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Molecular Dynamic Simulation of Side-Chain Liquid Crystalline Elastomer

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Summary: Molecular dynamic simulation of side chain liquid crystalline elastomer has been carried out. As an initial state a flexible polymer network in a low molecular liquid-crystal (LC) solvent was used. The LC solvent comprises of anisotropic rod-like semiflexible linear molecules (mesogens) composed of particles bonded into the chain by FENE potential. Rigidity of LC molecules was induced by a bending potential. All interactions between nonbonded particles are described by a repulsive Lennard-Jones potential. For the systems with different values of density and order parameter obtained after sufficiently long trajectory the attachment of ends of mesogens to the polymer network was simulated. The kinetic of the process of mesogens attachment to network was studied as well as morphology of attachment. The structural and dynamical behaviour of side chain LC elastomer was studied and compared with systems of polymer network in low molecular LC solvent.

Keywords: liquid crystalline elastomer; molecular dynamics

Introduction

Liquid crystal (LC) elastomers attracted the attention of researchers for a long time. They combine rubber-like mechanical properties due to the entropic elasticity of chains with long range orientational order and mobility characteristic for low molecular LC. LC elastomers are considered as slightly crosslinked networks consisting of polymers wearing the mesogenic groups. Similar to linear LC polymers two main types of LC elastomers are possible: main chain and side chain ones. In the first case mesogenic groups are directly included into the backbone. In the second case the backbone is a usual flexible polymer and mesogens are linked to it as side groups. Of course combined main-chain and side chain structures are possible as well [1]. In the present work we consider side-chain elastomers. There are many experimental works devoted to the synthesis, structure and outstanding mechanical properties of such materials [2,3]. The theoretical consideration of such systems is based on the continuum approach where the coupling between elastic and orientation modes is assumed. As to the molecular modelling there are only few works devoted to the computer simulation of main chain LC polymers [4–6]. As to our knowledge the simulations of side- chain LC elastomers are practically absent.

Recently we [7] have presented results of molecular dynamics simulations of a simple model of the polymer-dispersed liquid crystal. A flexible regular polymer network swollen in low molecular LC solvent was considered. As a model of low molecular LC the system of rod-like molecules with purely repulsive intermolecular interactions was used. At the sufficient concentra-

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tion and the shape anisotropy of molecules the solvent forms a lyotropic LC phase. It was shown that by the density decrease it goes through the same LC phase states as the pure solvent does: the smectic phase (S), the nematic (N) and the isotropic (I) phase. The presence of the network shifts only the region of the isotopic-nematic (I-N) transition to larger total densities but does not influence the position of the nematic-smectic (N-S) transition.

In the present work this model is used as a starting one for the preparation of the model of a polymer network with mesogenic side groups. The system was simulated by molecular dynamic method and its structure and dynamics were compared with those for the initial system of a polymer network in low molecular LC solvent.

Initial System

The mesogens are rod like semiflexible molecules composed of 7 beads each. The beads are bonded into linear chains by FENE potential. Rigidity is introduced by a bending potential:

$$U_{bend}(\theta) = 200[1 - \cos(\theta)] \tag{1}$$

where Θ is the valence bond angle. A network is a regular tetrafunctional diamond-like network consisting of flexible chains of 31 beads each, bonded only by FENE potential

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

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

All the beads in the system interact by repulsive Lennard-Jones (LJ) potential.

$$U_{LJ}(r) = 4\varepsilon\left(\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6} + \frac{1}{4}\right), \quad r \leq 2^{1/6}\sigma. \tag{3}$$

Here σ and ε are *LJ's* parameters and units of length and energy correspondingly ($\sigma = 1$, $\varepsilon = 1$).

The network containing 6 cells [7] along 0Z axis of order and 3 cells along 0X and 0Y axes is superimposed on the fully ordered initial structure of mesogens, aligned along 0Z axis into 6 layers. The procedure of preparation of the initial state and equilibration of the system is described more detail in our recent work [7].

The simulation was performed by the molecular dynamics method using a collisional thermostat [8] to keep the local thermal equilibrium. The equations of motion were integrated using "velocity Verlet" algorithm [9]. As a time unit $\tau_0 = \sigma\ (m/\varepsilon)^{1/2}$ was used. All calculations were performed at the same reduced bath temperature equal to unity. The integration step $\Delta\ t = 0.004$ was used. The equilibrium state was considered being achieved after the characteristics of the system (density and order parameter) became stable on a sufficiently long part of the trajectory. Equilibration of the systems was carried out using NPT ensemble. The series of calculations were conducted at progressively decreasing pressures, using NPT ensemble. After the equilibration procedure the productive runs were carried out using NVT ensemble (constant temperature and volume) and static and dynamic characteristics of the systems were calculated. At various densities system forms different phase states. Every system was simulated during 1×10^6 steps. The calculations were carried out using computer time provided by the Centre for Scientific Computing (CSC, Espoo, Finland) on IBM eServer Cluster 1600.

Preparation of a LC Elastomer

For the preparation of the polymer network with side chain mesogens (LC elastomer) the following procedure was used. As an initial system one consisting of flexible polymer network in low molecular LC solvent equilibrated at certain density was used. In this system the reaction of the attachment of ends of mesogens to the network was simulated. When one of the mesogen ends occurred to be at the distance less than one monomer length from a free chain monomer a new FENE bond was introduced between them. The parameters of FENE potential are same as for each bond in the chain. The mesogen can be attached to the polymer chain only by one of its ends and only one mesogen is allowed to be attached to a chain bead. Bond formation was carried out using the NVT ensemble until the degree of conversion equal to 99% was achieved. This attachment procedure was carried out for systems with different values of density and order parameter. Thus, we obtained polymer network with side chain mesogens at the same density as the initial system.

Kinetics of the Formation of Polymer Network with Side Chain Mesogens

The kinetic of LC elastomer formation was followed by the time dependence of the fraction of low molecular LC mesogens attached to the polymer network. The kinetics depends both on the phase state and on the density. Most rapidly attachment occurs when the initial system is in smectic phase, and most slowly – in nematic phase. To separate the effect of density and to reveal the effect of the ordering only the curves of fraction of attached mesogens are plotted in reduced time units $t' = tD$ where D is a diffusion coefficient of free mesogens in the initial system of polymer network + low molecular LC at the same density (Figure 1). In these coordinates the attachments still occurs most rapidly in the smectic phase. It can be explained by the fact that in the smectic phase the mesogens are aligned parallel to each other, chain monomers are mainly concentrated in interlayer regions and mesogen ends are close to potential points of joining. It leads to the increased rate of attachments in the first stage when 90% of mesogens attach to backbone chain. At the final stage the rate of the reaction become slower because free mesogens need some time to find a non-occupied monomer in the network to join.

In the nematic phase the reaction goes slower (in reduced time coordinates) than in the smectic phase but faster than in the isotopic phase up to the conversion degree about 80%. At larger conversion the reaction in isotropic phase goes a little faster. Practically full conversion in all the phases occurs for the same reduced time ~10Dτ_0.

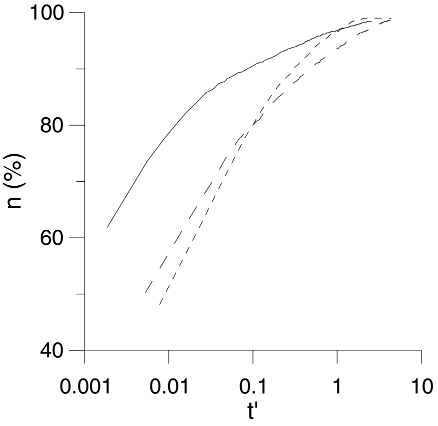

Figure 1.
Time dependence of the degree of conversion in smectic (solid line), nematic (long dashed line) and isotropic (short dashed line) phases.

Distribution of Mesogens Over Network Chains.

The average number $\langle n \rangle$ of mesogens per one chain in our system is 11,1. Mesogens are distributed nonuniformly over the chains. Figure 2 shows the number of chains $g\ (n)$ with given number n of attached mesogens.

These distributions are rather broad. All of them have maximums near$\langle n \rangle$. The narrowest distribution is observed for an isotropic state. It means that reaction of the attachment in this state leads to a more uniform distribution of mesoges over network chains. Practically any chain has at least several attached mesogens. In the smectic and nematic phases there are chains without mesogens at all and chains with highest possible value n = 31. In the same time in the isotropic phase we do not see chains with very large number of mesogens The distribution for an isotropic state is most symmetric one. The asymmetry of the distribution increases from I to S.

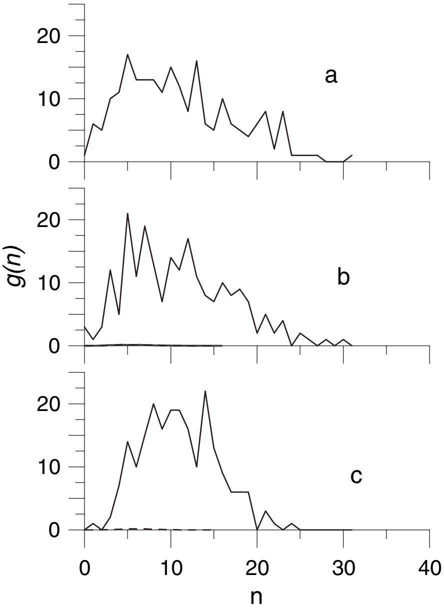

Figure 2.
Number of chains g (n) with given number n of attached mesogens.1-smectic phase, 2 -nematic phase, 3- isotropic phase.

The process of LC elastomer formation was stopped after achievement of 99% degree of conversion of the reaction of the attachment. After that the system was equilibrated using NVT ensemble. The equilibrium state was considered being achieved when the order parameter became stable. The duration of the equilibration run was about 5×10^6 time steps. Than productive runs were performed during 5×10^5 steps each. Structural and dynamical properties of the system were determined by the averaging over the trajectory for every run.

Structure Characteristics

Phase Behaviour

The order parameter S of mesogens is determined as

$$S = \frac{3}{2}\left\langle \cos^2\theta - \frac{1}{3} \right\rangle, \qquad (4)$$

where θ is the angle between the end-to-end vector of a mesogen and the director.

The director was calculated by the diagonalization of the ordering tensor. Averaging is performed both over the time of simulation and over all mesogens in the simulation box. Simulations show that in the ordered state of The LC elastomer mesogens remain to be oriented along the z-axis as in the initial system.

The density dependence of the order parameter of mesogens in the side chain elastomer and in the corresponding initial system low molecular LC+network is shown on Figure 3. Density of the system was calculated as a number density $\rho = N/V$, where N - number of all particles in the system.

It is seen that the attachment of mesogens to the network decreases the value of order parameter S at the same density.

To reveal, how the transformation into elastomer changes the structure and the phase state of the system, several structure characteristics were calculated and compared with those for an initial system.

Density Profiles and Distribution Functions

The structure of elastomer system can be characterised by number density profiles $\rho_{mes}(z)$ and $\rho_{net}(z)$ along OZ axis of beads

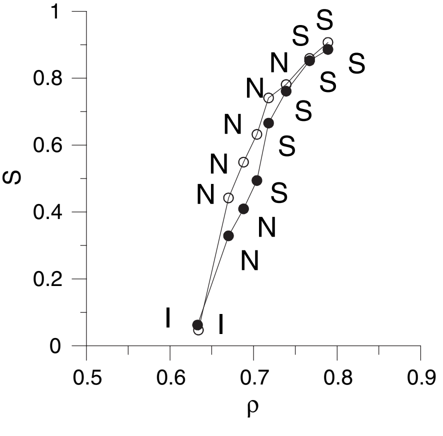

Figure 3.
Density dependence of the order parameter of mesogens in the side chain elastomer (filled circles) and in the corresponding initial system LC+network (open circles).

belonging to mesogens and to the network chains correspondingly.

$$\rho_A(z) = \left\langle \sum_i \delta(z - z_{Ai}) \right\rangle \quad (5)$$

where z_i– is a position of i-bead belonging to the network chain or to the mesogen and $A = mes$ or net.

Comparison with density profiles for the initial systems (Figure 4) shows that the attachment of mesogens to the network does not change remarkably the structure of the system. In the smectic phase mesogen and network beads remain to be distributed periodically in both systems and the maximum of $\rho_{mes}(z)$ corresponds to the minimum of $\rho_{net}(z)$ and vice versa. In the nematic and isotropic states there is no periodicity in the density distribution.

The distribution of network crosslinks in the system before and after the reaction of the attachment of mesogens was characterized by the binary function $g(z)$ defined as

$$g(z) = \frac{V}{N_{cr}^2} \left\langle \sum_i \sum_{j \neq i} \delta(z - z_{ij}) \right\rangle \quad (6)$$

where $z_{ij} = |z_i - z_j|$ is Z projection of distance between the crosslinks i and j; Ncr–the whole number of crosslinks in the system ($Ncr = 108$).

In the smectic phase for the initial system $g(z)$ shows a periodic character, and the number of peaks is equal to that of the layers of LC (Figure 5).

It means that crosslinks are concentrated in the interlayer regions. This periodical character remains in the elastomer system, but peaks become more narrow, therefore the attachment of mesogens to the network decreases the crosslinks fluctuations. In nematic and isotropic states network crosslinks are distributed uniformly both in the LC elastomer and in the initial system.

Main Chain Conformation

The effect of the elastomer formation on the conformations of main chains can be seen from the comparison of distribution function for end-to-end distances of the network chains in both systems (Figure 6).

In the isotropic phase the distribution does not change practically after the LC elastomer formation. In the nematic phase

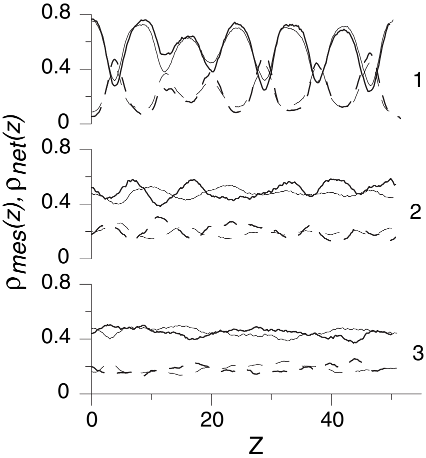

Figure 4.
Number density distribution of beads of side chain mesogens (solid line) and beads of polymer chain (dashed line) along the axis of order OZ. 1, 2 and 3 correspond to smectic, nematic and isotropic phases. Thick line –LC elastomer, thin line - system LC+net-network.

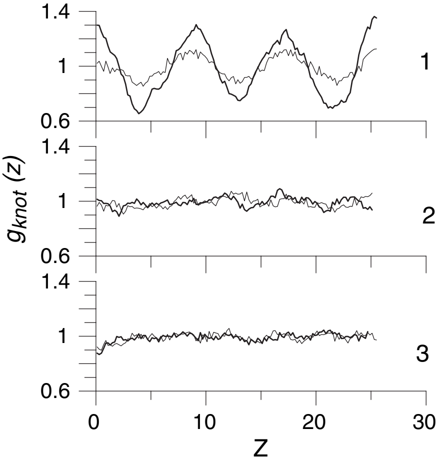

Figure 5.
Number density distribution of polymer network junctions along the axis of order OZ. 1,2 and 3 correspond to smectic, nematic and isotropic phases correspondingly. Thick line –LC elastomer, thin line – system LC+network

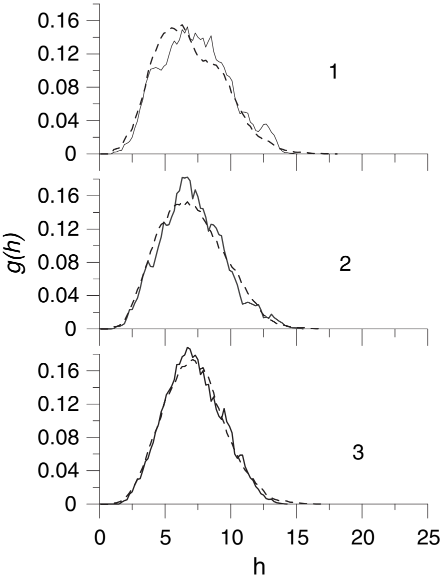

Figure 6.
Distribution function for end-to end distances *h* for chains of the polymer network for LC elastomer (solid line) and initial system LC+network (dashed line) in smectic (1), nematic (2) and isotropic (3) states.

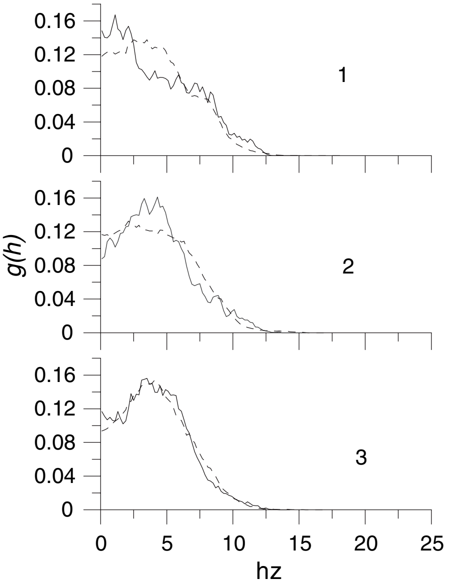

Figure 7.
Distribution function of projections of end-to end distances for chains of the polymer network on the axis of order OZ for LC elastomer (solid line) and initial system LC+network (dashed line) in smectic (1), nematic (2) and isotropic (3) states .

the distribution becomes slightly narrower. The most remarkable changes are in the smectic phase. The maximum of the distribution shifts to larger values of the end-to-end distance. It means that in the smectic state of the LC elastomer chains are more stretched than in the initial system where mesogens are not connected with the network.

Additional information can be obtained from the distribution function for the Z projections of end-to end distances (Figure 7).

In the smectic phase we observe the increase of the number of chains both with small and large OZ projection of end-to-end distance. It can be explained by the assumption that there are network chains which are situated inside the interlayer regions and chains which connect neighboring interlayer regions. The first ones are collapsed and the second ones are stretched in z-direction. Elastomer formation leeds to an additional compressing and stretching of these types of chains comparing to the initial system. For the nematic and isotropic states the behavior of the distribution function for z-projections by the formation of the LC elastomer is qualitatively similar to that of *g(h)*: the distribution becomes more narrow in the first case and doesn't change practically in the second case.

Dynamics

Translational Diffusion

The translational mobility of mesogens and main chain monomers can be characterized by the time dependence of mean squared displacement (MSD) of centres of mass of mesogens and chain beads correspondingly. In the initial system mesogens can move independently from chain beads. Therefore MSD for mesogens is a linear function of time. For chain beads MSD is a non-linear function of time due to the chain connectivity. In the LC elastomer the attachment of mesogens to the main chain restricts their displacements and MSD for mesogens becomes to be non-linear too.

Figure 8 shows the MSD for middle monomer of network chain $\langle \Delta r_m^2(t) \rangle$ and center of mass of mesogen $\langle \Delta r^2(t) \rangle$ for LC elastomer in different phase states. To separate the effect of the density on the mobility from the effect of the phase state the time units were scaled in such a way that the initial parts of curves for network chain corresponding to different phase states coincide. The same scaling was done separately for MSD of mesogens as well.

It is seen that the maximum restriction on the monomers displacement is observed for smectic phase, and the minimum - for isotropic one. Qualitatively this behaviour is the same as for the initial system LC+net [7] and agrees with the assumption that the network chains in the smectic phase are confined between the layers formed by attached mesogens.

Anisotropy of Diffusion

It is well known that low molecular LC exhibit 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, in the smectic state the situation is reverse. Such anisotropy is observed for the simulated systems also. For its quantitative description we have calculated the time dependence of the mean square displacements (MSD) of centres of mass of mesogens along the director $\langle \Delta r_{par}^2(t) \rangle$ and in the perpendicular direction $\langle \Delta r_{per}^2(t) \rangle$ (Figure 9).

For the isotropic phase there is of course no difference between $\langle \Delta r_{par}^2(t) \rangle$ and $\langle \Delta r_{per}^2(t) \rangle$. For the nematic phase $\langle \Delta r_{par}^2(t) \rangle$ exceeds $\langle \Delta r_{per}^2(t) \rangle$ at all times. For the smectic phase at short times $\langle \Delta r_{par}^2(t) \rangle$ is larger than $\langle \Delta r_{per}^2(t) \rangle$, but at longer times mesogens are more mobile in the normal direction than along the direction of ordering. Such a change of the anisotropy of motion is typical for low molecular LC [10] and was observed also for the case of polymer-dispersed liquid crystal. In all the cases the curves are nonlinear. This nonlinearity reflects the attachment of mesogen to the chains of polymer network, where increasing involvement of neighboring monomers into the movement increases of the displacement of a given monomer.

Due to the nonlinear character of MSD the value of anisotropy can be estimated as ratio MSD$_{per}$/MSD$_{par}$ vs. time (Figure 10).

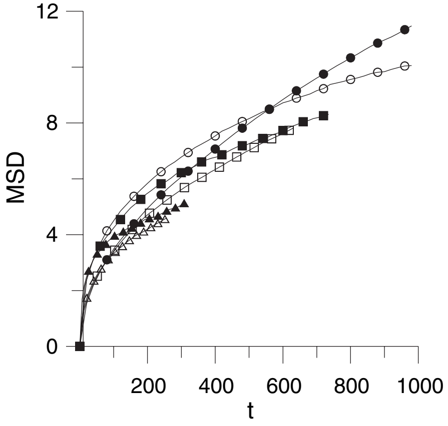

Figure 8.

Mean squared displacement of the middle chain monomer (open symbols) and mesogen (filled symbols) vs. scaled time. Triangles – smectic ($\rho = .740$), squares – nematic ($\rho = 0.700$) phase, circles ($\rho = 0.634$) -isotropic phase.

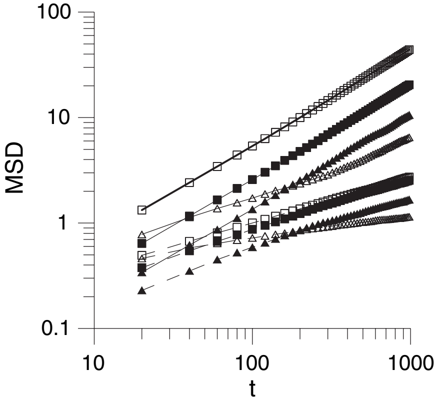

Figure 9.

Time dependences of MSD of mesogens for the system LC+network (solid line) and LC elastomer (dashed line): triangles – smectic ($\rho = 0.740$), squares – nematic ($\rho = 0.700$) phase. Open symbols – $\langle \Delta r_{(par)}^2(t) \rangle$, filled symbols - $\langle \Delta r_{(per)}^2(t) \rangle$.

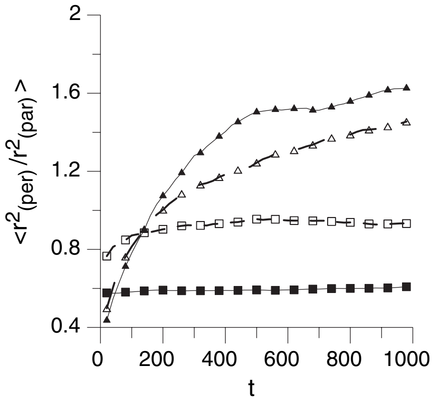

Figure 10.
Anisotropy of MSD of centers mass of of mesogens_vs.time. Triangles – smectic ($\rho = 0.740$), squares – nematic ($\rho = 0.700$) phase, in LC+network (filled symbols) and elastomer (open symbols).

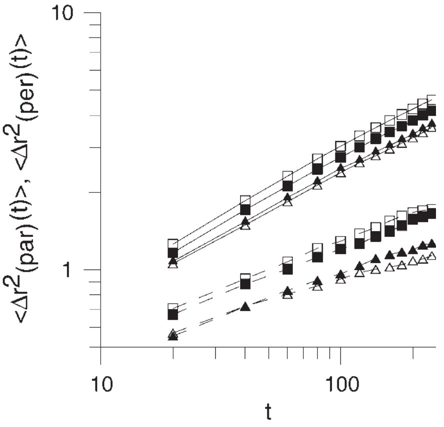

Figure 11.
Time dependences of MSD of middle chain monomers for the system LC+network (solid line) and LC elastomer (dashed line): triangles – smectic ($\rho = 0.740$), squares – nematic ($\rho = 0.700$) phase. Open symbols – $\langle \Delta r^2_{m(par)}(t) \rangle$, filled symbols - $\langle \Delta r^2_{m(per)}(t) \rangle$.

To demonstrate how the attachment of the mesogen to polymer network affects an anisotropy of translation diffusion of mesogens this ratio for the system of LC+ network at the corresponding densities was shown also. It is seen that the anisotropy of mesogens is less pronounced in elastomer compare to LC+network. This is connected with the decreased value of the order parameter in the elastomer at the same density.

The anistropy of diffusion of polymer chains arising by the ordering was estimated by calculation of MSD of middle chain monomer of the chain along the director $\langle \Delta r^2_{m(par)}(t) \rangle$and in the perpendicular direction$\langle \Delta r^2_{m(per)}(t) \rangle$. The comparison of the data for polymer network in low molecular LC solvent and LC elastomer system shows that attachment of mesogens to the polymer network leads to the increase of anisotropy of translational diffusion of chain monomers at least in the smectic phase (Figure 11).

On the base of both structural and dynamics data it is possible to perform the more precise attribution of the phase states of the LC elastomer. The phase states of the system are shown in Figure 3. Comparison with results for the initial system of LC+ network shows that the attachment of mesogens to the network results in decrease of the density region of nematic phase formation and shifts the formation of the smectic phase to lower densities.

Conclusions

The special procedure was elaborated for the formation of the LC elastomer with side chain mesogens from the system of flexible polymer network in a low molecular LC solvent. The kinetic of the process of mesogens attachment to network was studied as well as morphology of attachment. It was shown that attachment goes easier in the smectic phase. The morphology of the LC elastomer obtained depends of the state of the initial system.

The structural and dynamical behaviour of side chain LC elastomer was studied and compared with systems of polymer network in low molecular LC solvent. Formation of LC elastomer shifts the position of the nematic-smectic transition to the lower densities and favors the formation of smectic phase. LC elastomer has lower order parameter comparing to the initial polymer dispersed LC system at the same density. In the smectic phase the distribution of polymer network crosslinks becomes narrower, so the location of crosslinks in the interlayer of LC mesogen is more probable.

The attachment of low molecular LC to polymer network decreases the translational mobility of network monomers and mesogens. Same time the attachment increases the anisotropy of translational diffusion of polymer network strands especially in smectic phase.

The anisotropy of translational diffusion of mesogens attached to the network has the same sign as that of free mesogens in the low molecular LC system in polymer network, but its value is lower due to the lower order parameter in the LC elastomer system at the same density.

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