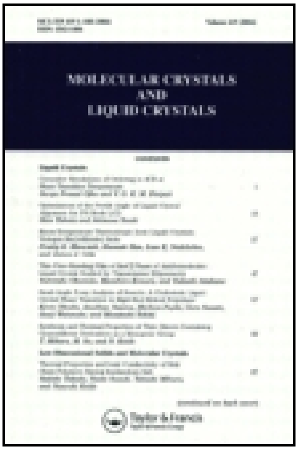

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Nicole Aβfalg [a], Andreas Greve [a] & Heino Finkelmann [a]
[a] Institut für Makromolekulare Chemie, Albert-Ludwigs-Universität Freiburg, Sonnenstr.5, D-79104, Freiburg

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Influence of a Mechanical Field on the Liquid Crystalline to Isotropic Phase Transformation

NICOLE AßFALG, ANDREAS GREVE and HEINO FINKELMANN

Institut für Makromolekulare Chemie, Albert-Ludwigs-Universität Freiburg; Sonnenstr.5, D-79104 Freiburg

The influence of external mechanical stress on the liquid crystalline to isotropic phase transformation of polysiloxane networks with mesogenic side groups is investigated by stress optical measurements. The hypothetical second order phase transformation temperature T^* and the critical exponent γ, as described by the phenomenological Landau – de Gennes theory, are determined. Different systems having nematic and smectic behaviour, respectively, are investigated. Furthermore, the crosslinking density is varied for the nematic system. While in previous investigations of side-on nematic polymer networks, the phase transformation temperature depends on the applied stress, this effect is not found for end-on nematic systems. For smectic elastomers a hypothetical phase transformation temperature T^* close to $T_{lc,i}$ is observed. In contrast to previous experiments, however, no smectic fluctuation could be identified above $T_{lc,i}$.

Keywords: nematic; smectic; lc-elastomers; birefringence; Landau-de Gennes; stress-optical measurements

INTRODUCTION AND THEORY

Phase transformations of nematic and smectic liquid crystalline (lc) elastomers are generally described by the phenomenological Landau-de Gennes theory [1,2]. The behaviour of such elastomers in the pretransformational regime can be described by a hypothetical second-order phase transformation temperature (T^*) and a critical exponent (γ). These parameters can be discerned from stress-optical experiments for nematic and smectic lc elastomers. In the pretransformational regime just above the phase transformation temperature, optical birefringence exhibits the following temperature dependence under the influence of an external mechanical field:

$$\Delta n \sim \left(T - T^*\right)^{-\gamma} \tag{1}$$

Because of very small values of the order parameter S (S<<1) in the pretransformational regime, measurement of birefringence is a suitable method for determination of macroscopical order. The anisotropy of the polarizability, coupled with the contribution of the mesogenic groups, results in macroscopical anisotropy of the polarizability, which is related to the birefringence by a modified Lorenz-Lorentz equation [3]. It immediately follows that the birefringence (Δn) is proportional to the order parameter S. According to the extrapolation procedure of Haller et al. [4,5], the order parameter S can be ascertained from stress-optical measurements in the lc phase.

Prior investigations of nematic elastomers in the pretransformational regime [6] showed a dependence of T^* on the strength of the external mechanical field. In these experiments the critical exponent γ was found to be one. Kaufhold et al. [7] have performed measurements on side-on lc elastomers based on methacrylate networks and have reported that $T_{n,i}$ is shifted to higher temperatures by different constant nominal stresses.

Investigations of smectic elastomers reveald a second characteristic temperature $T^{*\prime}$. The second hypothetical phase transformation temperature is explaind by the existence of smectic fluctuations in the pretransformational regime [8]. In order to establish if the previously reported stress-optical behaviour is general, we analyzed a series of nematic and smectic networks.

EXPERIMENTAL

Experimemtal set-up

Each elastomer film was stretched symmetrically by two stepping motors (Fig.1) and the stress was measured by a force transducer as a function of strain. The birefringence is determined simultaneously by the method of the rotating-analyzer [10]. Monochromatic light from a He-Ne laser passed successively through the polarizer, the sample, a quaterwave (λ/4) plate, and a rotating analyzer before reaching a photodiode. The polarizer and the axis of the quaterwave plate were aligned at 45° to the stress axis.

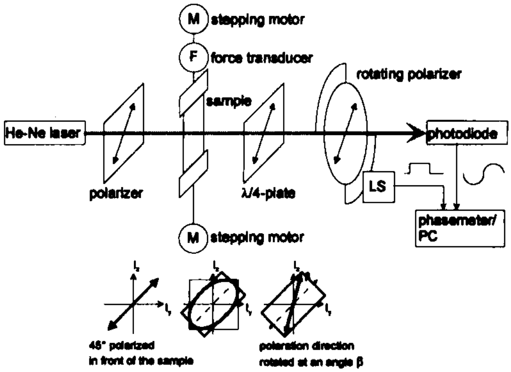


FIGURE 1 Schematic illustration for the stress-optical equipment

The polarization direction of the light that has passed the sample and the λ/4 plate was subsequently rotated by an angle β, which is proportional to the birefringence Δn.

Systems

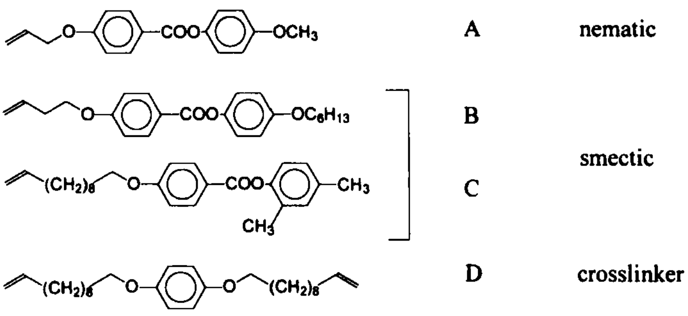


FIGURE 2 Chemical structure of the different compounds

Each of the monomeric compounds (A,B,C in Fig. 2), the crosslinker (D) anc poly(hydrogenmethylsiloxane) as the polymer backbone were dissolved ir toluene (Table 1). The lc elastomers were prepared by a platinium-catalyzec hydrosilylation reaction during spin-casting at 60°C for 3h. After crosslinking the elastomers were deswollen on a water surface (E1-E3, E11) or subjectec to a constant stress (E8) and dried in vacuum [9,11]. The non-stressed samples exhibited a polydomain structure, whereas the stressed sample possessec a monodomain structure, as characterized by x-ray scattering. The results o differential scanning calometry (DSC) measurements are shown in Table 1.

Table 1 Mesogenic groups, crosslinker density and DSC results of the synthesized elastomers examined here

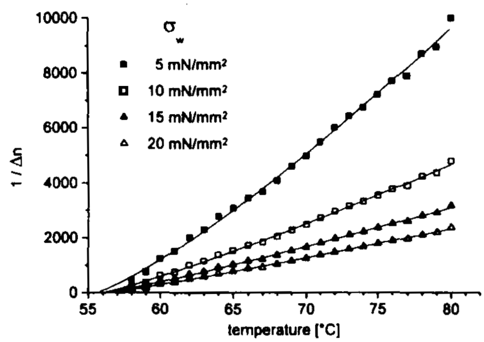
elastomer	mesogenic group	crosslinking density	$T_{lc,i}$ [°C]	$\Delta H_{lc,i}$ [J/g]
E1	A	7 mol%	56	1.4
E2	A	10 mol%	51	1.6
E3	A	20 mol%	26	0.8
E8	45% B 55% C	10 mol%	64	8.9
E11	C	10 mol%	59	8.5

RESULTS AND DISCUSSION

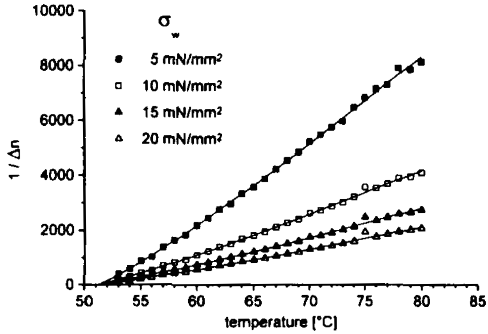
Nematic Systems (E1,E2,E3)

Stress optical measurements of the nematic elastomers E1, E2 and E3 are conducted just above the phase transformation temperature, up to $T_{lc,i}$ + 30K. The crosslinking density is increased from 7mol% to 20mol%. The dependence of the reciprocal birefringence on temperature for these elastomers is shown in figure 3a - 3c, with the different curves representing different stresses.

a)



b)



c)

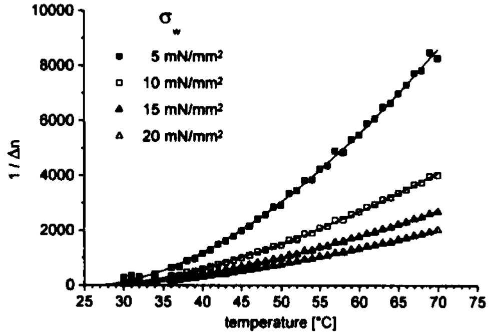


FIGURE 3 Reciprocal birefringence versus temperature for the nematic elastomers (a) E1 (b) E2 and (c) E3 as the true stress is increased from $5mN/mm^2$ to $20mN/mm^2$. The solid lines are shown in the plots correspond to Eq. (1).

Unlike former investigations [4] of acrylate-based networks the hypothetical second-order phase transformation temperature T^* is virtually independent of stress for the elastomers E1, E2 and E3, especially considering the uncertainty in the data. For the systems with low crosslinking density (E1, E2), the critical exponent γ is found to be 1.1±0.1. For the system with a higher crosslinking density (E3), the critical exponent increases to 1.6±0.1. A possible reason for this difference is that the crosslinker hinders the formation of nematic clusters. The phase transformation enthalphy $\Delta H_{lc,i}$ (Table 1) is much lower for the elastomer E3 than for the systems E1 and E2 (with lower crosslinking density). A similarly observed reduction in phase transformation enthalphy occurs with decreasing film thickness in thin lc films due to a „finite-size-effect“ [12,13], suggesting that the nematic clusters in E3 are smaller than those in E1 and E2.

Smectic Systems (E8, E11)

Stress optical measurements on smectic elastomers (E8, E11) have also been performed just above the phase transformation temperature up to $T_{lc,i}$ + 20K.

a)

b)

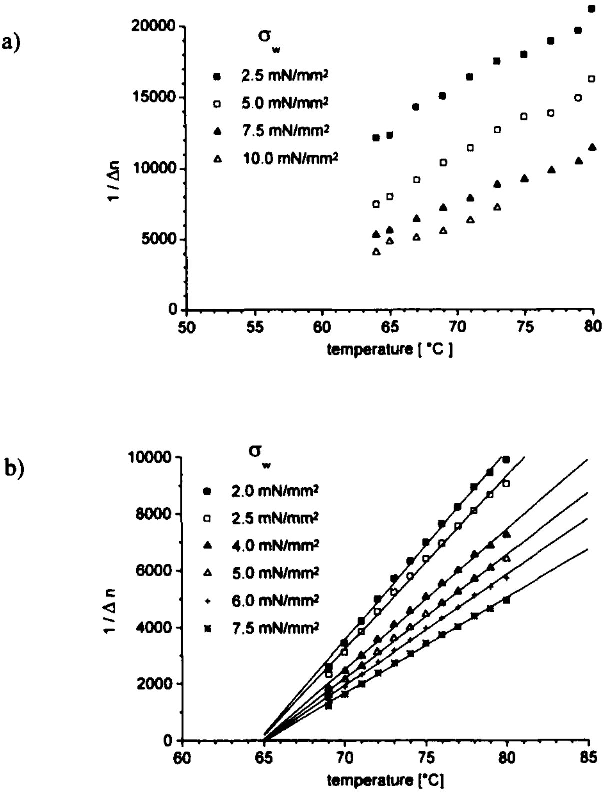


FIGURE 4 Reciprocal birefringence versus temperature for the smectic elastomers (a) E11 and (b) E8 for different true stresses over the range from 2.0mN/mm^2 to 10.0mN/mm^2.

The variation of reciprocal birefringence with temperature for these elastomers is shown in Fig. 4a and 4b, with different curves in the figures once again representing different stresses.

The smectic A systems (E8, E11) do not show any obvious evidence of second hypothetical phase transformation temperature $T^{*'}$ (Fig. 4a, Fig 4b), in marked contrast to former investigations [8] of siloxane-based smectic networks with slightly different substituted mesogenic groups. The systems investigated here possess only one unambiguos hypothetical phase transformation temperature T^* near the clearing temperature $T_{lc,i}$. Unlike the nematic elastomers, these elastomers always possess a critical exponent γ larger than unity.

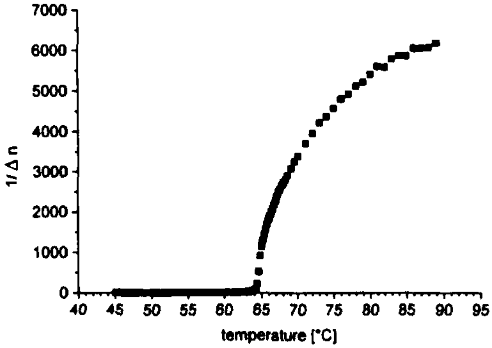


FIGURE 5 Temperatur-dependent reciprocal birefringence of the unstressed monodomain sample E8.

For the monodomain sample E8 (Fig. 5) it is possible to measure a value of birefringence up to the lc-phase. Since the variation of reciprocal birefringence with temperature is continuos, it appears that this the phase transformation is second-order but additional experiments must be conducted to verify this result.

CONCLUSIONS

At this stage of the present study, we can conclude that the hypothetical phase transformation temperature T^* is independent of applied stress for the investigated nematic and smectic systems, and the critical exponent γ lies in the range between one and two. The smectic systems do not exhibit a discernible second hypothetical phase transformation temperature $T^{*\prime}$ in contrast to former investigations of other smectic systems. Initial birefringence measurements from the isotropic phase into the smectic phase give reason to believe that the phase transformation is second-order.

Acknowledgments
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