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Influence of Network Topology on Polydomain−Monodomain Transition in Side Chain Liquid Crystalline Elastomers with Cyanobiphenyl Mesogens

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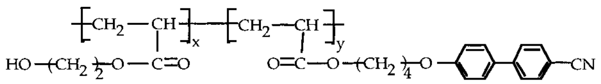
ABSTRACT: Orientation behavior of acrylate-based liquid crystalline (LC) networks containing different types of cross-links is studied and discussed. Cross-links incorporated by chemical reaction with cross-linking agent presumably distort LC order, whereas cross-links induced by γ-irradiation preserve and even stabilize the nematic phase. The comparison of the three different series of LC elastomers is given in terms of the macroscopic order parameter dependence on temperature and external mechanical field.

Introduction

Liquid crystalline (LC) elastomers are known to be a particular class of polymer systems with the coupling between nematic field and backbone conformations. These networks are interesting from both theoretical and practical viewpoints.[1−6] The overwhelming majority of the investigation was performed for siloxane-based side-chain LC networks that display rubber-like elasticity at room temperature. On the other hand, acrylate-based systems have a significantly higher glass transition temperature (T_g) due to much higher rigidity of the backbone when compared with siloxane-based polymers. Thus, the orientation of mesogens induced by external field can be frozen by cooling the system down to room temperature (far below T_g). Moreover, the coil anisotropy strongly depends on the interaction of the mesogens and is found to be fairly small for cyanobiphenyl-group-containing systems.[7,8]

The main objective of this paper is to investigate the influence of structure and spatial distribution of different cross-links on the macroscopic order parameter when a mechanical field is applied to systems possessing extremely low network anisotropy.

A random copolymer of the following structure



was used for the network preparation. The first series was obtained by chemical reaction with different amount of cross-linking agent; namely, 4,4′-methelynediphenyl diisocyanate (MDI) and 1,6-diisocyanatohexane (HMDI). Other networks were produced by γ-irradiation of the same linear copolymer at different doses, yielding a set of networks with varying cross-link density.

Experimental Section

The monomer, 4-(4-cyano-4′-biphenylyloxy)butyl acrylate, was synthesized accordingly to the procedure described by Gubina.[9] The copolymer containing 10 mol % of nonmesogenic units ($X = 10$) was prepared by copolymerization of the aforementioned monomer with 2-hydroxyethylacrylate in chlorobenzene at 65 °C for 35 h. 2,2′-Azoisobutyronitrile (0.1 wt % of the total weight of the monomers) was used as initiator. The copolymer was precipitated from 80/20 vol % 1,2-dichloroethane/acetonitrile into methanol. The composition of the copolymer was determined by UV spectroscopy using the value of the extinction coefficient reported for the homopolymer.

The molecular mass characteristics of the copolymer were determined by gel-permeation chromatography (GPC) using a Waters liquid-phase chromatograph equipped with a R401 differential refractometer ($M_w = 1.4\ 10^5$; $M_w/M_n = 3.02$). The glass transition (T_g) and nematic-to-isotropic phase transition (T_{n-i}) temperatures of the copolymer were determined by differential scanning calorimetry (DSC) to be 62 and 112 °C, respectively.

Chemical cross-linking was performed as follows: The linear copolymer and the cross-linking agents (i.e., MDI or HMDI) were dissolved in 80/20 vol % 1,2-dichloroethane/acetonitrile. After a homogeneous solution was obtained, the mixture of the solvents was evaporated. The copolymer containing the cross-linking agent was dried under reduced pressure at room temperature.

After 95% removal of the solvent, the sample was placed in a thermal chamber under reduced pressure, where cross-linking proceeded for 1 h either in the liquid crystal phase (20 °C) or at the isotropic melt temperature, which is 5−10 °C above the clearing point. The reaction was monitored by disappearance of the melting peak of the cross-linking agent (DSC) and by swelling of the samples in the 1,2-dichloroethanacetonitrile mixture.

Under the conditions of complete consumption of the sol-fraction and cross-linking agent, the cross-link density was calculated from the following stoichiometric ratio

$$M_c = m_{cop}/2\nu_c$$

where m_{cop} is the weight of the copolymer and ν_c is the number of moles of the cross-linking agent. The calculated values of the parameter M_c were in good agreement with those estimated from the slope of deformation curves.

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To perform cross-linking under the action of γ-radiation, polymer films were placed into ampules, which were evacuated for 1 h at room temperature at 0.133 Pa. The ampules were sealed and irradiated with doses from 0.1 to 3 MGy at 20 °C. The dose rate was 0.048 MGy/h (γ-radiation from a ^{60}Co source). The gel dose was determined by the standard technique from the gel fraction versus dose plots. To characterize the cross-link density in the networks formed under the action of γ-radiation, we used the parameter M_c calculated according to the following expression

$$M_c = M_w(R_g/R)$$

where R_g and R are the gel and the exposure doses, respectively.

The DSC measurements were carried out on a Mettler TA-4000 at heating rates of 15, 10, 5, and 2 K/min. The nematic-to-isotropic phase transition temperature was determined by extrapolating to 0 K/min heating rate. The parameter T_{red} represents the ratio T/T_{n-i}, where T is a current temperature in K and T_{n-i} is the nematic-to-isotropic phase transition temperature.

X-ray scattering measurements were performed using a Cu X-ray tube (wavelengh $\lambda = 0.154$ nm) coupled with a graphite monochromator and a 0.8-mm collimator. The incident beam was normal to the surface of the elastomer film. The scattered X-ray intensity was detected by an image plate system. The order parameter was calculated by an azimuthal scan applied to the nematic intermesogen reflexes.[10] The temperature dependence of X-ray scattering experiments was carried out after annealing the sample for 30 min at the desired temperature.

Stress–strain measurements were performed in a custom-made cell. All parameters including temperature were computer controlled as previously described.[11,12] The experiments were carried out under thermodynamical equilibrium conditions. Stress, as indicated, is the nominal stress σ_n in mN/mm^2 (force per unit of initial cross-section). The elongation λ is the ratio of the sample length with and without load (L/L_0).

Polydomain chemically cross-linked networks were obtained by casting a 30% solution of the linear copolymer in 80/20 vol % 1,2-dichloroethane/acetonitrile containing the required amount of cross-linking agent (MDI or HMDI) onto the polyamide tub-shaped substrate. The cross-linking reaction was controlled by swelling experiments. In both systems, the reaction did not occur until 95 wt % of the solvent was removed. At that point, the cross-linking starts to proceed at 20 °C and in 1 h the reaction is completed (no sol fraction is detected). After successive annealing at 120 °C, the polydomain films were peeled off the support. The thickness of the films was in the range of 250–300 ± 5 μm.

Polydomain γ-cross-linked networks were obtained by γ-irradiation of the linear copolymer film prepared in the manner just described (without the addition of cross-linking agent).

Monodomain networks were prepared by a two-step procedure: the polydomain chemically cross-linked sample was stretched at 90 °C up to $\lambda = 1.5$ and then cooled to room temperature (40 °C below T_g) while secured in the clamps. The frozen monodomain structure was then fixed by incorporation of additional cross-links produced by γ-irradiation in an evacuated ampule at $D = 2$ MGy. The sample was then heated to 100 °C, and, after complete relaxation of residual stresses, the transparent film possessing uniform alignment of mesogens in the direction of initial deformation without any external field was obtained.

Results and Discussion

The dependence of the orientational order parameter versus nominal stress for chemically and γ-cross-linked samples with different cross-link density is shown in Figure 1. The increase in concentration of cross-links is followed by a considerable drop in LC order for chemically cross-linked systems (Figure 1a; MDI is used as a cross-linking agent). Contrary to this, γ-cross-linked networks (Figure 1b) display a constant value of parameter S at high normal stress, although the actual value of the external field required to achieve plateau increases with the number of γ-incorporated cross-links. These data imply that the latter virtually do not disrupt LC order, whereas chemically induced cross-links presumably generate defects and their disordering role prevails.

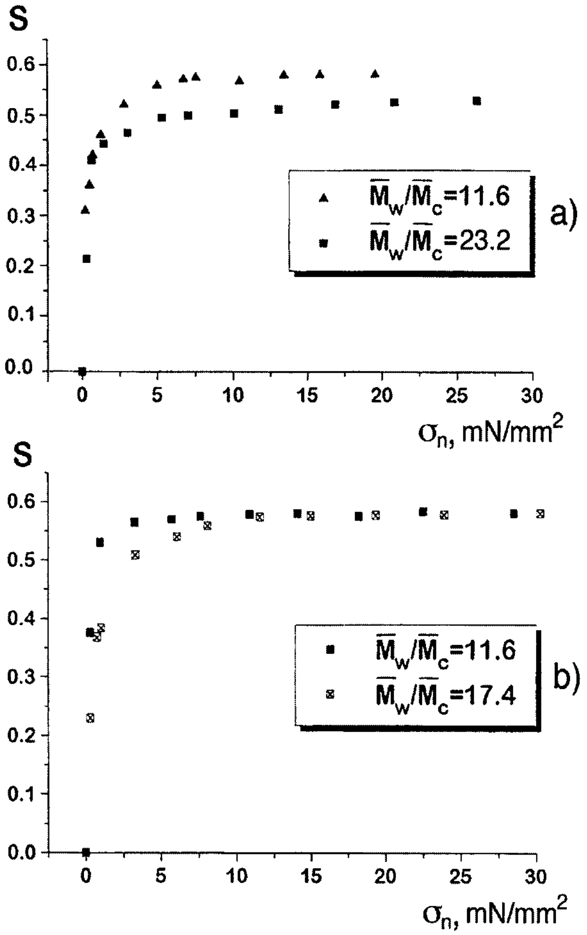

Figure 1. Orientational order parameter versus normal stress for samples cross-linked by MDI (a) and for γ-cross-linked samples (b) at $T_{red} = 0.953$.

Interestingly, the plateau level at $T_{red} = 0.953$ ($T = 94$ °C) corresponds to the same value of S for both systems with $M_w/M_c = 11.6$. However, the situation is drastically changed in the vicinity of phase transition temperature T_{n-i}. In Figure 2 $S(\sigma_n)$ curves for chemically (by means of MDI) and γ-cross-linked networks with $M_w/M_c = 11.6$ obtained at higher temperatures are shown. The closer the systems are to T_{n-i}, the higher is the difference in order parameter. This result is basically due to the significant decrease in order parameter caused by chemical cross-links while the S value for γ-cross-linked samples remains constant. Consequently, the destabilizing influence of chemically incorporated bulky cross-links on LC order increases when the system approaches the clearing point. The results indicate that "chemical" cross-links based on the rigid fragment of cross-linking agent MDI are located in close position to mesogenic units. On the other hand, γ-cross-links are formed by recombination of radicals that presumably emerge due to nonmesogenic hydroxyethylacrylate units, as found in our previous investiga-

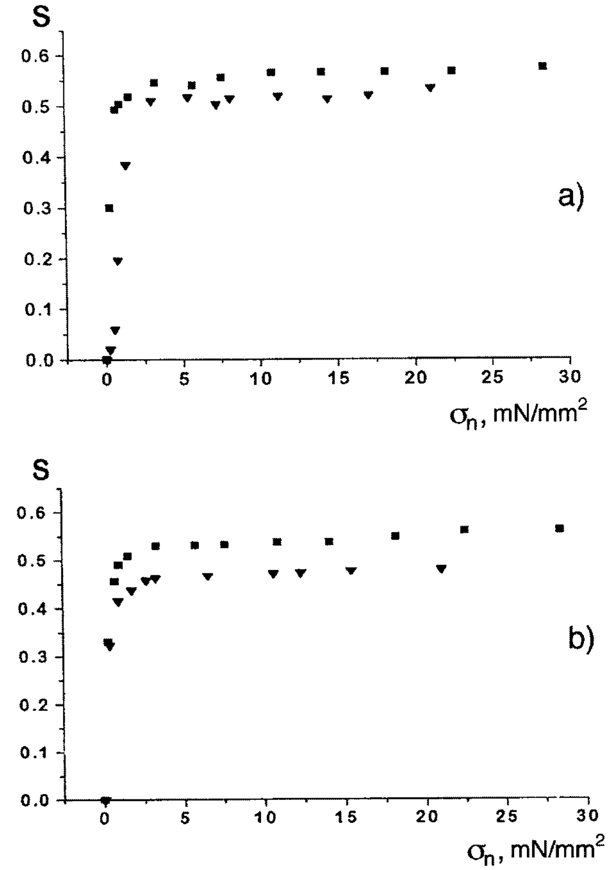

Figure 2. Orientational order parameter versus normal stress for γ-cross-linked samples (■) and for samples cross-linked by MDI (▼) at (a) $T_{\mathrm{red}} = 0.979$ and (b) at $T_{\mathrm{red}} = 0.992$ ($M_w/M_c = 11.6$).

tion.[10] Therefore, γ-cross-links are being formed and located within certain regions enriched in nonmesogenic units that serve as a shield preserving initial LC order. As a result, the destabilizing role of γ-cross-links is minimized and practically does not appear until the clearing point is reached.

Confirmation for the assumption just mentioned is derived from the temperature dependence of the macroscopic order parameter obtained for both systems with certain cross-linking density. The data presented next were collected for samples with monodomain structure sustained by an applied external mechanical field ($\sigma_n = 4$ mN/mm²). Figure 3 shows that γ-cross-linked systems demonstrate very high values of S through the whole temperature range studied. A sharp drop in the order parameter (from 0.4 to 0.2) occurs when the system overcomes phase transition from the nematic to paranematic phase caused by an external mechanical field. On the other hand, the chemically cross-linked sample (by MDI) displays a different shape of the $S(T)$ curve revealing a continuous decrease in LC order and only a weak drop in the S value in the vicinity of clearing point.

Thus, the disrupting role of rigid chemical cross-links is expressed to the highest extent when the system is close to the phase transition and, therefore, the disordering influence of the temperature itself on LC packing is increased because of the presence of this kind of cross-links. In contrast, γ-cross-links tend to stabilize the nematic phase and act in an opposite direction, providing the system with very high order parameter within the whole range of the nematic phase. These results are in good agreement with the data obtained from phase behavior investigations of these systems.[13,14] As an example, in Figure 4, the change in clearing point ΔT (the difference between clearing temperature of the linear polymer and that of the cross-linked sample) is given versus the cross-link density for γ-cross-linked and chemically cross-linked (by MDI) systems. The incorporation of γ-cross-links causes a significant increase (up to 5 °C) in the nematic–isotropic phase transition temperature. On the other hand, an increase in the concentration of rigid "chemical" cross-links (MDI fragments) is followed by a continuous drop in the clearing point.

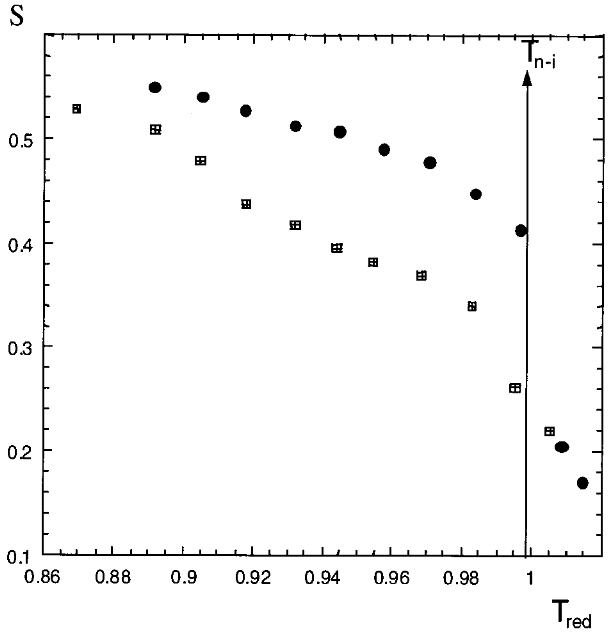

Figure 3. Orientational order parameter versus temperature for γ-cross-linked sample (●) with $M_w/M_c = 11.6$ and for sample cross-linked by MDI (⊞) with $M_w/M_c = 23.2$. External mechanical field $\sigma_{\mathrm{ext}} = 4$ mN/mm².

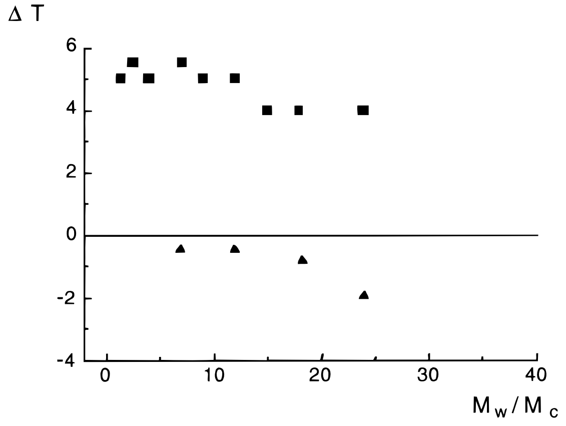

Figure 4. Change in the clearing temperature ΔT as a function of cross-link density: (■) γ-cross-linked networks; (▲) chemically cross-linked networks (by means of MDI). Both systems were cross-linked at 20 °C.

Based on data presented so far, we are led to the conclusion that spatial distribution of cross-links and the corresponding network topology are responsible for the strong difference in orientational behavior of systems having the same cross-link density and polymer chains with identical mesogenic groups. The γ-cross-linked system is characterized by a highly nonhomogeneous distribution of junction points when cross-links

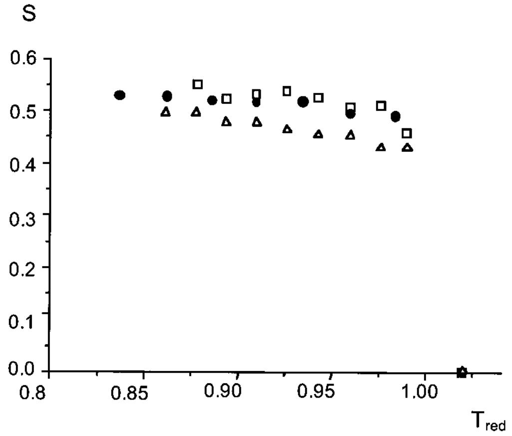

Figure 5. Orientational order parameter versus temperature for networks cross-linked by HMDI with different cross-link density M_w/M_c: 6.9 (□); 13.9 (●); 21.0 (△). External mechanical field σ_{ext} = 5 mN/mm^2.

are concentrated in nonmesogenic regions and isolated from cyanobiphenyl fragments. On the contrary, chemical cross-links with rigid methylene biphenyl fragments tend to be distributed within the network more homogeneously because, on one hand, they have certain similarity in chemical structure when compared with mesogenic units and, on the other hand, they are covalently attached to nonmesogenic hydroxyethylacrylate units.

In addition, the actual flexibility of "chemical" junction point is to be considered here because it may have a strong influence on the orientational behavior. That is why we also obtained $S(T)$ curves for chemically cross-linked systems based on a far more flexible cross-linking agent, HMDI. Figure 5 shows that these samples are very similar to γ-cross-linked systems because the orientational order parameter remains very high up to the clearing point. Moreover, the plateau level is not affected by significant increases in the cross-link density. These curves prove the idea about nonhomogeneous spatial distribution of cross-links within the network. Due to the decreased compatibility of the hexamethylene fragment with cyanobiphenyl mesogenic groups, they tend to be accumulated in microregions enriched in nonmesogenic units and because of much higher flexibility compared with MDI fragments, they can be shielded more effectively.

However, there is one particular characteristic that is the same for both systems. Figures 1 and 2 show that plateau of $S(\sigma_n)$ curves for all samples studied is reached at very low stress (compared with siloxane-based elastomers) and an almost discontinuous jump in S value occurs from zero to plateau level at ~0.5. It is to be pointed out that the stress just mentioned corresponds to several percent elongation (from 3 to 8% depending on temperature) of the chemically and γ-cross-linked samples. Such a small deformation causes complete transformation of the polydomain structure into monodomain one, which implies the absence of a mechanical field threshold when a monodomain structure can appear with no cost in external load. This unique property is only typical for acrylate-based LC networks with cyanobiphenyl mesogenic groups. Moreover, siloxane-based LC elastomers described in the literature demonstrate a certain critical stress of 20 mN/mm^2, which is necessary to achieve monodomain structure. As long as the external stress is less than a critical value, no orientation transition occurs and the sample remains polydomain.[11]

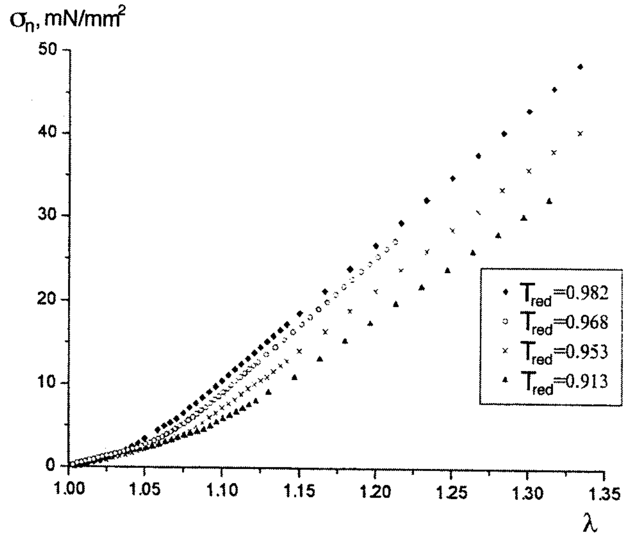

Figure 6. Deformation curves for the sample cross-linked by MDI (M_w/M_c = 11.6) at different temperatures.

A significant difference between our systems and siloxane-based elastomers was also found in the stress–strain curves. As an example, in Figure 6, σ_n (λ) dependencies obtained for chemically cross-linked sample at different temperatures are shown. These curves exhibit two ranges with different slope. However, contrary to siloxane-based LC elastomers, this system does not display a plateau corresponding to critical stress at which the orientation process can be started and proceed until monodomain structure is reached. Instead, the initial deformation of the sample is followed by only a very low increase in σ_n value that remains on the order of 2–4 mN/mm^2. In other words, the absence of the plateau also reveals a nonthreshold behavior of the system. When the deformation reaches a certain number in the range from 1.03 to 1.08 depending on the temperature, the sharp increase in slope of the curves occurs. At this point, polydomain–monodomain transition is completed and the film becomes transparent. Furthermore, the absolute value of σ_n that causes a sharp increase in the deformation curves slope is in good agreement with the stress at which the plateau level of orientation order parameter on $S(\sigma_n)$ curves (Figure 1) is reached.

Stress–strain curves were also obtained for chemically cross-linked samples containing variable amount of 1,6-diisocyanatohexane cross-links (Figure 7). These curves show that the stress value remains at zero level (within the experimental error) until a monodomain structure is reached ($\lambda \approx 1.1$). This feature appears to be typical for all investigated systems regardless of the actual cross-linking density.

Thus, extremely low elongation (several percent of initial length) of the systems under consideration results in full completion of orientation transition. This result is strongly different from siloxane-based LC elastomers. In our view, the main reason for this difference is associated with far lower network anisotropy of acrylate-based systems with cyanobiphenyl groups. Small-angle neutron-scattering experiments performed for linear homopolymer[7] with the same mesogenic groups demonstrate that coil anisotropy $\boldsymbol{r}$ does not exceed the 1.7 value even at the glass transition temperature. On the

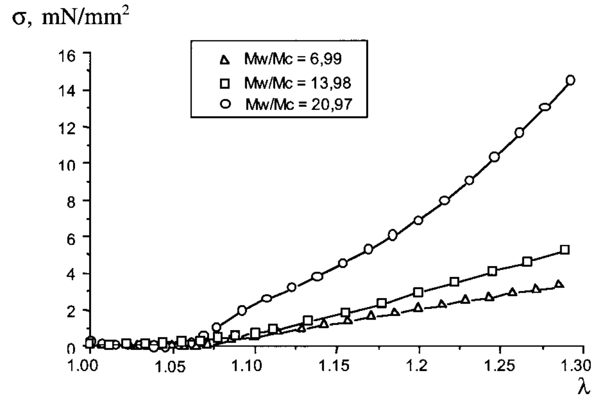

Figure 7. Deformation curves for the samples cross-linked by 1,6-diisocyanatohexane (T = 80 °C) with different cross-link density.

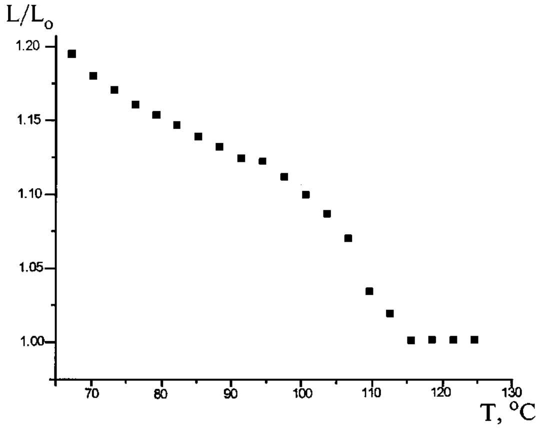

Figure 8. Spontaneous macroscopic elongation L/L_0 versus temperature for monodomain network obtained by γ-irradiation (D = 2 MGy) of preoriented sample cross-linked by MDI ($M_w/M_c = 11.6$).

other hand, in accordance with well-known theory developed by M. Warner,[15] the spontaneous macroscopic elongation of the monodomain LC network is directly connected to the coil anisotropy, when

$$L/L_0 = (\boldsymbol{r})^{1/3}$$

where L is the sample length in nematic state at a given temperature, L_0 is the sample length in isotropic phase that does not depend on temperature, and $\boldsymbol{r}$ is the coil anisotropy at the given temperature. Figure 8 shows the thermoelastic curve for the monodomain network obtained by γ-irradiation of the oriented chemically cross-linked sample (cross-linked by MDI). Within the particular temperature range studied (from $T_{red} = 0.953$ to $T_{red} = 0.992$ or from $T = 94.5$ to $T = 109$ °C) the elongation L/L_0 remains <1.13. In terms of M. Warner theory, it means that coil anisotropy is <1.45.

Thus, according to the theory, the lower the coil anisotropy, the lower the elongation necessary to cause and sustain the monodomain structure. That is why the plateau level of $S(\sigma_n)$ curves (Figures 1 and 2) is reached at very low, practically nonmeasurable, stress.

We believe that extremely low network anisotropy results from the strong tendency of cyanobiphenyl mesogenic groups to form smectic-like clusters. The presence of the latter is known to decrease anisotropy of prolate coils because smectic clusters provide local oblate packing within nematic matrix.

Conclusion

Orientation behavior of acrylate-based LC elastomers with cyanobiphenyl mesogenic groups is strongly influenced by network topology (i.e., structure and spatial distribution of junction points). Because of accumulation within nonmesogenic regions, γ-induced cross-links do not disrupt LC packing and tend to stabilize the nematic phase. In contrast, rigid chemical cross-links (MDI fragments) with a more homogeneous distribution significantly distort LC order. Yet, flexible chemical cross-links provide similar orientation behavior when compared with γ-cross-linked systems. This result is in good agreement with the phase transition temperature changes caused by a variation in network topology and the idea of a nonhomogeneous distribution of cross-links and their compatibility with the LC phase.

Extremely low coil anisotropy of the studied systems provides virtually nonthreshold orientation behavior when critical stress is nearly zero, and polydomain–monodomain transition takes place almost at no cost in external load.

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