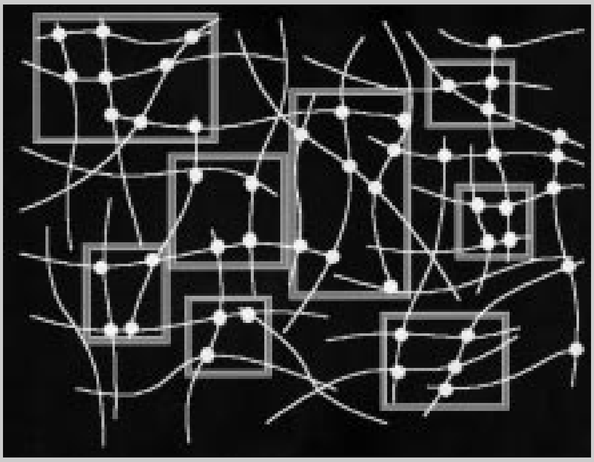
Full Paper: A dynamic model of a heterogeneous polymer network system is proposed. A polymer network is presented as an ensemble of cross-linked regions (domains) of different sizes, the domains have similarly regular internal structures. To a first approximation, these domains are treated independently of each other. Relaxation modulus, storage modulus, and loss modulus of the heterogeneous polymer network are calculated. For the purpose of averaging over all network domains the exponential number distribution of chain segments in domains is used. This type of distribution has been previously proposed by one of the authors in the frame of the aggregation model. It is shown that a structure heterogeneity introduced into a network model according to the above domain approach leads, at long times, to the stretched exponential type of time dependence of relaxation modulus instead of the power-law dependence predicted by the theories dealing with regular networks. The network heterogeneity also leads to a more rapid decrease in the storage modulus in the region of low frequencies, as compared with regular polymer networks. It is shown that the loss modulus in the region of its maximum is very slightly sensitive to the "long-range" network heterogeneity considered.



Dynamic model of a heterogeneous polymer network consisting of cross-linked regions (domains) of different sizes

Viscoelastic dynamic properties of heterogeneous polymer networks with domain structure

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Introduction

The dynamics of polymer networks is a very interesting and not completely understood problem of polymer physics. In most theories dealing with long-time network dynamics, regular polymer networks with different topologies have been studied[1–17] to describe the dynamic behavior of cross-linked polymers. A polymer network has been modeled as a collection of long flexible chains connected by junctions (cross-links). It has been assumed that all network chains have identical contour lengths and form a regular spatial structure of meshlike[1, 3–5, 13–17] or treelike topologies.[8, 10–12]

The main results of the previous theories of viscoelastic mechanical properties of regular polymer networks may be formulated as follows. The cross-linking of multi-segmental polymer chains in a network structure leads to the appearance of an additional long-time branch of the relaxation spectrum describing the collective interchain relaxation[1, 3, 12]. The characteristic time parameter corresponding to the maximum relaxation time τ_{chain} of a chain between neighboring network cross-links appears. This time parameter divides the total relaxation spectrum of a polymer network into two different regions. The first region is the intrachain spectrum with times smaller than the relaxation time of a chain between neighboring junctions τ_{chain}. This part of the spectrum is very similar to the spectrum of a linear not cross-linked polymer. The second region of the relaxation spectrum has times greater than

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τ_{chain} and corresponds to the long-scale interchain relaxation processes typical of polymer networks.[1, 3, 5, 12, 17] The relaxation spectrum $H(\tau)$ (or the distribution function of relaxation times τ on a logarithmic scale) is related to the relaxation modulus $G(t)$ as follows:[18]

$$G(t) = G_e + \int H(\tau)\ \exp\left[-t/\tau\right] d\ \ln\ \tau \tag{1}$$

where G_e is the equilibrium modulus of a polymer network. Both intra- and interchain parts of the relaxation spectrum of regular polymer networks show the power-law behavior. If a regular polymer network consisting of "bead and spring" Rouse chains[19] is considered, the intrachain part of the relaxation spectrum $H(\tau)$ has the usual Rousean behavior $\tau^{-1/2}$ (see, for example, ref.[1, 3, 5, 12, 17]). The behavior of the interchain part of the relaxation spectrum of a network depends considerably on the topology and connectivity of the network model considered. For example, in the case of infinitely large three-dimensional regular networks (cubic or tetrahedral) the interchain collective part of the relaxation spectrum behaves as $\tau^{-3/2}$, i.e., decreases more rapidly as compared with the intrachain spectrum component.[1,3,17] Such a type of relaxation spectrum behavior leads to the corresponding power-law time dependence of the relaxation modulus $G(t)$ of a regular polymer network. In the case of an infinitely large cubic network, the relaxation modulus $G(t)$ decreases as $t^{-1/2}$ at times smaller than the relaxation time τ_{chain} of a chain between cross-links and as $t^{-3/2}$ at longer times.

The usage of regular models of polymer networks represents the simplest approach to study the network dynamics and allows us to analyze qualitatively the effect of the cross-linking of polymer chains in a spatial network structure on the viscoelastic properties. However, the comparison of the predictions of regular network models with the experiment is often impossible because real cross-linked polymers have a heterogeneous structure as a rule. There is a great number of possible types of the network structure heterogeneity. It may be, for example, the distribution of molecular weights of network chains between cross-links, the existence of regions with different topology and cross-link density, the existence of not cross-linked amorphous domains, dangling chains etc. Therefore, the problem of structure heterogeneity is of great importance for theoretical considerations of viscoelastic properties of polymer networks. In this paper we shall confine ourselves to the consideration of one example of a network heterogeneity concerning the existence of regions with different properties in real polymer networks.

Dynamic model of a heterogeneous polymer network

A random character of the cross-linking process may lead to the existence of cross-linked as well as not cross-linked regions in a real network polymer. The cross-linked regions of different sizes may be separated by the regions consisting of the not cross-linked macromolecules. A first simplest approximation seems to consist of the independent treatment of different cross-linked regions. Therefore, we propose the following dynamic model of a heterogeneous network. A polymer network as a whole is presented as an ensemble of cross-linked regions (domains) of different sizes, which relax independently of each other (Fig. 1). It is assumed that each domain represents a regular cubic network consisting of $N \times N \times N$

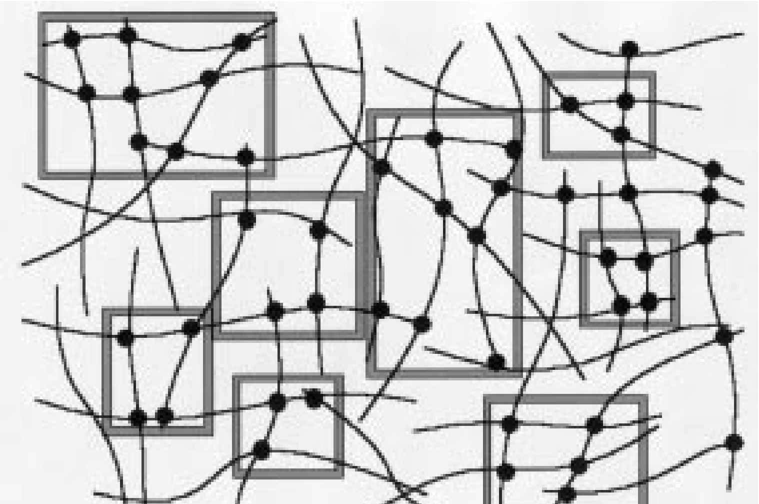

Fig. 1. Dynamic model of a heterogeneous polymer network consisting of cross-linked regions (domains) of different sizes

cells. The polymer chains between neighboring cross-links of the cubic network domains are modeled by "bead and spring" Rouse chains.[19] Each multi-segmental Rouse chain contains n_0 beads (segments). The quantity n_0 is the same for all the domains forming a heterogeneous network, the domains differ from each other only by the number of cubic network cells inside of the domains. The structure regularity (homogeneity) inside of network domains allows us to use (after some modifications) the results obtained in the theories dealing with regular polymer networks.

We assume that the cubic network domains have soft boundaries (boundary junctions are not fixed) and are embedded in an effective viscous medium which is "common" for all the domains. The viscoelastic response of an ensemble of the network domains to an external perturbation producing a longitudinal velocity gradient in the effective viscous medium is studied. In a certain sense, the heterogeneous network model considered is similar to a polymer solution in which a cross-linking process is in progress. In this case, the sufficiently large formations already having an internal network structure move in a real solvent and relax yet independently of each other.

Since a longitudinal velocity gradient produced by an external perturbation in an effective viscous medium is assumed to be the same for all network domains, the viscoelastic response of a collection of domains may be imitated by the behavior of a number of generalized Maxwell models[18] (corresponding to viscoelastic domains of different sizes) connected in parallel. Therefore, the total dynamic modulus of a heterogeneous polymer network as a whole is the sum of dynamic moduli of network domains with different weights. These relative weights (contributions) of dynamic moduli of different domains should be determined by domain size distribution. Since the non-interacting network domains of different sizes are assumed to relax independently, the domain model of a heterogeneous polymer network seems to be similar to the model of reversible aggregation.[20–22] The aggregation model has been proposed by one of the authors for describing the relaxation of amorphous polymers. Some related aspects of structure heterogeneity of polymers have been also discussed in ref.[23, 24] In this paper, the number distribution function of the aggregation model, which obeys the exponential law,[20, 22] will be used for the averaging over all the domains of a heterogeneous network. If each network domain is characterized by the number of chain segments ("beads") which it contains, the distribution function of the number of polymer segments in the network domains $n(y)$ is given by[20, 22]

$$n(y) = Cy^2 \exp[-ay] \tag{2}$$

where C is a normalization constant. Parameter a is determined as $a = U_0/k_BT$ where U_0 is the energy of the smallest domain.[20, 22] The size of the smallest domain must have an order of magnitude close to the size of a cubic network cell (not smaller).

Parameter determines the average number $\bar{y}$ of chain segments in the domains, i.e., the average domain size:

$$\bar{y} = \frac{\int yn(y)dy}{\int n(y)dy} \cong \frac{3}{a} \tag{3}$$

Note that the average domain size $\bar{y} \cong \langle y\rangle$ is very close to the quantity $\sqrt{\langle y^2\rangle} \cong 2\sqrt{3}/a$ for the number distribution function considered. The network domain of the average size should contain a number of chain segments much greater than those in a network cell because all domains have an internal network structure in the system considered and, therefore, should be larger (not smaller) than the cubic network cell. An elementary cell of a regular cubic network consists of $3n_0$ chain segments. Therefore, the condition $\bar{y} \gg 3n_0$ should be fulfilled. This means that the parameter $a \cong 3/\bar{y}$ of the number distribution function has to be much smaller than unity for sufficiently long chains, namely, $a \ll 1/n_0$.

Relaxation modulus

Relaxation modulus of a unique domain

At first, we consider the viscoelastic mechanical behavior of a unique domain that has a three-dimensional regular network structure. It has been shown[17, 25, 26] that in the consideration of viscoelastic dynamic properties of three-dimensional meshlike regular networks consisting of "bead and spring" Rouse chains, intra- and interchain relaxation processes can be treated separately. The contribution of small-scale intrachain motions to network dynamics is shown to be very similar to the contribution of not cross-linked chains with the same molecular weight as that of the chains between cross-links in a network. The interchain long-scale motions can be satisfactorily described using a simplified "coarse-grained" model of a network.[4, 11, 14–17, 25, 26] The coarse-grained model of a cubic network represents a collection of beads (junctions) connected by springs into a unified regular network structure. The elasticity constant K of a spring between neighboring junctions corresponds to that of a multi-segmental Rouse chain as a whole between these junctions. The friction constant ς of a junction relative to the effective viscous medium mimics the friction of halves of the network chains directly attached to the given junction. Thus, in order to obtain the total relaxation modulus $G(t)$ of a cubic polymer network of "bead and spring" Rouse chains, it is sufficient to a good approximation to sum the relaxation modulus $G_N(t)$ of a coarse-grained network model and the relaxation modulus $G_C(t)$ of not cross-linked polymer chains with the same molecular weight as those in the network.[17,25,26]

The relaxation modulus $G_N(t)$ is presented as a sum over all the relaxation times τ_N of a coarse-grained network model

$$G_N(t) = G_e + \frac{1}{V_{dom}} 3k_BT \sum_{\vec{\theta}} \exp[-t/\tau_N(\vec{\theta})] \tag{4}$$

where V_{dom} is the volume of a network domain and G_e is the equilibrium modulus of a network. The relaxation times $\tau_N(\vec{\theta})$ manifested in the mechanical relaxation of the coarse-grained network model are given by[14,16,25,26]

$$\tau_N(\vec{\theta}) = \frac{6\tau_{\min}}{3 - \cos\theta_1 - \cos\theta_2 - \cos\theta_3} \tag{5}$$

where $\tau_{\min}$ is the minimum relaxation time of a coarse-grained network model (at $\theta_{1;2;3} = \pi$):

$$\tau_{\min} = \frac{\varsigma}{24K} \tag{6}$$

The interchain wave vector $\vec{\theta} = (\theta_1, \theta_2, \theta_3)$ determines the phase shift between displacements of neighboring network cells. Its components in the case of a cubic network of finite size are given as follows:

$$\theta_{1;2;3} = \frac{\pi}{N} k_{1;2;3}; \quad k_{1;2;3} = 1, \ldots, N-1 \tag{7}$$

Since the network domain considered has finite size, the finite maximum relaxation time $\tau_{\max}$ exists as

$$\tau_{\max} = \frac{4}{\pi^2} N^2 \tau_{\min} \tag{8}$$

which is proportional to the square of number of junctions N along every Cartesian direction of a cubic network.

For the intrachain component $G_C(t)$ of the total relaxation modulus of a network domain we obtain

$$G_C(t) = \frac{1}{V_{dom}} \cdot 3N^3 \cdot 3k_BT \sum_{\psi} \exp[-t/\tau_C(\psi)] \tag{9}$$

where $3N^3$ is the number of polymer chains in a cubic network domain. The corresponding relaxation times $\tau_C(\psi)$ are given by:

$$\tau_C(\psi) = \frac{2\tau_0}{(1 - \cos\psi)} \tag{10}$$

Here τ_0 is the relaxation time of a single chain segment (at $\psi = \pi$)

$$\tau_0 = \frac{\varsigma_0}{8K_0} \tag{11}$$

where K_0 is the elasticity constant of a Gaussian subchain ("spring"), and ς_0 is the friction constant of a "bead" of the network chain between cross-links. The intrachain wave vector ψ corresponds to the phase shift between displacements of neighboring beads of a Rouse chain[19,27]

$$\psi = \frac{k\pi}{n_0 + 1} \quad k = 1 \ldots n_0 \tag{12}$$

where n_0 is the number of beads in the chain between cross-links.

The total relaxation modulus of a domain is the sum of relaxation moduli $G_N(t)$ and $G_C(t)$. Note that the minimum relaxation time $\tau_{\min}$ of a coarse-grained network model (Eq. (6)) has an order of magnitude equal to the maximum relaxation time τ_{chain} of a chain between neighboring junctions,[17] namely, $\tau_{\min} \cong (\pi^2/4)\tau_{chain}$. The quantity τ_{chain} is given by (see Eq. (10) at $\psi = \pi/(n_0 + 1)$):

$$\tau_{chain} = \frac{4}{\pi^2} (n_0 + 1)^2 \tau_0 \tag{13}$$

Since the distribution function of the number of chain segments in domains (Eq. (2)) will be used for the averaging over all domains, it is necessary to present the relaxation modulus of a unique domain as a function of the number of chain segments y in the domain. The cubic network domain consisting of y chain segments contains N^3 cubic network cells with $3n_0$ segments per cell (i.e. with three multi-segmental Rouse chains per network cell). Therefore, one can write the following simple interrelation:

$$y = 3n_0N^3 \tag{14}$$

Finally, the relaxation modulus $G(t;\, y)$ of a domain consisting of y chain segments is presented as follows

$$G(t;y) - G_e = 3\nu_{chain} k_B T n_0 \left[\frac{1}{n_0} \sum_{\psi} \exp[-t/\tau_C] + \frac{1}{y} \sum_{\vec{\theta}} \exp[-t/\tau_N] \right] \tag{15}$$

where ν_{chain} is the number of network chains per unit volume. The first term in Eq. (15) corresponds to the contribution of intrachain relaxation, and the second term describes the interchain collective relaxation of a network domain. The relaxation times manifested in $G(t;y)$ range from the relaxation time of a single chain segment τ_0 (Eq. (11)) to the maximum relaxation time $\tau_{\max}(y)$ of a cubic network domain of finite size (see Eq. (8)), which may be rewritten using Eq. (14) as:

$$\tau_{\max}(y) = \frac{4}{\pi^2} \left(\frac{1}{3n_0} \right)^{2/3} \tau_{chain} y^{2/3} \tag{16}$$

Using Eq. (15) one can evaluate the asymptotic time dependence of relaxation modulus $G(t;y)$ of a unique network domain. The corresponding calculations are very similar to those carried out in ref.[17] At short times $\tau_0 < t < \tau_{chain}$, the relaxation modulus $G(t;y)$ behaves as

$$G(t;y) - G_e \cong \nu k_B T \cdot \frac{1}{n_0} \cdot \frac{6}{\pi} \cdot \sqrt{\frac{\tau_{chain}}{t}} \tag{17}$$

where $\nu = n_0 \nu_{chain}$ is the number of chain segments per unit volume. This power-law time behavior of $G(t;\, y)$ is typical of a single Rouse chain.[18, 19, 27] At times from τ_{chain} to $\tau_{\max}(y)$ (see Eq. (16)) the relaxation modulus of a cubic network domain has the same time behavior as that of an infinite regular cubic network in the region of interchain collective relaxation,[1, 3, 14–17] namely:

$$G(t;y) - G_e \cong \nu k_B T \cdot \frac{1}{n_0} \cdot \frac{4\sqrt{3}}{\pi^2} \cdot \left(\frac{\tau_{chain}}{t}\right)^{3/2} \tag{18}$$

At longer times ($t > \tau_{\max}(y)$) we obtain the following asymptotic behavior for the relaxation modulus $G(t;\, y)$ of a network domain of finite size:

$$G(t;y) - G_e \cong \nu k_B T \cdot \frac{9\pi\sqrt{3}}{4} \cdot \frac{1}{y} \cdot \left(\frac{\tau_{\max}(y)}{t}\right) \cdot \exp\left[-\frac{t}{\tau_{\max}(y)}\right] \tag{19}$$

One can see that the relaxation modulus $G(t;y)$ of a three-dimensional network domain of finite size has an exponential decay at longest times because the relaxation spectrum of the domain is limited by the finite maximum relaxation time $\tau_{\max}(y)$ of the domain as a whole. In other words, each network domain consisting of y polymer chain segments at times greater than its maximum relaxation time $\tau_{\max}(y)$ shows a simple relaxation behavior with a single relaxation time. Note that the relaxation modulus $G(t;\, y)$ includes also the power-law term ($\tau_{\max}/t$) which has much more weak time dependence as compared with the exponential term.

Thus, the relaxation modulus $G(t;y)$ of a unique domain with internal cubic network structure has the power-law time dependencies $t^{-1/2}$ and $t^{-3/2}$ in the intra- and interchain regions of relaxation inside of the domain, respectively. At times greater than the maximum relaxation time of a network domain the relaxation modulus decreases rapidly according to the exponential law (Fig. 2).

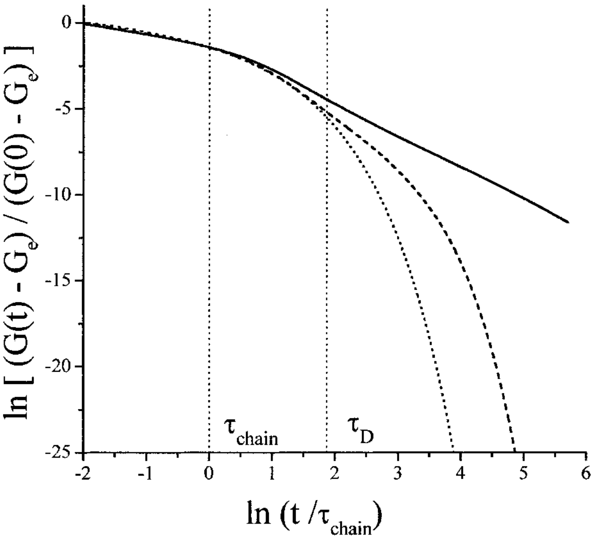

Fig. 2. Relaxation modulus $G(t)$ of the three-dimensional network systems considered: an infinitely large regular cubic network (solid line), a single cubic network domain of average size (dashed line), and a heterogeneous network with domain structure (dotted line); here $n_0 = 20$ and $a = 0.001$

Relaxation modulus of a heterogeneous polymer network with domain structure

A heterogeneous polymer network in the present paper is modeled as an ensemble of independent cross-linked domains of different sizes. As mentioned above, in order to obtain the relaxation modulus of the heterogeneous network as a whole, it is necessary to average the relaxation modulus $G(t;\, y)$ over all domains forming the network. The network heterogeneity considered is long-range, it begins to be manifested on a scale greater than the size of an elementary network cell. Therefore, the relaxation modulus $G(t)$ of a heterogeneous polymer network as a whole at times smaller than the relaxation time of a network chain τ_{chain} has the same time behavior as that of a unique domain (see Eq. (17)) because the polymer chains between neighboring cross-links inside of all domains consist of an identical number n_0 of chain segments.

At longer times ($t \gg \tau_{chain}$), the main contribution to relaxation modulus $G(t)$ of a heterogeneous network is provided by the time regions in which the exponential decay of moduli of network domains appears (see Eq. (19)). Just this exponential decay after averaging over all domains with number distribution function (Eq. (2)) determines the time dependence of $G(t)$ of a heterogeneous network as a whole. To evaluate the time behavior of relaxation modulus $G(t)$ at long times, one can use the Laplace method[28] of estimation of the asymptotic behavior of integral with large dimensionless parameter ($t/\tau_{chain} \gg 1$). Finally, at sufficiently long times ($t \gg \tau_{chain}$) we obtain the following asymptotic behavior of the relaxation modulus $G(t)$ for a heterogeneous network

$$(G(t) - G_e) \cong \bar{\nu}_{dom} k_B T \cdot C_1 \cdot (a n_0)^{1/5} \cdot \left(\frac{t}{\tau_{chain}}\right)^{3/10} \cdot \exp\left[-\left(\frac{t}{\tau^*}\right)^{3/5}\right] \tag{20}$$

where $C_1 = 2^{-9/5} \cdot 5^{-1/2} \cdot 3^{29/10} \cdot \pi^{21/10} \approx 34.4$ and $\bar{\nu}_{dom} = \nu/\bar{y}$ is the number of domains of average size per unit volume (ν is the number of chain segments per unit volume). The characteristic relaxation time τ^* in the stretched exponential term is close to the maximum relaxation time τ_D of the network domain of average size (see Eq. (16) at $y = \bar{y}$)

$$\tau_D = \frac{4}{\pi^2}\left(\frac{1}{an_0}\right)^{2/3}\tau_{chain} \tag{21}$$

namely,

$$\tau^* = C_2\tau_D \tag{22}$$

where $C_2 = 5^{-5/3}2^{2/3}3^{1/3} \approx 0.15$.

Eq. (20) indicates that the relaxation modulus of a heterogeneous polymer network after averaging over all domains has the stretched exponential type of time dependence: $\exp[-(t/\tau^*)^{3/5}]$. The appearance of the stretched exponential time dependence is caused by the existence of the exponential term in the number distribution function $n(y)$ of network domains (Eq. (2)). The algebraic term $(t/\tau_{chain})^{3/10}$ in Eq. (20) is characterized by a much weaker time dependence as compared with stretched exponential term and arises from the factor y^2 in the number distribution used (see Eq. (2)). It is also interesting to note that the relative decrease of the relaxation modulus $G(t)$ at times corresponding to the beginning of the region of stretched exponential dependence (i.e. at $t \cong \tau_D$) is given by $(G(\tau_D)-G_e)/(G(0)-G_e) \approx 0.14 \cdot a$. Hence, the relaxation modulus of a polymer network at $t \cong \tau_D$ becomes small because of the above condition $a \ll 1/n_0$ where n_0 is the number of beads in a Rouse chain between cross-links ($n_0 \gg 1$ for sufficiently long chains).

It should be especially emphasized that the stretched exponential time dependence of the relaxation modulus of heterogeneous network systems appears because the averaging over all domains is performed using the number distribution function $n(y)$ containing the exponential term (see Eq. (2)). Besides the number distribution function of the aggregation model[20–22], which has been used in this paper, there are many other examples of exponential distributions. The exponential distribution seems to be the general origin of time dependence of such a type. For example, the stretched exponential time dependence of the relaxation modulus may appear due to a broad distribution of the molecular weight of network chains, which also obeys the exponential law.[29] Another example may be a network system with a domain structure in which the number of cross-links inside of the domains fluctuates due to a random character of the cross-linking process and, therefore, is governed by the Gaussian distribution function $\exp[-(y-\langle y\rangle)^2/2\langle\delta y^2\rangle]$.

Thus, if a long-range heterogeneity of a cross-linked polymer is taken into account in the frame of the above domain approach, the decrease of the relaxation modulus of a network at long times becomes much more rapid as compared with a homogeneous network. The power-law time dependence of relaxation modulus $G(t) \sim t^{-3/2}$ of a regular three-dimensional network in the interchain region of relaxation is replaced by the stretched exponential type of time dependence of the relaxation modulus (Eq. (20)) in the case of a heterogeneous network system (Fig. 2).

Complex polymer systems often show decay obeying the stretched exponential law, i.e. more rapid relaxation than the power (algebraic) type of relaxation. Examples include the local segmental motions in non-crystalline polymers, the motions of polymer chains in entangled polymer melts, and relaxation phenomena in other complex correlated systems (see, for example, the well-known review of Ngai[30]). In these systems, the strong correlation between relaxing units has an effect in slowing down the relaxation. Another example is the dielectric relaxation in glassy materials, which has been treated in the frame of a defect diffusion model.[31, 32] In our case, the origin of the appearance of stretched exponential relaxation is related to the broad size distribution of non-interacting relaxing units (domains) in a heterogeneous polymer network. This is similar to the situation in disordered orientational glasses[33] where the non-exponential relaxation is also caused mostly by heterogeneous broadening.

The above considerable change of the time dependence of the relaxation modulus in the case of the heterogeneous polymer network as compared with the homogeneous one should be also manifested in the relaxation spectrum. The relaxation spectrum $H(\tau)$ is determined by Eq. (1). This is a very important quantity because all the viscoelastic characteristics corresponding to mechanical relaxation (e.g. dynamic modulus and viscosity) may be calculated with the use of the relaxation spectrum.[18] At short times smaller than the maximum relaxation time τ_{chain} of a chain between cross-links, the relaxation spectrum of a heterogeneous network with domain structure shows usual Rousean behavior:

$$H(\tau) \cong \nu k_B T \frac{1}{n_0}\,\frac{3}{\pi}\sqrt{\frac{\tau_{chain}}{\tau}} \tag{23}$$

Such a type of behavior is caused by the fact that the network chains between cross-links in all the domains of a network have identical contour lengths, i.e. the heterogeneity of the considered type does not influence the intrachain relaxation. At long times ($\tau \gg \tau_{chain}$ and $\tau \gg \tau_D$), the relaxation spectrum $H(\tau)$ shows very rapid decrease, namely,

$$H(\tau) \cong \bar{\nu}_{dom}k_B T(an_0)\tilde{C}\left(\frac{\tau}{\tau_{chain}}\right)^{3/2}$$

$$\exp[-3(\tau/\tau_D)^{3/2}] \tag{24}$$

where $\tilde{C} = 2^{-6/5}\,\pi^4\,3^{9/2}$, $\bar{\nu}_{dom}$, is the number of network domains of average size per unit volume, and τ_D is the maximum relaxation time of the network domain of average size (Eq. (21)). One can see from Eq. (24) that the relaxation spectrum $H(\tau)$ of a heterogeneous network in the long-time region of interchain (or "interdomain") relaxation is much narrower as compared with the spectrum of an infinitely large regular three-dimensional network, which has the power-law behavior $\tau^{-3/2}$ (for example, see ref.[1,3,14,16,17]).

Storage and loss moduli

Storage and loss moduli of a unique domain

With the use of Eq. (15), the complex dynamic modulus $G^*(\omega;y)$ of a unique domain consisting of chain segments is presented as follows:

$$G^*(\omega;y) = G_e + 3\nu k_B T\left[\frac{1}{n_0}\sum_{\psi}\frac{i\omega\tau_C}{1+i\omega\tau_C}\right.$$

$$\left.+\frac{1}{y}\sum_{\vec{\theta}}\frac{i\omega\tau_N}{1+i\omega\tau_N}\right] \tag{25}$$

Here ν is the number of chain segments per unit volume; τ_C are the intrachain relaxation times (see Eq. (10), (11), and (12)), and τ_N are the interchain relaxation times of a cubic network domain (see Eq. (5), (6), and (7)). Using Eq. (25), it is easy to obtain the storage modulus $G'(\omega)$ of a unique network domain (real component of complex dynamic modulus $G^*(\omega)$):

$$G'(\omega;y) = G_e + 3\nu k_B T\left[\frac{1}{n_0}\sum_{\psi}\frac{(\omega\tau_C)^2}{1+(\omega\tau_C)^2}\right.$$

$$\left.+\frac{1}{y}\sum_{\vec{\theta}}\frac{(\omega\tau_N)^2}{1+(\omega\tau_N)^2}\right] \tag{26}$$

The storage modulus $G'(\omega;\,y)-G_e$ of a network domain has the following behavior at extremely high frequencies $\omega \gg 1/\tau_0$ (here τ_0 is the relaxation time of a single chain segment (Eq. (11))):

$$G'(\omega;y) - G_e \cong 3\nu k_B T\left[1-\frac{\pi^4}{80}\,\frac{1}{(\omega\tau_0)^2}\right] \tag{27}$$

In the region of high frequencies ($1/\tau_0 > \omega > 1/\tau_{chain}$), the storage modulus of a domain behaves as:

$$G'(\omega;y) - G_e \cong \nu k_B T\frac{8}{\pi}\sqrt{\omega\tau_0} \tag{28}$$

Such a form of frequency dependence of the storage modulus is typical of a single Rouse chain.[18,19,27] In the region of low frequencies ($1/\tau_{chain} < \omega < 1/\tau_{\max}(y)$), the storage modulus of a network domain has the same behavior as that of a regular three-dimensional polymer network in the region of interchain cooperative relaxation,[14,16,25,26] namely,

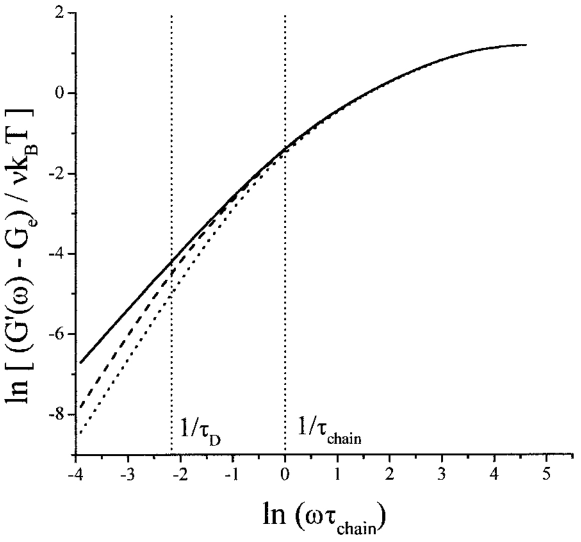

Fig. 3. Dynamic storage modulus $G'(\omega)$ of an infinitely large regular network (solid line), a single domain of average size (dashed line), and a heterogeneous network with domain structure (dotted line); here $n_0 = 10$ and $a = 0.001$

$$G'(\omega;y) - G_e \cong \nu k_B T\frac{1}{n_0}\,\frac{16\sqrt{3}}{\pi^2}(\omega\tau_{chain})^{3/2} \tag{29}$$

where τ_{chain} is the maximum relaxation time of a network chain between neighboring junctions (Eq. (13)). Note that for an infinitely large three-dimensional network such a type of frequency behavior holds up to zero frequency. In the case of a cubic network domain of finite size, which contains y polymer segments, the relaxation spectrum is limited by the finite maximum relaxation time $\tau_{\max}(y)$ of the domain as a whole (see Eq. (16)). Therefore, at lower frequencies ($\omega < 1/\tau_{\max}(y)$) we obtain the following asymptotic frequency behavior of the storage modulus $G'(\omega;\,y)-G_e$ of a network domain

$$G'(\omega;y) - G_e \cong \nu k_B T\frac{1}{n_0}\,\frac{12\sqrt{3}}{\pi^2}$$

$$\omega^2\left(\sqrt{\tau_{\max}(y)}\sqrt{\tau^3_{chain}}\right) \tag{30}$$

which differs from that of an infinitely large regular network (Eq. (29)). The decrease of $G'(\omega;\,y)$ at low frequencies becomes more rapidly in the case of a domain of finite size as compared with an infinitely large regular network (Fig. 3 and 4).

The loss modulus $G''(\omega)$ of a unique network domain (imaginary component of complex dynamic modulus $G^*(\omega)$) is given by (see Eq. (25)):

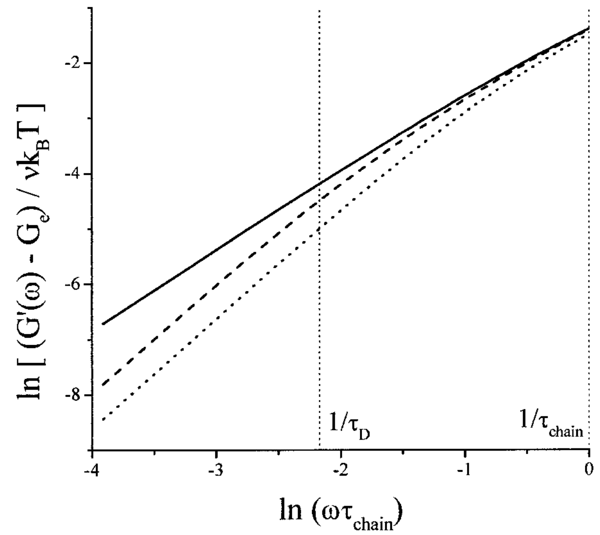

Fig. 4. The frequency dependence of dynamic storage modulus $G'(\omega)$ at $\omega < 1/\tau_{chain}$; the denotation of the curves is the same as in Fig. 3

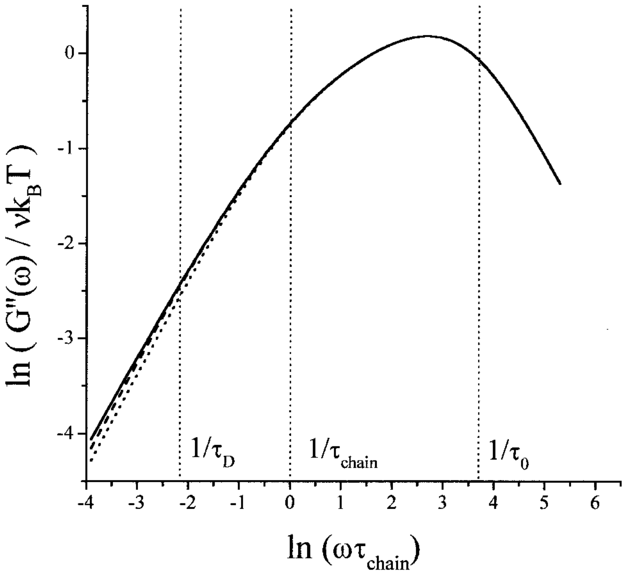

Fig. 5. Dynamic loss modulus $G''(\omega)$ of an infinitely large regular network (solid line), a single domain of average size (dashed line), and a heterogeneous network with domain structure (dotted line); here n_0= 10 and a = 0.001

$$G''(\omega;y) = 3\nu k_B T\left[\frac{1}{n_0}\sum_{\psi}\frac{\omega\tau_C}{1+(\omega\tau_C)^2} + \frac{1}{y}\sum_{\bar{\theta}}\frac{\omega\tau_N}{1+(\omega\tau_N)^2}\right] \tag{31}$$

The quantity $G''(\omega; y)$ is characterized by the existence of the maximum, its position is determined by the reverse relaxation time of a single Gaussian segment $1/\tau_0$ (see Fig. 5). At very high frequencies $\omega > 1/\tau_0$ (region on the right of the maximum of $G''(\omega; y)$) the loss modulus behaves as:

$$G''(\omega;y) \cong \nu k_B T\frac{\pi^2}{4}\frac{1}{\omega\tau_0} \tag{32}$$

With the decrease of frequency ($1/\tau_{chain} < \omega < 1/\tau_0$) (region on the left of the maximum of $G''(\omega; y)$) the loss modulus has the behavior:

$$G''(\omega;y) \cong \nu k_B T\frac{8}{\pi}\sqrt{\omega\tau_0} \tag{33}$$

Note that the frequency dependence of $G''(\omega; y)$ of a network domain at frequencies $\omega > 1/\tau_{chain}$ is the same as that of a single Rouse chain.[27] At low frequencies $1/\tau_{\max}(y) < \omega < 1/\tau_{chain}$, the quantity $G''(\omega; y)$ shows a behavior typical of a three-dimensional regular networks[14], namely:

$$G''(\omega;y) \cong \nu k_B T\frac{1}{n_0}\frac{12\sqrt{3}}{\pi^2}(\omega\tau_{chain})\left[1-\frac{4}{5}\sqrt{\omega\tau_{chain}}\right] \tag{34}$$

In the case of an infinitely large regular network, such a type of frequency dependence holds up to frequencies having an order of magnitude equal to $1/(10\,\tau_{chain})$. At lower frequencies, the loss modulus of an infinitely large regular network behaves as (cf. Eq. (34)):

$$G''(\omega;y) \cong \nu k_B T\frac{1}{n_0}\frac{12\sqrt{3}}{\pi^2}(\omega\tau_{chain}) \tag{35}$$

In the case of a network domain which is characterized by the finite maximum relaxation time $\tau_{\max}(y)$ (see Eq. (16)), we obtain the following asymptotic behavior for the loss modulus $G''(\omega; y)$ at low frequencies $\omega < 1/\tau_{\max}(y)$:

$$G''(\omega;y) \cong \nu k_B T\frac{1}{n_0}\frac{12\sqrt{3}}{\pi^2}(\omega\tau_{chain})\left[1-\sqrt{\frac{\tau_{chain}}{\tau_{\max}(y)}}\right] \tag{36}$$

It is seen that the slope of a curve of $G''(\omega; y)$ for a network domain of finite size at very low frequencies changes as compared to that for an infinitely large regular network. Note that this effect is very weak (Fig. 5 and 6). It is determined by the difference in the terms which are smaller than the main terms ($\sim\omega\tau_{chain}$) in the frequency dependence of $G''(\omega; y)$ by an order of magnitude (cf. Eq. (34) and (36)). The weakness of the effect is caused by the fact that the loss modulus $G''(\omega; y)$ at low frequencies (namely, the main second term in Eq. (31) at $\omega < 1/$

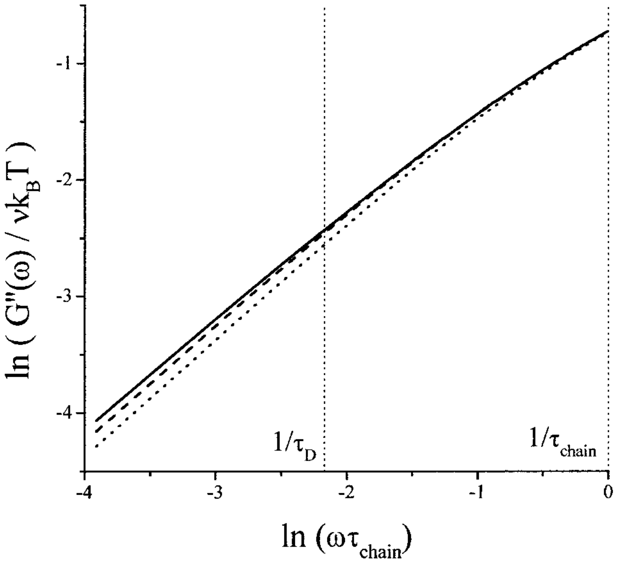

Fig. 6. The frequency dependence of dynamic loss modulus $G''(\omega)$ at $\omega < 1/\tau_{chain}$; the denotation of the curves is the same as in Fig. 5

$\tau_{\max}(y)$) is mostly determined by the relaxation time τ_{chain} of a network chain between cross-links (not the maximum relaxation time $\tau_{\max}(y)$ of a unique domain as a whole).

Storage and loss moduli of a heterogeneous polymer network with domain structure

To obtain the dynamic modulus $G^*(\omega)$ of a heterogeneous polymer network as a whole, it is necessary to average the dynamic modulus $G^*(\omega; y)$ of a unique network domain over all the domains in the system considered with the use of the number distribution function given by Eq. (2). Storage and loss moduli of a heterogeneous polymer network as a whole at frequencies greater than the reverse relaxation time of a chain between cross-links $1/\tau_{chain}$ have the same frequency behavior as those of a unique domain (see Eq. (27) and (28) for $G'(\omega)$ and Eq. (32) and (33) for $G''(\omega)$). This is caused by the feature of the type of the network heterogeneity considered which begins to be manifested on a scale greater than the average distance between neighboring cross-links (polymer chains between neighboring cross-links inside of all domains consist of an identical number n_0 of Gaussian segments).

In the region of low frequencies ($\omega \ll 1/\tau_{chain}$ and $\omega \ll 1/\tau_D$), which corresponds to the time region where the stretched exponential time dependence of relaxation modulus $G(t)$ appears, we obtain the following asymptotic behavior for the storage modulus $G'(\omega) - G_e$ of a heterogeneous polymer network

$$G'(\omega) - G_e \cong \bar{\nu}_{dom} k_B T \cdot \tilde{C}_1 \cdot (\omega\tau_D)^2 \qquad (37)$$

where $\tilde{C}_1 = \pi \cdot 7 \cdot 2^{-1} \cdot 5^{-1} \cdot 3^{13/6} \approx 23.7$ and $\bar{\nu}_{dom} = \nu/\bar{y}$ is the number of domains of average size per unit volume (ν is the number of chain segments per unit volume). Thus, the form of frequency dependence, which is typical of regular polymer networks in the region of interchain relaxation (see Eq. (29)), disappears in the case of a heterogeneous network with domain structure. In fact at low frequency, the storage modulus relaxes with a single relaxation time equal to the maximum relaxation time of the network domain of average size τ_D. The slope of the curve of $G'(\omega)$ on a logarithmic scale becomes greater in the case of the heterogeneous polymer network as compared with the homogeneous one (Fig. 3 and 4). Note that the reduced decrease of the storage modulus $(G'(\omega) - G_e)/(G'(\infty) - G_e)$ at $\omega \cong 1/\tau_D$ becomes equal to about $2.64 \cdot a$ and, therefore, is much smaller than unity because the distribution parameter a should be much smaller than $1/n_0$.

The loss modulus $G''(\omega)$ of a heterogeneous polymer network at low frequencies ($\omega \ll 1/\tau_{chain}$ and $\omega \ll 1/\tau_D$) has the following asymptotic behavior (cf. Eq. (36)):

$$G''(\omega) \cong \nu k_B T \frac{1}{n_0} \frac{12\sqrt{3}}{\pi^2} (\omega\tau_{chain}) \left[1 - \frac{3^{4/3}}{4}\sqrt{\frac{\tau_{chain}}{\tau_D}}\right] \qquad (38)$$

The position of the maximum of $G''(\omega)$ of a heterogeneous network is not shifted as compared to that of an infinitely large regular network (Fig. 5) because its position is determined by the characteristic frequency $1/\tau_0$ corresponding to the purely intrachain relaxation on a scale smaller than the distance between cross-links. On this scale, the “long-range” heterogeneity of a network is not manifested yet. As a result, the loss modulus $G''(\omega)$ is very slightly sensitive to the network heterogeneity of the domain type considered (see Fig. 5 and 6).

Conclusion

The main results of this paper may be stated as follows. If a heterogeneous polymer network is treated as an ensemble of non-interacting cross-linked domains of different sizes, the decrease of the relaxation modulus of a network at long times becomes much more rapid as compared with a homogeneous network. The algebraic time dependence of relaxation modulus $G(t)$ of regular cross-linked polymers is replaced by the stretched exponential type of time dependence of $G(t)$ for heterogeneous polymer network systems. A similar (but much weaker) effect is shown to be manifested in the storage modulus of a heterogeneous network. In the region of low frequencies, which corresponds to the region of stretched exponential time dependence of the relaxation modulus, the storage modulus behaves as ω^2, i.e., more rapidly as compared with a three-dimensional regular network in which $G'(\omega) \sim \omega^{3/2}$. In contrast to the viscoelastic characteristics corresponding to the energy storage, the loss modulus is shown to be very slightly sensitive to a heterogeneity of the domain type.

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