Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926090

X-ray investigation of combined main-chain/side-chain liquid-crystalline polymers

S. Diele[a]; M. Naumann[a]; F. Kuschel[a]; B. Reck[b]; H. Ringsdorf[b]
[a] Martin-Luther-Universität Halle-Wittenberg, Sektion Chemie, Halle/S., G.D.R. [b] Universität Mainz, Institut für Organische Chemie, Mainz, F. R. Germany

To cite this Article Diele, S. , Naumann, M. , Kuschel, F. , Reck, B. and Ringsdorf, H.(1990) 'X-ray investigation of combined main-chain/side-chain liquid-crystalline polymers', Liquid Crystals, 7: 5, 721 — 729

To link to this Article: DOI: 10.1080/02678299008036753

URL: http://dx.doi.org/10.1080/02678299008036753

LIQUID CRYSTALS, 1990, VOL. 7, NO. 5, 721–729

X-ray investigation of combined main-chain/side-chain liquid-crystalline polymers

by S. DIELE†, M. NAUMANN†, F. KUSCHEL†, B. RECK‡
and H. RINGSDORF‡
†Martin-Luther-Universität Halle-Wittenberg, Sektion Chemie, Postfach, Halle/S., 4010, G.D.R.
‡Universität Mainz, Institut für Organische Chemie, D-6500 Mainz, F.R. Germany

(*Received 19 June 1989; accepted 3 November 1989*)

Structural investigations on six combined liquid-crystalline polymers using the X-ray technique are described. The measurements have allowed a characterization of the liquid-crystalline phases and have led to our first ideas about the phase structures. All mesogenic groups are arranged parallel to each other, the shortest segment in the main-chain or in the side-chain determines the smectic layer spacing. A modified designation for liquid-crystalline phases of high polymers is proposed.

1. Introduction

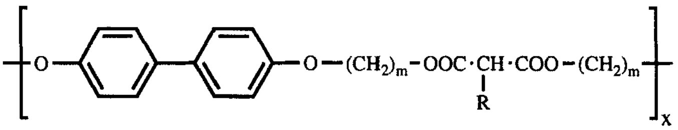
In recent years the liquid-crystalline properties of polymers have been significantly influenced by a systematic variation of their chemical structure. In connection with this, there exist many systematic structure investigations for main-chain as well as side-chain polymers. Now by the incorporation of mesogenic groups in the main-chain as well as in the side-chain a new type of liquid-crystalline polymeric architecture has been created [1]. It is of interest to know how the different mesogenic groups are involved in the formation of liquid-crystalline phases for such polymers. However only a few structural studies for polymers of this combined type have been reported up to now [2–8].

Here X-ray studies are described for six polymers of the combined type, which differ from each other in the lengths of the spacers in the main-chain and/or in the side-chain. The side-chain is linked with the flexible part of the main-chain, which yields polymorphic smectic phases. In contrast linkage of the side-chain with the rigid part of the main-chain seems to prevent smectic polymorphism [9, 10].

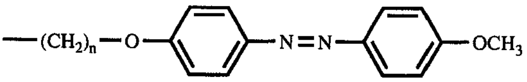
2. Experimental

The substances characterized in [1] have been investigated without any further purification. The transition temperature (see table 1, with respect to the designation see the later discussion) were examined by differential scanning calorimetry (DSC II, Perkin-Elmer Corp.) and polarizing microscopy. Non-oriented samples have been studied by means of a Guinier-equipment (Firma Huber) with monochromatic CuK$_\alpha$-radiation. In addition to this, oriented samples obtained by slow cooling from the nematic into the smectic A phase within a magnetic field of about 1·5 T or by drawing fibres below the clearing point were investigated.

Table 1. Chemical structure and transition temperature (in °C) of the polymers†.



R =



Code‡	*m*	*n*	Δ‖								
5a	2	2	2		P_C 148			P_{S_C} 163	P_{S_A} 176		P_I
5b	2	6	2		P_{CI} 124		P_{S_J} 129	P_{S_C} 153	P_{S_A} 162	P_N 181	P_I
5c	2	10	6	P_g 112	P_C 162					(P_N 159)§	P_I
5e	6	2	6		P_{CI} 109	P_{CII} 120				P_N 153	P_I
5f	6	6	2		P_{CI} 108		P_{S_J} 112	P_{S_C} 131	P_{S_A} 136	P_N 155	P_I
5g	6	10	2	P_g 72			P_{S_G} 120	P_{S_C} 139	P_{S_A} 154		P_I

† P_g: glass; P_C: crystalline; P_{S_G}: smectic G; P_{S_J}: smectic J; P_{S_A}: smectic A; P_{S_C}: smectic C; P_N: nematic; P_I: isotropic.

‡ As used in [1].

§ Monotropic nematic phase.

‖ $\Delta = |m - n + 2|$.

3. Results

The polymorphism of the polymers under discussion is strongly dependent on the spacer lengths. Consideration of the absolute difference of the distances of two successive mesogenic groups, e.g. two groups within the main-chain or a main-chain- and side-chain-group, expressed by

$$\Delta = |m - n + 2|$$

leads to a systematization. The estimation of the distances is performed by counting all of the linking atoms (O and C). In this way the distance between two main-chain groups is $2m + 7$ and the distance between the main-chain- and side-chain-group is $m + n + 5$. As is shown in the table, polymers 5c and 5e, exhibiting large differences, form only nematic phases. In all other cases characterized by nearly the same distance, a relative high degree of polymorphism is observed. A glass transition is observed only in polymers with long side-chain spacers (5c and 5g).

An example of the Guinier patterns is shown in figure 1 for polymer 5f taken with increasing temperature. The first strip represents a pattern of the crystalline state. The transition into the next phase is indicated by a loss of numerous weaker reflections and

Figure 1. Guinier patterns of polymer 5f. From top to bottom: T = 98°C (P_C), T = 110°C (P_{S_J}), T = 122°C (P_{S_C}), T = 134°C (P_{S_A}).

a small shift of the remaining outer reflections. The inner reflection caused by the layer periodicity is nearly unchanged. This type of pattern is very similar to those of the S_G or S_J phases found in low molar mass systems.

With the transition into the P_{S_C} phase a diffuse outer scattering maximum appears indicating the loss of order within the layers. The position of the inner reflection is clearly shifted to smaller values in the following P_{S_A} phase. An increase of the layer thickness takes place (see figure 2). On the basis of the values in the P_{S_C} and P_{S_A} phase, a tilt angle of about 17° is estimated.

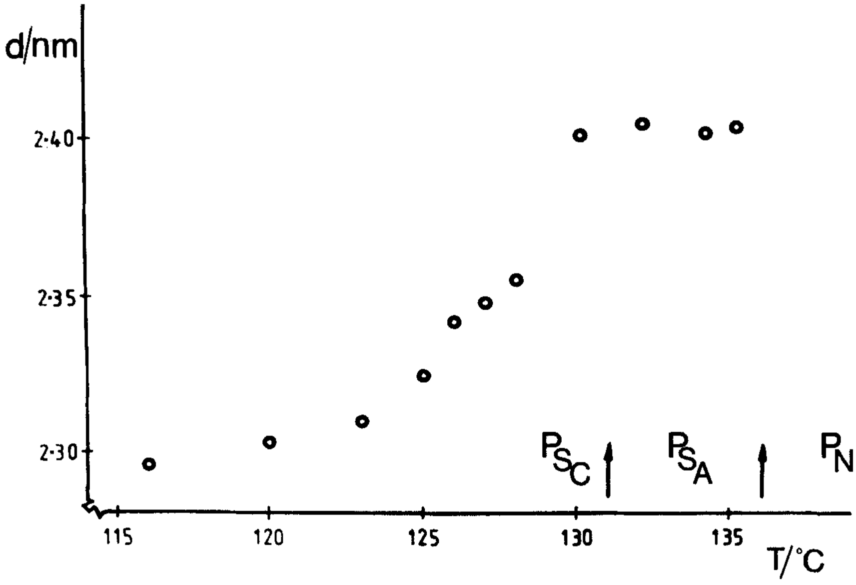
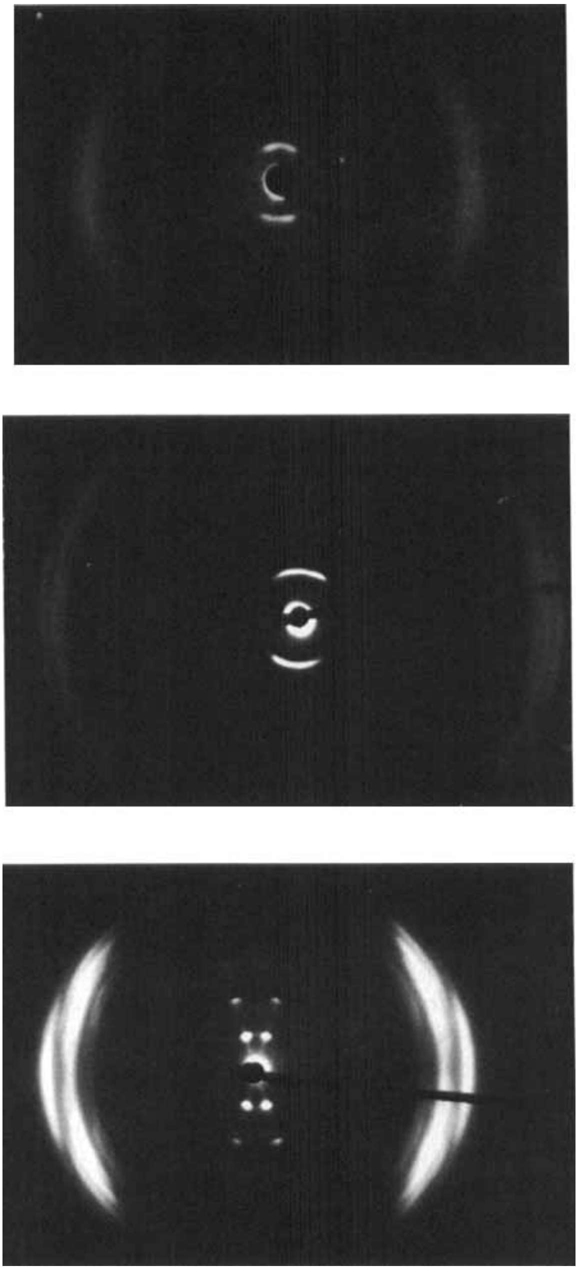


Figure 2. Layer thickness at the P_{S_C}–P_{S_A} transition of polymer 5f as a function of temperature.

The X-ray patterns of a sample of polymer 5f, oriented in the magnetic field, are shown in figures 3 (*a*)–(*d*). Additionally, in figure 3 (*e*) the direction of the irradiation was parallel to the preferred direction. The disappearance of the inner reflections proves the layer structure with a parallel arrangement of the mesogenic groups independently of the incorporation into the main-chain or the side-chain. The inner reflection is split off for the P_{S_C} phase (see figure 3 (*c*)). Since the maximum of the outer scattering is located on the equator of the pattern it is, in agreement with figure 2, a proof of the tilted structure of this phase. The pattern of the P_{S_A} phase exhibits only one strong reflection on the meridian (see figure 3 (*d*)).

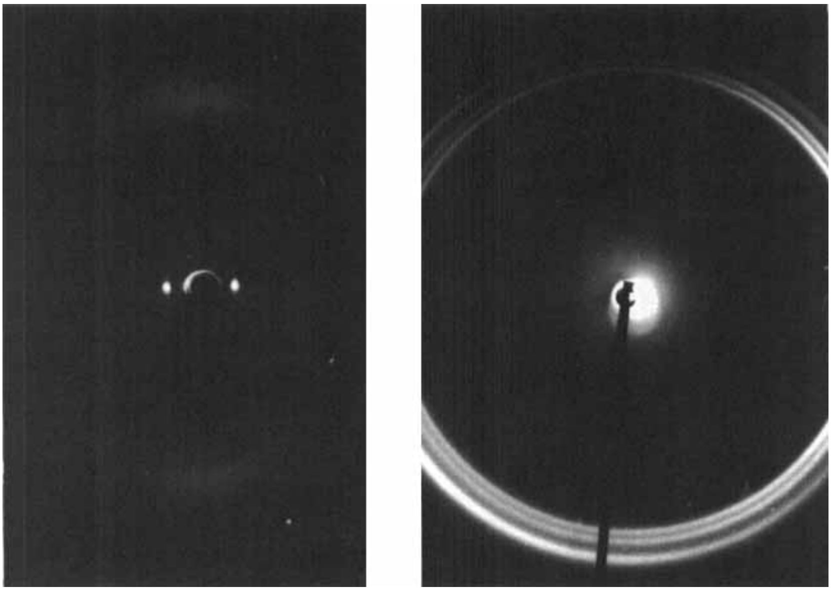
The polymers 5b, 5f and 5g exhibit a low temperature phase between the P_{S_C} phase and the crystalline one. The Guinier-patterns have been analysed on the basis of a monoclinic unit cell. The scattering patterns for oriented samples (see figure 4) have been explained in comparison with low molar mass systems as sketched in figure 5. Rotational disorder around the c^* axis and equally distributed up and down orientation of the c^* axis is assumed. It yields a ratio of the lattice constants $a/b < 1$, which characterizes the S_I, S_J and S_K phases found in low molar mass systems [11–13]. The Guinier patterns of 5b and 5f suppose an interpretation with P_{S_J}. The patterns of polymer 5g, however, can be indexed only if the existence of a P_{S_G} phase is assumed, exhibiting a ratio $a/b > 1$.



(*a*)

(*b*)

(*c*)



(*d*) (*e*)

Figure 3. X-ray patterns of oriented samples of polymer 5f. Sample-film distance: (*a*), (*c*), (*d*) 70 mm, (*b*), (*e*) 88 mm. (*a*) Crystalline, (*b*) P_{S_J}, (*c*) P_{S_C}, (*d*) P_{S_A}, (*e*) crystalline, direction of the incident beam is parallel to the direction of the magnetic field.

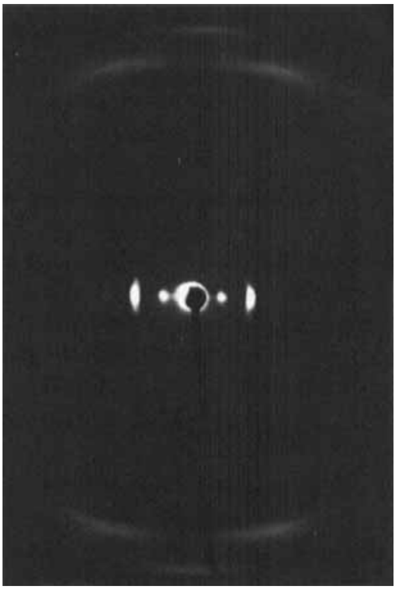


Figure 4. X-ray pattern of oriented sample of polymer 5b, P_{S_J} phase.

In this way the phases under discussion can be interpreted as liquid-crystalline phases of the ordered type [14]. This classification is supported by NMR studies [10] which yield similar dynamic properties as the low temperature phases of the low molar mass systems.

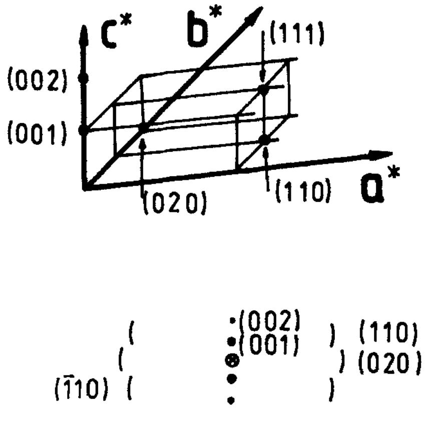


Figure 5. The reciprocal lattice for the P_{S_J} phase (see figure 4).

4. Some remarks about the nomenclature

The polymorphism of liquid-crystalline phases in polymeric systems requires a designation of the different types. In the literature the denotation introduced for low molar mass systems has been used without hesitation, that means the phases are labelled with S_A, S_B, S_C etc.

It must be emphasized that this denotation is based on the rule of uninterrupted miscibility. Phases, which are connected in binary systems by a complete miscibility, are labelled with the same symbol. After that it has been evidenced that each phase type (S_A, S_B, . . .) can be characterized by a definite structure type [14]. Therefore the X-ray patterns which are different for different phases can be used to classify phases of new substances in connection with the miscibility studies. The lack of an extended miscibility in polymeric systems and the difficulties in obtaining specific textures make the classification in the manner described for low molar mass systems doubtful. Therefore the notation is based mainly on the X-ray patterns which exhibit some common features with the corresponding phases of low molar mass systems. But that is the crucial problem. The X-ray patterns of the polymeric phases represent usually much more scattering phenomena (diffuse scattering maxima in the small as well as in the wide angle region, reflections incommensurable with the molecular structure etc.) indicating that the structures are more complicated than those of the low molar mass systems. For example a diffuse scattering in the patterns of the S_G phase in low molar mass systems [19] indicates characteristic properties of this phase type. Several reasons for the scattering in polymeric systems can be given (the position of the main chain, the tendency to a phase separation), but most of them seem to be connected with the presence of mesogenic as well as of non-mesogenic parts leading to incommensurable conditions. Especially, it can be assumed that the specific properties of polymeric phases are more significant in the low temperature phases.

Therefore, complete agreement between the known structures of low molar mass systems and polymeric ones, suggested by one and the same designation must be doubtful. To point to the differences as well as to the same common properties it would be helpful to use a symbol characteristic for polymeric systems but not quite different from that of low molar mass systems, e.g. P_{S_A}, P_{S_B} . . . P_{S_J}. It should be remembered that a similar situation is known in the case of discotic systems in which the specific structure is expressed by the symbol D [15, 16].

5. Conclusions

The systematic variation of the length of the main-chain segment L_1 as well as of the side-chain L_2 by the variation of the corresponding spacer length should give an insight into the packing of the two mesogenic parts of the polymer. The strong influence of L_1 and L_2 on the polymorphism limits such a discussion.

A biaxial arrangement [1] in which the main-chain and the side-groups are arranged perpendicular to each other could be excluded [2–8]. It would be in contradiction with the results under discussion. Especially by more recent studies of similar substances [7, 8] an analogous model to that used in this paper has been proved.

Table 2.

Polymer	Lengths of the main-chain (L_1) and side-chain segments (L_2) L_1/Å	L_2/Å	d/Å in P_{S_A}	Layer thickness estimated by models/Å
5a	22·0 ± 1·0	18·0 ± 1·0	16·5 ± 0·5	18·0 ± 2·0
5b	22·0 ± 1·0	23·0 ± 1·0	19 ± 0·5	38·0 ± 3·0
5c	22·0 ± 1·0	28·0 ± 1·0	44 ± 1 (crystalline)	44 ± 3.0
5e	32·0 ± 1·0	18·0 ± 1·0	18·5 ± 0·5 (crystalline)	19·0 ± 2·0
5f	32·0 ± 1·0	23·0 ± 1·0	23·5 ± 0·5	23·0 ± 2·0
5g	32·0 ± 1·0	28·0 ± 1·0	26·0 ± 0·5	27·0 ± 2·0

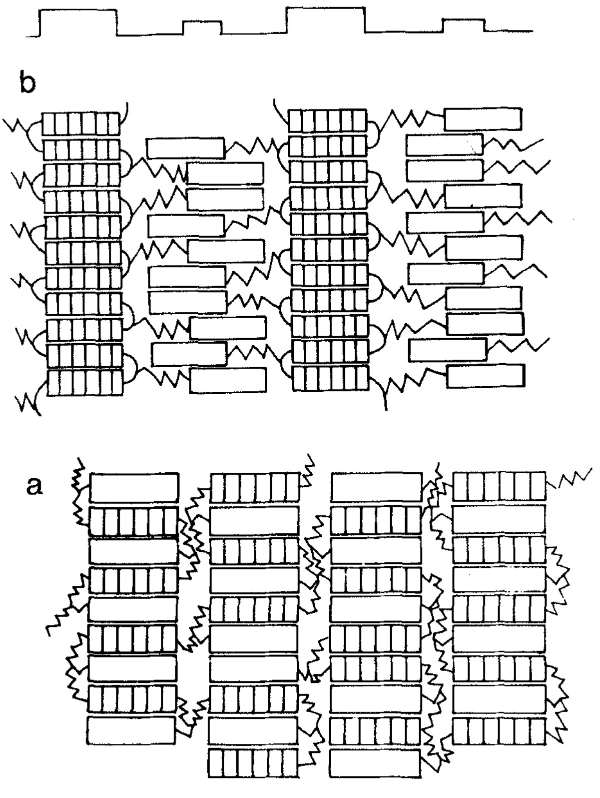


Figure 6. Sketch of a packing model in the smectic phases (*a*) of polymers 5a, 5e, 5f, 5g and (*b*) of polymer 5b.

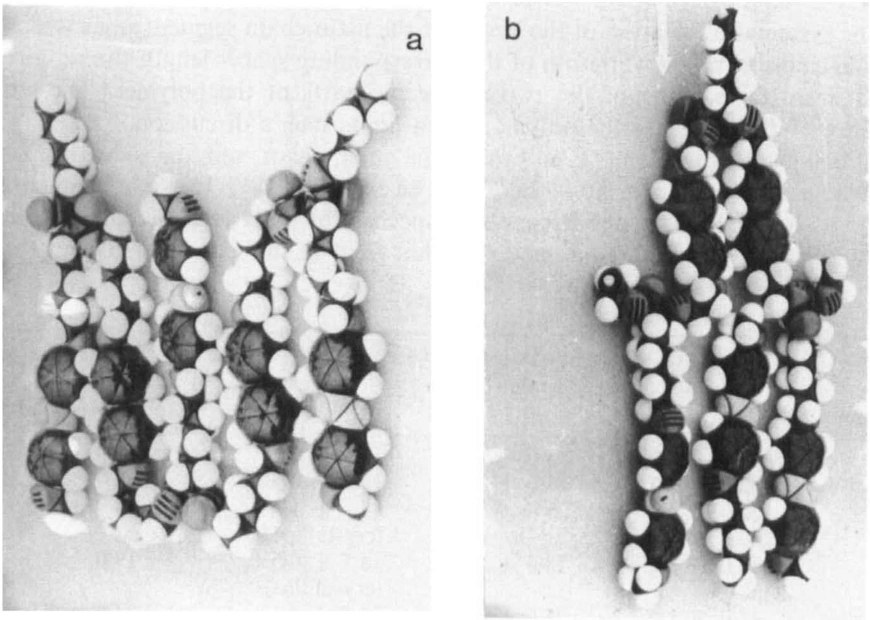


Figure 7. Molecular models typical for (*a*) polymers 5a, 5e, 5f, 5g and (*b*) polymer 5b.

Our interpretation of the structure is based on the assumption that a strong tendency for a parallel arrangement of the aromatic parts exists independently of their incorporation into the main-chain or into the side group. Of course, steric interactions as well as the flexibility of the segments may disturb this packing principle to a certain extent. Comparing the experimental d values with the length of the main-chain and side-chain segments, L_1 and L_2 respectively, it seems that the d-value is generally determined by the shorter segments (see table 2). With the exception of polymers 5b and 5c the determining segment is the side-group. The main-chain, which contains two spacers in the repeating unit, is flexible enough to form the packing as sketched in figures 6 (*a*) and 7 (*a*). It must be emphasized that this behaviour differs clearly from results for low molar systems. It has been shown [17, 18] that the layer period of mixtures can be calculated additively from the length of the pure components, also if the molecules are of quite different length. The non-applicability of this rule in the present case could be due to the chemical connection of the different mesogenic groups. For $L_1 = L_2$ (see polymer 5b, table 2), a layer thickness greater than L_1 or L_2 is found. This value could be explained only by a model in which a separation of the main-chain and side-chain segments into two sublayers is assumed (see figures 6 (*b*) and 7 (*b*)). The higher intensity of the 002 reflection with respect to the 001 reflection is interpreted by different amplitudes of the electronic density maxima as sketched in figure 6 (*b*).

References

[1] RECK, B., and RINGSDORF, H., 1985, *Makromolek. Chem.*, **6**, 291.
[2] ZENTEL, R., RECKERT, G., and RECK, B., 1987, *Liq. Crystals*, **2**, 83.
[3] ZENTEL, R., SCHMIDT, G. F., MAYER, J., and BENALIA, M., 1987, *Liq. Crystals*, **2**, 651.
[4] VOIGT-MARTIN, I. G., DURST, H., RECK, B., and RINGSDORF, H., 1988, *Macromolecules*, **21**, 1620.
[5] BUALEK, S., and ZENTEL, R., 1988, *Makromolek. Chem.*, **189**, 797.

[6] KAPITZA, H., and ZENTEL, R., 1988, *Makromolek. Chem.*, **189**, 1793.

[7] VOIGT-MARTIN, I. G., and DURST, H., 1989, *Macromolecules*, **22**, 168.

[8] ENDRES, B. W., EBERT, M., WENDORFF, J. H., RECK, B., and RINGSDORF, H., 1989, (in the press).

[9] RECK, B., and RINGSDORF, H., 1986, *Makromolek. Chem., rap. Commun.*, **7**, 389.

[10] RECK, B., 1988, Thesis.

[11] GANE, P. A. C., LEADBETTER, A. J., and WRIGHTON, P. G., 1981, *Molec. Crystals liq. Crystals*, **66**, 567.

[12] GANE, P. A. C., LEADBETTER, A. J., WRIGHTON, P. G., GOODBY, J. W., GRAY, G. W., and TAJBAKHSH, A. R., 1983, *Molec. Crystals liq. Crystals*, **100**, 67.

[13] DIELE, S., DEMUS, D., and SACKMANN, H., 1980, *Molec. Crystals liq. Crystals*, **56**, 217.

[14] DEMUS, D., DIELE, S., GRANDE, S., and SACKMANN, H., 1983, *Advances in Liquid Crystals*, edited by G. H. Brown, Vol. 6 (Academic), p. 1.

[15] DESTRADE, C., FOUCHER, P., GASPAROUX, H., HUU TINH, N., LEVELUT, A. M., and MALTHETE, J., 1984, *Molec. Crystals liq. Crystals*, **106**, 121.

[16] DUBOIS, J. C., and BILLARD, J., 1984, *Liq. Crystals and Ordered Fluids*, Vol. 4, edited by A. C. Griffin and J. F. Johnson (Plenum), p. 1043.

[17] DIELE, S., NASTA, L., and SACKMANN, H., 1977, *Krist. Techn.*, **12**, 1063.

[18] DIELE, S., and SACKMANN, H., 1989, *Ber. Bunsenges. phys. Chem.*, **93**, 467.

[19] LEVELUT, A. M., DOUCET, J., and LAMBERT, M., 1974, *J. Phys., Paris*, **35**, 773.