Sign Reversal of the Spontaneous Polarization in the C* Phase of a Side-Chain Polyacrylate and Its Monomer

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SIGN REVERSAL OF THE SPONTANEOUS POLARIZATION IN THE C* PHASE OF A SIDE - CHAIN POLYACRYLATE AND ITS MONOMER

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Abstract The electro-optic response in the C* phase of a side-chain polyacrylate and its monomer has been found to exhibit an anomalous dependence on temperature. The apparent tilt angle undergoes a sign reversal. The anomaly is attributed to a sign reversal of the spontaneous polarization, caused by molecular conformational changes in the monomer part.

Introduction

The tilted smectic phases of liquid crystals composed of chiral molecules or doped with chiral additives, exhibit ferroelectric properties i.e. existence of spontaneous polarization P_S /1/. In these phases a relationship is supposed to exist between molecular geometrical properties (conformational or rotational), molecular dipole moments and the macroscopic dipole moment /2-4/. The magnitude and the sign of spontaneous polarization P_S are determined by the magnitudes and positions of dipole moments and their relations to the chiral centers of the molecules and thus they will be sensitive to conformational changes of the chiral molecules /5/. The phenomenon of sign reversal of P_S in the C* phase of low molecular mass ferroelectric liquid crystal was first observed by Goodby et al. /6/. So far, only few examples are reported in the literature /3, 7-12/. Goodby et al. attributed this phenomenon to gradual conformational changes of the chiral molecules.

In the orthogonal chiral smectic phases A*, B* and E* an applied electric field E induces a molecular tilt (the electroclinic effect), i.e. induces a polarization P_i /13-17/.

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Recently, an anomalous behaviour of P_i , similar to that of P_S referred to above, was found in the B* and A* phases /18, 19/ and it was explained on the same basis of competing conformers (as in the case of sign reversal of P_S in the C* phase).

In the last few years, the synthesis of polymer ferroelectric liquid crystals has received a rapidly growing attention and in this paper we present a comparative investigation on a polymer ferroelectric liquid crystal material and its monomer, after having found a polarization anomaly in the former. What we asked ourselves was whether this anomaly could be traced to the properties of the monomer or if other, new effects play a role. As we shall see, both polymer and monomer exhibit a similar sign reversal of P_S in the C* phase and the phenomena seem to be well correlated.

General part

Synthesis and characterization

The reaction pathway leading to the racemic side chain polyacrylate **12** and its saturated monomer **10** is shown in scheme 1.

After one-sided protection of 1.9-nonadiol **1** as benzylether the second hydroxy group was oxidized by using dicyclohexylcarbodiimide(DCCI) and DMSO affording aldehyde **3**. The Horner-Wittig reaction of **3** with ethyl-phosphonoacetate yielded **4**, which was reduced to the allylic alcochol **5** using diisobutylaluminiumhydride (DIBAH).

The chiral oxirane was obtained by asymmetric epoxidation of **5** via the Sharpless procedure /20/.The enantiomeric exess of **6** was determined by the Mosher method /21/ (ee>95). The Mitsunobu reaction /22/ was used to etherificate hydroxymethyloxirane **6** with 4-hydroxy-(4'-decyloxy-biphenyl-4-yl)-benzoate **7** /23/ in presence of triphenylphosphine and diethylazodicarboxylate (DEAD) to yield **8**. In the next step the protecting group was removed by hydrogenation and the resulting alcohol **9** was treated with propionyl chloride and triethylamine (NEt₃) to give the saturated monomer **10**, which was used for the comparitive investigations. Monomer **11** was synthesized by reaction of **9** with acryloyl chloride and NEt₃. The polymerization of **11** in THF yielded the polymer **12** with a molecular weight M = 3500 g/mol (M_W / M_N = 1.31) /23/. For more quantitative experimental information the reader is referred to the Appendix.

The textures were identified by using a polarizing microscope together with a hot stage Mettler FP 52 and control unit FP 5. The phase sequences are included in scheme 1. The DSC-data for the monomer and the polymer are illustrated in Figure 1 a and b.

Electro-optic investigations

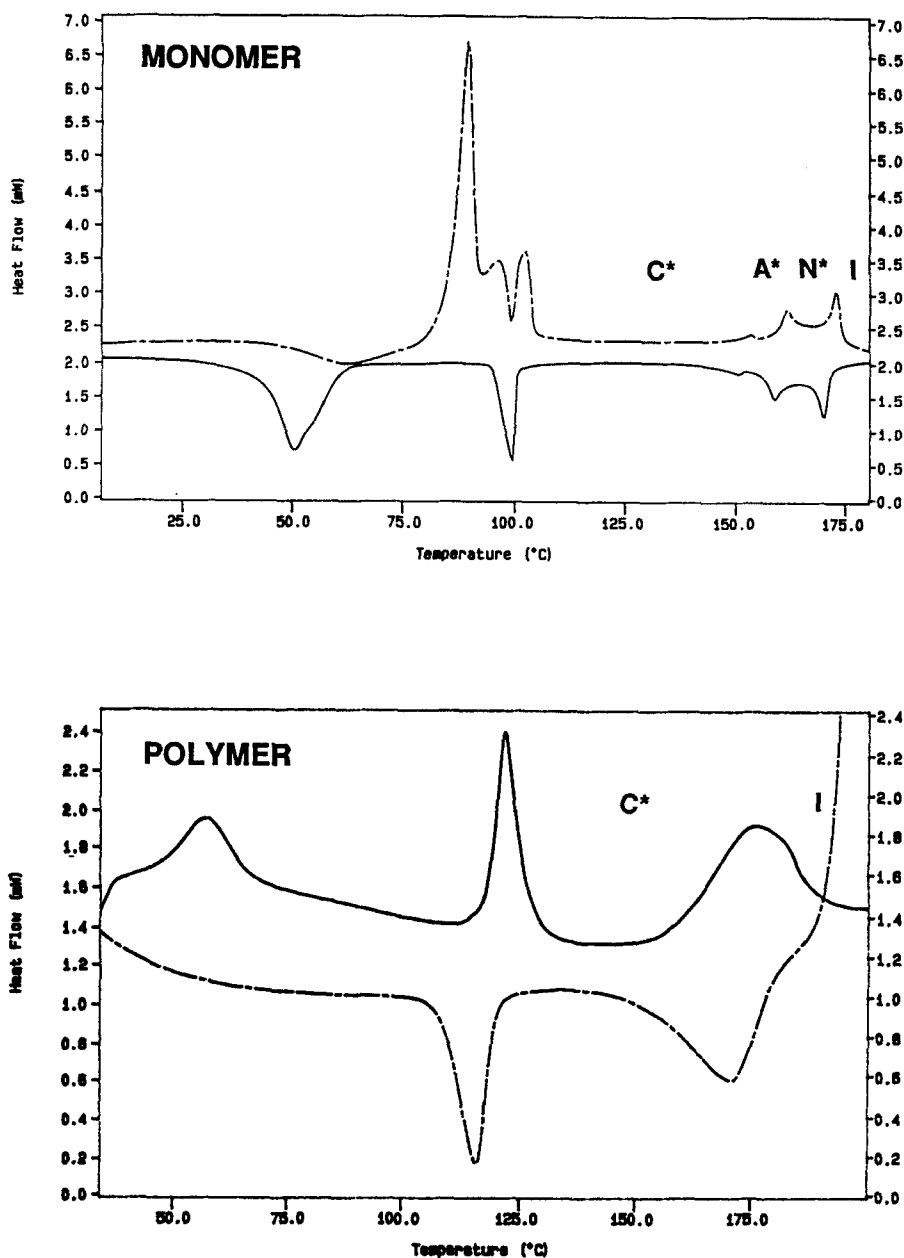In our experiments we have used thin cells of sandwich type with a spacing of about

Fig. 1   Differential calorimetry scans of monomer (top) and polymer (bottom) taken on heating and cooling (reversed peak direction) at rate of 10°C/min. The monomer is smectic C* between 102°C and 153°C and has above-lying A* and N* phases. The polymer is smectic C* between 122°C and 177°C.

2 μm. The liquid crystal material is filled into the cells in the isotropic phase and has been aligned into a bookshelf geometry (with smectic layers perpendicular to the glass substrates) by applying simultaneously a high electric field (150 volts peak to peak, $f \geq 1$ kHz) and mechanical shearing. In order to study the temperature dependence of the sign of P_S the sample has been mounted in a Mettler hot stage under the microscope with crossed polarizers. The electro-optic response is detected in the set-up shown in Fig.2. When the applied electric field is alternating its sign the molecules switch their position between two states at angle $2\theta_{app}$ (θ_{app} apparent tilt angle). Because molecular tilt θ and polarization P_S are linearly related it is possible to determine the sign of P_S from an observation of θ_{app}. According to the standard convention /24/ the sign of P_S (and thus of θ and θ_{app}), will be positive or negative if the layer normal $\mathbf{k}$ director $\mathbf{n}$ and P_S form a right- or left-handed coordinate system, respectively. From
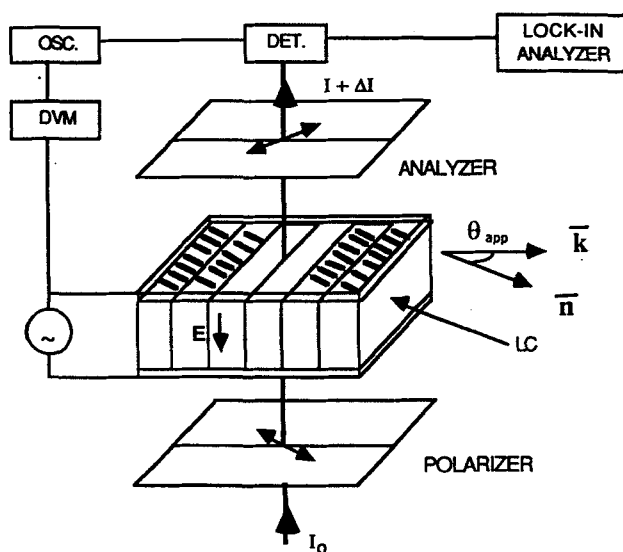
Fig.2 Set-up for electrooptic measurements.

the electrooptical response one can then extract the sign of P_S by extending the method described in /18/ (for the determination of the sign of the electroclinic coefficient) to the C* phase or to tilted smectic phases in general. The transmitted light intensity through the sample idealized with upright layers and placed between crossed polarizers at normal incidence is, in a uniaxial slab approximation

$$I = I_0 \sin^2 2\psi \sin^2 \delta/2 \qquad (1)$$

where ψ is the angle between the optic axis and transmission direction of the polarizer

and δ is the optical phase difference between extraordinary and ordinary rays after passage of the sample. When the sample satisfies the $\lambda/2$ plate condition i.e. $\delta = \pi$ then the phase factor is equal to one. In general it will deviate (though commonly not very much) from this value, but as it has no influence on the method as such we will omit it in the further consideration.

As derived in /25/ the equation (1) acquires a particularly simple shape in the case that we turn the crossed polarizer - analyzer away such that the polarizer makes the angle 22.5 degrees with the smectic layer normal. Then the modulated intensity is maximized and can be approximately expressed by the relationship

$$I = I_0\{ 1/2 + 2\, \theta_{app}(E) \} \qquad (2)$$

Equation (2) describes the electrooptic response which in turn depends on the shape of the function $\theta_{app}(E)$. In contrast to the electroclinic response $\theta_{app}(E)$ is not a linear function of the applied field E, hence we have to discuss a more general case. In Figure 3 are shown, schematically, three different response curves which correspond to observed behaviour. The case (a) is the idealized bistable case when a field reversal induces switching between extreme cone positions and the two polarization states have the polarization vector **P**
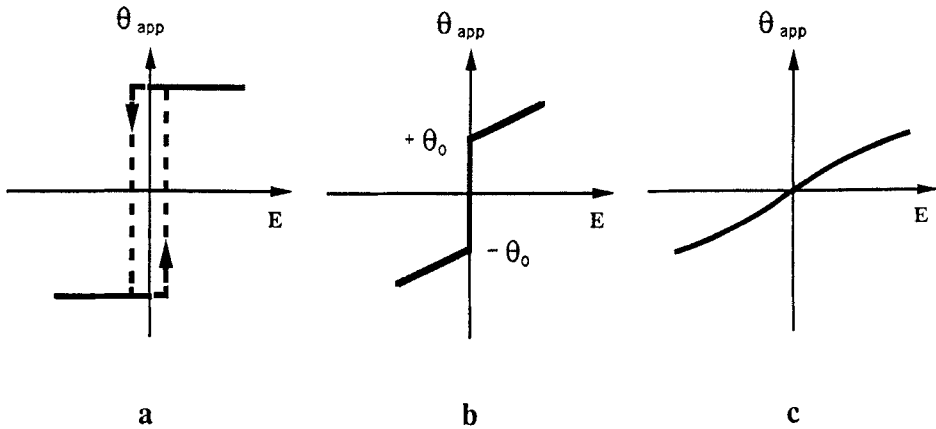
Fig.3   The three principal categories of FLC response function (in the symmetric case), going from pronounced bistability(a) to monostability (c). The hysteresis is only indicated in (a) whereas (b) is drawn as if the threshold field were negligibly small (in which case θ_0 is small, $\theta_0 << \theta$).

perpendicular to the sample. An increase in E thus has no influence on the observed tilt angle θ_{app} which is equal to the smectic tilt θ . In the case (b) the memorized (field-

free) states correspond to a value $\theta_{app} = \theta_0 < \theta$, and increasing the field will cause $\mathbf{P}$ to lign up further in the direction of E and thus move the optic axis further out on the smectic cone. In (c), finally, we have the extreme situation that the director $\mathbf{n}$ is strongly anchored in a preferred direction of alignment, having its projection along the layer normal and hence the polarization in the plane of the sample. This monostable state gives a response which in man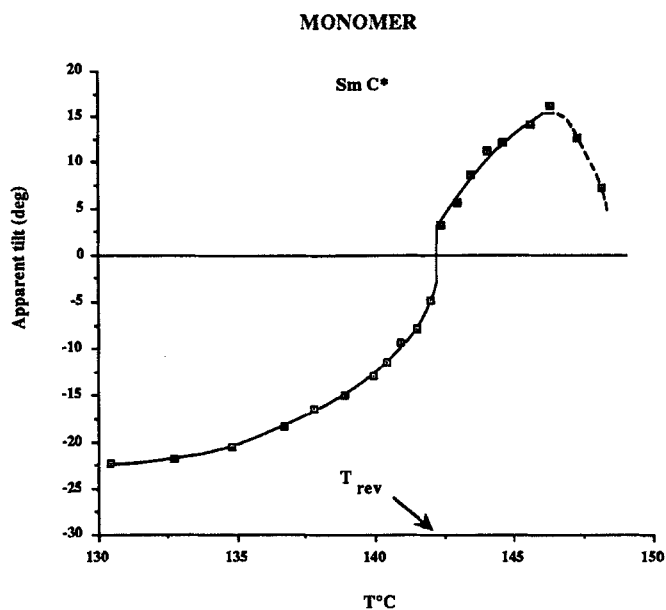y respects is similar to the electroclinic response. In practice the response functions will vary considerably (the cases (a) and (b) being less common) depending as it does on many factors, especially sample preparation. Nevertheless, all response functions are odd functions in the electric field. Therefore, a change of sign in $\mathbf{P_s}$, related as it is with a deflection of θ_{app} in the opposite direction, will be recognized as a phase shift of π between the electric field and the optical signal. The experimental results shown in Figures 4 and 5 illustrate this for both polymer and monomer. From the electrooptic response we find that both materials exhibit an anomalous behaviour of $\mathbf{P_s}$ with temperature in the sense that $\mathbf{P_s}$ goes to zero and changes sign at a certain temperature T_{rev} . In both cases $\mathbf{P_s}$ is reversing the sign from negative at low temperature to positive at high temperature, being zero at 131°C and 142°C, respectively. For the polymer a lower value of T_{rev} is thus found than for the monomer whereas the phase transition temperatures limiting the C* region are shifted to higher values on polymerization.

Discussion

When $\mathbf{P_s}$ approaches zero at T_{rev} the electrooptic switching will cease. The apparent tilt does not have to go to zero. We have measured it by turning the sample to the extinction states in the set-up of Figure 2. The results are shown in Figure 5 (a, b) for polymer and monomer. These curves give an independent (though less accurate) measurement of the temperature T_{rev} , and the values coincide with those extracted from the electrooptic signals. As we see from Figure 5 (a) the apparent tilt, in the case of polymer, actually goes to zero and has a fairly linear behaviour around T_{rev} . This is in agreement with the shape of the electroptic response signal which is not too much distorted and discloses a fairly linear response function, similar to that of Figure 3 (c). The response is less linear in the case of the monomer, thus rather in the category of Figure 3 (b), although the zero-field value (θ_0, corresponding to E=0 or $\mathbf{P_s}$=0) is only about 5 degrees, a small fraction of the actual tilt defined by the smectic cone. We have also verified, by checking the extinction position when going from the A* phase through all of the C* phase, that the cone tilt angle θ has a completely regular behaviour, and in particular no anomaly around $T = T_{rev}$. In order to interpret our results we then have to assume that on approaching T_{rev} the optic axis, in a fairly symmetric way (corresponding to opposite sign of the applied field) wants to approach the direction corresponding in projection to the smectic layer normal, c.f.

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ELECTRO-OPTIC   RESPONSE

U(pp) = 60 V   U(pp) = 110 V

137°C

$P_S > 0$

146°C

$P_S > 0$

131°C

$P_S = 0$

142°C

$P_S = 0$

125°C

$P_S < 0$

140°C

$P_S < 0$

POLYMER   **MONOMER**

a   b

Fig.4   Electooptic response signal in (a) the case of the polymer (for an applied
triangular voltage), and (b) in the case of the monomer (for sinusoidal
voltage) when passing the reversal temperature T_{rev} (131°C and 142°C,
respectively).
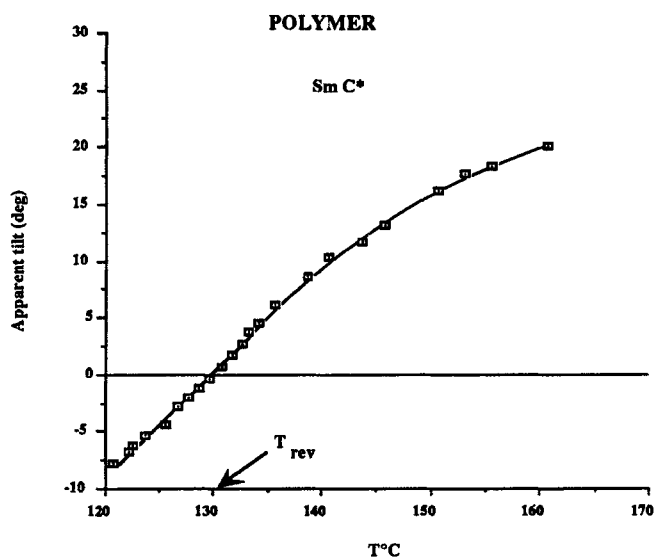
Fig.5   Measured values of apparent tilt (taken on heating) around the vicinity of the
reversal temperature in the case of polymer (a) and monomer (b). In the former
case the apparent tilt value actually goes through zero.

Figure 6. This means that in the absence of polar interaction the molecules prefer a homeotropic orientation. This is also in agreement with the experimental result found on the monomer, that its A* phase strongly prefers to be homeotropically aligned, to the point that no other alignment can be induced.

In contrast to the nematic case the polymerization of a smectogen may leave a lot of
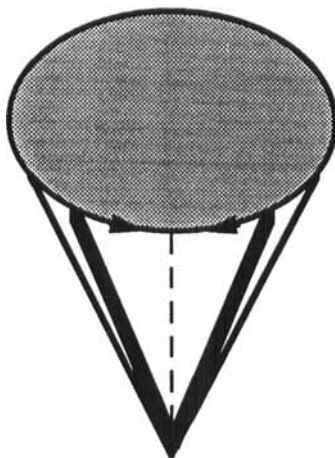

Fig.6　　Interpretation of the tendency for the relaxed states (i.e. in the absence of a ferroelectric torque) to shrink together and merge into a quasi-homeotropic state (looking at the sample from above).

flexibility for the internal motion corresponding to the electrooptic process. Thus the cone motion in the polymer smectic C* is not frozen, in the sense that the response time would be orders of magnitude higher than the value in the monomer. The difference is typically rather one order of magnitude. On a molecular level the motions and dynamics can be expected to be not too different, and this is confirmed by the fact that the shift in the balance of different conformers giving rise to a polarization reversal in the monomer must be very similar to the situation in the polymer, causing essentially the same phenomenon, and only a small change in T_{rev} . The competition between the different conformations of the molecule 11 in scheme 1 is thus kept essentially unaltered when it is being fixed at one end in the polymer state 12. One essential difference in the switching motion in the two cases is that, being bound at one end in the polymer state, the molecule is not free to rotate around its center of gravity as it does in the bulk of the monomer. (This situation is similar to what is supposed to take place at the outermost surface layers of a monomer SSFLC cell .) Hence the switching has to set up a counter motion of matter which will increase the effective viscosity and which may perhaps even be the dominating factor in the slowing down of the switching in the polymer. The rheological consequences of this counter motion have , so far, not been subject to any study.

Because of the vanishing ferroelectric torque at T_{rev} the electrooptic switching will cease and we should expect a smoothly diverging response time τ, when the temperature approaches T_{rev}, similar to the case reported in /7/. However, in this case, the deflection of the optic axis itself goes to zero (Figures 4 a and 6) which has the opposite effect. In reality we measure a dip rather than a divergence in τ as shown for
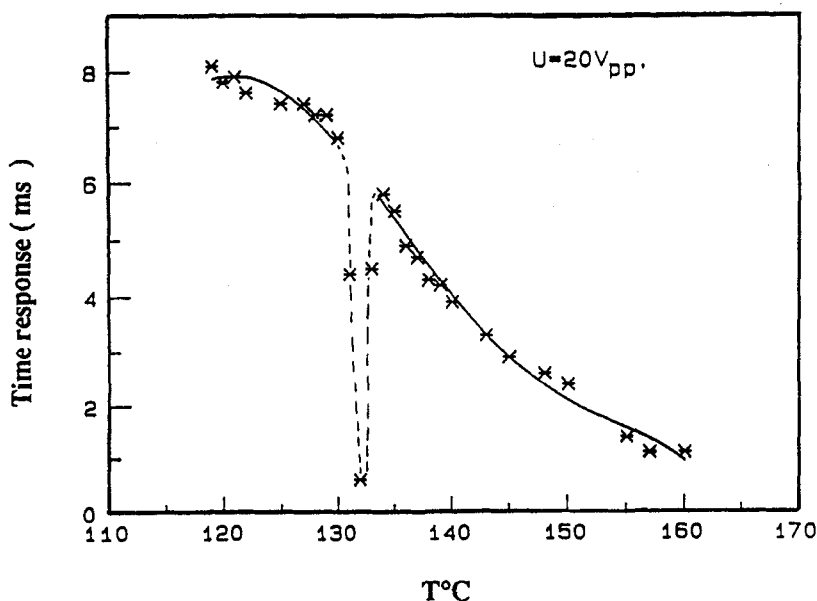

Fig.7   Temperature dependence of the electrooptic switching time in the polymer.

the polymer in Figure 7. The data for the monomer are similar with response times about one order of magnitude smaller. Measuring a vanishing response is difficult and gives rise to considerable scatter of data in the region around T_{rev}. We therefore have to regard these data as tentative. However, the tendency is the same for the monomer, with the measured τ being partcularly small around T_{rev}. In general the phenomena are so similar for the monomer and the polymer that we have to conclude that the rotational freedom of the monomer parts are surprisingly well kept in the polymeric state.

Acknowledgements

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Appendix

^{1}H-NMR: Bruker WM 400. M.S.: Varian MAT 711 (70·0eV). I.R.: Perkin Elmer PE 225 or PE 257. Specific rotation: Perkin Elmer PE 241 polarimeter.

<u>(2S,3S)-(-)-3-(8-propionyloxy)-octyl-2-[4-(4'-decyloxy-biphenyl-4-yl-oxycarbonyl)-phenoxymethyl]-oxirane (10).</u>

To a solution of (2S,3S)-(-)-3-(8-hydroxy)-octyl-2-[4-(4'-decyloxy-biphenyl-4-yl-oxycarbonyl)-phenoxymethyl]-oxirane **9** (91mg, 0,144mmol) and triethylamine (18 mg,0.18mmol) in 5ml dry THF, propionylchloride (15mg, 0.16mmol) was added dropwise at 0°C. The mixture was stirred for 1h at 0°C and thereafter evaporated under reduced pressure. The crude product was purified by F.C. on silica-gel using dichloromethane / petroleum ether as eluent followed by precipitation from THF solution with methanol.
Yield: 30 mg (30%),[α]$_D^{25}$=-10,2° (c=1.65, CHCl$_3$)
^{1}H-NMR: (400 MHz, CDCl$_3$): δ=0.89(t,J=7Hz;3H), 1.08(t,J=7Hz;3H), 1.23-1.52 (m;24H), 1.60-1.67(m;2H), 1.67(tt,J=7 and 6.5Hz;2H), 1.80(tt,J=7 and 6.5Hz;2H), 2.35(q,J=7Hz,2H), 2.99(ddd,J=6,5.5 and 2Hz;1H), 3.14(ddd,J=5.5,3.5 and 2Hz;1H), 4.00(t,J=6.5Hz;2H), 4.06;4.29(AB$_{dd}$,J=11Hz; part A: d,J=5.5Hz; part B: d,J=3.5Hz;2H), 4.15(t,J=6.5Hz;2H), 6.97;7.51(AA'BB',J=9Hz;4H), 7.01;8.17 (AA'BB',J=9Hz;4H), 7.24;7.58(AA'BB',J=9Hz;4H)

<u>(2S,3S)-(-)-3-(8-acryloyloxy)-octyl-2-[4-(4'-decyloxy-biphenyl-4-yl-oxycarbonyl)-phenoxymethyl]-oxirane (11).</u>

To a solution of **9** (0.99g, 1.57mmol) and triethylamine (0.174g, 1.73mmol) in 8 ml dry THF, acryloylchloride (0.171g, 1.88mmol) was added dropwise at 0°C. The mixture was stirred for 1h at 0°C and evaporated under reduced pressure. The crude product was purified by F.C. on silica-gel using dichloromethane as eluent. Yield: 0.49g (46%) [α]$_D^{25}$=-10° (c=1.65)
^{1}H-NMR: (400 MHz, CDCl$_3$): δ=0.89(t,J=7Hz;3H), 1.23-1.52(m;24H), 1.60-1.67(m;2H), 1.67(tt,J=7 and 6.5Hz;2H), 1.80(tt,J=7 and 6.5Hz;2H), 2.99(ddd,J=6,5.5 and 2Hz;1H), 3.14(ddd,J=5.5,3.5 and 2Hz;1H), 4.00(t,J=6.5Hz;2H), 4.06;4.29 (AB$_{dd}$,J=11Hz; Part A: d,J=5.5Hz; Part B: d.J=3.5Hz;2H), 4.15(t,J=6.5Hz;2H), 5.82(dd,J=10 and 1.5Hz;1H), 6.12(dd,J=17.5 and 10Hz;1H), 6.40(dd,J=17.5 and 1.5Hz;1H), 6.97;7.51(AA'BB',J=9Hz;4H), 7.01;8.17(AA'BB',J=9Hz;4H), 7.24;7.58(AA'BB',J=9Hz;4H).
IR: 2860,2940(CH$_2$),1735,1720(C=0),1635(C=C),1610,1500(Ar),1170,1080(C-0), 990(C=C) cm^{-1}.

MS(230°C): m/e = 684(10%, M$^+$), 668(2, M-O), 446(7, C$_{27}$H$_{34}$O$_4$), 359(86, M-C$_{22}$H$_{29}$O$_2$), 343 (7, M-C$_{22}$H$_{29}$O$_2$-O), 326(70, C$_{22}$H$_{30}$O$_2$), 186(64, C$_{12}$H$_{10}$O$_2$), 121(100, C$_7$H$_5$O$_2$), 97(11, C$_7$H$_{13}$), 83(20, C$_6$H$_{11}$), 57(32, C$_4$H$_7$), 55(67, C$_3$H$_3$O).

(9S,10S)-(-)-poly-10-[4-(4'-decyloxy-biphenyl-4-yl-oxycarbonyl)-phenoxymethyl]-9,10-epoxy-nonyl-acrylat (12)

The monomer 11 (0.47g, 0.69mmol) was polymerized with AIBN (2.3mg, $1.38 \cdot 10^{-2}$ mmol) in 3.5ml dry THF solution under an atmosphere of nitrogen. The polymerization was carried out at 60°C for 14h. The polymer was purified by reprecipitation from concentrated THF solution with methanol followed by F.C. on silica-gel with dichloromethane as eluent.
Yield: 0.19g (40%); $[\alpha]_D^{25} = -13.4$ (c=0.49)
$M_W/M_N = 1.31$; $M_W = 3.500$ g/mol