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Liquid Crystals

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Dye-containing S_C^* side-on/end-on copolymers

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Mesomorphic copolysiloxanes, which combine 'normal' end-on linked chiral mesogenic units inducing S_C^* phases and side-on fixed chromophores were prepared. The interplay of the different orientational tendencies of these moieties, which are perpendicular (end-on linked mesogenic groups) or parallel (side-on fixed chromophores) to the polymer chain, lead to a strong destabilization of the S_C^* phase. However, copolymers with up to about 10 mol % of chromophores still show a smectic C* phase. FTIR measurements show that both moieties orient parallel to each other and perpendicular to the polymer chains. These copolymers are interesting to consider as coloured guest–host S_C^* materials for coloured displays or as pyro-electric detectors.

1. Introduction

Low molar mass ferroelectric liquid crystals (FLCs) have attracted a lot of interest because of their potential for electro-optical applications (fast switching devices in the range of microseconds) [1]. FLC polymers have been studied since they may afford certain advantages, such as improved processability (preparation of flexible FLC polymer films) or the freezing of an ordered structure below the glass transition [2]. In addition, polymers offer new possibilities [3] like FLC elastomers (piezoelectric elements) [4] or, by copolymerization [3, 5], the formation of intrinsic mixtures between S_C^* mesogenic units and other comonomers that would be immiscible as low molar mass materials. This leads to FLC polymers combining several material properties. In this respect, we present here *S_C^* FLC copolymers incorporating new side-on fixed dye molecules.*

We selected copolymers with side-on fixed dye molecules within a S_C^* matrix of (normal) end-on linked mesogenic groups for the following reason. It is known from small angle neutron scattering [6] that the orientational tendency of mesogenic moieties (in this case, mesogens and mesogen-like dye molecules) with respect to the polymer chain is different for both types of fixation. The end-on fixed mesogenic groups used normally orient preferably perpendicular to the polymer chains. Side-on linked mesogenic units (for polymers of this type see [7–9]) orient preferably parallel to the polymer chain. This leads to a stretching of the polymer chain and has led to the expression 'jacketed' polymer chain [8]. The interplay of both types of fixation has not yet been studied for smectic phases. The question to be answered is whether the interaction of the mesogenic groups with the polymer chains can compete with the direct interaction of the mesogenic moieties. Two extreme situations can be envisaged: (i) if the interaction among the mesogenic moieties is strongly dominating, they will orient parallel to each other, independent of their fixation to the polymer chain; (ii) if the interaction with the polymer chain dominates, it may be possible to orient the mesogenic moieties at right angles to each other (see figure 1). This will, of course, strongly destabilize the LC phase, but

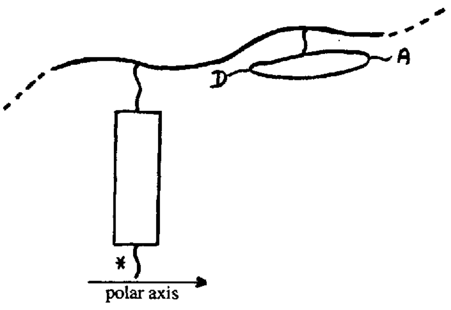

Figure 1. Possible mode of incorporation of side-on linked chromophores into S_C^* copolymers. ~ : polymer chain; *D*: donor group; *A*: acceptor group; ⬭ : conjugated electrons; *—▭— : chiral mesogen;.

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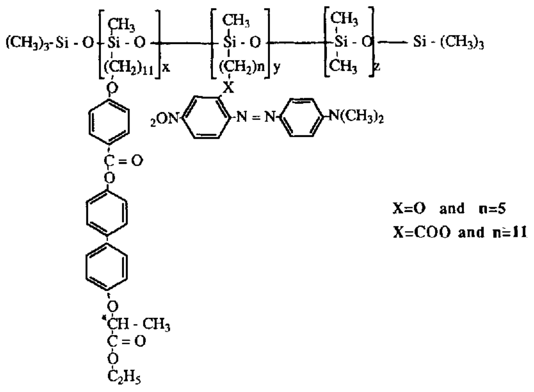
small concentrations of moieties oriented at right angles might be tolerable. In both cases LC polymers with new material properties will result from such dye-containing copolymers. In the first case, (i), these polymers can be regarded as guest–host smectic systems. Due to the linear optical dichroism of the dyes, they could be used in SSFLC electro-optical devices needing a single polarizer or in coloured displays [5]. In addition they may be interesting because of any pyroelectric effect for the detection of radiation [10]. If however, an orientation of the dye molecules perpendicular to the mesogenic groups can be obtained (case (ii)), then these materials would be interesting for non-linear optical (NLO) effects, for example, second harmonic generation (SGH) or the Pockels effect [11]. In this case of an organic NLO system, the polar ordering of the S_C^* mesophase may provide the required macroscopic non-centrosymmetric arrangement of the chromophores [3, 12]. Therefore, the donor–acceptor (D–A) systems of the chromophores should lie along the polar axis of the S_C^* phase. Compared to other concepts that use electron donor–acceptor groups oriented perpendicular to the long axis of the mesogen [13], the advantage of this concept would be that π-systems with extended conjugation can be used. The dye molecule to be used here is 2-(pent-4-enyloxy)-4-nitro-4′-*N*,*N*-dimethylamino-azobenzene.



The chromophore content is defined by : c=y/(x+y)
The polymers are labelled according to the following :
$P_{0.27}X.n.c$ if (x+y)/(x+y+z)=0.27
$P_{0.47}X.n.c$ if (x+y)/(x+y+z)=0.47

Figure 2. Chemical structures of the chiral copolymers.

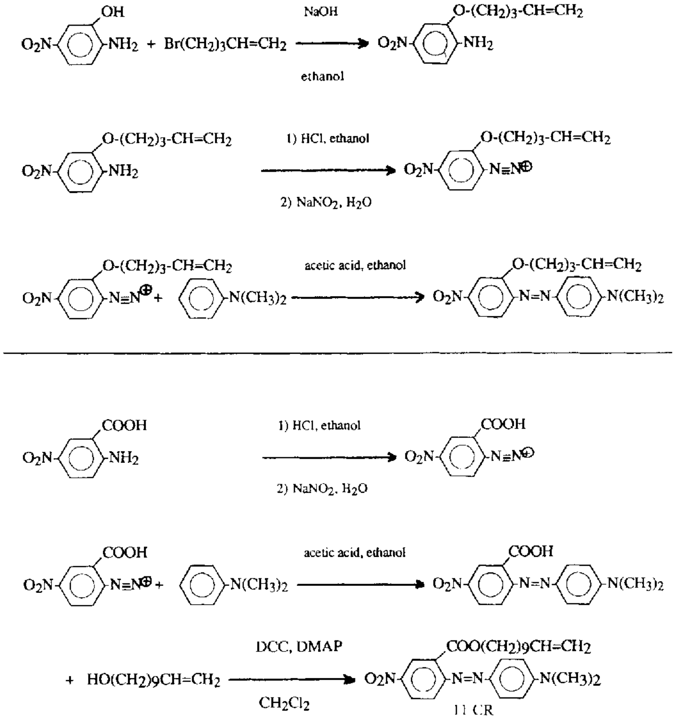


Figure 3. Synthesic schemes for the chromophores with terminal alkenyl groups.

2. Experimental

2.1. *Preparation of copolymers*

The general structures of the copolymer are given in figure 2. Two different poly(dimethyl-co-methylhydrogen)siloxanes were used as starting materials (gifts of Wacker Chemie, Burghansen)

$P_{0\cdot27}$: $(x+y)/(x+y+z) = 0\cdot27$ with $x+y+z=90$

or

$P_{0\cdot47}$: $(x+y)/(x+y+z) = 0\cdot47$ with $x+y+z=30$.

2.1.1. *Synthesis of 2-(pent-4-enyloxy)-4-nitro aniline*

2-Hydroxy-4-nitro aniline (Fluka) (5 g, 0·032 mol) was dissolved in a solution of ethanol (100 ml) and sodium hydroxide (1·6 g, 0·04 mol). The mixture was heated to reflux and 5-bromo-1-pentene (5·2 g, 0·035 mol) added dropwise. The reaction mixture was heated for 4 h. The ethanol was removed and the residue recrystallized from ethanol/water. A yellow powder of 2-(pent-4-enyloxy)-4-nitro aniline was obtained: 3 g (42 per cent yield). ^{1}H NMR (90 MHz, acetone), δ_{TMS}(ppm) = 1·80–2·10 (m, 2 H, $O{-}CH_2{-}\underline{CH_2}{-}CH_2$), 2·10–2·50 (m, 2 H, $O{-}CH_2{-}CH_2{-}\underline{CH_2}$), 4–4·20 (t, 2 H, $O{-}\underline{CH_2}{-}CH_2{-}CH_2$), 4·90–5·10 (m, 2 H, vinyl H), 5·50–6 (m, 2 to 3 H, vinyl H + NH_2), 6·70–6·90 (d, 1 H, Ar H), 7·60–7·80 (m, 2 H, Ar H). IR (KBr pellet), $\nu_{sN\text{-}H} = 3360\,cm^{-1}$, $\nu_{asN\text{-}H} = 3460\,cm^{-1}$, $\delta_{NH_2} = 1620\,cm^{-1}$ (primary amine), $\nu_{asC\text{-}NO_2} = 1525\,cm^{-1}$, $\nu_{sC\text{-}NO_2} = 1310\,cm^{-1}$.

2.1.2. *Synthesis of 2-(pent-4-enyloxy)-4-nitro-4′-N,N-dimethylaminoazobenzene*

2-(Pent-4-enyloxy)-4-nitro aniline (2 g, 0·009 mol) was dissolved in a solution of ethanol (50 ml) and conc. hydrochloric acid (3 ml). The mixture was cooled below 5°C in an ice bath. Then sodium nitrite (0·7 g, 0·01 mol) in water (40 ml) was added dropwise and the mixture stirred for 15 min. A solution of *N*,*N*-dimethylaniline (1·1 g, 0·009 mol) in ethanol (20 ml) and glacial acetic acid (1 ml) was now added dropwise. The reaction mixture was held for 30 min below 5°C and for 1 h between 10 and 20°C. Sodium acetate (1 g) was added. After recooling for a few hours below 3°C, the product was filtered off and recrystallized from ethanol: 2·7 g (95 per cent yield). Further purification was performed by chromatography on silica gel, eluting with toluene (and finally acetone); m.p. = 103°C. ^{1}H NMR (200 MHz, acetone), δ_{TMS}(ppm) = 1·90–2·10 (m, 2 H, $O–CH_2–\underline{CH_2}–CH_2$), 2·25–2·45 (m, 2 H, $O–CH_2–CH_2–\underline{CH_2}$), 3·05–3·20 (s, 6 H, $N(CH_3)_2$, 4·25–4·40 (t, 2 H, $O–\underline{CH_2}–CH_2–CH_2$), 4·90–5·15 (m, 2 H, vinyl H), 5·85–6·05 (m, 1 H, vinyl H), 6·80–6·90 (d, 2 H, ArH) 7·65–7·75 (1 H, ArH), 7·75–8 (m, 4 H, Ar H).

2.1.3. *Synthesis of 11CR*

The synthesis of 11CR was achieved in two steps. The first was an azo coupling between 2-amino 5-nitrobenzoic acid and *N*,*N*-dimethylaniline according to the procedure described above. The second step was an esterification using the alcohol, dicyclohexylcarbodiimide (DCC) and 4-*N*,*N*-dimethylaminopyridine (DMAP) [14].

2.1.4 *Synthesis of the chiral mesogen*

The procedures for the synthesis of the chiral mesogen have been described elsewhere [14, 15].

2.1.5. *Synthesis of copolysiloxanes*

Mesomorphic copolysiloxanes were prepared by a co-hydrosilylation reaction between an ω-alkenyl chromophore, an ω-alkenyl chiral mesogen and the Si–H bonds of poly(methylhydrogen-co-dimethyl)siloxanes. A typical procedure is described. In a dried apparatus, under a nitrogen atmosphere, $x + y$ mol of Si–H bonds, $1{\cdot}2c(x + y)$ mol of chromophore, $1{\cdot}2(1 - c)(x + y)$ mol of chiral mesogen and 1 to 4 mg of platinum catalyst ($PtC_{10}H_{12}Cl_2$) were dissolved in 5 ml of dried toluene. The solution was stirred during 2 days at 80°C. Then, another portion of catalyst together with a small amount of hex-1-ene (15 per cent molar ratio hexene/initial SiH) were added. The reaction was continued for another day. The polysiloxane was recovered by two precipitations in cold methanol. Each sample was checked by thin layer chromatography (total removal of monomers), ^{1}H NMR (200 MHz, $CDCl_3$), IR, and UV. Integration of the NMR spectra showed no evidence, within experimental error, for additional CH_2 groups resulting from any uptake of hexene at Si–H sites.

A few remarks concerning the preparation of the copolymers should be made. Copolymers with high chromophore contents ($y/(x + y) > 30$ per cent) tend to crosslink (insoluble fractions appear with time) whatever the reaction time, the use of several catalyst additions or the presence of an excess of alkenic bonds. The steric hindrance of the chromophores may prevent a complete substitution of the Si–H reactive bonds. In order to minimize this situation, hex-1-ene was added at the end of the reaction, but, as noted above, any uptake must be small. The comonomer ratios were evaluated by ^{1}N NMR (200 MHz) on the one hand, and by UV spectroscopy on the other. Both determinations were in good agreement, except for very low chromophore contents for which NMR is not accurate enough.

2.2. *Characterization*

2.2.1. *Calculations of the chromophore content*

The integration (i_m) of the ArH peak (8·15 ppm, 2 H) characteristic of the mesogenic moiety and the integration (i_c) of the $(CH_3)_2N$ peak (3·1 ppm, 6 H) characteristic of the chromophore from the ^{1}H NMR spectra give the chromophore content from: $c\text{NMR} = i_c/(i_c + 3i_m)$. The calculation of the chromophore content by UV spectroscopy is based on the maximum optical density of the chromophore at 476 nm and the Beer–Lambert relation ($\varepsilon_{476} = 27\,100\,\text{cm}^{-1}\,\text{mol}^{-1}\,\text{l}$).

2.2.2. *Mesomorphic properties*

The mesomorphic properties were studied by microscopic observations (Olympus BH2, Linkam hot stage THMS 600). The isotropic–mesophase transition temperatures are given from the microscopic observations, and were read on cooling at the end of the transition (tables 1 and 2). Differential scanning calorimetry (DSC Mettler TA 4000) was performed at 10 or 20°C min^{-1} on heating and 5 or 10°C min^{-1} on cooling. The DSC scans confirmed the isotropic–mesophase transitions and sometimes revealed the existence of higher ordered low temperature phases or crystalline phases (see figure 4 (*a*)); these could not be investigated further.

2.2.3. *Electro-optical measurements*

The samples were sandwiched between two ITO-coated glass plates. Two types of ITO cells were used: (*a*) 10 μm thick sealed cells (EHC Inc.) ready for use. The polymer was introduced into the cell by capillary forces above the clearing temperature. (*b*) Open ITO glass plates (Balzers Manufacturing) spin-coated with a rubbed polyimide layer (Merck Liquicoat 2650). The samples were sandwiched between the two plates. The thickness was not measured, but could be estimated to be between 5 and 10 μm. The plates were sheared at the I–S_C^* transition with a home-made shearing device.

The $\mathbf{P}_{0{\cdot}47}$ polymers could not be introduced into sealed 10 μm cells; therefore open cells were used in this case.

The $\mathbf{P}_{0\cdot27}$ polymers could always be introduced into EHC sealed 10 μm cells. Then the cells were placed into a hot stage and the ferroelectric properties (polarization, switching time) measured as a function of temperature using the reversal current method and an applied triangular or rectangular voltage at 5 Hz. The current through the cell was recorded versus time (see figure 5) and integrated to give the spontaneous polarization [16, 17]. The values of spontaneous polarization obtained with the two types of cells (open or sealed) differ slightly. We give correlated values with a maximum of 15 per cent difference between open and sealed cells.

2.2.4. *FTIR dichroism*

The spectra were recorded on a Brucker IFS 88 FTIR spectrometer, with a resolution of 4 cm^{-1} and a total of 32 scans. Polarization of the IR beam was obtained using a wire grid polarizer based on a KRS-5 substrate. Oriented polymeric films were obtained in a mechanical force field by applying a shear stress. The NaCl plates used as sample supports were coated with a thin polyimide layer to improve the surface properties. The shearing process was first performed in the isotropic state and then at the isotropic–S_C^* transition. Afterwards the temperature was gradually decreased to room temperature. The process was simultaneously analysed using polarizing optical microscopy. The samples were mounted in the spectrometer so that the direction of the applied shearing forces was vertical. By rotating the polarizer, spectra were recorded with light polarized parallel and perpendicular to this preferential direction.

3. Results and discussion

3.1. *Phase assignment*

Tables 1 and 2 first demonstrate that the reactivities, towards hydrosilylation, of the two comonomers are different. Therefore, the chromophore contents in the final copolymers differ from the initial ratios. This lower

Table 1. Chromophore contents and transition temperatures of the $\mathbf{P}_{0\cdot47}.X.n.c$ series.

c_0/per cent	c_{NMR}/per cent	c_{UV}/per cent	$T_{\text{isotropic-}S_C^*}$/°C	ΔH/J g^{-1}
$\mathbf{P}_{0\cdot47}$.O.5.c series				
0	0	0	130	7
8	—	4·5	116	6·5
16	12	11	98	4·5
17	12	14	93	3·5
23	18	17	Non-mesomorphic	—
100	—	—	Non-mesomorphic	—
$\mathbf{P}_{0\cdot47}$11.COO.c series				
8	—	4·75	118	6
30	26	20	Non-mesomorphic	—

C_0: initial chromophore ratio (introduced before reaction). c_{NMR}: final chromophore content determined by ^{1}H NMR (200 MHz) (after reaction). c_{UV}: Final chromophore content determined by UV at 476 nm (after reaction). $T_{\text{isotropic-}S_C^*}$: isotropic–$S_C^*$ transition temperature (determined by microscope). ΔH: isotropic–S_C^* clearing enthalpy.

Table 2. Chromophore contents and transition temperatures of the $\mathbf{P}_{0\cdot27}.X.n.c$ series.

c_0/per cent	c_{NMR}/per cent	c_{UV}/per cent	$T_{\text{isotropic-}S_C^*}$°C	ΔH/J g^{-1}
$\mathbf{P}_{0\cdot27}$.O.5.c series				
0	0	0	108	
4·6	4·1	5·4	87	5·5
9	8	7·7	75	
17	—	15	61	
22	20	20	Non-mesomorphic	

C_0: initial chromophore ratio (introduced before reaction). c_{NMR}: final chromophore content determined by ^{1}H NMR (200 MHz) (after reaction). c_{UV}: Final chromophore content determined by UV at 476 nm (after reaction). $T_{\text{isotropic-}S_C^*}$: isotropic–$S_C^*$ transition temperature (determined by microscope). ΔH: isotropic–S_C^* clearing enthalpy.

reactivity of the side-on chromophore may result from the steric hindrance arising from the lateral fixation. The same effect has been first observed by Gray *et al.* for a different side-on/end-on system [18].

Since a S_C^* phase is observed for the homopolymer [2], this was also to be expected for the dye containing copolymer. This was the case and was confirmed by the observation of bistable switching. The texture of this mesophase is however often uncharacteristic, even after annealing for several hours. In polymers with low chromophore contents (up to about 10 to 15 per cent) small focal-conic groups are however unambiguously observed, consistent with a smectic phase. However, on increasing the chromophore content, the apparent viscosity rises and the textures become poorly established.

Although the desired S_C^* phase is present in most compounds, it is drastically destabilized by the incorporation of the chromophore: the clearing temperatures and the corresponding enthalpies drop. Simultaneously, the DSC peaks become broader and less well defined (see figure 4). The S_C^* phase is lost at a fairly low chromophore content of 20 to 30 per cent. The rather contradictory mode of fixation of the two monomers and the fact that the chromophore itself does not give rise to any liquid crystalline properties account for such a destabilization. We note that analogous copolysiloxanes between the same chromophore and a two-ring chiral mesogen lose any mesomorphic behaviour at an even lower chromophore content (10 per cent).

3.2. *Ferroelectric behaviour*

The majority of the copolymers were switched in the SSFLC configuration by an electric field of 20 to 100 V (peak–peak) over a temperature range of at least 20°C below the clearing temperature. The switching is bistable; with a single polarizer (polarized input light), the chromophores clearly switch between a dark orange state and a pale yellow state. This demonstrates that the azo dye moieties orient within the liquid crystal phase, thus showing an alignment of the side-on fixed entities. On further cooling, the increase in viscosity prevents any detectable switching. For a cell filled with a copolymer comparable to **P**$_{0\cdot27}$O.5·5 a pyroelectric coefficient of $1\,\mathrm{nC\,K^{-1}\,cm^{-2}}$ has been determined at room temperature [19]. This value is smaller than for inorganic pyrroelectric materials. However, due to the lower dielectric constant of the S_C^* material, the figure of merit is excellent [10].

Polarization values were measured for **P**$_{0\cdot27}$.O.5·8. Figure 5 shows the oscilloscope traces of the applied voltage (see trace 1), the current response (see trace 2), the optical response (see trace 3). The temperature dependence of the polarization for **P**$_{0\cdot27}$.O.5·8 and the corresponding end-on homopolymer is shown on figure 6. The polarization values for this homopolymer are consistent with other measured values [2]. On the other hand, the dye-containing copolymer exhibits a strong decrease in polarization which is much greater than linear with chromophore content. Beyond the fact that those polymers

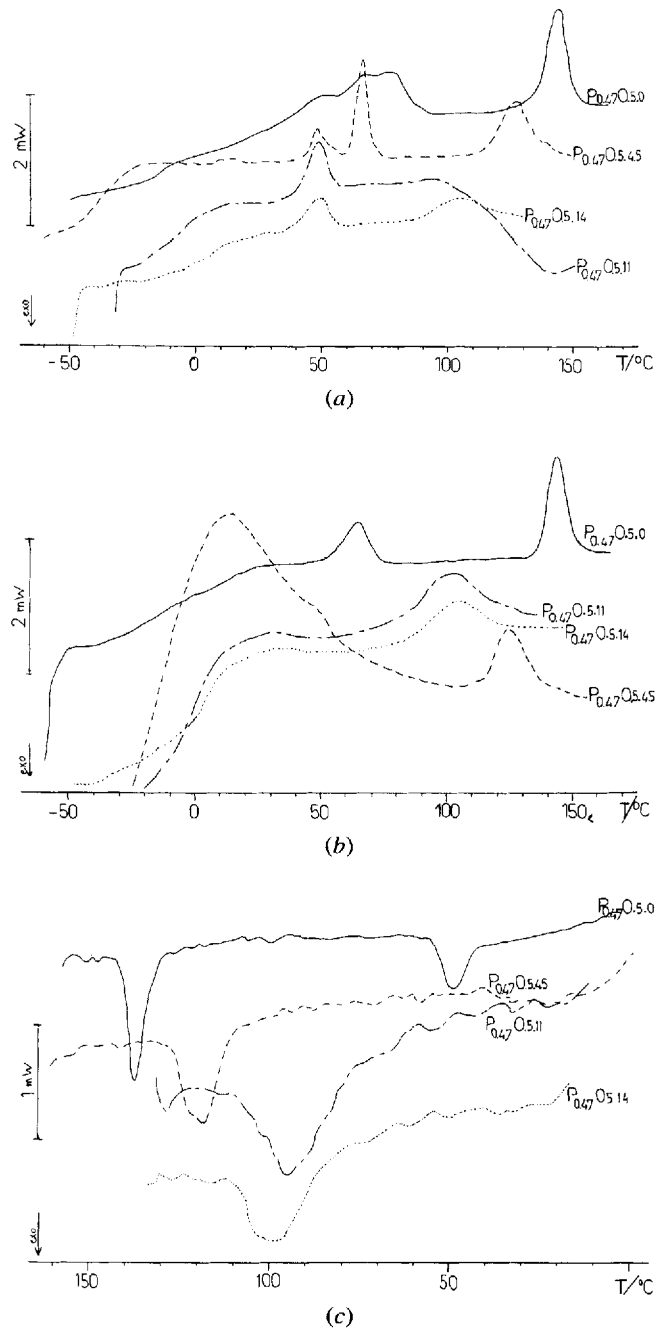


Figure 4. (*a*) DSC scans of the **P**$_{0\cdot47}$.O.5.*c* series. First heating scans (10°C min^{-1}). (*b*) DSC scans of the **P**$_{0\cdot47}$.O.5.*c* series. Second heating scans (20°C min^{-1}) after quenching from the isotropic state. (*c*) DSC scans of the **P**$_{0\cdot47}$.O.5.*c* series. Cooling scans (5°C min^{-1}).

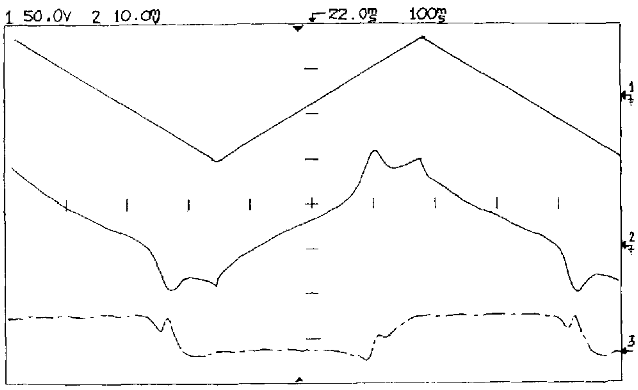


Figure 5. Oscilloscope traces of the applied voltage (trace 1), the current response (trace 2) and optical response (trace 3) for **P**$_{0\cdot27}$.O.5.8.

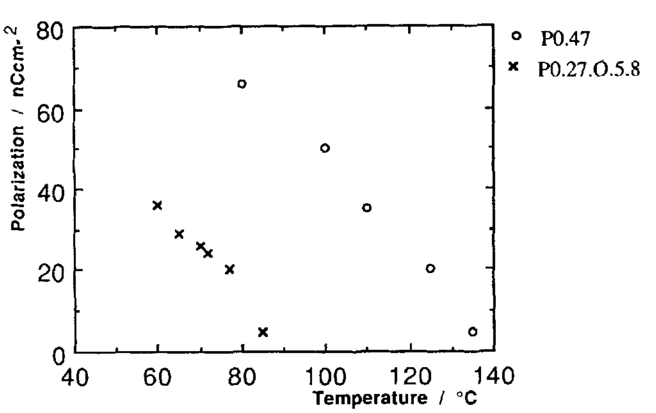


Figure 6. Temperature dependence of the spontaneous polarization for **P**$_{0\cdot27}$.O.5·8 (dye-containing S_C^* copolymer) and **P**$_{0\cdot47}$ (S_C^* homopolymer).

do not have the same dimethylsiloxane ratio [14], this polarization difference may originate from different alignments of the molecules, i.e. a different behaviour of the two polymers on orientation. The response time under 65 Vpp (1 Hz, 10 μm cell) was 5 ms for **P**$_{0\cdot27}$.O.5·8 at 75°C and 0·9 ms for the homopolymer at 125°C, $T_c - T = 5$°C approximately, in each case.

This raises the question as to how the side-on linked chromophores are incorporated in the smectic order of chiral mesogenic units. An important point is certainly to determine the relative orientation between the two units in the S_C^* phase.

In this context one might speculate about the possibility of a partial antiparallel orientation of the chromophore dipoles and the chiral mesogen dipoles. This would reduce the apparent polarization according to the dipole strength. We have to take into account that the NO_2–$N(CH_3)_2$ system represents a strong dipole moment, which might explain the observed drop in polarization.

3.3. *FTIR dichroism*

In order to determine the orientation of the mesogenic and dye units with respect to each other, FTIR dichroism measurements were performed on oriented samples. This helped to determine first the alignment of the main chain, the dyes and the mesogenic side groups relative to the shearing direction.

Figure 7 shows one of the polarization spectra of the sheared homopolymer. Specific absorption bands [20] can be assigned to the main chain, the spacer and the mesogenic side group, respectively. Characteristic absorptions of the mesogenic groups are the aromatic ring modes (1608 and 1500 cm^{-1}) and the ν(C=O) band (1734 cm^{-1}). These absorption bands are useful probes for determining the orientation of the mesogenic groups, whereas the anisotropy of the main chain is reflected by the δ_s(Si–CH$_3$) (1263 cm^{-1}), the ν(Si–O–Si) (1110 ... 1000 cm^{-1}) and the ν_{as}(Si(CH$_3$)$_2$) (802 cm^{-1}). The ν_{as}(C–O–C) absorption of the ester function located in the main chain is superimposed on the δ_s(Si–CH$_3$) band. The ν(CH$_2$) vibrations (2925 and 2852 cm^{-1}) can be assigned to the methylene groups of the spacer. From the dichroic behaviour of the above mentioned bands, it is possible to derive a model of the shear-induced alignment. The shearing stress leads to a predominant orientation of the mesogenic units in the direction normal to the deformation, whereas the main chain tends to orient parallel to this direction.

This description is based on the σ-dichroism of the aromatic ring modes. The transition moment for these absorptions is roughly parallel to the long axis of the mesogenic core. Also, a very weak π-dichroism for the ν(C=O) absorption is observed. Observation of σ-dichroism for the absorptions correlated with the main chain indicates ordering of the main chain backbone in the direction of the mechanical stress [21–22]. The alignment of the mesogenic part of the side chain should also induce an orientation of the methylene units in the spacer. The π-dichroism of the ν(CH$_2$) bands must be interpreted in terms of a preferential orientation of the methylene units in the spacer perpendicular to the shearing direction.

Figure 8 shows the polarization spectra of a sheared copolymer **P**$_{0\cdot27}$.O.5·8. The spectra and the dichroic behaviour of the absorptions are similar to those of the homopolymer spectra (see figure 7). A parallel alignment of the main chain and a perpendicular orientation of the spacer and the mesogenic units is obvious. Furthermore, there is a band at 1336 cm^{-1} in the copolymer spectrum which is not present in that of the homopolymer (marked by ↓). This absorption, which must be characteristic for the chromophore, exhibits σ-dichroism. It can be assigned to the ν_s(NO$_2$) absorption [20]. The relatively low absorption frequency of the ν_s(NO$_2$) band is due to conjugation of the NO$_2$ group with the aromatic ring. Furthermore, the

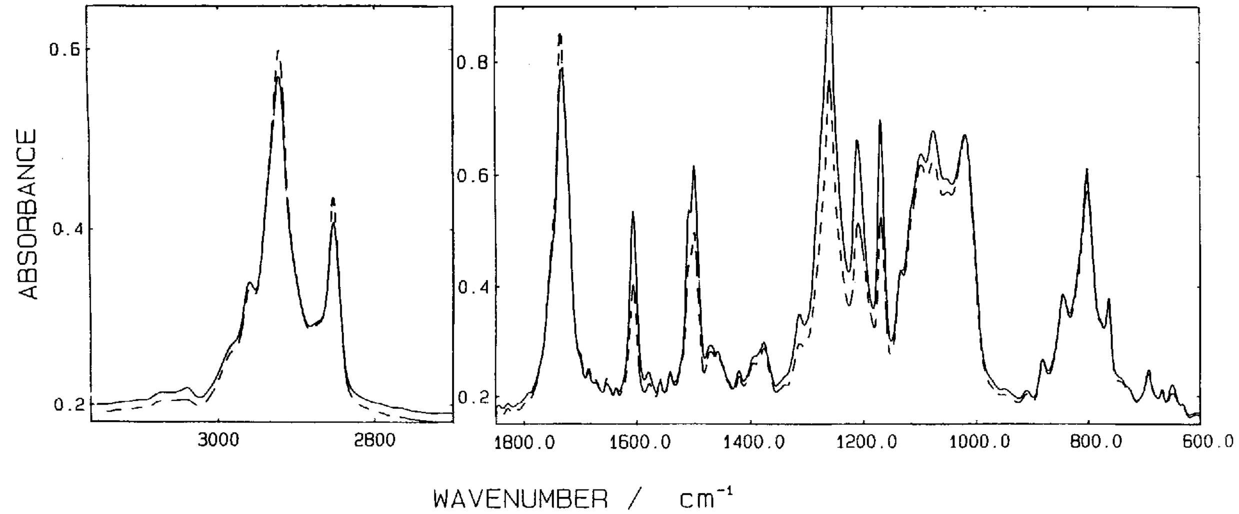


Figure 7. Absorption spectra of the sheared homopolymer for IR radiation polarized perpendicular (——) and parallel (– – –) to the shearing direction.

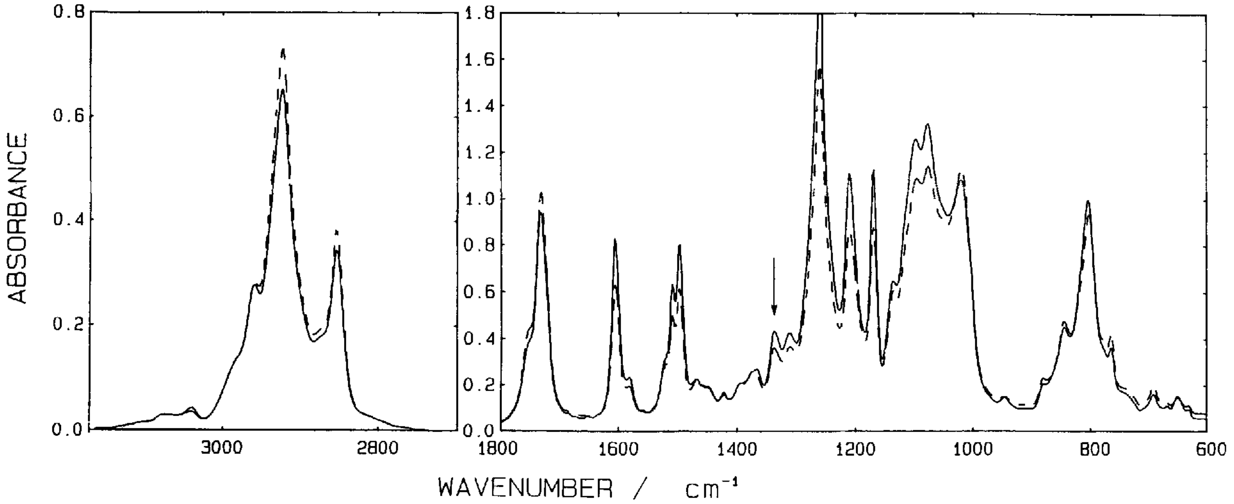


Figure 8. Absorption spectra of the sheared copolymer $\mathrm{P}_{0\cdot27}$.O.5·8 for IR radiation polarized perpendicular (——) and parallel (– – –) to the shearing direction.

$N(CH_3)_2$ group as an electron donor shifts the frequency to lower wavenumbers. The transition moment vector is directed along the axis of the azo-benzene group. The σ-dichroism of this absorption therefore supports a perpendicular orientation of the chromophore with respect to the shear direction. This would be parallel to the mesogenic groups. Unfortunately, the low chromophore content in the sample (around 8 per cent) makes further assignments of chromophore absorptions very difficult. Measurements carried out on samples which differ in spacer length and type of chemical bonding between spacer and chromophoric system show the same alignment tendency.

Although the order parameter S shows principally the same effect by a positive value over the whole sample area, a quantitative evaluation of S is not given due to the wide fluctuations in its magnitude. There are regions on the support where the phase shows significant alignment and regions where the order parameter is close to zero. This could be due to surface defects on the NaCl plates or insufficient contact between the two plates while the shearing process is performed.

4. Conclusions

The results of the IR spectroscopy show that the side-on fixed chromophores show an orientation in the S_C^* mesophase of our copolymer system which is parallel to the mesogenic moieties (see figure 9). Thus their orientation is dominated by the direct interaction among the

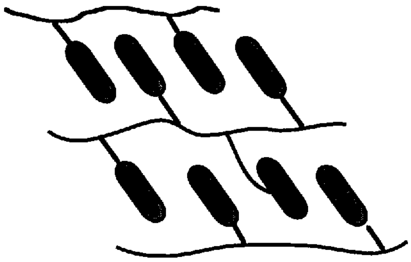


Figure 9. Schematic representation of the side chains in the investigated side-end-on/side-on copolymer.

mesogenic groups. These dye-containing copolymers may therefore not be useful for non-linear optics.

However, at least a tendency towards a perpendicular orientation is also detectable. The strong destabilization of the mesomorphic character (textures, clearing temperatures and enthalpies) and the drop in the polarization values is as would be expected for a parallel orientation of the chromophores to the polymer backbone, and consequently a perpendicular orientation of the chromophore to the chiral mesogen.

The copolymers presented here show, as expected, an interplay between two opposing orientational tendencies. The direct interaction among the rod-like dye molecules and the mesogenic units dominates; the different interaction with the polymer chain is, however, strong enough to lead to a destabilization of the LC phase.

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