Viscoelastic Dynamic Properties of Meshlike Polymer Networks: Contributions of Intra- and Interchain Relaxation Processes

Andrew A. Gurtovenko* and Yuli Ya. Gotlib
Institute of Macromolecular Compounds, Russian Academy of Sciences, Bolshoi Prospect 31, V. O.; St. Petersburg, 199004, Russia
Received October 6, 1999; Revised Manuscript Received March 10, 2000

ABSTRACT: The theory of intra- and interchain relaxation processes for the local dynamic characteristics of meshlike polymer networks has recently been proposed by the authors (Macromolecules 1998, 31, 5756). The extension of this theory to macroscopic viscoelastic characteristics is presented. A regular cubic network consisting of “bead and spring” Rouse chains embedded in an effective viscous medium is considered. The viscoelastic response of the polymer network to an external stress producing a longitudinal velocity gradient in the effective viscous medium is studied. The comparisons of contributions from intra- and interchain relaxation processes to the dynamic modulus and viscosity of the Gaussian network are made. The asymptotic behavior of dynamic quantities considered is estimated for various limiting regions of frequency. The possibility of a simplified description of the viscoelastic properties of a polymer network in terms of a coarse-grained network model and a melt consisting of un-cross-linked chains is demonstrated. The problem of hydrodynamic interactions in polymer networks is also discussed.

1. Introduction

The dynamic behavior of polymer networks is a very interesting area of polymer physics. The polymer chains in a network are connected with each other by means of cross-links in an unified spatial structure. As a result of this connectivity, long-range cooperative motions of macromolecules exist in a polymer network; they have characteristic scales greater than the average length of network chains between cross-links. The existence of these cooperative motions of polymer chains in the network is reflected in the relaxation processes manifested in cross-linked polymer systems and can lead to the difference between relaxation properties of cross-linked polymers and polymer solutions or melts consisting of un-cross-linked macromolecules.

The theoretical consideration of dynamic properties of real polymer networks is a rather difficult problem because of structure irregularity of the networks resulting in complex character of relaxation. Therefore, we use the well defined regular model of a network to study the effect of spatial network structure on the dynamic properties of a polymer. Recently, we have proposed the theory of intra- and interchain relaxation processes for the local dynamic characteristics of meshlike polymer networks.1 The mean-square displacements of network elements and the relaxation of end-to-end chain vectors between cross-links have been studied in terms of a regular cubic network model consisting of “bead and spring” Rouse chains.2 These local dynamic characteristics can be manifested in dielectric relaxation3,4 and dynamic light scattering in cross-linked polymers. The main goal of the present work is to extend this approach to macroscopic characteristics determining the viscoelastic response of polymer networks.

* Author to whom correspondence should be addressed. Permanent address: Institute of Macromolecular Compounds, Russian Academy of Sciences, Bolshoi Prospect 31, V. O., St. Petersburg, 199004, Russia. Telephone: 7-(812)-328-5601. Fax: 7-(812)-328-6869. E-mail: andrew@imc.macro.ru.

The paper is organized as follows. The total stress arising in a network under external perturbation and the frequency-dependent dynamic modulus and viscosity will be calculated using a regular Gaussian network model that takes into account both small-scale intra-chain and collective interchain motions. A comparison of contributions from intra- and interchain relaxation processes determining the viscoelastic characteristics considered will be made. The viscoelastic characteristics of a polymer network of multisegmental Rouse chains will be compared with those of a simplified coarse-grained network model in which each polymer chain between junctions is described by a single Gaussian spring. Moreover, the comparison of viscoelastic mechanical properties of the polymer network and the melt of un-cross-linked macromolecules with the same chain lengths as in the network will be made.

2. Theory

Viscoelastic mechanical properties of cross-linked polymers are considered in terms of a regular cubic network consisting of “bead and spring” Rouse chains (Figure 1). This dynamic network model allows the relative contributions from intra- and interchain net-
work motions to be studied. To study the viscoelastic mechanical properties of a polymer network, one can consider its response to an external perturbation (stress). It is assumed that the external stress is applied directly to the boundaries of a polymer sample. A dry polymer network without solvent is considered. According to the well-known approach developed for polymer melts, an effective viscous medium can be introduced into a concentrated polymer system. The effective medium describes viscous interactions of a given segment with all other segments; these interactions cannot be reduced to the intersegmental friction between a given pair of segments. Making an extension of this approach to cross-linked bulk polymers (elastomers), one can assume that a similar effective medium exists in a dry polymer network. This medium takes into account the stochastic character of contacts of network chain segments and the degrees of freedom which are not included in the network model (e.g., elements smaller than the Gaussian segment, side groups, dangling chains, etc.).

It is assumed that an external stress \( \sigma_{\text{ext}} \) applied to the opposite boundaries of a network (Figure 1) consists of two parts

\[
\sigma_{\text{ext}} = \sigma_0 + \delta \sigma_{\text{ext}} \exp(i \omega t) \tag{1}
\]

The constant stress component \( \sigma_0 \) stretches the network system and ensures its fixed average volume. This corresponds to the approach of James and Guth, who have introduced internal pressure into the three-dimensional Gaussian network model to prevent its collapse to infinite density. The second stress component \( \delta \sigma_{\text{ext}} \exp(i \omega t) \) determines the periodic motion (at a frequency \( \omega \)) of network boundaries about their average positions fixed by the stress \( \sigma_0 \). It is essential that the effective viscous medium of a network system relaxes much more rapidly than the degrees of freedom of the network (junctions and nonjunction beads of network chains). This means that external perturbation affects at first (at small times) only the effective viscous medium and produces a certain velocity field in it. This perturbation does not yet affect the network degrees of freedom. After the medium is perturbed, the network elements (junctions and nonjunction beads) begin to move with respect to the effective medium which is already perturbed by external perturbation. The above approach is quite analogous to that for polymer melts.

The small periodic displacements of network boundaries with respect to their average positions are assumed to produce a longitudinal velocity gradient of an effective viscous medium. If the medium is purely viscous and its viscosity is \( \eta_0 \), the internal stress \( \sigma_m \) resulting from the deformation of medium is given by

\[
\sigma_m = G \eta_0 \tag{2}
\]

where \( G \) is the longitudinal velocity gradient. There is some uncertainty related to the viscosity value \( \eta_0 \) of the effective medium. In dynamic theory of polymer melts, the quantity \( \eta_0 \) has been assumed to be close to the viscosity of a melt consisting of polymer monomers. A similar assumption may also be used for the dry polymer network considered.

Let an external stress \( \sigma_{\text{ext}} \) (see eq 1) act on the network along the X axis of the Cartesian coordinate system (Figure 1). A cross-linked polymer sample as a whole is incompressible. The constancy of the network volume \( V_0 \) under a small deformation means that the network extension \( \delta X \) along the X axis should lead to the compression along the Y and Z axes. The following condition must be fulfilled: \( \delta X = -\left(\frac{1}{2}\right)Y - \left(\frac{1}{2}\right)Z \). In other words, when an external stress produces a small longitudinal velocity gradient in the effective medium along the X axis, the internal pressure in the network sample leads to the appearance of longitudinal gradients in normal directions. In the case of a network consisting of Gaussian chains, the motions of X, Y, and Z components of position vectors of network elements are independent of each other. The equations of motion of each Cartesian component are linear and have identical forms. Therefore, it is sufficient to consider only the network deformation along the direction of an external stress, i.e., along the X axis (Figure 1). The consideration of network deformations along the directions normal to the X axis is analogous.

A longitudinal velocity gradient \( G \) of effective viscous medium is given by

\[
G = G_0 \exp(i \omega t) \tag{3}
\]

where \( G_0 = |G| \) is the absolute value of velocity gradient. Since the effective viscous medium of a dry polymer network is modeled by stochastic interactions between the degrees of freedom of the same network, the motion of this medium should be self-consistent with the macroscopic deformation of cross-linked polymer sample. The network deformation \( L(t) \) along the X axis is determined as

\[
L(t) = L_0 + \delta L(t) \tag{4}
\]

where \( L_0 \) is the average linear size of the cross-linked polymer along the X axis and \( \delta L(t) \) is the network deformation with respect to the average linear size \( L_0 \). Then the longitudinal velocity gradient \( G \) of an effective viscous medium is directly related to the deformation \( \delta L(t) \) of a polymer sample:

\[
G = \frac{d}{dt} \frac{\delta L(t)}{L_0} \tag{5}
\]

Equation 5 describes the interconnection between the motion of an effective viscous medium and the macroscopic deformation of a polymer network.

In the simplest hypothetical case, when the network elements (junctions and nonjunction beads) do not interact with an effective viscous medium, the viscoelastic response of the polymer network sample may be described by a simple Voigt element consisting of a spring and a dashpot, which are connected in parallel. The spring constant of the spring corresponds to the equilibrium modulus \( G_e \) of polymer network. Then the internal stress \( \sigma \) arising in the polymer network as a response to an external perturbation would be given by the sum of two independent components: the stress \( \sigma_m \) corresponding to the deformation of the medium (eq 2) and the stress \( \sigma_{\text{el}} \) resulting from the deformation of elastic Gaussian springs which form the network. The latter stress component is given by

\[
\sigma_{\text{el}} = \frac{\delta L(t)}{L_0} G_e \tag{6}
\]
If the interactions between the network and the effective viscous medium are taken now into consideration, an additional stress component \( \sigma_{\text{int}} \) corresponding to these viscous interactions appears. It is this stress component that determines the frequency and time dependences of viscoelastic characteristics of a polymer network. Hence, the total internal stress \( \sigma \) arising in a bulk cross-linked polymer has the form

\[
\sigma = \sigma_m + \sigma_{\text{el}} + \sigma_{\text{int}}
\]

(7)

where the stress components \( \sigma_m \) and \( \sigma_{\text{el}} \) are given by eqs 2 and 6, respectively. It should be emphasized that there are two main features which distinguish the network model proposed from the dynamic model of polymer melts. Firstly, in cross-linked polymers there is the nonzero equilibrium modulus \( G_0 \) and, therefore, an additional stress contribution \( \sigma_{\text{el}} \) absent in melts. Secondly, the polymer chains in a network are connected with each other in a three-dimensional spatial structure. This leads to a more complicated form of the main nontrivial stress component \( \sigma_{\text{int}} \) determining the frequency dependences of dynamic moduli as compared with those of polymer melts.

To obtain the stress component \( \sigma_{\text{int}} \) and, therefore, to calculate the dynamic modulus and viscosity of a polymer network, we use the method of calculation of the additional work \( A_{\text{add}} \) which is made by the network owing to the friction of polymer chains against an effective viscous medium. This is a widely used standard approach, and it may be found elsewhere.\(^5\) In general, the additional work \( A_{\text{add}} \) per unit volume and per unit time, which arises from the motion of network chains in an effective viscous medium, is given by

\[
A_{\text{add}} = \frac{1}{V} \int_{T_{\omega}}^{T_{\omega} + \delta T} \sum_{X} (F_{fr}(X)V_{m}(X)) \, dt
\]

(8)

Here \( V \) is the volume of a network, \( T_{\omega} \) is the period of an external force acting at a frequency \( \omega \), \( V_{m}(X) \) is the complex conjugate of velocity of an effective viscous medium in the vicinity of a network element \( X \), and \( \langle ... \rangle \) means the configurational average. Note that eq 8 determines the additional work due to network extension along the \( X \) axis. As mentioned above, in an incompressible polymer sample this extension should be accompanied by the compression in the normal directions. The calculations of corresponding additional works arising from network compressions along the \( Y \) and \( Z \) axes are quite analogous to those for the deformation along the \( X \) axis (longitudinal velocity gradient \( G \) should be replaced by the quantity \( \langle V_{m} \rangle \)).

We shall make all the calculations of \( A_{\text{add}} \) in terms of the Rouse model,\(^2\) i.e., the hydrodynamic interactions between the network chains and the viscous medium will be neglected. At the end of the paper (section 3.4) we shall discuss the problem of hydrodynamic interactions. In the Rouse approximation, the friction force \( F_{fr}(X) \) acting on the network elements from a perturbed effective viscous medium has the form \( \zeta[V_{m}(X) - \chi] \) where \( \zeta \) is the friction constant of a given network element (junction or nonjunction bead) and \( V_{m}(X) = G_0X \exp(\text{i}\omega t) \) is the velocity of the viscous medium in the vicinity of network element \( X \). As has been shown,\(^1,11\) the exact analytical solution for relaxation times of a regular cubic network consisting of "bead and spring" Rouse chains can be obtained if the friction constant of a junction is three times greater than that of a nonjunction bead (in other cases the solution can be found using numerical calculations). Hence, friction forces acting on the junctions and nonjunction beads of network chains differ from each other. They are given by \( 3V_{g}(V_{m}(X) - \chi) \) and \( V_{g}(V_{m}(X) - \chi) \) for a junction and a nonjunction bead, respectively (here \( V_{g} \) is the friction constant of a nonjunction bead).

As mentioned above, the network system considered is characterized by the fixed average volume ensured by the constant component \( \sigma_0 \) of an external stress (see eq 1). This means that the average values of projections of position vectors of the network elements are not equal to zero. This distinguishes them from the "unstrained" polymer networks embedded in a viscous medium (see, for example, ref 12), and polymer solutions and melts.\(^5,10\) In a Gaussian network having a fixed average volume, the \( X \) projection of the position vector of a given network element \( X(t) \) consists of the nonzero average value \( \langle X \rangle \) and the time-dependent fluctuating part \( \delta X(t) \), i.e., \( X(t) = \langle X \rangle + \delta X(t) \). The quantities \( \langle X \rangle \) are determined by the average positions of network elements in space and would have to provide an additional contribution to the work \( A_{\text{add}} \) as compared with the "unstrained" polymer networks for which \( \langle X \rangle = 0 \). This contribution corresponds to the spectrum of average values of displacements of network elements \( \langle \delta X(t) \rangle \). However, the above-mentioned interconnection between the motion of an effective viscous medium and the macroscopic network deformation (eq 5) leads to an affine (homogeneous) deformation of a polymer network. As a result, the average velocities of network elements are equal to those of the effective viscous medium in the vicinity of these network elements: \( \langle \delta X(t) \rangle = \langle V_{m}(X) \rangle \). In other words, the average value of friction force acting on a network from a viscous medium is equal to zero and does not make any contributions to the additional work \( A_{\text{add}} \) (eq 8). This means that only the relaxation spectrum of mean squares \( \langle \delta X^2(t) \rangle \) of displacements of network elements is excited in this system (spectrum of average values \( \langle \delta X^2(t) \rangle \) does not appear). This fact was rigorously demonstrated in the frame of a simplified coarse-grained network model\(^9\) and may be easily extended to a network model consisting of multisegmental Rouse chains.

Taking into account the difference between the friction constants of a junction and a nonjunction bead and all the above considerations concerning the average values \( \langle X \rangle \), the additional work \( A_{\text{add}} \) (see eq 8) may be rewritten as

\[
A_{\text{add}} = \frac{1}{V} \int_{T_{\omega}}^{T_{\omega} + \delta T} \sum_{X} (F_{fr}(X)V_{m}(X)) \, dt
\]

(9)

where

\[
I(\delta X) = \sum_{\Omega} \int (\delta X_0(t) \delta X(t)) \, dt
\]

(10)

Here \( \delta X_0(t) \) and \( \delta X(t) \) are the fluctuating parts of \( X \) projections of junctions and nonjunction beads, respectively. An elementary cell of a cubic network consisting of a junction and three "bead and spring" Rouse...
chains. All the network chains have the identical contour lengths. A Rouse chain between cross-links (junctions) consists of n “beads” with a friction constant \( V_0 \) and \( (n + 1) \) “springs” with an elasticity constant \( K_0 \). As mentioned above, the case when the friction constant of a network junction is equal to \( 3V_0 \) is considered. Each junction of a regular cubic network is marked by a three-component index \( \Omega = (\alpha, \beta, \gamma) \). The quantities \( \alpha, \beta, \) and \( \gamma \) range from unity to the number of network junctions \( N \) along a given Cartesian direction. The total number of the junctions in a network is equal to \( N^3 \). Each nonjunction bead in a chain between network junctions is marked by the number \( \Omega = (\alpha, \beta, \gamma) \) of a cubic network cell, by the number \( p \) of a chain in the cubic cell \( (p = 1...3) \), and by the number \( j \) of the bead along the network chain (\( j \) ranges from 1 to \( n \)).

In contrast to a simplified coarse-grained network model \(^9\), \(^12\) where a chain between junctions is modeled by a single Gaussian spring and all the network elements (junctions) are identical, the network model considered contains the elements of two sorts: junctions and nonjunction beads in the chains between junctions, which differ in their friction constants. Therefore, the main problem in the calculation of an additional work \( A_{\text{add}} \) is in the determination of different weights contributed by network junctions \( \delta X_\Omega(\Omega; t) \) and nonjunction beads \( \delta X_p(\Omega_j; t) \) to the quantity \( A_{\text{add}} \) (eqs 9 and 10). To obtain the additional work \( A_{\text{add}} \) we use the normal mode treatment. It is assumed that an external perturbation applied to a network is small. It corresponds to the smallness of a longitudinal velocity gradient of an effective viscous medium. Therefore, the normal modes of a network which is not perturbed by an external stress may be used. The transformation from Cartesian coordinates to normal modes for elements of a nonperturbed cubic network has been obtained previously \(^1\) and may be written in the following form:

\[
\begin{align*}
\delta X_p(\Omega_j; t) & = \sum_{\psi} \sum_{\theta} C_p(\Omega_j; \theta, \psi) Q(\psi, \theta; t) \\
\delta X_\Omega(\Omega, t) & = \sum_{\psi} \sum_{\theta} C_\Omega(\Omega; \theta, \psi) Q(\psi, \theta; t)
\end{align*}
\]  

(11a)

(11b)

Here \( \psi \) is the intrachain wave vector determining the phase shift between displacements of neighboring beads in a network chain and \( \theta \) is the interchain wave vector describing the phase shift between network cells. Note that the coefficients \( C_p(\Omega_j; \theta, \psi) \) and \( C_\Omega(\Omega; \theta, \psi) \) may be complex values.

The normal mode transformation allows the potential energy \( U(X) \) and dissipation function \( R(X) \) of a cubic network consisting of “bead and spring” Rouse chains to be diagonalized simultaneously. In the case of dissipation function, this means that the following condition should be fulfilled: \(^1\)

\[
\sum_{\Omega} \left[ 3C_\Omega(\Omega; \theta, \psi) Q(\psi, \theta; t) + \sum_{p=1}^{n} \sum_{j=1}^{n} \delta X_p^2(\Omega_j; t) \right] = \sum_{\psi} \sum_{\theta} Q^2(\theta, \psi; t)
\]  

(12)

Substituting the normal mode transformation (eqs 11) into this condition, one can obtain the relation between the coefficients of the normal mode transformation:

\[
\sum_{\Omega} [3C_\Omega(\Omega; \theta, \psi) C_\Omega^*(\Omega; \theta, \psi) + \sum_{p=1}^{n} \sum_{j=1}^{n} C_p(\Omega_j; \theta, \psi) C_p^*(\Omega_j; \theta, \psi)] = 1
\]  

(13)

Using this relation and the normal mode transformation (eq 11), eq 9 for the additional work \( A_{\text{add}} \) may be rewritten as

\[
A_{\text{add}} = -\frac{G_0 V}{2} \int_{t_0}^{t} \frac{1}{2} \left( V \left[ -i \omega t \right] \frac{d}{dt} (Q) - G_0 V(\psi) \right) dt
\]

(14)

where

\[
I(\psi) = \sum_{\theta} \left( Q^2(\theta, \psi; t) \right)
\]

(15)

One can see from eqs 14 and 15 that the additional work \( A_{\text{add}} \) is determined by the mean squares of normal modes \( \langle Q^2 \rangle \). They may easily be obtained from the equations of motion of a Gaussian network with the use of condition of the smallness of an external perturbation (or a velocity gradient \( G_0 \)).

The equations of motion of the network elements with respect to an effective viscous medium in which a longitudinal velocity gradient \( G = G_0 \exp[i\omega t] \) exists have the following forms for a nonjunction bead (cf. ref 1)

\[
\frac{d}{dt} \delta X_p(\Omega_j; t) - G_0 \delta X_p(\Omega_j; t) \exp(i\omega t) + K_0 \left[ 2\delta X_p(\Omega_j; t) - \delta X_p(\Omega_j + 1; t) - \delta X_p(\Omega_j - 1; t) \right] = F_B(\delta X_p(\Omega_j; t))
\]

(16a)

and for a network junction

\[
3 \frac{d}{dt} \delta X_\Omega(\alpha, \beta, \gamma; t) - G_0 \delta X_\Omega(\alpha, \beta, \gamma; t) \exp(i\omega t) + K_0 \left[ 6 \delta X_\Omega(\alpha, \beta, \gamma; t) - \delta X_1(\alpha, 1, \gamma; t) - \delta X_1(\alpha, 1, \beta; t) - \delta X_2(\alpha, \beta, 1; t) - \delta X_2(\alpha, \gamma, 1; t) - \delta X_3(\alpha, \beta, \gamma; t) - \delta X_3(\alpha, 1, \beta; t) - \delta X_3(\alpha, 1, \gamma; t) \right] = F_B(\delta X_\Omega(\alpha, \beta, \gamma; t))
\]

(16b)

Here \( F_B(\delta X) \) is the stochastic Brownian force. Using normal mode transformation (eqs 11) one can obtain the equations of motion of normal modes \( Q \)

\[
\frac{d}{dt} Q(t) = G_0 Q(t) \exp(i\omega t) + K_0 2(1 - \cos \psi_0) Q(t) = F_B(\langle Q \rangle)
\]

(17)

After multiplying eq 17 by \( Q \) and averaging the equation over all the configurations of a network system, the equations of motion for the mean squares of normal modes \( \langle Q^2 \rangle \) can be obtained

\[
\frac{1}{2} \frac{d}{dt} \langle Q^2 \rangle - G_0 \langle Q^2 \rangle \exp(i\omega t) + K_0 2(1 - \cos \psi_0) \langle Q^2 \rangle = k_B T
\]

(18)

Then one can use the perturbation theory with a small parameter, namely, the solution of eq 18 may be expanded in the power series of a small velocity
gradient including terms up to first power of \( G_0 \), i.e., 
\[
(Q^2) = C_1 + C_2 G_0 \exp(\iota \omega t).
\]

Finally, we obtain the following expression for the additional work \( A_{\text{add}} \) arising from the friction of network chains against to a viscous medium

\[
A_{\text{add}} = G_0^2 2 \pi k_B T \sum \tau(\psi) \quad (19)
\]

where \( \psi \) is the number of cross-links per unit volume and \( N^3 \) is the total number of cross-links (junctions) in the cubic network considered. The set of relaxation times \( \tau(\psi) \) manifested in mechanical relaxation of a network is given by

\[
\tau(\psi) = \frac{2 \tau_0}{(1 - \cos \psi)} \quad (20)
\]

Here \( \psi \) is the intrachain wave vector and \( \tau_0 \) is the relaxation time of a single Gaussian subchain

\[
\tau_0 = \frac{\zeta_0}{8 \pi k_0} \quad (21)
\]

where \( \zeta_0 \) is the friction constant of a nonjunction bead and \( k_0 \) is the elasticity constant of a “spring” between neighboring beads. The relaxation times manifested in mechanical relaxation of a network are two times smaller than those determining local relaxation properties (see eq 5 of ref 1). This is caused by the fact that the spectrum of mean squares of normal modes \( Q^2 \) is excited in macroscopic mechanical relaxation. This situation differs from that in the local relaxation phenomena (e.g., dielectric relaxation of polymer networks)\(^3,4\) in which the spectrum of average values of normal modes \( \bar{Q} \) is manifested. Note that the structure of the expression for the additional work \( A_{\text{add}} \) obtained for a network consisting of “bead and spring” Rouse chains (eq 19) is the same as that for a coarse-grained network model\(^9,10\) (and for polymer solutions\(^8,10\) and melts\(^9\) as well) with corresponding sets of relaxation times. This fact confirms the result obtained by Golovachev\(^13\) that the above structure of the expression for an additional work \( A_{\text{add}} \) holds for network systems with arbitrary topologies if the interchain friction interactions are neglected.

The additional work \( A_{\text{add}} \) determines the stress contribution \( \sigma_{\text{int}} \) arising from viscous interactions between the network chains and the effective medium: \( \sigma_{\text{int}} = A_{\text{add}}/G_0 \) (see, for example, refs 8 and 10). It is also essential to take into account the contributions to the additional work \( A_{\text{add}} \) provided by the network compression along the axes normal to the direction of an external stress (the \( X \) axis). These contributions may be calculated in an analogous way as the additional work arising from the deformation along the \( X \) axis and are given by equations similar to eq 19 (quantity \( G_0 \) should be replaced by \( (1/2)G_0 \)). Finally, the stress \( \sigma_{\text{int}} \) in which we are interested (see eq 7) is given by

\[
\sigma_{\text{int}} = \frac{G_0^3 \pi k_B T}{N^3} \left[ \sum \frac{\tau(\psi_1)}{1 + \iota \omega \tau(\psi_1)} + 2 \sum \frac{\tau(\psi_2)}{1 + \iota \omega \tau(\psi_2)} \right] \quad (22)
\]

Here the quantities \( \psi_1 \) and \( \psi_2 \) represent two sets of intrachain wave vectors of a cubic network consisting of “bead and spring” Rouse chains. They are given by

\[
\psi_1 = \frac{2 \pi}{n + 1} \left( \frac{1}{n + 1} \right)^{1/2} \cos \left( \frac{\theta_1 + \theta_2 + \theta_3}{3} \right); \quad l = 0 \ldots n/2 (23a)
\]

\[
\psi_2 = \frac{\pi}{n + 1} k; \quad k = 1 \ldots n (23b)
\]

where the number of beads \( n \) in the network chain is believed to be even. The interchain wave vector \( \theta = (\theta_1, \theta_2, \theta_3) \) determines the phase shift between displacements of neighboring network cells. Its components \( \theta_1, \theta_2, \) and \( \theta_3 \) are given by

\[
\theta_{1,2,3} = \frac{2 \pi S_{1,2,3}}{N - 1}; \quad S_{1,2,3} = 0, \ldots, N - 1 (24)
\]

where \( N \) is the number of cross-links along the given Cartesian direction in a network. A cubic network as a whole contains \( N^3 \) junctions, and the interchain wave vector \( \theta \) has an infinitely large number of values in the case of an infinitely large (macroscopic) network.

Using the expression obtained for the stress component \( \sigma_{\text{int}} \) arising from viscous interactions between the network elements and the effective medium (eq 22) and taking into account the stress components \( \sigma_0 \) and \( \sigma_0 \) (eq 7), one can obtain the expressions for complex dynamic modulus \( G^*(\omega) \) and viscosity \( \eta^*(\omega) \) (see, for example, ref 8):

\[
G^*(\omega) = G_0 + 3 \pi k_B T \sum \frac{1}{N^3} \left[ \sum \frac{\iota \omega \tau(\psi_1)}{1 + \iota \omega \tau(\psi_1)} + 2 \sum \frac{\iota \omega \tau(\psi_2)}{1 + \iota \omega \tau(\psi_2)} \right] \quad (25)
\]

\[
\eta^*(\omega) = \eta_0 + 3 \pi k_B T \sum \frac{\tau(\psi_1)}{N^3} \left[ \sum \frac{\tau(\psi_1)}{1 + \iota \omega \tau(\psi_1)} + 2 \sum \frac{\tau(\psi_2)}{1 + \iota \omega \tau(\psi_2)} \right] \quad (26)
\]

Here \( G_0 \) is the equilibrium modulus of a network and \( \eta_0 \) is the viscosity of an effective viscous medium.

One can see that the frequency dependences of dynamic modulus and viscosity are determined by two sets of relaxation times \( \tau(\psi_1) \) and \( \tau(\psi_2) \). The main and more complicated set of relaxation times \( \tau(\psi_1) \) is determined by the phase shift along the network chain (first term in eq 23a) as well as by the phase shift between network cells \( \theta \) (second term in eq 23a). Just these relaxation times \( \tau(\psi_1) \) include the interchain collective branch of network relaxation. If nonzero value of \( l \) is fixed (see eq 23a), the broadening of relaxation time line of a single chain is observed due to the change of the interchain wave vector \( \theta \), i.e., due to the existence of a spatial network structure. The corresponding relaxation processes have characteristic times which range from the relaxation time of a single Gaussian subchain \( \tau_0 \) (eq 21) to the maximum relaxation time of a chain between cross-links (see eq 20 at \( \psi = \pi (n + 1) \))

\[
\tau_{\text{chain}} = \frac{4}{\pi^2} (n + 1)^2 \tau_0 \quad (27)
\]
and may be treated as intrachain relaxation processes. If we put \( l \) equal to zero in eq 23a, we obtain a purely interchain cooperative branch determined only by the phase shift \( \theta \) between network cells. The corresponding relaxation processes have characteristic times ranging from \( t_{\text{chain}} \) to infinitely long times and may be treated as interchain relaxation processes. Besides the relaxation times \( \tau(\psi_1) \), there is also a doubly degenerated set of relaxation times \( \tau(\psi_2) \) determined by the purely intrachain phase shift \( \psi_2 \) (eq 23b). These relaxation times correspond only to the intrachain relaxation processes, namely, to the relaxation of a single Rouse chain with fixed ends. In the next section the relative contributions from intra- and interchain relaxation processes to viscoelastic mechanical characteristics of a polymer network will be compared.

3. Discussion

3.1. Dynamic Modulus of Elasticity of a Network. The dynamic modulus of elasticity \( G'(\omega) \) (real part of complex dynamic modulus \( G^*(\omega) \)) of a polymer network consisting of “bead and spring” Rouse chains has the form (eq 25)

\[
G'(\omega) = G_e + 3\nu k_BT \left[ \frac{1}{N^2} \sum_{\psi_1} \frac{(\omega \tau(\psi_1))^2}{1 + (\omega \tau(\psi_1))^2} + 2 \sum_{\psi_2} \frac{(\omega \tau(\psi_2))^2}{1 + (\omega \tau(\psi_2))^2} \right]
\]

Here \( \tau(\psi) \) are the relaxation times manifested in mechanical relaxation (eqs 20 and 21), \( \nu \) is the number of cross-links per unit volume, and \( G_e \) is the equilibrium modulus of a polymer network. To compare the relative contributions from intra- and interchain relaxation processes to the dynamic modulus and to estimate the frequency dependence of \( G'(\omega) \) on various limiting regions of frequency one can use the following approximation. The wave vector \( \psi_1 \) at \( l = 0 \) (see eq 23a) corresponds only to interchain relaxation. The quantity \( \psi_1 \) at \( l \neq 0 \) contributes to the relaxation from intrachain motions and is determined by the phase shift \( 2\pi l/(n+1) \) along the chain and by the phase shift \( \theta \) between network cells. The change of interchain wave vector \( \theta \) at fixed \( l \neq 0 \) influences slightly the relaxation times \( \tau(\psi_1) \). To a first approximation, one can assume for sufficiently long chains that the wave vector \( \psi_1(l) \neq 0 \) does not depend on the phase shift \( \theta \) between network cells. This means that we neglect the broadening of the relaxation spectrum of a polymer network in the region of intrachain relaxation (see also ref 1).

In the consideration of viscoelastic properties of a Gaussian network, two characteristic frequencies appear. The first frequency is equal to the inverse relaxation time \( t_0 \) of a single Gaussian subchain. The second one is equal to the inverse maximum relaxation time \( t_{\text{chain}} \) of a chain between network junctions. The characteristic frequencies determine the following frequency regions: the region of extremely high frequencies \( \omega \gg 1/t_0 \) corresponding to the network relaxation on a scale smaller than a Gaussian subchain size, the intermediate high-frequency region \( 1/t_{\text{chain}} \ll \omega \ll 1/t_0 \) corresponding to the relaxation on a scale-up to the dimension of a chain between cross-links, and the low-frequency region \( \omega \ll 1/t_{\text{chain}} \) corresponding to the large-scale collective network relaxation.

The dynamic modulus of elasticity \( G'(\omega) \) of a polymer network in the low-frequency region \( (\omega \ll 1/t_{\text{chain}}) \) behaves as

\[
G'(\omega) - G_e \approx \nu k_BT (\omega t_{\text{chain}})^{3/2} 6\sqrt{3}\pi
\]

The interchain relaxation processes provide the main contribution to the dynamic modulus in this frequency region (Figure 2). The dynamic modulus \( G'(\omega) \) of a network consisting of “bead and spring” Rouse chains has the same asymptotic frequency dependence in the low-frequency region as that for a simplified coarse-grained network model describing the collective interchain relaxation only. With increasing frequency, the contribution from interchain motions to frequency dependence of \( G'(\omega) \) becomes smaller. At \( \omega \approx 1/t_{\text{chain}} \) the interchain relaxation processes provide only the constant contribution to dynamic modulus \( G'(\omega) \) (see Figure 3). In the high-frequency region \( (1/t_{\text{chain}} \ll \omega \ll 1/t_0) \), the frequency dependence of \( G'(\omega) \) is mostly determined by the intrachain relaxation processes (Figure 4) and has the form

\[
G'(\omega) - G_e \approx \nu k_BT (n+1)\sqrt{\omega/\omega_0^2}\frac{24}{\pi}
\]

Figure 4 indicates that the dynamic modulus \( G'(\omega) - G_e \) of a polymer network in the high-frequency region has a similar behavior as the dynamic modulus of a melt consisting of un-cross-linked polymer chains, which has an additional constant component corresponding to the high-frequency limit of an interchain contribution to
$G'(\omega)$ of the polymer network. It should be noted that all the curves in Figures are plotted using exact analytical expressions without any approximations (see eq 28 in the case of $G'(\omega)$). The approximation mentioned in this Section is used only to estimate the asymptotic behavior of viscoelastic mechanical characteristics considered.

3.2. Dynamic Viscosity of a Network. For dynamic viscosity $\eta'(\omega)$ of a polymer network (real part of complex dynamic viscosity $\eta^*(\omega)$) we have (see eq 26)

$$
\eta'(\omega) = \eta_m + 3v_k B T \left[ \frac{1}{\sqrt{\omega \tau_0}} + \frac{2}{\sqrt{\omega \tau_0^3}} \right]^{3/2}
$$

where $\eta_m$ is the viscosity of an effective viscous medium. In the region of high frequencies ($1/\tau_{\text{chain}} \ll \omega \ll 1/\tau_0$), the dynamic viscosity $\eta'(\omega)$ of a network is determined by the intrachain relaxation processes and behaves as

$$
\eta'(\omega) \approx \eta_m = v_k B T (n + 1) \frac{1}{\sqrt{\omega \tau_0}} \frac{24}{\sqrt{3\pi}}
$$

This is typical of a melt of un-cross-linked macromolecules. With decreasing frequency, the influence of the intrachain motions on frequency dependence of dynamic viscosity $\eta'(\omega)$ becomes weaker. At $\omega \approx 1/\tau_{\text{chain}}$, the intrachain relaxation processes begin to provide only the constant contribution independent of frequency (Figure 5). In the region of low frequencies ($\omega \ll 1/\tau_{\text{chain}}$) the frequency dependence of $\eta'(\omega)$ is governed by the interchain relaxation processes (Figure 5). In this low-frequency region, the quantity $\eta'(\omega)$ behaves as

$$
\eta'(\omega) \approx \eta_m + \eta'(0) - v_k B T \tau_{\text{chain}} \sqrt{\omega \tau_0} \frac{18\sqrt{3\pi}}{5}
$$

where $\eta'(0)$ is the dynamic viscosity of a polymer network at zero frequency

$$
\eta'(0) \approx v_k B T \tau_0 (n + 1)^2 [C_{\text{intra}} + C_{\text{inter}}]
$$

Here $C_{\text{intra}}$ and $C_{\text{inter}}$ are numerical constants. The constants $C_{\text{intra}} \approx 5.1$ and $C_{\text{inter}} \approx 6.3$ correspond to the contributions from intra- and interchain relaxation processes to the dynamic viscosity $\eta'(0)$ of a network at zero frequency, respectively. The interchain contribution to $\eta'(0)$ is slightly greater than the intrachain contribution; the interrelation $C_{\text{inter}}/C_{\text{intra}} \approx 1.2$ does not depend on molecular weight of a chain between network junctions.

It should be especially emphasized that the contributions from intra- and interchain relaxation processes to dynamic viscosity at zero frequency have the same order of magnitude. The quantity $\eta'(0)$ represents the sum of all relaxation times of a network (see eq 31 at $\omega = 0$). The contribution from intrachain motions to dynamic viscosity at zero frequency $\eta_{\text{intra}}'(0)$ is given by

$$
\eta_{\text{intra}}'(0) \sim v_k B T \int_{\tau_0}^{\tau_{\text{chain}}} \frac{H(\tau)}{\tau} \, d(\ln \tau)
$$

Here $H(\tau)$ is the relaxation spectrum (or the distribution function of relaxation times on a logarithmic scale) manifested in mechanical relaxation of a polymer network. The relaxation spectrum $H(\tau)$ of a polymer network consisting of “bead and spring” Rouse chains has the usual Rouse-like behavior $\tau^{3/2}$ in the short-time region $\tau_0 < \tau < \tau_{\text{chain}}$ (see ref 1). Therefore, the function under the integral sign in eq 35 increases as $\sqrt{2}\tau$, and the quantity $\eta_{\text{intra}}'(0)$ is determined by the maximum relaxation time of intrachain motions, namely, by the maximum relaxation time of a chain between cross-links $\tau_{\text{chain}}$ (eq 27). The contribution from interchain motions to dynamic viscosity $\eta_{\text{inter}}'(0)$, in turn, has the form

$$
\eta_{\text{inter}}'(0) \sim v_k B T \int_{\tau_{\text{chain}}}^{\infty} \frac{H(\tau)}{\tau} \, d(\ln \tau)
$$

As shown in ref 1, the relaxation spectrum $H(\tau)$ of a polymer network in the long-time interchain region $\tau > \tau_{\text{chain}}$ decreases as $\tau^{-1/2}$, i.e., more rapidly than the spectrum in the intrachain region. Therefore, the function under the integral sign in eq 36 behaves as $\tau^{-1/2}$. As a result, the quantity $\eta_{\text{intra}}'(0)$ is mostly governed by the minimum relaxation time of large-scale interchain motions, i.e., by the same relaxation time $\tau_{\text{chain}}$. Thus, the contributions from intra- and interchain relaxation processes to dynamic viscosity at zero frequency are approximately equal. This is an essential result. It means that the intrachain motions provide noticeable contribution to macroscopic viscoelastic characteristics.
of a polymer network (e.g., to the dynamic viscosity) even in the low-frequency region corresponding to large-scale interchain relaxation. In contrast, local dynamic characteristics of the network are mostly governed by interchain motions on a scale greater than the average distance between cross-links.

### 3.3. Simplified Description of Viscoelastic Properties of a Network

As shown in ref 1, the local dynamic characteristics of a polymer network (e.g., the mean-square displacement of a network junction) may be described to a rather good approximation by an simplified coarse-grained network model at times greater than the maximum relaxation time of a chain between cross-links. In the consideration of macroscopic viscoelastic characteristics of the network, the situation is more complicated because all network elements provide contributions to the macroscopic quantities. We begin with the comparison of dynamic viscosity \( \eta(\omega) \) of a network model consisting of “bead and spring” Rouse chains and of a coarse-grained network model. The coarse-grained model of a network consists of junctions with the friction constant \( \zeta \) and Gaussian springs with the elasticity constant \( K \), which connect the junctions into a spatial network structure.\(^\text{1,3,4,9,12,14,15} \)

The elasticity constant of a spring corresponds to the elasticity of a multisegmental Rouse chain between neighboring junctions. The friction constant of a junction corresponds to the friction of chain halves directly attached to the junction. The relaxation times of the coarse-grained model of a cubic network, which are manifested in mechanical relaxation, are given by\(^\text{9,12} \)

\[
\tau(\theta) = \frac{6r_{\text{min}}}{(3 - \cos \theta_1 - \cos \theta_2 - \cos \theta_3)}
\]  

(37)

where \( r_{\text{min}} = \zeta \cdot 24K \) is the minimum relaxation time of the coarse-grained network model. The relaxation times of the coarse-grained network are determined only by the interchain wave vector \( \theta = (\theta_1, \theta_2, \theta_3) \) describing the phase shift between network cells (eq 24). The characteristic times of a simplified network model and a more realistic network model considered in the paper are related to each other by the following equation:\(^\text{1} \)

\[
\tau_{\text{min}} = (n + 1)^2 \tau_0
\]  

(38)

The dynamic viscosity \( \eta_{\text{CG}}(\omega) \) of a coarse-grained network under an external stress producing a longitudinal velocity gradient in effective viscous medium is given by\(^\text{9} \)

\[
\eta_{\text{CG}}(\omega) = \eta_m + 3n_k B T \left[ \frac{1}{N^2 \sum_{\theta} \tau(\theta)} \right]
\]  

(39)

In Figure 6 we plot the dynamic viscosity \( \eta(\omega) \) of a network of “bead and spring” Rouse chains, the contribution from interchain relaxation processes to \( \eta(\omega) \) of this network model, and the dynamic viscosity of a coarse-grained network model. The dynamic viscosity of the coarse-grained network is found to be very close to the contribution from interchain motions to the dynamic viscosity \( \eta(\omega) \) of a more realistic network model. Apart from the interchain relaxation processes, the small-scale interchain motions also provide considerable contribution to dynamic viscosity \( \eta(\omega) \) of a polymer network in the low-frequency region (see previous section). Therefore, the total dynamic viscosity of a network of “bead and spring” Rouse chains cannot be described only in terms of the coarse-grained network model even in the region of large-scale interchain relaxation. Hence, there is a certain difference between the macroscopic and local dynamic characteristics of a polymer network as regards the possibility of the above simplified description using the coarse-grained network model only.

It is also interesting to compare the dynamic viscosity \( \eta(\omega) \) of a polymer network and a melt consisting of un-cross-linked chains at the same number of chains per unit volume \( \nu_{\text{chain}} \). In the case of a regular cubic network, the quantity \( \nu_{\text{chain}} \) is related to the number of cross-links per unit volume \( v \) by a simple equation: \( \nu_{\text{chain}} = \frac{3}{4} v \).

The dynamic viscosity of a polymer melt has been studied, for example, in ref 5 for the case of a shear velocity gradient of the effective viscous medium. In the case of a longitudinal velocity gradient, the dynamic viscosity \( \eta(\omega) \) of the melt of un-cross-linked chains having the same lengths as in a network may be presented in the form (in the Rouse-like region)

\[
\eta_m(\omega) = \eta_m + 3n_{\text{chain}} k_B T \sum_{\psi} \frac{\tau(\psi)}{1 + (\omega \tau(\psi))^2}
\]  

(40)

Here \( \tau(\psi) \) are the relaxation times of a “bead and spring” Rouse chain consisting of \( n + 1 \) subchains. They are given by eq 20 with wave vector \( \psi = kx/(n + 1) \) where \( k = 1..n \) (see, for example, refs 2, 5, and 8). One can see from Figure 7 that the dynamic viscosity \( \eta(\omega) \) of the melt is close to the contribution from interchain relaxation processes to dynamic viscosity \( \eta(\omega) \) of a polymer network. The dynamic viscosity \( \eta(0) \) of melt at zero frequency is found to be about two times smaller than that of a network at the same number of chains per unit volume \( (v_{\text{chain}}) \). In the high-frequency region (\( \omega \gg 1/\tau_{\text{chain}} \)), the polymer network behaves like a melt consisting of un-cross-linked chains (Figure 7).

One can conclude that the frequency dependence of dynamic viscosity \( \eta(\omega) \) of a polymer network may be described to a good approximation in the low-frequency region (\( \omega \ll 1/\tau_{\text{chain}} \)) by a coarse-grained network model and in the high-frequency region (\( \omega \gg 1/\tau_{\text{chain}} \)) by a melt of un-cross-linked macromolecules having the same molecular weight as polymer chains in the network. It
is essential that the contribution from intrachain relaxation processes to the total dynamic viscosity of a polymer network cannot be omitted even in the low-frequency region. This intrachain contribution practically does not change with frequency at sufficiently low frequencies (Figure 5) and is shown to be close to the dynamic viscosity at zero frequency of the melt of un-cross-linked macromolecules. This means a certain "redefinition" of the concept of an effective viscous medium: now it depends on the scale of network motions. For the motions having characteristic scale smaller than the average distance between cross-links, the viscosity \( \eta \) of an effective viscous medium is assumed to be equal to that of a melt consisting of polymer monomers. It is quite analogous to the approach developed for polymer melts.\(^5\) For larger scale of network motions, the viscosity of the effective medium of a polymer network may be assumed to be close to that of a melt of polymer chains not connected in a spatial network structure.

### 3.4. Problem of Hydrodynamic Interactions

The results of this paper were obtained in terms of the dynamic network model in which the hydrodynamic interactions between the network elements and effective viscous medium are neglected. The network elements move against the viscous medium which is perturbed by a longitudinal velocity gradient. It is essential that we need the velocity gradient only to excite the mechanical relaxation spectrum, the relaxation times themselves correspond to those of a network system at a zero velocity gradient. If the hydrodynamic interactions are taken into account, the situation becomes more complicated. When the scales of motions smaller than the distance between neighboring cross-links are considered, the dynamic behavior of network chains is very close to that of un-cross-linked polymer chains in the melt. Therefore, the results obtained in the theory of dynamics of polymer melts can be used for the intrachain relaxation of polymer networks. In the polymer melt the motion of a single chain is considered as the motion in an effective medium which includes the effect of the other polymer chains (at least, in the Rouse-like region).\(^5,16\) The viscosity \( \eta_m \) of this medium is assumed to be close to that of a liquid consisting of polymer monomers. On a small scale, the velocity profile \( V(r) \) of the effective viscous medium at a distance \( r \) from a given chain segment decreases as \( 1/r \) according to the Oseen formula. On a large scale, the velocity profile obeys the macroscopic hydrodynamics, i.e., the velocity of medium should decrease as \( 1/r \) where \( \eta \) is the macroscopic viscosity of melt. If \( \eta_m \ll \eta \) the velocity field falls rapidly on the scale with an order of magnitude of tens of segments, and the so-called hydrodynamic screening takes place.\(^5,16,17\) As a result of the hydrodynamic screening, the dynamic behavior of a single polymer chain in the melt becomes Rouse-like. Hence, for the relaxation times corresponding to the intrachain motions of a network, the hydrodynamic interactions are negligible.

If the scale of network motions larger than the distance between cross-links is considered, the contribution of the hydrodynamic interactions becomes noticeable as compared with that of stochastic Brownian forces. The hydrodynamic interactions are controlled by viscosity close to that of a melt of un-cross-linked chains \((V(r) \sim 1/r)\). Thus, for large-scale collective motions of network chains the hydrodynamic interactions between the network and the effective medium may be important. To study this effect, a simplified coarse-grained network model describing only the collective interchain dynamics may be used. A bulk cross-linked polymer as a whole is an incompressible system, i.e., its volume and average distances between cross-linked are fixed. One can assume that an effective viscous medium has the properties of a real liquid, i.e., it represents an incompressible medium. Therefore, the combined consideration of the interacting network and mobile incompressible medium can be carried out. This approach has been developed by the authors in refs 18 and 19. The resulting relaxation spectrum is shown to depend considerably on the compressibility of a network component of the "network and incompressible medium" system.\(^18,19\) The network elements (junctions in the case of a coarse-grained network model) do not include all the degrees of freedom of an incompressible bulk polymer. Therefore, the network component may be either compressible or incompressible. If a network component itself is compressible, the set of relaxation times \( \tau(\tilde{\theta}) \) excited in the "network and medium" system is found to be the same as that of a network system in which the hydrodynamic interactions are absent (see eq 37). If the network component of the "network and medium" system is incompressible, another set of relaxation times \( \tau^{**}(\tilde{\theta}) \) appears:

\[
\frac{1}{\tau^{**}(\tilde{\theta})} = \frac{1}{\tau(\tilde{\theta})} + \frac{1}{\tau^{**}}
\]

Here \( \tau(\tilde{\theta}) \) are the relaxation times corresponding to the compressible network component (eq 37), and \( \tau^{**} = h_0/\eta \) where \( \eta \) is the viscosity of an effective viscous medium, \( K \) is the elasticity constant of a Gaussian spring between cross-links of a coarse-grained network model, and \( h_0 \) is the average distance between neighboring cross-links. This spectrum is restricted by the finite maximum relaxation time equal to \( \tau^{**} \). Moreover, one can show that it is a rather narrow spectrum. The relaxation spectrum of this type corresponds to the cooperative motion of the network and the medium. The effective viscous medium is partly carried along by the motion of network elements so that for large-scale motions \((|\tilde{\theta}| \to 0)\) the network and the medium move in

### Figure 7. Dynamic viscosity \( \eta(\omega) \) of a network consisting of "bead and spring" Rouse chains (solid line), intrachain contribution to dynamic viscosity of this network (lines with solid squares (■)), and dynamic viscosity \( \eta(\omega) \) of melt consisting of un-cross-linked chains (lines with open squares (□)). Here \( n = 20 \).
synchronizm. A more detailed discussion of the hydrodynamic interactions in polymer networks may be found in refs 18 and 19.

To conclude, one can say that the hydrodynamic interactions do not influence the relaxation times and viscoelastic characteristics of a polymer network on the scales of motions smaller than the distance between neighboring cross-links. For greater scales the hydrodynamic interactions may be negligible if the network component itself of the “network and medium” system is compressible. This means that there is at least one situation when the results obtained hold for a network system in which the hydrodynamic interactions are taken into account. If the network component itself is incompressible, another very narrow relaxation spectrum appears. The influence of this spectrum on dynamic moduli of a polymer network will be a subject of our further publications.

4. Conclusion

In this work we have discussed the features of viscoelastic dynamic behavior of polymer networks, which are related to the existence of a spatial network structure. A simple dynamic model of a regular network consisting of “bead and spring” Rouse chains has been considered. This regular network model allows us to investigate the effect of connectivity of all the network chains with each other and the influence of this connectivity on various viscoelastic characteristics of a polymer. In particular, the comparative role of small-scale intrachain motions of segments and specific network interchain motions has been studied for the dynamic modulus and viscosity of a polymer network. A certain simplified description of macroscopic viscoelastic properties of cross-linked polymers is proposed. In addition, the problem of long-range hydrodynamic interactions in polymer networks was briefly discussed.

Acknowledgment. It is a pleasure to acknowledge the financial support of the Russian Foundation of Basic Research (Grant 99-03-33313), Russian Federal Program “Integration” (Grant 326.38), INTAS (Grant 99-1114), and Volkswagenstiftung (Grant 1/72 638).

References and Notes