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Thermal reversibility of ordered, photocrosslinked liquid crystalline poly(vinyl ether)s

F. Sahlén, H. Andersson, A. Hult and U. W. Gedde*
Department of Polymer Technology, Royal Institute of Technology, S-100 44 Stockholm, Sweden

and F. Ania
Instituto de Estructura de la Materia, Consejo Superior de Investigaciones Cientificas, Calle Serrano, 119-123, E-28006 Madrid, Spain
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Anisotropic networks were prepared by photoinitiated cationic bulk polymerization of aligned liquid crystalline mixtures of mono- and bifunctional vinyl ethers. The thermal reversibility of the macroscopic order of the networks was assessed by infra-red spectroscopy measuring the dichroic ratio of the oriented samples at different temperatures between 20°C and 200°C. The order parameter gradually decreased with increasing temperature and the relative reduction decreased with increasing crosslink density. For systems showing smectic mesophase transitions, the decrease in order parameter was concentrated in the transition temperature ranges. The almost complete recovery of alignment after cooling to 20°C was due to the network character of these polymers. A permanent loss in order parameter of about 15% after the first heating and cooling cycle was recorded. This was attributed to a thermally induced polymerization occurring during the first heating scan. Copyright © 1996 Elsevier Science Ltd.

(Keywords: liquid crystalline polymers; poly(vinyl ether)s; crosslinking)

INTRODUCTION

Oriented polymers exhibit anisotropic mechanical and optical properties. Liquid crystalline (LC) materials possess the intrinsic property, on a microscopic level, of directing the mesogenic groups along a common so-called director[1]. An external field of a mechanical, electrical, magnetic or surface nature[2] may orient the microdomain directors along a director common to an entire macroscopic sample. A necessary condition for a material to exhibit non-linear optical (chi-2) properties is that the material should have a high degree of orientation[2]. Polymers prepared for this application must thus be initially highly oriented and they must retain their orientation on storage at ambient or elevated temperatures. The degree of orientation of a globally oriented LC polymer may decrease with increasing temperature. There is thus a need to stabilize or make permanent the orientation in this class of polymer. This has mainly been accomplished in two different ways: (1) by synthesis of LC polymers with a high glass transition temperature[3], in which case the orientation is retained at temperatures below the glass transition temperature; and (2) by crosslinking LC bifunctional monomers[4] or side-chain LC polymers (SCLCP)[5]. Both methods have been used to thermally stabilize main-chain and side-chain polymers for non-linear optically active materials[6,7], where the alignment of the chromophores is crucial for the non-linear optical response. Lightly and densely crosslinked SCLCPs, with, for example, siloxane, acrylate or vinyl ether backbones, have been synthesized. Siloxanes that are slightly crosslinked give elastomeric properties[8], whereas densely crosslinked acrylates[9] and vinyl ethers[10-12] are used in making thin films. Recently, new bifunctional crosslinkable LC vinyl ether monomers have been synthesized[13]. These monomers have been used in this study. The order parameter of aligned SCLCPs and crosslinked SCLCPs has previously been determined mostly by measurement of birefringence[14], infra-red dichroic ratio[15-18] and X-ray scattering[19].

This paper presents data for macroscopically oriented, photocrosslinked liquid crystalline poly(vinyl ether)s on mesogenic group orientation as a function of temperature. The order parameter was obtained from infra-red dichroic ratio data. Films of different degrees of crosslinking were prepared from a series of mixtures of monofunctional and bifunctional LC vinyl ether monomers.

EXPERIMENTAL

Monomers and initiators

The monomers, 4-[11(vinyloxy)undecyloxy]-4-ethoxyphenylbenzoate, 4-[11-(vinyloxy)undecyloxy]-4-[2-(vinyloxy)ethyloxy]phenylbenzoate, and 4-[11(vinyloxy)undecyloxy]-

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* To whom correspondence should be addressed

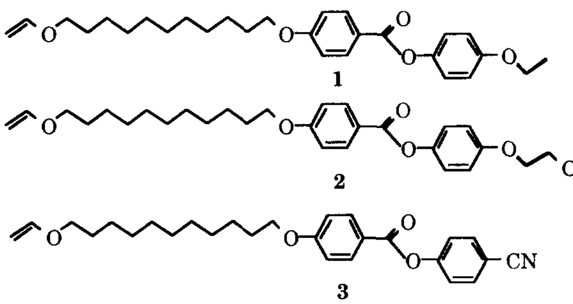

Figure 1 Liquid crystalline vinyl ether monomers **1**, **2** and **3**

Table 1 Thermal data of studied monomers and polymers[a]

Compounds	Thermal transitions[b] (°C) Heating	Cooling
1	k66n76i	i70n59s_A28k
2	k64s_A66n70i	i66n63s_A48s_B25k
3	k68i	i64n50k
poly(**1**)	g37s_B66s_A134i	i123s_A57s_B31g
poly(**2**)	smectic polymer network[c]	
poly(**3**)	g37s_C65s_X76s_A154i	i150s_A40s_C37g

[a] Data refer to first cooling and second heating scans

[b] g, glass; k, crystalline; s_B, smectic B; s_A, smectic A; n, nematic; i, isotropic

[c] Polymerization from the nematic and smectic A phases of the monomer resulted in smectic A polymer network structures, whereas polymerization from the smectic B phase of the monomer resulted in a smectic B polymer network structure, see ref. 13

4-cyanophenylbenzoate, designated **1**, **2** and **3** respectively, were synthesized as reported elsewhere[13,20,21]. Their chemical structures are shown in *Figure 1* and their thermal characteristics are shown in *Table 1*.

The assessments of the liquid crystalline phases of the monomers were made by X-ray diffraction on aligned samples, polarized light microscopy and differential scanning calorimetry (d.s.c) in accordance with refs 13 and 20. Phenacyltetramethylenesulfonium hexafluoroantimonate was used as photoinitiator for the ultraviolet photopolymerizations, and phenothiazine was used as photosensitizer. The initiator was synthesized according to a procedure described in ref. 22 and the photosensitizer was obtained from Aldrich.

Sample preparation and analysis methods

The initiator was added to a mixture of monofunctional and bifunctional monomers as a dilute CH_2Cl_2 solution. The monomer–initiator blend was then dissolved in CH_2Cl_2 and thoroughly mixed while the solvent was allowed to evaporate. The resulting solid mixture was then dried in a vacuum oven overnight. The molar ratios of monofunctional-to-bifunctional monomer 100:0, 90:10, 80:20, 60:40, 20:80 and 0:100, which gave polymers with different degrees of crosslinking. The samples are referred to as 0, 10, 20, 40, 80 and 100% (mol/mol) of bifunctional monomer. The monomer-to-initiator molar ratio was in all cases 250:1 (mol/mol).

All monomer mixtures were photopolymerized in a Mettler FP-82 hot-stage under isothermal conditions. The monomer–initiator mixtures were heated above the isotropization temperature and cooled to the nematic phase at reduced temperatures, T_r (polymerization temperature/isotropization temperature (T_p/T_i), both given in K) of 0.96–0.99, prior to the polymerization. *Figure 2* shows the phase diagram, recorded on cooling, of the different mixtures of monomers **1** and **2**. The polymerization temperature is indicated by a broken line.

To make samples suitable for infra-red dichroic measurements, the monomers were photopolymermized between two KBr pellets. The pellets were coated with a polyimide film on the inside which was uniaxially rubbed to induce orientation of the monomers. Photopolymerization of the monomers in an oriented state resulted in oriented polymer films. The infra-red dichroic measurements were carried out on a Perkin-Elmer 1760X Fourier transform infra-red spectrometer equipped with a Perkin-Elmer KRS-5 infra-red polarizer. Infra-red spectra of the samples were recorded between room temperature and 200°C. The KBr cells containing the oriented films were mounted in a PID-controlled resistive oven. The oven was then placed in the sample compartment of the infra-red spectrometer in line with an infra-red polarizer which could be rotated through 360° to change the polarization angle. The order parameters of the samples were calculated on the basis of the recorded spectra while the temperature was raised by 10°C increments to 200°C. The samples were then cooled in the same manner. Each temperature measurement was made after a 5 min wait, assuming that temperature equilibrium had then been established. The heating and cooling rates were 2°C min^{-1}, and the samples were exposed to 10 consecutive heating and cooling cycles. The liquid crystalline phases and phase transition temperatures were determined by a differential scanning calorimeter (Perkin-Elmer DSC-7, scanning rate 10°C min^{-1}). Small-angle X-ray scattering (SAXS) patterns of different liquid crystalline phases were recorded on a Statton camera equipped with a resistive oven, using CuKα radiation generated by a Philips PW 1830 generator. A polarized light microscope (Leitz Ortholux POL BK II equipped with a Mettler hot-stage FP-82) was used for textural and thermal characterizations and an OSRAM Ultra-Vitalux lamp (300 W) served as ultraviolet source for the photopolymerizations. Dynamic

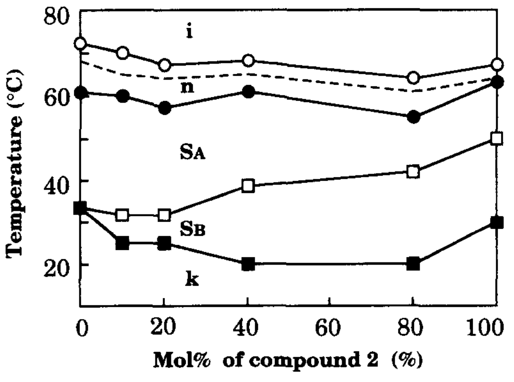

Figure 2 Phase diagram, obtained on cooling from the isotropic (i) state of mixtures of monomers **1** and **2** showing nematic (n), smectic A (s_A), smectic B (s_B) and crystalline (k) phases. All polymerizations were carried out from the nematic phase at the temperature represented by the broken line

mechanical measurements were carried out on a Polymer Laboratories dynamic mechanical thermal analyser at a frequency of 1 Hz.

RESULTS AND DISCUSSION

The order parameter, s, is obtained from the dichroic ratio R, i.e. the ratio of the absorbance of radiation with the electrical field parallel to ($A_{\parallel}$) and perpendicular to ($A_{\perp}$) the director:

$$s = \left[\frac{2}{3\cos^2\delta - 1}\right]\left[\frac{R-1}{R+2}\right] \tag{1}$$

where δ represents the angle between the mesogenic group long axis and the transition moment[17]. In this work, the absorption at 1510 cm^{-1} representing the transition moment of the asymmetric vibration of the *para*-substituted benzene ring[23] (C=C) has been used. The transition moment of the cyano stretching vibration at 2230 cm^{-1} of compound **3** is known to be parallel to the cyano group[15], and thus to be mainly parallel to the long molecular axis of the outer phenyl group of the mesogen. To determine whether the transition moment at 1510 cm^{-1} and 2230 cm^{-1} was mainly parallel to the long axis of the mesogen, a copolymer of monomers **1** and **3** (1 : 1 molar ratio) was made. The monomer mixture was polymerized from the nematic phase, at 70°C, forming a network with s_A organization. The absorption of polarized infra-red radiation by copoly(**1**/**3**) at 1510 cm^{-1} and 2230 cm^{-1} exhibited a similar polarization angle dependence, with clear maxima and minima in both cases at the same polarization angles (*Figure 3*). A comparison of the dichroic ratios obtained for the two absorption bands indicates that the angle between the transition moment vectors is close to 8°. Thus the two stretching vibrations have similar angles between the transition moment vectors and the long axis of the mesogenic groups.

For simplicity, it has been assumed that the angle δ is zero and equation (1) then simplifies to:

$$s = \left[\frac{R-1}{R+2}\right] \tag{2}$$

The order parameter calculated from equation (2) can be considered as an order parameter for the actual groups involved in the vibration. The order parameter adopts values between −0.5 and 1, where the limiting values are associated with, respectively, perpendicular and parallel alignment along the director. In practice, however, with a δ angle deviating slightly from zero, the range of the order parameter becomes less extensive.

The structures of compounds **1** and **2** used in this study are described in *Figure 1*, and data for the thermal characterization are presented in *Table 1*. Monomer **1** showed enantiotropic nematic and monotropic smectic A LC phases, whereas monomer **2** showed enantiotropic nematic, smectic A and smectic B LC phases. No signs of phase separation were observed in the mixtures of monomers **1** and **2**. The mixtures of **1** and **2** showed enantiotropic nematic, smectic A and smectic B mesophases where the temperature ranges of the different phases depended on the compositions (*Figure 2*). Photopolymerization of the monomer blends from the nematic phase yielded polymers with smectic A mesomorphism. The structural assignment was based on data obtained by polarized light microscopy and X-ray scattering. The absorbance spectra of the polymer containing 20% bifunctional monomer obtained using infra-red light polarized perpendicular to and parallel to the main director of the mesogenic groups are shown in *Figure 4*. Infra-red bands with transition moment vectors parallel to the mesogenic long axis, e.g. the C=C stretch appearing at 1510 cm^{-1}, show the strongest absorption of the parallel polarized infra-red light, whereas infra-red bands with transition moment vectors perpendicular

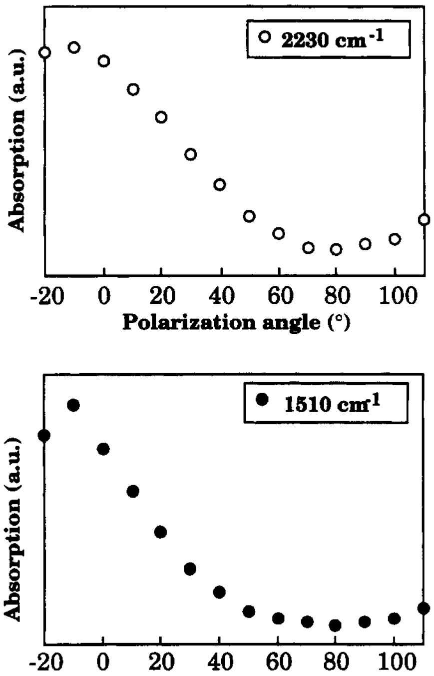

Figure 3 The infra-red absorbance at 1510 cm^{-1} and 2230 cm^{-1} as a function of the polarization angle of the incident infra-red light for poly(**1**/**3** (50/50))

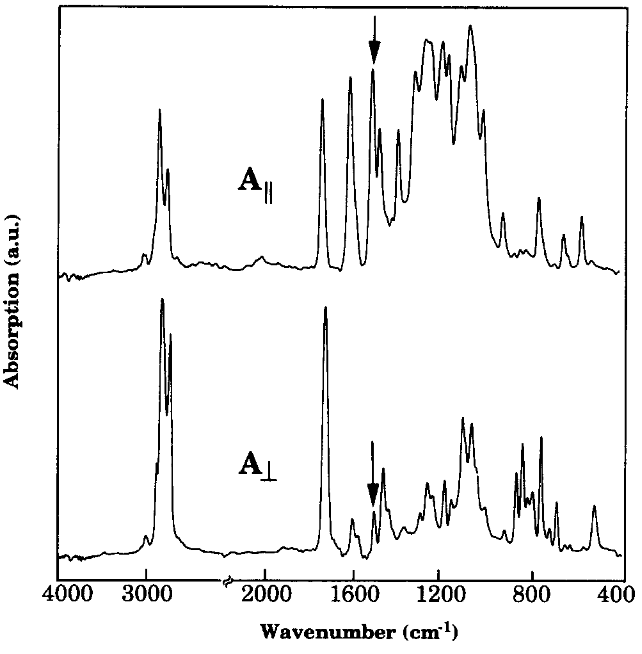

Figure 4 Infra-red spectra for aligned poly(**1**/**2**) (20 mol% of **2**) using polarized infra-red parallel to ($A_{\parallel}$) and perpendicular to ($A_{\perp}$) the director. The absorption band at 1510 cm^{-1} is indicated by arrows

to the mesogenic long axis, e.g. the carbonyl stretch at 1744 cm^{-1}, show the strongest absorption for infra-red light polarized in the perpendicular direction.

Infra-red dichroic absorption spectra of the samples were obtained between 23°C and 200°C. The absolute values of the order parameter did not appear to be exactly the same for different samples prepared with the surface alignment technique. Based on the absorbance value at 1510 cm^{-1} in *Figure 4*, the order parameter of the sample with 20% bifunctional monomers at 23°C was, according to equation (2), equal to 0.52. To compare the changes in the order parameter values among the samples, the values were normalized. The order parameter at 23°C was set to unit (s_0) and the variation in order parameter with temperature is given with reference to this initial value (s/s_0). *Figure 5* shows a graph where the normalized order parameters are plotted *versus* temperature for samples with different crosslink densities. The graph represents the first heating and cooling cycle of the samples.

The normalized order parameter of poly(**1**) decreases very strongly (transitional) at 60°C and then more gradually with increasing temperature and approaches zero at 130°C. The transitional drop in order parameter coincides with the transition from smectic B to smectic A phase and the final establishment of isotropy with the isotropization temperature at 130°C as obtained by d.s.c. This polymer remained globally non-oriented on cooling. The polymer with 10% bifunctional monomer also exhibited a transitional decrease in order parameter at 60°C, again associated with the smectic B to smectic A transition, and it reached an isotropic state ($s = 0$) at 150°C. When the sample was cooled, the order parameter increased gradually with decreasing temperature. A transitional change in order parameter occurred in this particular sample at 70°C, again consistent with the temperature for the smectic A to smectic B phase transition (*Figure 5*). Thus, the introduction of 10% of crosslinks is sufficient to yield thermal reversibility of the order parameter. Samples with 40 mol% or more of the bifunctional monomer also preserved their mesophase at very high temperatures, i.e. the isotropic phase was never reached (*Figure 5*). These samples showed a gradual decrease in order parameter with increasing temperature. These samples showed no first order phase transition as revealed by d.s.c. (*Figure 6*), in sharp contrast to the behaviour of polymers with a lower content of crosslinks (10 mol% of **2**). The latter showed two phase transitions, i.e. from smectic B to smectic A at 58°C and from smectic A to isotropic phase at 133°C. Each phase transition caused a pronounced change in order parameter. About 10% of the mesogens need to be crosslinked in order to achieve recovery of the alignment on cooling. Introduction of 10 mol% of **2** in poly(**1**) caused a slight shift in the s_B–s_A transition towards lower temperatures whereas the isotropization temperature remained unchanged. The transition enthalpies associated with s_B–s_A and s_A–I were slightly lower in poly(**1**/**2**) than in poly(**1**); 3.9 and 4.0 kJ mol^{-1} compared to 4.7 and 4.5 kJ mol^{-1}, respectively. The smectic phase was permanent in polymers with more than 20 mol% of bifunctional monomers and none of the first order phase transitions was visible by d.s.c.

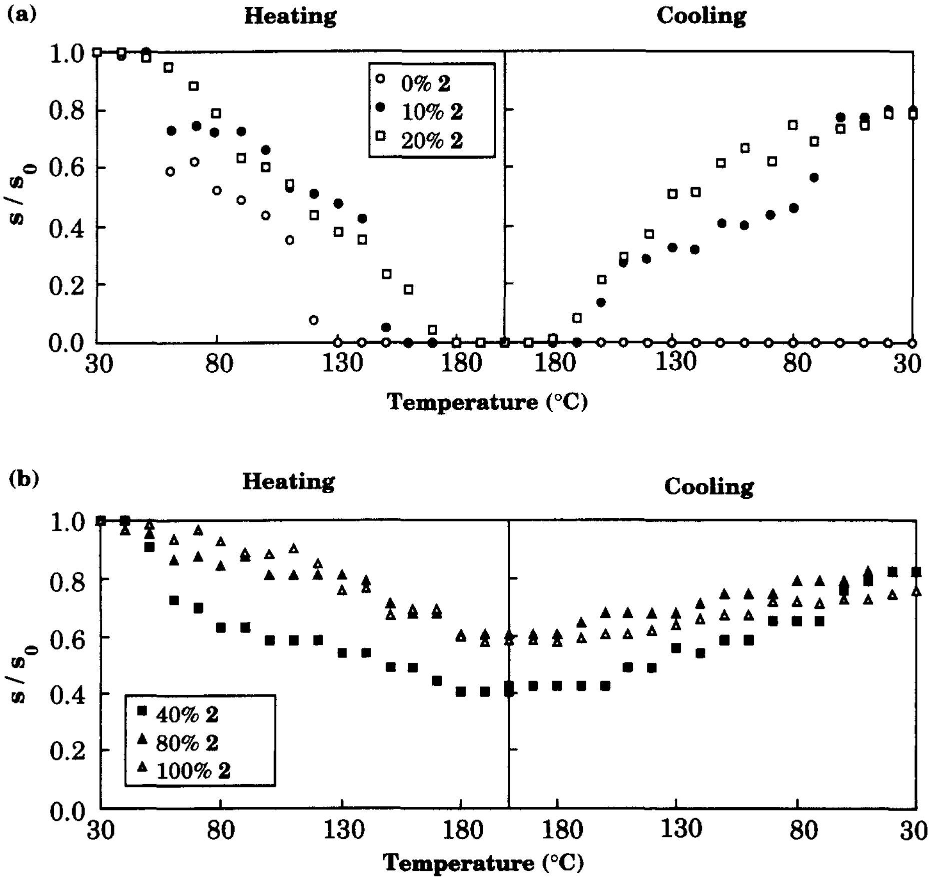

Figure 5 Normalized order parameter (s/s_0) as a function of temperature for: ○, poly(**1**); ●, poly(**1**/**2**) of molar ratio 90:10; □, poly(**1**/**2**) of molar ratio 80:20; ■, poly(**1**/**2**) of molar ratio 60:40; ▲, poly(**1**/**2**) of molar ratio 20:80; and △, poly(**2**)

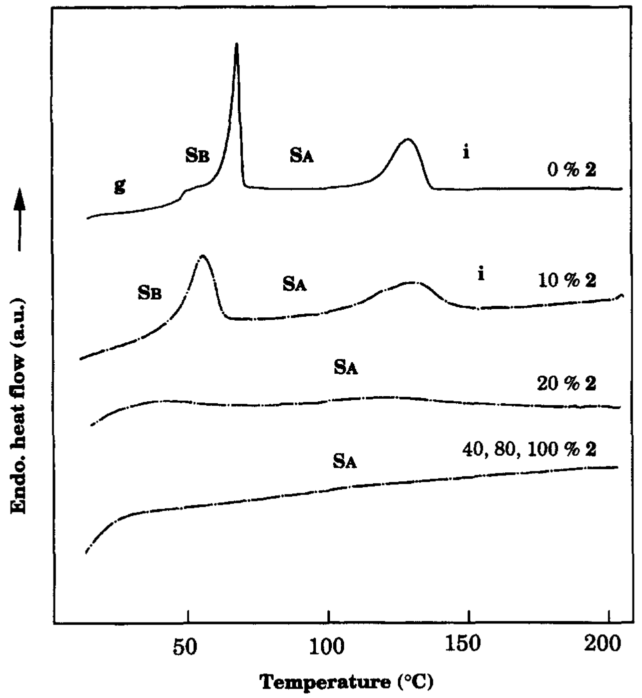

Figure 6 Thermograms of poly(**1**/**2**) with different molar fractions of **2** as shown in the figure

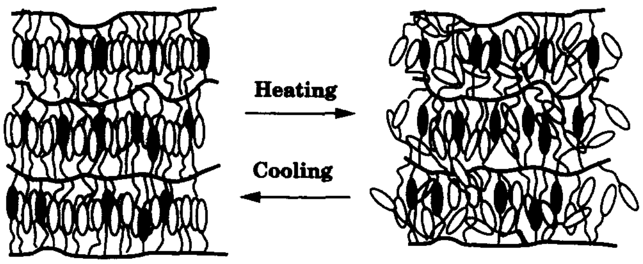

Figure 7 Schematic representation of the reorganization of an organized network (poly(**1**/**2**) of molar ratio 90:10), during heating and cooling. Side groups that are linked to the network at one end (white ovals) can move and adopt an 'isotropic' organization, whereas side groups linked to the backbones at both ends (grey ovals) are constrained

Figure 5 shows that about 85% of the initial order parameter of the crosslinked samples is retained after the first heating and cooling cycle. This value was the same for all the studied samples. The aligned monomer mixtures were polymerized in the nematic state below the glass transition temperature (T_g) of the polymer. At some stage in the polymerization, the crosslink density becomes sufficiently high to cause vitrification of the polymers. When the polymer network reached a T_g above the polymerization temperature, the reaction stopped and the monomer residue was frozen in, vitrified. During the first heating to 200°C, the monomer residue should enter the isotropic phase at 70°C and start to polymerize, essentially forming an isotropic polymer, which would explain the irreversible decrease in order parameter. This explanation is supported by the fact that the order parameter of the crosslinked samples remained the same after the second heating and cooling cycle until the tenth time of testing. The T_g of poly(**2**) was 85°C at 1 Hz according to dynamic mechanical data. This is higher than the polymerization temperature used for the samples. Broer *et al.*[24] presented evidence in favour of the presence of monomer residue in vitrified SCLCPs.

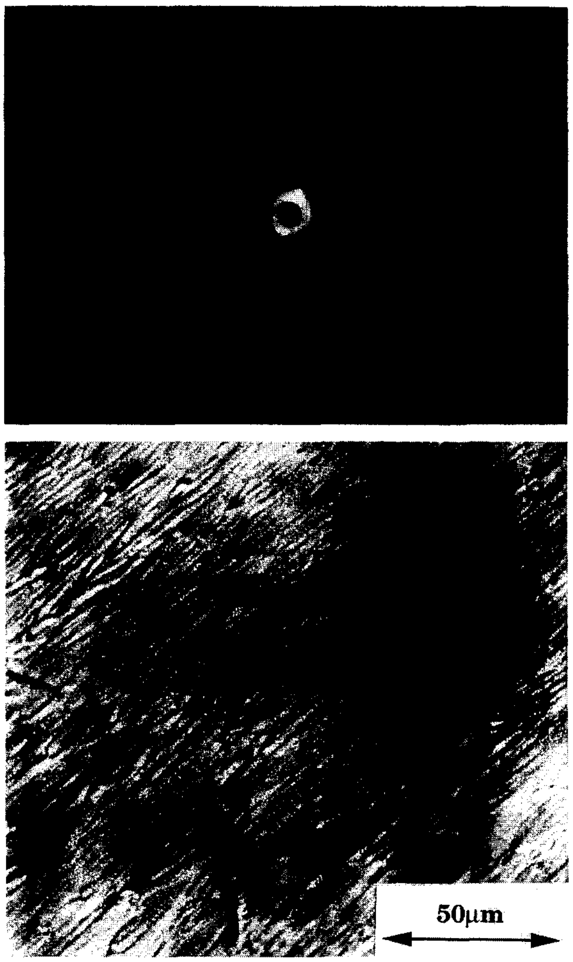

Figure 8 Polarized photomicrograph of a macroscopically aligned poly(**1**/**2**) with a molar ratio of 90:10 at room temperature. The X-ray scattering pattern of the same sample showed a smectic B phase organization

The reorientation of the pendent groups in the polymer network is illustrated in *Figure 7*. The side groups, which are linked to the network at one end, are free to move and may reach an 'isotropic' state at elevated temperatures, whereas the pendent groups that are linked to the network at both ends are highly constrained. The constrained bifunctional units act as directors for the monofunctional units on cooling, and the alignment is essentially completely recovered.

The decrease in order parameter with increasing temperature was also revealed by polarized light microscopy. The birefringence was assessed in the microscope using the Michel-Lévy colour chart. At 200°C, the polymer network containing 10% crosslinks appeared to be white-yellow, close to the black region of the Michel-Lévy colour chart. When the crosslinked polymer was cooled to room temperature, the sample went through five orders of spectral changes, equivalent to a birefringence greater than 0.18. *Figure 8* shows a polarized photomicrograph of an aligned polymer network containing 10% bifunctional units at 25°C. This sample showed smectic B mesomorphism at 25°C according to X-ray scattering (*Figure 8*). The sharp inner reflections ($d = 3.3$ nm)—four orders are seen—

indicate the alignment of the smectic layers and the outer arc-shaped reflections ($d = 0.43$ nm) demonstrate the alignment of the mesogenic groups. Estimated molecular lengths for monomers **1** and **2** are 3.2 nm and 3.4 nm respectively, according to an all-*trans* conformation model of the molecules.

CONCLUSIONS

Oriented LC networks obtained by polymerizing mixtures of aligned mono- and bifunctional LC vinyl ethers decreased their order parameter on heating, reaching a globally isotropic state at 200°C. Cooling of polymers with more than 10 mol% bifunctional monomers led to an almost complete recovery of the original orientational order. Polymers with more than 20 mol% of bifunctional monomer exhibited no first order mesomorphic and isotropization transitions according to d.s.c.

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