Molecular Crystals and Liquid Crystals

Sign Reversal of the Dielectric Anisotropy in the Chiral Nematic Phase of a Copolysiloxane

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Abstract   A chiral copolysiloxane was synthesized that exhibited an N* phase in the 9-41 °C temperature range. A linear electro-optical response with the applied electric field was detected in the N* phase due to the electroclinic effect. At high electric fields, the linearity of the response was strongly affected by dielectric coupling. It was found, however, that the influence of dielectric coupling on the electro-optical response became zero at a particular temperature ($T = 37$ °C), which was attributed to a sign reversal of the dielectric anisotropy.

INTRODUCTION

The electroclinic effect [1] has mainly been studied in orthogonal chiral smectic phases, most typically the SmA* phase in so-called bookshelf geometry [2,3]. This effect has also been observed in the N* phase [4,5]. An important requirement for detecting the

electroclinic effect in the N* phase is a complete unwinding of the helical molecular order.

Chiral liquid crystal polymers, especially those possessing ferroelectric SmC* phase and, to a much lower extent, those with paraelectric SmA* phase, have attracted interest in recent years because of the electro-optical responses that take place in these materials due to ferroelectric and electroclinic effects, respectively [6]. Lately, we have given the first report on the electroclinic effect that can also operate in long-pitch N* polymers when a suitable electric field was applied perpendicular to the long molecular axis of the mesogenic units in the essentially unwound state [7].

As known, the electroclinic effect, at moderate electric fields, gives rise to a linear electro-optical effect due to the linear coupling between the field-induced polarization and the applied field. At higher electric fields, however, the dielectric response, which is quadratic with the field, affects the linearity of the response due to the electroclinic effect (similar to the case of the influence of dielectric response on the linear flexoelectro-optical response [8]).

In this work we present a new example of an electroclinic response in the N* phase of a polymer, namely the chiral copolysiloxane copoly(**1**)-*co*-(**2**), in which we furthermore found a sign reversal of the dielectric anisotropy in the N* phase on changing temperature.
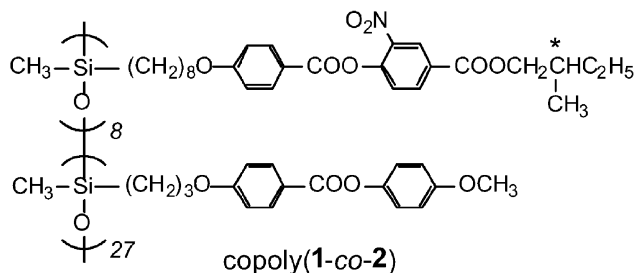
EXPERIMENTAL PART

Synthesis of monomer (1)

4-(7-Octenyl-1-oxy)benzoic acid (**5**): 5.00 g (0.026 mol) of 8-bromooctene (**4**) was added dropwise to a solution of 3.61 g (0.026 mol) of 4-hydroxybenzoic acid (**3**), 3.22 g (0.057 mol) of KOH and 0.36 g (0.002 mol) of KI in 80 ml of ethanol and 20 ml of water, and the mixture was refluxed for 3 days. The solvent was then evaporated under vacuum and the residue was dispersed in water and acidified (pH • 1) with HCl. The solid was then filtered, dried and crystallized from *n*-hexane, giving 4.93 g (yield 76%) of (**5**): m.p. 76-77 °C.

^{1}H-NMR (CDCl$_3$) δ (ppm): 11.6 (s, 1H, OH), 8.1 (d, 2H, aromatic), 6.9 (d, 2H, aromatic), 5.8 (m, 1H, CH$_2$=C$\underline{H}$), 5.0 (m, 2H, C$\underline{H}_2$=CH), 4.0 (t, 2H, C$\underline{H}_2$OAr), 2.1 (m, 2H, CH$_2$=CHC$\underline{H}_2$), 1.8 (m, 2H, C$\underline{H}_2$CH$_2$OAr), and 1.4 (m, 6H, aliphatic).

(+)-(*S*)-2-Methylbutyl 3-nitro-4-hydroxybenzoate (**8**): 10.00 g (0.055 mol) of 3-nitro-4-hydroxybenzoic acid (**6**), 4.81 g (0.055 mol) (-)-(*S*)-2-methylbutanol (**7**) and 1 g of *p*-toluenesulfonic acid were dissolved in 150 ml of toluene in a Dean-Stark apparatus. The reaction mixture was refluxed for 27 h; the solution was then diluted with CH$_2$Cl$_2$, washed with 5% NaHCO$_3$, water, and dried over Na$_2$SO$_4$. The solvent was evaporated leaving 3.34 g (yield 24%) of (**8**) as a yellow oil: $[\alpha]^{25}_D$ = +4.5 (CHCl$_3$).

^{1}H-NMR (CDCl$_3$) δ (ppm): 10.8 (s, 1H, OH), 8.8 (s, 1H, aromatic), 8.2 (d, 1H, aromatic), 7.2 (d, 1H, aromatic), 4.2 (m, 2H, COOCH$_2$), 1.8 (m, 1H, COOCH$_2$C$\underline{H}$), 1.5, 1.3, and 1.0 (3m, 8H, aliphatic).

(+)-(*S*)-2-Methylbutyl   3-nitro-4-[4'-(7-octenyl-1-oxy)benzoyloxy]-benzoate (**1**): 1.46 g (0.006 mol) of acid (**5**), 1.50 g (0.006 mol) of phenol (**8**) and 0.12 g (0.0008 mol) of pyrrolidinylpyridine (PPy) were dissolved in 60 ml of anhydrous CH$_2$Cl$_2$ under inert atmosphere. 1.22 g (0.006 mol) of dicyclohexylcarbodiimide (DCC) in 25 ml of anhydrous CH$_2$Cl$_2$ was then slowly added. The reaction mixture was maintained at room temperature for 2 days. The precipitate formed was filtered off and the organic solution was washed with 5% HCl, water, 5% NaHCO$_3$ and dried over Na$_2$SO$_4$. After evaporation of the solvent, the residue was purified by flash chromatography (silica gel 230-400 mesh, Merck) with *n*-hexane-ethyl acetate (9:1 mixture by vol) as the eluent, giving 2.40 g (yield 84%) of (**1**) (R$_f$ = 0.35) as a yellow viscous oil: $[\alpha]^{25}_D$ = +1.7 (CHCl$_3$).

^{1}H-NMR (CDCl$_3$) δ (ppm): 8.7 (s, 1H, aromatic), 8.3 (d, 1H, aromatic), 8.1 (d, 2H, aromatic), 7.5 (d, 1H, aromatic), 7.0 (d, 2H, aromatic), 5.8 (m, 1H, CH$_2$=C$\underline{H}$), 5.0 (m, 2H, C$\underline{H}_2$=CH), 4.2 (d, 2H, COOC$\underline{H}_2$), 4.0 (m, 2H, C$\underline{H}_2$OAr), 2.1 (m, 2H, CH$_2$=CHC$\underline{H}_2$), 1.8 (m, 3H, COOCH$_2$C$\underline{H}$ + C$\underline{H}_2$CH$_2$OAr), 1.4, 1.3, and 1.0 (3m, 14H, aliphatic).

Synthesis of monomer (2)
Monomer (**2**) was synthesized according to literature [9].

Synthesis of copolysiloxane copoly(1)-co-(2)
0.19 g (0.40 mmol) of (**1**), 0.45 g (1.60 mmol) of (**2**), 0.12 g (1.80 mmol of Si-H groups) of (**9**) and 56 μl of a 2% solution of platinum (divinyltetramethyl disiloxane) (Pt-DVDS) were dissolved in 20 ml of anhydrous toluene under dry nitrogen atmosphere. The reaction mixture was maintained at 50 °C for 22 h, after which it was poured into *n*-hexane. The coagulated polymer was purified by precipitations from CH$_2$Cl$_2$ solutions into methanol (yield 89%): $[\alpha]^{25}_D$ = +0.4 (CHCl$_3$).
^{1}H-NMR (CDCl$_3$) δ (ppm): 8.7 (s, 0.23H, 2-aromatic (**1**)), 8.3 (s, 0.23H, 6-aromatic (**1**)), 8.1 (s, 2.00H, 2'- and 6'-aromatic (**1**) + 2- and 6-aromatic (**2**)), 7.4 (s, 0.23H, 5-aromatic (**1**)), 7.0 and 6.8 (2s, 5.09H, 3'- and 5'-aromatic (**1**) + 3-, 5-, 2'-, 3'-, 5'-, and 6'-aromatic (**2**)), 4.2 (s, 0.46H, COOCH$_2$), 3.9 and 3.8 (2s, 4.31H, C$\underline{H}_2$OAr + OCH$_3$), 1.9, 1.7, 1.2, and 1.0 (3s and m, 6.34H, aliphatic), 0.5 (s, 2.00H, SiCH$_2$), and 0.1 (s, 3.50H, SiCH$_3$).

Sample preparation
For studying the electro-optical response of the liquid crystal polymer in the N* phase, the polymer was introduced into a conventional sandwich cell consisting of two glass substrates with electrodes deposited on the inner sides of the substrates. The distance between the substrates was fixed by evaporated SiO$_x$ spacers to be of about 2 μm. For achieving a uniform planar alignment of the liquid crystal, the electrodes were coated by a unidirectionally rubbed polymer layer. In

addition, a gentle mechanical shear was applied to the liquid crystal layer in order to increase the uniformity of the planar alignment.

The cell was placed in a Mettler FP-52 hot stage mounted in a polarizing microscope. The optical and electro-optical studies of the sample were carried out between crossed polarizers. The electro-optical response was detected in a set up described in [3] at a position of the cell optic axis corresponding to an angle of 22.5° with respect to one of the polarizers.

RESULTS

The new chiral monomer (1) was synthesized following the procedure outlined in Figure 1. Its chemical structure had been designed in such a way as to give a chiral nematic phase when incorporated along with nematogenic monomer (2) into a copolysiloxane structure.
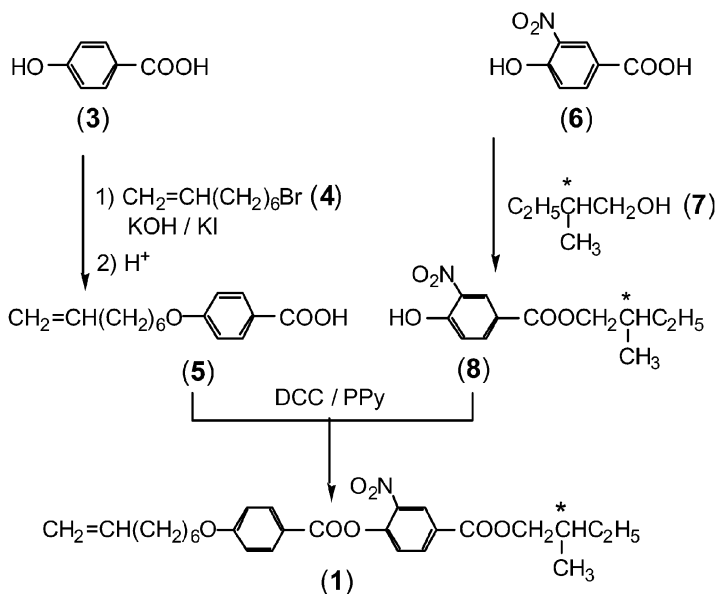
FIGURE 1. Reaction scheme for the synthesis of monomer (1).

Copolysiloxane copoly(**1**)-*co*-(**2**) was synthesized by a Pt-catalyzed hydrosilylation reaction of a mixture of monomers (**1**) and (**2**) (20:80 by mol) onto a preformed poly(hydrogenmethyl)siloxane (**9**) (DP_n = 35), as is shown in Figure 2.

The copolymer formed an N* phase up to 41 °C (T_i), which on cooling remained locked in the glassy state below 9 °C (T_g). The sample after cooling from the isotropic phase was aligned in a uniform planar texture with the optic axis being parallel to the glass substrates. The helical order appeared to be completely suppressed by the liquid crystal/surface interactions. Some additional studies on copoly(**1**)-*co*-(**2**) indicated that the pitch of its N* was indeed long and, therefore, possible to be suppressed.

A linear electro-optical response was detected in the N* phase because of the field induced tilt of the optic axis due to the electroclinic effect that resulted in the in-plane switching of the liquid crystal molecules. The amplitude of the induced tilt was rather small ($\phi \approx 0.02°$) (U_{pp} = 100-300 V, f = 40 Hz) but large enough to trace a sign reversal of the dielectric anisotropy, see below.
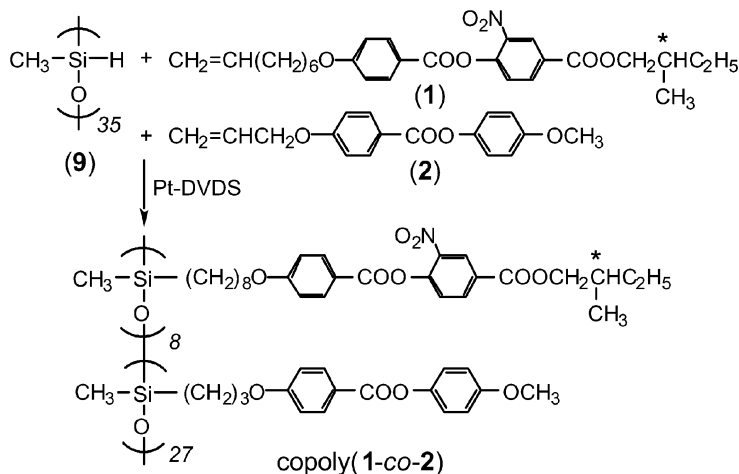

FIGURE 2. Reaction scheme for the synthesis of copolysiloxane copoly(**1**)-*co*-(**2**).

With increasing applied electric field ($U_{pp} > 300$ V) a deformation of the linear response occurred due to dielectric coupling that increased with the field in a quadratic fashion. The character of the deviation from linearity of the response changed with temperature, as illustrated in Figure 3. This deviation corresponded to the out-of-plane switching of the liquid crystal molecules by the applied electric field due to dielectric coupling. As seen, both the dark and the bright states of the switching process were affected by the out-of-plane switching of the molecules. The out-of-plane switching, however, changed the macroscopic birefringence (Δn) of the liquid crystal layer due to the change in the molecular tilt with respect to the confining substrates. This tilt was increasing at positive and decreasing at negative dielectric anisotropy ($\Delta \varepsilon$) when applying an electric field across the sample. The changes of Δn due to the changes in the molecular tilt affected the intensity of the light transmitted through the cell. The distortion reversed its sign below 37 °C (Figure 3B) becoming zero at this particular temperature.

To eliminate the influence of dielectric coupling $\Delta \varepsilon$ should be zero [8]. The detected electro-optical response at different temperatures indicated that $\Delta \varepsilon$ of copoly(**1**)-*co*-(**2**) was negative at 39 °C, since the dielectric coupling increased Δn thereby distorting the minimum and the maximum in the transmitted light intensity in such a way that they both became brighter. On lowering the temperature, however, $\Delta \varepsilon$ decreased and the dielectric influence on the response also decreased. At 37 °C, $\Delta \varepsilon = 0$ and therefore the response was essentially undisturbed. In contrast, at lower temperatures $\Delta \varepsilon$ was positive and now the dielectric coupling decreased Δn thus resulting in a decrease of the brightness of the maximum in the transmitted light intensity and in an increase of the darkness of the minimum.

DISCUSSION

When the sample is placed between crossed polarizers, and its optic axis is oriented along either the analyzer or the polarizer, the sample shows a high degree of extinction of the transmitted light.
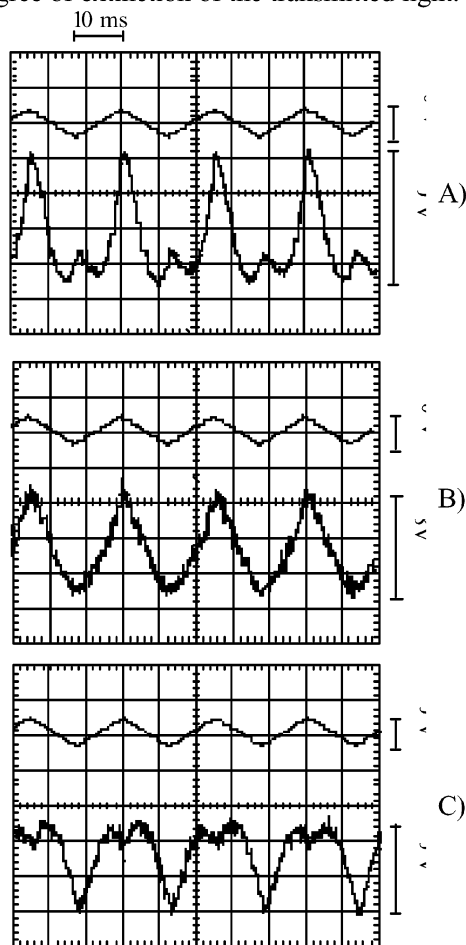
10 ms

FIGURE 3. Electro-optical response in the N* phase of copoly(**1**)-*co*-(**2**) at 39 °C (A), 37 °C (B), and 35 °C (C).

Due to the field-induced deviation of the optic axis, the transmitted light intensity (I) through the sample becomes modulated. The modulation of the light intensity is defined as $\Delta I \approx I(E, \Psi_0) - I(0, \Psi_0)$, where Ψ_0 denotes the angle between the optic axis of the sample and the polarizers axis at zero field.

At low electric fields the transmitted light intensity $I(E, \Psi_0)$ is given by [3]:

$$I(E_z, \Psi_0) = I_0 \sin^2[2(\Psi_0 + \phi(E_z))] \sin^2(\pi d \Delta n / \lambda) \qquad (1)$$

where $\phi(E)$ is the field-induced in-plane deviation of the optic axis due to the electroclinic effect and E_z is the component of the applied electric field normal to the sample substrates, d is the sample thickness, Δn the effective birefringence, and λ the wavelength of the incident light in vacuum, respectively. The first factor of this equation, $\sin^2[2(\Psi_0 + \phi(E_z))]$, is giving the modulation of the transmitted light intensity due to the in-plane switching of the cell optic axis whereas the second factor gives the light modulation due to the out-of-plane switching. Setting the angle Ψ_0 to be $\pm 22.5°$ and assuming that the sample is satisfying the half-wave plate condition ($2\pi d\Delta n / \lambda = \pi$) and Δn is constant with the field (i.e. the dielectric coupling can be neglected, so-called low field approximation) then the second factor in eq.(1) approaches one. Expanding eq.(1) in a Taylor series around Ψ_0, it transforms to:

$$I_{\lambda/2}(E_z, \pm \pi/8) = I_0 \{1/2 \pm 2\phi(E_z) \mp 2/3[2\phi(E_z)]^3 ....\} \qquad (2)$$

At low fields, only the first harmonic is of importance and the induced deviation $\phi(E)$ of the optic axis could be approximated to:

$$\phi(E) = e_c E \qquad (3)$$

where e_c is the electroclinic coefficient. Inserting eq.(3) in eq.(2), one realizes that the modulation of the transmitted light through the cell will be linear with the field. The second factor in eq.(1) will be

constant only if $\Delta\varepsilon = 0$, i.e. when no dielectric coupling is present. However, if $\Delta\varepsilon$ is not zero then dielectric coupling will result in out-of-plane switching of the molecules in a quadratic fashion. In this case Δn is no longer constant and the second factor in eq.(1) does change [8]. The decrease of Δn, the case of positive $\Delta\varepsilon$, lowers the transmitted light intensity. On the contrary, Δn increases with the field in the case of negative $\Delta\varepsilon$, which causes an increase in light intensity.

In conclusion, we have synthesized a new N* polymer that exhibited a linear electro-optical response in the N* phase due to the electroclinic effect (albeit of rather modest intensity). A dielectric coupling was also detected which affected the electro-optical response. Although the linear electro-optical response due to electroclinic effect was small, it was enough to estimate the sign of the dielectric anisotropy. This reversed with changing temperature (being $\Delta\varepsilon = 0$ at 37 °C), because of the changed polarization of the mesogenic units. This might be associated with conformational changes in the polymer side chains.

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