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## Liquid Crystals

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# Frustrated liquid crystalline side group polymers for optical storage

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The phase formation and thermodynamic properties of side group copolymers composed of different concentrations of mesogenic azobenzene side groups and non-mesogenic side groups were investigated. Such kinds of polymers can be used for optical data storage. The storage process is caused in this case by a light-induced reorientation of the chromophores. The basic idea was that the introduction of non-mesogenic units should lead to frustration effects in the sense that amorphous polymers are obtained, which can be handled more easily than liquid crystalline polymers yet which still possess strong orientational interactions between the side groups allowing cooperative switching processes. The results of thermodynamic, structural and dynamical investigations indicate that this goal can be achieved on the basis of such copolymers.

## 1. Introduction

Side group liquid crystalline polymers (SGLCPs) containing azobenzene derivatives as mesogenic units have been used with surprising success as materials for optical storage [1–4]. Digital and holographic recording as well as the manufacturing of holographic optical components have been documented in the literature [5–8]. The basic mechanism involved in the storage process is a reorientation of the chromophore in the presence of polarized light, the reorientation being a consequence of light-induced isomerization cycles [1, 9, 10].

Homogeneously oriented monodomain films with frozen-in ordering in the glassy state were used as storage media. The basic idea was that the liquid crystalline environment should result in an amplification effect for the reorientational motion. The drawback of the storage material described so far is that it requires the manufacture of optically homogeneous monodomain films. This becomes increasingly complex as the size of the storage device increases. Large film areas of good optical quality can, on the other hand, be produced easily from amorphous polymers including amorphous side group polymers. Yet, amorphous polymers might not give rise to the strong amplification effect described above.

Our concept to overcome this problem consisted in using side group polymers which were constructed in such

a way that they can be prepared as amorphous films, but keep their tendency to develop liquid crystalline orientational order [11–14]. The goal can be achieved along different routes. One route consists in placing the glass transition temperature close to the temperature where the transition from the isotropic melt to the liquid crystalline state takes place. Depending on the rate of cooling and the annealing conditions, either amorphous or liquid crystalline films can be prepared [11].

A second approach, and the one discussed in this contribution, consists in the replacement of parts of the mesogenic side groups by non-mesogenic groups in a side group polymer [12–14]. The expectation is that the tendency of the polymer to exhibit a liquid crystalline phase becomes exceedingly frustrated as the concentration of the non-mesogenic comonomers is increased. The optimum choice with respect to optical storage should be a copolymer which allows the formation of amorphous films, yet develops orientational order in the course of irradiation in the solid film. Such materials should have an enhanced sensitivity due to the presence of cooperative orientational interactions.

This contribution describes the synthesis of such copolymers and the characterization of their thermodynamic and structural properties, as well as their optical properties. In addition, we will briefly discuss selective results of Monte Carlo simulations on the storage process in the absence and presence of liquid crystalline orientational interactions.

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## 2. Experimental

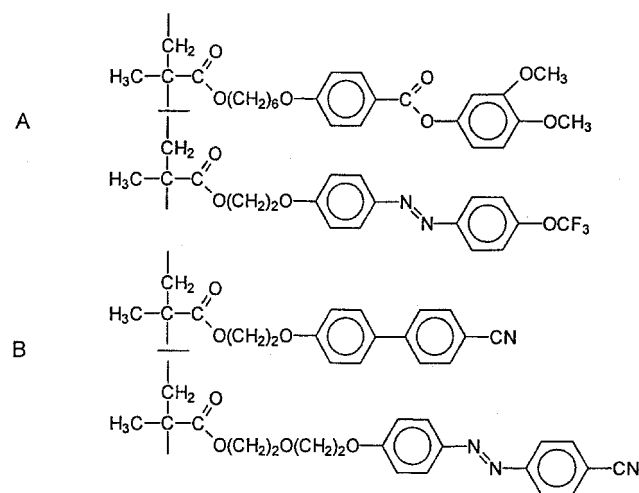
### 2.1. Samples

We considered a set of copolymers (copolymers A/4–A/1) in which the concentration of mesogenic and non-mesogenic side groups was varied over a broad range. The azo side chain has a terminal  $-\text{OCF}_3$  substituent in order to show a dipole moment suitable for Kerr measurements. The chemical compositions are given in the scheme. We considered, in addition, an amorphous copolymer (copolymer B) which also contained both mesogenic and non-mesogenic side groups. The chemical structure is also given in the scheme.

### 2.2. Characterization

#### 2.2.1. Chemical analysis

Purification control of the monomers was given by thin layer chromatography (Merck Kiesegel 60F 2654/ methylene chloride or chloroform:methanol 10:1, UV detection). For elemental analysis an analyser 1106, Carlo Erba, was used. Molecular weights and the polydispersity index  $E$  of the polymers were determined by size exclusion chromatography, Waters C-150 (stationary phase: ultra styragel column  $10^5$ ,  $10^4$ ,  $10^3$  nm, polystyrene calibration standards, Polymer Laboratories Ltd., UV detection: 254 nm, Unicam PU 4021, Philips, eluent: tetrahydrofuran).



Copolymer	Mol % azo side chain	Behaviour
A/4	90	LC
A/3	70	LC
A/2	50	LC
A/1	0	amorphous
B	60	amorphous

Scheme. Chemical structure and composition of the copolymers investigated.

#### 2.2.2. Thermal analysis

The glass transition and melting temperatures were determined using a differential scanning calorimeter (Perkin Elmer DSC 7). The heating and cooling rates were  $10 \text{ K min}^{-1}$ ; all data reported were obtained after the first heating run which was performed to erase the thermal history.

#### 2.2.3. Structural and dynamic investigations

A Siemens D 5000 diffractometer was used to perform the wide angle X-ray analysis. Ni-filtered  $\text{Cu K}\alpha$  radiation was used in all cases. For dielectric studies we used a Hewlett-Packard impedance analyser HP 4284 A which covers the frequency range from 20 Hz to 1 MHz. The temperature of the samples could be controlled in a temperature range from 100 to 650 K, using a nitrogen gas heating system, with an accuracy of 0.2 K.

#### 2.2.4. Kerr effect studies

The experimental set-up has been described in previous publications [15]. The experiment consists in applying an electric field to the fluid state in a cell fitted with a thermostat. The field causes the molecules to orient partially, giving rise to birefringence. The birefringence is analysed by passing a light beam through the cell perpendicular to the direction of the applied field. A linear detection system including a quarter wave plate was used to analyse the magnitude of the birefringence. The polarizer was oriented at an angle of  $45^\circ$  with respect to the electric field and the analyser was rotated by a known angle  $\alpha$  relative to the direction of the field.

#### 2.2.5. Grating experiments

In order to test the capability of the frustrated side group polymers for optical storage we performed grating experiments on films with a thickness of about  $1 \mu\text{m}$ . Gratings were obtained by the interference of two planar waves in a Mach Zehnder interferometer. An argon ion laser operating at 488 nm single mode single frequency was used as the light source. The writing intensity was  $90 \text{ mW cm}^{-2}$ . A helium neon laser operating at 632.8 nm was used to read the induced optical modulation. The intensity diffracted into the first order was recorded by a photodiode and normalized to the intensity of the incident read-out beam to obtain the diffraction efficiency.

## 3. Synthesis

### 3.1. Synthesis and properties of the monomers

#### 3.1.1. 3,4-Dimethoxyphenyl 4-methacryloyloxyhexadecyloxybenzoate (**1**)

The synthesis of this compound was done according to Finkelmann *et al.* [16].

The last step was realized by the reaction of 0.032 mol of methacryloyloxyhexadecyloxybenzoyl chloride with

0.032 mol of 3,4-dimethoxyphenol (solvent 150 ml toluene, reaction time 10 h, temperature 55°C, TL-controlled). The crude monomer was purified by column chromatography on a silica gel column (375 g, 0.2–0.5 nm) with elution by a 10:1 mixture of trichloromethane/methanol, followed by filtration through Al<sub>2</sub>O<sub>3</sub>. This was followed by repeated crystallization from *n*-hexane. Yield 9.8 g, m.p. 74–76°C. The monomer did not show liquid crystalline behaviour.

### 3.1.2. 4-Methacryloyloxy pentadiyloxy-4'-trifluoromethoxyazobenzene (2)

The synthesis of this compound followed the synthetic route for azobenzene-basic-components for side group polymethacrylates described by Ringsdorf and Schmidt [17]. The first step was realized by the diazotation of 13.5 g of 4-trifluoromethoxyaniline [18]. After coupling with phenol (solution of 7.5 g of phenol, 3 g of NaOH, 47 g of Na<sub>2</sub>CO<sub>3</sub> and 270 ml of water), etherification of the 4-hydroxy-4'-trifluoromethoxyazobenzene was effected with 1,5-dibromopentane (solvent 200 ml of acetone, reaction time 15 h, temperature 35°C, TL-controlled). The recrystallized (*n*-hexane) 4-bromopentadiyloxy-4'-trifluoromethoxyazobenzene was mixed with a solution of potassium methacrylate in 100 ml of dimethylformamide. The mixture was stirred for 10 h at 60°C. After cooling, the precipitate was filtered off, dried, purified by column chromatography and finally recrystallized from *n*-hexane. Yield 54%, m.p. 68–70°C, F-content: calc. 13.06, found 12.47%. The monomer did not show liquid crystalline behaviour.

### 3.2. Polymerization

The radically initiated polymerization (2 mol % of bis-azoisobutyronitrile) was carried out by using solutions of 10 wt % of monomer or mixtures of monomers in dimethylformamide at 70°C in a nitrogen atmosphere. After 24 h the polymerization was terminated by precipitation in ethanol. The crude products were dissolved in tetrahydrofuran or methylene chloride and reprecipitated four times with ethanol. The polymers were dried in vacuo at 40°C until a constant weight was reached. Yields after purification and drying were between 40 and 84%.

The results of copolymer characterization are summarized in table 1.

## 4. Result of Monte Carlo simulations on the role of cooperative effects

Monte Carlo simulations were performed in order to find out whether the interactions characteristic for the formation of liquid crystalline phases affect the reorientation of the azo chromophores in the presence of light, even in the case of frustrated amorphous systems.

Table 1. Molecular weights and the polydispersity index  $E$  of the polymers.

Copolymer	$M_w/\text{kg mol}^{-1}$	$M_n/\text{kg mol}^{-1}$	$E$
A/4	95.2	29.2	3.2
A/3	53.7	26.8	2.0
A/2	57	30	1.9
A/1	54	29	1.9

Details of the simulations are published elsewhere [10]. The basis of this simulation can be described as follows. The model consists of a three dimensional lattice of chromophore cells. The state of each cell can be 'trans' or 'cis'. For simplicity, the chromophores were regarded as rigid rods.

For the description of the orientational state of the system, the orientation factor method, as introduced by Michl and Thulstrup [19], was applied. The orientation factors are defined as

$$K_{uU} = \langle \cos^2 uU \rangle$$

giving the tensor projections of the molecular axes  $u = a, b, c$  to the laboratory axes  $U = X, Y, Z$ . The sample lies in the  $XY$ -plane, and  $Y$  is the polarization direction of the light. The interaction energy between a molecule and its neighbours was represented by

$$E = -\frac{1}{2} \sum_{ij} J_{ij} (3 \cos^2 \theta_{ij} - 1)$$

according to the theory of Maier and Saupe [20] for liquid crystals.  $\theta_{ij}$  is the angle between the molecular long axes. and  $J_{ij}$  represents the individual interaction energy. The thermodynamic properties of this system are known from the original work of Lebwohl and Lasher [21]: the system exhibits a liquid crystalline–isotropic first order phase transition at  $\epsilon/kT = 0.89$  with an order parameter  $S = 1/2 \langle 3 \cos^2 \theta - 1 \rangle = 0.33$ .

The results of the simulations are shown in figure 1. The observation is that the anisotropic interactions between the rigid molecules cause the formation of oriented domains in amorphous systems and biaxiality occurs. In the plots of figure 1,  $K_{aX}$  is higher than expected for a uniaxial system. Even for small interactions,  $\epsilon/kT \approx 0.2$ ,  $K_{aX}$  may exceed the maximum value which is allowed for a uniaxial system ( $K_{aX} = 0.5$ ). The interaction energy which is required for the formation of domains is substantially lower than  $\epsilon/kT = 0.89$ , the value required in the Lebwohl–Lasher model for the occurrence of liquid crystalline phases. The light field is predicted to promote the formation of ordered structures. For real materials, this can be very important: for example, the occurrence of such ordered domains is expected for side group polymers which are amorphous,

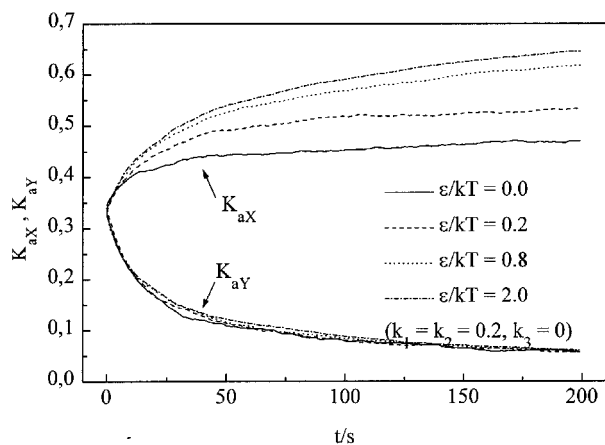


Figure 1. Evolution of the orientation factors  $K_{aX}$  and  $K_{aY}$  for an isotropic system with cooperative interactions.

but at the border of liquid crystallinity. Such amorphous polymers with anisotropic rigid side groups should exhibit no liquid crystalline phases, but ‘cooperative effects’ should arise.

## 5. Experimental results and discussion

### 5.1. Thermodynamic properties

All the side group polymers display a glass transition, the location of which depends on the copolymer composition as is obvious from table 2. In addition, we observe a transition from the liquid crystalline state into the isotropic state with the exception of the copolymer A/1. Figure 2 shows characteristic DSC diagrams both for the heating and the cooling cycle for copolymer A/3. The results on the location of the transition peaks and on the enthalpy of transition are given in table 2. It is apparent that the transition temperatures do not vary smoothly as a function of the comonomer composition despite the fact that all the molecular weights are rather close to each other. The enthalpy of the transition decreases, however, with increasing concentration of the non-mesogenic units in the polymer chain. X-ray results to be described below indicate that the liquid crystalline

Table 2. Results of the DSC analysis of the thermodynamic properties.

Copolymer	$T_g/^\circ\text{C}$	$T_{NI}/^\circ\text{C}$ (on heating)	$T_{NI}/^\circ\text{C}$ (on cooling)	$\Delta H/\text{J g}^{-1}$ (on heating)
A/1	47	—	—	—
A/2	52	103	— <sup>a</sup>	2
A/3	47	80	69	4.2
A/4	52	116	106	9.1

<sup>a</sup> No signal could be detected on cooling for this transition which is probably so strongly smeared out that it is not detectable by DSC.

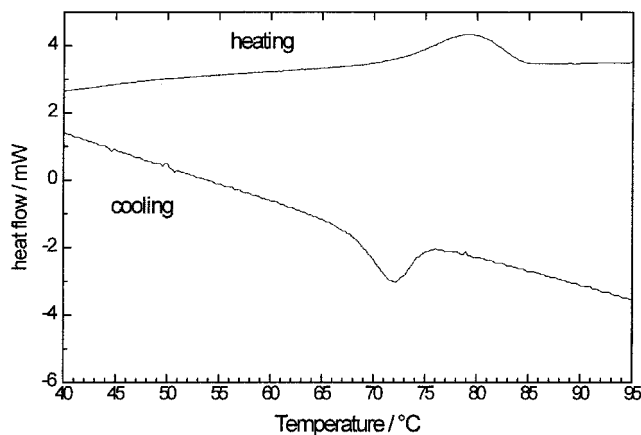


Figure 2. DSC diagram of A/3 for the heating and cooling cycle. The nematic phase can be supercooled by up to 10 K.

side group polymers display a nematic phase which is subsequently frozen-in into an ordered glassy state.

An interesting observation is that the nematic phases may be supercooled substantially. The isotropic nematic transition can, in general, be supercooled only slightly, typically by about 2 up to 4 degrees at moderate cooling rates ( $5\text{--}20\text{ K min}^{-1}$ ) provided that the glass transition temperature is not close to the liquid crystalline transition temperature. The copolymers considered here display supercoolings as large as 11 K. We take these results as first indications of frustrating processes experienced by the copolymers.

### 5.2. Phase assignment

The X-ray diagrams of all the copolymers were characterized by the occurrence of amorphous halos which are expected either for truly amorphous materials or for nematic materials (figure 3). The observation of birefringence in the polarizing microscopy studies showed that the polymers A/4 to A/2 do not display an amorphous

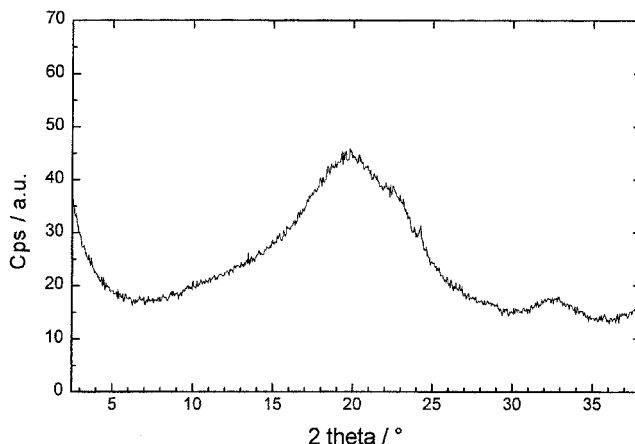


Figure 3. X-ray diffraction diagram of A/3. No peaks indicate that a higher than nematic order occurs.

state at lower temperatures, i.e. they are nematic. In fact, we were able to induce monodomains on glass slides covered with rubbed polyimide. The copolymer A/1 proved to be amorphous based on these investigations.

### 5.3. Dielectric relaxation studies

Glass forming organic materials including side group polymers display, in general, an  $\alpha$ -relaxation due to the motion of the backbone, in addition to high frequency secondary relaxations. The  $\alpha$ -process obeys in the majority of cases the WLF [22] or Vogel Fulcher relations [23]. For the  $\alpha$ -relaxation an activation plot of the logarithm of the frequency  $\ln \omega$  versus  $1/T$  does not give a straight line as in the case of the secondary relaxations which are thermally activated, but rather a curved line. This line can be fitted, for instance, to the WLF equation:

$$\log(v_T/v_{T_g}) = C_1(T - T_g)/(C_2 + (T - T_g))$$

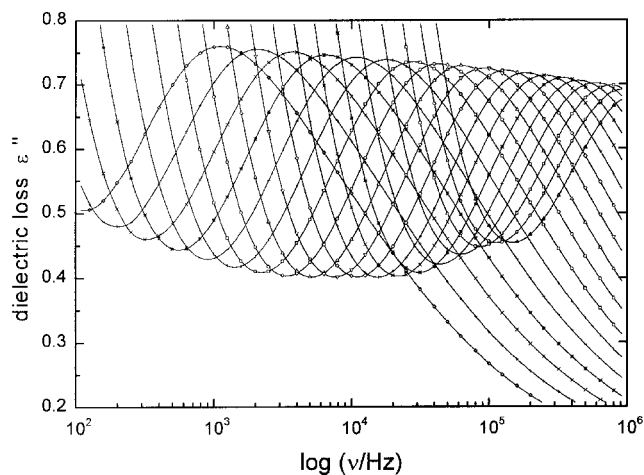
where the WLF constants  $C_1$ ,  $C_2$  are frequently close to some quasi-universal constants [22].

We were interested in the effect of the structural frustration on the relaxation properties. Figure 4(a) shows characteristic relaxation spectra for a side group copolymer A/2 with a low concentration of the mesogenic unit considered here, figure 4(b) displays the corresponding activation diagram. In figures 5 and 6 the analogous data for A/4, a system with a high concentration of the mesogenic units, are given. The observation is that the low frequency relaxation of the copolymer with the high concentration of non-mesogenic groups figure 4(b), corresponds closely to an  $\alpha$ -relaxation with WLF parameters expected for amorphous systems and with low frequency values obtained for  $T_g$ , corresponding to the values obtained by DSC.

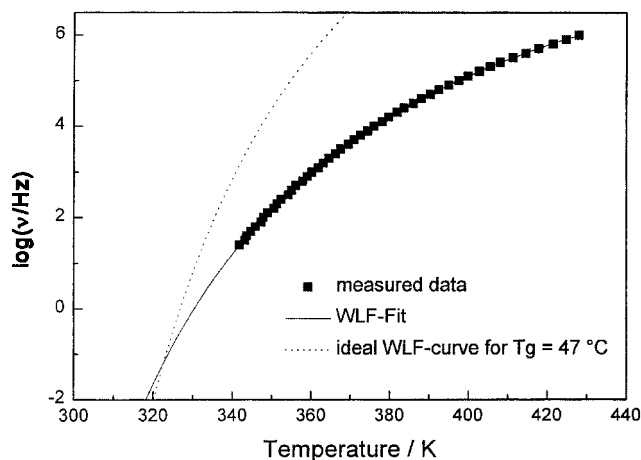
A significantly different result is obtained for the copolymer having the highest concentrations of the mesogenic unit, i.e. copolymer A/4 (figures 5 and 6). The spectra show a sudden increase of the relaxation strength around  $T_{NI}$ . The activation plot displays a straight line, the slope of which shows a significant change in the temperature range 114–117°C, apparently related to the phase transition, and a small one at 105–107°C. The activation energy for the relaxation process changes. This may be due to an enhanced alignment of the dipoles of the azo groups in the LC phase.

### 5.4. Kerr effect investigation

Nematic liquid crystals are known to display unusual electro-optical properties within the isotropic phase as the nematic–isotropic transition temperature is approached [24–28]. The electric field induced birefringence  $\Delta n$ —which increases proportionally to the square of the



(a)



(b)

Figure 4. (a) Dielectric loss  $\varepsilon''$  vs frequency for A/2. The temperature ranges between 88 and 160°C in temperature steps of 4 K; (b) activation diagram for the  $\alpha$ -relaxation of A/2.

electric field  $E$

$$\Delta n = \lambda B E^2$$

(where  $B$  is the Kerr constant and  $\lambda$  the wavelength of the light)—diverges at a temperature  $T^*$  which in the majority of cases is located slightly below the transition temperature  $T_{NI}$ .

De Gennes [25] has treated this phenomenon using a Landau expansion of the free energy of the system with respect to the orientational order parameter  $S$ . He has argued that pretransitional fluctuations should occur, the magnitude of which grows with decreasing temperature similarly to the case of critical systems. Using the approach described above one may represent the temperature dependence of the Kerr constant  $B$  as

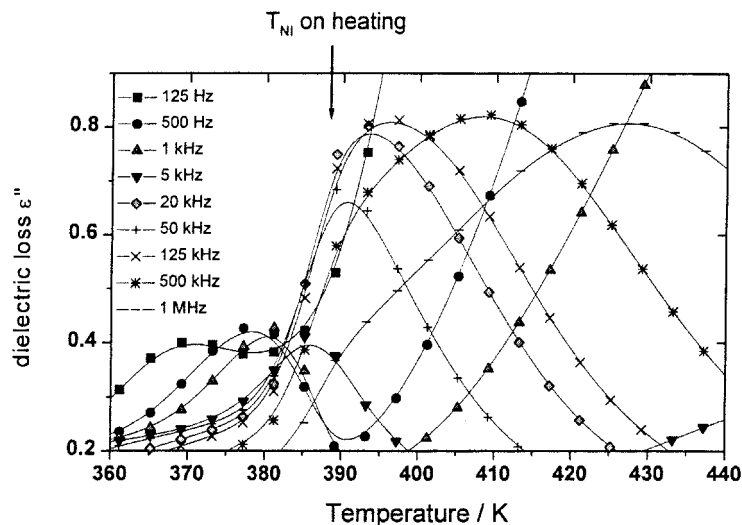


Figure 5. Dielectric loss  $\epsilon''$  vs temperature for A/4. The frequency ranges between 125 Hz and 1 MHz.

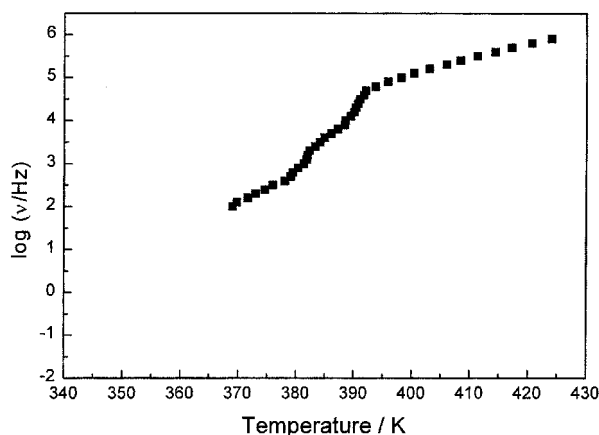


Figure 6. Activation diagram for the system with the highest concentration of the mesogenic side group, A/4.

follows:

$$B \propto 1/(T - T^*).$$

Using a statistical mechanical treatment we may trace back the divergence of the Kerr constant to the divergence of the orientational correlation factor  $g_2$  defined as [26]

$$g_2 = 1 + \frac{1}{2} \sum_{i \neq j} \langle 3 \cos^2 \theta_{ij} - 1 \rangle$$

where  $\theta_{ij}$  is the angle between the long axes of the molecules  $i$  and  $j$ . A common finding is that the correlation factor  $g_2$  is of the order of  $10^2$  at the transition temperature  $T_{NI}$  and that the characteristic temperature  $T^*$  is located about 1 K below the first order phase transition [27, 28].

The results obtained for the side group polymers discussed here are displayed in figures 7–9. It is obvious that the side group polymers obey the Kerr law, since

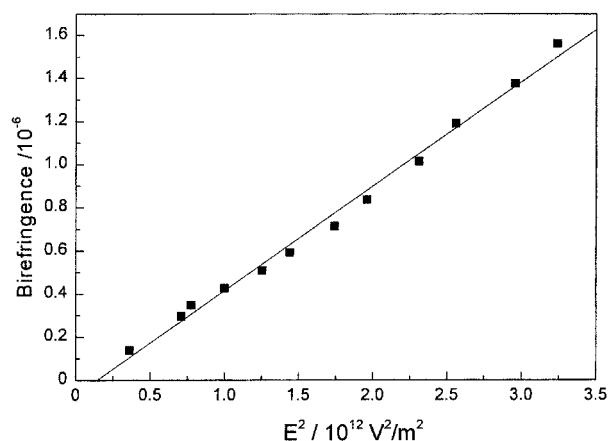
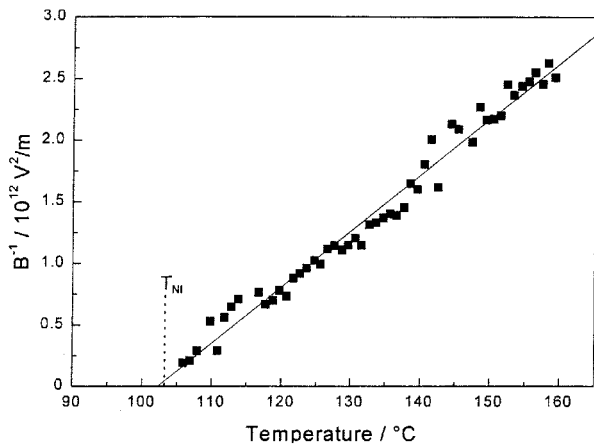


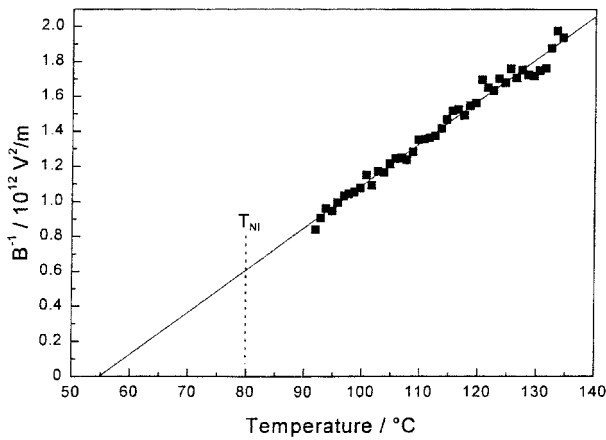
Figure 7. Electrically induced birefringence for A/3. The systems obey the Kerr law.

the induced birefringence is found to increase linearly with the square of the applied field (figure 7). The Kerr constant is found in all cases to increase strongly with decreasing temperature, as expected. A plot of the inverse of the Kerr constant versus the temperature yields a straight line which can be extrapolated to obtain the characteristic temperature  $T^*$ . These plots are shown in figures 8(a) and 8(b). The surprising finding is that the characteristic temperatures may lie well below the actual phase transition temperatures (table 3). The difference for A/3 is as large as 25 K, as is obvious from table 3: again we may take these results as indications of the frustration of the liquid crystalline structure. A further unexpected observation is that the amorphous side chain polymer A/1 also displays pretransitional effects. This is obvious from figure 9.

Such pretransitional effects reported here for an amorphous side chain polymer do not seem to be unique. Figure 10 displays the results obtained for the amorphous



(a)



(b)

Figure 8. Inverse of the Kerr constant vs temperature for (a) A/2 and (b) A/3. A linear dependence can be observed with a characteristic temperature considerably below  $T_{NI}$ .

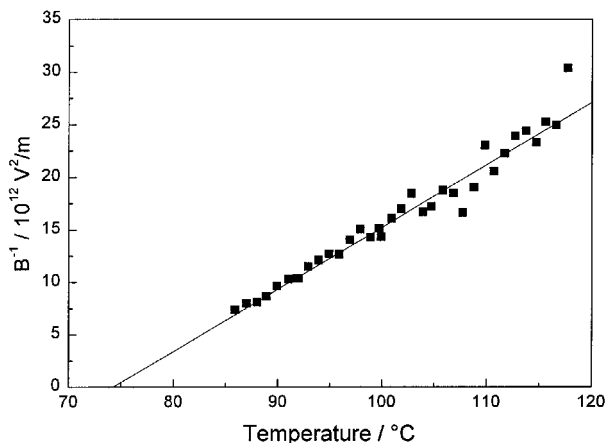


Figure 9. Inverse of the Kerr constant vs temperature for the amorphous copolymer A/1. The same linear dependence as for liquid crystalline materials can be observed.

Table 3. Characteristic temperatures  $T^*$  from Kerr effect investigations.

Copolymer	$T^*/^{\circ}\text{C}$	$T_{NI}-T^*/^{\circ}\text{C}$
A/2	101	2
A/3	55	25
A/4	95	21

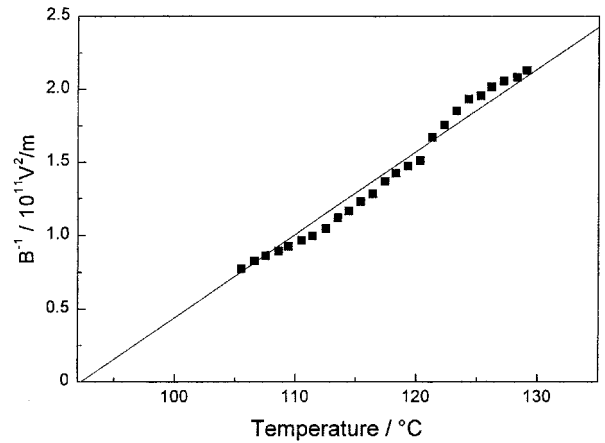


Figure 10. Inverse of the Kerr constant vs temperature for the amorphous copolymer B. Pretransitional effects are also indicated for this amorphous system.

side chain polymer B (see the scheme). The Kerr constant is found in this case to diverge at a temperature of  $92^{\circ}\text{C}$ . It thus seems that weak cooperative interactions still exist in these systems despite their amorphous nature.

### 5.5. Results of grating experiments

Figure 11 displays the result of the grating experiments on the side chain polymer A/3. Displayed here is the diffraction efficiency as a function of the irradiation time. The diffraction efficiency reaches a value of 11.3% which corresponds to a change of the refractive index  $n_1$  of  $4.8 \times 10^{-2}$ . These results have to be taken as an

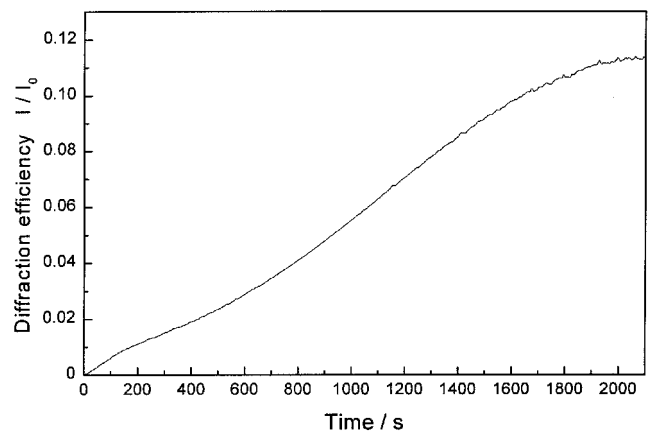


Figure 11. Holographic response curve for A/3.



indication that, in fact, the concept described here works and that the predictions of the Monte Carlo simulations hold for the polymers considered here.

## 6. Conclusions

The combination of mesogenic and non-mesogenic side groups in a copolymer can lead to systems that form amorphous films, either for kinetic reasons during film formation or even as the stable state, in which nevertheless cooperative orientational interactions do appear. Such copolymers display frustration effects caused by a competition between the tendency of the mesogenic side groups to form a nematic phase and the non-mesogenic side groups to form an amorphous phase.

An amplification effect due to cooperative interactions in the system controls the photoinduced reorientation.

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