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Combined main chain/side chain polymers

A new class of liquid crystalline polymers with unusual structural, thermodynamic and dynamic properties

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Combined main chain/side chain polymers carry rigid rod-like mesogenic units both in the side chain and along the chain backbone. The properties of such combined systems are expected to be controlled by the competition of the interactions between the mesogenic units in the side and main chains as well as the tendency of the chain backbones to maximize their entropy. The thermodynamic, structural and dynamic properties of such combined main chain/side chain liquid-crystalline polymers were investigated for various chain architectures. The combined systems were found to display properties corresponding in many cases to a favourable superposition of properties characteristic of both main and side chain systems. These include high transition temperatures (up to 530 K) and broad ranges of stability of liquid-crystalline phases (up to about $\Delta T = 170\,\mathrm{K}$). The orientational order parameter was found to approach values of 0.9 and it was possible to orient some of the polymers in weak external fields such as 1 T for instance, for magnetic fields. Smectic antiphase formation corresponding to that observed in low molar mass systems carrying strong longitudinal dipoles and resulting from the presence of incommensurable lengths were observed in those cases in which the side groups were attached directly to the rigid part of the chain backbone whereas no such effects occurred if the side groups were fixed to the flexible part of the main chain. The reorientational motion of the mesogens about their short axis, which couples to dielectric and electro-optical properties was found to have a surprisingly low activation energy (as low as 115 kJ/mol) and a strong anisotropy of the dielectric constant ($\Delta\varepsilon = 7$) despite a relatively small concentration of dipoles. It thus seems that the combined systems may be the material of choice for many future applications.

1. Introduction

Chain molecules have a tendency to maximize their entropy in the condensed fluid state, as is apparent from the random coil conformation displayed by flexible chain molecules in the melt [1]. This tendency is, however, opposed for liquid-crystalline polymers by orientational ordering effects resulting from anisotropic interactions between the anisometric mesogenic units. The expectation is therefore that the structure which evolves in liquid-crystalline polymers as well as their thermodynamic and dynamic properties are controlled by this competition between driving forces and will depend strongly on details of the chain architecture [2–7]. Semiflexible main chain polymers in which the mesogenic units are linearly incorporated into the chain backbone can be envisaged to display properties which differ strongly, for instance,

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from those of side chain polymers in which the mesogenic units are attached via flexible spacers to a flexible chain backbone.

Both of these cases have been investigated experimentally and treated theoretically in some detail [2–6]. The prediction for semiflexible main chain polymers is that the chain backbone units prefer to orient parallel to the director, so causing a chain extension along this direction which increases with increasing strength of the nematic phase, i.e. with increasing magnitude of the nematic order parameter S. The drive towards entropy maximization gives rise, according to theoretical concepts, to the formation of defects such as hair pins [7] rather than of chain folds known to occur for non-thermotropic flexible chain molecules.

For side chain polymers, on the other hand, the predictions are that, just because of the competitions between entropy maximization and the ordering effects of main chain and side chain elements, different nematic phases may be displayed. Their formation depends on the concentration of side chains, the length of the side chains, the flexibility of the chain backbone and the coupling of side group and main chain elements [6]. These phases differ with respect to the alignment of either just the side groups, the chain backbone units or both side group and chain backbone units along the director and consequently with respect to the anisotropy of the chain dimensions parallel and perpendicular to the director. Experimental results obtained by neutron scattering studies or N.M.R. studies seem to indicate that the chain backbone may actually be extended along the director or perpendicular to it depending on the chemical structure of the side chain polymer [8–12]. Oblate or prolate shapes are thus displayed by the chain molecules.

On the basis of these considerations it is, first of all, tempting from a theoretical point of view to investigate structure formation processes and related thermodynamic properties for the case that both the side chain and the main chain contain mesogenic units [13, 14]. The anisotropic interaction between side chain and main chain units are strongly enhanced and the main chain has an increased tendency to extend and orient parallel to the director. This might lead to a destructive superposition of structure formation processes (frustration) or to a constructive one creating synergistic effects, for instance, or even the formation of a biaxial nematic phase.

The exploration of the properties of combined main chain/side chain polymers is, however, of great interest also from an application point of view. Semiflexible liquid-crystalline polymers tend to display satisfactory mechanical properties, frequently a broad range of thermodynamic stability of liquid-crystalline phases [15–18]. In addition, they tend to have a high orientational order. Their optical or electro-optical properties on the other hand are poor and it is difficult to orient them with external electric or magnetic fields.

Side chain polymers, on the other hand are easy to orient by external fields, they possess in the majority of cases acceptable optical, electro-optical or non-linear optical properties but poor mechanical properties, limited ranges of thermodynamic stability of the liquid-crystalline phase and often rather low glass transition temperatures [15–18]. In addition, the orientational order is generally low. It seems possible therefore that combined main chain/side chain polymers may offer a combination of favourable properties characteristic of the main chain polymers on the one hand and the side chain polymers on the other hand.

So, for these reasons, thermodynamic properties and structural properties of combined main chain/side chain polymers were investigated. In addition, dielectric relaxation studies were performed as a function of the chain architecture. The motivation, first of all, is that the dielectric response depends strongly on the intrinsic orientational order of the liquid-crystalline phase as well as on restrictions of reorientational motions imposed by the coupling of main chain and side chain units. In addition, it is known that electro-optical and switching properties are strongly controlled by such reorientational motions as the reorientation of the mesogenic unit about its short axis [19–21].

2. Experimental

2.1. *Chemical structures of the combined main chain/side chain polymers*

Two types of liquid-crystalline combined polymers were investigated: those in which the side groups are attached to the chain backbone at the flexible part of this (type *a*, figure 1 (*a*)) and those in which the mesogenic units of the chain backbone are effective laterally substituted by side chains (type *b*, figure 1 (*b*)).

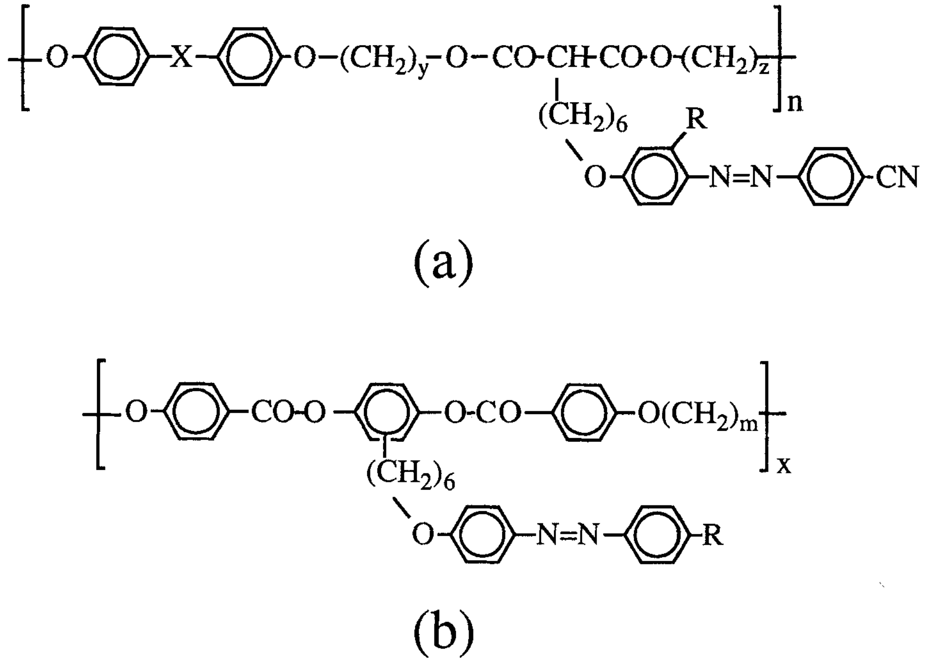


Figure 1. Chemical structures of the combined main chain side chain polymers (*a*) type *a* and (*b*) type *b*. The modifications performed are listed in table 1.

Polymers 1–5 (see table 1) belong to the first type of combined polymers displayed in figure 1 (*a*). Polymer **1** contains azobenzene groups as well as $(CH_2)_n$ spacer units ($n = 6$) both in the chain backbone and in the side chain. The side group finally contains a strong longitudinal dipole (CN). The chemical modifications which were performed consisted in varying the length of the spacer units in the chain backbone, the nature of the mesogenic unit in the chain backbone and in the side chain. The length of the flexible units in the chain backbone was varied by using equal amounts of co-monomers containing either 6 or 2 (CH_2)-units along the chain backbone for the polymer 2 (see table 1) and in the case of polymer **3** by incorporating only $(CH_2)_2$ spacer units into the chain backbone. These variations also cause an increase of the concentration of side chains. The mesogenic units were modified either by replacing

Table 1. Chemical structures of the combined main chain/side chain polymers investigated, their molecular weights as well as their approximate chain length.

Polymer	Structure	$\bar{M}_{GPC}$ [g mol^{-1}]	Chain length *n*
	Type *a*		
1	X = N=N, $Y = 6$, $Z = 6$, R = H	55·000	70
2 Copol 50/50	X = N=N, $Y_1 = 6$, $Z_1 = 6$, $Y_2 = 2$, $Z_2 = 2$, R = H	30·000	40
3	X = N=N, $Y = 2$, $Z = 2$, R = H	—	—
4	X = $Y = 6$, $Z = 6$, R = H	—	—
5 Copol 50/50	X = N=N, $Y_1 = 6$, $Z_1 = 6$, $Y_2 = 2$, $Z_2 = 2$, $R = CH_3$	27·000	35
Type *b*			
6	$m = 6$, $R = OCH_3$	38·000	55
7	$m = 9$, $R = OCH_3$	45·000	60
8 a	$m = 10$, $R = OCH_3$	20·000	25
b	$m = 10$, $R = OCH_3$	112·000	145
9	$m = 10$, R = CN	10·000	15

the azobenzene moities in the chain backbone by a biphenyl unit (polymer **4**, table 1) or by a lateral CH_3-substitution in the side chain at the phenyl group closest to the main chain (polymer **5**).

The coupling between main and side chain units is strongly modified by moving the coupling from the flexible part of the chain backbone to the rigid part as shown in figure 1 (*b*). The number of flexible spacer units (CH_2) was varied between 6 (polymer **6**), 9 (polymer **7**) and 10 (polymers **8** and **9**) as shown in table 1 and the end group of the side chain was either a CN group (polymer **9**) or a methoxy group (polymers **6**–**8**).

Table 1 contains the average molecular weights obtained from gel chromatographic investigations, using a polystyrene standard. It is apparent that the chain length is of the order of about 20 to 150 repeat units, which corresponds to a chain contour length of the order of 50 to 450 nm. Neither microscopical studies nor the DSC studies (width of the transitions, see figure 2 as an example) revealed any indication of biphasic behaviour. This indicates a rather narrow distribution of the molecular weights.

2.2. *Techniques employed*

The wide angle X-ray experiments were performed for unoriented samples with a wide angle goniometer (D500, Siemens, Erlangen) and for oriented samples with a flat film camera and a Kratky pin hole camera. Nickel-filtered CuK_α radiation ($\lambda = 0.154$ nm) was used in all cases. The calorimetric studies were performed with a Perkin Elmer DSC 4 and the dielectric studies by using a General radio bridge (1621) as well as by using a Hewlett Packard bridge (4192 A LF). The dielectric studies were performed isothermally, increasing the temperature stepwise prior to each measurement at a given temperature.

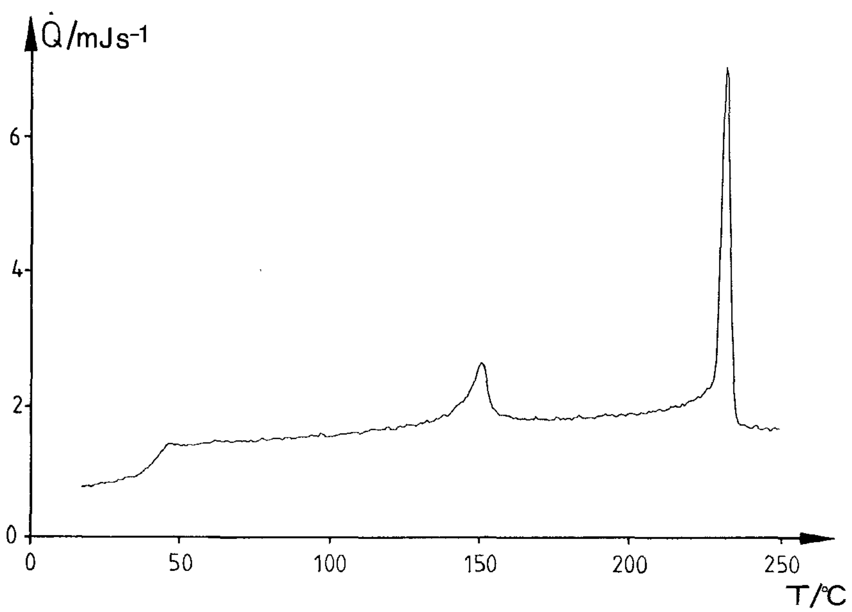


Figure 2. D.S.C. trace for the combined polymer **8b** (see table 1), showing a glass transition and two first order phase transitions.

3. Thermodynamic properties and transitions

3.1. *The glass transition*

The combined main chain/side chain polymers display in all cases a glass transition at low temperatures and one or two first order phase transitions at elevated temperatures. Figure 2 gives an example for the particular case of polymer **8b**. Table 2 displays the location of the glass transition temperature of the combined systems *a* (polymer **1–5**) and *b* (polymers **6–9**) as a function of the chain architecture. The general finding is that the location of the coupling sites of the side chains (at the rigid or flexible part of the chain backbone) does not influence the location of the glass transition temperature significantly and that decreasing the number of CH_2-units leads to an increase of the glass transition temperature, as expected. The increase is, however, moderate. A surprisingly strong increase results from the replacement of the azobenzene units in the chain backbone by biphenyl units (polymer **4**, type *a*). This might be interpreted as being due to the enhanced rigidity of the latter unit. The locations of the glass transitions of semiflexible main chain polymers having about the same length of the flexible spacer and of side chain polymers with flexible backbones such as acrylate, methacrylate or polyester chain backbones are in the same temperature range [15–18]. So in general, the impact of the chain architecture on the location of the glass transition is evident but moderate, amounting to shifts of the order of 15 K.

3.2. *Phase transitions*

Both types of combined main chain/side chain polymers studied here exhibit at elevated temperatures one and in a few cases two anisotropic phases which are, in any

Table 2. Glass transition temperatures, phase transition temperatures, heats of transition and entropies of transition of the combined main chain/side chain polymers.

Sample				
1	g 37	C? 93°C 12·5 kJ mol^{-1} 34·2 J K^{-1} mol^{-1}	S_B 196°C 11·8 kJ mol^{-1} 25·2 J K^{-1} mol^{-1}	I
2	g 39		S_A 182°C N 191°C † 7·6 kJ mol^{-1} 16·4 J K^{-1} mol^{-1}	I
3	g 53		S_A 202°C 5·6 kJ mol^{-1} 11·9 J K^{-1} mol^{-1}	I
4	g 60	C? 112°C 9·5 kJ mol^{-1} 24·5 J K^{-1} mol^{-1}	S_A 180°C 13·3 kJ mol^{-1} 29·4 J K^{-1} mol^{-1}	I
5	g 31		N 143°C 2·5 kJ mol^{-1} 6·1 J K^{-1} mol^{-1}	I
6	g 51	$S_{\tilde{A}}$ 172°C 0·6 kJ mol^{-1} 1·3 J K^{-1} mol^{-1}	N 257°C 8·7 kJ mol^{-1} 16·2 J K^{-1} mol^{-1}	I
7	g 41	$S_{\tilde{A}}$ 68°C 0·6 kJ mol^{-1} 1·8 J K^{-1} mol^{-1}	N 216°C 6·6 kJ mol^{-1} 13·5 J K^{-1} mol^{-1}	I
8a	g 37	$S_{\tilde{A}}$ 129°C 1·5 kJ mol^{-1} 3·8 J K^{-1} mol^{-1}	N 214°C 9·8 kJ mol^{-1} 18·1 J K^{-1} mol^{-1}	I
8b	g 39	$S_{\tilde{A}}$ 144°C 1·9 kJ mol^{-1} 4·7 J K^{-1} mol^{-1}	N 228°C 9·1 kJ mol^{-1} 20·0 J K^{-1} mol^{-1}	I
9	g 43		N 208°C 9·3 kJ mol^{-1} 19·3 J K^{-1} mol^{-1}	I

First lines: Transition temperature (°C), (kJ mol^{-1}), (J K^{-1}mol^{-1}); g, glass; C, crystalline; S, smectic; N, nematic.

Second lines: enthalpy of transition.

Third lines: entropy of transition.

† Not resolved.

case, liquid-crystalline phases. Polymers of type *a* may also display a low temperature ordered phase (see §4) which can, however, be suppressed by rapid cooling to room temperature. The polymers of type *b* have only low temperature liquid-crystalline glassy states. The distortions introduced into the chain structure are apparently sufficiently large to prevent the formation of a well ordered low temperature state. The distortions on the other hand are not strong enough to disrupt the liquid-crystalline structure.

The rather unexpected finding is that all combined systems *a* and *b* are characterized by a relatively high transition temperature as far as the transition into the isotropic phase is concerned. This is evident from table 2 and from a comparison with the transition temperatures of semiflexible main chain and of side chain polymers of similar chemical structure. The transition temperatures are of the order of 200°C. The main chain polymer (Azo 6, 6) corresponding to polymer 1 possesses a monotropic liquid-crystalline phase which transforms at about 150°C into the isotropic melt, the main chain liquid-crystalline polyesters corresponding to polymer 6 to 9 are characterized by somewhat larger transition temperatures of the order of 380°C ($n = 6$) to 270°C ($n = 10$) [22] and the side chain polymers with similar side groups and acrylate, methacrylate or polyester chain backbones exhibit transitions into the isotropic phase in the temperature range between 100 and 120°C [23]. So it seems that the thermodynamic properties are controlled by a constructive superposition of energetic and entropic contributions resulting from main and side chain elements thus causing the high transition temperature. This holds even when the coupling sites are located at the rigid parts of the chain backbond.

A decrease of the total length of the CH_2 spacers in the chain backbone from 12 (polymer **1**) to effectively 8 (polymer **2**) and finally to 4 (polymer **3**) is expected to lead to a large increase of the transition temperature of the order of 100 K or more as judged from the corresponding behaviour of semiflexible main chain polymers and to a certain degree also as judged from the behaviour of side chain polymers [23]. It is the stiffness of the chain backbone (siloxane, acrylate, methacrylate units in the chain backbone, for instance) which has an appreciable impact on the transition temperature for side chain polymers. In contrast to this expectation we find that this reduction of the spacer length leads only to negligible variations of the transition temperature for polymers of type *a*. The replacement of the azobenzene unit in the chain backbone by a biphenyl unit, which seems to stiffen the chain backbone as judged from its effect on the glass transition temperature, even causes a decrease of the transition temperature. A somewhat stronger decrease of the transition temperature with increasing spacer length is, however, found for polymers *b*.

These findings seem to indicate that the transition from the liquid-crystalline state into the isotropic phase is not at all or only weakly controlled by the length of the flexible spacer units in the chain backbone. This conclusion is, however, incorrect as is apparent from the dependence of the transition enthalpy and the transition entropy on the chain architecture (see table 2). The transition entropy is strongly reduced with decreasing spacer length. The absolute value of the transition entropy and its variation agree qualitatively with those found for semiflexible chain molecules. The strong dependence of the transition entropy on the number of CH_2-units suggests conformational changes accompanying the smectic or nematic to isotropic transition [4, 23].

The reason why the transition temperatures of polymers of type *a* do not increase with decreasing spacer length evidently is that the transition enthalpy is also a function of the spacer length as is also apparent from table 2. This dependence obviously is stronger than for main chain polymers. So it seems that the side chain arrangement and their interactions among themselves and with the mesogenic units of the chain backbone have also to play a substantial role in controlling the transition. This is directly apparent from the fact that the lateral substitution of the azobenzene group in the side chain with a CH_3 group causes a drastic decrease of the transition temperature, connected both with a strong decrease of the transition entropy and the transition enthalpy. On the other hand the shift of the side group coupling from the flexible to the rigid part of the backbone (type *b*, polymers **6–9**), which might be expected to lead to strong modifications of the tendency towards liquid-crystalline phase formation, does not disturb the structure formation in such a way that a low transition temperature arises. On the contrary, the transition temperatures are extremely high and stay so despite the fact the flexible spacer is long and despite the fact that a nematic phase is formed at elevated temperatures (see table 2).

Data on the transition temperature and on the entropy of transition which are available for similarly constructed semiflexible main chain polymers and side chain polymers reveal that the transition entropies found for the combined polymers resembles that of main chain polymers but are much larger (up to a factor of 10) than encountered for side chain polymers [23]. (It has to be pointed out, however, that these values tend to depend on the chain length, to a certain extent.) Nevertheless, both findings taken together with the results reported here for the laterally substituted polymer indicate again the occurrence of a constructive superposition of the structure forming processes controlled by side and main chain elements, leading to an ordered structure. The major contribution to the transition properties seems to result, in general, from the main chain.

In the discussion of transition properties so far no distinction was made between the different kinds of liquid crystal phases which are formed by the combined systems. In general we observe, as for semiflexible main chain polymers, the formation of a smectic phase, as will become apparent later either of disordered ones such as the smectic A phase or ordered ones corresponding to the smectic B phase. The copolymer (polymer **2**) forms both a nematic and a smectic phase at elevated temperatures, the laterally substituted combined systems just a low temperature nematic. An interesting result is that the transition entropy and the transition enthalpy are frequently the largest for the high temperature transition, independent of whether it is a nematic- or a smectic–isotropic transition in comparison to the values found for lower temperature transitions. This seems to indicate that conformational changes of the chain backbone drive the transition into the isotropic phase and that only minor changes occur at subsequent lower temperature transitions.

4. Results of structural investigations

4.1. *General discussion of the structure of the combined polymers of type a*

Some of the combined main/chain side chain polymers display a low temperature ordered state. This is apparent from the wide angle X-ray pattern for polymer 1 shown in figure 3 (*a*). This state is characterized, evidently, by a layer structure, giving rise to a triplet of equally spaced small angle X-ray reflections and by a well defined order within the layer. The number of reflections is too low in order to allow a reliable structure assignment. It seems, however, that the solid state does not correspond to a really three dimensional ordered crystalline state, as judged from the patterns obtained for oriented samples. No reflections were found which could be assigned to mixed reflections (*hkl*), as we would expect for a crystalline state. The transition enthalpies and entropies observed for the transition into the liquid-crystalline state are of the same order as the corresponding values found for the nematic or smectic to isotropic transition. This topic will be considered in a separate paper.

The transition into the liquid-crystalline phase leaves the layer intact whereas the order within the layers is reduced. This is evident from figure 3 (*b*), which shows just one rather broad reflection, indicative of the absence of a long range order or of the presence of a disturbed long range order. The wide angle reflection observed for polymer **1** is, however, too narrow of a disordered smectic phase such as the smectic A phase, for instance and it resembles that of a smectic B modification. This is apparent from the X-ray pattern of the isotropic phase displayed in figure 3 (*c*). The

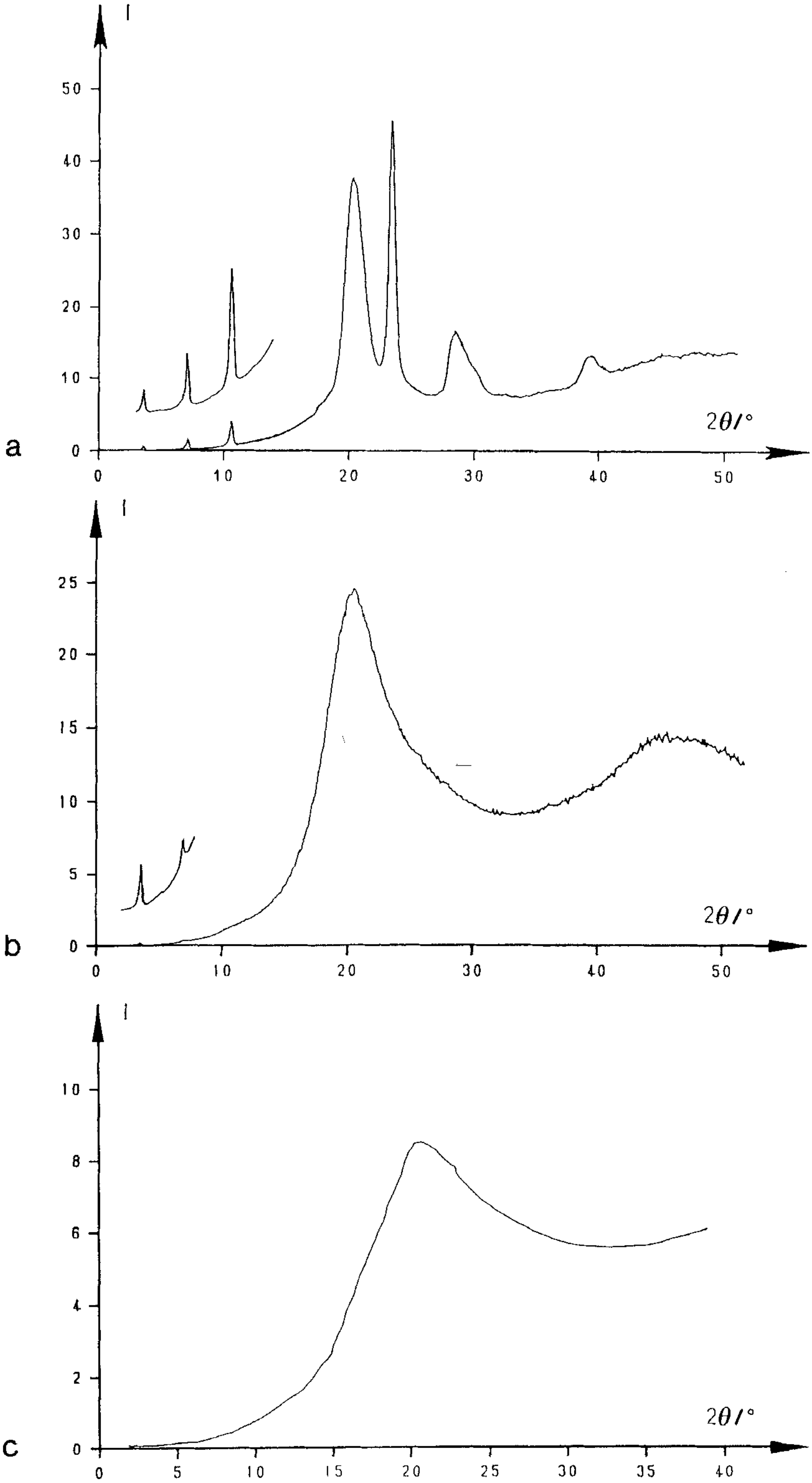


Figure 3. Wide angle X-ray diffraction pattern of the combined polymer **1** (see table) in the ordered state (*a*), the smectic state (*b*) and the isotropic phase (*c*).

reflection is, on the other hand too broad for a highly ordered smectic phase. We conclude tentatively that the packing of the molecules is probably hexagonal and this is in agreement with room temperature electron microscopy on quenched samples by Voigt-Martin *et al.* [24]. Voigt-Martin observed furthermore a slight tilt of about 16° between the layer normal and the director, a feature which was not apparent from the X-ray fibre patterns. The other smectic polymers both of type a and of type *b* evidently possess a disordered smectic A phase. The differences in the optical textures between these two types of smectic phases are small and inconclusive as is often the case for polymer liquid crystals. The distance *a* of the two dimensional hexagonal lattice within the layers is given in table 3. The packing within the layer perpendicular to the director seems to be similar in all cases.

The layer distance obtained from the small angle reflections for the polymer **1** and for the chemical modifications exhibiting also smectic phases, i.e. polymers **2–4**, are given in table 3. The layer distance corresponds roughly to the length of the chain backbone repeat unit and it is apparent that a shortening of the spacer incorporated in the main chain leads to a corresponding decrease of the layer distance. This is an indication of the impact of the main chain structure on the structure formation process. The results seem to indicate the presence of a single layer rather than a double layer structure as often found for side chain polymers with strong longitudinal dipole moments. This topic will be considered again later in some detail.

So far the smectic phase which is formed by the majority of the combined systems of type a studied here was discussed. A nematic phase or both a nematic or a smectic phase are observed if the chain structure is distorted in some way, for instance by copolymerization or by lateral substitution of the side chain mesogen. Figure 4 shows the flat camera diffraction pattern obtained for a sample of the laterally substituted

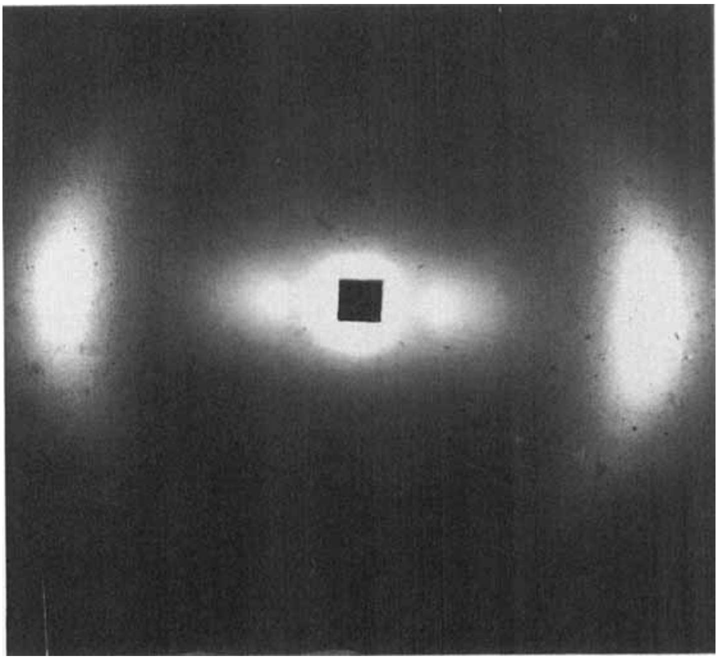


Figure 4. Flat camera diffraction pattern of the polymer **9**, oriented within the nematic phase by a magnetic field (1 T).

polymer **9** which was aligned in a magnetic field. The finding is that the nematic order parameter is rather large and surpasses easily values of the order of 0·85, as determined from X-ray results on oriented samples. This is a characteristic feature of the main chain polymers whereas the ease of orientation in external fields is a feature characteristic of side chain polymers. The chain conformation formed by the nematic systems seems to be similar to that which is characteristic of the smectic phase, as is evident from similar transition entropies and from the rather high orientational order parameter.

4.2. *Conclusions on the chain conformation*

Next the problem of the competition between entropy maximization imposed by the interactions between the mesogenic units will be addressed. The question to be answered is to what extent the mesogenic units in the chain backbone and in the side groups are orientationally correlated and what conformation the chain backbone will assume. To this end structural models which are based on such considerations will be discussed based on the experimental results given so far.

In the first model (see figure 5(*a*)) a case is considered which is based on the assumption that the competition between the interactions among mesogenic units and the tendency of the main chain to maximize its entropy is such that the side chain

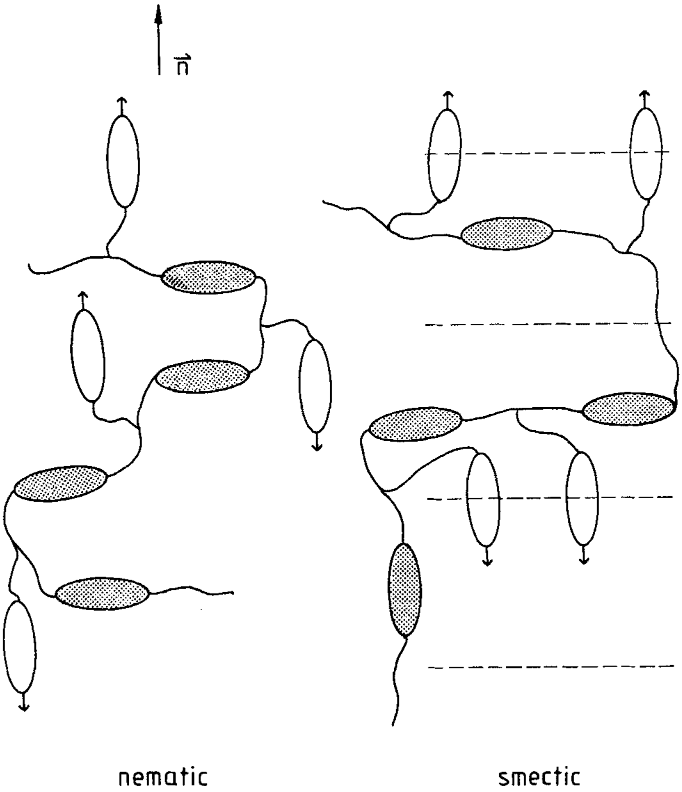
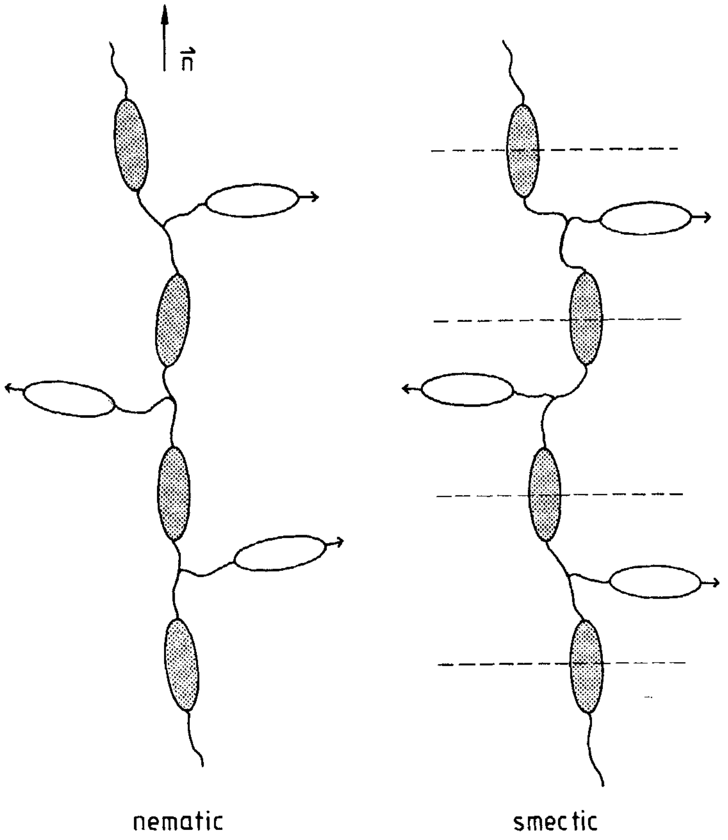


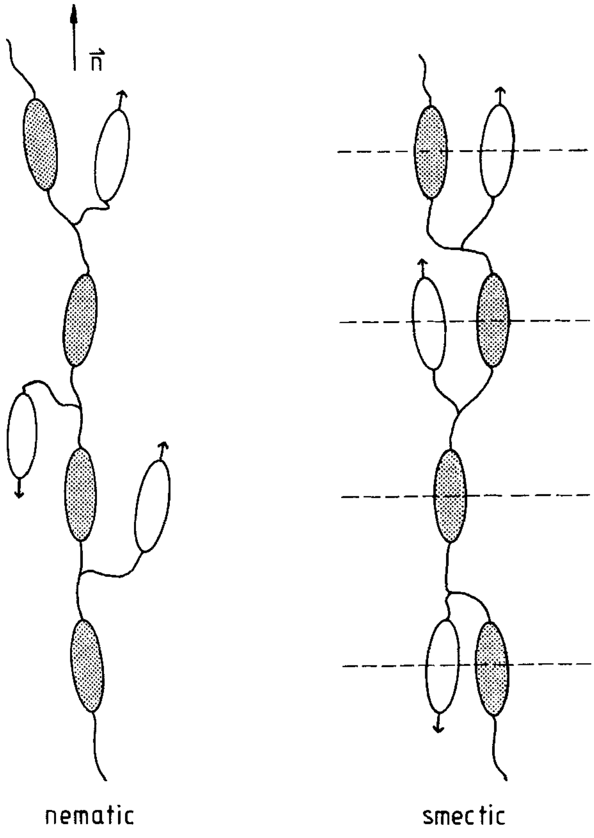
Figure 5.



b
Figure 5.

units possess a positive order parameter, that the smectic layers are formed predominantly by the side groups and that the mesogens of the main chain take part in the layer only in those cases where the chain backbone crosses the layer in order to be able to maximize its entropy by the formation of a coil conformation, i.e. layer hopping takes place. Such a structure is not expected to give rise to large entropies of transition at the isotropic transition, in contrast to experiment. This model, furthermore, seems to be at variance with the observation that the smectic layer distance is related to the length of the spacer along the main chain. However a stronger evidence against this model is needed in order to discard it.

In the second case the assumption is that the interactions between side chain units and main chain units are weak and that it is the main chain unit which possesses a positive order parameter whereas the side group has a negative one. The chain backbone units form the smectic structure, giving rise to a kind of biaxial phase (see figure 5 (*b*)). The problem with this model is that modifications performed on the side chains should only have a negligible influence on the transition properties in this case in contrast to the experiment. The dielectric properties, to be discussed later, which display a positive anisotropy of the dielectric constant are also in contradiction with this model as are packing considerations. So this model does not seem to be correct.



c

Figure 5. Structural models for the distribution of the mesogenic units of the chain backbone (▨) and of the side groups (☐) within the nematic phase and a smectic phase. (*a*) The order parameter of the side groups is positive, the side groups form the smectic layers, the chain backbone assumes a random coil type conformation. (*b*) The order parameter of the chain backbone units is positive, that of the side groups is negative, the main chain units form the smectic layers. (*c*) The order parameters both of the side and chain backbone units are positive, both form the smectic layers.

Finally the model is considered where the interactions between all mesogenic units are assumed to be such that both the side chain and the chain backbone units possess positive order parameters (see figure 5 (*c*)). For a smectic phase this will cause both the side chain and the main chain mesogens to form the smectic layers as shown schematically in figure 5 (*c*) for the polymers of type *a*. The dielectric studies which are described later will show that the side groups have to point both up and down as indicated in figure 5 (*c*). The chain conformation has to correspond more or less to that of a rod with the possible exceptions of the presence of hairpin defects. This conformation is imposed by the ordering of the mesogenic units incorporated in the chain backbone. We expect, as found experimentally, large transition entropies to occur at the transition into the isotropic phase for such a model if the chain backbone assumes a random coil conformation in the isotropic phase.

Further discussions of these models will be based on packing arguments, comparing the densities as calculated from the X-ray data with experimental. The calculation of the effective volume taken by a chain unit in the liquid-crystalline state, however, is not as straightforward as the calculation of the volume of an unit cell for a crystalline structure. We consider the smectic phase. Our principal assumption is that a nearly hexagonal packing of chain elements exists in all cases and that this packing controls together with the layer distance d an effective volume V:

$$V = a^2 (\sin 60^\circ) d,$$

where a and d are the lattice dimensions of the quasi-hexagonal lattice obtained from the small angle and wide angle reflections, respectively (see table 3). One monomer unit composed of the main chain and the side chain units either takes one or two such effective volume units depending on the model used and shown in figures 5 (*a*)–(*c*). For model *c* the conclusion is that two aromatic rigid mesogenic units are incorporated into the core of the smectic layers, in the spirit of the McMillan approach [25], per monomer unit taking thus two volume units defined here. It is only one mesogenic unit, on the other hand, for models *a* and *b* displayed in figure 5 since the smectic layers are formed predominantly either by main chain or by side chain units. The effective cross section of the mesogenic units is of the order of 21·5 Å^2 for polymers of type *a*. The volume of the elementary cell is then obtained from the X-ray results on the distance d (see table 3). Table 3 gives the densities expected for the various polymers for model *c*. Twice these values are expected for models *a* and *b*. The table also contains the experimental densities. The finding is that the predictions of model *c* agree closely with experiment. The conclusion is therefore that the smectic layers are equally formed by mesogenic units incorporated in the chain backbone and in the side chains. This seems to indicate also that the chain backbone is more or less extended.

This conclusion is in agreement with the results of the thermodynamic analysis revealing large entropy changes at the transition. Such changes are expected if the transition is accompanied by strong variations of the chain conformation, such as from an extended to a coiled one in the case considered here. The decrease of the enthalpy of transition with increasing chain stiffness is a direct consequence of constraints imposed on the side chain ordering due to the rather inflexible chain backbone and a possible mismatch of the length of the side chain and of the chain repeat unit, the mismatch not being strong enough to prevent the smectic structure

Table III. Structural data and density data obtained for the combined main chain/side chain polymers. (*a*) derived from the small angle reflections, using the Bragg equation; (*b*) derived from the wide angle reflection, assuming a hexagonal packing; (*c*) calculated from the X-ray results.

Polymer	$d^{(a)}_{\mathrm{layer}}$ Å	$a^{(b)}_{\mathrm{hex}}$ Å	$\varrho^{(c)}_{\mathrm{X\text{-}ray}}$ g cm^{-3}	ϱ_{exp} g cm^{-3}
		Type *a*		
1	22·5	5·0	1·18	1·17
2	22·6	5·0	1·23	–
3	19	5·0	1·38	–
4	25	5·0	1·15	–
5	–	–	–	–
		Type *b*		
6	25·7	4·7	1·23	1·21
7	28·4	4·7	1·18	–
8	29·5	4·7	1·15	1·20
9	–	–	–	–

formation. A stronger mismatch leads eventually to the formation of a nematic phase or both of a smectic and a nematic phase as found for some of the polymers. Based on the observation that the polymers studied here display single layer smectics we have to conclude that either all dipoles (i.e. side chain mesogens) point along the same direction or statistically up and down. A non-centrosymmetric structure which displays a permanent polarization would result in the first case. The dielectric results to be reported later seem to indicate that the latter case is correct (see figure 5 (*c*)).

4.3. *Structures formed by the combined polymers of type b*

So far structural models were discussed for polymers of type *a*. The data on thermodynamic properties, on the densities obtained for the polymers of type *b* indicate that a similar structure has to exist as for polymers of type *a*. The shift of the coupling sites from the flexible to the rigids units along the chain backbone apparently does not disrupt liquid crystal formation. The impact of the shift of the coupling sites is that the polymers of type *b* have a tendency to form a nematic rather than a smectic phase at elevated temperatures. Figure 6 shows the schlieren texture which is observed within the high temperature anisotropic phase ($T = 185°C$) for polymer **8a**. The polymers **6–8** can be completely aligned by a magnetic field of 7 T just a few degrees above the low temperature transition to a smectic phase. The order parameter which is deduced from fibre diffraction patterns after orientation in the magnetic fields or by fibre drawing is large in these phases, similar to those discussed for the nematic phases of polymers type *a*.

The combined polymers of type *b* (with the exception of polymer **9**) form a smectic phase at lower temperatures. The layer distances found for these phases are also given in table 3. The average distance between the molecules within the smectic layers is smaller than for polymers of type *a* as apparent from the location of the amorphous

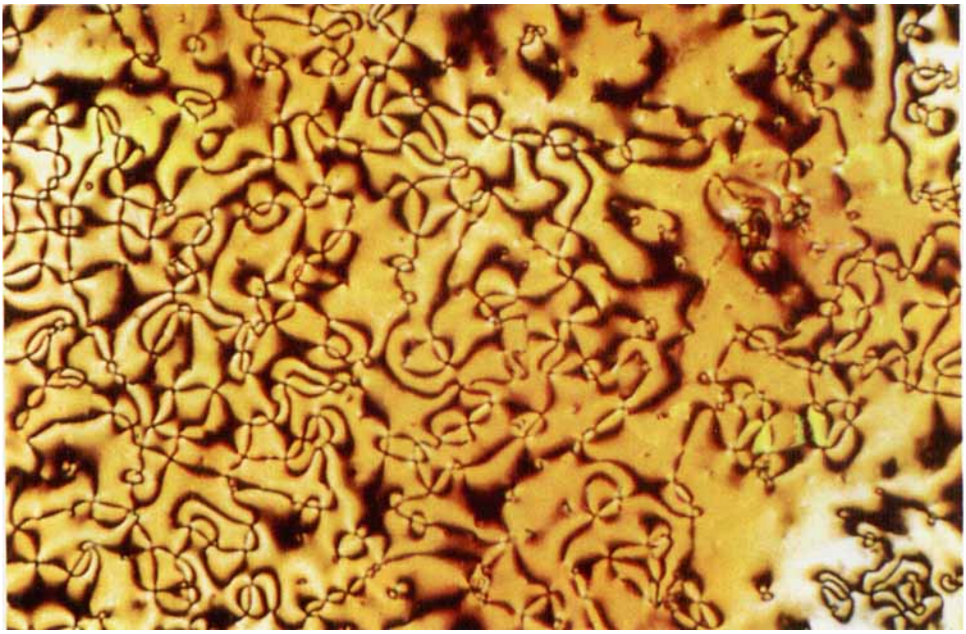


Figure 6. Schlieren texture observed by polarizing microscopy for the polymer **8a** (see table 1) within the nematic phase at a temperature of 185°C.

halo in the wide angle scattering range. The effective cross section amounts to about 18·9 Å^2. This has to be taken as an indication that structural differences have to exist between the two types of polymers. The peculiar nature of this smectic state will be discussed next in some detail.

4.4. *The particular nature of the smectic phase displayed by polymers 6–8*

Polymers **6–8**, characterized by the fact that the side groups are attached to the main chain backbone at its rigid parts display a very peculiar smectic phase. This is evident from the X-ray patterns obtained for drawn fibres or magnetically oriented samples shown in figure 7. The fibre pattern of the two kinds of samples agree very closely. This fact and some recent N.M.R. results [26] indicate that a parallel ordering of side and main chain elements occurs in these polymers, as shown schematically in figure 5 (*c*) for polymers of type *a*. Nevertheless, structural differences exist for the two types of combined polymers. We observe for the polymers **6–8**, in addition to the halo on the equator, a four point pattern in the direction of the meridian, a single reflection along the meridian followed again by a four point pattern for the polymers carrying a OCH_3 group at the end of the side group. The other meridional reflections seem to be higher order reflections.

The scattering patterns are reminescent of those reported for the frustrated smectic phases, in particular for the antiphase $S_{\tilde{A}}$. Such phases have been observed for low molar mass systems carrying strong longitudinal dipoles [27, 28]. Frustration effects arise in such systems because of the incommensurability of two types of characteristic lengths, namely the molecular length and the pair length, the pair formation being controlled by dipolar forces. The structure is characterized by the

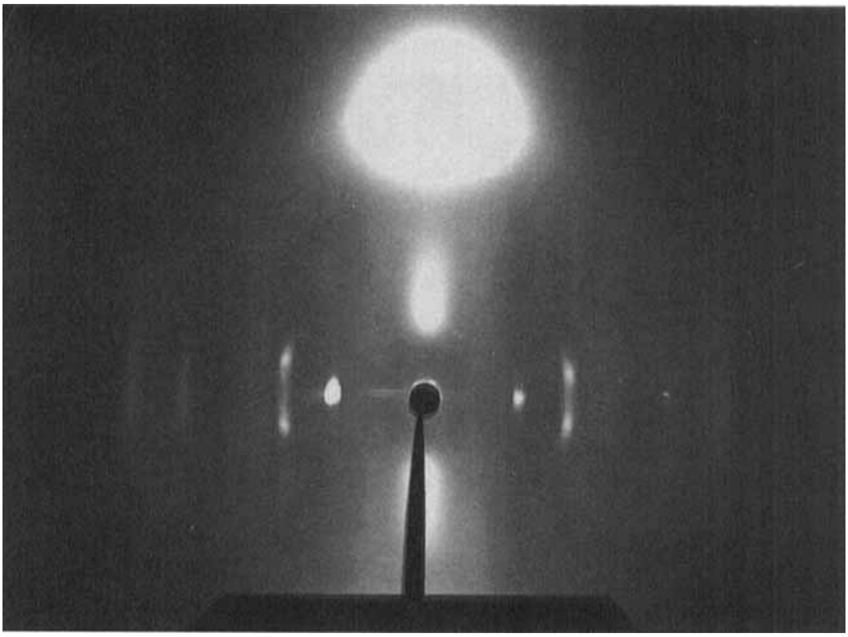


Figure 7. X-ray diffraction pattern for the combined main/chain side chain polymer **6** (type (**b**).

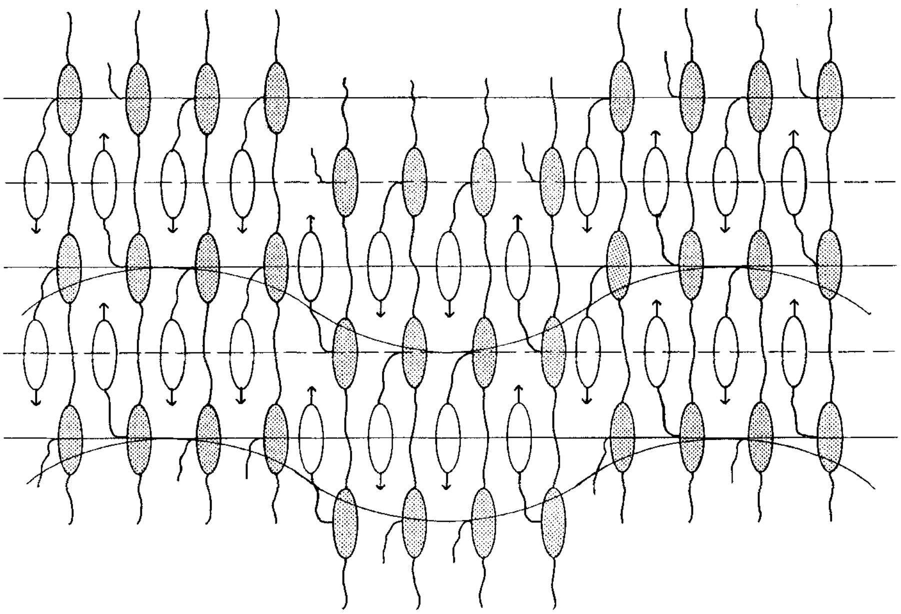


Figure 8. Structural model displaying the arrangement of the mesogenic units in the smectic antiphase $S_{\tilde{A}}$.

fact that locally an antiparallel arrangement of molecules exists and thus a bilayer or partial bilayer structure in which, however, the local orientation various periodically along a direction perpendicular to the layer normal. This gives rise on average to a single layer structure, (see figure 8).

In the case considered here it seems conceivable that a similar frustration effect occurs although for a different reason. The incommensurability refers to the side chain lengths and the main chain repeat unit length and the resulting packing is characterized by a periodic up and down of the side groups. Using the concept developed for the frustrated smectic phases we propose tentatively a structural model according to which the internal structure of the smectic layers displays undulation perpendicular to the layer normal (see figure 8). The bilayer is formed by the repeat units of the chain backbone and the single layers both by the chain backbone units and the side group units. The locations of the side chains vary periodically within the layers in the direction perpendicular to the layer. These undulations cause the four point pattern and the single layers the meridional reflections. So the interesting finding is that apparently frustrated smectic phases can be induced not only due to strong dipolar forces causing pair formation but also by an appropriate design of chain molecules. This arrangement allows a denser packing inside the layers than expected for those shown in figure 5 (*c*) for polymers of type *a*. A detailed analysis of the structures displayed by polymers **6–8** will be published elsewhere. Such an incommensurability could also have been expected for systems of type *a*. The attachment of the side groups on the main chain, however, seems to allow a sufficient flexibility in those cases to overcome frustration in contrast to the case of polymers of type *b*. It is interesting to note that polymer 9 which possesses a strong longitudinal dipole moment in the side chains is not able to form a smectic A antiphase.

It is a peculiar feature of the low temperature phase of polymers of type *b* that the intensities of the layer reflections are very weak, much weaker than for the smectic phase formed by polymers of type *a*. One reason apparently is that the layers are strongly distorted, due to the unfavourable coupling of the side groups to the rigid part of the main chain. A second factor is that the structure is no longer characterized by a microphase separation of aliphatic and aromatic units even in the cores of the smectic layering. This leads to a decrease of the amplitudes of the electron density fluctuations along the layer normals. This interpretation is in agreement with the finding that the average intermolecular distance within the layers is smaller than for polymers of type *a*.

Finally the problem of biaxiality will have to be addressed. Experimental evidence based on N.M.R. studies indicates a weak biaxiality in the combined systems [26], which seems to disagree with the model shown in figure 8. Prost [29], however, has pointed out that the smectic antiphase displays a weak biaxiality. So there does not seem to exist a discrepancy between spectroscopic and scattering data.

5. Results of dielectric relaxation studies

Additional information on the local arrangement of the side groups in the nematic and smectic states is available from dielectric relaxation studies, particularly from those performed on oriented samples. Furthermore information is obtained on the restrictions imposed on the reorientational mobility of the side groups due to their different modes of coupling to the main chain.

It is a characteristic feature of low molar mass liquid crystals that they display a strongly anisotropic low frequency dielectric relaxation process which has been attributed to the reorientational motion of the mesogens about their short axes [19–21]. This motion controls, in principle, the electro-optical and dielectric properties of the liquid-crystalline systems. The coupling of this reorientational motion to the anisotropic neighbourhood is the reason for the shift of this process to low frequencies. Side chain liquid-crystalline polymers also display this δ-process which takes place at temperatures well above the glass transition at a given frequency [30–32]. Such reorientational motions are, of course, strongly restricted in rigid main chain but also in semiflexible main chain liquid-crystalline polymers. It is, therefore, of interest to investigate combined main chain/side chain polymers with respect to the occurrence of the δ-process [33]. The experimental observation is that all combined systems display at least two relaxation processes, a low temperature (high frequency) glass relaxation process and a high temperature (low frequency) δ-process. In addition, low temperature secondary relaxation processes taking place within the glassy state are observed.

To start with combined systems which form just the nematic phase or the nematic phase in addition to a smectic phase will be considered. The advantage of these polymers is that it is possible to orient them, for instance in a magnetic field, allowing thus the determination of the anisotropy of the dielectric behaviour. Figure 9 shows the dielectric constant and the dielectric loss ($\tan \delta$) both parallel and perpendicular to the director (in a homogeneous and in a homeotropic texture) at a given frequency as a function of the temperature for copolymer **2** (type *a*, polymer **2**). It is apparent that a nearly isotropic relaxation process takes place at a temperature of about 50°C and a second very anisotropic one at a temperature of about 100°C. The low temperature process which only gives rise to a small increase of the dielectric constant has

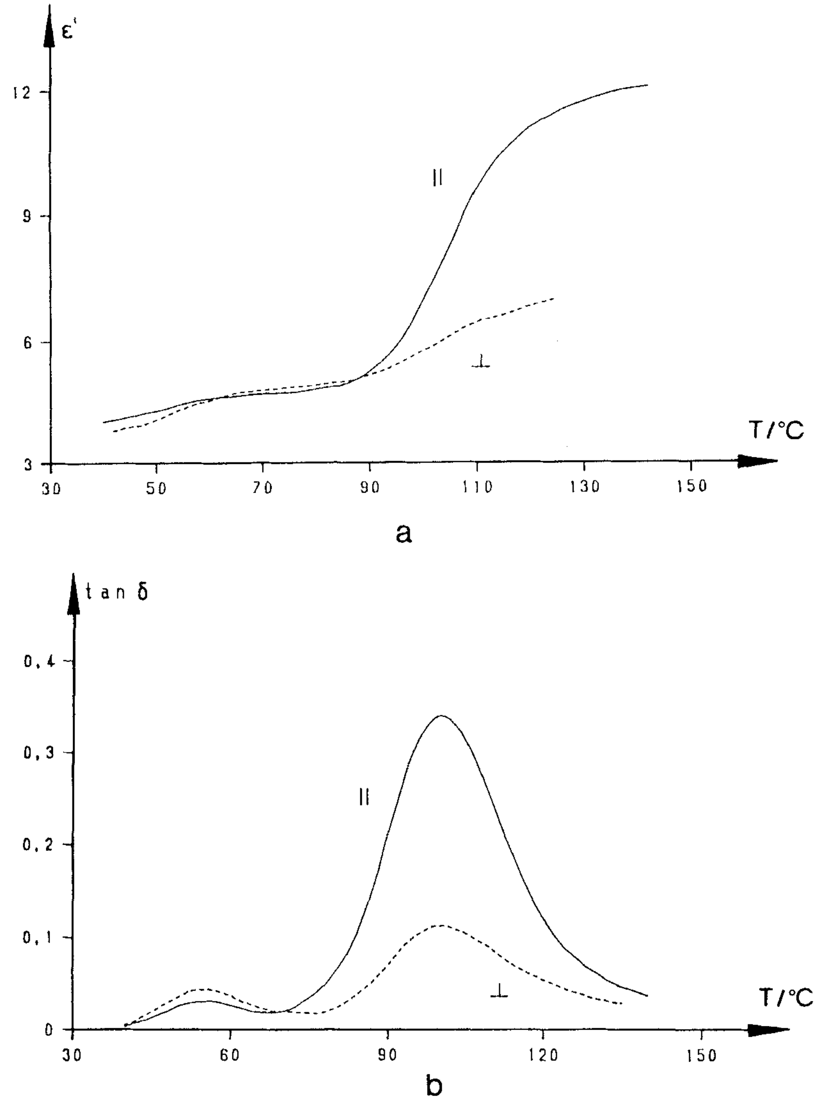


Figure 9. (*a*) Dielectric constant ε' and (*b*) loss tangents as obtained for polymer **2** in the oriented state (frequency 1 kHz).

to be attributed to the glass relaxation process whereas the high temperature (low frequency) process is due to the onset of the δ-process. This is obvious from the strong increase of the magnitude of the dielectric constant, from the strong increase of the anisotropy of the dielectric constant due to the onset of this motion and finally from the observation that the process is characterized by a very narrow distribution of relaxation times. The latter fact is evident from figure 10 *a* which shows the Cole–Cole plot. The semi circle which is obtained to a good approximation corresponds ideally to the presence of just one relaxation time, i.e. the relaxation corresponds to a Debye relaxation. The low temperature process on the other hand is characterized by a very broad distribution of characteristic relaxation times, as can be seen from the corresponding Cole–Cole diagram (see figure 10 (*b*)). The fact that the dielectric anisotropy

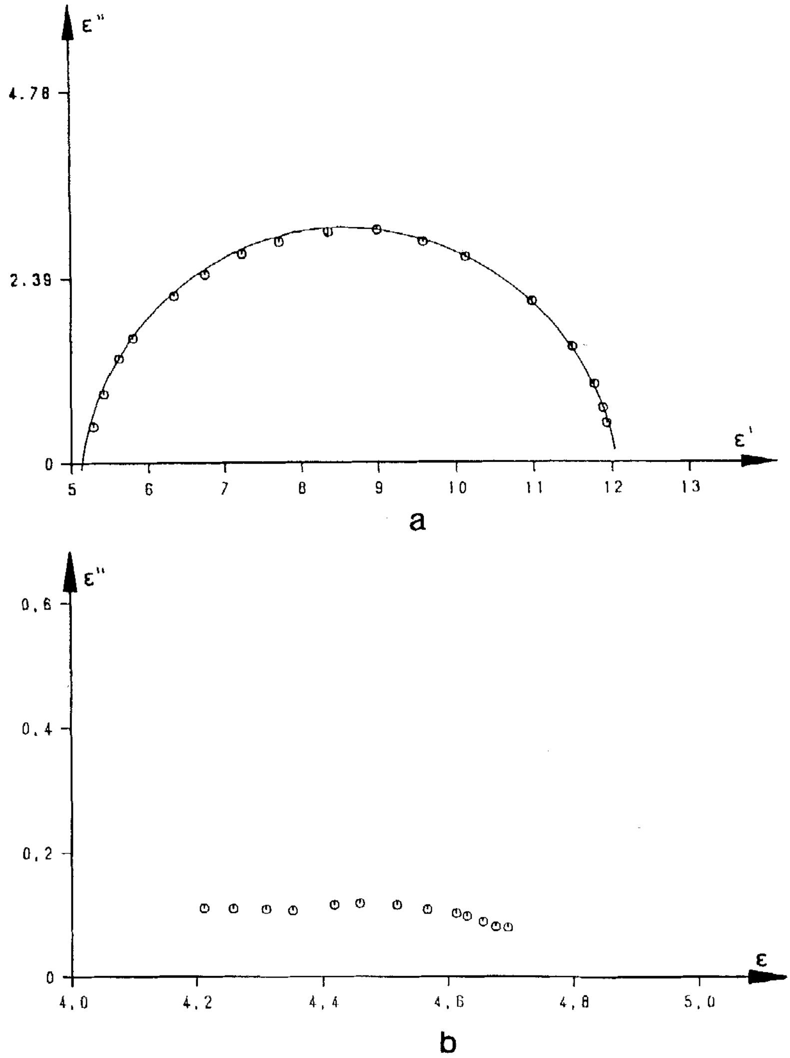


Figure 10. Cole–Cole plot of the dielectric data, shown in figure 9 for polymer 2; (*a*) δ-process, (*b*) glass process.

is large and positive shows beyond any doubt that the order parameter of the side groups is positive, as assumed in model *c* (see figure 5 (*c*)) or in model *a* (see figure 5 (*a*)) which, however, was ruled by earlier considerations.

Next the absolute value of the relaxation times observed for the combined polymers is discussed for the δ-process. We choose for this purpose a reference temperature of 100°C and consider the characteristic relaxation time or characteristic relaxation frequency as a function of the chain architecture. The results are displayed in table 4. First of all it is apparent that the absolute magnitude is within the range also observed for side chain polymers. The magnitude is, however, definitely dependent on the chain stiffness. The characteristic frequency decreases from about 5 or 10 kHz, found for the chain molecules with effectively 12 CH_2-units in the chain backbone to 100 Hz for that containing effectively only four such units. Polymer **2** having an

Table 4. Dielectric relaxation properties of the combined main chain/side chain polymers. E_a, activation energy; ν, relaxation frequency as obtained for a reference temperature of 373 K.

Polymer	E_a/kJ mol^{-1}	ε	ν/kHz
	Type *a*		
1	115	Iso 3·5	5
2	121	Aniso 7·0	1
3	134	Iso 3·7	0·1
4	–	Aniso 3·0	–
5	132	Aniso 7·0	10
	Type *b*		
9	139	Aniso 7·5	0·1

intermediate number of such units displays also an intermediate magnitude of relaxation frequency. It has to be pointed out that polymer **9** (side group fixed to the rigid part of the chain backbone) shows a rather low characteristic frequency as judged from the number of CH_2-units along the chain backbone.

There is apparently no direct relation between chain stiffness and activation energy. The δ-process is approximately linearly shifted to higher temperatures with increasing frequency. It is characterized therefore by a constant activation energy. The features described so far correspond closely to those observed for side chain liquid-crystalline polymers and to low molar mass liquid crystals. The interesting observation is that the activation energy, which amounts to 115 to 140 kJ/mol is well below the range of values usually found for side chain liquid-crystalline materials. Those values are of the order of 150 to 200 kJ/mol or even larger. The magnitude of the activation energy is intermediate between that characteristic of side chain polymers and that observed for low molar mass liquid crystals. This is a general trend for all combined main chain/side chain polymers studied here, as is apparent from table 4 displaying the activation energies of the δ-process. The obvious conclusion is that the restrictions imposed on the reorientational dynamics of the mesogenic units, located in the side groups, by their coupling to the chain backbone are weaker in combined systems as compared to side chain systems. This seems to be a direct consequence of the parallel orientation of the mesogenic units and the chain backbone, since motions about a short axis do not necessarily require larger changes in the chain conformation. So, variations of the chain stiffness, which had some effects on the glass relaxation process and the absolute time scale of the relaxation do not seem to influence the activation energy of the relaxation to an appreciable extent. For side chain polymers with longitudinally attached side groups and even more so for side chain polymers with laterally attached side groups we observe much larger activation energies since the process requires conformational changes.

The magnitude of the anisotropy of the dielectric constant found for macroscopically oriented combined systems with CN groups is of the same size or even larger than for side chain polymers carrying the same mesogenic unit, as is apparent from table 4. The same is true for the absolute value of at high temperatures (see table 4). This is rather surprising since only those mesogenic units which are located in the side chains carry strong longitudinal dipoles. The total number of dipoles amounts to about 2 × $10^{21}/\mathrm{cm}^3$ for the combined polymers and to about 4 × $10^{21}/\mathrm{cm}^3$ for the corresponding side chain polymers.

One reason for the nearly identical magnitude of the dielectric effects quite evidently is the much larger orientational order parameter characteristic of the combined polymers as is apparent from

$$\varepsilon'_{\parallel} - \varepsilon'_{\perp} = (NFh/\varepsilon_0)(\Delta\alpha - F(\mu^2/2kT)(1 - 3\cos^2\beta))S.$$

Here S is the order parameter, N the number of dipoles per unit volume, F and h are internal field corrections, μ is the dipole moment, β is its orientation relative to the long axis and $\Delta\alpha$ is the anisotropy of polarization. So the decrease of N seems to be partially compensated for by the corresponding increase in S. Differences in the dipolar coupling may also contribute to the rather large values found here, as shown later. The rather high value of the order parameter is also the reason why the perpendicular component of the dielectric response is less than that observed for side chain polymers.

Additional information on the local arangement of the side chains is available from the analysis of the anisotropy of the dielectric contant as well as of the relaxation strength of the δ-process. These quantities allow the determination of the effective longitudinal component of the dipole moment. The result is that it is about 15 × $10^{-30}\,\mathrm{cm}^2$. This value is very close to that expected just from the dipolar configuration of the side group. The Kirkwood correlation factor is thus of the order of unity whereas, for side chain polymers Kirkwood factors of the order of 0·4 have been observed, indicative of anticorrelations [34]. Again this result has to be taken as an indication that the reorientational motion of the side groups is quite unrestricted, as expected from the structure proposed in figure 5 (*c*).

6. Conclusions

Combined main chain/side chain liquid-crystalline polymers turn out to be a new class of liquid-crystalline polymer which combine favourable properties characteristic of the main chain polymers on the one hand and of side chain liquid-crystalline polymers on the other. Characteristic features are high transition temperatures as far as the transition into the isotropic phase is concerned, a broad range of stability of the smectic or nematic phase, a high orientational order parameter both in the nematic and in the smectic phase, a strong coupling to external fields allowing the induction of a macroscopic orientation in weak magnetic fields and finally the occurrence of strongly anisotropic dielectric relaxation process having low activation energies. These features seem to be the direct consequence of the parallel arrangement of the chain backbone units and the side chain units and of the apparently considerable extension of the chain backbone in the anisotropic phases. It seems evident that such side chain polymers may well play a major role in future applications.

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