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Investigation of Local Motions in Polymers by the Method of Molecular Dynamics

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ABSTRACT: The main features of local motions in linear polymer chains and in cross-linked macromolecules were studied by the method of molecular dynamics. The chain model consists of particles connected by rigid bonds and interacting with each other and with solvent particles with Lennard-Jones potential forces. Chains with various numbers of units were considered at various concentrations and temperatures. The characteristics of local motions (translational and rotational mobility), normal modes, and cooperative motions and the effect of cross-linking on local chain mobility were investigated. The results of numerical experiments (NE) are compared with analytical results for a viscoelastic Hearst-Harris (H-H) model. It is shown that the characteristics of both local motions and normal modes are close to those of viscoelastic models. The dependence of the characteristic relaxation times of normal modes on the wavenumber virtually coincides with that for the H-H model. The present study suggests that in cross-linked systems the translational and rotational mobility of the cross-link and the adjoining chain elements are greatly hindered. The relationship between the characteristic times obtained in NE and experimental results on dielectric relaxation and polarized luminescence is discussed.

The molecular theory of equilibrium properties of polymers in solution, in the melt and in bulk, is based on the principles and methods of conformational statistics of macromolecules developed by Flory and co-workers,[2] Volkenstein,[3a] Ptitsyn and Birshtein,[3b] and others. This theory started from simple models of a polymer chain describing qualitatively the observed relationships. Models of real chains as developed at present permit the determination of numerical values of physical parameters. In contrast, in the molecular theory of the nonequilibrium relaxation process in polymers we are only at the beginning of our path. The dynamic theory of polymers uses mainly semiphenomenological viscoelastic models that describe the average motion of chain segments containing many units. The transition to models in which the kinetic element is represented by a rigid link or a monomer unit rather than by a flexible subchain is difficult, because their analytical description involves substantial mathematical difficulties. These difficulties increase on passing from the description of the motion of a single chain in a continuous viscous medium to a more detailed description in which the interactions of polymer particles with each other and the solvent are explicitly taken into account.

Computer simulation of molecular motion is the most suitable method for solving these problems. According to the degree of precision desired, different models and corresponding methods of motion simulation may be used. In lattice chain models, motion occurs as a result of random local rearrangements of chain elements. The mechanism of local mobility (various types of elementary jumps) is postulated and its manifestations in various dynamic chain characteristics are considered. Monte-Carlo methods are used for computer simulation of the motion of such models.[4-8]

The method of Brownian dynamics[9-12] consists of numerical solution of Langevin equations. This method makes it possible to take into account rigid bonds, valence angles, and the potential energy of internal rotation.[11] Ceperley and co-workers[12] take into account also the spatial interactions of chain particles separated from each other along the chain contour. Just as for viscoelastic models, the medium surrounding the macromolecule is described as a continuous viscous liquid which is also a source of random Brownian forces affecting chain elements.

The method of molecular dynamics (MD) provides an even more detailed description; it takes into account explicitly both the interactions between chain units and the interactions with solvent particles. During the last two decades this method has been widely used in the physics of liquids.[13-15] It was developed for polymer chains by Balabaev, Grivtsov, and Shnol[16-18] and applied to the investigation of relaxation properties of polymers by the present authors.[19,20] The MD method seems to be the most suitable for describing highly condensed systems, for which it is doubtful whether the medium surrounding a given macromolecule can be described as a continuous liquid. Because computer time is limited, a combination of these complementary methods probably offers the best solution. The results obtained by a more detailed method may provide the basis for a more "grain-coarsed" description.

The present work deals with some results of a study of local mobility in macromolecules in the liquid phase (in solution and in the melt) by the MD method. The study was carried out with the simplest model for a polymer chain: a chain of point-like particles with mass m bonded by rigid bonds and interacting with each other and with similar solvent particles with Lennard-Jones potential forces. This model is a polymeric analogue of a model widely used for studying the properties of simple liquids by the MD method.[14] Recently works of other authors dealing with the MD of oligomers and polymers have also appeared.[21-23] They consider mainly the mathematical

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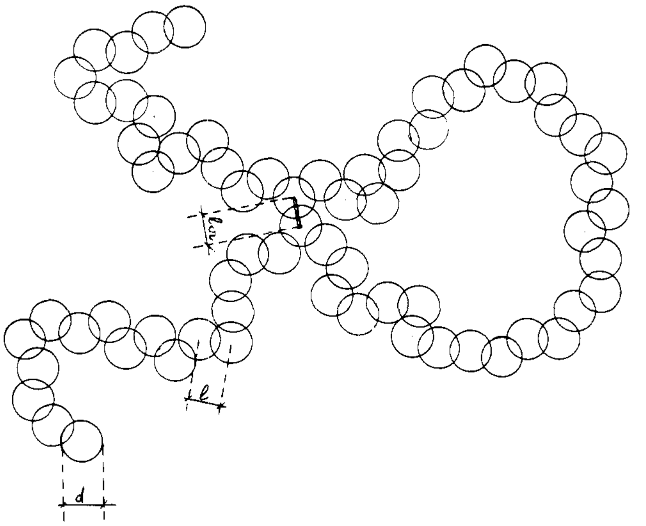

Figure 1. Chain model (cross-link was introduced only for system V): $l = 0.69\sigma$ is the bond length, $d = 1.12\sigma$ is the "diameter" of a chain particle determined as the minimum of the Lennard-Jones potential $U(r)$; $U(\sigma) = 0$; $U(\mathrm{d}) = -\epsilon_0$; $l_{cr} = l$ is the cross-link length (for system V).

aspects of the application of the MD method for polymers.

Model and Method of Calculation

The chain model (Figure 1) consisted of N_1 point particles of mass m bonded by rigid bonds of length l and interacting with each other and with N_2 similar solvent particles with the Lennard-Jones potential

$$U(r) = 4\epsilon_0\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right] \qquad (1)$$

where r is the distance between the centers of interaction, $U(\sigma) = 0$ and $U(2^{1/6}\sigma) = -\epsilon_0$. The bond length l was selected in such a manner that the tetrahedral bond angle between the jth and the $(j + 1)$th bonds should correspond to the minimum of the potential energy of interaction between the jth and $(j + 2)$th chain particles. The characteristic length scale of the problem is σ and the time scale is $t_0 = \sigma(m/\epsilon_0)^{1/2}$, where m is the mass of a polymer or solvent particle. Hereafter linear dimensions are expressed in units of σ. Equations of motion for a chain consisting of $N_1 - 1$ rigid bonds can be written in two ways.[24,16] Either $3N_1 - (N_1 - 1)$ generalized coordinates are introduced or the bonds are taken into account by using Lagrangian multipliers in a Cartesian coordinate system. We used the second method developed for a polymer chain consisting of rigid links.[16-18] In this case the number of equations becomes $3N_1 + (N_1 - 1)$, where $3N_1$ is the number of motion equations and $N_1 - 1$ is the number of bond equations.

$$m_i\ddot{\mathbf{r}}_i = -\frac{\partial U}{\partial \mathbf{r}_i} + \sum_{k=1}^{N_1-1} \lambda_k \frac{\partial \varphi_k}{\partial \mathbf{r}_i} \qquad i = 1, \ldots, N_1 \qquad (2)$$

$$\varphi_k = \frac{1}{2}[(\mathbf{r}_{k+1} - \mathbf{r}_k)^2 - l^2] = 0 \qquad \mathrm{k} = 1, \ldots, N_1 - 1 \qquad (3)$$

where m_i, $\mathbf{r}_i$ are the mass and the coordinates of the ith particle, respectively, l is the bond length, and λ_k is the Lagrangian multiplier corresponding to the kth bond.

Further, it is possible to obtain $4N_1 - 1$ finite difference equations for $r_i(t + \Delta t)$ and $\lambda_k(t)$ by using the simplest finite difference approximation $\ddot{r}(t) = [r(t + \Delta t) - 2r(t) + r(t - \Delta t)]/(\Delta t)^2$. Since this system is linear for $\lambda_k(t)$ and nonlinear for $\vec{r}_i(t + \Delta t)$ it is possible to solve it by the Newtonian method, obtaining for each iteration a linear triagonal system for $\lambda_k(t)$. Two or three interations were sufficient for maintaining the constant bond length with high precision. The algorithm is described in greater detail by Balabaev, Grivtsov, and Shnol.[16-18] The system should satisfy periodic boundary conditions permitting a high degree of volume filling by the particles of the chain and the solvent. This degree, i.e., the ratio of the total volume of the chain and solvent particles to the volume occupied by nonbonded particles with closest packing, was usually taken as 0.82. The overall energy of the system, E, is predetermined at the beginning of the calculations and should remain constant. The calculation step $\Delta t = 0.004t_0$ selected in these NE led to deviations of E from the given value not exceeding 0.1 to 1%. The temperature of the system T^* (measured in T_0 units, $T_0 = \epsilon_0/k$ where k is Boltzmann's constant) was determined from the average kinetic energy per degree of freedom. For each set of values of the parameters several experiments were carried out under different initial conditions, and the results were averaged over these NE. Each NE consisted of 13000–20000 steps and took about 2 h of computer time. (An ABESM-6 computer was used.)

The following systems were considered: a monomer in a solvent (system I: $N_1 = 2$ and $N_2 = 106$) and a polymer chain in a solvent (system II: $N_1 = 10$ and $N_2 = 98$; system III: $N_1 = 60$ and $N_2 = 58$; and system IV: $N_1 = 123$ and $N_2 = 4$). Furthermore a variation of system IV, a polymer chain with a cross-link, was considered (system V).

Local Motions in Linear Chains. 1. Characteristics of Local Motions.

In each NE time dependences were calculated for the following quantities

$$P_1(t) = \langle \cos\,[\theta(t)] \rangle \qquad (4)$$

$$P_2(t) = \tfrac{3}{2}\langle \cos^2\,[\theta(t)] - \tfrac{1}{3} \rangle \qquad (5)$$

where $\theta(t)$ is the angle of rotation of the vector $\mathbf{l}$ characterizing the orientation of a chain element and $\langle\ \rangle$ indicates averaging over the total time of calculations for each NE and over the different initial conditions. Appart from the $P_{1,2}(t)$ values for systems II–V the autocorrelation function

$$M(t) = \langle \mu(\pi,0)\ \mu(\pi,t) \rangle \qquad (6)$$

was calculated for the vector of the dipole moment of a chain which has links with dipole moments of equal value and alternating sign:

$$\mu(\pi,t) = \sum_{p=1}^{N_1-1} (-1)^p \mathbf{l}_p(t) \qquad (7)$$

where $\mathbf{l}_p$ is the vector of the pth unit.

It has been shown[19] that for a long chain $\mu(\pi,t)$ corresponds to the shortest mode of chain motion with the wavenumber $\psi = \pi$. To calculate the quantities of eq 4 and 5 from viscoelastic models to be compared with the results of NE, it is necessary to know the effective diffusion coefficient of a chain particle. Hence, the coefficients of translational diffusion were also calculated. They were determined from the mean-square displacements of chain particles as functions of time.

2. Characteristics of Local Motion in the Viscoelastic Hearst–Harris Model. Phenomenological viscoelastic models are widely used to describe the motion of polymer chains.[25-29] The kinetic units of these models imitate subchains, i.e., chain segments containing a large number of links. Their interaction with the medium is determined by viscous friction whereas the interaction with neighboring chain elements is determined by elastic forces. In the Hearst–Harris (H–H) model[27] the angle between links is prescribed by the introduction of elastic interactions between second-nearest-neighboring elements, which was not taken into account in the earlier model of Kargin-Slonimskii-Rouse.[25,26] For a single "link" in the H-H model, consisting of a relatively large number of elements with the "valence" angle θ, the expression for $P_1(t)$ obtained previously[30] is given by

$$P_1(t) = \frac{\int_0^\pi \Lambda_c^{-1}(\psi) \exp\left[-\frac{t(1-\cos\psi)\Lambda_c(\psi)}{\tau_0} \right] d\psi}{\int_0^\pi \Lambda_c^{-1}(\psi)\, d\psi} \tag{8}$$

where

$$\Lambda_c(\psi) = \frac{1 + 2\cos\theta\cos\psi + \cos^2\theta}{1 - \cos^2\theta} \tag{9}$$

Here ψ is the wavenumber of a normal mode, $\tau_0 \sim \langle l^2 \rangle / D$ is the characteristic time of a single elastic dumbbell (one unit in the H-H model) in the same solvent, D is the translational diffusion coefficient of a chain particle, and $\langle l^2 \rangle$ is the mean square of unit length. In calculating $P_2(t)$ for viscoelastic models the following equation is generally used[31]

$$P_2(t) = P_1^2(t) \tag{10}$$

It should be noted that eq 10 is not valid for a single rigid particle in a solvent. In this case we have

$$P_2(t) = P_1^3(t) \tag{11}$$

3. Calculation of the Rotational Link Mobility. a. Single Link in a Solvent. For a single "monomer" ($N_1 = 2$) both log $P_1(t)$ and log $P_2(t)$ are close to linear functions of t. If they are described by linear dependences with single relaxation times τ_1 and τ_2, respectively, then over the investigated temperature range we have $\tau_1/\tau_2 \approx 2.7$. For the isotropic Brownian motion of a rigid dumbbell in a viscous medium[31,32] one has

$$\tau_1/\tau_2 = 3 \tag{12}$$

The dependence of τ_1/τ_2 on the monomer length l has been investigated previously.[33] It was shown that eq 12 holds for values of $l \gtrsim 1.5$–2. The monomer considered here is of a lower length, $l \approx 0.7$, and this explains the observed discrepancy with hydrodynamic theory.

b. Mobility of a Chain Link. For a link incorporated in a polymer chain the experimental dependence of ln $P_1(t)$ on t is essentially nonlinear, which indicates the occurrence of a relaxation-time spectrum. Figure 2 shows as an example the results for the systems II–IV (chains with different link numbers) at $T = 2.0$. These systems differ slightly in the value of the diffusion constant of solvent particles D_{trans}. For comparison with the H-H model it is necessary to obtain the value of D_{trans} in a given medium. It may be assumed that $\tau_{0,\text{med}}/\tau_{0,\text{sol}} = D_{\text{trans,sol}}/D_{\text{trans,med}}$ where $\tau_{0,\text{med}}$, $\tau_{0,\text{sol}}$, D_{trans}, and $D_{\text{trans,sol}}$ are the values of τ_0 and D_{trans} in the medium (systems II–IV) and in the solvent (system I), respectively. Experimental points for ln $P_1(t)$ fall between the ln $P_1(t)$ curves for an H-H model with "valence" bond angle $\theta = 109° \, 30'$ and $\theta = 120°$. Statistical chain characteristics obtained from NE[19] also give the bond angle value of $109°\,30' < \theta < 120°$. The "experimental" dependence of ln $P_2(t)$ is close to linear over the same range as seen in Figure 2 for ln $P_1(t)$ corresponding eq 10. However, for virtually all systems the "experimental" dependence ln $P_2(t)$ is adequately described by eq 11. Hence, the relaxation of an average cosine of the rotational angle $P_1(t)$ for a unit incorporated in a chain consisting of rigid interacting links both in low molecular solvent (system II) and in more condensed systems (III and IV) occurs in the same manner as the relaxation of the orientation of an element of a viscoelastic H-H model with the same number of elements and the same average angle between them. However, the relationship between the values of $P_1(t)$ and $P_2(t)$ as expressed by eq 11 is valid for the diffusive motion of a single rigid dumbbell in a viscous medium, rather then by eq 10 which is applicable to viscoelastic models. The spectrum of the $P_1^3(t)$ function is narrower than that of $P_1^2(t)$. Thus, it might be suggested that real chains consisting of rigid elements have a narrower spectrum of relaxation times for $P_2(t)$ than that of viscoelastic models.[29]

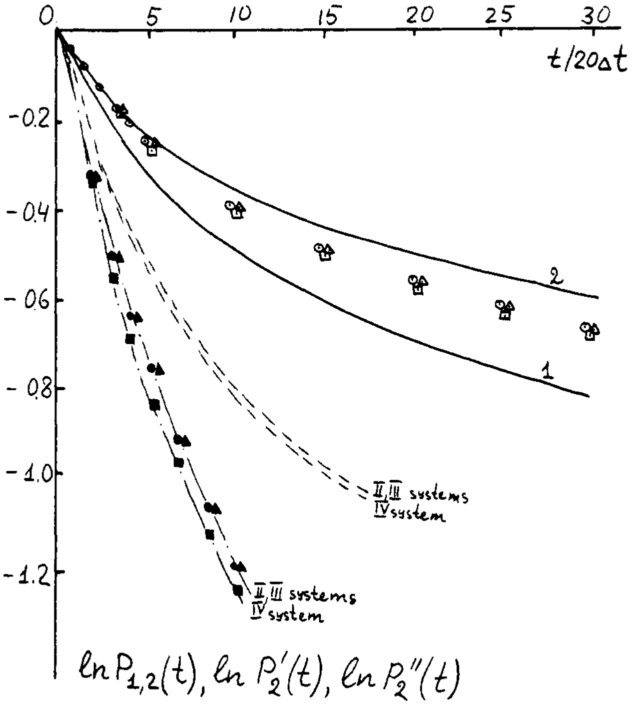

Figure 2. Dependences ln $P_1(t)$ and ln $P_2(t)$ for a chain unit at a temperature T^* of 2.0. Full lines: 1, ln $P_1(t)$ for an H-H model with a θ angle of 109° 30′; 2, ln $P_1(t)$ for an H-H model with a θ angle of 120°. Results of NE for ln $P_1(t)$: ⊙, system II; △, system III; □, system IV. Results of NE for ln $P_2(t)$: ●, system II; ▲, system III; ■, system IV. The dotted line indicates ln $P_2'(t) = 2$ ln $P_1(t)$ and the dashed line ln $P_2''(t) = 3$ ln $P_1(t)$.

c. Dielectric and Luminescent Relaxation Times. Methods of dielectric relaxation (DR) and polarized luminescence (PL) are widely used to study local motions in polymers. In the DR method the relaxation of the projection of the total dipole moment vector on a field direction is investigated. In PL the decay of the fluctuations of the square cosine of the orientation angle of the luminescent marker emitting oscillator is manifested. The properties of PL are expressed by the value of $P_2(t)$ for labeled chain links. The relaxation of the projection of the overall dipole moment of the chain on field direction M_ϵ is determined by the distribution of dipole moments of chain links: $M_\epsilon = \sum_j \mu_j \cos \Theta_j$ were μ_j is the dipole moment directed along the chain link or transverse to it. Only for some particular distributions of dipole moments is DR expressed by the $P_1(t)$ value. This occurs for single dipoles at a large distance from each other along the chain (copolymers with a small amount of a polar component). A similar case is observed when negative and positive values of μ_j alternate randomly along the chain (one of the "transverse" branches of relaxation motions for polar atactic polymers).

Table I
Characteristic Relaxation Times of "Dielectric" (τ_1) and "Luminescent" (τ_2) Types[b]

system	τ_1	τ_2	τ_1/τ_2
I (monomer)	10.7	4.0	2.7
IV (monomer inserted in the chain)[a]	17	5.9	2.9
IV ($\tau(\pi)$)	1.7		

[a] Times for a unit in the chain were determined from the initial slope. [b] Emitting oscillator and dipole are directed along the chain unit.

Hence, the difference in the characteristic times (and relaxation spectra) for DR and PL depends on different time behavior of $\langle\cos\Theta_j\rangle$ and $\langle\cos^2\Theta_j\rangle$ and on the distribution μ_j and orientation of the dipole moments and emitting oscillators with respect to the main chain; i.e., it depends on the specific chemical structure of the main chain, side groups, and markers.

Table I lists as an example comparison of the PL times for an emitting oscillator oriented along the chain link and of the DR times for a single dipole oriented in the same direction and of DR time $\tau(\pi)$ (see ref 6 and 7), corresponding to an alternating distribution of the signs of longitudinal components of μ_j along the chain (e.g., for chains of the CH_2–CHCl type).

For a rigid spherical particle or a rigid dumbbell the standard ratio of times τ_1/τ_2 is 3.[31-33] The results of NE given in Table I show that for identical orientations (along the link) of the oscillator (in PL) and the dipole moment (in DR) the τ_{DR}/τ_{PL} ratio is $\tau_1/\tau_2 = 2.9$, i.e., only slightly lower than the standard value. However, the value of $\tau(\pi)$ is lower than any type of time considered. The calculated values of τ_{DR} and τ_{PL} can be compared to those calculated from the H–H model. The ratios of τ_1 and τ_2 of the same type have already been considered in eq 10 and 11. The ratio $\tau_2/\tau(\pi)$ for the H–H model is equal to 4 for a tetrahedral angle between the elements ($\theta = 109°\ 10'$) and equal to 10.8 for $\theta = 120°$. The $\tau_2/\tau(\pi)$ ratio obtained from NE is close to the value calculated by using the H–H model with $\theta = 109°\ 30'$: $\tau_2/\tau(\pi) = 4$ at $T^* = 1.2$. However, it decreases in our NE slightly with increasing temperature, $\tau_2/\tau(\pi) = 3$ at $T^* = 2.0$ and $\tau_2/\tau(\pi) = 2.5$ at $T^* = 3.3$.

4. Translational Diffusion of Chain Particles. To characterize translational diffusion of the particles of the chain and the solvent the value of the mean square displacement $\langle\Delta r^2(t)\rangle = \langle(\mathbf{r}(0) - \mathbf{r}(t))^2\rangle$ was calculated as a function of time t (the values of the vectors $\mathbf{r}(0)$ and $\mathbf{r}(t)$ represent the coordinates of a particle at the corresponding times). Figure 3 shows the time dependences $\langle\Delta r^2(t)\rangle$ for a middle chain particle, the chain end, and the solvent particle in system IV. This dependence is linear for a free ("solvent") particle and curvilinear for a particle incorporated in the chain. In the time interval considered, this dependence for the chain end is close to a straight line with a slope which is less steep than that of a free particle. Similar results were also obtained for particles of a polymer chain in solution. The curvilinearity of $\langle\Delta r^2(t)\rangle$ for a particle incorporated in the chain reflects the fact that as the displacement of the particle increases, the chain parts increasingly distant from it are involved in the motion. The initial slopes for the end and middle chain particles virtually coincide, whereas the $\langle\Delta r^2(t)\rangle_{\text{end}}/\langle\Delta r^2(t)\rangle_{\text{middle}}$ ratio increases with time and at the end of the time interval considered attains the value of 1.55. For the viscoelastic chain models considered by de Gennes, Jannink, and coworkers[37,38] the dependences $\langle\Delta r^2(t)\rangle$ for particles are also curvilinear and at high t increase as $t^{1/2}$. It is easy to show that for these models, at high t, $\langle\Delta r^2(t)\rangle_{\text{end}} = 2\langle\Delta r^2(t)\rangle_{\text{middle}}$.

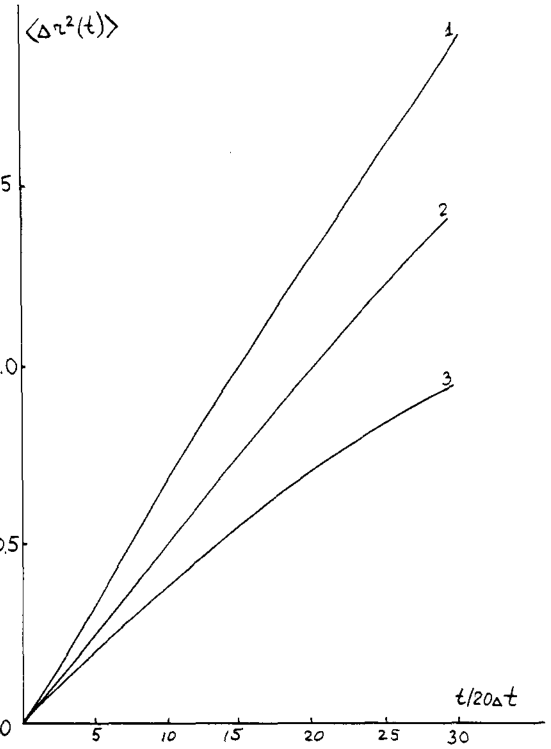

Figure 3. Mean square displacement $\langle\Delta r^2(t)\rangle$ for: 1, a free particle; 2, a chain end; and 3, a middle chain particle vs. time. $T^* = 2.0$ for system IV.

The initial slopes of $\langle\Delta r^2(t)\rangle$ for the terminal and middle chain segments of viscoelastic models coincide with and are equal to the slope of $\langle\Delta r^2(t)\rangle$ for a single particle in the same medium. In our NE the slope of this dependence for a single particle is slightly higher. Probably, this reflects the hydrodynamic effect of the inclusion of a particle into a short rigid bond.

Normal Modes and Cooperative Motions in the Linear Polymer Chain. 1. Characteristics of Cooperative Motions. Viscoelastic models of a polymer chain exhibit a set of normal modes (types of motion), i.e., linear combination $M(\psi)$ of chain-element coordinates x_j

$$M(\psi) = \sum_{j=1}^{N} (x_{j+1} - x_j) \sin j\psi = \sum_{j=1}^{N} u_j \sin j\psi \qquad (13)$$

where x_j is the x coordinate of the jth chain particle, $u_j = x_{j+1} - x_j$ is the projection of the jth chain unit bonding the $(j + 1)$th and the jth particles, and $\psi = k\pi/(N + 1)$ ($k = 1, 2, \ldots, N$) is the wavenumber of the kth normal mode (or the phase shift between the displacements of projections of neighboring chain links). N is the number of chain links.

The autocorrelation functions of these normal modes

$$\rho(\psi,t) = \langle M(\psi,0)\, M(\psi,t)\rangle \qquad (13')$$

(where ⟨ ⟩ is the averaging over a statistical ensemble) decay exponentially with the characteristic relaxation time $\tau(\psi)$

$$\rho(\psi,t) = \rho(\psi,0) \exp[-t/\tau(\psi)] \qquad (14)$$

The dependence of $\tau(\psi)$ on the wavenumber ψ for the simplest model of Kargin–Slonimskii–Rouse[25,26] is given by

$$\tau(\psi) = \frac{2\tau_{\min}}{1 - \cos\psi} \qquad (15)$$

where $\tau_{\min}$ is the minimum relaxation time.

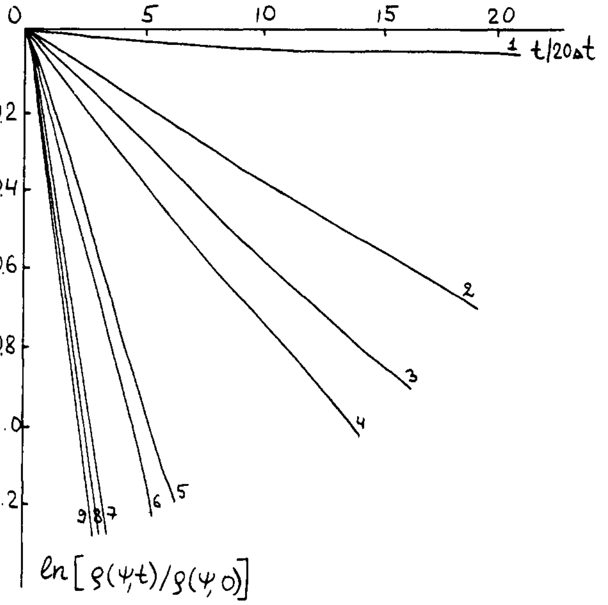

Figure 4. Normalized autocorrelation functions of normal modes for system IV vs. time at different k (where $\psi = k\pi/10$ and $k = 1, 2, \ldots, 9$), $T^* = 2.0$.

For an H–H chain model,[27] where additional elastic interaction leading to chain-bending rigidity is introduced, we have

$$\tau(\psi) = \frac{2\tau_{\min}}{1 - \cos\psi} \frac{(1 - \cos\theta)^2}{1 + 2\cos\theta\cos\psi + \cos^2\theta} \tag{16}$$

where cos θ is the average value of the cosine of the "valence" angle between the neighboring chain elements which is the measure of bending rigidity.

The following problems are considered in the next section: first, to determine whether the exponential dependence (eq 14) characteristic for normal modes (linear combinations $M(\psi)$) is retained in the chain model consisting of rigid interacting links considered here and, second, to find the characteristic relaxation times for this chain model and compare their dependence on the wavenumber ψ with the corresponding dependences for the viscoelastic model.

For this purpose the time autocorrelation functions $\rho(\psi,t)$ have been calculated by NE for various values of the wavenumber ψ.

2. Calculations of Relaxation Times and Normal Modes Analysis. Time dependences of ln $\rho(\psi,t)$ for some values of ψ corresponding to the high-frequency region of the relaxation spectrum (from $\psi = \pi$ to $\psi = \pi/10$) are shown in Figure 4. The variation of ψ from π to $\pi/10$ corresponds to a change in the length of the "wave" $L = 2\pi l/\psi$ characterizing the scale of motion from $L = 2l$ to $L = 20l$. For the slowest large-scale motions considered here ($\psi = \pi/10$), the change in the $\rho(\psi,t)$ value during the time t_{corr} is small, and this prevents a reliable determination of the quantitative characteristics of the corresponding motions. Over the range $\pi/5 < \psi < \pi$ the time dependence of ln $\rho(\psi,t)$ is linear at least up to an e-fold decrease in $\rho(\psi,t)$ as compared to the initial value of $\rho(\psi,0)$. Hence, linear combinations $M(\psi)$ are close to normal modes for this chain model. Relaxation times $\tau(\psi)$ were determined from the slope of ln $\rho(\psi,t) = f(t)$. The dependences $\tau_{\min}/\tau(\psi)$ in Figure 5 are monotonic and for the long chain minimal time $\tau_{\min} \simeq \tau(\pi)$ corresponds to the smallest-scale mode ($\psi_{\min} = \pi$). The results of NE are compared to the corresponding dependences $\tau_{\min}/\tau(\psi)$ for the Kargin–Slonimskii–Rouse model and the Hearst–Harris model with

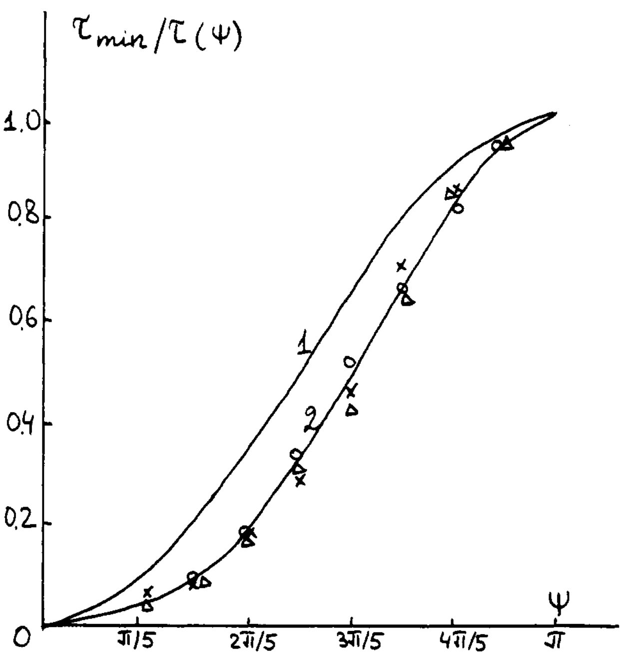

Figure 5. Ratios of relaxation times $\tau_{\min}/\tau(\psi)$ (where $\tau_{\min}$ is the minimal relaxation time) vs. wavenumber ψ for $T^* = 2.0$: ×, system II; △, system III; ○, system IV. Full lines: 1, dependence $\tau_{\min}/\tau(\psi)$ for the subchain model; and 2, the same dependence for the H–H model.

$\cos\theta = -{}^1/_3$, which corresponds to a tetrahedral angle between the bonds. The "experimental" points fall mainly between these two dependences shifting toward the dependence for the H–H model with decreasing temperature.

Hence, for this chain model, linear combinations of chain coordinates exist which relax according to a simple exponential law (eq 14) with a single relaxation time. The shape of these normal modes (coefficients of linear combinations) is similar to that of the normal modes for linear viscoelastic models, i.e., for chains consisting of beads (centers of viscous friction and quasielastic springs). Over the investigated range of $L(\psi) = (2\text{–}10)l$, the dependences of $\tau_{\min}/\tau(\psi)$ are also close to the corresponding dependences for viscoelastic models. It is of great interest that the ψ dependence of $\tau_{\min}/\tau(\psi)$ does not differ from those for linear viscoelastic models of a polymer chain in spite of steric hindrances due to strong nonlinear interactions of chain links distant along the chain. Hence, the correlated motion of chain segments arranged close to each other does not affect the shape of the normal modes and the $\tau(\psi)$ dependences even in a densely packed polymer medium. (This is true at least for local motions.) It is important that the shape of the dependence $\tau_{\min}/\tau(\psi)$ characteristic for viscoelastic models is retained up to the shortest normal modes, the "size" of which is comparable to the length of a rigid bond.

Chain with a Cross-Link. 1. Model. The study of the structure and relaxation properties of cross-linked polymer systems comprises the analysis of the local mobility of both the junctions (or bridges) themselves formed by the cross-linking agent and the chain units in a cross-linked polymer system. At present the relaxation properties of cross-linked systems are being investigated by several methods: NMR, dielectric relaxation, and polarized luminescence (PL). In particular, the orientational mobility of cross-linking bonds can be studied by experiments with labeled chain fragments (PL of EPR) if the marker is introduced directly into the bridge formed by the cross-linking agent.[34] Some authors[35,36] have shown that in polymer systems intramolecular mobility is greatly

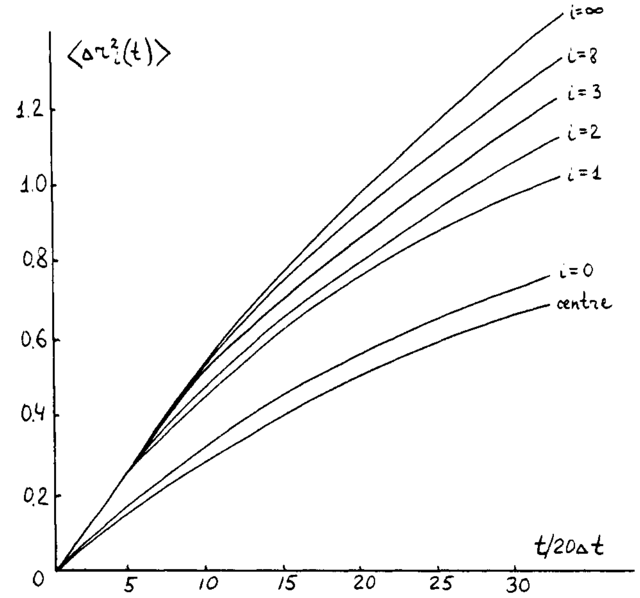

Figure 6. Mean square displacement $\langle\Delta r^2(t)\rangle$ for particles located at a distance i links from the cross-link vs. time t.

dependent on the extent of cross-linking. In this connection a question arises about the origin of the influence of cross-linking on mobility. Cross-linking can hinder the local mobility of chain elements both owing to the existence of kinematic and dynamic constraints along the chain and owing to a change in the local environment of a chain element near a junction in a swollen cross-linked polymer.

The mobility of a cross-link as compared to that of chain parts without cross-linking and the scale and nature of restrictions imposed by it on the local mobility of chain elements depend on the structure, length, and flexibility of the cross-link and the thermodynamic and kinetic flexibility of cross-linked chains.

In this work we considered a chain with one cross-link with average length equal to that of a rigid bond (Figure 1). Two particles distant from each other along the chain but located close to each other in the initial configuration were chosen for cross-linking. An additional "cross-linking" potential between them was assumed

$$U(r) = K\epsilon_0(r^2 - l^2)^2 \qquad (17)$$

where r is the distance between the particles of the cross-link and K characterizes the cross-link rigidity.

The value of the K parameter was chosen in such a manner that the maximal deviation of the cross-link length from the average value l should not exceed 10-15%. NE were carried out at various values of K (9, 18, 36). In the range of K considered, the results were virtually independent of cross-link rigidity (at a given average, cross-link length). The length of the loop formed simultaneously with the cross-link was also varied. No systematic dependence of the results of NE on loop length was observed.

2. Translational Mobility of Cross-Link and Chain Particles. Data of NE on the translational mobility of chain particles and that of the center of the cross-link, as given in Figure 6, show a clearly defined curvilinear time dependence of the square displacement $\langle\Delta r^2(t)\rangle$. This result corresponds qualitatively to the predictions of the analytical theory[37,38] for a viscoelastic model consisting of noninteracting elements. This dependence is connected with successive inclusion into the diffusive motion of increasing chain parts adjoining the given selected particle. NE show that the particles constituting the cross-link experience the slowest motion. As the distance to the cross-link along the chain increases, the time dependence $\langle\Delta r^2(t)\rangle$ of chain segments approaches that for segments of a noncross-linked chain. For example, even for a particle 6th from the cross-link $\langle\Delta r_6^2(t)\rangle$ is equal to $0.9\langle\Delta r_\infty^2(t)\rangle$ (where $\langle\Delta r_6^2(t)\rangle$ and $\langle\Delta r_\infty^2(t)\rangle$ are mean square displacements for the 6th particle from the cross-link and for a particle of the noncross-linked chain, respectively). To obtain the expression for the mean square displacement of the cross-link center $\langle\Delta r_c^2\rangle$ the results of NE for the translational diffusion of particles in the cross-link $\langle\Delta r_0^2(t)\rangle$ and the rotational diffusion of the cross-link itself $P_1(t)$ were used. The value of $\langle r_0^2(t)\rangle$ is expressed as follows:

$$\langle\Delta r_c^2(t)\rangle = \langle\Delta r_0^2(t)\rangle + \tfrac{1}{2}l^2(P_1(t) - 1) \qquad (18)$$

For comparison with the results of NE the time dependence of the mean square displacement of the cross-link center $\langle\Delta r_0^2(t)\rangle$ is obtained for a model of Gaussian subchains with a junction between two chains. This dependence was obtained by generalization of the corresponding derivation for the diffusion of a unit of a chain without branching.[37,38]

The mean square displacement of the bridge (cross-link) center obtained in NE is half that of a particle distant from the cross-link along the chain. The same result is obtained theoretically in a model of Gaussian subchains for a cross-link bonding two chains.

3. Rotational Mobility of Cross-Link and Chain Bond. In the investigation of the rotational mobility of chain elements, just as in that of translational mobility, the main problem was to establish the scale of action of a junction. Time dependences $\ln P_1(t)$ and $\ln P_2(t)$ for the cross-link and for chain elements at various distances along the chain from the junction are nonlinear, which shows that a spectrum of relaxation times exists. Over the range investigated a relationship between the dependences $P_1(t)$ and $P_2(t)$ is observed, $P_2(t) = P_1^3(t)$, just as for the orientational relaxation of a single rigid dumbbell in a viscous liquid[33] and for that of a rigid unit in a chain without cross-linking (Figure 2). The rotational mobility of the cross-link is appreciably lower than that of chain links. However, the effect of the cross-link on neighboring links (dependences $\ln P_1^{(i)}(t)$ and $\ln P_2^{(1)}(t)$ where i is the number of chain elements reckoned from the junction) decreases rapidly with increasing distance from the junction. For the quantitative characterization of the rotational mobility it is possible to introduce characteristic relaxation times $\tau_{1,2}^{i}(\Delta)$, the time during which the corresponding function $\ln P_1^{(i)}(t)$ or $\ln P_2^{(i)}(t)$ decreases by the value Δ. Since during the correlator calculation time $t \leq t_{\mathrm{corr}}$ the value of $\ln P_1^{(0)}(t)$ for the cross-link decreases only by $\Delta = 0.4$, the time $\tau_1(0.4)$ is chosen to characterize the decrease in $\ln P_1(t)$. The value of $\ln P_2(t)$ decreases with time much more rapidly. Hence, to characterize the rate of decay of $P_2(t)$ the usual time of the e-fold decrease in the function $\tau_2(1.0)$ can be used also. Over the range of changes in $P_1^{(i)}(t)$ and $P_2^{(i)}(t)$ considered here the effect of the junction on the orientational mobility becomes apparent only for units directly adjoining the cross-link ($i = 1$). Even for second-nearest neighbors ($i = 2$) the orientational mobility is actually the same as that for units in a chain without the cross-linking. Thus the insertion of a cross-link (bridge), the length of which is close to that of a rigid chain segment, profoundly affects local diffusion and relaxation properties of chain particles located near the cross-link. The mobility of the cross-link itself differs greatly from that of free chain particles. For example, characteristic relaxation times $\tau_1^{(0)}(0.4)$ and $\tau_2^{(0)}(1.0)$ for cross-links are almost sixfold longer than the corresponding times for links in a chain without a cross-link, $\tau_1^{(\infty)}(0.4)$ and $\tau_2^{(\infty)}(1.0)$. For

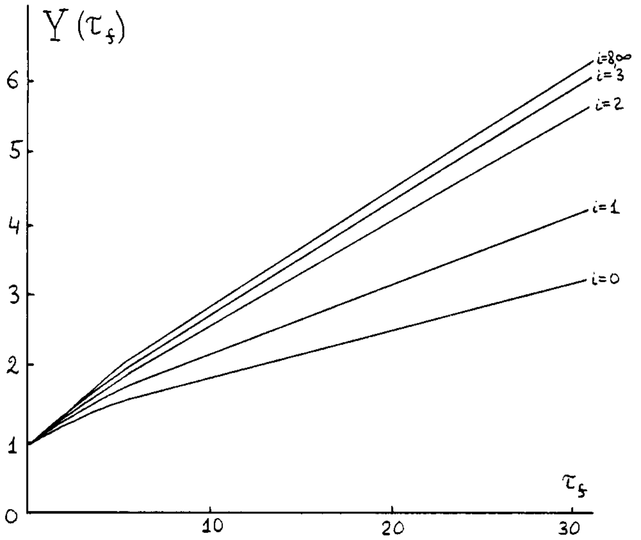

Figure 7. Reduced reciprocal polarization of luminescence $Y = (1/P + {}^1/_3)/(1/P_0 + {}^1/_3)$ (where $1/P$ is the inverse of polarization; $1/P_0$ is the inverse of limiting polarization) vs. the lifetime τ_f of an oscillator in the excited state for the cross-link and for chain elements at a distance of i units from it.

the initial part of the dependence of P_2 we have $\tau_2^{(0)}/\tau_2^{(\infty)} \approx 2$.

The difference between the orientational mobilities of the bridge and the units of a free chain can be determined experimentally in "labeling" dynamic experiments, e.g., by polarized luminescence (PL) if the luminescent marker is incorporated into the cross-link.[34] The dependences $P_2^{(i)}(t)$ obtained in NE were used to calculate the value of the quantity $Y = (1/P + {}^1/_3)/(1/P_0 + {}^1/_3)$ which is measured directly in PL experiments, where $1/P$ is the inverse of polarization of the luminescence and $1/P_0$ is the inverse of limiting polarization. The theory[39] shows that

$$Y = \left(\frac{1}{\tau_f} \int_0^\infty e^{-t/\tau_f} P_2(t) \, dt \right)^{-1} \qquad (19)$$

where τ_f is the lifetime of the oscillator in the excited state, t is the time, and $P_2(t)$ is determined by eq 5. Usually, in PL experiments the dependence of Y on T/η is obtained (T is the temperature and η is the viscosity of the solvent). The slopes of the linear part of the curves $Y(T/\eta)$ at high T/η are used to determine the characteristic time τ_w. Similar information can also be obtained from the dependence $Y(\tau_f)$ at a fixed value of T/η. Figure 7 shows the dependence $Y(\tau_f)$ obtained in NE for a marker inserted in the cross-link and for markers inserted in units located at different distances from the junction along the chain. The usual experimental range of changes in $Y(\tau_f)$ is from 1 to 5–6.[39] In this range the dependences $Y(\tau_f)$ obtained in NE are virtually linear with the exception of a small initial part. The slopes of the linear parts of $Y(\tau_f)$ for a marker in the cross-link and for a marker distant from the cross-link differ two- or threefold. Hence the mean luminescent time τ_w for the cross-link is two or three times longer than that for a marker in the main chain. The value obtained for the time ratio is close to the values obtained for the luminescent marker in junctions of a cross-linked system based on PMMA.[34]

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