transformed to (*S*)-2-chlorocarboxylic acids, which on treatment with thionyl chloride gave (*S*)-2-chlorocarboxylic acid chlorides. The products were obtained by esterification of 2-(4-hydroxyphenyl)-5-(4-*n*-hexyloxyphenyl)-pyrimidine with the respective (*S*)-2-chlorocarboxylic acid chloride. All compounds have been purified by chromatography over silica gel using methylene chloride as eluent and then by recrystallization with ethanol till the transition temperatures remained constant.

EXPERIMENTAL

Phase transition temperatures were determined optically using a Leitz SM-Lux-Pol polarizing microscope fitted with a Mettler FP-2 microheating stage as well as by DSC measurements using a Perkin Elmer DSC 7. Miscibility studies were done first by contact method followed by investigating mixtures with singular concentrations. For these investigations terephthalylidene-bis-4-*n*-butylaniline (**TBBA**), *n*-pentyl-4-(4-*n*-dodecyloxybenzylideneamino)-cinnamate, 2-(4-*n*-pentylphenyl)-5-(4-*n*-hexyloxyphenyl)-pyrimidine, 2-(4-*n*-decyloxyphenyl)-5-[4-(2-chloro-3-methylpro-

panoyloxy)-phenyl]-pyrimidine (**2e–10**) and 2-(4-*n*-hexyloxyphenyl)-5-[4-(2-chloro-4-methylbutanoyloxy)-phenyl]-pyrimidine (**2f–6**) have been used as reference compounds. X-ray studies of nonoriented samples were carried out using a Guinier film-camera and a small angle scattering equipment as described in Reference 9. Tilt angles were determined by comparing the layer thickness of the tilted smectic modifications with the layer thickness of the SmA phase. Values of spontaneous polarization were measured using a Diamant bridge. The layer thickness of the planar oriented samples was 9 μm.

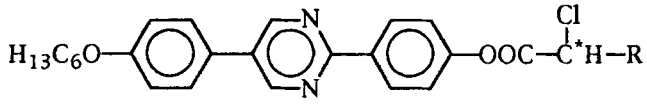
RESULTS AND DISCUSSION

Liquid Crystalline Properties

On the basis of texture observations and miscibility studies the 2-[4-(2-chloroalkanoyloxy)-phenyl]-5-(4-*n*-hexyloxyphenyl)-pyrimidines have been found to possess a rich variety of polymorphism including six different smectic phase types (see Table I). In order to classify these smectic modifications miscibility studies in combination with X-ray investigations have been carried out. As examples, the classification of the smectic modifications of the compounds **4b**, **4g**, **4c** and **4d** will be described in the following section. Summarizing the results of the DSC measurements, texture observations, miscibility studies as well as X-ray investigations

TABLE I

Polymorphy, transition temperatures (°C) and transition enthalpies (kJ/mol) of 2-[4-(2-chloroalkanoyloxy)-phenyl]-5-(4-*n*-hexyloxyphenyl)-pyrimidines



Comp.	R=	Cr	SmH*	SmG*	SmJ*	SmM'*	SmC*	SmA	I
4a	$-CH_3$	° 161.0	-	(° 159.2)	-	-	° 189.6	° 237.7	°
				3.66			0	7.67	
4b	$-C_2H_5$	° 99.6	° 99.9	° 142.0	-	-	° 179.0	° 218.1	°
			3.00	3.75			0	6.37	
4c	$-C_3H_7$	° 97.1	-	-	° 114.8	° 117.5	° 158.9	° 200.3	°
					0.59	0.78	0.07	5.72	
4d	$-C_4H_9$	° 99.7	-	-	(° 94.9)°	107.9	° 148.5	° 194.3	°
					0.17	0.57	0	5.91	
4e	$-CH(CH_3)_2$	° 100.1	-	-	(° 94.2)	-	° 141.0	° 182.8	°
					2.4		0	4.61	
4f	$-CH_2CH(CH_3)_2$	° 100.9	-	-	(° 94.3)	-	° 140.9	° 182.7	°
					2.47		0	4.75	
4g	$-\overset{*}{C}H(CH_3)C_2H_5$	° 97.0	-	(° 94.6)°	107.9	-	° 148.5	° 179.7	°
				0.66	3.06		0.27	3.86	

the polymorphy, transition temperatures and transition enthalpies of seven 2-[4-(2-chloroalkanoyloxy)-phenyl]-5-(4-*n*-hexyloxyphenyl)-pyrimidines are presented in Table I.

Classification of the Smectic Modifications by X-ray Investigations and Miscibility Studies

In Figure 1 the phase diagram between the compounds **4b** and **TBBA** is shown. SmA, SmC, SmG and SmH phases of **TBBA** are uninterruptedly miscible with the respective modifications of **4b** indicating thereby a phase sequence of SmH*—SmG*—SmC*—SmA with increasing temperature for compound **4b**. This result is confirmed by a continuous evolution of the positions and intensities of the X-ray diffraction pattern of both SmG (Figure 2) as well as SmH phases (Figure 3) within the investigated binary system (**4b/TBBA**). From the X-ray diffractograms of the SmG* and SmH* phases of **4b** the following cell parameters have been calculated:

SmG* (T = 130°C): a = 10.17 Å, b = 5.40 Å, c = 28.0 Å, β = 119.8°

SmH* (T = 102°C): a = 9.58 Å, b = 5.61 Å, c = 28.4 Å, β = 119.6°

The phase diagram between the compounds **4g** and **TBBA** is shown in Figure 4. SmA, SmC and SmG phases of **TBBA** are uninterruptedly miscible with the respective modifications of **4g**. Again, the classification of the SmG phase is confirmed by a continuous evolution of the positions and intensities of the X-ray diffraction pattern within the investigated binary system. In between SmC* and SmG* phases of **4g** another smectic modification occurs. By the obtained X-ray diffractogram this smectic modification is identified as SmJ*. The designation of the reflections

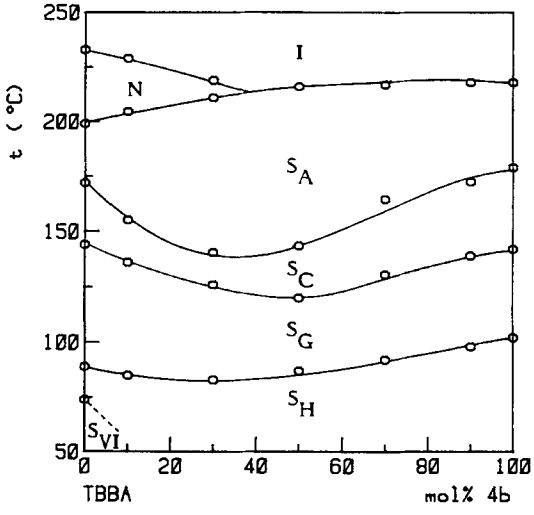


FIGURE 1 Binary diagram of state between compounds **TBBA** and **4b**.

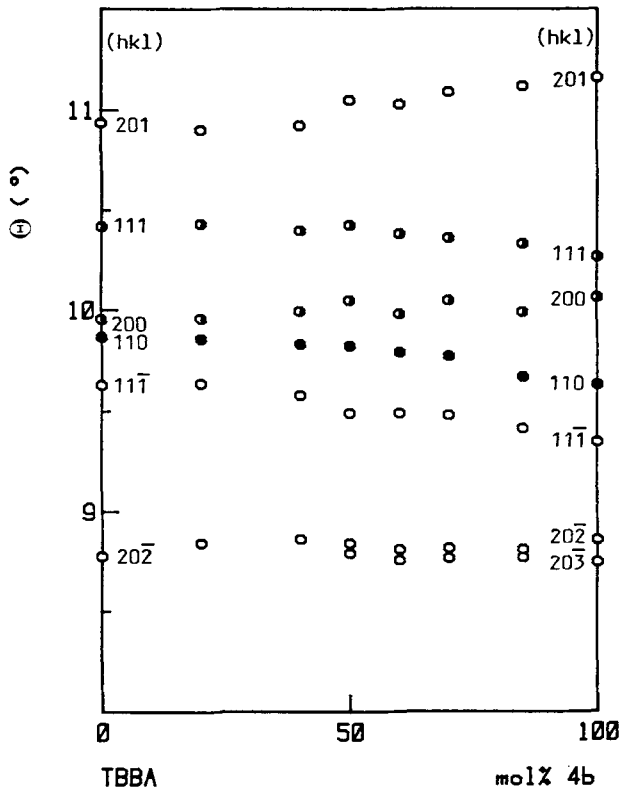


FIGURE 2 Positions and intensities of the X-ray diffraction pattern of the SmG phase within the binary system **TBBA/4b**. Strength of reflections are indicated as ● = strong, ◑ = medium and ○ = weak.

and the cell parameters for the SmJ* and SmG* phases of **4g** are listed in Table II. A SmJ—SmG transition as established for compound **4g** is a very unusual phase sequence. Up to the knowledge of the authors a SmJ—SmG phase sequence has been observed so far only for one pure compound (chiral and racemic **CE8**: 4-(2′-methylbutyl)-phenyl-4′-*n*-octylbiphenyl-4-carboxylate.[10–13]

On the basis of miscibility studies between compounds **4c** and **4d**, **4g** and **4c** as well as **4g** and **4d** an identical phase sequence of SmJ*—Sm3*—SmC*—SmA with increasing temperature has been established for the compounds **4c** and **4d**. To prove the classification of the SmJ* phase the evolution of the X-ray diffraction pattern within the binary system **4g/4c** has been investigated. Due to the recrystallization of compound **4d** close to the SmJ*—Sm3* transition temperature no similar investigations on the binary system **4g/4d** were possible. As can be seen in Figure 5 with the exception of reflection no. 7 of compound **4c** a continuous evolution of the positions and intensities of the X-ray diffraction pattern is found. The additional reflection which is observed for the SmJ* phase in case of the pure compound **4c** can be only explained assuming a doubling of the cell parameter c (c = 21) leading to the designation and cell parameters given in Table III. Such a doubling of the cell parameter c, which indicates an ABAB . . . interlayer ordering

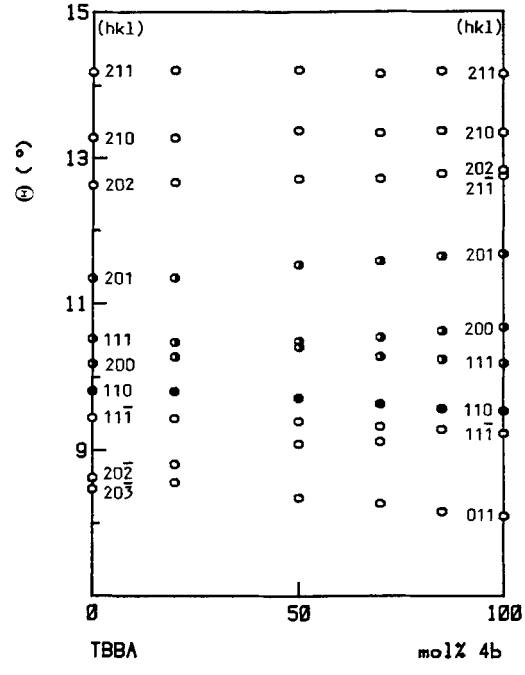


FIGURE 3 Positions and intensities of the X-ray diffraction pattern of the SmH phase within the binary system **TBBA/4b**. Strength of reflections are indicated as ● = strong, ◑ = medium and ○ = weak.

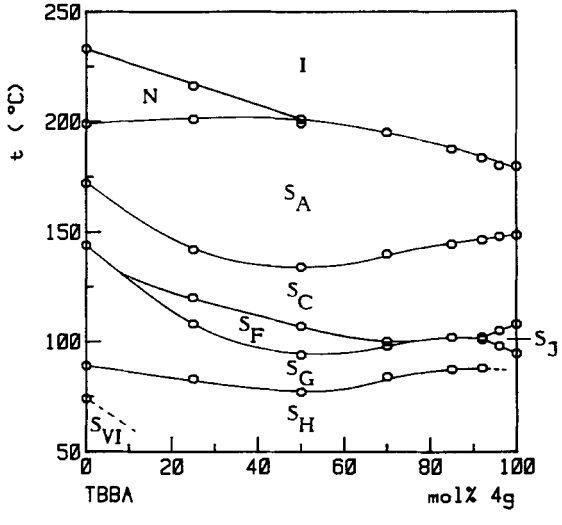


FIGURE 4 Binary diagram of state between compounds **TBBA** and **4g**.

TABLE II

Observed and calculated reflections for the crystalline smectic phases of compound **4g**

tempe-rature	reflex no.	inten-sity	hkl	Θ/° obs.	Θ/° calc.	$\Delta\Theta$/°	cell parameters
102°C	1	VS	001	1.890	1.890	0	a=6.34Å
SmJ*	2	M	002	3.780	3.780	0	b=9.97Å
	3	VW	$11\bar{3}$	8.390	8.300	0.090	c=29.5Å
	4	VW	$11\bar{2}$	8.490	8.440	0.050	β=127.8°
	5	S	020	8.900	8.900	0	
	6	M	021	9.170	9.100	0.070	
	7	M	110	9.914	9.914	0	
	8	M	111	11.066	11.089	0.023	
	9	W	112	12.417	12.456	0.039	
94°C	1	VS	001	1.850	1.850	0	a=10.8Å
SmG*	2	M	002	3.700	3.700	0	b=5.61Å
	3	VW	$20\bar{3}$	8.200	8.220	0.020	c=29.4Å
	4	VW	$20\bar{2}$	8.410	8.500	0.090	β=125.7°
	5	VW	$11\bar{1}$	8.960	8.975	0.015	
	6	VW	$20\bar{1}$	9.200	9.170	0.030	
	7	S	110	9.390	9.390	0	
	8	M	200/ 111	10.140	10.140	0	
	9	M	201	11.330	11.340	0.010	
	10	W	202	12.770	12.720	0.050	

Strenght of reflections are indicated as VS=very strong, S=strong, M=medium, W=weak, VW=very weak

has been observed so far only for SmB (crystalline) and SmE phases (Reference 14 and references therein).

In between SmC* and SmJ* phases of compounds **4c** and **4d** another smectic modification occurs, which exhibits either a schlieren or a broken focal conic fan texture with small round bands. The X-ray powder diffraction photographs of this smectic modification show a sharp reflection in the small angle region which corresponds to the thickness of the smectic layers as well as to diffuse outer scattering maxima corresponding to the molecular order within the smectic layers. With decreasing temperature the intensity of the first diffuse scattering maximum (at lower Θ values) as well as the distance between both maxima increases (see Figure 6). A similar diffractogram has been observed in case of a recently discovered new type of tilted smectic phase for which the notation SmM has been introduced.[7]

In order to confirm that the investigated smectic modification of compounds **4c** and **4d** belongs to the SmM* and not to the SmI* or SmF* phase miscibility studies

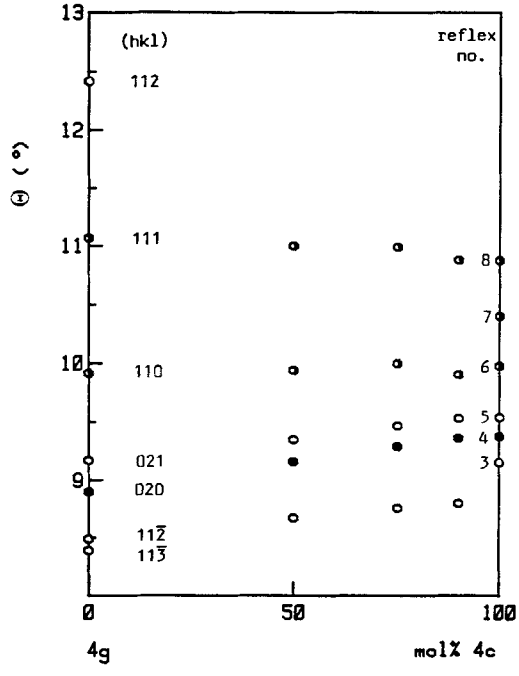


FIGURE 5 Positions and intensities of the X-ray diffraction pattern of the SmJ* phase within the binary system **4g/4c**. Strength of reflections are indicated as ● = strong, ◑ = medium and ○ = weak.

TABLE III

Observed and calculated reflections for the SmJ* phase of compound **4c**

tempe-rature	reflex no.	inten-sity	hkl	Θ/° obs.	Θ/° calc.	ΔΘ/°	cell parameters
100°C	1	S	002	1.775	-	-	a=5.98Å
	2	W	004	3.550	-	-	b=9.46Å
	3	VW	11$\bar{2}$	9.150	9.240	0.090	c=59.0Å
	4	S	020	9.375	-	-	β=122.5°
	5	W	022	9.540	9.550	0.010	
	6	M	110	9.975	-	-	
	7	M	111	10.400	10.430	0.030	
	8	M	112	10.875	10.940	0.065	

Strenght of reflections are indicated as VS=very strong, S=strong, M=medium, W=weak, VW=very weak

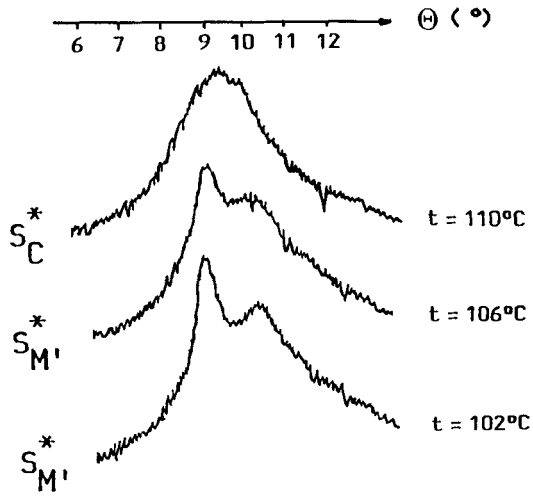
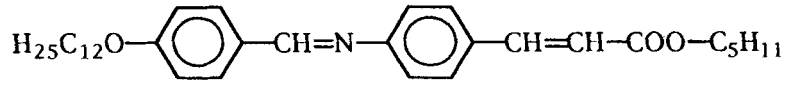
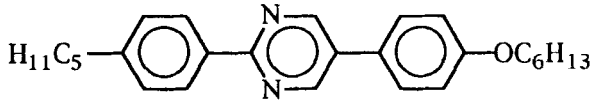


FIGURE 6 Photometer curves of the X-ray powder diffraction photographs of compound **4d**.

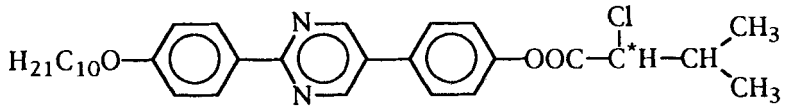
between compound **4d** and the following SmI, SmF as well as SmM* reference compounds have been performed.



Cr 73.9 (S_{IV} 71) S_I 95.0 S_C 106.7 S_A 134.2 I (A)



Cr 65 S_G 98.8 S_F 116.5 S_C 153.5 S_A 211.0 I (B)



Cr 113.6 (S_J^* 105.5) S_M^* 121.7 S_A 189.0 I (2e–10)

As indicated by the observation of a phase transition between the respective smectic phases (see Figure 7 and Figure 8) the investigated smectic modification (denoted as SmM′) is different from SmI and SmF phases. However, the SmM′* phase of compound **4d** and the SmM* phase of the reference compound **2e–10** are separated by an induced smectic modification (presumably SmF) thus the relationship between these phases cannot be ascertained (see Figure 9). The same result has been obtained using 2-(4-*n*-hexyloxyphenyl)-5-[4-(2-chloro-4-methyl-butanoyloxy)-phenyl]-pyrimidine (**2f–6**) instead of compound **2e–10** as SmM* reference compound.

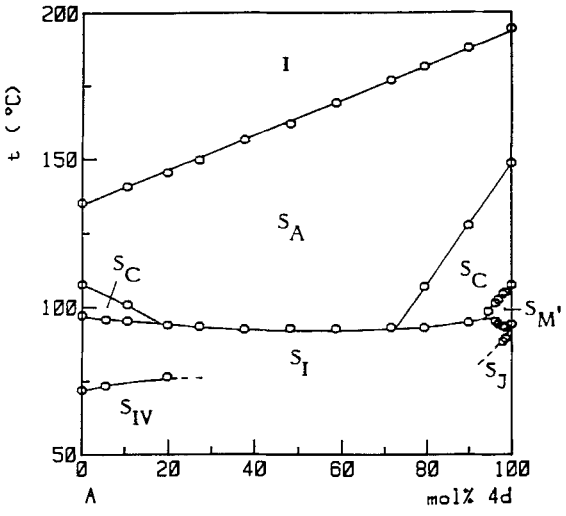


FIGURE 7 Binary diagram of state between the reference compound **A**: *n*-pentyl-4-(4-*n*-dodecyloxy-benzylideneamino)-cinnamate and compound **4d**.

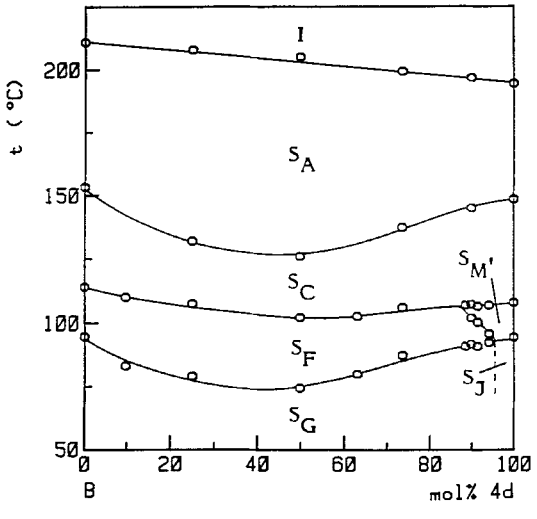


FIGURE 8 Binary diagram of state between the reference compound **B**: 2-(4-*n*-pentylphenyl)-5-(4-*n*-hexyloxyphenyl)-pyrimidine and compound **4d**.

Although the results obtained for the SmM'* phase of compounds **4c** and **4d** (texture observations, X-ray investigations and occurrence between SmC* and SmI* phases) suggest that this phase is identical with the SmM* phase, any attempt to prove the equivalence by miscibility studies have failed so far. Thus we propose to use the notation SmM'* until the relationship to the SmM* phase is clarified.

Ferroelectric Properties

From the performed X-ray measurements the temperature dependence of the tilt angle was calculated by comparing the layer thickness of the tilted smectic modi-

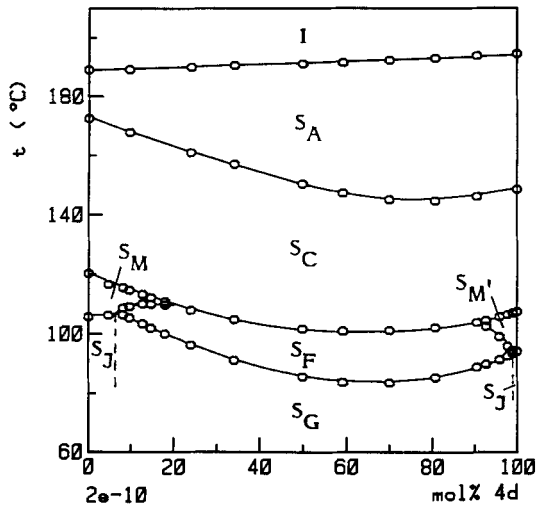


FIGURE 9 Binary diagram of state between the reference compound **2e–10**: 2-(4-*n*-decyloxyphenyl)-5-[4-(2-chloro-3-methylpropanoyloxy)-phenyl]-pyrimidine and compound **4d**.

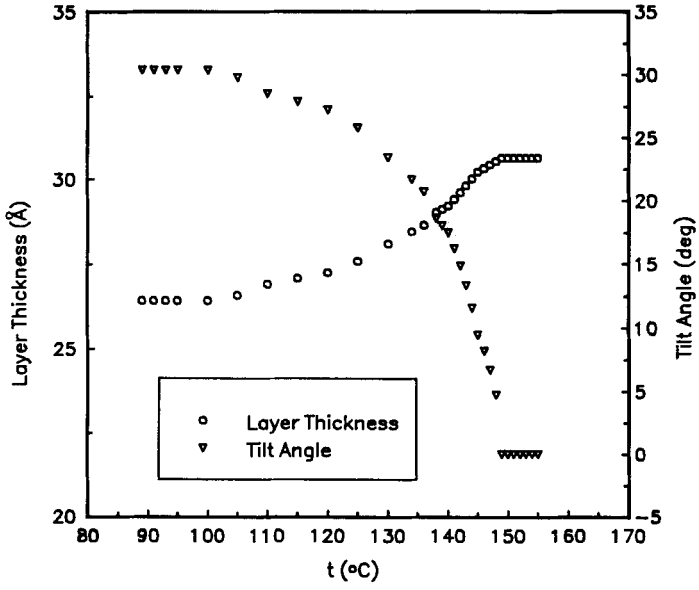


FIGURE 10 Temperature dependence of layer thickness and tilt angle of compound **4d**.

fications with the layer thickness of the respective SmA phase. As an example the temperature dependence of layer thickness and tilt angle of compound **4d** are shown in Figure 10. For all compounds a typical temperature dependence of the tilt angle of the SmC* phase is observed reaching maximum values between 28° (for compounds **4a** and **4b**) and 35° (for compound **4g**). In the SmM'* phase the tilt angle is found to increase slightly with decreasing temperature whereas in the crystalline smectic modifications temperature independent tilt angle are obtained.

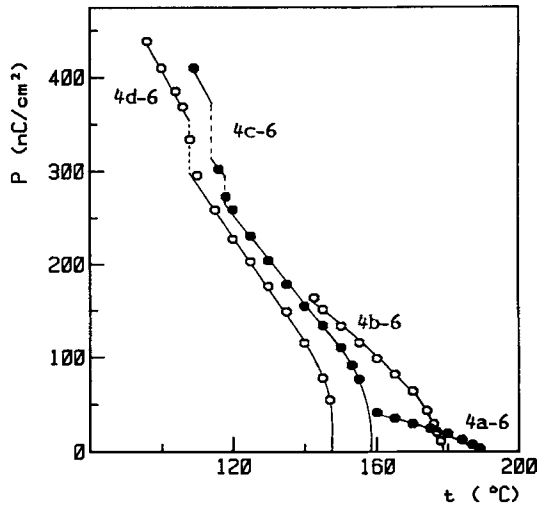


FIGURE 11 Temperature dependence of spontaneous polarization of the 2-[4-(2-chloroalkanoyloxy)-phenyl]-5-(4-*n*-hexyloxyphenyl)-pyrimidines derived from linear 2-chlorocarboxylic acids.

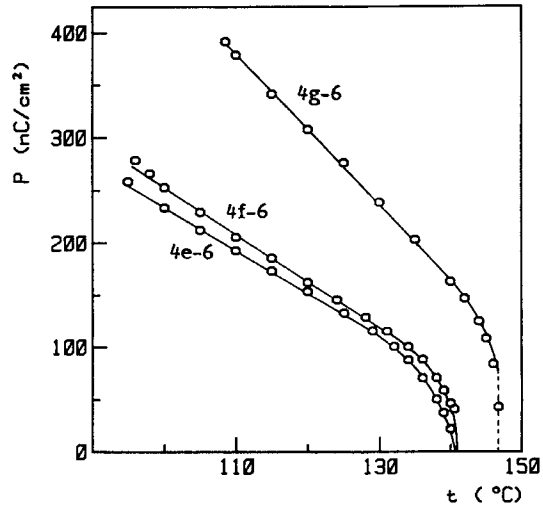


FIGURE 12 Temperature dependence of spontaneous polarization of the 2-[4-(2-chloroalkanoyloxy)-phenyl]-5-(4-*n*-hexyloxyphenyl)-pyrimidines derived from branched 2-chlorocarboxylic acids.

The temperature dependence of the spontaneous polarization of the 2-[4-(2-chloroalkanoyloxy)-phenyl]-5-(4-*n*-hexyloxyphenyl)-pyrimidines is shown in Figure 11 (esters of linear 2-chlorocarboxylic acids) and Figure 12 (esters of branched 2-chlorocarboxylic acids). Within the homologous series of compounds derived from linear 2-chlorocarboxylic acids (**4a**, **4b**, **4c** and **4d**) a strong increase of spontaneous polarization with increasing length of the chiral side chain is found. Whereas **4a** exhibits only a maximum polarization of about 30 nC/cm^2 a ten times higher value is observed for the SmC* phase of **4d** close to the SmC*—SmM'* transition temperature. The maximum polarization of the esters of branched 2-chlorocarboxylic

acids (**4e**, **4f** and **4g**) varies between 260 nC/cm^2 (for **4e**) and 390 nC/cm^2 (for **4g**). These values are of the same order as the maximum values of other esters of branched 2-halogenocarboxylic acids.[5, 15–21].

Below the SmC* phase of compounds **4c** and **4d** the SmM'* phase occurs. As shown in Figure 11 the SmM'* phase exhibits ferroelectric properties. At the SmC*—SmM'* transition temperature a jump of spontaneous polarization is observed indicating thereby an increase of the molecular order within the smectic layers. With decreasing temperature the spontaneous polarization of the SmM'* phase of compound **4d** is found to increase linearly whereby the slope of the curve is slightly higher than in the SmC* phase.

Under our experimental conditions (electric field strength up to about 15 V/μm) a ferroelectric switching behaviour of the crystalline smectic modifications (SmJ*, SmG* and SmH*) could be observed only in case of the SmJ* phase of compound **4c** close to the SmM'* to SmJ* transition temperature.

CONCLUDING REMARKS

The results presented show that a smectic modification being similar to the recently discovered SmM* phase occurs also in two of the investigated 2-[4-(2-chloroalkanoyloxy)-phenyl]-5-(4-*n*-hexyloxyphenyl)-pyrimidines. Assuming that SmM* and SmM'* belong to the same phase type altogether nine compounds exhibiting this novel smectic modification are reported so far. As a result of the performed X-ray investigations the SmM* phase can be described as a tilted smectic phase without long range positional order within the smectic layers. However the structural peculiarities of this phase could not yet be determined because all attempts to obtain a well oriented sample of one of these compounds have failed so far. It was suggested that SmM belongs to the group of hexatic phases exhibiting long range bond orientational order,[7] which also should apply to the SmM' phase. In agreement with this assumption the pronounced increase of the helical pitch and of the pitch controlling elastic constant being observed with decreasing temperature for the SmM* phase of compound **2f–6** could be explained as a consequence of the growing bond orientational order.[22]

Acknowledgment

The authors would like to thank the Deutsche Forschungsgemeinschaft (Sonderforschungsbereich 335, "Anisotrope Fluide") and the Volkswagen-Stiftung for financial support.

References

1. R. B. Meyer, L. Liebert, L. Strzlecki and P. Keller, *J. Phys. (Paris) Lett.*, **36**, L-69 (1975).
2. J. Dijon, *Liquid Crystals—Applications and Uses*, edited by Birendra Bahadur, Vol. 1, 305–360, World Scientific Publishing Co. Pte. Ltd. (1990).
3. A. D. L. Chandani, Y. Ouchi, H. Takezoe and A. Fukuda, *Jpn. J. Appl. Phys.*, **27**, L729 (1988).

4. J. W. Goodby, M. A. Waugh, S. M. Stein, E. Chin, R. Pindak and J. S. Patel, *Nature*, **337**, 449 (1989).
5. G. Heppke, D. Lötzsch and N. K. Sharma, Poster P71 presented at the 1st Int. Symp. on Ferroel. Liq. Cryst., Arcachon (1987).
6. G. Heppke, B. Kampa, D. Lötzsch, K.-D. Scherf and H. Zaschke, Poster F19 presented at the 12th Int. Liq. Cryst. Conf., Freiburg (1988).
7. G. Heppke, D. Lötzsch, D. Demus, S. Diele, K. Jahn and H. Zaschke, *Mol. Cryst. Liq. Cryst.*, **208**, 9 (1991).
8. S. J. Fu, S. M. Birnbaum and J. P. Greenstein, *J. Am. Chem. Soc.*, **76**, 6054 (1954).
9. K. Jahn, Dissertation, Martin-Luther-Universität, Halle-Wittenberg (1991).
10. J. Budai, R. Pindak, S. C. Davey and J. W. Goodby, *J. Phys. (Lett.)*, **45**, L1053 (1984).
11. J. Przedmojski, R. Dambrowski, B. Pura, K. Zickert and S. Gierlotka, *Mol. Cryst. Liq. Cryst.*, **151**, 171 (1987).
12. J. Przedmojski and S. Gierlotka, *Liq. Cryst.*, **3**, 409 (1988).
13. S. Gierlotka, J. Przedmojski and B. Pura, *Liq. Cryst.*, **3**, 1535 (1988).
14. D. Demus, S. Diele, S. Grande and H. Sackmann, *Advances in Liquid Crystals*, edited by Glenn H. Brown, Vol. 6, 1–107, Academic Press, Inc. (1983).
15. J. Bömelburg, G. Heppke and A. Ranft, *Z. Naturforsch.*, **44**, 1127 (1989).
16. G. Y. Bak, D. Joachimi, C. Tschirske and H. Zaschke, Poster E29 presented at the 8th Liq. Cryst. Conf. of Socialist Countries, Krakow (1989).
17. T. Sakurai, N. Mikami, R. Higuchi, M. Honma and K. Yoshino, *Ferroelectrics*, **85**, 469 (1988).
18. N. H. Tinh, C. Salleneuve and C. Destrade, *Ferroelectrics*, **85**, 435 (1988).
19. Ch. Bahr, Dissertation, Technische Universität, Berlin (1988).
20. G. Heppke, D. Lötzsch, N. K. Sharma and Ch. Hänsel, *Ferroelectrics*, **132**, 153 (1992).
21. G. Heppke, D. Lötzsch, B. Kampa, K.-D. Scherf and H. Zaschke, *J. Prakt. Chem.* **335**, 549 (1993).
22. Ch. Bahr, G. Heppke and K. Wuthe, *Liq. Cryst.*, **12**, 997 (1992).