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Relaxation Modulus of Heterogeneous Polymer Networks with the Domain Structure[1]

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Abstract—A dynamic model for the viscoelastic properties of inhomogeneous polymer networks is proposed. A polymer network is modeled as an assembly of noninteracting crosslinked regions (domains) of various sizes. Network domains are represented as regular cubic networks of finite dimensions made of crosslinked multisegmental Gaussian chains. The domains differ from one another in the number of network cells. For averaging over all network domains, an exponential distribution function of the number of polymer segments in domains is used, which was earlier proposed by one of the authors within the framework of the aggregate model. The time dependence of the relaxation modulus of the polymer network with domain-type heterogeneity was shown to follow a stretched exponent law. In contrast, the theory predicts a power-law dependence of the relaxation modulus for infinite regular polymer networks. This conclusion can be extended to other exponential functions for the distribution of segments in network domains; i.e., to a rather wide range of heterogeneous network systems.

INTRODUCTION

Crosslinked polymer systems possessing rubber elasticity (elastomers) have been a subject of intense research for many decades because of their wide practical application. While the statistical properties of crosslinked polymers have been studied fairly well, the understanding of the dynamic properties of crosslinked polymer systems remains far from being complete as compared to those of polymer solutions or melts. This is primarily due to the complex nature of physical phenomena occurring in polymeric systems and a large number of factors that determine the dynamic properties of crosslinked polymer systems. One of such factors is the structural heterogeneity of crosslinked polymers (polymer networks). There is a wide variety of possible types of polymer network heterogeneity. As an example, the length distribution of polymer chains connecting the crosslinks, the existence of regions with different topology and crosslink density, or the presence of uncrosslinked amorphous regions together with crosslinked regions may be named.

Most of the theoretical approaches that were developed to describe the dynamics (and, especially, the aspects of dynamic behavior at long times) of polymer networks are based on the use of idealized regular (homogeneous) network models [1–18]. In these models, a polymer network is represented as a set of long elastic chains with the ends crosslinked at the network junctions. In this case, it is assumed that all network chains have the same contour length and form a regular three-dimensional structure of different topology. The use of such regular network models is the simplest approach to rationalizing the dynamics of crosslinked systems and it allows the effect of crosslinking of macromolecules to a united structure on the viscoelastic properties of polymers to be qualitatively analyzed. However, the predictions of the theory are often difficult to compare with the experiment in this case because the structural heterogeneity inherent in crosslinked polymer systems can significantly interfere with the effects due to linkage of macromolecules in the three-dimensional network structure. Thus, allowance for the heterogeneity of polymer networks is an important problem in the theoretical description of the dynamic properties of polymer networks. In this work, we will consider a rather general type of heterogeneity associated with the existence of regions with different properties in a real crosslinked polymer.

DYNAMIC MODEL

Since the crosslinking process of polymer chain has a random character, a real network polymer can have both crosslinked and uncrosslinked regions. For exam-

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ple, crosslinked regions of different sizes may be separated with “soft” regions composed of uncrosslinked macromolecules. The simplest approach to the description of a crosslinked polymer system of this sort consists in treating the relaxation of different crosslinked network regions independently of one another. Therefore, the following dynamic model of a heterogeneous network is proposed. The polymer network is represented as an assembly of crosslinked regions (domains) of different sizes which relax independently of each other (Fig. 1). It is assumed that each domain is a regular cubic network composed of $N \times N \times N$ cells. The polymer chains that connect contiguous junctions are modeled by the Kargin–Slonimskii–Rouse multisegmental chains [19, 20] comprising n_0 segments. The value of n_0 is assumed to be equal for all network domains of the system; thus, the domains differ from one another only in the number of cubic cells inside a domain. Such homogeneity of the inner network structure of domains makes it possible to use (after some transform) the results obtained in the theories of dynamic properties of regular polymer networks.

It is assumed that all cubic domains of the network have “soft” boundaries (the boundary junctions are not fixed in space) and the domains move against the background of a “common” effective viscous medium. What is examined is the viscoelastic behavior of the heterogeneous polymer network under the action of an external perturbing force which creates a longitudinal velocity gradient in the effective viscous medium. In a certain sense, the system under consideration resembles a polymer solution in which the process of crosslinking of macromolecules into a network takes place. If the network formation process is not completed, rather large entities that have already got the inner network structure relax independently of one another against the solvent. The velocity gradient of the effective viscous medium is supposed to be identical for all network domains; therefore, the viscoelastic behavior of the heterogeneous polymer network as a whole can be described with the set of generalized viscoelastic Maxwell elements [21] connected in series. Then, the total dynamic modulus of the network system of interest will be the sum of moduli of network domains. In this case, the relative contribution of network domains to the total modulus is determined by the size distribution of domains in the system. For averaging over all heterogeneous-network domains, a distribution function from the aggregate model, which was earlier proposed by one of the authors to rationalize the relaxation of amorphous polymers [22–24], is used. This distribution function is exponential. By the end of the paper, we will consider a more general form of function for the exponential behavior of the number of segments in domains. If each network domain is characterized by the number of Gaussian segments contained in it, y, according the accepted model of heterogeneous network, the distribution function for the number of segments in domains $n(y)$ is defined by [22–24]

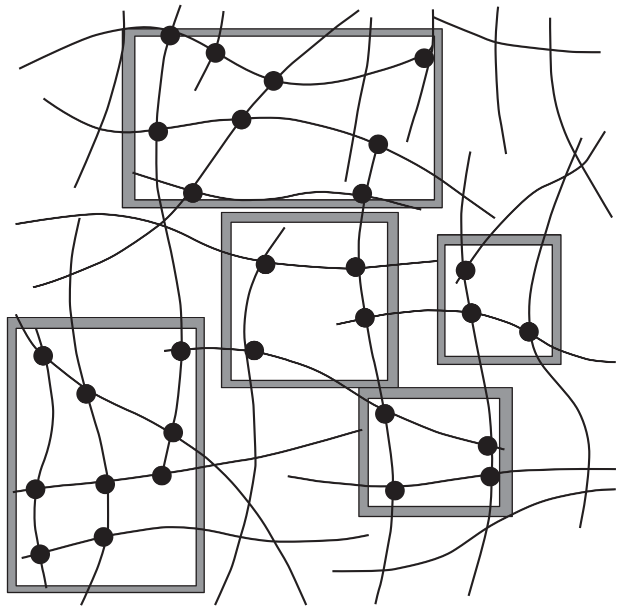

Fig. 1. Dynamic model of heterogeneous polymer network composed of crosslinked regions (domains) of different size.

$$n(y) = Cy^2 \exp[-ay], \tag{1}$$

where C is the normalization constant. The parameter a defines the average number $\bar{y}$ of chain segments in domains: $a \cong 3/\bar{y}$. Note that the physical meaning and the temperature dependence of a (or $\bar{y}$) may be different in systems with another character of heterogeneity. For example, the parameter a in the aggregate model [22–24] is defined by U_0/k_BT, where U_0 is the energy of the smallest domain.

The size of the smallest network domain in the considered system must be of the order of dimensions of the cubic network cell. In addition, since we consider the system in which each domain possesses the inner network structure, an average domain must contain the number of segments much larger than the number of polymer segments in the cubic cell of the network. Recall that the unit cell of the cubic network comprises three multisegmental Gaussian chains and, correspondingly, contains $3n_0$ segments. Therefore, the condition $\bar{y} \gg 3n_0$ must be observed, which implies that the distribution parameter $a \cong 3/\bar{y}$ must be much smaller than unity for sufficiently long polymer chains: $a \ll 1/n_0$.

THEORY

First, let us consider the dynamic viscoelastic behavior of an individual polymer network domain represented by a regular cubic network of a finite size. In the studies of macroscopic viscoelastic properties of an infinite cubic polymer network [18, 25, 26], it was shown that small-scale intrachain and cooperative interchain relaxation processes can be considered separately. The contribution of intrachain network motions turns out to be close to the contribution that would be made by uncrosslinked polymer chains of the same molecular mass as in the network. Intrachain relaxation processes of a larger scale were shown [18, 25, 26] to be fairly well described in terms of the simplified coarse-grained network model [4, 11, 14–18, 25, 26]. This coarse-grained dynamic network model represents a set of junctions connected by elastic springs to form a three-dimensional network structure. In the case, the elasticity constant K of a spring connecting two neighboring junctions corresponds to that of the multisegmental Gaussian chain between these junctions, and the friction coefficient ς of a junction is that of the friction of the halves of multisegmental chains originating from this junction. Thus, in order to find the dynamic modulus of the polymer network composed of crosslinked multisegmental Gaussian chains, it is sufficient (with reasonable accuracy) to sum the moduli of the coarse-grained polymer network model and uncrosslinked polymer chains of the same molecular mass as in the network [18, 25, 26].

For the relaxation modulus $G(t; N)$ of a cubic network domain composed of N^3 cells, we get

$$G(t;N) = G_e + \frac{1}{V_{\mathrm{dom}}} 3k_{\mathrm{B}}T \sum_{\boldsymbol{\theta}} \exp[-t/\tau_n(\boldsymbol{\theta})] + \frac{1}{V_{\mathrm{dom}}} 3N^3 3k_{\mathrm{B}}T \sum_{\psi} \exp[-t/\tau_c(\psi)], \quad (2)$$

where V_{dom} is the volume of a cubic network domain and G_e is the equilibrium modulus of the polymer network. The second term reflects the contribution of the coarse-grained dynamic network model to the relaxation modulus (interchain relaxation processes). The last term is the dynamic modulus of noncrosslinked polymer chain of the same length as in the network (intrachain relaxation processes).

Relaxation times $\tau_n(\boldsymbol{\theta})$ for the coarse-grained network model are as follows [14, 17, 25, 26]:

$$\tau_n(\boldsymbol{\theta}) = \frac{6\tau_{\min}}{3 - \cos\theta_1 - \cos\theta_2 - \cos\theta_3}, \quad (3)$$

where the minimum time for the relaxation of the coarse-grained network model (at $\theta_1 = \theta_2 = \theta_3 = \pi$) is

$$\tau_{\min} = \frac{\varsigma}{24K}. \quad (4)$$

The relaxation times $\tau_n(\boldsymbol{\theta})$ are determined by the three-component interchain wave vector $\boldsymbol{\theta} = (\theta_1, \theta_2, \theta_3)$ which describes a phase shift between displacements of neighboring cubic network cells:

$$\theta_{1;2;3} = \frac{\pi}{N} k_{1;2;3}, \quad k_{1;2;3} = 1, \ldots, N-1 \quad (5)$$

(N is the number of junctions along one of the three orthogonal directions in the cubic polymer network).

Relaxation times $\tau_c(\psi)$ corresponding to the contribution of intrachain relaxation to the modulus in Eq. (2) are given by

$$\tau_c(\psi) = \frac{2\tau_0}{(1 - \cos\psi)}. \quad (6)$$

Here, the minimum relaxation time of a network domain is the relaxation time of the chain segment ($\psi = \pi$)

$$\tau_0 = \frac{\varsigma_0}{8K_0}, \quad (7)$$

where K_0 is the spring constant of a Gaussian subchain and ς_0 is the friction coefficient of an individual segment. The intrachain wavenumber ψ corresponds to the phase shift between displacements of neighboring segments in a multisegmental Gaussian chain [19, 20, 27, 28]:

$$\psi = \frac{k\pi}{n_0 + 1}, \quad k = 1 \ldots n_0 \quad (8)$$

(n_0 is the number of segments in a chain between network junctions).

Since the domains have finite dimensions, each network domain is characterized by its own finite maximum relaxation time

$$\tau_{\max} = \frac{4}{\pi^2} N^2 \tau_{\min}, \quad (9)$$

which is proportional to the squared number of junctions N in a cubic domain along one of the directions in the Cartesian coordinate system. Recall that relaxation times of an infinite regular network have no finite limit [1, 3, 14–18, 25, 26]. It should be also noted that the minimum relaxation time $\tau_{\min}$ given by Eq. (4) for the simplified coarse-grain model of a polymer network is close in value to the maximum relaxation time of the chain connecting neighboring network junctions, τ_{chain} [18], which is defined as follows (see Eq. (6) at $\psi = \pi/(n_0 + 1)$)

$$\tau_{\mathrm{chain}} = \frac{4}{\pi^2}(n_0 + 1)^2 \tau_0. \quad (10)$$

Further, we will deal only with one of these two quantities, namely, the relaxation time τ_{chain}.

Inasmuch as we are going to use distribution (1) of the number of segments y in domains to average the relaxation modulus over all domains of the heterogeneous polymer network, it is necessary to represent the dynamic characteristics of each domain as a function of y. The cubic network domain including y chain segments is composed of N^3 network cells, each containing three multisegmental Gaussian chains (or $3n_0$ Gaussian segments). Hence, the following simple relationship is observed for domains of these sort:

$$y = 3n_0N^3. \tag{11}$$

Using relationship (11), we may rewrite Eq. (2) for the relaxation modulus of an individual cubic domain of the heterogeneous polymer network in the following form:

$$\begin{aligned} &G(t;\, y) - G_e \\ &= 3\nu_{\text{chain}}k_{\text{B}}Tn_0\left[\frac{1}{y}\sum_{\theta}\exp[-t/\tau_n] + \frac{1}{n_0}\sum_{\psi}\exp[-t/\tau_c]\right], \end{aligned} \tag{12}$$

where ν_{chain} is the number of network chains in unit volume and the relaxation times τ_n and τ_c are as defined by Eqs. (3) and (6). Relaxation times that are manifested in the mechanical relaxation of an individual domain of a finite size fall in the interval between the relaxation time of a Gaussian segment τ_0 (Eq. (7)) and the maximum relaxation time of a domain $\tau_{\max}(y)$ which may be represented in the following form using Eq. (11):

$$\tau_{\max}(y) = \frac{4}{\pi^2}\left(\frac{1}{3n_0}\right)^{2/3}\tau_{\text{chain}}y^{2/3}. \tag{13}$$

Using Eq. (12) for the relaxation modulus $G(t;\, y)$ of the individual domain, it is easy to represent its asymptotic time behavior within different characteristic time intervals.

In the short-time region $\tau_0 < t < \tau_{\text{chain}}$, the domain relaxation modulus $G(t;\, y)$ behaves as follows:

$$G(t;\, y) - G_e \cong \nu k_{\text{B}}T\frac{1}{n_0}\frac{6}{\pi}\sqrt{\frac{\tau_{\text{chain}}}{t}}, \tag{14}$$

where $\nu = n_0\nu_{\text{chain}}$ is the number of segments in unit volume. Such “power-law” behavior of the relaxation modulus is characteristic of individual uncrosslinked Gaussian chains [20, 21, 28]. This region of the asymptotic time behavior of the relaxation modulus as defined by (14) extends up to the time periods of the order of the relaxation time of chains connecting neighboring junctions, τ_{chain}, as given by Eq. (10). In this case, the decay of the relaxation modulus at $t \cong \tau_{\text{chain}}$ with respect to the magnitude of the modulus at the initial point of time is inversely proportional to the number of segments n_0 in a chain between junctions: $(G(\tau_{\text{chain}}) - G_e)/(G(0) - G_e) \sim 1/n_0$.

At times longer than the relaxation time of the chain between junctions τ_{chain}, but shorter than the maximum domain relaxation time $\tau_{\max}(y)$, the time dependence for the relaxation modulus of a cubic network domain is the same as that for the modulus of the infinite regular cubic network in the region of predominant large-scale interchain relaxation [1, 3, 14–18]

$$G(t;\, y) - G_e \cong \nu k_{\text{B}}T\frac{1}{n_0}\frac{4\sqrt{3}}{\pi^2}\left(\frac{\tau_{\text{chain}}}{t}\right)^{3/2}. \tag{15}$$

In this region, the relaxation modulus also decays following a power law; moreover, the decay is faster than in the region of predominant intrachain relaxation (14). At longer times ($t > \tau_{\max}(y)$), the finite size of a domain begins to have an effect, and we obtain the following asymptotic behavior of the relaxation modulus:

$$\begin{aligned} &G(t;\, y) - G_e \\ &\cong \nu k_{\text{B}}T\frac{9\pi\sqrt{3}}{4}\frac{1}{y}\left(\frac{\tau_{\max}(y)}{t}\right)\exp\left[-\frac{t}{\tau_{\max}(y)}\right]. \end{aligned} \tag{16}$$

The relaxation modulus of the cubic network domain of a finite size starts to decay by an exponential law since the set of relaxation times for an individual domain is limited by the maximum relaxation time $\tau_{\max}(y)$ of the domain as a whole. This is the major difference in the viscoelastic properties of infinite and finite regular polymer networks (Fig. 2). At the points of time when the exponential decay of the relaxation modulus of a network domain of a finite size becomes noticeable ($t \cong \tau_{\max}(y)$), the following estimate can be obtained for the relative decrease in the relaxation modulus: $(G(\tau_{\max}) - G_e)/(G(0) - G_e) \sim (1/n_0)(1/N^3)$, where N^3 is the total number of cubic cells in a network domain.

Now, let us consider the viscoelastic dynamic properties of the heterogeneous polymer network as a whole. As noted above, in order to find the relaxation modulus of the network, it is necessary to average the modulus of its individual domain over all network domains using corresponding distribution function (1). Because the network heterogeneity type discussed in this work begins to manifest itself on a scale greater than the network cell size, the relaxation modulus $G(t)$ of the polymer network as a whole within time periods shorter that the relaxation time of the chain between junctions τ_{chain} will behave in the same manner as the modulus of the individual domain (Eq. (14)). At longer times ($t \gg \tau_{\text{chain}}$), the main contribution to the relaxation modulus $G(t)$ of the heterogeneous polymer network is made by the time regions corresponding the exponential decay of moduli of individual domains (Eq. (16)). In order to get the asymptotic time behavior of the relaxation modulus of the network at longer periods, it is necessary to use the Laplace transform [29] for determining the asymptotic behavior of an integral with a large dimensionless parameter $(t/\tau_{\text{chain}}) \gg 1$. Ultimately, we obtain the following expression for the relaxation modulus $G(t)$ of the heterogeneous polymer

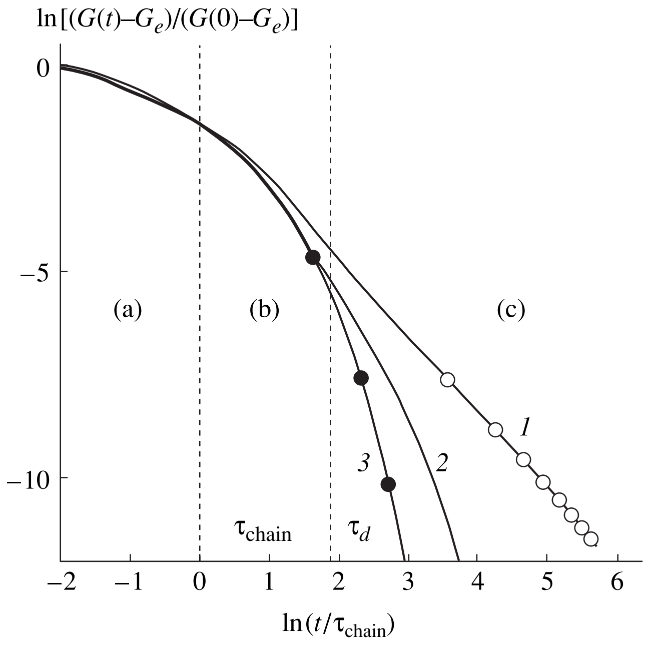

Fig. 2. Time dependence for the relaxation modulus $G(t)$ of three network systems: (*1*) infinite regular cubic network: $G(t) \sim t^{-1/2}$ at $t < \tau_{\text{chain}}$ (region a) and $G(t) \sim t^{-3/2}$ at $t > \tau_{\text{chain}}$ (regions b and c); (*2*) cubic network domain containing the average number of polymer segments: $G(t) \sim t^{-1/2}$ at $t < \tau_{\text{chain}}$ (region a), $G(t) \sim t^{-3/2}$ at $\tau_{\text{chain}} < t < \tau_d$ (region b), and $G(t) \sim \exp[-t/\tau_d]$ at $t > \tau_d$ (region c); and (*3*) heterogeneous polymer network with the domain structure: $G(t) \sim t^{-1/2}$ at $t < \tau_{\text{chain}}$ (region a) and $G(t) \sim \exp[-t/\tau^*)^{3/5}]$ at $t \gg \tau_{\text{chain}}$ (regions b and c). The curves were constructed with the parameters $n_0 = 20$ and $a = 0.001$.

network with the domain structure in the region of sufficiently long times ($t \gg \tau_{\text{chain}}$):

$$(G(t) - G_e) \cong \bar{\nu}_{\text{dom}} k_{\text{B}} T C_1 (a n_0)^{1/5} \left(\frac{t}{\tau_{\text{chain}}}\right)^{3/10} \exp\left[-\left(\frac{t}{\tau^*}\right)^{3/5}\right], \tag{17}$$

where $C_1 = 2^{-9/5} \times 5^{-1/2} \times 3^{29/10} \times \pi^{21/10}$ and $\bar{\nu}_{\text{dom}} = \nu/\bar{y}$ is the number of domains of the average size in unit volume (recall that ν is the number of segments in unit volume). The characteristic relaxation time τ^* is close in the order of magnitude to the maximum relaxation time τ_d of a network domain containing the average number of segments $\bar{y}$

$$\tau^* = C_2 \tau_d, \tag{18}$$

where $C_2 = 5^{-5/3} 2^{2/3} 3^{1/3} \approx 0.15$ and τ_d is given by (see Eq. (13) at $y = \bar{y} \cong 3/a$)

$$\tau_d = \frac{4}{\pi^2} \left(\frac{1}{a n_0}\right)^{2/3} \tau_{\text{chain}}. \tag{19}$$

Note that the region in which the relaxation modulus would decay as $t^{-3/2}$, which corresponds to the region of pure interchain relaxation of an individual network domain as given by (15), is not displayed in the heterogeneous network system under consideration. This is due to the fact that the averaging over all domains is performed starting from the smallest domain which actually does not possess the inner network structure since its size is equal to the dimensions of the cubic network unit cell.

From Eq. (17), we can see that the relaxation modulus of the heterogeneous polymer network at sufficiently long times exhibits stretched-exponential behavior: $\exp[-(t/\tau^*)^{3/5}]$. The stretched-exponential time behavior of the network relaxation modulus is due to exponential form (1) of the number distribution function $n(y)$ of segments in domains, which was used to average the modulus over all the domains of the system. The powered term $(t/\tau_{\text{chain}})^{3/10}$ in Eq. (17) affects very insignificantly the form of function $G(t)$ as compared to the stretched-exponential factor, and it appears because of the presence of the squared factor y^2 in the applied distribution function (1). At times corresponding to the onset of the stretched-exponential behavior ($t \cong \tau_d$), the decay of the relaxation modulus with respect to its value at the initial point of time is given by $(G(\tau_d) - G_e)/(G(0) - G_e) \approx 0.14 \cdot a$. It is obvious that, at these times, the relaxation modulus of the heterogeneous polymer network having sufficiently long chains ($n_0 \gg 1$) decreases rather strongly now (recall that the conditions $a \ll 1/n_0$ should be fulfilled in the system under consideration).

Thus, if a heterogeneous polymer network is composed of domains having a homogeneous network structure and there is a size distribution of domains in the system, the decay of the relaxation modulus at longer times corresponding to interchain relaxation occurs much faster than in homogeneous polymer networks (i.e., when the domain size tends to infinity). The power-law dependence of the relaxation modulus $G(t) \sim t^{-3/2}$ of a regular three-dimensional network in the region of interchain relaxation is replaced by stretched-exponential behavior (17) of the time dependence of the modulus in the case of the heterogeneous polymer network with the domain structure (Fig. 2). If there were no size distribution of domains (all domains had identical finite dimensions), the decay of the relaxation modulus would be exponential, i.e., even faster than in the considered heterogeneous network system.

It is especially important to note that complex polymer systems frequently exhibit the stretched-exponential relaxation behavior. As examples, local segmental motions in noncrystalline polymers, motions of macromolecules in strongly entangled polymer melts, and relaxation phenomena in other strongly correlated systems can be mentioned [30]. In such systems, strong correlations between relaxing units lead to the delay of relaxation with respect to the ordinary exponential decay for systems with one relaxation time and to the appearance of the stretched-exponential time behavior. Another example is dielectric relaxation in glassy polymers, which may be described in terms of the imperfection diffusion model [31, 32]. And, finally, the stretched-exponential relaxation behavior is also observed in disordered orientation glasses. In the latter case, it is mainly due to the inhomogeneity of a system, i.e., caused by the same factor as in the case of the heterogeneous polymer network with the domain structure considered in the present work. It is essential that all of the above examples deal with local relaxation processes having a sufficiently short characteristic time. In contrast, the dynamic model of the heterogeneous polymer network considered in this paper describes the large-scale intrinsic interchain network relaxation with characteristic times longer than the maximum relaxation time of a polymer chain between network crosslinks.

The strong difference in the behavior of the relaxation modulus in the long-time region for inhomogeneous and homogeneous polymer networks is also reflected by the relaxation spectrum. Recall that the relaxation spectrum $H(\tau)$ (or relaxation time distribution function) is related to the relaxation modulus $G(t)$ by [21]

$$G(t) = G_e + \int H(\tau)\exp[-t/\tau]d\ln\tau, \tag{20}$$

where G_e is the equilibrium modulus of a polymer network. The relaxation spectrum $H(\tau)$ is a very important characteristic as it uniquely determines all viscoelastic properties of a system [21]. Inasmuch as the heterogeneity of the type under consideration begins to have an effect on a scale greater than the network cell size, the network relaxation spectrum $H(\tau)$ at short times $\tau < \tau_{\text{chain}}$ does not differ in the least from the spectrum of an individual multisegmental Gaussian chain

$$H(\tau) \cong \nu K_{\text{B}} T \frac{1}{n_0}\frac{3}{\pi}\sqrt{\frac{\tau_{\text{chain}}}{\tau}}. \tag{21}$$

In the long-time region ($\tau \gg \tau_{\text{chain}}$ and $\tau \gg \tau_d$), a very strong decay of the relaxation spectrum takes place:

$$H(\tau) \cong \bar{\nu}_{\text{dom}} K_{\text{B}} T(an_0)\tilde{C}\left(\frac{\tau}{\tau_{\text{chain}}}\right)^{3/2}\exp[-3(\tau/\tau_d)^{3/2}], \tag{22}$$

where $\tilde{C} = 2^{-6/5}\pi^4 3^{9/2}$, $\bar{\nu}_{\text{dom}}$ is the number of domains of the average size in unit volume, and τ_d is the maximum relaxation time of a network domain of the average size as defined by Eq. (19). Thus, the relaxation time spectrum $H(\tau)$ for the heterogeneous polymer network in the region of large-scale interchain (interdomain) relaxation turns out to be extremely narrow. In this respect, it strongly differs from the relaxation spectrum of the regular three-dimensional network, which is characterized by the power-law behavior $\tau^{-3/2}$ in the interchain relaxation region [1, 3, 14, 17, 18].

Let us emphasize once more that the main reason for the appearance of the stretched-exponential time behavior of the relaxation modulus of an inhomogeneous polymer network consists in the exponential form of the number distribution $n(y)$ of segments in network domains (Eq. (1)). In addition to the aggregate-model distribution function [22–24] used in this work, there are many other examples of exponential distribution. For example, the stretched-exponential time behavior of the relaxation modulus may appear as a result of the existence of a broad molecular mass distribution of network chains, which also obeys the exponential law $\exp[-n/\bar{n}]$, where $\bar{n}$ is the average number of segments in chains between the crosslinks [34]. Another example is a network system with the microdomain structure in which the number of crosslinks inside a domain fluctuates about the mean value from one domain to another because of the randomness of chain crosslinking and, hence, is determined by the Gaussian distribution function $\exp[-(y - \langle y\rangle)^2/2\langle\delta y^2\rangle]$. This distribution function has the form $\exp[-ay^2]$ at a large number of segments in domains. The physical nature of such structurally inhomogeneous systems is different from the aggregate structure proposed previously [22–24].

Therefore, it is very interesting to extend the results obtained in this work using distribution function (1) developed for the aggregate model to the case of exponential distribution of the general type. Let the number distribution $\tilde{n}(y)$ of polymer segments in domains be defined as

$$\tilde{n}(y) \sim y^{\sigma}\exp[-ay^{\delta}], \tag{23}$$

where a is the distribution parameter, and σ and $\delta > 0$ are the power indexes that may take arbitrary values. The parameter a determines the average number of polymer segments $\bar{y}$ in a domain: $a \cong 1/\bar{y}^{\delta}$. After averaging with distribution function (23) over all domains, which are assumed to be regular cubic networks of a finite size as previously, the relaxation modulus of the heterogeneous polymer network at sufficiently long times ($t \gg \tau_{\text{chain}}$) will be given by

$$G(t) - G_e$$

$$\sim \nu k_{\text{B}} T\left(\frac{t}{\tau_{\text{chain}}}\right)^{\frac{\sigma-(3/2)\delta}{\delta+(2/3)}}\exp\left[-\left(\frac{t}{\tilde{\tau}^*}\right)^{\frac{\delta}{\delta+(2/3)}}\right], \tag{24}$$

where $\tilde{\tau}^*$ is a certain characteristic time of the polymer network having a domain-type heterogeneity. Thus, even rather weak exponential dependence of the distribution function $\tilde{n}(y)$ (at $\delta > 0$ in Eq. (23)) results in the stretched-exponential behavior of the time dependence of the relaxation modulus $G(t)$ (the power index $\delta/(\delta + 2/3)$) in the exponent of Eq. (24) is always less than unity at $\delta > 0$). For the distribution given by the aggregate model ($\sigma = 2$ and $\delta = 1$, see Eq. (1)), expression (24) of the general type transforms into relationship (17). For example, another stretched-exponential behavior of the network relaxation modulus is obtained for the Gaussian distribution function ($\sigma = 2$): $\exp[-(t/\tilde{\tau}^*)^{6/8}]$ (cf. Eq. (17)). In addition, averaging in a similar manner with the distribution function $\tilde{n}(y)$, it may be shown that the relaxation spectrum $H(\tau)$ of the heterogeneous polymer network in the large-scale interchain relaxation region exhibits the following behavior:

$$H(\tau) \sim \nu k_B T\left(\frac{\tau}{\tau_{\text{chain}}}\right)^{3/2(\sigma-\delta)}\exp\left[-\left(\frac{\tau}{\tilde{\tau}^*}\right)^{3/2\delta}\right]. \qquad (25)$$

We can see that, at a sufficiently long time, the relaxation spectrum of a polymer network having the domain inhomogeneity becomes narrow with the arbitrary exponential distribution $\tilde{n}(y)$ of the number of polymer segments in domains as well. Thus, the principal results of the present work can be generalized to the case of a distribution function of rather common type (23).

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