Theory of Intrachain Relaxation Spectra for Polymer Networks Possessing a Short- or Long-Scale Ordering. Effects of the Nematic Ordering on the Relaxation Spectrum of a Polymer Network with Included Rods

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Summary: We discuss the relaxation properties of polymer networks possessing either short-scale ordering caused by rigidity of network strands or long-scale liquid crystalline order. The main topics of the paper are the equilibrium and local dynamic properties of a polymer network ordered due to nematic-like interactions of the network segments with included rod-like particles. A simplified three chain network model is used. Lagrange multipliers in the equations of motion of hard rods are replaced by their averaged values. This approximation corresponds to modelling the rod-like particles by elastic Gaussian springs, their mean-square lengths independent of the ordering. Nematic-like interactions between network segments and rods are taken into account in terms of the Maier-Saupe mean-field approximation. Nematic ordering of rods induces ordering of the network segments. Relaxation spectrum of the ordered network splits into two main branches for the parallel and perpendicular components of the chain segments with respect to the director. We calculate the relaxation times of a polymer network as functions of the wave number. The relaxation spectrum of an isotropic network and that of the ordered network with included rods are compared.

Keywords: liquid-crystalline polymers; networks; relaxation; relaxation spectra; rods in a network

Introduction

Many characteristic features of the relaxation spectra of polymer networks manifesting in experimental methods such as NMR, polarised luminescence, dielectric and mechanical relaxation, etc. are determined by different types of ordering of network chain fragments (both short- and long-scale ordering). Short-scale ordering may be caused by the chain structure and rigidity of macromolecules. Recently,[1,2] the authors considered the relaxation spectra for high-frequently torsional vibration dynamic processes in densely crosslinked polymer networks where the short-scale ordering is due to the torsional rigidity of network strands. In densely crosslinked polymer networks, the degree of crosslinking may be so high that the

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average contour length of network strands is about the Kuhn segment. In this case, the main conformation of a network strand remains unchanged and the motions have a character of torsional vibrations of chain elements transversal to the network strand. For describing this type of motions, the chain model of elastically coupled rotators[3] was used in refs.[1,2] It was shown that the autocorrelation function $P_2(t)=<3\cos^2\theta(t)-1>/2$ manifested in NMR and polarised luminescence obeys stretched exponential time behaviour $\sim\exp[-(t/\tau_*)^{1/2}]$ for torsional vibrations due to superposition of motions of different scales in network strands.[1,2] Here $\theta(t)$ is the rotational angle of a chain element during the time t. The relaxation times distribution function, $L(\tau)$,

$$[P_2(t) - P_2(t=\infty)] / [P_2(t=0) - P_2(t=\infty)] = \int L(\tau) \exp[-t/\tau]\, d\ln\tau \qquad (1)$$

for this type of time behaviour for $P_2(t)$ is sufficiently narrow and described by exponential dependency, $L(\tau) \sim \exp[-\tau/\tau_*]$.

Another reason of the short-scale ordering in a polymer network may be the bending rigidity of network strands. In a rarely crosslinked polymer network, each network strand may consist of a number of Kuhn segments. In this case, the main type of molecular mobility of network strands is the bending motion. For describing the bending motions of macromolecules, the Gaussian subchain models are used in the literature.[3-7] Using the freely-jointed Gaussian subchain model (Rouse model), it was shown[3,4] that for bending motions, the relaxation times distribution function, $L(\tau)$, for correlator $P_2(t)$ is broader than that for torsional vibrations and obeys the power-type law, $L(\tau) \sim \tau^{-1}$. Recently,[8] the authors considered the effect of bending rigidity of macromolecules on the relaxation spectrum for bending motions using the Hearst-Harris chain model. The bending rigidity produces an additional maximum on $L(\tau)$ at relaxation times corresponding to the motion of the scale of a Kuhn segment. This maximum shifts to the greater relaxation times with increasing the bending rigidity.[8]

Together with the short-scale ordering, the effects of long-scale LC-ordering on the relaxation spectra of polymer networks (e.g., nematic elastomers) are of great importance because of the every-increasing use of liquid crystal technology. The equilibrium properties of nematic elastomers have been studied by many authors.[9-13] Recently,[14,15] the authors calculated the mean-square fluctuational characteristics which determine the relaxation times of a nematic elastomer. It was shown that the relaxation spectrum of an ordered nematic elastomer splits into two branches corresponding to the relaxation of parallel and perpendicular components of network segments with respect to the director.

The present paper is a further development of a theory of relaxation spectra for LC-ordered polymer networks proposed in refs.[14,15] and deals with the two-component system "a polymer network — included rod-like particles" ordered due to the orientational interactions between the network segments and the rods. We hope that this work will be instrumental for understanding the molecular processes in recently synthesised network gels containing the molecular rods[16-18] which are able to form LC-ordered structures. As in refs.,[14,15] we restrict ourselves by consideration of relaxation spectra for so-called intrachain motions. According to refs.,[5-7] all the complicated motions in a polymer network can be represented as a superposition of two main types of motions. The first type corresponds to intrachain motions and is manifested at the times smaller than the maximal relaxation time of a chain between network junctions. In this time region, it is possible to consider the dynamics of each network strand separately from another chains taking into account average chain stretching between network junctions. At the greater times, the collective interchain network motions are manifested. In a good approximation, the intra- and interchain relaxation spectra can be considered separately.[5-7] The intrachain motions are of great importance because they determine the initial stage of relaxation.

Our interest is restricted to the dynamics of the simplest case when the mixture of a polymer network with included rods remains a homogeneous one-phase system. Consideration can be applied to one of the coexisting phases in a many-phase system or to a homogeneous state. According to ref.,[13] there is a broad region of parameters for a polymer network placed into nematic environment where it remains one-phase ordered system.

Model of a Polymer Network with Included Rods

A simplified three chain network model is used for describing the network structure of a crosslinked polymer. This model was originally introduced by James and Guth[19] for non-ordered rubbers and was modified by Monnerie[9] and by the authors[14,15] for ordered polymer networks. This model represents an elementary cell of a regular cubic network and consists of three identical polymer chains, end-to-end vectors of which are mutually perpendicular and form a rectangular coordinate system *XYZ* (Figure 1). The director of an ordered network is chosen parallel to the *OZ*-axis.

Orientational and dynamic properties of the included rods and of the rod-like rigid chain segments in a polymer network are described here by a simplified method proposed earlier in refs.[20-23] According to this method, the time dependent Lagrange multipliers in the equations

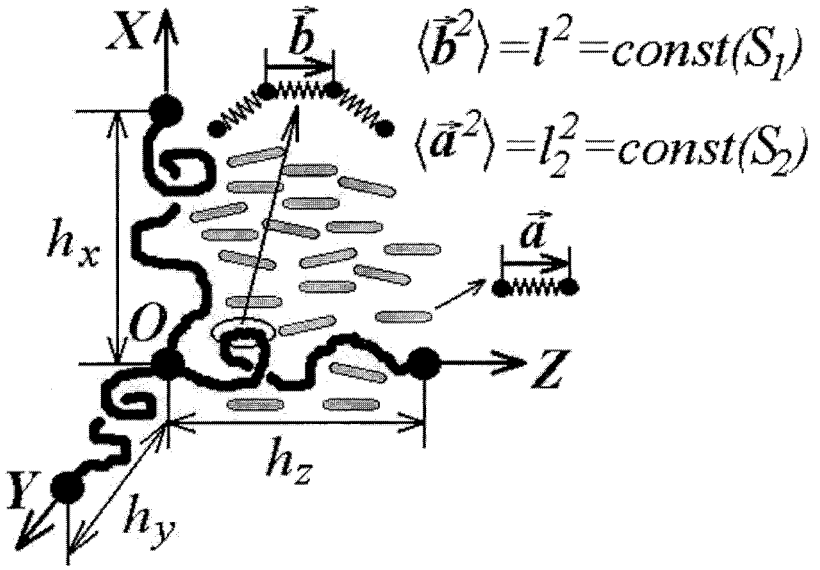

Figure 1. The elementary cell of the three chain network model with included rods.

of motion for rigid rod-like elements can be replaced in a good approximation by the constants equal to the averaged values of the multipliers. This approximation corresponds to modelling the rod-like elements by elastic Gaussian subchains. The elasticity constants of the subchains (equal to the averaged values of the Lagrange multipliers) change with ordering in such a way that the mean-square lengths of the subchains remains unchanged (see Figure 1) and equal to the length of the rod-like elements to be modelled.[20-23]

The chains between junctions of the network cell consist of N Gaussian subchains with mean-square length, l, which is constant during the ordering. For undeformed isotropic network with included rods, the end-to-end distances of the three chains in the cell are identical and assumed to be equal to the average end-to-end distance of network strands, h_0: $h_x=h_y=h_z \equiv h_0$ (Figure 1). The dimensionless parameter, h_0 / Nl, characterises the average strain of network strands and depends on the degree of cross-linking (or on the degree of polymerisation of network strands, N) and on the volume fraction of a polymer network in the system. For a dry polymer network (i.e. for a network without the rods), the specific form of the relationship between $h_0^{(dry)}/ Nl$ and N is determined by the procedure of polymer network preparation.[15,24] For example, if a polymer network is prepared by instantaneous cross-linking of polymer chains in a melt (e.g., with γ-rays), the end-to-end vector distribution in the network will be Gaussian, and $h_0^{(dry)}/ Nl \approx N^{-1/2}$. [15,25] The value of h_0 for a polymer network containing the

rod-like particles is greater than that for the dry network, $h_0^{(dry)}$. If Φ_1 is volume fraction of a polymer network we have for a homogeneous one-phase system, $\Phi_1 = [h_0^{(dry)}]^3 / h_0^3$, and

$$h_0 = h_0^{(dry)} \cdot (\Phi_1)^{-1/3} \tag{2}$$

Hence, the dimensionless parameter h_0 / Nl characterising the chain stretching in a polymer network with included rods is a complicated function of the degree of cross-linking and volume fraction of the network. We will obtain below the dependence of relaxation times of ordered polymer network on the parameter h_0 / Nl.

Mean-Field Approximation for Orientational Interactions of a Polymer Network with Included Rods. Equilibrium Values of the Order Parameters

Nematic-like interactions between a polymer network and the rods are taken into account here in terms of the mean-field approximation for nematic mixtures.[13,26-29] The free energy per the cell is written as follows (cf. with refs.[13,26-29]):

$$F(S_1, S_2) = -(1/2)\alpha_{11}\Phi_1^2 S_1^2 - (1/2)\alpha_{22}\Phi_2^2 S_2^2 - \alpha_{12}\Phi_1 \Phi_2 S_1 S_2 + \\ + kT\,\Phi_1\,(1/3) \sum_{n=X,Y,Z} \int \boldsymbol{db}\, f_1^{(n)}(\boldsymbol{b}) \ln f_1^{(n)}(\boldsymbol{b}) + kT\,\Phi_2 \int \boldsymbol{da}\, f_2(\boldsymbol{a}) \ln f_2(\boldsymbol{a}) \tag{3}$$

where S_1 and S_2 are the order parameters of a polymer network and rods, respectively:

$$S_1 = (1/3) \sum_{n=X,Y,Z} \int \boldsymbol{db}\, f_1^{(n)}(\boldsymbol{b})\, (3\cos^2\vartheta - 1)/2 \tag{4a}$$

$$S_2 = \int \boldsymbol{da}\, f_2(\boldsymbol{a}) (3\cos^2\vartheta - 1)/2 \tag{4b}$$

Here ϑ is the angle between a particle (a network segment or a rod) and the director (Oz-axis). In Equation (4a), the integral denotes the averaging with orientation distribution function, $f_1^{(n)}(\boldsymbol{b})$, over all segments in the chain stretched along an axis $n=X,Y,Z$ and the sum is over three chains in the cell. In Equation (4b), the averaging with orientation distribution function, $f_2(\boldsymbol{a})$, is over all the rods in the system; $\boldsymbol{a}$ and $\boldsymbol{b}$ are the vectors connecting the ends of the subchains modelling the rods and the network segments, respectively. The sum of the first three terms in Equation (3) represents the energy of nematic-like interactions; Φ_1 and Φ_2 are the volume fractions of network segments and the rods, respectively; the quantities α_{ij} are the parameters of nematic-like interactions. The parameter of interactions between the network segments, α_{11}, is connected with the temperature of isotropic-to-nematic phase transition, $T_C^{(net)}$, for non-crosslinked network chain segments ($\Phi_1=1$, $h_0=0$): $\alpha_{11}=2.701 \cdot kT_C^{(net)}$.[15,21] Parameter of interactions between the rods, α_{22}, is connected with the transition temperature

for a pure system of rods ($\Phi_2=1$): $\alpha_{22}=2.701 \cdot kT_C^{(rods)}$.[15,21] The parameter of interactions between the chain segments and the rods, α_{12}, is varied here for different systems.

The last two terms in Equation (3) represent the orientational entropy of the three chains in the cell and of the rods, respectively. Orientation distribution functions, $f_1^{(n)}(\boldsymbol{b})$, and $f_2(\boldsymbol{a})$ are calculated as an exponents of total potentials affecting the particles:

$$f_1^{(n)}(\boldsymbol{b})=C_1^{(n)} \cdot \exp[(V_1/kT)\cos^2\vartheta-(K_1^{(n)}/2kT)\boldsymbol{b}^2+(A^{(n)}/kT)b_n] \quad (5a)$$

$$f_2(\boldsymbol{a})=C_2 \cdot \exp[(V_2/kT)\cos^2\vartheta-(K_2/2kT)\boldsymbol{a}^2] \quad (5b)$$

The first terms in the exponents of Equations (5a), and (5b) correspond to the contributions of self-consistent molecular fields affecting the network and the rods; $V_{1,2}$ are the magnitudes of the fields. The second terms are related to the contributions of Gaussian potentials of the subchains; $K_1^{(n)}$ and K_2 are the elasticity constants of the subchains modelling the segments of the three chains and the rods, respectively. The third term in the exponent of Equations (5a) describes the effect of the stretching force applied to the ends of network strands; $A^{(n)}$ is the average magnitude of the stretching force. We calculated the nine parameters of the distribution functions, $V_{1,2}$, $K_1^{(X,Y,Z)}$, K_2, $A^{(X,Y,Z)}$ as functions of S_1 , and S_2 solving the system of nine equations: Equations (4a), and (4b), three equations determining the interrelation between the magnitudes of the stretching forces, $A^{(n)}$, and the end-to-end distances of the three chains in the cell, h_x, h_y, h_z, and four conditions of fixing the mean-square lengths of the subchains modelling the network segments and the rods:

$$\int \boldsymbol{db}\, f_1^{(n)}(\boldsymbol{b})\, \boldsymbol{b}^2 = l^2 \ (n=X,Y,Z); \qquad \int \boldsymbol{da}\, f_2(\boldsymbol{a})\, \boldsymbol{a}^2 = l_2^2 \quad (6)$$

Knowing $f_1^{(n)}(\boldsymbol{b})$, and $f_2(\boldsymbol{a})$ as functions of S_1 , and S_2 we calculated the dependence of the free energy on the order parameters, S_1, and S_2, using the Equation (3). The equilibrium values of the order parameters are determined by the condition of minimising the free energy.

At high values of the temperature ($kT/\alpha_{ij} >> 1$), the main contribution to free energy is the entropy one, the dependence $F(S_1 , S_2)$ has a single minimum at $S_1 = S_2 = 0$, and the system is isotropic. As the temperature decreases, an additional local minimum of $F(S_1 , S_2)$ appears at some values $S_1 > 0$ and $S_2 > 0$, this minimum being above the minimum at $S_1 = S_2 = 0$. At the transition temperature, the two minima mentioned are of the same level and the system becomes ordered. Figure 2 show the dependence of equilibrium values of the order parameters of a polymer network and of the rods on the reduced temperature $T / T_C^{(rods)}$ for different values of volume fraction of the network. We consider the case when the polymer

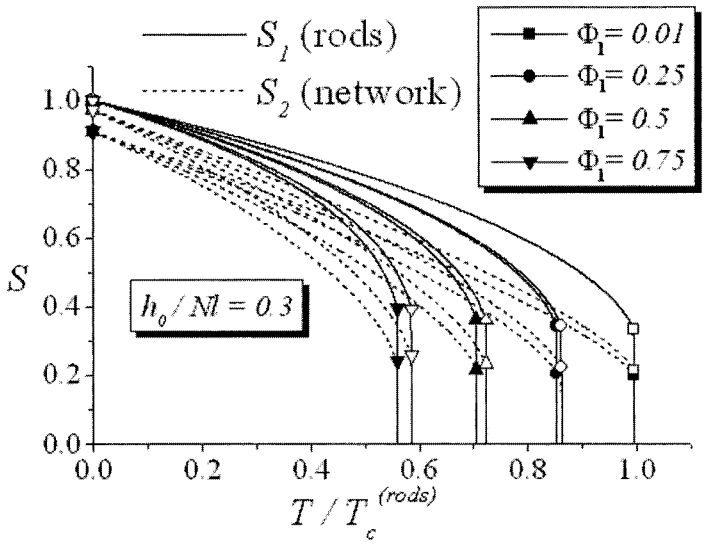

Figure 2. Dependences of equilibrium values of order parameters for rods, S_1 (solid lines), and for a polymer network, S_2 (dashed lines), on the reduced temperature, $T / T_C^{(rods)}$. Filled symbols correspond to a polymer network with fixed boundaries, open ones are related to the polymer network with free boundaries. $T_C^{(net)}/T_C^{(rods)}=\alpha_{11} / \alpha_{22}=0.5$, $\alpha_{12} = (\alpha_{11}\, \alpha_{22})^{1/2}$.

network is a weak nematic as compared with the system of rods and $T_C^{(net)}=T_C^{(rods)}/2$. It can be seen that ordering of the rods induces the ordering of the polymer network. The change of the volume fraction, Φ_1, shifts the transition temperature and changes only slightly the values of the order parameters S_1 and S_2 at the transition point.

We also analyse the effects of boundary conditions on the equilibrium values of the order parameters. Two variants of the ordering in the system are investigated. In the first case, the network boundaries are assumed to be fixed during the ordering. This situation can be implemented, e.g., when a polymer network with included rods is placed between two hard boundaries (planes) fixed in space. In this case, the degree of ordering of the network is varied due to the reorientation of chain segments at fixed average positions of chain ends. In the second case, the network boundaries are assumed to be free and a polymer network is stretched during the ordering along the director according to the condition of minimising the free energy. This situation can be implemented, e.g., when a swollen polymer network is in a free state in the system of rods which is considered as an "effective" nematic solvent. As it can be seen from Figure 2, for a polymer network with free boundaries, the values of order parameters both of a polymer network and of the included rods are higher than those for the polymer network with fixed boundaries (at given values of all external parameters –

temperature, concentrations, parameters of interactions etc.). Moreover, the isotropic-to-nematic phase transitions in the system with free boundaries are displayed earlier than those in the system with fixed ones. These facts may be explained by additional degree of ordering of a polymer network with free boundaries as compared with that for the network at fixed boundaries due to stretching of the network along the director.

Dynamics of the Ordered Rods Included into a Polymer Network

In our approximation, the equations of motions for the rods and for the chain segments of a polymer network may be written separately. However, the nematic-like interactions between the rods and the network change the magnitudes of self-consistent fields, $V_{1,2}$, and influence the relaxation times both of the rods and of the polymer network. For a rod-like particle affected by nematic-like field of the magnitude, V_2, the dependences of the relaxation times for projections of the rod along, $\tau_{||}^{(r)}$, and perpendicular, $\tau_{\perp}^{(r)}$, to the director are given by:[23]

$$\tau_{||}^{(r)} = 2\,\tau_0^{(r)}\,(1-S_2)/(1+2\,S_2), \quad \tau_{\perp}^{(r)} = \tau_0^{(r)} \exp[-V_2(S_2)/kT]/[1+(V_2(S_2)/kT)^{3/2}] \qquad (7)$$

where $\tau_0^{(r)}$ is a time of orientational diffusion of a single rod-like particle in the absence of any orientation fields. Equation (7) was derived in ref.[23] for the system of the rods where the magnitude of molecular field, V_2, is caused by the nematic-like interactions between the rods only. For the rods included into a polymer network, the magnitude of molecular field affecting the rods, V_2, is determined by the nematic-like interactions not only between the rods but also between the rods and network segments. Thus, the relaxation times of the rods included into a polymer network depend on the volume fraction and on the degree of crosslinking of the network.

Figure 3 illustrates the relative changes of the relaxation times, $\tau_{||}^{(r)}$, and $\tau_{\perp}^{(r)}$, in the point of isotropic-to-nematic phase transition for the rods included in a polymer network with respect to the times for the rods without the network. Interactions of the rods with a polymer network increase the relaxation time $\tau_{||}^{(r)}$ and decrease the time $\tau_{\perp}^{(r)}$. We consider the case when the polymer network is a weak nematic as compared with the system of rods, and $T_C^{(net)}=T_C^{(rods)}/2$. In this case, the relative changes of relaxation times, $\tau_{||}^{(r)}$, and $\tau_{\perp}^{(r)}$, are small at $\Phi_1<0.6$ and even at $\Phi_1 \to 1$, they may reach only 40 %. Thus, a weakly nematic network changes the relaxation times of the rods only slightly at the point of isotropic-to-nematic phase transition.

For a single particle, the relaxation spectrum is discrete and the relaxation time distribution function, $L(\tau)$, for correlator $P_2(t)$ represents a sum of delta-functions corresponding to the

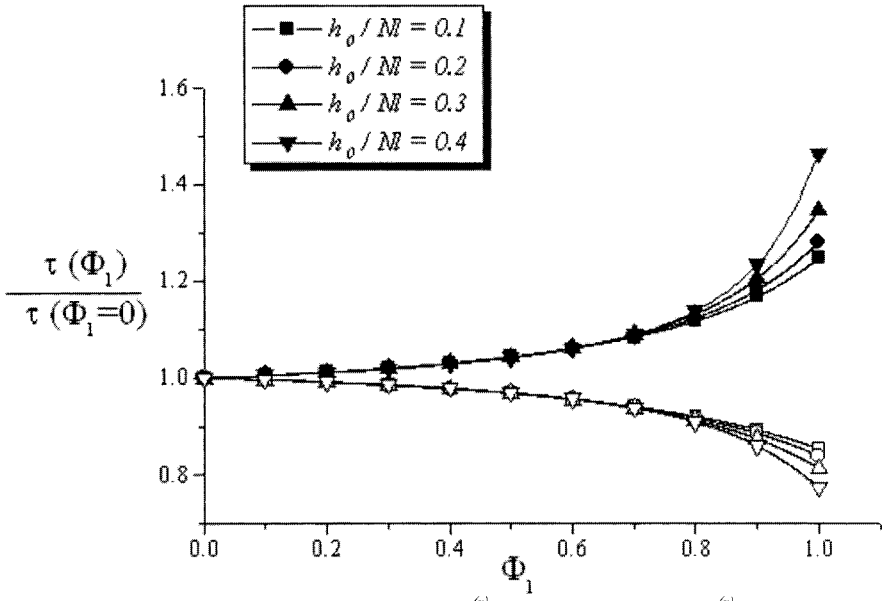

Figure 3. Relative changes of relaxation times, $\tau_{||}^{(r)}$ (filled symbols) and $\tau_{\perp}^{(r)}$ (open symbols), in the point of isotropic-to-nematic phase transition for the rods included in a polymer network with respect to the times $\tau_{||}^{(r)}$ and $\tau_{\perp}^{(r)}$, respectively, for the rods without the network. Φ_1 is the volume fraction of the network. Φ_2=1- Φ_1 , $T_C^{(net)}/T_C^{(rods)}$ =0.5, $\alpha_{12} = (\alpha_{11}\,\alpha_{22})^{1/2}$.

relaxation times $\tau_{||}^{(r)}/2$ and $\tau_{\perp}^{(r)}/2$.[3] As it can be seen from Figure 3, the interactions of the rods with a polymer network shift the lines corresponding to the relaxation times $\tau_{||}^{(r)}$, and $\tau_{\perp}^{(r)}$ from each other and the relaxation spectrum becomes broader. These effects may be manifested in the time behaviour of the correlator $P_2(t)$.

Dynamics of an Ordered Polymer Network with Included Rods

The equations of intrachain motions for an ordered polymer network were recently derived by the authors in ref.[15] for nematic elastomers where the orientational molecular field is caused by strong nematic-like interactions between the chain fragments of the network. Here, the equations derived in ref.[15] are applied for an ordered polymer network with included rods where the orientational field is due to the nematic-like interactions between the rods and network fragments. The interest of the ref.[15] was restricted to the calculation of statistical characteristics of the relaxation times of an ordered network. In the present paper, we also take into account the dissipative contribution into the relaxation times of a polymer network.

According to refs.,[20-23] the dynamics of hard fragments of network strands can be described in a good approximation by Gaussian subchains, their the dissipative function includes the diagonal, R_1, and the first non-diagonal, R_2, terms. In this approximation, the dissipative function of a chain stretched along the axis n (n=X,Y,Z) in the cell is written as follows:

$$R^{(n)}=(1/2)\sum_j[R_{1\parallel}^{(n)}(z'_j)^2+R_{1\perp}^{(n)}\{(x'_j)^2+(y'_j)^2\}]+$$
$$+(1/2)\sum_j[R_{2\parallel}^{(n)}z'_jz'_{j+1}+R_{2\perp}^{(n)}\{x'_jx'_{j+1}+y'_jy'_{j+1}\}] \quad (8)$$

Here x'_j, y'_j, and z'_j are the Cartesian projections of the velocity of j-th bead of the chain; the indexes "$\parallel$" and "$\perp$" denote the friction coefficients for the motions of beads parallel and perpendicular to the director (Oz-axis). The equations of motion of chain segments are written as follows using the Equation (8) for dissipative function (cf. with ref.[15]):

$$R_{1\xi}^{(n)}b'_{j,\xi}+(1/2)R_{2\xi}^{(n)}[b'_{j-1,\xi}+b'_{j+1,\xi}]+K_{eff}^{(n,\xi)}[2b_{j,\xi}-b_{j-1,\xi}-b_{j+1,\xi}]=(F_{j,\xi})^{(Br)}-(F_{j-1,\xi})^{(Br)} \quad (9)$$

where $b_{j,\xi}$ is the ξ–component (ξ=x,y,z) of the vector $\boldsymbol{b}_j$ connecting the ends of j-th subchain, $b'_{j,\xi}$=(d$b_{j,\xi}$/dt), and $(F_{j,\xi})^{(Br)}$ is the ξ–component of Brownian force exerted on j-th bead in the chain. The quantities $K_{eff}^{(n,\xi)}$ in Equation (9) are "effective" elasticity constants[15] which are determined by the equilibrium values of the mean-square fluctuations of b_ξ:

$$K_{eff}^{(n,\xi)}=kT/[<(b_{\xi,n})^2>-<b_{\xi,n}>^2] \quad (10)$$

The system of equations (9) is solved here in terms of normal modes, q_Ψ: [3,4,15,20-23]

$$<b_{j,\xi}^{(n)}(t)>=\sum_\Psi \exp[ij\Psi]\cdot\exp[-t/\tau_\xi^{(n)}(\Psi)]\cdot q_{\xi,\Psi}(0) \quad (11)$$

where Ψ is the wave number (phase shift between neighbouring elements for a certain normal mode). Substituting the Equation (11) into (9), we obtain the expression for relaxation times:

$$\tau_\xi^{(n)}(\Psi|\,S_1)=[R_{1\xi}^{(n)}(S_1)+R_{2\xi}^{(n)}(S_1)\cdot\cos\Psi]/[2K_{eff}^{(n,\xi)}(S_1)\cdot(1-\cos\Psi)] \quad (12)$$

It can be seen, that relaxation times contain the contributions of two factors. "Statistical" factor, $K_{eff}^{(n,\xi)}(S_1)$, is determined by statistical characteristics of segment orientation, see Equation (10). Using distribution functions, $f_1^{(n)}(\boldsymbol{b})$, derived above, we have calculated the averaged quantities included into the right-hand side of Equation (10) which determine $K_{eff}^{(n,\xi)}$ as functions of the order parameter, S_1, and of the chain stretching between network junctions, h_0 / Nl. "Dynamic" factor is related to dissipative effects in the system and is determined by friction coefficients, $R_{k,\xi}^{(n)}$. The coefficients of dissipative functions, $R_{k,\xi}^{(n)}$, are calculated as functions of S_1 and (h_0 / Nl), using the equality of translational and orientational relaxation

times for a single Gaussian spring and a single hard dumbbell to be modelled by the spring when they are in the same molecular field. This equality gives for $R_{k,\xi}^{(n)}$:[20,23]

$$(R_{1,2})^{(n)}{}_{||}=[\varsigma \pm 4\, K_{eff}^{(n,,||)}\cdot\tau_{||}^{(d)}]/2, \qquad (R_{1,2})^{(n)}{}_{\perp}=[\varsigma \pm 4\, K_{eff}^{(n,,\perp)}\cdot\tau_{\perp}^{(d)}]/2 \tag{13}$$

where ς is the friction coefficient of dumbbell ends; $\tau_{||}^{(d)}$ and $\tau_{\perp}^{(d)}$ are the relaxation times of dumbbell projections along and perpendicular to the director, respectively. The dependences of $\tau_{||}^{(d)}$ and $\tau_{\perp}^{(d)}$ on the order parameter, S_1, are determined by Equation (7) where all the quantities for a rod ($\tau_{||}^{(r)}$, $\tau_{\perp}^{(r)}$, S_2, and $\tau_0^{(r)}$) should be replaced by the corresponding quantities for the dumbbell representing the network segments ($\tau_{||}^{(d)}$, $\tau_{\perp}^{(d)}$, S_1, and $\tau_0=l^2\varsigma/4kT$); τ_0 is the relaxation time for a single dumbbell in the absence of any orientational fields. Using the Equations (10), (12), and (13), we have calculated the relaxation times of an ordered polymer network with included rods.

An ordered polymer network with included rods at fixed boundaries. For an ordered polymer network with fixed boundaries, the relaxation times, $\tau_{\xi}^{(n)}$, characterising the relaxation of segment projections along a chosen axis ξ are independent of the orientation of the end-to-end vector of the chain with respect to this axis (see also ref.[15]). This is due to the fact that the stretching degrees for the three chains in our model are the same for undeformed network with fixed boundaries. In this case, the set of the relaxation times consists only of two relaxation times corresponding to the relaxation of segment components parallel, $\tau_{||}$, and perpendicular, $\tau_{\perp}$, to the director. Both $\tau_{||}$, and $\tau_{\perp}$ are equal for three chains in the cell.

Figure 4 shows the relative changes in the relaxation times, $\tau_{||}$, and $\tau_{\perp}$, of ordered network with respect to these times for the same network without the rods (isotropic network). Parameters of interactions, α_{ij}, are chosen so that $T_C^{(net)}=T_C^{(rods)}/2$ If $T_C^{(rods)}$ is about of the room temperature, then $T_C^{(net)} \approx$ -150°C, i.e. the pure network is transformed into a glass-like state rather than in a nematic state with decreasing temperature (weakly nematic network). With ordering of the rods, the order parameter of a polymer network increases and the branches corresponding to the relaxation times, $\tau_{||}$, and $\tau_{\perp}$, shift from each other. The relaxation times $\tau_{||}$ for an ordered polymer network with included rods can reach the values three times higher than the relaxation times for the same network without the rods. In other words, even for weakly nematic network, the relative changes in the relaxation times of the network due to ordering of the rods may be high. However, the effects of a weakly nematic network on the relaxation times of included rods are sufficiently weak (see above). This fact

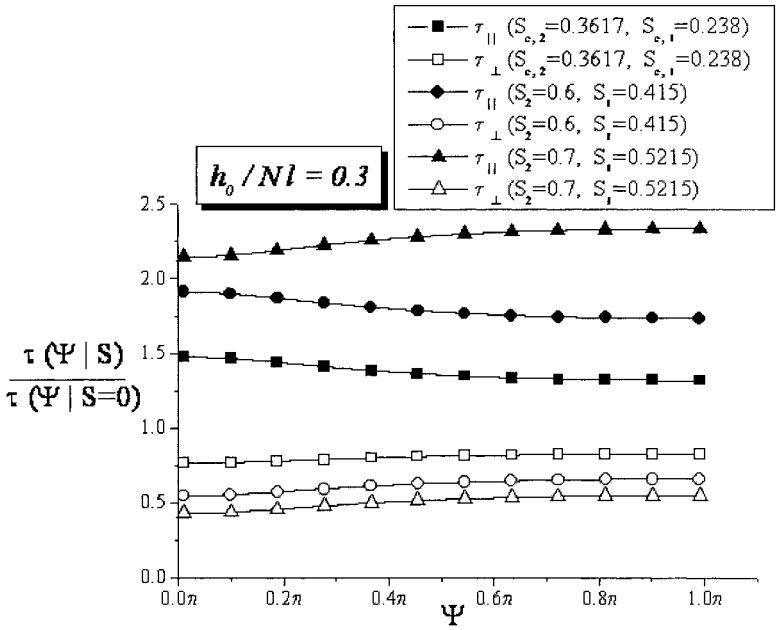

Figure 4. Relative changes of relaxation times, $\tau_{||}$ (filled symbols) and $\tau_{\perp}$ (open symbols), for an ordered polymer network with respect to these times for the same network without the rods (isotropic network) as functions of the wave number, Ψ, at different values of S_1. $\Phi_1=\Phi_2=0.5$, $h_0 / Nl=0.3$, $T_C^{(net)}/T_C^{(rods)}=0.5$, $\alpha_{12}=(\alpha_{11}\,\alpha_{22})^{1/2}$.

may be used for investigating the mobility of the rods by means of incorporation of the rods into a weakly nematic polymer network with further measurement of the relaxation properties of the network, the effects of the network on the mobility of the rods being neglected.

The changes in relaxation times of any polymer system are known to be influence strongly the time behaviour of the correlator $P_2(t)$.[23] We expect that the changes in the values of the relaxation times for a polymer network due to nematic-like interactions with the rods should shift the maximums of the relaxation time distribution function, $L(\tau)$, for correlator $P_2(t)$. These effects may be manifested in NMR and polarised luminescence techniques.

An ordered polymer network with included rods at free boundaries. A polymer network with free boundaries is stretched along the director during the ordering. In the stretched network, the degree of chain stretching for network strands stretched along the director becomes higher than that for the strands stretched perpendicular to it. The relaxation times for the more strained chains stretched along the director, $\tau^{(Z)}$, are lower than the relaxation times for the chains stretched perpendicular to it, $\tau^{(X)}=\tau^{(Y)}$. Therefore, each of the two branches

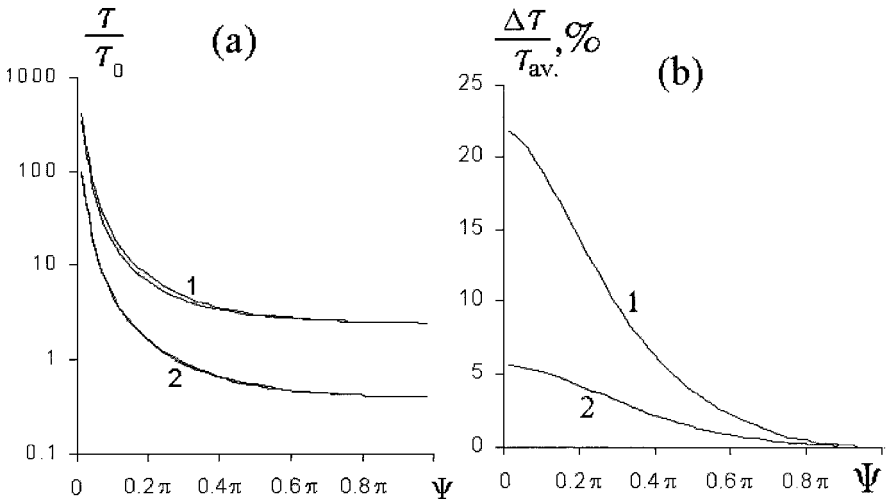

Figure 5a. Relaxation times for an ordered polymer network at free boundaries as functions of the wave number, Ψ. The filled areas 1 and 2 illustrate the continuous branches corresponding to the relaxation times, $\tau_{||}$, and $\tau_{\perp}$, respectively. $h_0 / Nl=0.3$, $S_l=0.5$.

Figure 5b. The relative breadths, $\Delta\tau/\tau_{av.}\cdot 100\%$, of the continuous branches of the relaxation spectrum as functions of Ψ. The curves 1 and 2 correspond to the relaxation times $\tau_{||}$, and $\tau_{\perp}$, respectively. $\Delta\tau_{||,\perp}=\tau_{||,\perp}^{(X)}-\tau_{||,\perp}^{(Z)}$, and $(\tau_{av.})_{||,\perp}=(\tau_{||,\perp}^{(X)}+\tau_{||,\perp}^{(Z)})/2$. $h_0 / Nl=0.3$, $S_l=0.5$.

related to the relaxation times $\tau_{||}$, and $\tau_{\perp}$, splits additionally into two sub-branches ($\tau_{||}^{(Z)}$, $\tau_{||}^{(X)}$ and $\tau_{\perp}^{(Z)}$, $\tau_{\perp}^{(X)}$) corresponding to the chains stretched parallel, $\tau_{\xi}^{(Z)}$, and perpendicular, $\tau_{\xi}^{(X)}=\tau_{\xi}^{(X)}$, to the director. Thus, the relaxation spectra for three chain network model is characterised by four branches, $\tau_{||}^{(Z)}$, $\tau_{||}^{(X)}$ and $\tau_{\perp}^{(Z)}$, $\tau_{\perp}^{(X)}$.

For a more realistic network model consisting of an ensemble of chains with chaotically oriented end-to-end vectors, each of the two branches related to the relaxation times $\tau_{||}$, and $\tau_{\perp}$, splits into continuous regions of the relaxation spectrum. The relaxation times $\tau_{||}^{(Z)}$, $\tau_{||}^{(X)}$ and $\tau_{\perp}^{(Z)}$, $\tau_{\perp}^{(X)}$ for the three chain network model determine the boundaries of the continuous branches $\tau_{||}$, and $\tau_{\perp}$, respectively, for the network model with chaotically oriented end-to-end vectors of chains. The continuous relaxation spectrum for a stretched polymer network is shown on Figure 5a by filled areas. The boundaries of the filled areas correspond to the relaxation times $\tau_{||}^{(Z)}$, $\tau_{||}^{(X)}$ and $\tau_{\perp}^{(Z)}$, $\tau_{\perp}^{(X)}$ for the three chain network model.

For short-scale motions (when $\Psi\rightarrow\pi$), the breadths of the continuous branches of the relaxation spectrum for a stretched polymer network tend to zero, $\Delta\tau_{||,\perp}=\tau_{||,\perp}^{(X)}-\tau_{||,\perp}^{(Z)}\rightarrow 0$, and the set of the relaxation times degenerates into only two times corresponding to $\tau_{||}^{(d)}$ and $\tau_{\perp}^{(d)}$ for a system of ordered dumbbells. This means that the collective intrachain motions of the

segments are not manifested at short times and the network system behaves like a system of separate non-crosslinked segments (dumbbells). The relative breadths of the continuous branches of the relaxation spectrum with respect to an average times, $(\tau_{av.})_{||,\perp}=(\tau_{||,\perp}^{(X)}+\tau_{||,\perp}^{(Z)})/2$, increase with decreasing the wave number, Ψ, and reach the maximums at $\Psi \rightarrow 0$ (Figure 5b). The relative breadth of the branch $\tau_{||}$ is higher than that for $\tau_{\perp}$. We expect that the splitting of the branches $\tau_{||}$, and $\tau_{\perp}$, of the relaxation spectrum for a stretched polymer network should widen the peaks of the relaxation time distribution function, $L(\tau)$, and may be manifested in NMR and polarised luminescence techniques. More detailed analysis of $L(\tau)$ as well as of the correlator $P_2(t)$ will be carried out in future.

Conclusion

Effects of nematic order in a polymer network with included rods on the relaxation spectra both of the polymer network and of the rods have been considered using a simplified three chain network model. The nematic-like interactions between a polymer network and the rods have been taken into account in terms of the Maier-Saupe mean-field approximation. We have considered the case when a polymer network is a weak nematic with respect to the rods. Nematic ordering of the rods induces the ordering of network segments. Nematic-like interactions of the rods with a weakly nematic network change strongly the relaxation spectrum of the network and change only slightly the relaxation times of the rods. This allow us to conclude that the mobility of the rods can be investigated by means of incorporation of the rods into a weakly nematic polymer network with further measuring the relaxation properties of the network. We expect that the changes in the relaxation times of a polymer network due to interactions with included rods may be measured by NMR and polarised luminescence techniques.

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