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K. Kühnpast^a; J. Springer^a; G. Scherowsky^b; F. Gießelmann^c; P. Zugenmaier^c

^a Institut für Technische Chemie, Fachgebiet Makromolekulare Chemie, Technische Universität Berlin, Berlin 12, Germany ^b Institut für Organische Chemie, Technische Universität Berlin, Berlin 12, Germany ^c Institut für Physikalische Chemie, Technische Universität Clausthal, Clausthal-Zellerfeld, Germany

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Ferroelectric liquid-crystalline side group polymers Spacer length variation and comparison with the monomers

by K. KÜHNPAST†, J. SPRINGER*†, G. SCHEROWSKY‡,
F. GIEBELMANN§ and P. ZUGENMAIER§

† Institut für Technische Chemie, Fachgebiet Makromolekulare Chemie,
Technische Universität Berlin, D 1000 Berlin 12, Germany

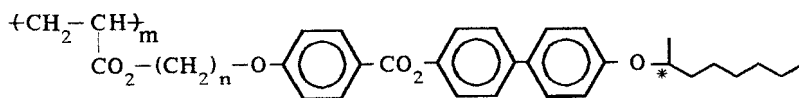
‡ Institut für Organische Chemie, Technische Universität Berlin,
D 1000 Berlin 12, Germany

§ Institut für Physikalische Chemie, Technische Universität Clausthal,
D 3392 Clausthal-Zellerfeld, Germany

The phase behaviour and the ferroelectric properties of liquid-crystalline side group polyacrylates containing an (*R*)-4''-(1-methylheptyloxy)-4'-biphenyloxy-carbonyl-4-phenoxy moiety are compared with the properties of their monomers. A S_C^* phase polymorphism including monolayer and bilayer structures was found for the polymers. Some of the S_C^* subphases, consisting of smectic mono- or bi-layers, do not exhibit ferroelectric properties. These unusual properties do not exist for the corresponding monomeric acrylates. Therefore, one has to take into account that the polymer chain exerts a strong influence on the phase behaviour and the ferroelectric properties.

1. Introduction

Recently the influence of the spacer length ($n = 2, 6, 8$ and 11 methylene groups) and molecular weight on the polymorphism and the ferroelectric properties of liquid-crystalline side group polyacrylates (**P/n**) has been described [1]. All polymers showed S_C^* phases, and in one case a S_C^* phase was in evidence. A S_C^* phase polymorphism was found for most of the polymers. In some of these S_C^* subphases, no ferroelectric properties could be detected. This unusual behaviour is in contrast to low molecular mass ferroelectric liquid crystals. Recently similar observations have been made for another liquid-crystalline side group polymer [2].



P/n

$n = 2, 6, 8, 11$

The question arises as to what extent the polymer chain is responsible for the extraordinary properties of these polymers. A first approach to this question is to compare them with the corresponding monomers. In this paper the phase behaviour and results of electro-optic measurements for the monomers **M/n** are presented and compared with the properties of their polymers **P/n**.

* Author for correspondence.

2. Experimental

The synthesis of the monomers and polymers was described in a separate paper [1]. The phase behaviour was determined by polarizing microscopy (Olympus, BHN-POL) and differential scanning calorimetry (DSC) (Perkin Elmer, DSC-7). The smectic layer thicknesses d were determined by X-ray measurements. The sample was aligned by slowly cooling from the isotropic phase to the liquid crystal phase in a magnetic field (0.7 T) and the diffraction patterns were recorded on a flat film [3].

Electro-optical properties were investigated using commercial $4\ \mu\text{m}$ -cells (E.H.C., Japan) with a rubbed polyimide layer on each of the glass substrates inducing planar orientation. The cells were filled using the temperature gradient method. The spontaneous polarization P_s was measured by the triangular wave method [4]. The response time $\tau_{10/90}$ was determined from the change in the transmitted light intensity (10–90 per cent) on applying a rectangular wave voltage. The set-up for the measurement of the director reorientation during the switching process has been described elsewhere [5].

3. Results and discussion

The transition temperatures and the liquid crystal phases of the monomers and the polymers are summarized in the table.

The monomers only show smectic phases with a monolayer structure (subscript 1). This was deduced from the smectic periodicity obtained from the X-ray measurements. For instance, the smectic periodicity of $44.2\ \text{\AA}$ for the S_{B_1} phase (see figure 1) of M/11 is in good agreement with the side group length of $44\ \text{\AA}$ estimated using Stuart and Briegleb stereomodels with an extended conformation. In the $S_{C_1}^*$ phase the smectic periodicity decreases to $40\ \text{\AA}$ due to the tilt of the molecules in the layers and increases again to $41.3\ \text{\AA}$ in the S_{A_1} phase. In the S_{A_1} phase, where the orientation of the molecules

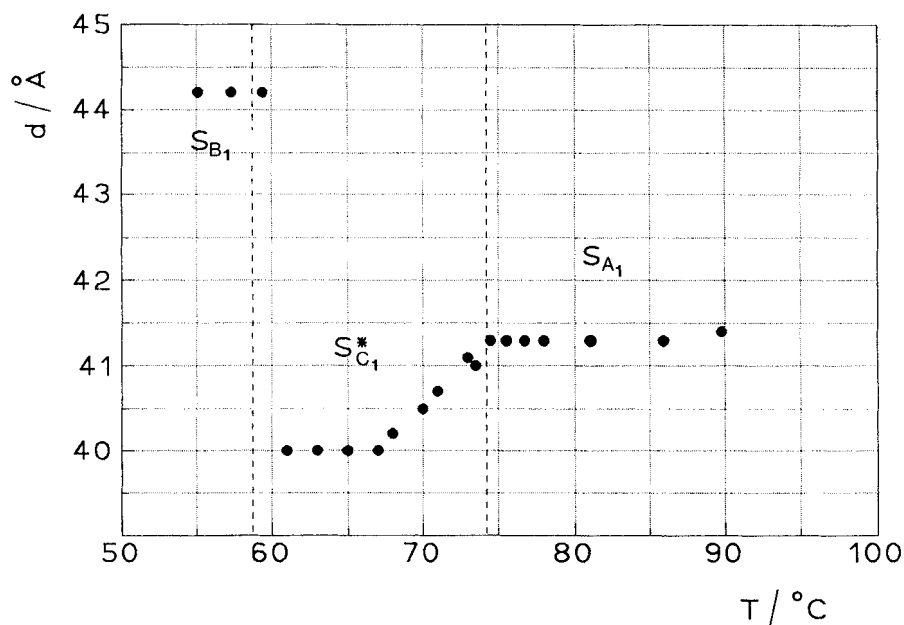


Figure 1. Smectic periodicity d of monomer M/11 as a function of temperature (the broken lines denote the transition temperatures measured by DSC).

is on average parallel to the layer normal, the smectic periodicity is nearly 6 per cent less than the extended length of the molecules. This can be explained by a random tilt of the molecules in the layers and/or shortening by *gauche* conformations of terminal alkyl chains. Some theories of the S_A phase propose that the molecules are randomly tilted within the layers, giving a tilt angle from 10–25° [6].

The smectic phases of the polymer samples are mainly bilayer structures (subscript 2). Only if a long spacer is introduced (polymer **P/11**) two modifications of a monolayered S_C^* phase appear ($S_{C_{1x}}^*$ and $S_{C_{1y}}^*$, see figure 2). Below these phases, a S_C^* phase was observed. This phase is presumed to have a S_{C_2} type structure, with bilayer regions of alternating anti-parallel polarity. It is very similar to the $S_{\bar{A}}$ phase [7], but the molecules are tilted with respect to the layer normals. The results of the X-ray investigations on the polymers are described in detail in a separate paper [1].

The appearance of bilayer structures in low molecular mass liquid crystals is restricted to molecules with strong longitudinal dipoles [8]. The monomers **M/n** do not contain strong dipoles derived from groups such as nitro or cyano. Hence only smectic monolayers are observed. Nevertheless, the polymers **P/n** exhibit bilayer structures. In fact, Mauzac *et al.* have shown that liquid crystal side group polymers do not need strong dipoles to form bilayer structures [9]. They claim that the coupling of the mesogens to the polymer chain leads to a high anisotropy and is decisive for such behaviour.

The table further shows that some of the polymers exhibit S_C^* subphases, which do not show ferroelectric switching properties. This puts the 'polymeric' S_C^* phases in contrast to the 'monomeric' ones. The occurrence of a ferroelectric switching behaviour in our polymers does not depend on whether they have mono- or bi-layer structures (compare **P/6** with **P/11** in the table). In polymer **P/11**, there are two S_C^* phases with an identical X-ray pattern showing different electro-optical behaviour [1, 10]. Those

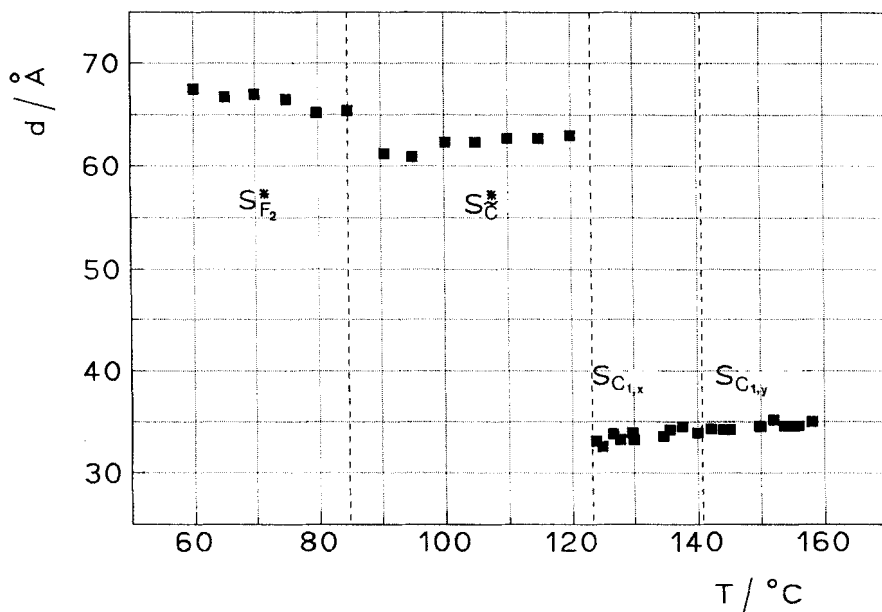


Figure 2. Smectic periodicity d of polymer **P/11** as a function of temperature (the broken lines denote the transition temperatures measured by DSC).

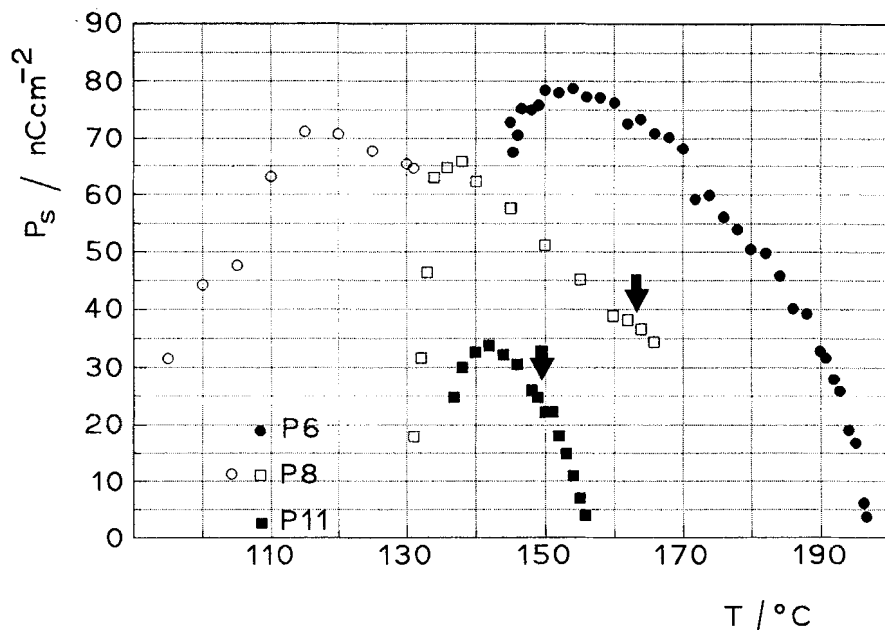


Figure 3. Spontaneous polarization P_s of the polymers P/6, P/8 and P/11 as a function of temperature (the arrows indicate the temperatures at which the polymers begin to clear); in the case of polymer P/8, both $S_{C_2}^*$ phases (x and y) exhibit ferroelectric properties.

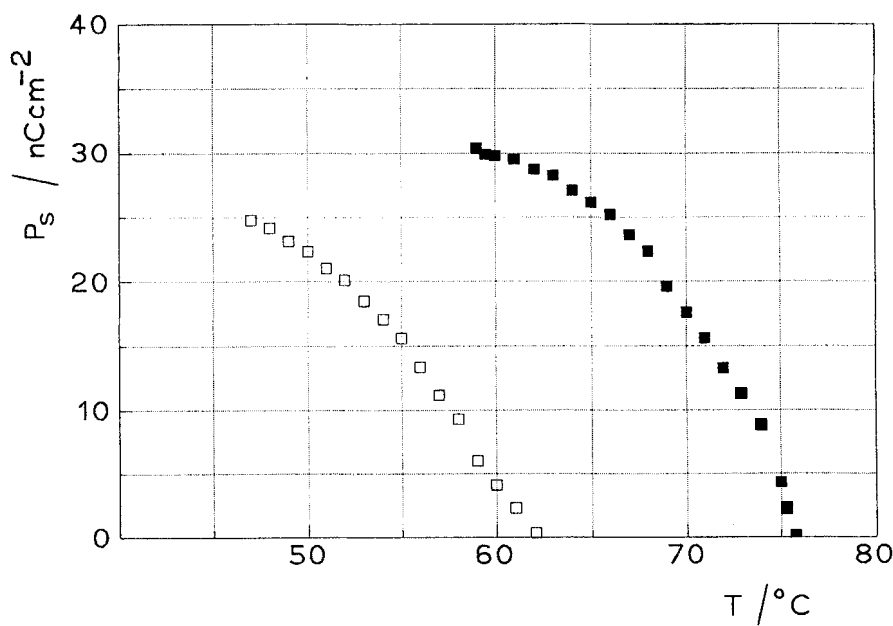


Figure 4. Spontaneous polarization P_s of the monomers M/8 (□) and M/11 (■) as a function of temperature.

phases are marked by the subscript *x*, for the low temperature phase, and *y* for the high temperature phase. In the high temperature $S_{C_{1y}}^*$ phase of polymer **P/11**, ferroelectric switching can be observed and a spontaneous polarization can be measured by polarization reversal (see figure 3). The low temperature $S_{C_{1x}}^*$ phase shows no ferroelectric switching at the maximum field strength applied. Therefore, no spontaneous polarization could be determined by polarization reversal measurements. This does not mean, that the $S_{C_{1x}}^*$ phase exhibits no spontaneous polarization at all; instead a spontaneous polarization may exist, which may be detectable by pyroelectric measurements [11].

The lack of ferroelectric switching in the $S_{C_x}^*$ phases in the polymers **P/6** and **P/11** could be due to a threshold behaviour. Ferroelectric switching in the S_{C_x} phase of polymer **P/8** could only be observed at electric fields higher than $25 \text{ V } \mu\text{m}^{-1}$. In the case of polymer **P/6**, stronger electric fields could be applied, but no switching was observed. The threshold seems to be higher due to the higher elastic constants caused by the shorter spacer. On applying such strong fields to polymer **P/11**, the cells suffer short circuiting.

In contrast to the polymers, neither a S_C^* polymorphism nor non-switchable S_C^* phases were observed for the respective monomers. Figure 4 shows the spontaneous polarization of **M/8** and **M/11**. The values of the spontaneous polarization for the polymers tend to be higher compared with the corresponding monomers. This may be due to a slight increase in the rotational hindrance of the mesogens around their molecular long axes as a result of the link to the polymer chain. The high viscosity of the polymers is responsible for the longer switching times in comparison with those observed for the monomers (for instance see figures 5 and 6). It should be mentioned that there are characteristic viscosities related to the different dynamic processes [12], which will not be discussed in detail.

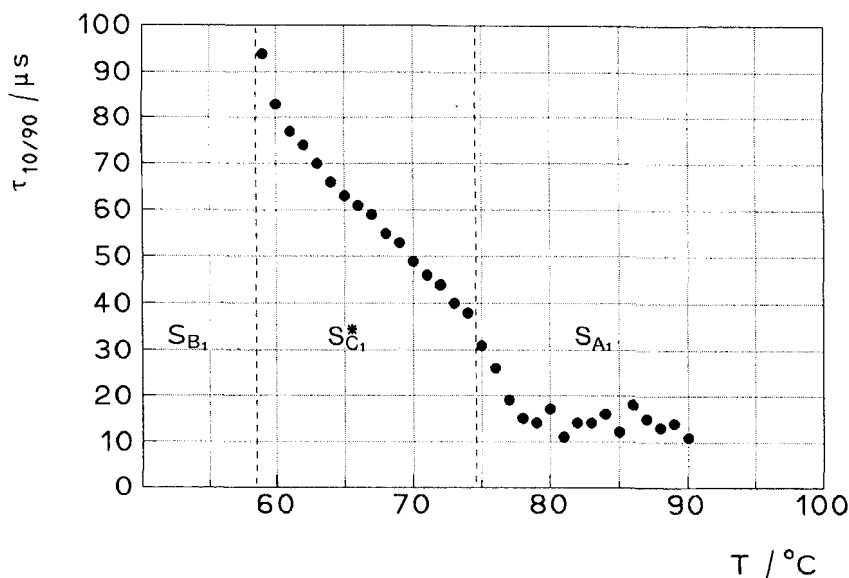


Figure 5. Response time $\tau_{10/90}$ of monomer **M/11** as a function of temperature—measured by applying an electric field of $2.5 \text{ V } \mu\text{m}^{-1}$ (the broken lines denote the transition temperatures measured by DSC).

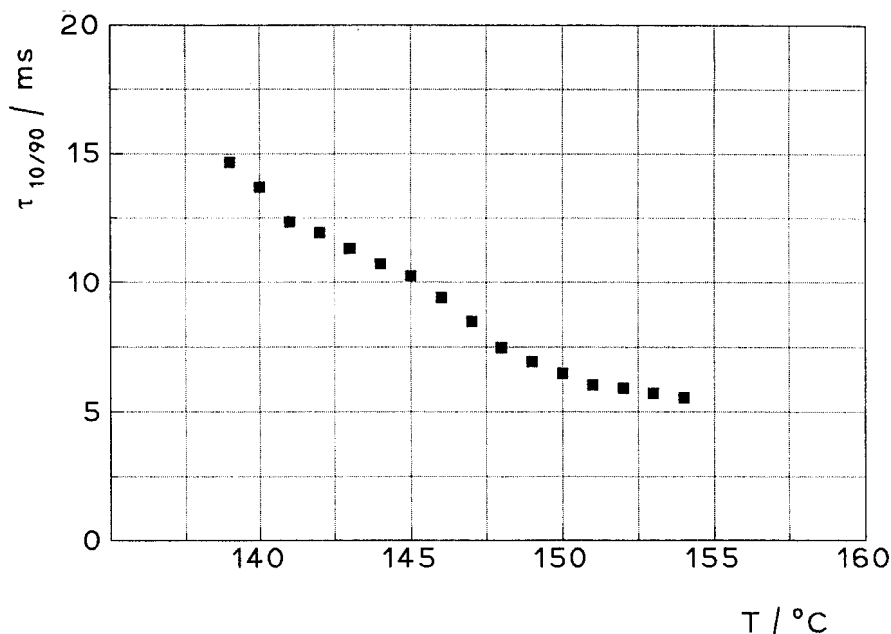


Figure 6. Response time $\tau_{10/90}$ of polymer P/11 as a function of temperature—measured in the ferroelectric $S_{C_{1y}}^*$ phase by applying an electric field of $2.5 \text{ V } \mu\text{m}^{-1}$.

To obtain more information about the nature of the $S_{C_x}^*$ and $S_{C_y}^*$ phases we have determined respectively the director reorientation during the switching processes at 135°C and 146°C for polymer P/11 (see figure 7). The in-plane angle describes the orientation of the director in a-plane parallel to the glass substrates of the cell and is often denoted as the apparent tilt angle (see figure 8). The inclination of the director with respect to the substrate plane will be described by the off-plane angle. At 146°C in the $S_{C_{1y}}^*$ phase the director describes a strongly distorted semicircular trajectory between the two optically uniform ferroelectric switching states A and B. A semicircular trajectory corresponds to the well known reorientation of the director on a cone during the ferroelectric switching process [13]. The offset value off the off-plane angle (about 10°) in the ferroelectric switching states could be due either to a layer tilt or an inaccurate estimation of the refractive indices (necessary for an evaluation of the trajectory). At 135°C , for the $S_{C_{1x}}^*$ phase, only electroclinic switching is observed, giving low contrast. The director distribution of the liquid crystal sample remains optically uniform, since the cell can be set to a dark position between crossed polarizers. The director oscillates on the apex of the trajectory (in-plane angle of 0°). The trajectory determined at 135°C agrees excellently with theoretically predicted director trajectories [13] of electroclinic reorientations. The average position is located accurately between the two ferroelectric states and represents a third state. This state appears very similar to the third switching state which recently has been detected in a liquid crystal side group polymer with a 1,3-dioxolane-4-carboxylic acid as chiral moiety [15, 16]. In the latter polymer, contrary to P/11, the three switching states occur in the same liquid crystal phase. This behaviour has been explained by assuming a conformational interaction between the side groups and the polymer chain [16]. Since the tilt cone symmetry is broken by the polymer chain in the polymeric S_C^* phases, the director orientations along the tilt cone possess different potential energies. This leads to two

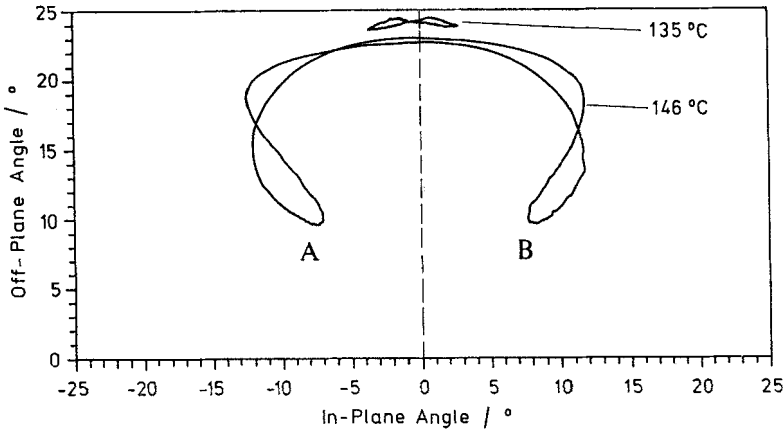


Figure 7. Director reorientation of polymer P/11 at 135°C and 146°C; 4 μm -cell, ± 30 V, 50 Hz, triangular waveform.

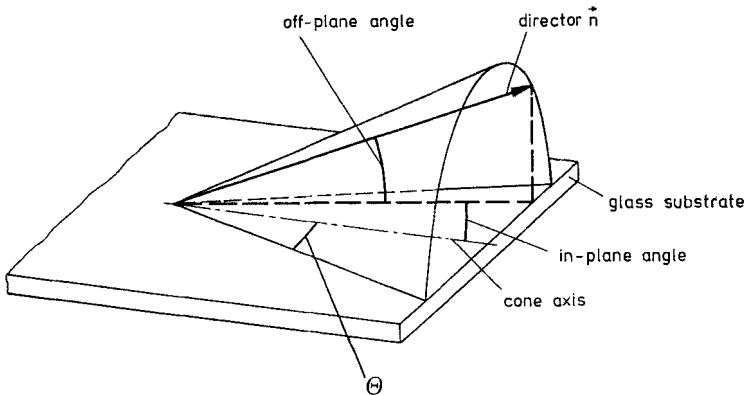


Figure 8. Schematic representation of the director reorientation on a cone and definitions of in-plane and off-plane angles.

states where the projection of the director on to the smectic layers is in the eclipsed conformation with respect to the polymer chain. These unfavourable states, considering the repulsive forces between polymer chain and side group, are identical to the ferroelectric switching states and appear at the high electric fields applied. If the external field is switched off or low electric fields are applied, a state with minimized repulsive conformational interactions between the polymer chain and the side groups is preferred. This is the case if the projection of the director is directed perpendicular to the polymer chain, i.e. the director lies on the apex of the trajectory. This state was observed as a third optically uniform switching state. The proposed explanation assumes that a certain long range orientational correlation exists between different polymer chains, which are placed preferably between the smectic layers.

Similar interactions between polymer chain and side groups may be responsible for the unusual properties observed in polymer P/11. Contrary to the behaviour described above, the $S_{C_i}^*$ phase of P/11 could not be forced into the ferroelectric switching states A, B. Only the intermediate (third) state is observed. This may be due to a stronger

interaction between the polymer chain and the side groups in polymer P/11. More experimental results are necessary to verify this assumption. However, the comparison of the polymers with the corresponding monomers shows that an influence of the polymer chain must be taken into account.

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