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A. S. Merekalov[a]; J. Berkmans[a]; E. R. Zubarev[a]; N. A. Plate[a]; R. V. Talroze[a]; H. Finkelmann[b]
[a] A. V. Topchiev Institute of Petrochemical Synthesis, Russian Academy of Sciences, Leninskii pr. 29, Moscow 117912, Russia, [b] Institute of Macromolecular Chemistry, Freiburg University, Stefan-Meier Str. 31, Freiburg D-79104, Germany,

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Pretransitional phenomena in acrylate-based liquid crystal networks

A. S. MEREKALOV, J. BERKMANS, E. R. ZUBAREV, N. A. PLATE', R. V. TALROZE*
A.V. Topchiev Institute of Petrochemical Synthesis, Russian Academy of Sciences,
Leninskii pr. 29, Moscow 117912, Russia

and H. FINKELMANN
Institute of Macromolecular Chemistry, Freiburg University, Stefan-Meier Str. 31,
Freiburg D-79104, Germany

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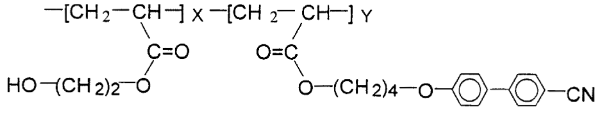
The static Kerr effect is used to study the pretransitional phenomena in polymer networks even in the presence of inherent optical anisotropy of crosslinked materials. The pretransitional phenomena in a liquid crystal polymer and its networks are sensitive to the structure of the crosslinks and their distribution within the network. The bulky network junctions distributed more or less homogeneously within the network serve as defects which decrease the hypothetical second order phase transition temperature T^* and suppress the nematic fluctuations in the polymer network above the clearing point.

1. Introduction

One of the most important phenomena in liquid crystal science is related to heterophasic fluctuations that emerge at the isotropic to nematic phase transition. Here nematic fluctuations are embedded within the isotropic matrix. The formation of fluctuations, their stabilization and the increase in the average correlation radius promote significant changes in physical characteristics, thus reflecting the cooperative nature of the liquid crystalline (LC) medium. The Kerr constant is one of these characteristics which gives a unique opportunity to trace the appearance and development of fluctuations.

Investigations of static and equilibrium characteristics of nematic systems carried out in the last few years [1–4] show many similarities in the pretransitional phenomena for both low molecular mass and polymer liquid crystals. The main goal of this paper is addressed at answering the following: to what extent and under which conditions can the crosslinking of linear LC polymers influence the formation of nematic fluctuations in the isotropic medium? We report on the observation of pretransitional phenomena in acrylate networks prepared by chemical and γ-induced crosslinking of a random copolymer with the following structure:



The first series of networks was obtained by chemical reaction with given amounts of crosslinking agents, namely, 4,4′-methylenediphenyl di-isocyanate (MDI) and 1,6-di-isocyanatohexane (HMDI). The other type of network was produced by γ-irradiation of the same linear copolymer at a prescribed dose.

2. Experimental

The monomer, 4-(4-cyano-4′-oxybiphenyl)butyl acrylate, was synthesized as previously described [5]. The copolymer containing 10 mol % of non-mesogenic units ($X = 10$) was prepared by copolymerization of the above-mentioned monomer with 2-hydroxyethyl acrylate in chlorobenzene at 65°C for 35 h. 2,2′-Azoisobutyronitrile (0.1% of the total weight of the monomers) was used as initiator. The copolymer was precipitated from a mixture of 1,2-dichloroethane and acetonitrile (4 : 1 by vol.) into methanol; yield 60%. The composition of the copolymer was determined by UV spectroscopy using the value of the extinction coefficient of the homopolymer.

The molecular mass characteristics of the copolymer were determined by gel permeation chromatography using a Waters liquid-phase chromatograph equipped with an R401 differential refractometer ($M_w = 1.4 \times 10^5$, $M_w/M_n = 3.02$).

The preparation of chemically crosslinked and γ-crosslinked samples was carried out as described in [6]. The

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*Author for correspondence; e-mail: rtalroze@ips.ac.ru

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temperature of phase transition was determined calorimetrically by linear extrapolation of the dependence of peak position on the temperature scale on the heating rate to the zero value of the latter. On the other hand the Kerr effect technique could be used to identify the nematic–isotropic transition as the temperature at which strong light scattering appeared in the melt. The related data are given in the table where $T_{ni} = T_{NI}$ = nematic–isotropic transition temperature.

The hand-made instrument for measuring the static Kerr effect was developed as described in [7] and allows measurement of the electric field induced optical birefringence in the presence of permanent birefringence resulting from the static network anisotropy. Elliptical compensation with phase modulation of the He-Ne laser beam was used. The initial polarization vector of the laser beam was oriented at 45° to the electric field direction. The analyser was crossed in order to obtain the minimum signal in the registration channel. The temperature control unit based on a thermoregulator Proterm 100 regulated the temperature in a large aluminium chamber where the Kerr cell was kept in the temperature region from 300–500 K. The accuracy of the isothermic regime was about 0.07 K. The sample cell consisted of two polished copper electrodes between which two thin glass plates were glued. The distance between the electrodes was 1–2 mm. The temperature was measured directly in the ground electrode using a Pt100 thermoresistor.

3. Results and discussion

The linear copolymer forms a nematic phase with the transition temperature T_{ni} = 385 K. As was shown before [8, 9], both crosslinking agents and γ-rays can be used for the crosslinking of this material. In the first case, the hydroxyl groups of non-mesogenic hydroxyethyl acrylate units are involved in the crosslinking process and urethane-containing junction points are formed. In contrast, the chemical structure and the location of network junctions induced by γ-rays cannot be particularly defined due to the non-selective effects of γ-irradiation. However, intensive studies of systems containing hydroxyl groups clearly indicate that γ-irradiation initially generates free OH radicals which promote crosslinking or even degradation of polymers [10, 11]. For example, our previous studies have shown that the gel dose for the copolymers under consideration is 10 times lower than that for the LC homopolymer [12].

Several alternative routes can lead to formation of the final crosslinks via recombination of various radicals. FTIR experiments (figure 1) reveal that the spectral band at 3500 cm^{-1} corresponding to the hydroxyl groups does not change appreciably after γ-induced crosslinking, but on the other hand, a noticeable decrease in the intensity of the spectral bands at 2800–2900 cm^{-1} is clearly observed. These bands correspond to the vibration of methylene groups. Therefore, the decrease in intensity indicates their contribution to the crosslinking process. We assume that initially generated free OH radicals preferentially attack the C–H bonds of the methylene groups located either in the backbone or in the side groups, resulting in formation of secondary radicals. The final recombination process would then form crosslinks containing carbon–carbon bonds. Thus, the hydroxyethyl acrylate (HEA) units are responsible for the formation of both types of networks. The proposed schematic representation of the junction's structure is illustrated in figure 2.

Above the clearing point, the linear copolymer forms an isotropic phase and the application of an electric field results in induced birefringence which is given as a function of the square of the field intensity in figure 3.

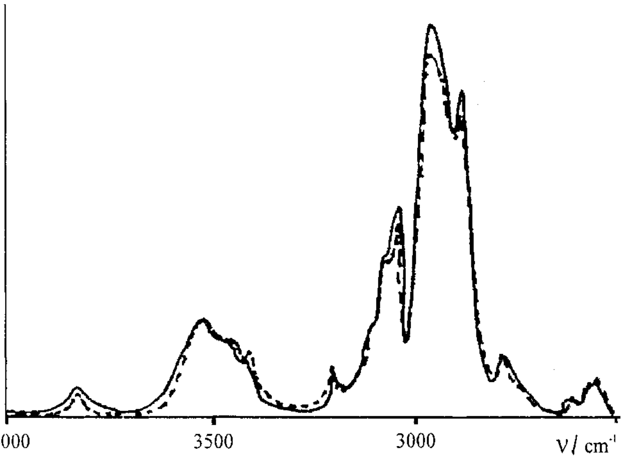

Figure 1. FTIR spectra of copolymer CP before (solid line) and after (dashed line) γ-crosslinking.

Table. Some thermodynamics parameters of nematic–isotropic phase transition for copolymers.

Sample	$T_{ni(Kerr)}$/K	T^*/K	$\Delta T = T_{ni}$-T^*/K	a_0/J K^{-1} mol^{-1}	$\Delta B^{-1}/\Delta T$/V^2 m^{-1} K^{-1}
CP	386.0 ± 0.1	385.3 ± 0.1	0.7 ± 0.1	14.78	(8.1 ± 0.4) × 10^{10}
CP-γ	392.0 ± 0.1	391.0 ± 0.1	1.0 ± 0.1	21.67	(4.7 ± 0.4) × 10^{10}
CP-HMDI	384.0 ± 0.2	383.0 ± 0.2	1.0 ± 0.2	26.53	(3.68 ± 0.08) × 10^{10}
CP-MDI	382.0 ± 0.2	373.7 ± 0.3	6.3 ± 0.3	134.40	(1.03 ± 0.08) × 10^{10}

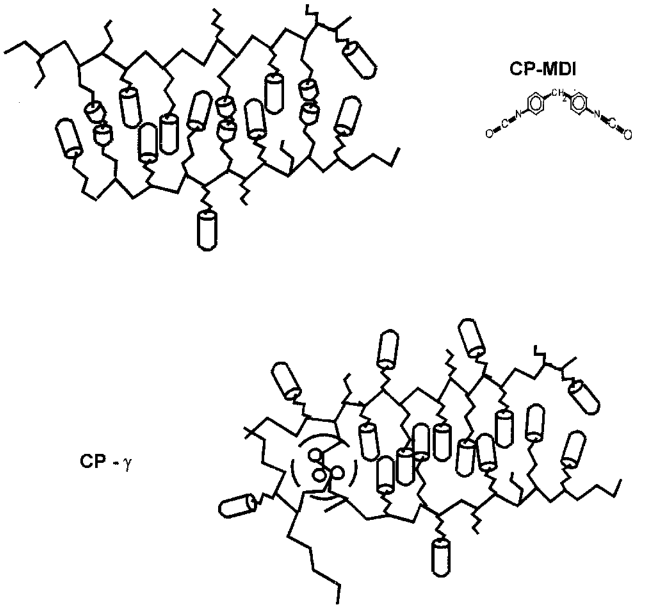

Figure 2. The structure of the network junctions from different crosslinking conditions.

The linearity of this curve within certain temperature and electric field ranges indicates that the system obeys the Kerr law. Contrary to a linear copolymer, the crosslinked materials show a non-zero optical background anisotropy above the clearing point so that the term 'optically isotropic medium' is no longer valid for these systems. This may be due to an inherent anisotropy of the network, which originates from the crosslinking process even if it occurs in the presence of solvent (presumably in the isotropic state of the linear copolymer). In order to avoid the inherent birefringence of the network, the method for the compensation of the electrically induced birefringence described in [7] has been used. This allows one to take into consideration and to compensate for an initial non-zero anisotropy of the medium. The curves for the induced optical anisotropy of the crosslinked samples as a function of the square of the electric field are given in figure 4. The observed linear $\Delta n(\mathbf{E}^2)$ dependence is similar to that for the initial copolymer and therefore proves the validity of the Kerr law for the crosslinked samples as well. The slope of the curves remains positive and increases with decreasing temperature. These data support the idea of the existence of heterophasic fluctuations existing in the vicinity of the isotropic–nematic phase transition, even in crosslinked systems where the presence of fluctuations also appears to be independent of the structure of network junctions.

The Kerr constant B calculated for chemically and γ-crosslinked samples is plotted versus temperature in figure 5. As the system approaches the clearing temperature from the isotropic melt, the value of the Kerr constant increases, which is indicative of critical behaviour in the vicinity of the phase transition. This suggests that the pretransitional behaviour of the LC networks in general is similar to that of the linear copolymer and therefore is not significantly altered by either the crosslinking conditions or agent.

The reciprocal Kerr constant B^{-1} changes linearly with temperature, which allows us to estimate the hypothetical second order transition temperature T^* for all the systems studied. Therefore, the Landau–de Gennes description of the nematic network to isotropic network phase transition theoretically may be used for calculation of the thermodynamic coefficient a_0 known from the

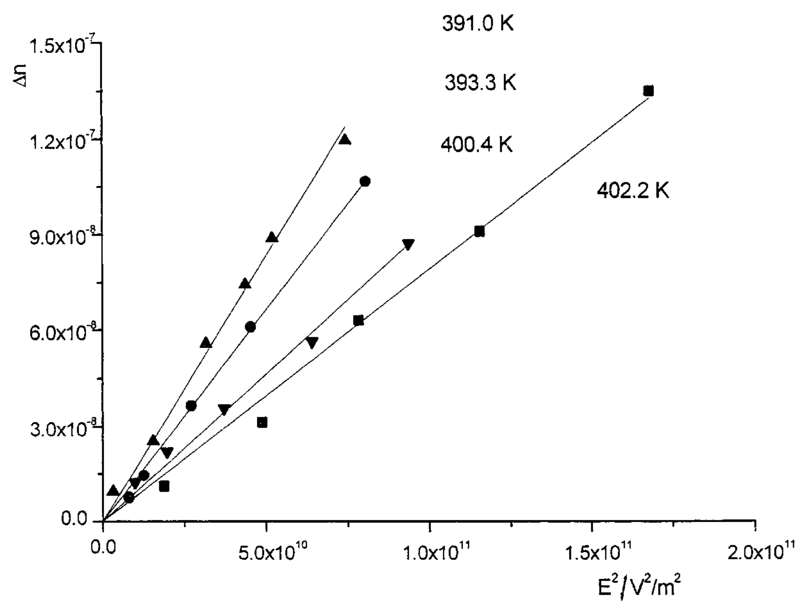

Figure 3. The induced birefringence as a function of the square of the electric field intensity for the linear copolymer CP.

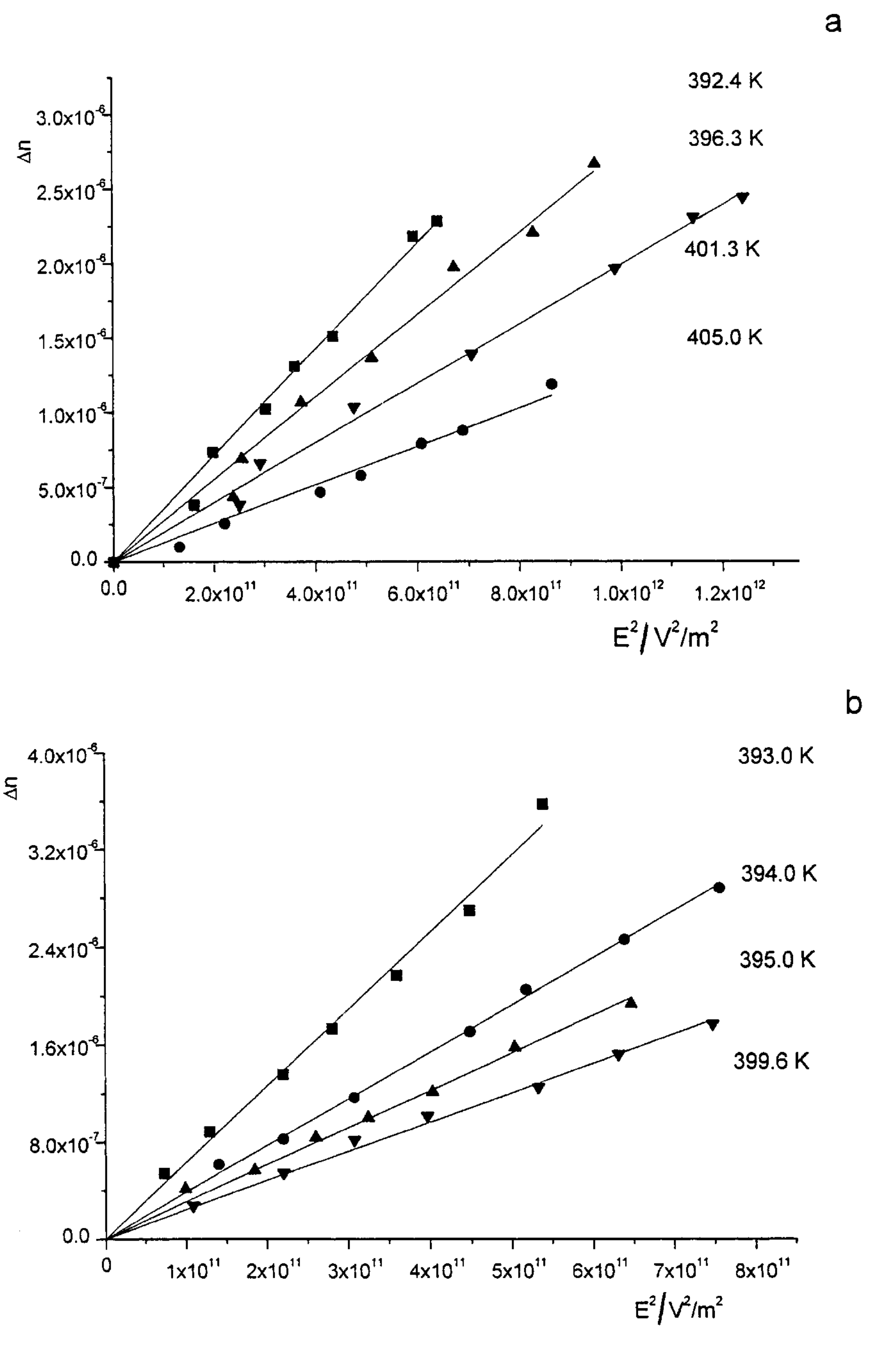

Figure 4. The induced birefringence as a function of the square of the electric field intensity for the crosslinked copolymers: CP-HMDI (*a*) and CP-γ (*b*).

following equation [13]:

$$F(T,S) = F_0(T) + [a(T)/2]S^2 - [b(T)/3]S^3 + [c(T)/4]S^4 + \dots \qquad (1)$$

and

$$a(T) = a_0(T - T^*)^{\gamma} \qquad (2)$$

where

$$a_0 = 2\Delta H / T_{\mathrm{ni}}(\Delta S_{\mathrm{ni}})^2. \qquad (3)$$

It is necessary to point out that the analysis of X-ray pattern azimuthal scans [6] does not give a real, accurate value of ΔS. Thus it is not possible to calculate and discuss the absolute values of the a_0 coefficients. However one may compare the estimated a_0 coefficients for the systems under study having parameters measured for similar conditions. The T^* values, the difference $\Delta T = T_{\mathrm{ni}} - T^*$, and the related a_0 coefficients, are given in the table. The ΔT for the linear and γ-crosslinked copolymers are estimated to be within the range

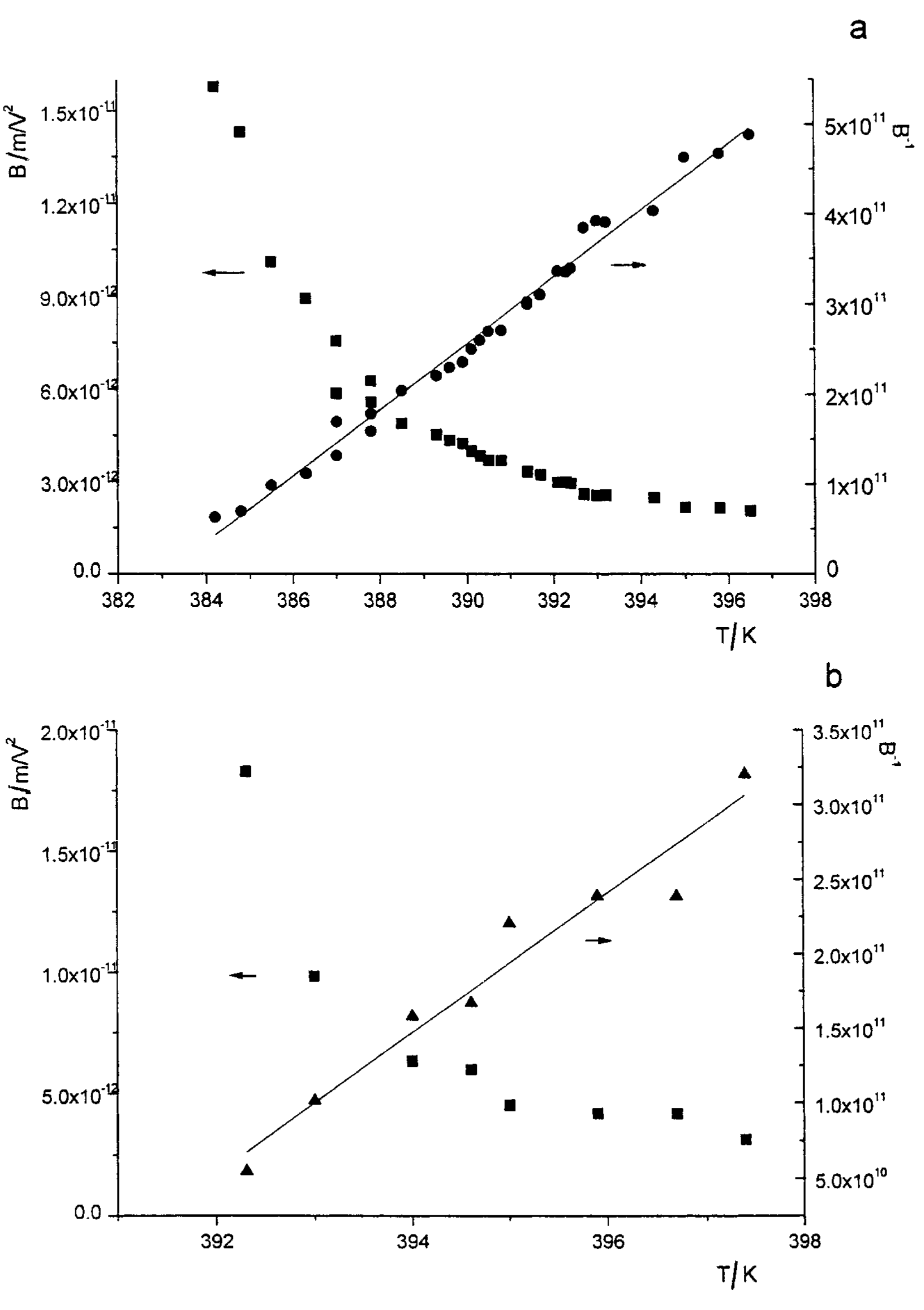

Figure 5. The Kerr constant B and B^{-1} versus temperature for (*a*) chemically (CP-HMDI) and (*b*) γ-cross-linked (CP-γ) samples.

0.7–1.0 K. This is in good agreement with parameters predicted by the Landau–de Gennes theory that have already found experimental confirmation for some low molecular mass liquid crystals [14, 15] and linear side group polymers [1, 2]. At the same time, however, the ΔT value is equal to 6.3 K for the network prepared with the MDI crosslinking agent. Thus, in this particular system, the network structure has the strongest impact on the nematic–isotropic phase transition. This conclusion is also supported by comparison of the temperature dependences of the global order parameter described in [6]. As was shown before, below the glass transition temperature T_g all the samples previously studied are characterized by the same order parameter S. However, above the T_g value, the samples crosslinked by MDI exhibit a significant and continuous decrease in S value at temperatures far below the nematic to isotropic phase transition temperature.

The structure of the network junctions also affects the correlation length of the heterophasic fluctuations and therefore the average number of molecules that form the nematic phase clusters. Taking into consideration the a_0 coefficients estimated above, one may compare the correlation radius g_2 calculated for different networks from the following equation [13]:

$$g_2 = (45NkT)/[(n^2+2)^2 a_0(T - T^*)]. \tag{4}$$

In figure 6 correlation radii values are plotted versus temperature for the different systems studied. These curves clearly show the effect of crosslinking on the size of fluctuations. The g_2 value calculated for the linear copolymer is consistent with data obtained for other systems [4, 13]. The γ-induced crosslinking slightly influences the fluctuation size, whereas the introduction of the network junctions based on MDI essentially limits this size. On the other hand, the slope of the temperature curves for the reciprocal Kerr constant (figure 7) changes in the opposite direction: CP > CP-γ > CP-HMDI > CP-MDI. This slope can be considered as a rate of reduction of the correlation radius with increasing the temperature. It implies that the size of the fluctuations in the linear copolymer decreases faster than it does in the crosslinked materials.

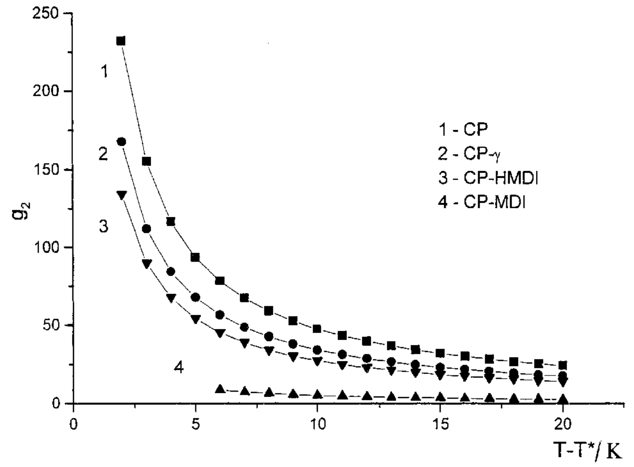

Figure 6. The correlation radius as a function of temperature for different copolymers.

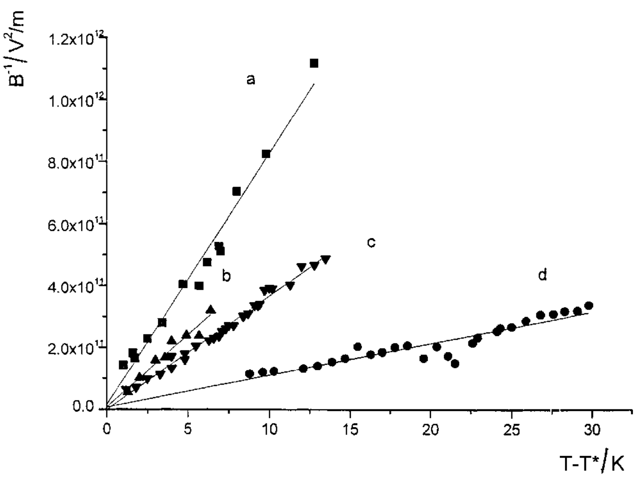

Figure 7. Reciprocal Kerr constant as a function of temperature for CP (a), CP-γ (b), CP-HMDI (c) and CP-MDI (d).

The question arises as to the reason for such a strong decrease in both T^* and correlation radii when the type of chemical agents and crosslinking conditions are varied. To answer this, one has to consider the distribution of comonomeric units within the bulk of the linear copolymer. We believe that because of the marked difference between the structures of the mesogenic and non-mesogenic units, the copolymer should contain microphase segregated domains enriched with hydroxyethyl acrylate (HEA) units. These domains can serve as spacially confined regions where the γ-induced crosslinks are being accumulated and are most likely to form due to a high local concentration of hydroxyl groups. These regions essentially 'shield' the network junctions from the mesogenic groups and prevent their deteriorating influence on the nematic order.

As for the chemically crosslinked systems, in which the junction points are based on fragments of crosslinking agent, the difference in their behaviour in comparison with the γ-crosslinked materials may have two causes. First, the molecules of the crosslinking agent MDI are fairly large in size and have a rather rigid structure. As a result, complete 'shielding' of these junctions cannot be achieved. Second, the chemical structures of the MDI fragments and mesogenic groups are somewhat similar. Therefore, during the crosslinking process, the MDI molecules are likely to penetrate into mesogenic domains where a small number of HEA units are still present. This leads to a more homogeneous distribution of crosslinks within the bulk material, causing the decrease in the global order parameter T^*, and the fluctuation in correlation length, as well as in the broadening of the phase transition.

Finally, the networks containing the HMDI fragments as junction points occupy an intermediate position between CP-γ and CP-MDI because they are far more flexible and should have a low compatibility with the LC phase. As a result, these crosslinks do not strongly affect the pretransitional phenomena and the global order parameter [6, 16].

4. Conclusion

Static Kerr effect measurements are found to be a powerful tool for the study of pretransitional phenomena in polymer networks, even in the presence of inherent optical anisotropy of the crosslinked materials. The formation of nematic fluctuations in the polymer networks can be described in terms of Landau–de Gennes theory. However, analysis of the pretransitional phenomena in a LC polymer and its networks shows their sensitivity to the structure of the crosslinks and their distribution within the network. One may conclude that bulky junctions distributed more or less homogeneously within the network serve as defects, which decrease the hypothetical second order phase transition temperature T^* and suppress the nematic fluctuations in the polymer network above the clearing point.

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