Anisotropic networks obtained by *in situ* cationic polymerization of liquid-crystalline divinyl ethers

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Anisotropic networks were obtained by photoinduced cationic polymerization of liquid-crystalline (LC) divinyl ethers. For this purpose two new LC divinyl ethers were synthesized. Transition temperatures, phase behaviour and the temperature dependence of the order parameter for the two systems were determined before polymerization. Subsequently the polymerization of the system was induced upon obtaining long-range uniaxial orientation of the molecules in the nematic state. In this way highly oriented networks were obtained. These anisotropic networks showed temperature-stable optical properties. Thermo-mechanical properties were found also to be anisotropic and highly dependent on relaxation mechanisms effective within the networks.

(Keywords: divinyl ether; liquid crystal; photopolymerization; anisotropic network; birefringence; modulus; thermal expansion)

INTRODUCTION

In situ photopolymerization of liquid-crystalline (LC) diacrylates has been shown to lead to the formation of anisotropic networks with a range of anisotropic properties[1–5]. The technique of *in situ* photopolymerization involves the macroscopic orientation of low-molar-mass LC molecules and subsequent initiation of polymerization to form a three-dimensional network. In the case of anisotropic networks obtained by photopolymerization of LC diacrylates, it was shown that the polymerization proceeded at a high rate, leading to a high degree of conversion of the acrylate groups. Using homologous series of LC diacrylates it was shown that the optical[3] and thermo-mechanical[5] properties of the network could be adjusted by varying the length of the flexible spacer between the rigid central unit and the acrylate end groups, and by varying the structure of the rigid central unit. Substitution of a methyl group on the rigid unit was also studied. Recently the mobility within anisotropic networks formed by photopolymerization of binary mixtures of mono- and diacrylates was studied[4] using dielectric spectroscopy, i.r. dichroism and refractive index measurements, showing that the glass transition temperature and other properties of the network depended to a large extent on the crosslink density within the system. Furthermore the use of LC diacrylates in the formation of anisotropic gels and plasticized networks was also shown[6]. These novel systems are formed by photopolymerization of mixtures of LC diacrylates and low-molar-mass conventional LC molecules, leading to the formation of a three-dimensional anisotropic network containing free molecules. These materials can be used in various ways for display applications[7].

Apart from photoinduced free-radical polymerization of acrylates, photoinduced cationic polymerization can also be used. LC diepoxides have been polymerized to form ordered crosslinked networks[8]. The photoinduced *in situ* cationic polymerization of LC monovinyl ethers to form side-chain LC polymers has also been described[9]. Here we describe the synthesis of two LC divinyl ethers **1a** and **1b**, which can be photopolymerized cationically to form anisotropic networks. The properties of the molecules in the nematic state and after polymerization will also be given.

EXPERIMENTAL

Monomer synthesis

The synthetic routes to monomers **1a** and **1b** are outlined in *Scheme 1.*

6-Chlorohexyl vinyl ether (**3**). This compound was made in 44% yield from 6-chlorohexanol and ethyl vinyl ether according to the method of Watanabe *et al.*[10]. It was purified by elution over alumina with CH_2Cl_2 followed by distillation (b.p. = 104–106°C at 21 mmHg).

4-(6-Vinyloxyhexyloxy)benzoic acid (**4**). A solution of 5.0 g of ethyl 4-hydroxybenzoate, 1.6 g of sodium methanolate, 0.6 g of NaI and 4.1 g of 6-chlorohexyl vinyl ether (**3**) in 25 ml of 2-butanone was boiled for 16 h. After evaporation of the 2-butanone, 50 ml of diethyl ether and 50 ml of water were added. After separation, the organic layer was extracted twice with 25 ml of 5% NaOH solution. After evaporation of the ether, a solution of 30 mmol of KOH in 80 ml of 30% ethanol was added and the mixture was boiled until a clear solution was obtained. After cooling to about 0°C, the solution was

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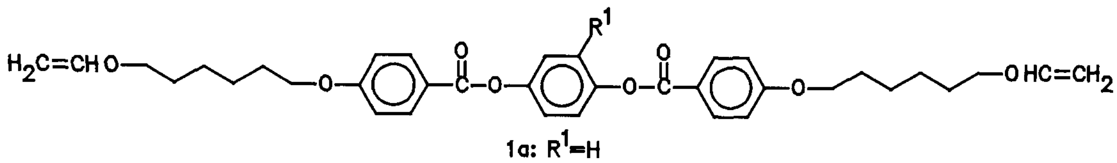
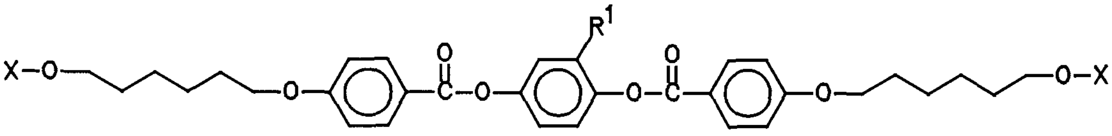


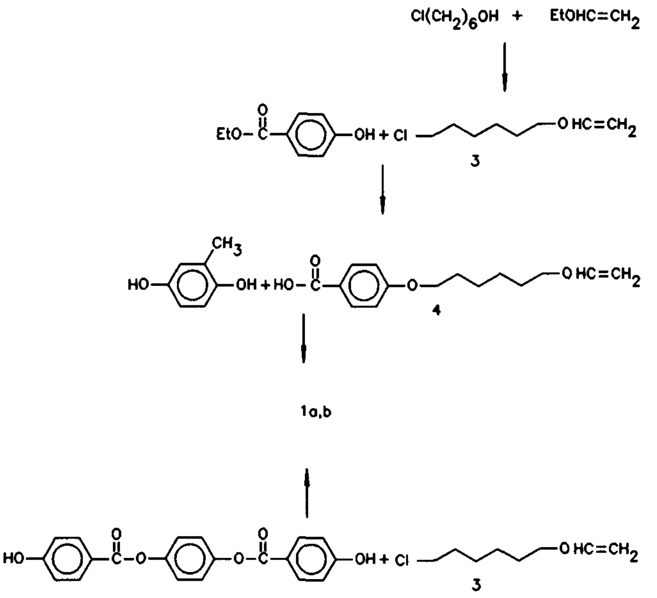
1a: R^1=H
1b: R^1=CH_3.

Table 1 Transition temperatures and enthalpies of the LC divinyl ethers **1a** and **1b**, and corresponding diacrylates **2a** and **2b**



	X	R^1	T_m (°C)	T_c (°C)	ΔH_c ($kJ\,mol^{-1}$)
1a	CH_2=CH	H	110	194	1.94
1b	CH_2=CH	CH_3	87	148	2.13
2a[a]	CH_2=CHCO	H	108	155	0.92
2b[a]	CH_2=CHCO	CH_3	86	116	1.60

[a] Data from ref. 3



Scheme 1 Synthetic routes to divinyl ethers **1a** and **1b**

acidified carefully with 27 mmol of HCl in about 25 ml of water. The precipitated acid was collected by filtration and washed thoroughly with 50 ml of water. After drying over SiO_2 under vacuum, 4.7 g of **4** (71%) was obtained as a white powder, which was ^1H n.m.r. pure (80 MHz).

1,4-Di-[4-(6-vinyloxyhexyloxy)benzoyloxy]benzene (**1a**). A mixture of 3.0 g of 1,4-di-(4-hydroxybenzoyloxy)-benzene[11], 2.7 g of K_2CO_3, 1.0 g of NaI and 3.1 g of 6-chlorohexyl vinyl ether (**3**) in 50 ml of 2-butanone was boiled for 60 h. The warm solution was filtered, evaporated and the residue was dissolved in 25 ml of CH_2Cl_2. This solution was filtered and eluted over SiO_2 with a 5:95 (v/v) mixture of ethyl acetate and CH_2Cl_2. Subsequently, 3 g of **1a** (58%) was obtained as white needles after crystallization from ethanol. Its ^1H n.m.r. spectrum (80 MHz) is in accordance with its structure. Its transition temperatures are shown in *Table 1*.

1,2-Di[4-(6-vinyloxyhexyloxy)benzoyloxy]-2-methylbenzene (**1b**). To a boiling mixture of 2.6 g of 4-(6-vinyloxyhexyloxy)benzoic acid (**4**), 0.6 g of 2-methylhydroquinone and 0.1 g of 4-*N*,*N*-dimethylamino-pyridine in 20 ml of CH_2Cl_2 is added slowly a solution of 2.3 g of *N*,*N*-dicyclohexylcarbodiimide in 10 ml of CH_2Cl_2. After boiling for another 3 h, the mixture was cooled, filtered and evaporated. Some 0.7 g of pure **1b** (23%) was obtained as described above for **1a**.

Physical measurements and polymerization procedures

^1H n.m.r. spectra were obtained with a Bruker WP-80 spectrometer. Transition temperatures and the enthalpies and the polymerization kinetics of the monomers were determined using a Perkin–Elmer DSC-2C provided with a u.v. source ($0.2\,mW\,cm^{-2}$). In the d.s.c. experiments sample quantities of 5 mg were used under a nitrogen atmosphere. The optical properties of the materials were studied using a polarizing microscope provided with a rotary compensator and a Mettler heating stage. Cells with a gap of about 6 μm provided with uniaxially rubbed polymer layers were filled with the LC material in order to obtain uniaxially aligned samples. For the refractive index measurements an Abbe refractometer that could be thermostated up to 140°C was used. For the infra-red measurements a Bruker IFS45 *FT*i.r. spectrometer equipped with a wire grid polarizer was used. Uniaxially oriented samples for i.r. measurements were obtained between KBr plates provided with uniaxially rubbed nylon layers. In order to initiate polymerization, the LC monomeric divinyl ethers were provided with 1% w/w Irgacure 651 (Ciba Geigy) and 1% w/w diphenyliodonium tetrafluoroborate. In some cases, in order to prevent thermal polymerization, small amounts of 4-methoxyphenol were also added to the systems.

Upon polymerization in the cells free-standing films were produced after removal of the glass substrates. Dynamic mechanical thermal analysis of the polymerized films was carried out using Polymer Laboratories d.m.t.a. equipment in the tensile mode.

RESULTS AND DISCUSSION

Synthesis and properties of the monomers

Scheme 1 outlines the synthetic routes to **1a** and **1b**. Owing to the fact that the formation of an acid chloride out of **4** is not compatible with the vinyl ether functionality, esterification of **4** with hydroquinone and 2-methylhydroquinone was tried with the aid of *N,N*-dicyclohexylcarbodiimide[12] to form **1a** and **1b**, respectively. In the case of **1a** only very low yields could be obtained with this method, which made it impossible to purify this compound. However, **1b** could be obtained in 23% yield in this way. Compound **1a** could be obtained in 58% yield by alkylation of 1,4-di-(4-hydroxybenzoyloxy)benzene in a procedure similar to that described for the formation of 1,4-di-(4-hexyloxybenzoyloxy)benzene[13].

D.s.c. heating and cooling scans of **1a** and **1b** are shown in *Figure 1*. The transition temperatures and enthalpies of these molecules together with those of their acrylate counterparts **2a** and **2b** are shown in *Table 1*. When the transition temperatures of the monomers **1a** and **1b** are compared, it can be seen that the transition temperatures for **1a** are higher than those for **1b**. The same behaviour is observed for monomers **2a** and **2b**, which contain acrylate groups instead of vinyl ether groups. This effect is associated with the disturbance of the packing of the molecules with a methyl group attached to the central rigid unit. It is also interesting to compare vinyl ethers **1a** and **1b** with their acrylate counterparts **2a** and **2b**, respectively. In both cases the acrylates and the vinyl ethers melt around the same temperature, while the isotropic transition temperatures (T_c) of the vinyl ethers are almost 40°C higher than those of their acrylate analogues. This behaviour is associated with the bulkiness of the acrylate groups as opposed to the smaller vinyl ether groups. However, the change in the polarity and the conformation may also contribute to the observed behaviour. It will become more clear later in the text that the increase in T_c also results in the increase of the anisotropic properties at a given temperature.

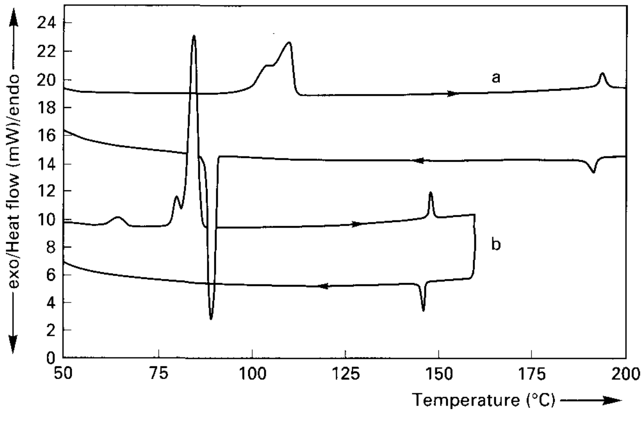


Figure 1 D.s.c. scans of **1a** (curve a) and **1b** (curve b)

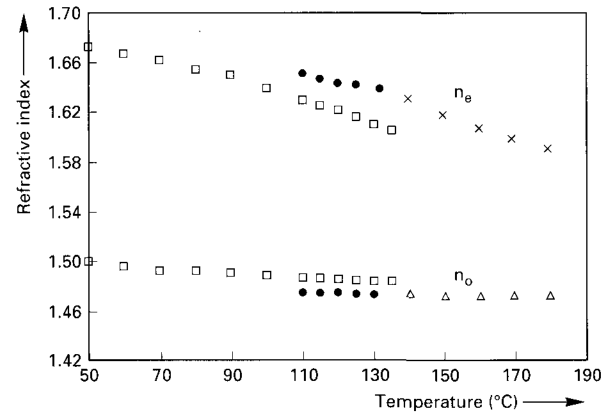


Figure 2 Refractive indices of **1a** (●) and **1b** (□) determined with the refractometer, and **1a** (×, △) estimated from birefringence

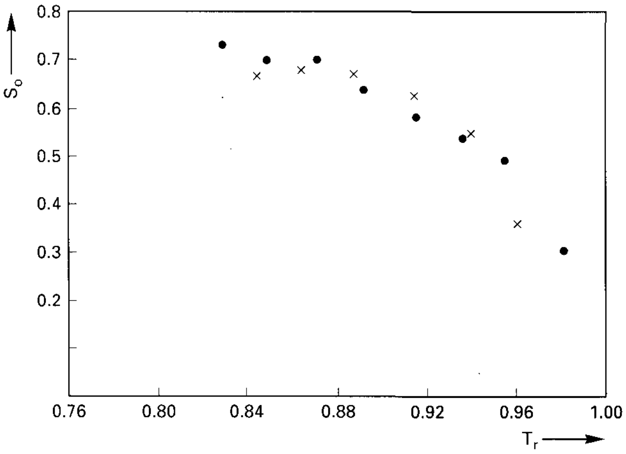


Figure 3 Order parameter of **1a** (●) and **1b** (×) as a function of reduced temperature

In *Figure 2* the refractive indices of **1a** and **1b** are plotted as a function of temperature. In the case of **1b** both the ordinary (n_o) and the extraordinary (n_e) refractive indices were measured directly using the refractometer. It shows a common behaviour for nematics, where n_o remains almost constant as a function of temperature, while n_e decreases with increasing temperature. We have directly measured the refractive indices of **1a** only, using the refractometer up to 140°C. Above this temperature we assumed n_o to be constant and estimated n_e from the measured values of birefringence for the material. It can be seen that at given temperatures the n_e of **1a** is higher than that of **1b**, whereas the n_o shows the opposite behaviour. These effects are associated with the order parameters of LC molecules. In order to estimate the order parameter of the systems, i.r. dichroism was used. The quantity S_0, related to the order parameter S, is given by[14]:

$$S_0 = \frac{\varepsilon_{\parallel} - \varepsilon_{\perp}}{\varepsilon_{\parallel} + 2\varepsilon_{\perp}} = S(1 - 3/2 \sin^2 \theta) \qquad (1)$$

where $\varepsilon_{\parallel}$ and $\varepsilon_{\perp}$ are the extinctions measured with the i.r. beam polarized in the direction parallel and perpendicular to the director of the uniaxially oriented system, respectively; θ is the angle between the direction of the molecular orientation and the vibrational transition moment. In *Figure 3*, S_0, which is estimated from the aromatic vibrations at 1580 cm^{-1}, is shown as a function of the reduced temperature T_r ($= T/T_c$). Within

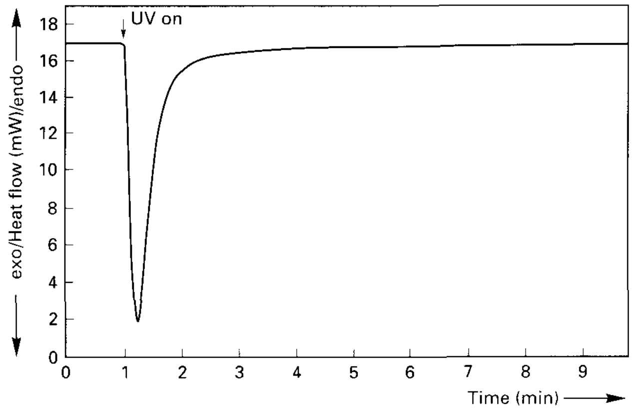


Figure 4 Heat of polymerization for **1b** as a function of time at 100°C

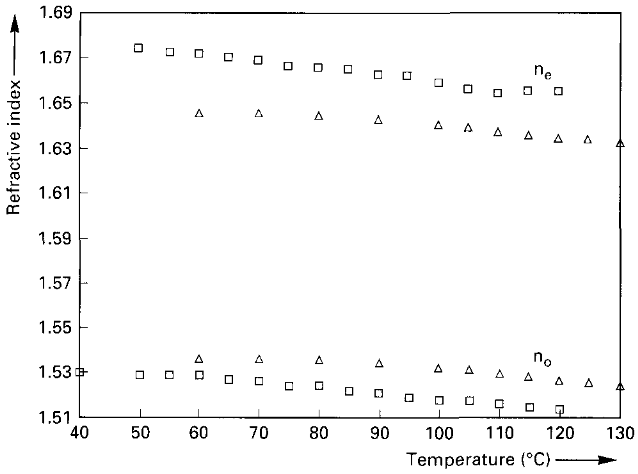


Figure 5 Refractive indices as a function of temperature for networks formed from **1b** produced at 100°C (□) and at 135°C (△)

the experimental error, S_0 has the same value for both **1a** and **1b**. In return, the refractive indices of the compounds are nearly equal when compared at the same T_r.

Formation and properties of the anisotropic networks

Before describing the properties of the networks it is appropriate to describe the polymerization behaviour of the monomers as recorded by d.s.c. In the case of **1a** it was found that already during the heating of the samples (i.e. containing the initiator) in the d.s.c. above their melting temperature early thermal polymerization was induced around the melting temperature of the sample. Therefore it was not possible to align the sample to form a monodomain before polymerization. As the melting temperature of **1b** is lower, the sample could be heated up to 100°C and the polymerization could be photochemically induced without the problem of early polymerization. In *Figure 4* the heat of reaction for **1b** is plotted as a function of time. The reaction starts as soon as the u.v. light is turned on and it is completed within about 2 min. Using the value of 60 kJ $\mathrm{mol^{-1}}$ for the polymerization of vinyl ether groups[15], the conversion of these groups was calculated to be more than 90%. This conversion is quite similar to the values obtained for the acrylate groups of LC diacrylates **2a** and **2b** polymerized by a radical mechanism[1]. As the polymerization of **1a** was not possible in a controllable way, we could only study the properties of networks obtained from **1b**.

Compound **1b** was polymerized at two different temperatures (after alignment at 100°C) and the optical properties of the anisotropic poly(vinyl ether) networks were investigated. In *Figure 5* the refractive indices of the networks formed at 100 and 135°C are shown as a function of temperature. The network formed at 135°C has higher values for n_o, whereas the values of n_e are lower. This indicates that the network obtained at 100°C has a higher order parameter than the network obtained at 135°C. This is associated with the initial order parameter of the system in the monomeric state, as shown in *Figure 3*. Furthermore it can be seen that the refractive indices decrease with increasing temperature. This behaviour is partly due to the decrease in the density caused by thermal expansion and partly due to the decrease in the order. To estimate the order parameter S_0, i.r. dichroism was used together with the refractive index measurements. The order parameter S_0 is related to the refractive indices as[16]:

$$S_0=\frac{C(n_e^2-n_o^2)}{(n_e^2+n_o^2-3)} \tag{2}$$

where C is a constant associated with the polarizability of the molecules. In *Figure 6*, S_0 obtained from i.r. and the refractive index measurements are shown as a function of temperature. The S_0 of the network formed at 100°C is indeed higher than that formed at 135°C. Furthermore in both cases the decrease in the order parameter with increasing temperature is small, showing the stability of the networks. It is also interesting to compare the order parameters in the monomeric state and after polymerization. In the case of 100°C there is almost no change in S_0 upon polymerization. At 135°C, however, S_0 increases considerably, showing that the degree of molecular orientation increases upon polymerization.

A network formed from **1b** at 100°C was used for the thermo-mechanical measurements. In *Figure 7* the tensile modulus of the sample is shown together with the loss tangent (tan δ) measured at 1 Hz as a function of temperature. Here, as also observed for anisotropic acrylate networks, three tan δ peaks are visible[5]. In order of decreasing temperature they are called α, β and γ

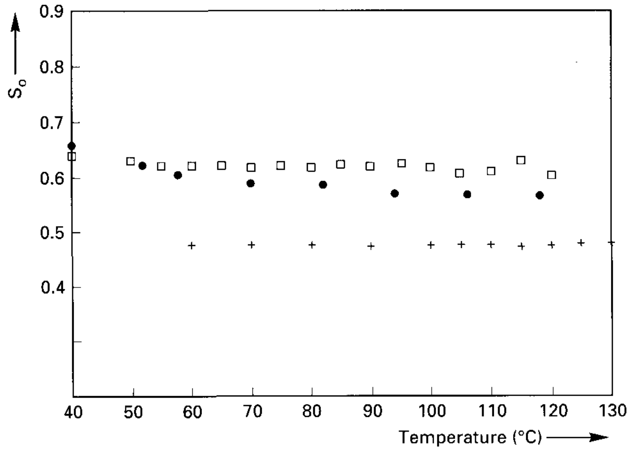


Figure 6 Order parameters estimated for the network formed from **1b** produced at 100°C (□) and at 135°C (+) determined with the refractometer, and produced at 100°C (●) determined from i.r. measurements

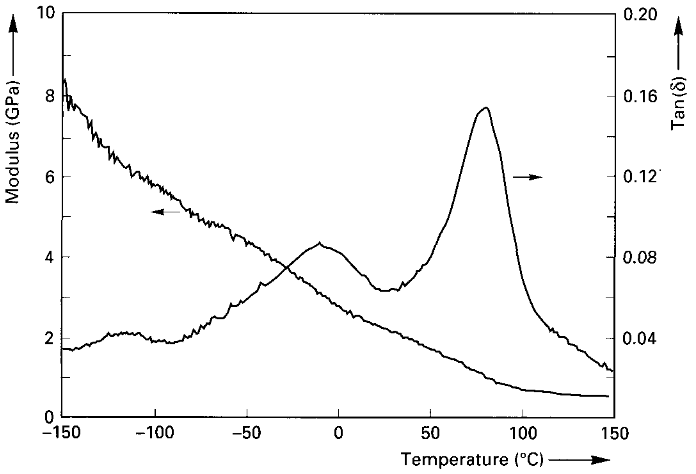


Figure 7 Loss tangent and tensile modulus of an anisotropic network formed from **1b** produced at 100°C, measured along the director

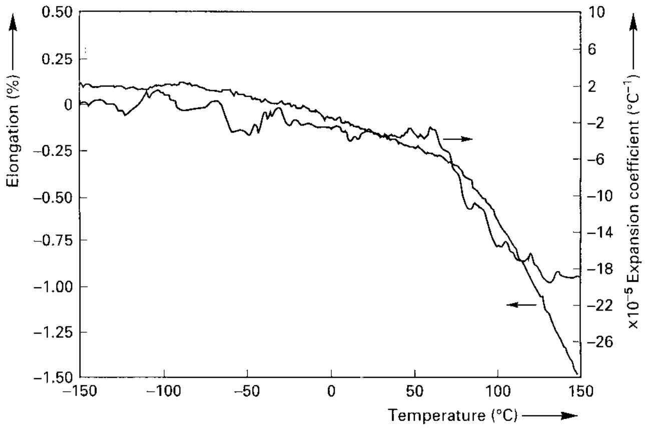


Figure 8 Thermal expansion and expansion coefficient of an anisotropic network formed from **1b** produced at 100°C, measured along the director

relaxations. The γ and β peaks are associated with the crankshaft motion of the methylene spacer and motion of the central rigid unit, respectively. They appear at about the same positions as observed for anisotropic polyacrylate networks formed from **2b**. The α relaxation is related to the relaxation of the network. It has been shown to be associated with the density of crosslinks[4,5]. Here the position of the α peak was found to be around 80°C, which is almost the same as the value observed[5] for the polyacrylate network formed from **2b**. However side-chain LC polymers with stiff acrylate backbones are known to have higher glass transition temperatures than the more flexible vinyl polymers[17]. Thus, the fact that both networks formed from divinyl ether **1b** and diacrylate **2b** have the same transition temperature indicates that the network density is a more important parameter than the polymer backbone in determining the relaxation of the network. *Figure 7* shows also that the modulus decreases very rapidly with increasing temperature up to the γ transition. In the rubbery state the network retains some of its modulus due to the crosslinks, showing the importance of secondary relaxations within the system. Finally, in *Figure 8* the thermal expansion of the anisotropic vinyl ether network in the direction of molecular orientation is shown as a function of temperature. In this figure the influence of various relaxation processes on the thermal contraction behaviour of the anisotropic network can be seen. The sample shows almost no expansion up to −100°C, corresponding to the end of the γ relaxation. From this temperature up to 70°C, corresponding to the span of the β relaxation, it contracts, and the coefficient of contraction in this range is about 20 ppm/°C. Above the α relaxation the sample starts to contract rapidly and the coefficient of contraction reaches the value of 180 ppm/°C. Contraction with increasing temperature in the direction of molecular orientation is a well known phenomenon in oriented polymeric systems[18]. Here the effect on this contraction of various relaxations within the system is also clearly shown.

CONCLUSIONS

Anisotropic networks were obtained by *in situ* cationic polymerization of LC vinyl ethers. The thermal instability of the polymerization initiator may cause problems in obtaining completely aligned samples at higher temperatures. The networks obtained by this method showed anisotropic optical and thermo-mechanical properties. The anisotropic optical properties remained even at elevated temperatures. The thermo-mechanical properties of the networks were found to be very dependent on the relaxation processes within the networks. The tensile modulus showed a sharp increase below the secondary relaxation temperature. The main relaxation peak associated with the network relaxation appeared at about the same position as that observed for an analogous acrylate network, demonstrating the importance of the network density as opposed to the main-chain flexibility. Finally, the anisotropic networks contracted in the direction of molecular orientation at different rates in different temperature regions, showing a relation between the relaxation processes and the thermal contraction.

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