Molecular Dynamic Simulation of Side-Chain Liquid Crystalline Elastomer Under Load

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Summary: We present a molecular dynamic simulation of a side chain liquid crystalline elastomer (LCE) under load. The LCE is composed of a flexible tetrafunctional diamond like network with rod-like mesogens attached to the network. As a precursor of the LC elastomer a flexible polymer network in a low molecular liquid-crystal (LC) solvent was used. The phase behavior of the LCE under uniaxial stretching up to the deformations of $\lambda = 1.5$ and 2.0 at different densities was studied. As in the non-stretched case upon density increase an isotropic to nematic phase transition occurs. However, in contrast to thermotropic side chain LC elastomers the stress induced shift transition is not observed. The stretching slightly increases the anisotropy of translational diffusion of mesogens in the nematic state. The stress-strain dependence for LCE both in the isotropic and the nematic states is obtained. Elastic modulus increases at high values of order parameter.

Keywords: elastomer; liquid-crystalline polymers; networks; simulations

Introduction

Side chain liquid crystal (LC) elastomers attracted attention of researchers for a long time due to their outstanding mechanical properties. The combination of the entropic elasticity of flexible polymer network chains with long range orientational order and mobility of mesogenic groups attached to polymer network in LCE systems has found promising applications as artificial muscles and mechanical actuators. LCE and their unique response to external forces are intensively studied experimentally and a few theoretical studies were reported, however, to author's best knowledge no computer simulation studies of side chain LCE[1–8] have been reported thus far.

As in the case of low molecular LC the ordering in LC elastomers can occur due to the dependence the interaction energy on the mutual orientation of mesogens or due to the anisotropic shape of mesogens. In the first case the LC transition is induced by the decrease of the temperature (thermotropic LC polymer). In the second case the LC transition occurs at some polymer concentration due to entropic reasons (lyotropic LC polymers).[4] Thermotropic LC elastomers show exceptional properties under load. The theory describing the effect of stress on the isotropic-nematic transition (NI) in thermotropic LC elastomers with backbone mesogens was first developed by de Gennes (see for example Finkelmann[6] and references in it). The theory predicts a shift of T_{NI} upon applied stress. It was shown that a similar approach is applicable also for the side chain LCE.[3] For such polymers the shift of T_{NI} under stress was also observed experimentally.[6,9]

Recently we have presented results of molecular dynamics simulations of a LC elastomer with side chain mesogens.[10] As

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a precursor of the LC elastomer the flexible polymer network swollen in a low molecular LC solvent was considered. The low molecular solvent consisted of rod-like molecules with purely repulsive intermolecular interactions. Upon a density increase of the low molecular solvent the following phase behavior is observed: from isotropic to nematic and than to the smectic phase. These LC phases are of lyotropic nature.

The formation of the LC elastomer comprising the attachment of ends of mesogens to the network was simulated at densities corresponding to different phases of the LC solvent. The structural and dynamical properties of the resulting created LC elastomer were studied and compared with those of the precursor. It was shown in particular that the formation of the LC elastomer shifts the region of the stability of the smectic phase to lower densities.

In the present work we study the effect of the deformation on the structure and dynamics of this LC elastomer model. The stretching procedure is simulated as an affine deformation of the network. The behavior of the stretched LC elastomer is compared with that of non-stretched one.

Model and Simulations

As a network model we use the regular tetrafunctional diamond-like network consisting of flexible chains composed of 31 beads each.

The beads interact with each other by repulsive Lennard-Jones (LJ) potential.

$$U_{LJ}(r) = 4\varepsilon\left(\left(\frac{\sigma_b}{r}\right)^{12} - \left(\frac{\sigma_b}{r}\right)^{6} + \frac{1}{4}\right), \quad r \leq 2^{1/6}\sigma_{\mathrm{b}}. \qquad (1)$$

Here σ_{b} and are *LJ's* parameters and units of length and energy correspondingly ($\sigma_b = 1$, $\varepsilon = 1$).

The side group mesogens consisted of linear sequence of 7 beads similar to those of the main chain. The beads both in the main chain and in mesogens are bonded by the FENE potential.

$$U_{bond}(r) = U_{LJ}(r) - \frac{\varepsilon_2 R_0^2}{2\sigma_b^2}\ln\left(1 - \left(\frac{r}{R_0}\right)^2\right), \quad r < R_0 \qquad (2)$$

where $R_0 = 1.5\sigma_b$, $\varepsilon_2 = 30\varepsilon$.

Rigidity of mesogens was introduced by an additional bending potential:

$$U_{bend}(\Theta) = 200[1 - \cos(\Theta)] \qquad (3)$$

where Θ is the angle between neighboring bonds in the mesogen.

The mesogens were attached by one end to the network beads through the FENE potential (2) (Figure 1).

As usual the temperature T of the system was determined as $T = 2K/3N$ where K is the total kinetic energy of the system and N is the total number of beads All simulation were performed at $T = 1$.

In the present work we study the effect of the stretching only for the LC elastomer formed from the precursor in the isotropic state (number density ($\rho = 0.55$)). The number density was determined as $\rho = N/V$, where N - number of all particles in the system The simulation box contained 6 network cells along 0Z axis and 3 cells along 0X and 0Y axes.[10] The average number of mesogens per one chain between junctions was equal to 10. The periodic boundary conditions were used.

Simulation of LC Elastomer Under Load

To simulate the behaviour of the elastomer under load the affine deformation of the whole system was performed along the X-axis of simulation box, keeping the volume constant. The dimensions of the simulation box along the X,Y and Z axes were changing with a deformation rate

Figure 1.
Layout of the side chain LC elastomer model.

$\lambda(t) = 1 + {}^{a}\!/_{x_o} t$ according to

$$x = \lambda(t)x_0,\ y = \frac{1}{\sqrt{\lambda(t)}}y_0, \\ z = \frac{1}{\sqrt{\lambda(t)}}z_0 \tag{4}$$

where x_o, y_o, z_o are the dimensions of the simulation box of the non-deformed state.

The value of the rate constant $a = 0.01$ was chosen. The process of the deformation was performed until the definite value λ of the deformation was achieved. In the present study final values $\lambda = 1.5$ and 2.0 were considered.

To obtain systems at various densities the external pressure was applied simultaneously with the deformation of the simulation box. The values of the pressure which are necessary for the formation of the system with the given density were determined earlier for non-deformed LC elastomer.[10] After the achievement of the given deformation and density the systems were equilibrated using NVT ensemble.

The equilibrium state was considered being achieved when the order parameter and stress became stable. The duration of the equilibration run was about 5×10^6 time steps. The reduced units for time $\tau = \sigma_b (m/\varepsilon)^{1/2}$ and length σ_b were used as usual. The integration step $\Delta t = 0.01$ was selected. Than productive runs were performed during 5×10^5 steps. Structural and dynamical properties of the system were determined by the averaging over whole trajectory of the productive run. The calculations were carried out using computer time provided by the Centre for Scientific Computing (CSC, Espoo, Finland) on IBM eServer Cluster 1600.

In contrast to the non-stretched case the simulations were performed in the more narrow density region (from $\rho = 0.55$ to $\rho = 0.70$). At larger densities the process of the equilibration occurs to be too slow to reach the equilibrium state in reasonable computer time.

Phase Behaviour

The order parameter S of mesogens is determined as

$$S = \frac{3}{2}\left\langle \cos^2\theta - \frac{1}{3}\right\rangle, \tag{5}$$

where θ is the angle between the end-to-end vector of a mesogen and the director. The director was determined by the diagonalization of the ordering tensor:

$$Q_{\alpha\beta} = \frac{1}{N_m}\sum_{j=1}^{N_m}\frac{3}{2}n_{j\alpha}n_{j\beta} - \frac{1}{2}\delta_{\alpha\beta}, \tag{6}$$

where $n_{j\alpha}$ are components of the normalized end-to-end vector of the molecule j; α, $\beta = x, y, z$; δ is the delta function. The eigenvector corresponding to the maximum eigenvalue λ_1 shows the direction of the preferred orientation of the molecules. The value of λ_1 gives the value of S. In our system the direction of the orientation of mesogens coincides with the direction of the stretching.

Figure 2 shows the change of the instaneous value of order parameter (averaged over all mesogens) in the process of

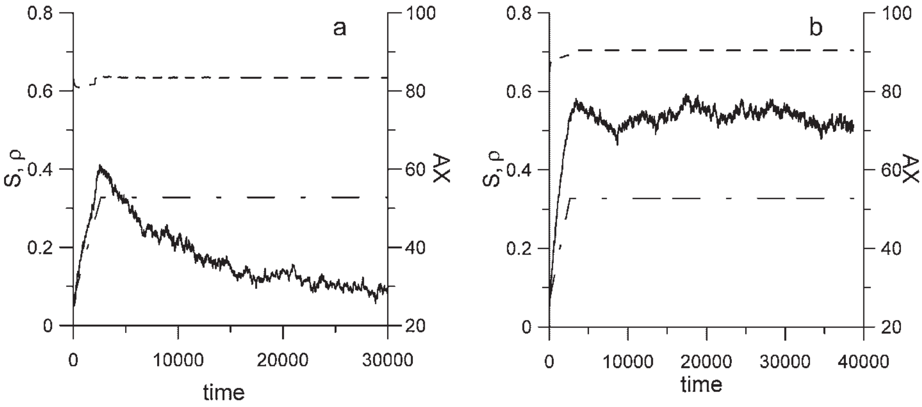

Figure 2.
Instaneous change of order parameter, density and x-dimension of the simulation box vs. time. a) $\rho = 0.634$, b) $\rho = 0.704$.

the deformation and compression of the systems. In the same plots the changes of the density and x-dimension of the simulation box are shown. At low densities the ordering of mesogens starts to increase during the process of the deformation but disappears continuously after the cell deformation was stopped (Figure 2a). At larger densities the ordering remains after the stopping of the deformation process (Figure 2b).

The dependence of the equilibrium value of the order parameter of mesogens (averaged both over the time of simulation and over all mesogens in the simulation box) on the density ρ for the non-stretched and stretched LC elastomer is shown in Figure 3. The data for the system of network/LC solvent, where mesogen were not attached to the network are shown on the same plot. It is seen that the values of the order parameter for stretched network coincide practically with those for non-streched one at the same densities. We show only data for the LC elastomer stretched up to the deformation value $\lambda = 2$. The data for other deformations differ only slightly.

The analysis based on the structural and dynamical data shows that this LC phase corresponds to the nematic. Snapshots (Figure 4) confirm this conclusion.

Therefore the stretching of lyotropic LC elastomer does not result in a shift of the LC transition along the density axis. For thermotropic LC side-chain elastomers the stretching corresponding even to smaller values of λ leads to a remarkable shift of the temperature of the I-N transition.[10] This shift is explained in frame of the de Gennes theory by the coupling between the orientation of side-chain mesogens and the network deformation. In the expression for the free energy of the deformed LC elastomer this coupling is described by the

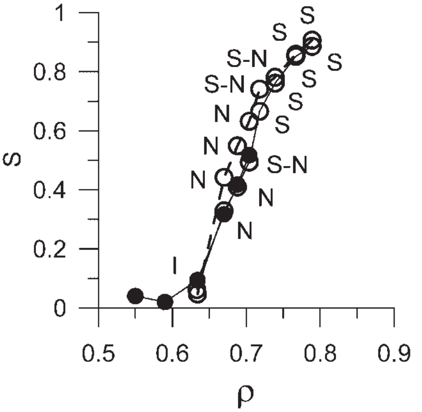

Figure 3.
Order parameter vs. density: I – isotrop, N-nematic, S - smectic phase. Filled circles – stretched LC elastomer, open circles - LC elastomer.

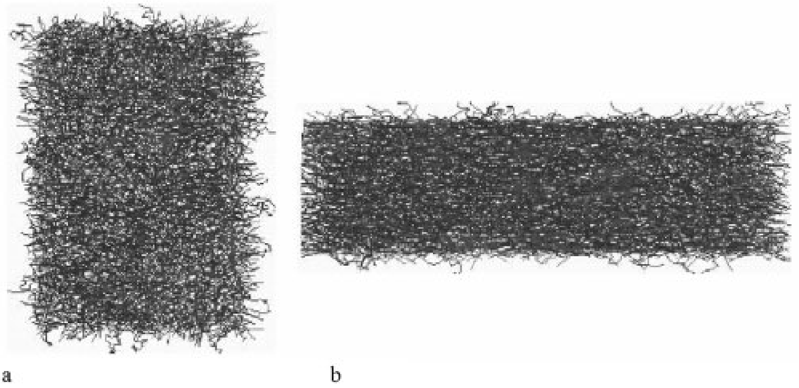

Figure 4.
Snapshots of nonstretched $\rho = 0.634$ (a) and stretched LC elastomer $\rho = 0.704$ (b).

additional term $-US(\lambda-1)$. In our case of the lyotropic LC side-chain elastomer the formation of the LC phase is determined by the entropic reasons. The absence of the effect of the deformation on the phase behavior means that the above mentioned coupling is small.

Chain Conformations in the Deformed Network

The effect of the stretching on conformations of network chains of LC elastomer in isotropic and nematic phases can be seen from the comparison of the distribution function for end-to-end distances of chains with that for non-deformed system (Figure 5).

In the isotropic phase (Figure 5b) the stretching shifts the distribution maximum to higher h. The distribution itself becomes wider for stretched system, but remains symmetric. A similar effect of deformation was observed by Everaers and al.[11] in simulation of usual flexible networks. At the densities corresponding to the nematic state the deformation leads not only to the

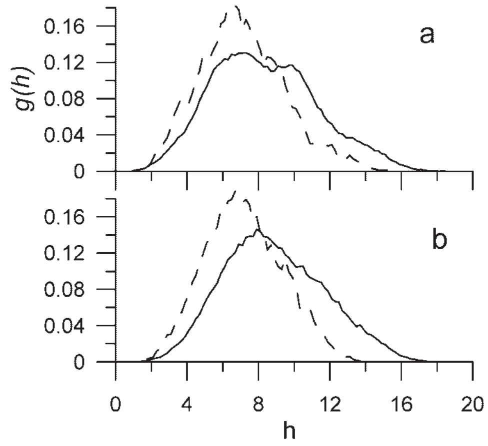

Figure 5.
Distribution function for end-to end distances h for chains of the polymer network for stretched LC elastomer (solid line) and initial system LC+network (dashed line) in (a) nematic ($S = 0.4$, $\rho = 0.704$) and (b) isotropic ($\rho = 0.634$) states.

broadening of the distribution but also to the remarkable changes of its shape (Figure 5a). Instead of the one maximum two maximums appear. The first maximum remains practically in the same place and the second one shifts to higher *h*. It means that the part of chains in the nematic state is stretched more than in the isotropic case due to the mesogens ordering.

Translational Diffusion

The translational mobility of network chain monomers and mesogens can be characterized by the time dependence of mean squared displacement $\langle \Delta r^2(t) \rangle$ (MSD) of chain beads and centres of mass of mesogens correspondingly. Figure 6 shows these data for stretched and nonstretched LC elastomer in isotropic and nematic states.

The time dependence of MSD for chain beads is nonlinear due to the chain connectivity. The stretching of the network decreases beads displacements for the same time both in the isotropic and nematic phases.

Due to the attachment of mesogens to the network chains the time dependence of MSD for mesogens is non-linear too (Figure 6). In the isotropic phase the stretching decreases slightly the diffusion of mesogens in comparison to the non-deformed case. In the nematic phase the diffusion of mesogens is slightly higher in the stretched LC elastomer.

Anisotropy of Diffusion

It is well known that LC ordering in low molecular systems leads to an anisotropy of the translational diffusion. In the nematic state the self- diffusion of LC molecules along the director is easier than that in the normal direction. Such an anisotropy is observed also for mesogens attached to the network. As can be seen from comparison of the time dependence of MSD of centres of mass of mesogens along the director $\langle \Delta r^2_{par}(t) \rangle$ with that in the perpendicular direction $\langle \Delta r^2_{per}(t) \rangle$ (Figure 7). Due to the limited computer time our data is reliable only for displacements smaller than the mesogen length (of order of several bond lengths).

In the isotropic phase there is no remarkable difference between $\langle \Delta r^2_{par}(t) \rangle$

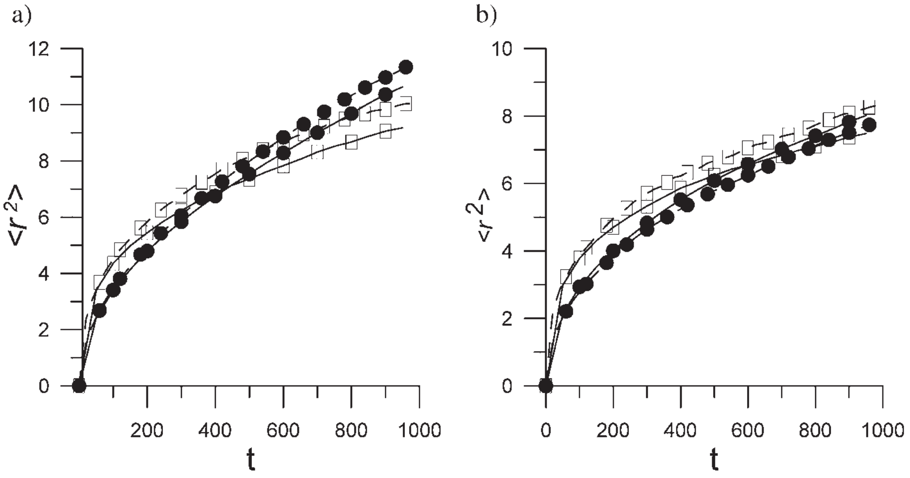

Figure 6.
Time dependences of MSD for the stretched (solid line) and nonstretched LC elastomer (dashed line): ● - centers of mass of mesogens, □ – middle chain monomers, a - nematic phase (ρ = 0.704), b – isotropic phase (ρ = 0.634).

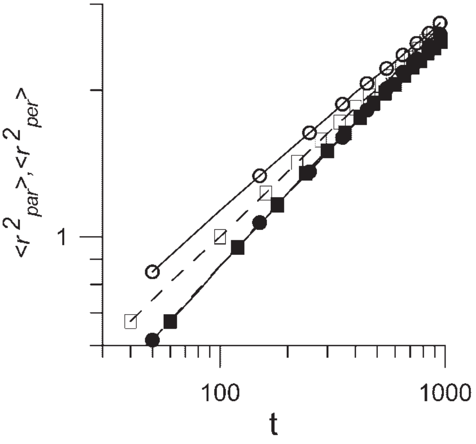

Figure 7.
Time dependence of MSD of mesogens for the stretched LC elastomer (solid line) and nonstretched LC elastomer (dashed line) in nematic phase ($\rho = 0.704$). Open symbols - $\langle \Delta r^2_{m(par)}(t) \rangle$, filled symbols - $\langle \Delta r^2_{m(per)}(t) \rangle$.

and $\langle \Delta r^2_{per}(t) \rangle$ both in the non-deformed and deformed networks. For the nematic phase $\langle \Delta r^2_{par}(t) \rangle$ exceeds $\langle \Delta r^2_{per}(t) \rangle$ in the whole time range. In the deformed system the anisotropy of the diffusion is stronger than that in the non-deformed network at the same density.

Elastic Properties

The elastic modulus of the network can be determined from the stress-strain dependence. To obtain the values of the stress the components P_{aa} of the pressure tensor were measured. The normal stress is given by the formula

$$\sigma = P_{xx} - {}^1\!/_2(P_{yy} + P_{zz}) \qquad (7)$$

Figure 8 shows the deformation of the network after applying the stress. During the first stage when the deformation increases with time the stress increases too. When the process of the deformation stops the stress begins to relax to the

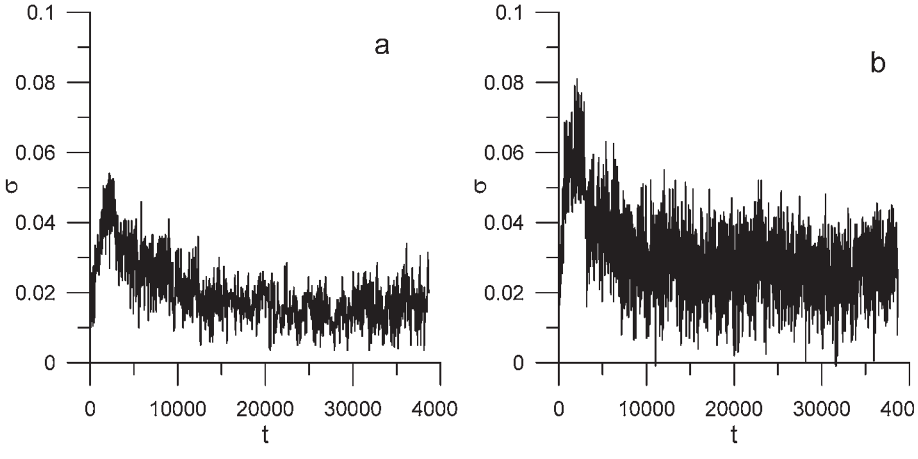

Figure 8.
Stress relaxation for the LCE system of different densities under load ($\lambda = 2$): a) $\rho = 0.634$, b) $\rho = 0.704$.

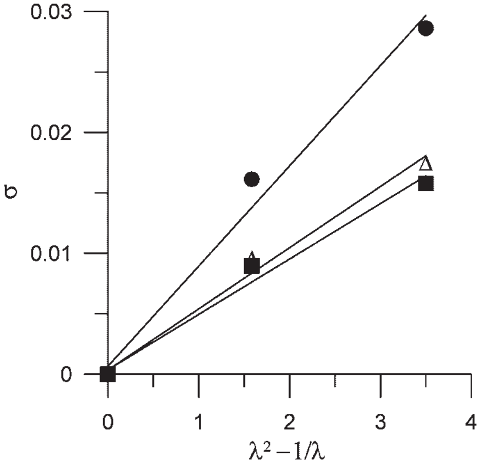

Figure 9.
Stress-strain curve. ●- $\rho = 0.704$, Δ- $\rho = 0.670$, ■ -$\rho = 0.634$.

equilibrium values characteristic for the given values of the final deformation. Even in the equilibrium state in the plateau region the values of stress fluctuate. The value of the elastic modulus G was calculated from the slope of the stress-strain dependence.

$$G = \sigma/(\lambda^2 - 1/\lambda) \tag{8}$$

To obtain this dependence we have calculated the average values of the stress in the plateau region. The resulting stress-strain dependence for different densities is shown in Figure 9. The stress-strain dependence is close to a linear function both in isotropic and nematic states.

The dependence of elastic modulus G vs. order parameter is shown in Figure 10. The value of the modulus calculated for the system network/low molecular LC solvent in the isotropic state is shown on the same plot. As can be seen the attachment of mesogens to the network increases the

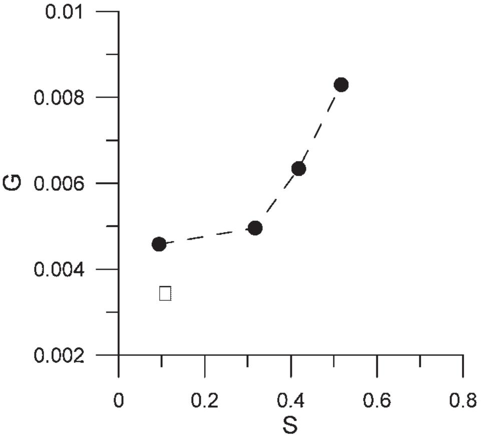

Figure 10.
Elastic modulus as a function of order parameter of LCE system. □ – value of the modulus for corresponding system of network swollen in the LC solvent.

value of the modulus even in the isotropic state. In the LC state the modulus of the LC elastomer doesn't change until the order parameter exceeds 0.4 and increases at larger S. It was shown[9] that the modulus of the thermotropic LC elastomer does not change after the transition to the nematic state but increases with the formation of the smectic phase.

Our previous simulation of the non-deformed LC elastomer[10] has shown that at larger values of density the transition from the nematic to the smectic phase is observed (Figure 3). Possibly the observed increase of the modulus in our case is connected with the initiation of the smectic phase.

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