

Electro-optic studies on novel chiral liquid crystalline polysiloxanes with the N* phase

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Summary

The electro-optical response of two novel side chain liquid crystalline polysiloxane copolymers containing chiral pendant groups was investigated. It was found that both copolymers possessed N* phase with a long pitch and therefore the origin of the electro-optical response detected in this phase was considered to be the electroclinic effect.

Introduction

The existence of spontaneous polarization in chiral tilted smectic phases was predicted by Meyer more than twenty years ago (1). Since then many research activities have been focused on ferroelectric liquid crystals. Garoff and Meyer (2) found that in the A* phase, which is an orthogonal smectic phase, the applied electric field can induce a molecular tilt and consequently a polarization. In the A* phase, as the molecular tilt fluctuations arise on approaching C*-A* phase transition, the smectic layer compressibility also diverges, the so-called soft mode. However, the tilt fluctuations in the A* phase are connected with local polarization fluctuations along the smectic layers and perpendicular to the plane of molecular tilt and layer normal. Therefore, a molecular tilt can be induced in the A* phase by applying an electric field along the smectic layers. This was termed the electroclinic effect. By using the bookshelf geometry alignment, with the smectic layers perpendicular to the confining glass plates, the electroclinic effect in A* phase shows features very attractive for applications in the field of electro-optics. The field-induced molecular tilt θ in the A* phase is found to be linearly dependent on the applied field (E), at least for small fields:

$$\theta = e_c E \quad (1)$$

where e_c is electroclinic coefficient given by

$$e_c = \frac{\mu}{\alpha (T - T_c)} \quad (2)$$

and μ is the structural coefficient, α is the first constant in the Landau free-energy expansion and T_c is the temperature of the A*-C* transition. As shown in eq. 2, the induced tilt is strongly temperature dependent and it diverges at A*-C* transition, a typical behaviour of the electroclinic effect in liquid crystal materials possessing such a phase transition. The electroclinic effect in A*

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phase is also characterized by a short response time being essentially in the microsecond range. Moreover, the response time is a field independent quantity.

The electroclinic effect has also been observed in chiral nematics with an unwound helix (long pitch N^*) (3,4). In describing the effect, the same symmetry arguments used in the case of A^* phase can be applied, since both the A^* and N^* phase have the same D_2 symmetry. Although the response time of the electroclinic effect in the N^* phase is much shorter than that of the A^* phase, the field-induced molecular tilt is generally much smaller. However, in some materials the induced tilt of several degrees was measured in the N^* phase, which is sufficient for some electro-optical applications. Therefore, it is worthwhile to study the effect in a variety of different liquid crystalline materials.

A similar linear electro-optic response can be obtained with a N^* phase oriented in a uniform lying helix (ULH) texture on applying an electric field perpendicular to the helix axis (6-8). This is called the flexoelectro-optic effect. The case of short pitch material (with pitch less than the light wave length) is of special interest since with an appropriate choice of material one can get a linear modulation of the transmitted light without losses due to the diffraction by the helical order of molecules. The field-induced tilt of the optic axis θ is a linear function of the applied field E

$$\theta \approx \frac{e_f E}{Kq} \quad (3)$$

where e_f is an average flexoelectric coefficient, K is the elastic constant ($K_{11} = K_{22} = K$) and q is the wave vector modulus, $q=2\pi/p$ (p is the spatial period of the helix).

In some liquid crystalline materials with a temperature independent pitch, a large field-induced tilt of the optic axis was observed, being linear with the field as well as temperature independent (7,9). Moreover, the response time was found to be in the range of 10-100 μ s. In the present paper we report on electro-optic response in the N^* phase of two novel chiral liquid crystalline copolymers. The aim of this study was first to clarify which of the above mentioned effects (either electroclinic or flexoelectro-optic) is the origin of the detected electro-optic response in these materials and then to measure the magnitude of the field-induced tilt of the optic axis as a function of the electric field and temperature.

Experimental

Polymer precursors: These materials had been made previously (6). The chiral monomer (**1**) synthesis is outlined in Scheme 1.

Copolymer synthesis: The chiral copolymers (**K91**, **K64**) were prepared previously (6) using the method outlined in Scheme 2. Poly(hydrogenmethylsiloxane) (1 mol. equiv.), the benzoate (**2**) (0.9 or 0.6 mol. equiv.) and the cyanohydrin ester (**1**) (0.1 or 0.4 mol. equiv.) were dissolved in dichloromethane (25 ml) and allowed to stir for a few minutes at ambient temperature while under an atmosphere of nitrogen. Added to this solution was platinum divinyltetramethyldisiloxane complex (10 μ l), which was followed by heating under reflux for 72-96 hours, after which time the reaction was shown to be complete by the absence of the Si-H peak in the infrared spectrum (~ 2160 cm^{-1}). The resultant solution was concentrated and the polymer precipitated using a 5 fold excess of methanol. The polymer was subsequently collected by centrifuging. Each polymer

was precipitated 5 times, yielding cream-colored gums. Drying was performed under high vacuum.

DSC measurements were carried out under nitrogen using a Perkin Elmer DSC 7 with a scanning rate of 10°C/min.

Optical study of the samples was done by means of polarizing microscope. A very weak optical activity was detected in the N* phase of the polymers thus indicating a long pitch helical order of the molecules.

Electro-optic measurements: Sandwich cells of conventional type with a gap of about 2 μm and with transparent conductive electrodes deposited onto the inner surfaces of the glass substrates were used. The liquid crystalline material was injected into the cell gap in the isotropic phase. By special surface treatment and mechanical shear prior to addition, a uniform alignment of the N* phase was achieved. The electro-optic characteristics were measured in a set-up as described in (11). The cell was inserted in a Mettler MP52 hot stage with the temperature controlled to within 0.1°C. The hot stage was fixed on the rotating table of a polarizing microscope with crossed polars. The field-induced tilt of the optic axis was evaluated following the method used in (11). As the detected magnitude of the field-induced tilt was very small, measurements were performed at the frequency of the applied electric field below the cut-off. This allows comparison between the response of the two materials.

Results and Discussion

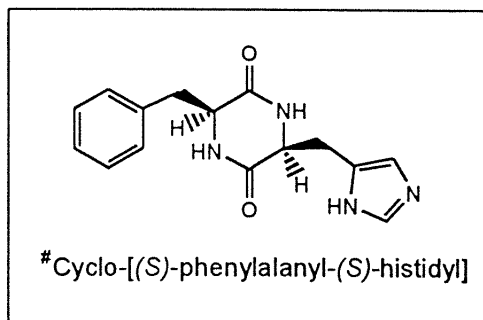
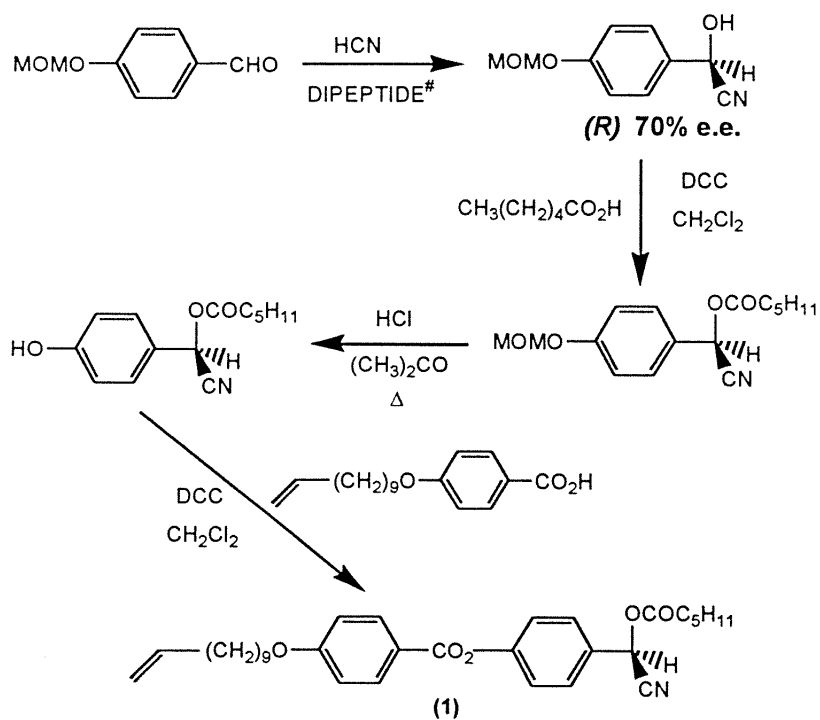
The syntheses for the chiral polymer precursor and the copolymers prepared in this work are outlined in Schemes 1 and 2. The thermal data for the chiral copolymers (**K91**, **K64**) are presented in Table 1. It is evident that these asymmetric materials are non-crystalline and that the T_i values for these types of copolymers dramatically decrease upon increasing the amount of the chiral pendant group. This is presumably due to the introduction of the chiral moiety disrupting the stable smectic phase of the corresponding non-chiral homopolymer (R₁ : R₂ = 100 : 0) in order to form the N* phase (10), even though the ΔH_i values for the chiral copolymers (**K91**, **K64**) were higher (3.0 and 2.4 J/g respectively) than the range normally expected with phase changes in such polymers (0.4-1.0 J/g) (12).

It was found that these materials exhibited very low optical activity and neither the texture or the optical behaviour revealed a helical order of the molecules in the samples of the two copolymers. Samples with good uniform planar alignment (completely unwound helical structure) were prepared. Application of an electric field across the cell resulted in a field-induced tilt of the optic axis θ(E). This caused a modulation of the light transmitted through the cell. In general, the transmitted light intensity through such a sample is given by (13):

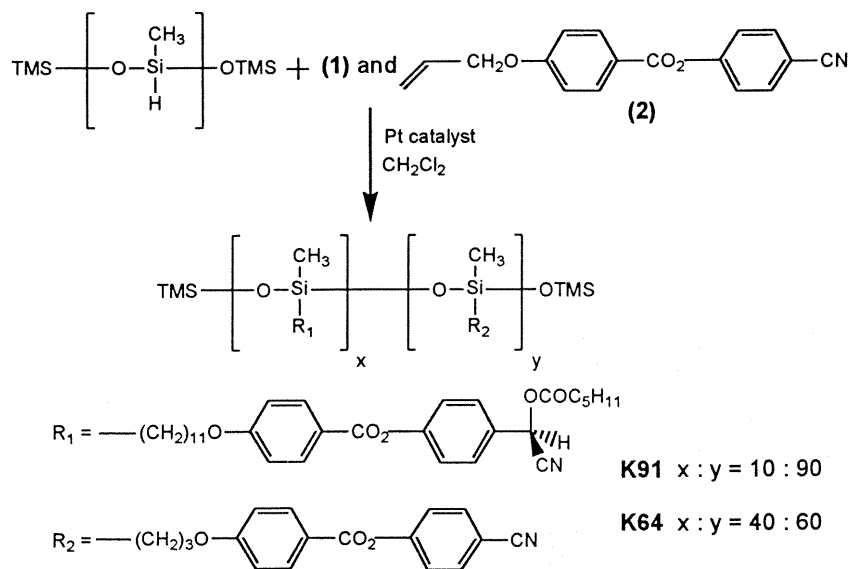
$$I = I_0 \sin^2 (2 [\Psi_0 + \theta(E)]) \sin^2 \left(\frac{\pi d}{\lambda} \Delta n \right) \quad (4)$$

where I₀ is a constant, depending on the incident light intensity and polarizer quality, Ψ₀ is the angle between the direction of the first polarizer and the optic axis of the sample, θ(E) is the field-induced deviation of the optic axis, λ is the wave length of the incident light in vacuum, d is the thickness of the sample and Δn is the birefringence of the liquid crystal material. The factor

$\sin^2(\pi d \Delta n / \lambda)$ is field independent in our case and it is approximately one for the liquid crystal cell of 2 μm thickness. The field-induced tilt $\theta(E)$, due to the electroclinic effect, for moderate fields is linear in the field and if Ψ_0 is set to be 22.5° then the electro-optic response is also linear function of the field (11). The polymers under study exhibited such a behaviour. This behaviour is demonstrated in Fig. 1 for the case of the polymer **K91** where the electrooptic response in the N^* phase on applying triangular voltage is depicted. The field-induced molecular tilt is measured as a function of the applied field and temperature (Fig. 2). As can be seen from Fig. 2, the induced tilt angles in the N^* phase in both materials have small values, especially in **K91**. In both cases the induced tilt is linear in the field and decreases on approaching the glass or isotropic phase transition, behaviour specific for the electroclinic effect. Hence, we may conclude that the electro-optic response detected in the unwound N^* phase of the polymers **K64** and **K91** is due to the electroclinic effect in the N^* phase of these materials. Moreover, comparing the magnitude of the induced tilt we see that increased chiral content in the copolymer material leads to larger induced tilt.



Scheme 1



Scheme 2

Table 1 Thermal characteristics of the copolymers **K91** and **K64**

Polymer	T_g (°C)	T_m (°C)	T_i (°C)	Peak Width [†] (°C)	ΔH_i (J/g)	ΔS_i (10^{-3} J/gK)
K91	*	-	84	38	3.0	8.4
K64	5	-	54	18	2.4	7.3

*Glass transition not observed

[†]Baseline peak width of clearing transition from DSC

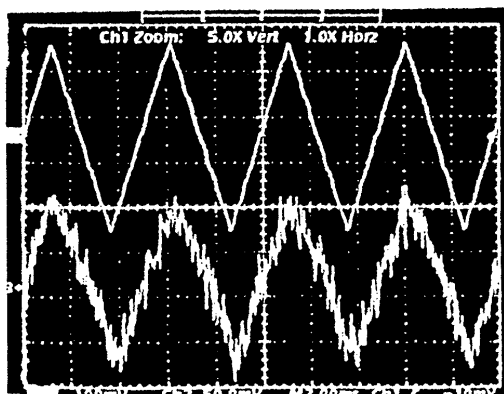


Fig. 1 Electro-optic response (lower curve) of cell with **K91** on applying triangular voltage (upper curve)

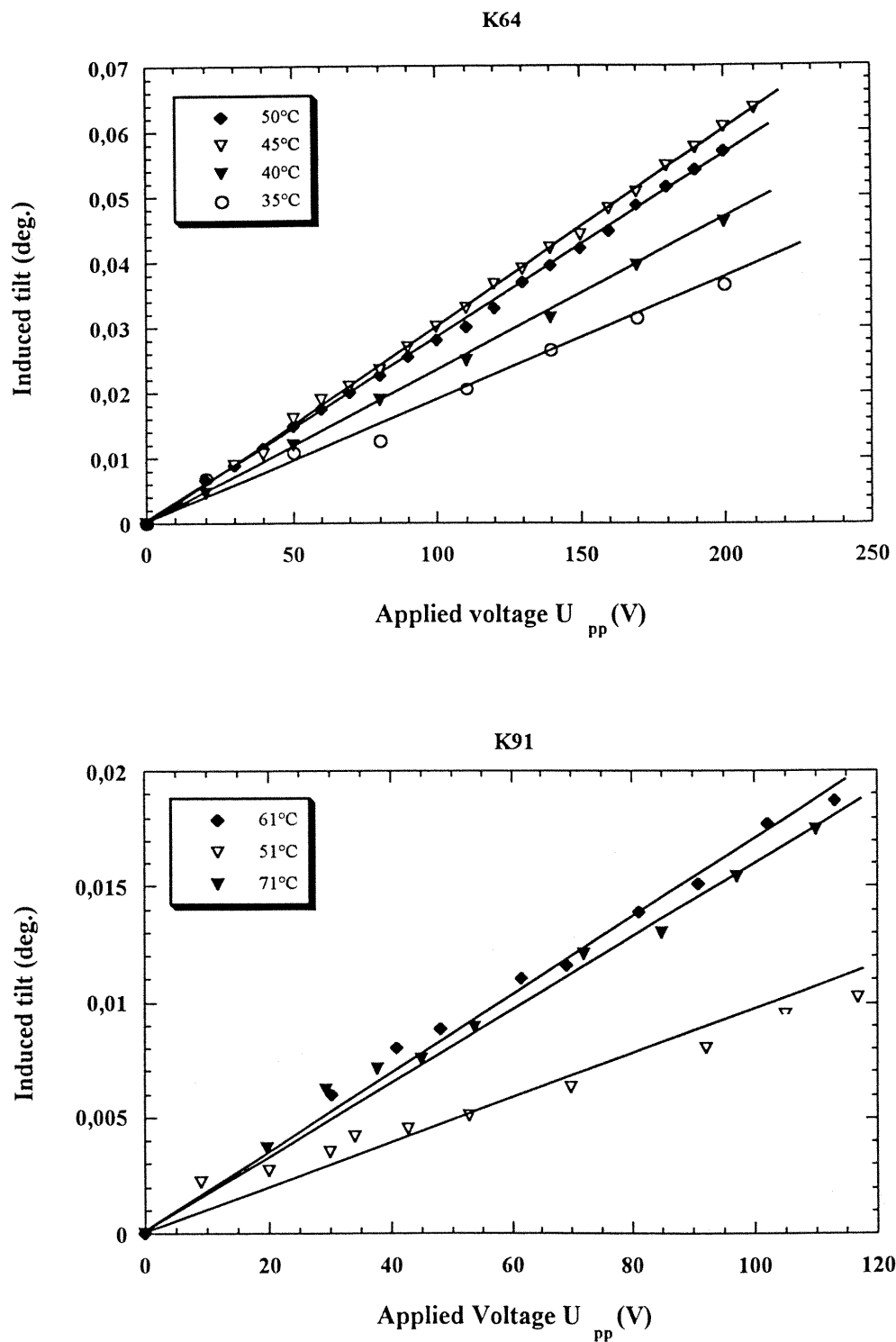


Fig. 2 The field-induced tilt in the cell with copolymer **K64** (top) and in the cell with **K91** (bottom) as a function of the applied voltage and temperature

Conclusion

Recently field-induced tilt of the optic axis, due to the electroclinic effect in the unwound N^* phase, with amplitude of about 5-8 degrees has been reported (14). Thus, the large magnitude of the induced tilt makes the electroclinic response in N^* phase attractive for applications. However, to date, the electroclinic response has been studied only in low molar mass liquid crystalline materials. For the first time, we present an investigation performed on the electro-optical response of two novel chiral liquid crystalline side chain copolymers possessing a long pitch N^* phase. This study has shown that the origin of the detected response in the N^* phase is the electroclinic effect and therefore it shows a pronounced linear behavior with the field. The response first increases on cooling down from the isotropic phase and then continuously decreases on approaching the glass transition. The comparison of the magnitude of the response in the two materials at the same reduced temperature $T_i - T$ shows that the concentration of the chiral moiety is of importance. Even though it is difficult to conclude unambiguously, it seems the higher is this concentration, the greater is the response. Further studies with similar polymeric materials, a greater variety of structures (particularly in the nature and content of the chiral group) are necessary in order to extend our knowledge about the electroclinic effect in the N^* phase of polymeric liquid crystalline materials.

Acknowledgements

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