Anisotropic Networks with Tunable Optical and Mechanical Properties

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ABSTRACT: Binary mixtures of liquid crystal diacrylates with a stilbene moiety were produced. The mixtures were uniaxially oriented and subsequently photopolymerized, resulting in anisotropic networks with a uniaxial molecular orientation containing stilbene groups in the *E* (trans) form. In order to avoid *E*–*Z* (trans–cis) isomerization of the stilbene groups during polymerization, the wavelength used to initiate polymerization was chosen to be beyond the absorption band of the stilbene molecules. Transformation of the stilbene groups within the uniaxially oriented networks from the *E* to the *Z* form was carried out using UV radiation. As a result of the transformation, the conformation and the polarizability of the stilbene molecules were altered, leading to a decrease in the birefringence of the anisotropic networks. The magnitude of the decrease could be varied by the UV exposure time and the fraction of stilbene moieties within the networks. The *E*–*Z* isomerization also caused anisotropic dimensional changes and altered the anisotropic thermal expansion behavior of the networks.

Introduction

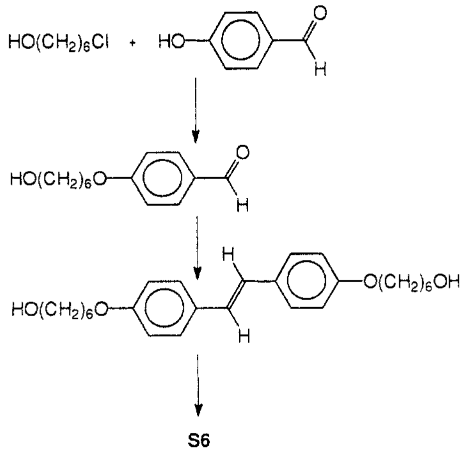
Anisotropic networks are new kinds of materials obtained by photopolymerization of liquid crystal (LC) molecules with reactive end groups in the macroscopically oriented state.[1-3] The macroscopic orientation within low-mass LC molecules is induced with ease at specially treated interfaces, in electric and magnetic fields. Subsequently, polymerization is initiated using UV radiation in order to freeze-in the anisotropic properties of the monomeric state. An important factor determining the anisotropic properties of an oriented system, such as birefringence, is the degree of orientational order within the system. The order parameter of the LC monomer is determined by the temperature, and it decreases with increasing temperature. The polymerization of the LC monomer proceeds isothermally; therefore, varying the temperature of polymerization produces anisotropic networks with different order parameters and associated anisotropic properties.[1] The anisotropic networks described so far[1-3] have permanently fixed properties which cannot be altered. However, in some cases it is desirable to be able to adjust the properties of an anisotropic network. Here we describe a LC system which can be used in the production of anisotropic networks with photosensitive groups, enabling the anisotropic properties of the network to be altered.

Photochromism of various molecules in the literature is well described.[4-7] Molecules containing azobenzene and stilbene chromophores are known to undergo *E* to *Z* (trans to cis) isomerization under the influence of UV radiation. It has already been shown that the properties of linear and cross-linked molecules containing such photosensitive groups can be altered by UV radiation. The effect is associated with the conformational changes as a result of *E*–*Z* isomerization. In the case of low-mass LC molecules containing such photosensitive groups, *E*–*Z* isomerization is shown to cause an isothermal nematic to isotropic transition.[8] It is well-known that rodlike molecules have the tendency to show mesomorphic behavior. LC azobenzene and stilbene derivatives in the *E* state have an extended conformation and they are rodlike. In the *Z* state, however, the molecules do not have the linear form required for liquid crystallinity. It is therefore as a result of such a drastic change in the conformation that the systems become isotropic isothermally under UV radiation. In some cases the systems thermally revert back to the *E* state and the LC state is recovered. Photochromism in side-chain LC molecules has also been shown, and the possibility of using them in optical data storage has been suggested.[9] Polarized light is used in order to irradiate such a side-chain LC polymer. As the absorbance of the molecules is the highest along the long axis of the molecules, the distribution of the orientation of the molecules in the direction perpendicular to the polarization direction becomes maximum during irradiation with polarized light. In this way, therefore, it is possible to change the mean orientation direction by changing the direction of polarized light.

In this article we describe the properties of a system containing stilbene molecules before and after polymerization in the nematic state to form a three-dimensional anisotropic network. The properties of the anisotropic networks after *E*–*Z* isomerization induced by UV radiation are also discussed.

Experimental Section

Synthesis. The synthesis of C10 is described in ref 2. S6 was synthesized in three steps as follows:



1. **4-[(6-Hydroxyhexyl)oxy]benzaldehyde.** To a boiling solution of 12.2 g of 4-hydroxybenzaldehyde, 12 g of 6-chlorohexanol, and 2 g of potassium iodide in 40 mL of ethanol is added

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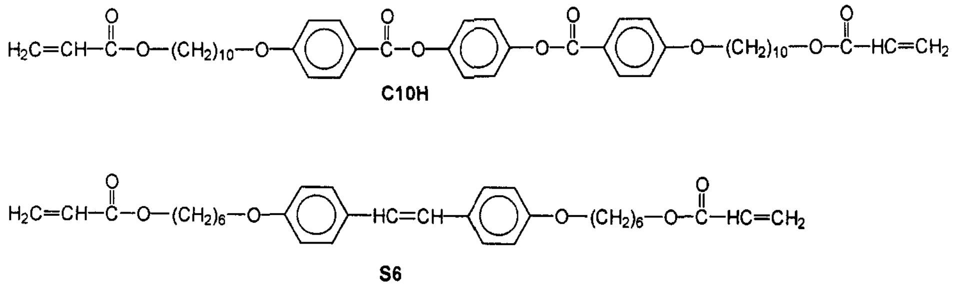

Figure 1. Structure of the LC monomers.

dropwise a solution of 6.6 g of potassium hydroxide in 10 mL of water. After boiling for another 18 h, the mixture is poured onto a mixture of 40 mL of water and 40 g of ice, followed by two extractions with 20 mL of chloroform. The combined chloroform layers are extracted subsequently with 40 mL of water and 40 mL of a 5% sodium hydroxide solution, dried over magnesium sulfate, and evaporated. A total of 15.6 g of the crude product is obtained as a yellow oil which slowly crystallizes. It is used without further purification in the next step.

2. **(*E*)-4,4′-Bis[(6-hydroxyhexyl)oxy]stilbene.** To a vigorously stirred mixture of 18 mL of titanium tetrachloride and 100 mL of tetrahydrofuran cooled in an ice bath is added in portions 35 g of powdered zinc. After addition of 14 mL of pyridine a black suspension is obtained to which is added the product of the first step dissolved in 200 mL of tertrahydrofuran. After boiling for 10 h and cooling to room temperature, 200 mL of chloroform is added. The crude product obtained by filtration, is crystallized from a mixture of ethanol and dimethylformamide. A total of 4.4 g of the product is obtained as a light yellow powder (20% yield), mp = 200 °C.

3. **(*E*)-4,4′-Bis[[6-(acryloyloxy)hexyl]oxy]stilbene (S6).** A mixture of 4.1 g of the product of the previous step, 1.8 mL of acryloyl chloride, 3.0 mL of triethylamine, and 20 mg of di-*tert*-butylmethylphenol in 50 mL of dioxane is stirred for 24 h at 50 °C. After cooling, the solution is filtered and poured into 200 mL of water. The crude product obtained by filtration is eluted with dichloromethane over aluminum oxide and recrystallized from ethanol. A total of 3.0 g of the product is obtained as white plates (57% yield). ^{1}H-NMR (300 MHz, $CDCl_3$, δ in ppm, J in Hz): δ 7.43 (d, J = 8.5, 4H, $-CH{-}CCH{=}CH$), 6.92 (s, 2H, $-CH{=}CH-$), 6.89 (d, J = 8.5, 4H, $-CH{-}COCH_2$), 6.40 (dd, J^1 = 1.7, J^2 = 17.3, 2H, $HHC{=}CHCO_2$), 6.13 (dd, J^1 = 10.2, J^2 = 17.3, 2H, $-HHC{=}CHCO_2$), 5.82 (dd, J^1 = 10.2, J^2 = 1.7, 2H, $HHC{=}CHCO_2$), 4.20 (t, J = 6.7, 4H, $-CH_2CH_2OCO-$), 4.02 (t, J = 6.7, 4H, $-CH_2CH_2OC(CH-)_2$), 1.86 (m, 4H, $-CH_2CH_2OC(CH-)_2$), 1.73 (m, 4H, $-CH_2CH_2OCO-$), 1.48 (m, 8H, $-(CH_2)_2-$).

Physical Measurements and Polymerization Procedures. Transition temperatures and the polymerization of the mixtures were followed using a Perkin-Elmer DSC-2C provided with a light source. In the experiments sample quantities of 5 mg were used and the atmosphere in the DSC was nitrogen. Optical properties of the materials were studied using a polarizing microscope provided with a photomultiplier, 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 in order to obtain uniaxially aligned samples. In order to initiate polymerization of the mixtures, they were provided with 1% w/w Lucirin LR8728 (BASF). After the uniaxial alignment of the monomers in such cells polymerization was initiated photochemically as described below to produce the uniaxially oriented networks. For the refractive index measurements an Abbe refractometer which could be thermostated was used. The thermal expansion behavior of the polymers was analyzed using Perkin-Elmer TMA7, and UV-vis spectroscopy was carried out using a Philips PU8740 spectrometer.

Results and Discussion

Monomers. The structure of the diacrylates C10 and stilbene S6 are shown in Figure 1. According to the ^{1}H-NMR spectrum of S6 it contains only the *E* isomer as revealed by the singlet at δ 6.92 ppm. The mesomorphic behavior of C10 and S6(*E*) studied by DSC and optical microscopy and the phase behavior of the system are shown in Figure 2. The mixtures show a pronounced eutectic point at around 80 °C. After complete melting, the system shows mesophases. The smectic-C phase shown by C10 is also observed in almost the whole composition range, while the two unidentified smectic modifications observed for the pure S6 rapidly disappear. The nematic to isotropic transition temperature (T_c) and the temperature range of the phase decreases with the decreasing weight fraction of C10. At concentrations above 70% w/w S6 the nematic phase disappears completely. In our further investigations we used the mixtures containing 20% and 50% w/w S6, as they show nematic phases where the molecules can be oriented uniaxially.

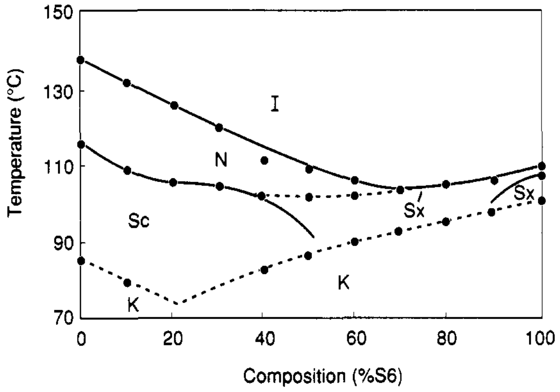

Figure 2. Phase diagram of C10 and S6.

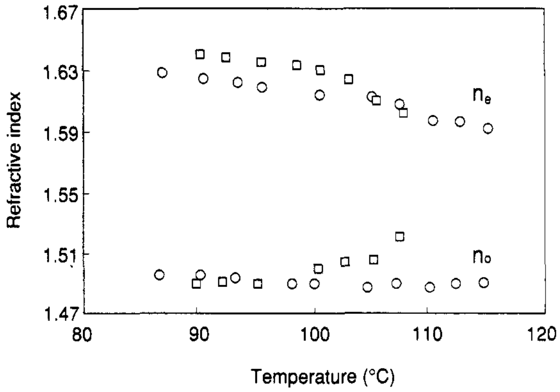

Figure 3. Refractive indices of various mixtures before polymerization: (○) 20% w/w S6; (□) 50% w/w S6.

The refractive indices of the monomeric mixtures measured by the Abbe refractometer are shown in Figure 3. It can be seen that with increasing temperature the ordinary refractive index (n_o) remains almost constant as a function of temperature, while the extraordinary refractive index (n_e) decreases with increasing temperature, showing a typical behavior for nematics.

Polymerization of the Mixtures. It has already been stated that the main aim of this study was to produce anisotropic networks containing photoisomerizable groups. Therefore, in order to avoid *E*-*Z* isomerization taking place

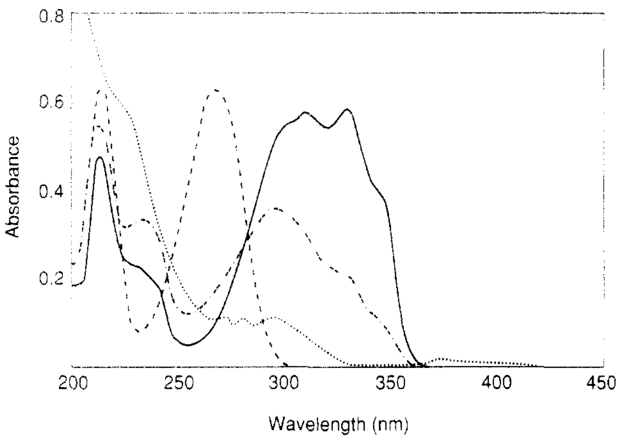

Figure 4. Absorption spectra of various substances: (- - -) C10; (—) S6 (*E*); (– • –) S6 (*Z*); (···) Lucerine.

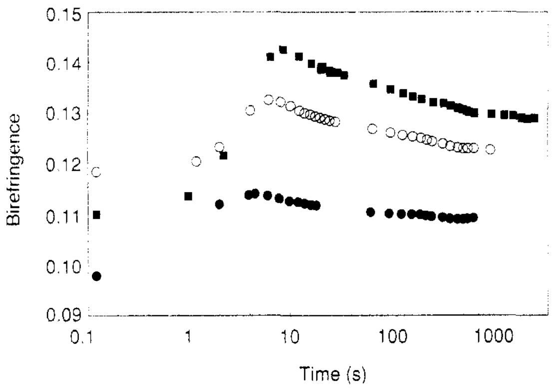

Figure 5. Change in birefringence of various mixtures during polymerization at various temperatures: 50% S6 (■) 103 °C; 20% S6 (●) 120 °C, (○) 108 °C.

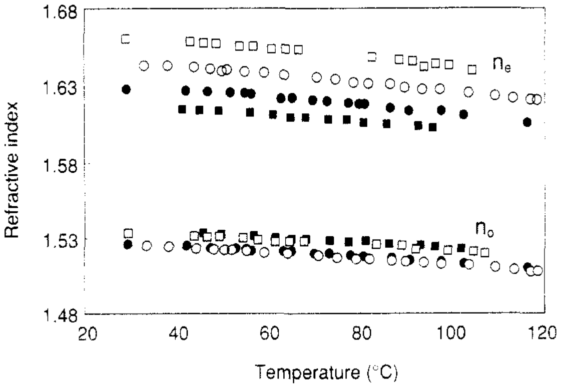

Figure 6. Refractive indices of anisotropic networks containing (○) 20% S6 and (□) 50% S6. Open symbols are before and filled symbols are *after irradiation to induce E–Z isomerization.*

during the photoinitiation of polymerization, the wavelength used should fall outside the absorption band of the stilbene molecule. In Figure 4 the absorption spectra of S6 before (in the *E* form) and after exposure to UV (366 nm) irradiation (mixture of *Z* and *E*) are shown together with the spectra of the photoinitiator Lucerine and C10 in tetrahydrofuran (0.2 mg/cm^3) in a cell with a thickness of 1 mm. It can be seen that in both cases the absorption peaks tail off around 360 nm. Therefore, the polymerization of the mixtures was carried out by irradiation with 405 nm (1 mW·cm^{-2}), where the initiator shows absorption. DSC was used in order to follow the exothermic heat of the polymerization reaction. It was found that the polymerization proceeds at a very fast rate, and using the value of 78 kJ/mol for the heat of the polyaddition reaction of acrylate groups, it was calculated that within 3 min the conversion of the reactive groups approach 90%. Fourier transform infrared measurements on polymerized samples did not show the vinyl absorption band at 1636 cm^{-1} corresponding to the acrylate groups, supporting the DSC data for a high conversion. This is in accordance with the previous work[2] using both methods where a high conversion (>90%) of acrylate groups is obtained. As the mesogenic groups also form the cross-link, this means that the system has a cross-link density of about 90% and only a very few pendent and end groups. Optical changes occurring during polymerization were investigated by measuring the transmitted intensity (546 nm) through crossed polarizers with the cell between the polarizers, where the molecular orientation is set to be at 45° to one of the polarizers. The intensity of the light through the polarizers is related to the birefringence (Δn) and the cell thickness (d) as

$$I = I_0 \sin^2(\pi \Delta n d/\lambda) \qquad (1)$$

The birefringence of the uniaxially oriented samples was measured before and after polymerization also using the compensator in order to ensure that the change measured in the intensity was caused by the change in birefringence. It was also found that the uniaxial orientation of the system remained during polymerization. In Figure 5 the changes in the birefringence (calculated from the intensity data) during polymerization of samples containing 20% w/w S6 at various temperatures, as well as the sample containing 50% w/w S6 at 103 °C, are shown. It can be seen that in all cases soon after the initiation of polymerization the birefringence increases rapidly to reach a maximum, before starting to decrease gradually. The initial increase in the birefringence, as suggested before,[1] is associated with the increase in the order parameter of the system as a result of polymerization. The subsequent decrease is however more difficult to explain; however it can be caused either by *E–Z* isomerization, which will be discussed further in the text, or by steric hindrance caused at higher conversions of the acrylate groups. The temperature dependence of the refractive indices of the anisotropic networks containing various amounts of S6 is plotted in Figure 6. It can be seen that after polymerization the anisotropic networks show high thermal stability and the refractive indices decrease only slightly with increasing temperature. We associate this decrease with the decrease in the density as a result of thermal expansion. Here it is important to note that the networks obtained here are three-dimensionally cross-linked and even when they were heated above 200 °C their uniaxial orientation was sustained and no phase transitions were observed.

***E–Z* Isomerization within the Networks.** In Figure 7 *E* and *Z* isomers of S6 in the most extended conformations are shown. It can be seen that in the *Z* state the rodlike nature of the mesogenic group changes. As a result of the *E* to *Z* isomerization optical and dimensional changes are expected to occur. In order to investigate the changes occurring as a result of *E–Z* isomerization of the stilbene moieties in the networks with a uniaxial molecular orientation, we measured in-situ the birefringence and dimensional changes during irradiation with UV (366 nm, 5 mW·cm^{-2}). The change in birefringence was measured by measuring the intensity of light through crossed polarizers, as described above, and the results are shown in Figure 8. It can be seen that at all temperatures the birefringence decreases continuously as a function time. The magnitude of the decrease at a given time increases at higher temperatures. The decrease in the birefringence is caused partly by the decrease in the degree of order

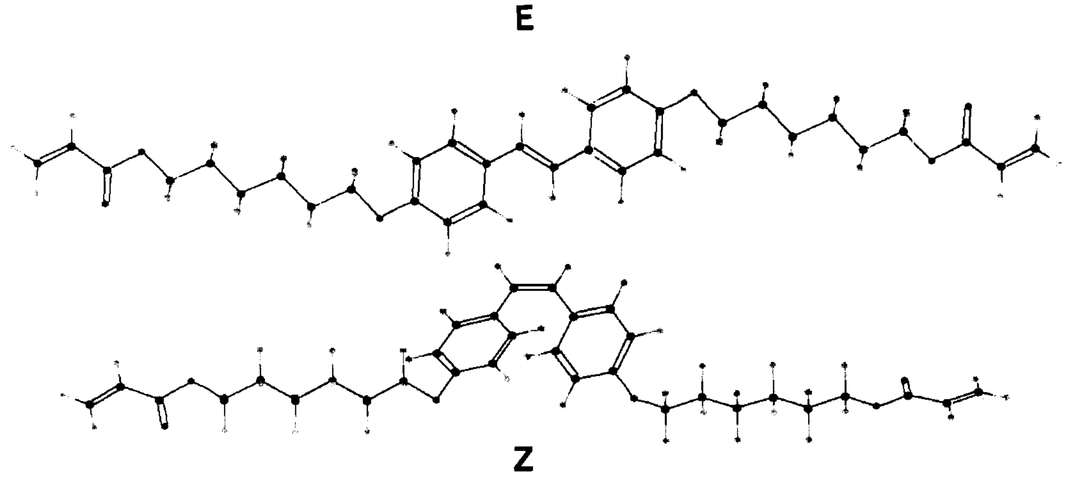

Figure 7. *E* and *Z* forms of S6 in the most extended conformations.

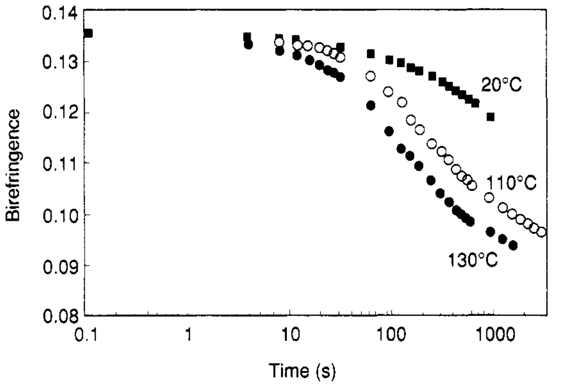

Figure 8. Change in birefringence of an anisotropic network containing 50% S6 during irradiation to induce E–Z isomerization at various temperatures.

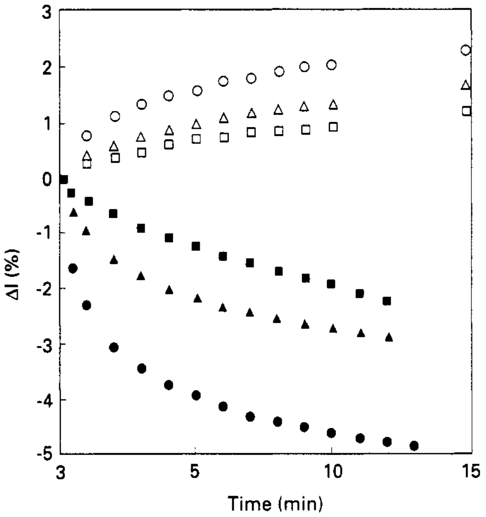

Figure 9. Dimensional changes in the anisotropic network containing 50% S6 during irradiation to induce E–Z isomerization at various temperatures: (○) 130 °C; (△) 90 °C; (□) 60 °C; (filled symbols) in the direction of molecular orientation; (open symbols) in the lateral directions.

within the system and partly due to the decrease in the anisotropy in molecular polarizability of the stilbene moieties as a result of the E–Z isomerization. If we consider that the birefringence of pure C10 is about 0.13 and assume no anisotropic contribution from S6 to the birefringence upon E–Z isomerization, then the birefringence of the system would be expected to decrease to 0.065. The fact that the birefringence upon isomerization is reduced to about 0.09 indicates that the stilbene moieties contribute to the birefringence of the system. As opposed to the un-cross-linked systems, the highly cross-linked network described here probably prevented the total disorder and no visible local isotropization on a macroscopic scale as a result of the E–Z isomerization could be observed. During the E–Z isomerization polymerized S6 molecules change their conformation, which can induce anisotropic dimensional changes during the UV irradiation. In order to follow these dimensional changes, a linear displacement transducer was used during the irradiation of the anisotropic networks containing 50% S6 at 366 nm, and the results are shown in Figure 9. It can be seen that as a result of E–Z isomerization the system shows a shrinkage in the direction of molecular orientation, while expanding in the lateral directions. The end to end distances of the E and the Z forms of S6 in the extended conformations shown in Figure 7 are estimated to be 360 and 330 nm, respectively. Assuming that the shrinkage is caused by the dimensional change as a result of the transformations between the states shown in Figure 7, one expects a shrinkage of about 10%. Therefore in a network containing 50% S6 the expected shrinkage of about 5% is in good agreement with the maximum measured value of 5% in the direction of molecular orientation. In Figure 9 it can also be seen that the shrinkage obtained in the direction of molecular orientation is about twice as much as the expansion measured in the direction perpendicular to the molecular orientation. This indicates that during the E–Z isomerization the change in the volume is negligible. The degree of conversion of the E molecules to the Z form was also estimated by measuring the IR absorption band at around 960 cm^{-1}, associated with the =C—H out-of-plane vibration in the E state. At long irradiation times the conversion was found to reach above 90%. The IR absorption band was also monitored at room temperature over 3 months, and no change in its intensity was found. This result shows the stability of the stilbene in the Z form.

Here we like to discuss two effects influenced by the mobility within the system. In Figure 9 it is also clear that with increasing irradiation temperature the dimensional changes proceed at a higher rate. It is known that at the photostationary state the ratio of E/Z isomers depends on the relative extinction coefficients of the E and Z isomers and on the quantum yields of the photoisomerization for both directions at the wavelength used to induce isomerization. The rate of the isomerization is on the other hand determined by the quantum efficiency and the intensity of the light. In the case of no overlap of the absorption bands of the E and Z isomers selective irradiation of one converts it to the other.[10] In the present study at the wavelength of 366 nm used in the isomerization the *E* form absorbs to a higher extent than the *Z* form; as a result during irradiation the population of the *Z* form increases. This decrease in the population of the *E* form is accompanied by a strong decrease in the absorption band obtained from the system (Figure 4) in the wavelength region used in isomerization. The fact that the rate of change decreases with increasing temperature indicates the importance of the mobility within the system. For the low-mass species it has been documented[11] that with increasing viscosity of the medium the activation energy involved in the transformation can increase, slowing down the process. Here the increased temperature increases the mobility within the network, causing the *E–Z* isomerization to take place at a faster rate. It was also found that after the end of irradiation the networks did not show any further changes. For stilbenes thermal back-reaction is not reported, as it does not readily take place.[10] However for azo compounds and spiropyrans the thermally induced back-reaction (*Z–E* isomerization) is known to be influenced to a large extent by the host medium. In the case of the photoisomerizable species introduced into a polymer hosts without chemical linking, it was found that with increasing rigidity (glass temperature) of the host matrix the decay rate decreased even though the activation energy of the process is not influenced. This indicated that the decay was coupled to the secondary relaxations within the system. At a given temperature the low-mass liquids showed a factor of 30 higher decay constants than polymeric glasses.[12] In the case of the systems where the photoisomerizable moiety is attached to the polymer, the rate decreased even further and the activtion energy showed a temperature dependence.[13] In the present system the extra constraint exerted by the oriented network also probably contributes to the stability of the *Z* form.

Having followed the changes occurring during the *E–Z* isomerization, we also studied the thermal and optical properties of the anisotropic networks following *E–Z* isomerization at 130 °C. Temperature dependence of the refractive indices of the networks before and after *E–Z* isomerization are compared in Figure 6. It can be seen that after the isomerization the extraordinary refractive index decreases considerably, while the ordinary refractive index (n_o) remains almost the same. In cases where only the order parameter of the network decreases,[1] n_e shows a decrease while n_o increases. The fact that n_o remains constant during the isomerization indicates a decrease in the polarizability of the system. Indeed, if we compare the mean refractive index ($\langle n \rangle = [n_e + 2n_o]/3$) of the networks, it can be seen that upon isomerization a decrease in $\langle n \rangle$ is observed. In order to investigate the effects of the change in the order parameter and the polarizability further, we measured the dispersion in birefringence of the anisotropic networks before and after *E–Z* isomerization. Anisotropic networks were placed between crossed polarizers, and the transmission was measured as a function of wavelength. In eq 1 it can be seen that the intensity through the crossed polarizers is a function of the wavelength. Knowing the birefringence at 546 nm and the thickness of the film using the transmission spectra before and after *E–Z* isomerization, the dispersion in the birefringence was calculated and the results are shown in Figure 10. It can be seen that the shift in the dispersion curves as a result of isomerization is not parallel. The decrease in birefringence at higher wavelengths is smaller than that at shorter wavelengths close to the absorption band, showing again the effect of changes in the polarizability of the molecule as a result of the isomerization.

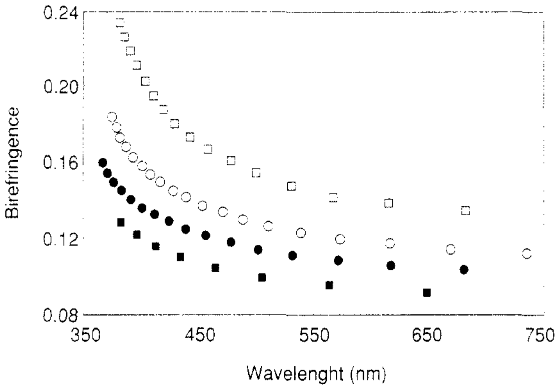

Figure 10. Dispersion of the birefringence for anisotropic networks containing (○) 20% S6 and (□) 50% S6. Open symbols are before and filled symbols are after irradiation to induce *E–Z* isomerization.

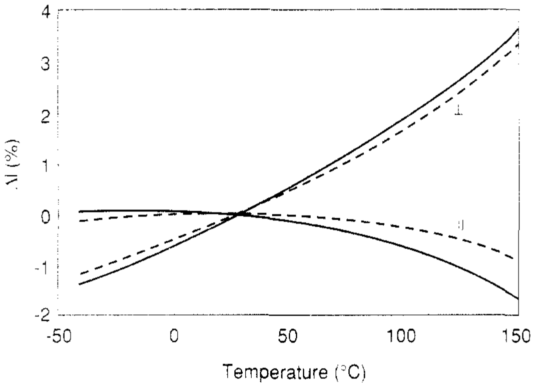

Figure 11. Thermal expansion of an anisotropic network containing 50% S6 (—) before and (- - -) after irradiation to induce *E–Z* isomerization.

The effect of the *E–Z* isomerization on the thermal properties of the networks was also studied. For this purpose, the thermal expansion of a network containing 50% C10 was used. In Figure 11 the thermal expansion curves of the network in the direction parallel and perpendicular to the molecular orientation before and after *E–Z* isomerization are shown. It can be seen that before isomerization, in the direction of molecular orientation, the slight expansion observed at low temperatures becomes thermal contraction at higher temperatures. In the direction perpendicular to the molecular orientation, however, the system expands across the whole temperature range, as also observed for other oriented systems before.[14] Upon *E–Z* isomerization the contraction observed for the network in the direction of the molecular orientation and the expansion in the lateral directions become smaller. This behavior is again associated with a decrease in the degree of orientational order within the system. It shows that, apart from the optical properties, the thermal expansion behavior of the anisotropic networks can also be altered by the isomerization.

Conclusions

It has been shown that anisotropic networks containing photoisomerizable groups can be produced. For this purpose it was necessary to use a photoinitiator so that the wavelength used to induce polymerization could be chosen to be beyond the absorption band of the stilbene molecules, so that *E–Z* isomerization during polymerization could be avoided. Oriented networks containing stilbene groups in the *E* form showed anisotropic optical properties and thermal expansion. When the networks were irradiated with UV light in the region of absorption of the stilbene molecules, *E* to *Z* isomerization could be induced, resulted in anisotropic dimensional changes of the oriented networks, accompanied by changes in their refractive indices and the expansion coefficients. The changes in the optical properties, namely the decrease in the extraordinary refractive index, was associated with the decrease of order within the system as well as the decrease in the polarizability of the stilbene moieties. The effect of the change in the polarizability also was manifested strongly in the change in the dispersion of birefringence. The magnitude of the changes could be controlled by the duration of exposure to UV irradiation to induce *E*–*Z* isomerization or by the concentration of the stilbene molecules within the system. The anisotropic networks containing stilbene moieties in both the *E* and the *Z* form were found to be stable, and at room temperature in the absence of UV light no change in their properties could be observed.

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