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RELAXATION PROPERTIES OF THE ROUSE CHAIN WITH INHOMOGENEOUS LINKS

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The relaxation properties of the Rouse chain with inhomogeneous links have been investigated. The problem has been solved by direct integration of systems of differential-difference equations which describe the relaxations of the chain length and stress. It has been shown that these two processes are different in both the set of relaxation modes and the characteristic of the spectrum. The influence of the chain structure on these parameters has been demonstrated. The effect of "packing" of the relaxation modes has been revealed; it appears on introduction of links with an increased coefficient of friction into the chain and manifests itself in the fact that the high-frequency modes come closer together and even merge, so that their total number becomes substantially smaller than that in the case of the Rouse model.

Introduction. The Rouse model suggested for the first time in [2] has found wide application for description of the relaxation properties of polymer chains [1]. In this representation, the chain consists of sequentially connected Maxwell elements (links). A significant assumption for calculation of the Rouse model is that the number of links n is rather large ($n >> 1$); therefore, the discrete system of differential-difference equations describing the movement of the links can be represented in continuous form [3–5] as one equation in partial derivatives of second order. It was shown that the numbers of the relaxation modes and links of the chain are equal, while the relaxation times λ_i obey the Rouse relation

$$(\lambda_i^{-1})_{\mathrm{R}} = 4\sin^2\left(\frac{\pi}{2}\frac{i}{n+1}\right), \tag{1}$$

here, the first number of the mode refers to the maximum relaxation time.

It is obvious that for rather short chains the continuity approximation cannot be satisfactory and the discreteness of the system containing a relatively small number of differential equations must be considered in explicit form. Moreover, it is necessary to allow an arbitrary distribution of the links differing in relaxation characteristics over the chain. Both these requirements are physically reasonable. Indeed, it is generally believed that a link of the Rouse chain corresponds in its elastic properties to a Kuhn segment, i.e., it can contain more than ten monomeric links. And this means that the number of Rouse links in the actual polymer chain is not equal to the number of monomeric links and, consequently, is not so large as to allow the continuity approximation in solving the kinetic problem. In addition, different chain links in copolymers can have differing relaxation properties. Even the links of homopolymeric macromolecules in melts and in concentrated solutions can possess different friction coefficients because of the presence of density fluctuations.

Generalized Model of Relaxation. Let us consider the relaxation of the chain removed from the equilibrium state by the force F applied to the first link:

$$\underset{n}{\mathrm{O}}\vee\vee\vee\underset{n-1}{\mathrm{O}}\vee\vee\ldots\ldots\vee\underset{i}{\mathrm{O}}\vee\vee\vee\ldots\ldots\vee\vee\vee\underset{2}{\mathrm{O}}\vee\vee\vee\underset{1}{\mathrm{O}}\vee\vee\vee \to F\,.$$

In this scheme, O denotes the friction element, while $\vee\vee\vee$ denotes the elastic element of the chain link.

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In the case where the force applied to the first link leads to extension of the chain and then becomes equal to zero, the chain length decreases, i.e., the strain relaxation occurs. For the stress relaxation, the model assumes that the force F is applied instantly through a spring with an elastic modulus E (the stress in the spring decreases due to the displacement of the chain links).

The relaxation of the length of the chain consisting of n links and removed from the equilibrium state is described by the system of n differential equations

$$
\begin{gathered}
\tau_1 \dot{x}_1 = - x_1 + x_2 \, , \\
\tau_2 \dot{x}_2 = x_1 - 2x_2 + x_3 \, , \\
\dots\dots\dots\dots \\
\tau_i \dot{x}_i = x_{i-1} - 2x_i + x_{i+1} \, , \\
\dots\dots\dots\dots \\
\tau_n \dot{x}_n = x_{n-1} - x_n \, .
\end{gathered}
\tag{2}
$$

The relaxation characteristics of the links, attributable to the difference in their friction coefficients due to the interaction with a medium, are described by the parameter τ_i. Solution of (2) makes it possible to find the equations of motion for all the chain links and the change in the chain length $L = x_n - x_1$ provided that the initial conditions are specific. As conditions of this kind, we can take $L(0) = 1$ and $x_i(0) = (i - 1)/(n - 1)$.

The kinetics of change in the chain length that can be expressed as the combination of exponentials

$$
L = L\,(0) \sum_{i=1}^{n} h_i \exp\left\{- p_i t\right\}
$$

is determined by the roots $z_i = \tau_i p_i$ of the polynomial D_n [7]:

$$
D_n = \begin{vmatrix}
z_1 - 1 & 1 & 0 & 0...0 & 0 & 0 \\
1 & z_2 - 2 & 1 & 0...0 & 0 & 0 \\
\dots & \dots & \dots & \dots & \dots & \dots \\
0 & 0 & 0 & 0...1 & z_{n-1} - 2 & 1 \\
0 & 0 & 0 & 0...0 & 1 & z_n - 1
\end{vmatrix} = 0 \, .
\tag{3}
$$

Transformation of Eq. (3) yields the determinant

$$
B_n = \begin{vmatrix}
z_1 - 2 & 1 & 0 & 0...0 & 0 & 0 \\
1 & z_2 - 2 & 1 & 0...0 & 0 & 0 \\
0 & 1 & z_3 - 2 & 1...0 & 0 & 0 \\
\dots & \dots & \dots & \dots & \dots & \dots \\
0 & 0 & 0 & 0...1 & z_{n-1} - 2 & 1 \\
0 & 0 & 0 & 0...0 & 1 & z_n - 1
\end{vmatrix} = (z_1 - 2)\, B_{n-1} - B_{n-2} \, .
\tag{4}
$$

Thus,

$$
D_n = (z_1 - 1)\, B_{n-1} - B_{n-2} = B_n + B_{n-1} = 0 \, .
\tag{5}
$$

The stress relaxation is described by the system of $n + 1$ equations

$$\tau_1 \dot{F} = -F + E\,(x_1 - x_2)\,,$$

$$\tau_1 \dot{x}_1 = \frac{F}{E} - x_1 + x_2\,,$$

$$\tau_2 \dot{x}_2 = x_1 - 2x_2 + x_3\,, \tag{6}$$

$$\ldots\ldots\ldots$$

$$\tau_i \dot{x}_i = x_{i-1} - 2x_i + x_{i+1}\,,$$

$$\ldots\ldots\ldots$$

$$\tau_n \dot{x}_n = x_{n-1} - x_n\,.$$

For the sake of simplicity, it is assumed that the quantity E is identical for all the links, whereas the difference of the links in the relaxation times, as in the previous case, is caused by that in the friction coefficients. The initial conditions for Eq. (6) are as follows: $F(0) = 1$ and $x_i(0) = 0$. Solution of system (6) for the stress relaxation

$$F = F\,(0) \sum_{i=1}^{n} h_i \exp\left\{-p_i t\right\}$$

in the form of a combination of exponentials is determined by the roots $z_i = \tau_i p_i$ of the polynomial

$$D_n = \begin{vmatrix} z_1 - 1 & E & -E & 0 & 0\ldots0 & 0 & 0 \\ \frac{1}{E} & z_1 - 1 & 1 & 0 & 0\ldots0 & 0 & 0 \\ 0 & 1 & z_2 - 2 & 1 & 0\ldots0 & 0 & 0 \\ \ldots & \ldots & \ldots & \ldots & \ldots & \ldots & \ldots \\ 0 & 0 & 0 & 0 & 0\ldots1 & z_{n-1} - 2 & 1 \\ 0 & 0 & 0 & 0 & 0\ldots0 & 1 & z_n - 1 \end{vmatrix} = 0\,, \tag{7}$$

whose transformation gives

$$D_n = z_1 B_n = 0\,. \tag{8}$$

As is seen, Eqs. (5) and (8) are different. This means that the relaxations of strain (of the chain length) and of stress are characterized by different sets of the relaxation times $\lambda_i = p_i^{-1}$. Numerical solution of Eqs. (5) and (8) can easily be obtained, since it is possible to represent the determinant B_n in the form of the recurrence series

$$B_1 = z_n - 1\,,$$

$$B_2 = (z_{n-1} - 2)\,B_1 - 1\,,$$

$$B_3 = (z_{n-2} - 2)\,B_2 - B_1\,, \tag{9}$$

$$\ldots\ldots\ldots$$

$$B_i = (z_i - 2)\,B_{i-1} - B_{i-2}\,,$$

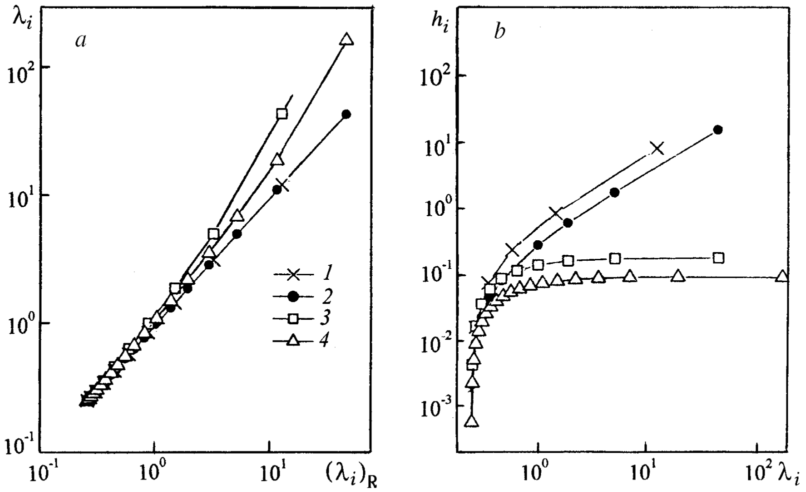


Fig. 1. Correlation between the relaxation times λ_i and $(\lambda_i)_R$ (a) and the relaxation spectra (b) for the strain relaxation (1, 2) and the stress relaxation (3, 4) in the case of 10- (1, 3) and 20-link (2, 4) chains.

....

$$B_n = (z_1 - 2)\, B_{n-1} - B_{n-2}\,.$$

The relaxation spectrum h_i is calculated by solving the system of equations with the initial conditions

$$\frac{d^k L}{dt^k}(t=0) = \sum_i \,(-1)^k p_i^k h_i\,, \quad \frac{d^k F}{dt^k}(t=0) = \sum_i \,(-1)^k p_i^k h_i\,,$$

where $k = 0, 1, ..., n-1$.

It should be noted that although the viscoelastic characteristics for the short chains can be obtained by direct solution of systems (2) and (6), it seems worthwhile to consider the influence of the chain structure on the spectral characteristics. This is due to the fact that the question of the correlation between the spectrum of relaxation times and the structure of polymeric chains is the key to establishing a relationship, for example, between the molecular-mass distribution and the relaxation properties of the polymer. The structure of the macromolecule can be modeled by introducing the links with different friction coefficients into an oligomeric chain. The solution of Eqs. (5) and (8) for the corresponding systems makes it possible to calculate the spectrum of relaxation times and in this way to establish its relationship with the chain structure.

First of all, we will consider the relaxation characteristics of a homogeneous Rouse chain. Figure 1a presents the results of solution of systems (2) and (6) for an 11-segment chain with identical links in the coordinates of Eq. (1), which, as is seen from this figure, adequately describes the strain relaxation. At the same time, the stress relaxation is characterized by the higher values of the times compared to $(\lambda_i)_R$. In the case of the chain-length strain, the spectrum (coefficients h_i in the exponential expansion) also corresponds to the well-known Rouse solution

$$h_i = \frac{1}{2n}\left(\tan\left(\frac{i\pi}{2n}\right)\right)^{-2}$$

for the odd values of i; for the even values we have $h_i = 0$ (Fig. 1b). However, for the stress relaxation the spectrum is quite different: as the value of λ_i increases, the quantity h_i reaches a plateau. This behavior correlates with the well-known formula $h_i = 1/n$ [4] with the only difference being that in the plateau region $h_i \approx 2/n$, although the mean value of $\langle h_i \rangle$ is exactly equal to $1/n$. Moreover, in contrast to the strain relaxation, all the modes (both the odd modes and the even ones) contribute to the spectrum.

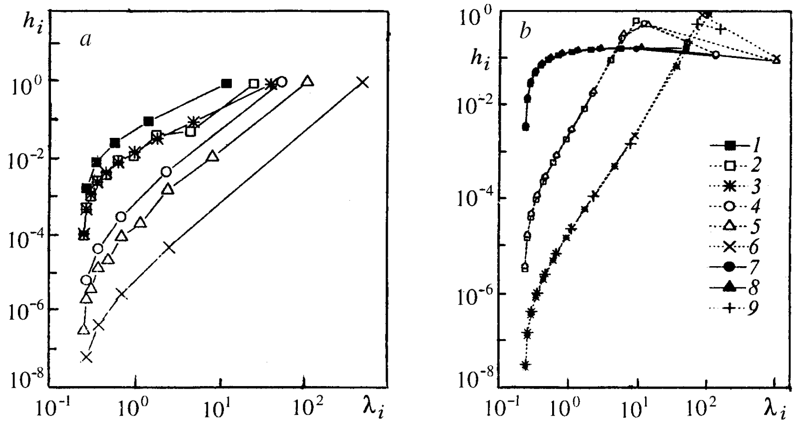


Fig. 2. Relaxation spectra of 11-link chains with modified end links (the first and the last) in the regime of strain relaxation (a) and stress relaxation (b): 1) τ_a/τ = 1 and 1, 2) 10 and 1, 3) 100 and 1, 4) 10 and 10, 5) 10 and 100, 6) 100 and 100; 7) 1 and 10, 8) 1 and 100 and 9) 100 and 10.

Thus, in the present model the Rouse law is satisfied only for the strain relaxation, whereas the stress relaxation is described by another set of relaxation modes and another relaxation spectrum.

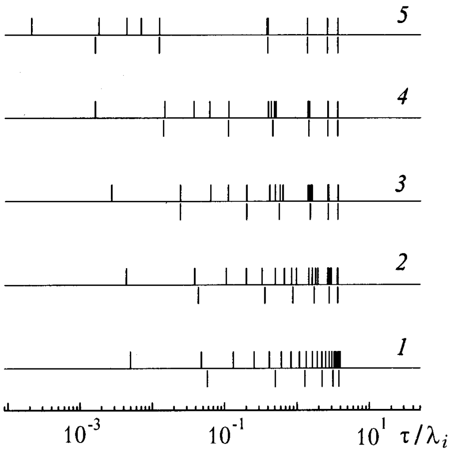
Inhomogeneous (Modified) Rouse Chain. We will represent the inhomogeneous Rouse chain in the form of a sequence of links with a different friction coefficient, for example, a-b-b-b-b-b-a, where at the ends there are modified links of the type "a"; the type "b" corresponds to unmodified links. The friction coefficient of a modified link τ_a will be expressed in terms of the ratio τ_a/τ, where τ is the friction coefficient of the "b" link. In this case, it is convenient to write the relaxation structure of the chain in the form of a set of figures each of which is the value of the friction coefficient. Thus, for the case $\tau_a/\tau = 5$ the chain has the form 5-1-1-1-1-1-5.

Figure 2a illustrates the relaxation spectra of the chains with end modified links (strain relaxation). As is evident, the maximum value of the relaxation time (λ_{max}) grows considerably; the greater the λ_{max}, the higher the friction coefficient of the end link. The symmetric chains (the "a" links at both ends of the chain) are characterized only by the odd modes, whereas for the asymmetric chains (there is a modified link only at one end of the chain) the number of modes is equal to that of the chain links minus unity. However, one may notice that the even modes in this case are also characterized by a relatively lower value of the pre-exponential factor h_i, i.e., the curve of the spectrum has a nonmonotone form which is the more pronounced, the lower the quantity τ_a/τ.

Modification of both end links and the increase in their friction coefficient make the spectral curve steeper: the statistical weight of the term with the longest relaxation time virtually becomes equal to unity, while the short times are characterized by a very low value of the statistical weight (see, for example, curves 1 and 6).

In the case of the stress relaxation, modification of the end links exerts an even stronger influence on the spectrum behavior. As is evident from the data given in Fig. 2b, the curves are of a monotone nature only in the case where the first link, to which the force is applied, has the same friction coefficient as middle links of the type "b" (curves 1, 7, and 8). As this quantity increases, the curves acquire a nonmonotone form; the statistical weight h_1 of the mode with the longest relaxation time λ_1 turns out to be smaller than λ_2. At the same time, the quantity λ_1 virtually is the same for the chains with an identical end link. The quantities λ_2 are close for the chains with an identical first link. The spectral curves in the region of short relaxation times merge together provided that the first links are identical, while the values of the statistical weights differ by orders of magnitude for the chains whose first links are different (see, for example, curves 1 and 3 or 8 and 9). Consequently, the spectral characteristics clearly respond to the structure of the chain.

The inclusion of the links with an increased value of the friction coefficient (of the type "a") into the middle of the chain leads to a significant change in the set of relaxation modes. As is seen from the data on strain relaxation, presented in Figs. 3–5, the growth in the number of these links subdividing the chain into the blocks of "b"-type links, increases the total number of the modes. However, higher-frequency modes are grouped together into "packets", i.e., form groups with a close relaxation time, with the relaxation time being the closer, the higher the value of the friction



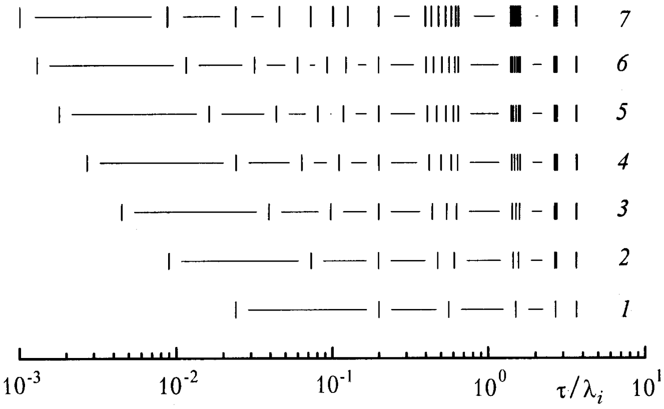


Fig. 3. Relaxation modes for the structure a-(b-b-b-b-b-a)$_m$. Below the straight lines, the number of blocks is m = 1; above the straight lines, m = 4: 1) τ_a/τ = 1, 2) 2, 3) 5, 4) 10 and 5) 100.

Fig. 4. Relaxation modes for the structure a-(b-b-b-b-b-a)$_m$, τ_a/τ = 2: 1) m = 1, 2) 2, 3) 3, 4) 4, 5) 5, 6) 6, and 7) 7.

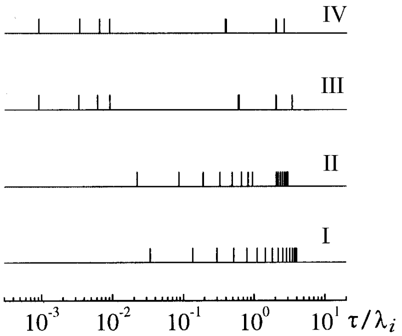
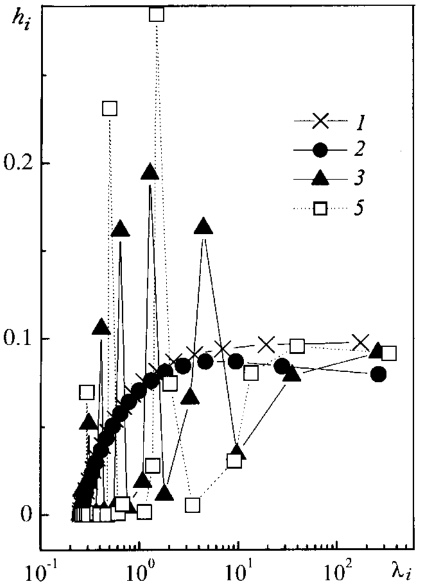


Fig. 5. Relaxation modes for chains with different structures of the block: I) 1-(1-1-1-1)$_3$-1-1-1-1; II) 2-(1-2-1-2)$_3$-1-2-1-2; III) 100-(1-1-1-100)$_3$-1-1-1-100; IV) 100-(1-2-1-100)$_3$-1-2-1-100; V) 100-(1-10-1-100)$_3$-1-10-1-100. The quantity τ_a/τ is denoted by the figures. The number of blocks is denoted by the subscript.

coefficient of "a"-type links (Fig. 3). In the spectrum of relaxation times of the homogeneous Rouse chain, it is difficult to assign particular modes to the definite links. The inclusion, into the chain, of "a"-type links differing little in their relaxation ability from the main links (τ_a/τ = 2) allows separation of the "packets" of modes, which, being different in value, are noticeably grouped together near the values available in the initial block. As is shown in Fig. 3, the modes converge the closer, the higher the value of τ_a/τ. Thus, the links with a high friction coefficient isolate as it were the blocks from each other and in any chain one can separate modes characterizing links with different relaxation properties.

From a comparison of the multiblock chains and the "single-block" chain (Fig. 4) it is evident that the high-frequency modes are grouped near the values characteristic of the corresponding block. The number of the modes entering into the packet turns out to be equal to the number of the blocks. (In Fig. 4, we present the data for τ_a/τ = 2 so as to differentiate order that the components entering into the packet). In the limit, the growth in the chain length due to the increase in the number of blocks leads to the fact that the number of modes becomes smaller than the total number of the links, since the high-frequency modes simply merge together.

Figure 5 presents the frequency characteristics of a 17-link chain with different structure. It is seen that even a comparatively weak change in the relaxation properties of the links (structure II, τ_a/τ = 2 for the odd links) causes a significant increase in the quantity λ_{max}; the formation of two "packets" of relaxation modes in the high-frequency



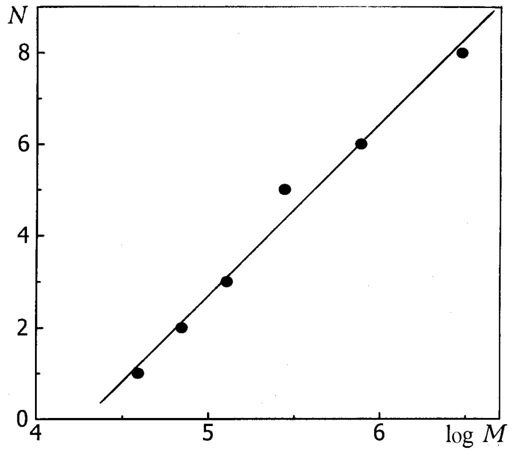


Fig. 6. Relaxation spectra of the chains listed in Table 1 under Nos. 1, 2, 3, and 5.

Fig. 7. Correlation between the molecular mass of the polymer M and the number of modes in the relaxation spectrum of monodisperse polystyrene N according to the data of [8].

region is observed. If the chain is modified in such a way that there are three mobile links (structure III) between the "a"-type links (even with a higher value of $\tau_a/\tau = 100$), then the quantity $\lambda_{\min}$ virtually is the same as for the Rouse chain (structure I). This means that $\lambda_{\min}$ characterizes the high-mobility link between the same links. The decrease in the mobility of the adjacent links (structures IV and V) leads to a sharp displacement of $\lambda_{\min}$ to the low-frequency region. Thus, each mode can be assigned to a link of a definite type with account for its immediate surroundings. In turn, the lowest-frequency modes characterize low-mobility links; the influence of the high-frequency component on this dependence is very weak: chains III–V containing an identical number of "a" links ($\tau_a/\tau = 100$) demonstrating the same set of low-frequency modes (four, since the number of blocks is four). It should be noted that in this case no "packing" is observed.

Similar effects are also observed in the regime of stress relaxation. The subdivision of the chain of homogeneous links into blocks by the links with a higher friction coefficient causes the appearance of inhomogeneities in the relaxation spectrum, even though these blocks have different lengths. Thus, Fig. 6 illustrates the spectra of chains whose structure is given in Table 1. The appearance of a modified link at the end of the chain increases somewhat the quantity $\lambda_{\max}$ but decreases the statistical weight of this mode. On the curves of the spectrum, peaks are observed when the chain is subdivided into the blocks: the number of the peaks is larger when there are two blocks, and their number is three when there are four blocks in the chain. It is obvious that this is a manifestation of the decrease in the number of high-mobility links due to the shortening of the sequence of "b" links. Thus, here, too, the relationship between the spectrum character and the chain structure is seen.

It is well known that the rheological properties of the system (viscosity and stationary compliance) are determined by the mean values of the relaxation times

$$\langle\lambda\rangle_n = \sum_{i=1}^{20} h_i\lambda_i\,,\quad \langle\lambda\rangle_w = \frac{\sum\limits_{i=1}^{20} h_i\lambda_i^2}{\sum\limits_{i=1}^{20} h_i\lambda_i}$$

TABLE 1. Block Structure of the 20-Link Chains

Number of the chain	Structure of the chain
1	$F \leftarrow (1)_{20}$
2	$F \leftarrow (1)_{19}$-5
3	$F \leftarrow (1)_6$-5-$(1)_{12}$-5
4	$F \leftarrow (1)_6$-5-$(1)_6$-5-$(1)_8$-5
5	$F \leftarrow (1)_3$-5-$(1)_4$-5-$(1)_6$-5-$(1)_3$-5
6	$F \leftarrow (1)_3$-5-$(1)_4$-5-$(1)_5$-5-$(1)_2$-5-1-5

Note: The quantity τ_a/τ is denoted by the figures; the number of links in the block is denoted by the subscripts.

TABLE 2. Values of the Mean Times of the Stress Relaxation for the 20-Link Chains

Number of the chain	λ_{max}	$<\lambda>_n$	$<\lambda>_w$	γ
1	170.4	20	143.5	7.175
2	261.4	25	219.8	8.79
3	257.0	27	228.0	8.44
4	281.9	32	238.5	7.45
5	330.8	36	282.0	7.83
6	392.9	40	336.95	8.42

and by their ratio γ rather than by the quantity λ_{max}. In Table 2 we present the values of these characteristics for the chains whose structure is illustrated in Table 1, while the spectral characteristics of some of them are given in Fig. 6 (chains 1–3 and 5) in comparison with the value of the maximum relaxation time, which, as is seen, is significantly higher than the mean values. The width of the distribution function by relaxation times which is characterized by the parameter γ also depends on the chain structure. This quantity is the least for the homogeneous chain.

CONCLUSIONS

From the comparison of the results obtained and the data on the relaxation characteristic of high-molecular-weight polymers it is possible to draw the following conclusions. It is assumed that, because of the large length of the chains, the relaxation spectrum can be considered as continuous. Only a few attempts to analyze the frequency dependence of the relaxation elastic modulus for determining the relaxation spectrum point to the fact that the latter is adequately characterized by a limited set of modes, the number of which is the larger, the higher the molecular polymer mass, however, this increase is far from proportionality. Thus, according to the data of [6], the correlation between the number of modes and the molecular mass is expressed in the form of a logarithmic dependence (Fig. 7). Here, the spectrum of relaxation times is not described by the Rouse or Doi–Edwards models. For example, in [6] a nonmonotonic increase in the pre-exponential factor with growth in the relaxation time was observed: the term with the maximum time enters with a smaller statistical weight than the previous one. It is possible that these features are of the same origin as in the case considered in the present work, i.e., the result of the relaxation nonequivalence of the chain links. This nonequivalence can be understood within the framework of the model of a grid of physical relationships, according to which some of the chain links are related to other macromolecules by long-lived physical nodes. The rupture of the chain links is accompanied by energy dissipation, which is equivalent to the significantly higher value of the friction coefficient than that for the links not entering into such nodes. Thus, in solving the problem on establishing a relationship between the relaxation characteristics of the polymer and its molecular-mass distribution, it is necessary to take into consideration the possibility of relaxation inhomogeneity of the polymer chains.

As has been shown in the present work, the presence of the links with different relaxation characteristics is manifested as the set of relaxation modes. It would seem that this fact allows one to consider the Bartenev approach

[7] developed in recent decades, to be valid, since this approach relates definite relaxation times to specific molecular groups. Possibly, for vibrational spectra this representation is true. However, it is obvious that in the case of mechanical relaxation the structure–property relationship cannot be simple and unambiguous. Indeed, as has been shown above, the position of a mode on the frequency scale is affected not only by the relaxation characteristic of the link, but also by the surroundings in which it is located with consideration not only of the near neighbors in the chain but also of those at a larger distance. A rather extended sequence of single-type links demonstrates the Rouse behavior, i.e., the number of differing modes corresponds to the number of links in this sequence (Figs. 3–5).

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NOTATION

i, number of the link or mode x_i, coordinate of the ith link of the chain; τ_i, relaxation characteristic of the ith link; λ, relaxation time; $(\lambda_i)_R$, relaxation time according to the Rouse equation (1); $p_i = \lambda_i^{-1}$, E, elastic modulus of the Maxwell element; L, chain length; F, force; n, number of links in the chain; t, time; h_i, spectrum of relaxation times; D_n and B_n, determinants; $\langle\lambda\rangle_n$ and $\langle\lambda\rangle_w$, numerical-mean and weighted-mean relaxation times; γ, ratio of the weighted-mean relaxation time to the numerical-mean relaxation time; τ_a, relaxation characteristic of a modified "a"-type link; M, molecular mass of the polymer; N, number of modes in the relaxation spectrum of monodisperse polystyrene. Subscripts: max, maximum; min, minimum; n, numerical-mean; w, weighted-mean; a, "a"-type link.

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