

THE MOLECULAR DYNAMICS OF POLYMER CHAINS WITH RIGID BONDS. LOCAL RELAXATION TIMES*

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Local movements of small elements (one or a pair of chain units) of the chain composed of parts joined by rigid bonds have been examined by molecular dynamics. The chain was immersed in a solvent of low molecular weight. The interactions between the particles or between them and similar solvent particles are described by the Lennard-Jones potential. Chains possessing various numbers of units were examined at various temperatures and concentrations. The results of numerous experiments have been compared with the analytical results for the elastic Hearst-Harris model. The relaxation of the average cosine of angles of rotation of the rigid chain elements is identical in practice with that of the equivalent pseudo-elastic elements of the Hearst-Harris model. Each elastic element in the model is equivalent to one rigid chain unit and the average angle between the elements in the elastic model is similar to that between rigid chain units. The relaxation of the mean square cosine of angles of rotation is more rapid than in the elastic model. The ratio of t , the average and the mean square cosine of angles of rotation is similar to that for a separate, rigid, anisotropic particle in a viscous solvent. Pronounced anisotropy of the local relaxation properties is shown to exist; the values of the various times which can elapse in dielectric relaxation and the depolarization of luminescence have been established.

ONE OF the specific features of the polymer chain as a mechanical system is the presence of fixed valency angles and bonds in it; these impose kinematic restrictions upon the shifts and the rates of movements of individual chain parts. As regards the viscoelastic model used nowadays in polymer chain dynamics, the chains consist of deformed, pseudo-elastic elements. If such models are valid in describing larger scale movements, and confirmation of this is found by comparison with the experiment, one remains still doubtful of whether they describe local movements within a scale comparable with the length of a rigid chain part. Furthermore, the medium surrounding the polymer molecule in these models (the solvent, other macromolecules) are regarded as a viscous, continuous liquid. Such a homogenization of the medium must be well founded if the particle dimensions of the surrounding medium are to be comparable with those of the moving chain.

The consecutive consideration of the rigidity of chain units, the discreteness

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of the surrounding medium, as well as of the intra- and inter-molecular reactions of chains can be made by the method of molecular dynamics. This method was used previously [1] to examine a chain model composed of rigid interacting units. The collective deformation-orientation movements appearing in chronological order as linear functions of chain unit projections were mainly investigated. The ratios of the wave numbers to relaxation times were found to be retained, even in such a model in the high temperature range for the respective modes typical of models composed of visco-elastic elements (the Hearst-Harris model [2, 3]).

This report describes the results of examining the local movements of small chain parts on the same model. Such movements are to be found in dielectric, nuclear, magnetic and electron paramagnetic relaxations, in polarized luminescence, etc. In contrast with the work carried out before [1] we investigated the behaviour in time of not only the linear but also the square functions of the cosine of angles of rotation of chain units (Q-functions). In addition to the systems having compacted polymer chains we examine here those in which the chains are present in a low mol.wt. solvent. A model for comparison is also the movement of a single chain unit (monomer) or of two joined together (a dimer) in the solvent.

Description of models. The chain model consists of n_1 particles of weight m joined by rigid bonds of length l . The chain is immersed in a solvent composed of n_2 similar particles. The reactions of all the particles, i.e. of chain and solvent, are described by the Lennard-Jones potential:

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

in which r are distances between the centres of 2 particles; ϵ_0 and σ — parameters of the potential. The whole system fits into a cell of $5\sigma \times 5\sigma \times 5\sigma$ with periodic limiting conditions. The bond length $l=0.69\sigma$ so that the minimum of the reaction energy between two proximate particles in the chain which are not joined by a rigid bond (other neighbours) is given by a tetrahedral "valence" angle between the units. Numerous experiments simulated the movements of the system in some time interval (step Δt) in which the movement equations were solved for all the particles present in the system. The algorithm of the calculation was described in detail by Balabayev and co-workers [4, 5]. A random configuration of the chain particles was selected as the starting point for the numerical experiment, and also of the solvent. The system temperature depends on the full energy given it and is determined [4] from the average of the kinetic energy for one degree of freedom. The numerical values for the temperature were expressed in units of ϵ_0/k , in which k is the Boltzmann constant.

The following systems were dealt with: one "monomer" molecule in a solvent (system I: $n_1=2$, $n_2=106$); one "dimer" molecule in solvent (system II: $n_1=3$, $n_2=105$), and the polymer chain in solvent (system III: $n_1=10$, $n_2=98$; system IV: $n_1=60$, $n_2=58$; system V: $n_1=123$, $n_2=4$).

The complete number of particles present in the system was selected in such a way that the volume of the cell was filled to the same extent by all the systems. The particle volume was that of a sphere of 1.12σ diameter, i.e. the distance of the Lennard-Jones minimum potential (the volume occupied by the polymer chain was calculated while considering the overlap of particles linked by rigid bonds). The temperature was the same for all the investigated systems [1] ($T=1.2$; 2.0 ; 3.3), and the numerical experiment was normally carried out several times for each system by starting out from various configurations; the results were then averaged. Each experiment consisted of 1400–20,000 steps in period Δt (1–2 hr of computer time), $\Delta t=0.004 t_0$, in which $t_0=\sigma\sqrt{m/\epsilon_0}$; all the period of time will be subsequently expressed as Δt . The time interval t_{cor} , in which the time dependence of various correlation functions was studied amounted to $1/30$ of the total counting period, so as to ensure that enough material was available for averaging.

Local movement characteristics. In each experiment the time dependences of the values were calculated

$$P_1(t)=\langle \cos \theta(t) \rangle \quad (2)$$

$$P_2(t)=\frac{3}{2} \left\langle \cos^2 \theta(t) - \frac{1}{3} \right\rangle, \quad (3)$$

$\theta(t)$ is the angle of rotation vector characterizing the orientation of the chain element; the brackets, $\langle \rangle$, meaning the averaging in time of the numerical results.

The selected element was the bond and a pair of chain units. The latter can be modelled as a repetitive unit present in a number of carbon chain polymers. The orientation of the p -th unit was characterized by a single vector, \mathbf{l}_p , pointing downwards and the orientation of the pair of chain units was given by two mutually orthogonal vectors [5]

$$\mathbf{l}_{\parallel}=\frac{\mathbf{l}_p+\mathbf{l}_{p+1}}{|\mathbf{l}_p+\mathbf{l}_{p+1}|} \quad (4)$$

$$\mathbf{l}_{\perp}=\frac{\mathbf{l}_p-\mathbf{l}_{p+1}}{|\mathbf{l}_p-\mathbf{l}_{p+1}|} \quad (5)$$

$P_j(t)$ ($j=1, 2$) will refer to the chain unit from now on, and $P''_j(t)$ to vector \mathbf{l}_{\parallel} , while $P'_j(t)$ to vector \mathbf{l}_{\perp} .

In addition to the $P_j(t)$ values we calculated for the systems III–V the auto-correlation function

$$M(t)=\frac{\langle \mathbf{M}(\pi, 0) \mathbf{M}(\pi, t) \rangle}{\langle \mathbf{M}^2(\pi, 0) \rangle} \quad (6)$$

for the vector with a dipole moment in which the chain has alternating signs in

front and equal values (singular) of dipole moments of the units

$$\mathbf{M}(\pi, t) = \sum_{k=1}^{n_1-1} \mathbf{l}_k (-1)^k \quad (7)$$

We showed in earlier work [1] that $M(\pi)$ equals the smallest-scale mode of chain movements with wave number $\psi=\pi$. The calculations (2) and (3) of the values based on the visco-elastic models make it necessary to know the efficiency coefficients of the diffusion of chain particles. The comparison of the results of experiments with analytical theory in this work therefore required the calculation of the diffusion coefficients.

The characteristics of the local movements in the Hearst–Harris visco-elastic model. The molecular dynamic method had shown [1] the high frequency normal modes for the average chain unit projections and the typical relaxation times for these modes to be the same in our model as those of the Hearst–Harris visco-elastic one [2], namely that the number of elements equals the number of chain units, and that the average angle between elements were close to tetrahedral. The angles between the units in the Hearst–Harris model were given by introducing an elastic reaction between the nearest non-adjacent elements which contrasts with what was done in the Kargin–Slonimskii–Rauz model [6]. The local movement characteristics got here will also be compared with the respective one got on the basis of the Hearst–Harris model.

The expression for $P_1(t)$ got for the individual “unit” of the latter model possessing a fairly large number of elements with a “valence” angle of θ by Gotlib [7] was:

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

in which

$$\lambda_c(\psi) = \frac{1+2 \cos \theta \cos \psi + \cos^2 \theta}{1-\cos^2 \theta}, \quad (9)$$

for which ψ is the wave number of the normal mode; $\tau_0 \sim \langle l^2 \rangle / D$ — typical rotation time of an isolated, elastic rod (dumb-bells — single unit of model) in the same solvent; D — translational diffusion coefficient of the chain parts; $\langle l^2 \rangle$ — mean square chain length.

In the case of the dimer, i.e. a chain consisting of two units (3 parts) one can write for $P_1(t)$

$$P_1(t) = \frac{1}{2} [(1-\cos \theta) e^{-t/2\tau_0(1-\cos \theta)} + (1+\cos \theta) e^{-3t/2\tau_0(1-\cos \theta)}] \quad (10)$$

The initial slope of dependence (10) agrees with that for $P_1(t)$ of the isolated unit (dumb-bell) in the Hearst-Harris model consisting of two parts in the same medium. The $P_1(t)$ measurement for the dumbbell, i.e. the "monomer", is a simple exponential function having the relaxation time τ_0 ,

$$P_1(t) = \exp(-t/\tau_0) \quad (11)$$

According to Gotlib [7] we have for $P_1^{\parallel}(t)$ and $P_1^{\perp}(t)$:

$$P_1^{\parallel, \perp}(t) = \frac{\int_0^{\pi} \frac{(1 \pm \cos \psi)}{\lambda_c(\psi)} \exp\left[-\frac{t(1 - \cos \psi) \lambda_c(\psi)}{\tau_0}\right] d\psi}{\int_0^{\pi} \frac{(1 \pm \cos \psi)}{\lambda_c(\psi)} d\psi} \quad (12)$$

The relaxation for each of the $P_1^{\parallel}(t)$ and $P_1^{\perp}(t)$ values takes place in the case of the dimer by a single, typical time

$$P_1^{\parallel}(t) = \exp[-t/2\tau_0(1 - \cos \theta)] \quad (13)$$

$$P_1^{\perp}(t) = \exp[-3t/2\tau_0(1 + \cos \theta)] \quad (14)$$

The following equation is normally used to calculate the $P_2(t)$ for the visco-elastic models [8]:

$$P_2(t) = P_1^2(t) \quad (15)$$

Condition (15) will not be fulfilled for an individual (separate) rigid part in the solvent, for which one has to use

$$P_2(t) = P_1^3(t) \quad (16)$$

The mobility of the chain unit. The isolated unit present in the solvent, i.e. the "monomer" ($n_1=2$) will have near-linear $\ln P_{1,2}(t)$ functions (Fig. 1). Their description by linear dependences with a single relaxation time (τ_1 or τ_2) means that $\tau_1/\tau_2 \approx 2.5$ in the studied temperature range. For the isotropic Brownian movement of the rigid dumbbell in a viscous medium [9, 10] we get

$$\tau_1/\tau_2 = 3 \quad (17)$$

The τ_1/τ_2 dependence on the length l of the monomer unit was found in earlier work [11] to meet the requirement of eqn. (17) when $l > (1.5-2) \sigma$. The monomer examined in the present work is shorter ($l \approx 0.7\sigma$) which explains the found deviation from the theoretical hydrodynamics.

Dimer. The $\ln P_{1,2}(t)$ dependence for the unit present in the dimer ($n_1=3$; Fig. 2) is non-linear (the calculations were made for a single temperature). The theoretical analysis of the unit in the dimer of the Hearst-Harris model (10) also gives a non-linear $\ln P_1(t)$ function with two relaxation times (also in ac-

cordance with eqn. (15) for $\ln P_2(t)$). A τ_0 value is required for comparison purposes of the $\ln P_{1,2}(t)$ functions found by experiment and the theoretical analysis (for the Hearst-Harris model). As the movement of the dimer is examined in the same medium as that of the monomer, one will naturally take the τ_0 in formulae (8), (10), (13) and (14) to equal τ_1 got for the monomer in accordance

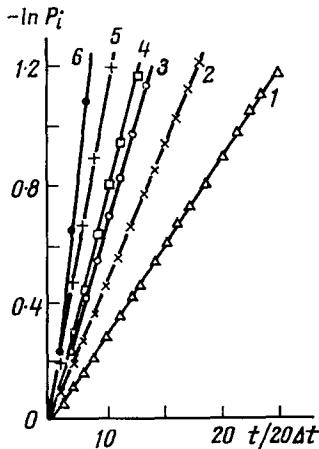


FIG. 1

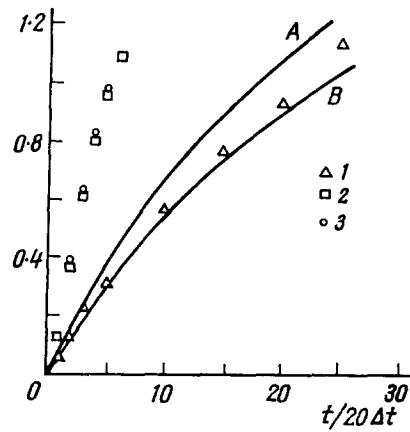


FIG. 2

FIG. 1. The temperature dependence of $\ln P_1(t)$ and $\ln P_2(t)$ for the isolated chain unit in a solvent: 1-3— $\ln P_1(t)$ for T of: 1-1.2; 2-2.0; 3-3.3; 4-6— $\ln P_2(t)$ for T of: 4-1.2; 5-2.0; 6-3.3.

FIG. 2. The dependence of: 1— $\ln P_1(t)$; 2— $\ln P_2(t)$; 3—the unit in the dimer, on $T=2.0$. Continuous lines: analytical solution of $\ln P_1(t)$ for the Hearst-Harris model. A: $\theta=109^{\circ}30'$; B— $\theta=120^{\circ}$.

with eqn. (11). The results of the experiment and of the theoretical $\ln P_1(t)$ function are in close agreement in the examined time interval when the valence angle selected for the Hearst-Harris model is $\theta \approx 120^{\circ}$. The experimental $\ln P_2(t)$ function is very well described by eqn. (16), but not by (15) as is being assumed for the visco-elastic models. The connection in relaxation behaviour of the first and second harmonics of rotation angles (P_1 and P_2 respectively) for the unit in the dimer is the same as for the rigid particle in a viscous medium.

The unit in the chain. The unit included in the polymer chain gives experimental $\ln P_1(t)$ functions which are essentially non-linear; this point to the existence of a relaxation time spectrum. The examples illustrated by Fig. 3 are the results for the systems III-V (branches with various numbers of units) at $T=2.0$. The examined systems have slightly differing diffusion coefficients for the solvent particles (D_{post} ; Table 1). Any comparison with the Hearst-Harris model requires the knowledge of τ_0 in the particular medium. One can say that

$$\tau_0 \text{ ep}/\tau_0 \text{ p} = D_{\text{post. p}}/D_{\text{post. ep}},$$

in which $\tau_{0\text{ cp}}$, $\tau_{0\text{ p}}$ and $D_{\text{post, cp}}$, $D_{\text{post, p}} - \tau_{0\text{-}}$ and D_{post} -values in the medium (systems III-V) and in the low mol.wt. solvent (system I). The experimental $\ln P_1(t)$ points fall within the space between the $\ln P_1(t)$ curves for the Hearst-Harris model for $\theta=109^\circ 30'$ and $\theta=120^\circ$ (8).

TABLE 1. THE TRANSITIONAL DIFFUSION COEFFICIENT D_{post} FOR THE SOLVENT PARTICLES

T	D_{post} -values (in $\sigma^2/20At$ units) for the systems				
	I	II	III	IV	V
1.2	0.56	—	0.46	0.45	0.64
2.0	0.98	0.98	0.86	1.00	1.05
3.3	1.51	—	1.38	1.36	1.39

We found our model [1] that the $\tau(\psi)$ as a function of the wave number of the normal mode ψ is similar to that for the Hearst-Harris model with a valence angle θ which is intermediate between a tetrahedral ($\theta=109^\circ 30'$) and $\theta=120^\circ$. The statistical characteristics of the chain from experiment [1] also gave the same angles. The $\ln P_2(t)$ experimental functions were near-linear in the examined $P_2(t)$ range, but its progress is steeper than that of the $2 \ln P_1$ which is equivalent to eqn. (15). The $\ln P_2(t)$ experimental function is described well by eqn. (16) for practically all the systems. The relaxation of the average cosine of the angle of rotation of the $P_1(t)$ unit incorporated in the chain with rigid, interacting chain units is thus identical in a low mol.wt. solvent (system III) and in more condensed systems (IV and V) with the relaxation of the chain unit orientation of the Hearst-Harris visco-elastic model having the same number of units and average angle between them. The $P_1(t)$ is linked with $P_2(t)$ by eqn. (16) which is correct for the diffusive movement of the isolated, rigid dumbbells in the viscous medium, rather than by eqn. (15). As the spectrum of the $P_1^3(t)$ function is narrower than $P_1^2(t)$ one can assume true chains consisting of rigid elements to have a narrow spectrum of relaxation times for $P_2(t)$ than any visco-elastic model [12].

The anisotropy of local relaxation properties. The presence of a noticeable anisotropy of local relaxation properties had been established on discrete [13] and visco-elastic [7] polymer chain models. This anisotropy becomes apparent in a variety of unit movements rigidly linked into a chain and with differing orientations relative to it. This was noticed specifically in the rates of change of the vector orientation \mathbf{l}_\parallel (4) pointing along the bisected angle between two adjacent dimer units.

The isolated dimer in the solvent. Anisotropy is noticeable already on the isolated dimer in a solvent (system II, Fig. 4a). The $\ln P_1^\parallel(t)$ and $\ln P_1^\perp(t)$ experimental points fall on the linear function for the Hearst-Harris model consisting of two units (eqn. (13) and (14)) with a tetrahedral angle between the two units (the ratio $\omega_1 = \tau_1^\parallel/\tau_1^\perp$ of the τ_1^\parallel and τ_1^\perp relaxation times which typify the slopes of

the $\ln P_1^{\parallel}(t)$ and $\ln P_1^{\perp}(t)$ response lines are close to the theoretical value of $\omega_1 \approx 6$. The $P_2^{\parallel}(t)$ and $P_1^{\parallel}(t)$ are linked by eqn. (16), but the experimental points for the $\ln P_2^{\perp}(t)$ are situated closer to the eqn. (15) response line. This deviation for a rotation around the long axis of the dimer could be due to the small lateral dimension of the latter when compared with the solvent particles size [11]. The anisotropy $\omega_2 = \tau_2^{\parallel}/\tau_2^{\perp}$ is slightly smaller for this reason, i.e. about 4.

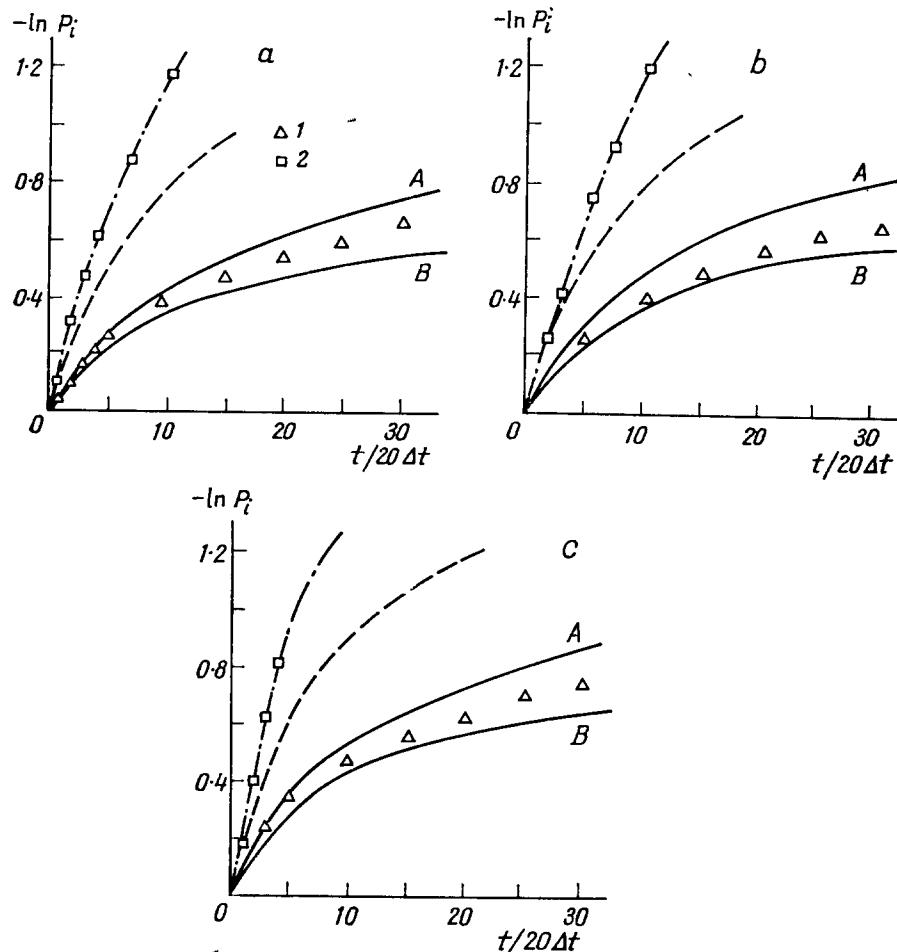


FIG. 3. The $\ln P_1(t)$ and $\ln P_2(t)$ for the central unit in the chain and the systems: *a*—III; *b*—IV; *c*—V, at $T=2.0$. Results of numerical experiments: 1— $\ln P_1(t)$; 2— $\ln P_2(t)$. Continuous lines: analytical solution of $\ln P_1(t)$ for the Hearst-Harris model at *A*— $\theta=109^{\circ}30'$; *B*— $\theta=120^{\circ}$. Dashes: numerical experiment with $2 \ln P_1(t)$. Dots and dashes: $3 \ln P_1(t)$.

The dimer and the chain. The $\ln P_1^{\parallel}(t)$ relaxation is slower for the dimer incorporated in the chain than for the unit (monomer). This value will drop at the lowest of the examined temperatures, i.e. $T=1.2$, to $A \ln P_1^{\parallel}=0.2$, in time

$t_{\text{cor.}}$, and to 0.5 at the highest, i.e. $T=3.3$. The relaxation time of $\ln P_1^{\parallel}(t)$ will be faster at the same time. Figure 4b gives the results for system V ($n_1=123$, $n_2=4$) and $T=2.0$. The $\ln P_1^{\parallel}(t)$ functions are non-linear, which reflects the exist-

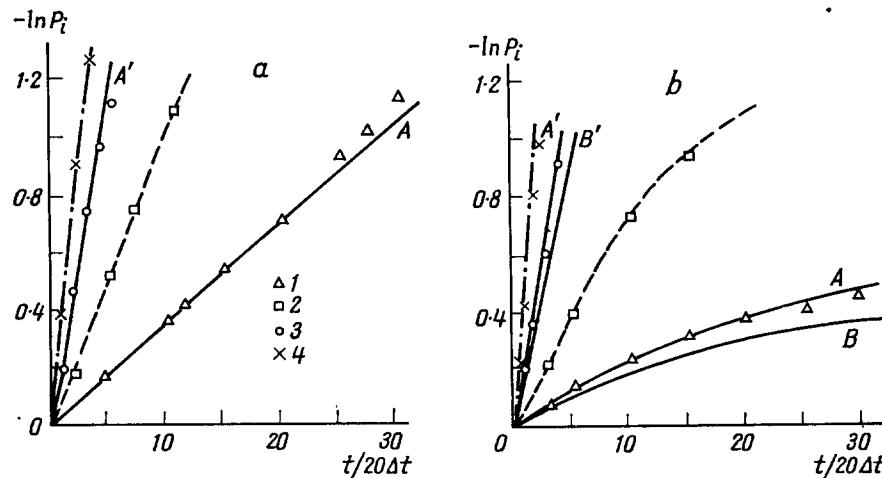


FIG. 4. The $\ln P_{1,2}^{\parallel}(t)$ and $\ln P_{1,2}^{\perp}(t)$ for the isolated dimer in: *a*—the solvent; *b*—the chain, at $T=2.0$. Numerical experiments: 1— $\ln P_1^{\parallel}(t)$; 2— $\ln P_2^{\parallel}(t)$; 3— $\ln P_1^{\perp}(t)$; 4— $\ln P_2^{\perp}(t)$. Continuous lines: analytical solutions for the Hearst-Harris model: *A*, *A'* for $\theta=109^{\circ}30'$, *B*, *B'* for $\theta=120^{\circ}$. *A*, *B*— $\ln P_1^{\parallel}(t)$, *A'*, *B'*— $\ln P_1^{\perp}(t)$. Dashes: line got in numerical experiment for 3 $\ln P_1^{\parallel}(t)$; dots and dashes: for 2 $\ln P_1^{\perp}(t)$.

ence of a time relaxation spectrum. The experimental points for $\ln P_1^{\parallel, \perp}(t)$ will be situated between the curves plotted from eqn. (12) for the Hearst-Harris model at $\theta=109^{\circ}30'$ and $\theta=120^{\circ}$. Correspondingly, the anisotropy $\omega_1(\Delta)$

TABLE 2. THE ANISOTROPY OF LOCAL MOVEMENT $\omega_1(\Delta)$ FOR THE DIMER INSIDE THE CHAIN

T	$\omega_1(\Delta)^*$ values					Hearst-Harris model with "valency" angle of	
	II	III	IV	V			
						109°30'	120°
1.2	7 (0.2)	8.5 (0.2)	11 (0.2)	10 (0.2)	7 (0.2)	13 (0.2)	
2.0	7 (0.4)	10 (0.4)	13 (0.4)	12.5 (0.4)	10 (0.4)	23 (0.4)	
3.3	7 (0.5)	12 (0.5)	13 (0.5)	15 (0.5)	12 (0.5)	30 (0.5)	

* The values in the brackets are the Δ in $P_1(t)$ at which the ω_1 was calculated.

$=\tau_1^{\parallel}(\Delta)/\tau_1^{\perp}(\Delta)$ (Table 2) will be intermediate between the $\omega_1(\Delta)$ for these models. ($\tau \Delta$ —time in which $\ln P(t)$ drops by Δ). The $\omega_1(\Delta)$ for the dimer in the chain is above the ω_1 for the isolated dimer and will become larger with increasing Δ , which is due to the steadily increasing $P_1^{\parallel}(t)$ relaxation times. The connection between $P_1(t)$ and $P_2(t)$ for I_{\parallel} and I_{\perp} when the dimer is present in the chain (as well as for the isolated dimer) will be different. Although the $P_2^{\parallel}(t)$ relaxation

is described well by eqn. (16), the experimental points for $P_2^{\perp}(t)$ in the case of the "lateral" vector will be near the curve (15). This difference is of the same type as for isolated dimer not incorporated in the chain. The $\omega_2(\Delta) = \tau_2^{\parallel}(\Delta)/\tau_2^{\perp}(\Delta)$ for $P_2^{\parallel, \perp}$ is much smaller than the $\omega_1(\Delta)$. For example, $\omega_2(0.2) = 4$ at $T = 1.2$, $\omega_1(0.4) = 3.3$ for system V, and the corresponding $\omega_2(0.2) = 10$, while $\omega_1(0.4) = 12.5$.

TABLE 3. TYPICAL RELAXATION TIMES* OF "DIELECTRIC" (τ_1) AND "LUMINESCENCE" (τ_2) TYPE

System	τ_1	τ_2	τ_1/τ_2
Separate rigid particle	10.7	4.0	2.7
Unit in chain (l_p)	17	5.9	2.9
Dimer in chain (l_p^{\parallel})	36.0	12.5	2.9
Dimer in chain (l_p^{\perp})	4.3	2.5	1.7
$\tau(\pi)$	1.7	—	—

* The relaxation times were determined from the initial slope of the respective curves.

It thus follows from the numerical experiments that the τ_1/τ_2 ratio differs for l_{\parallel} and l_{\perp} , eqn. (16) applying to l_{\parallel} , while the above ratio is smaller than 3 for l_{\perp} . The Hearst-Harris model which well describes the anisotropy for $P_1(t)$ which is linear with respect to the cosine of angles of rotation of chain units make the anisotropy too large for the square values of $P_2(t)$.

Dielectric and luminescence relaxation times. The relaxations of dielectrics and polarized luminescence are widely used to study the local movements in polymers. The first method is used to study the vector projection of the overall dipole moment on to the field orientation. The second method shows the resolutions of the scatter by the quadratic cosine angle of the oscillator orientation for the luminescence marker (relative to the vector of electric excitation by the light). The properties of polarized luminescence are expressed by the $P_2(t)$ values for the labelled chain unit. In contrast with the tensor type of relaxing values to be found in polarized light, the relaxation of the vector projection of total dipole moment of the chain on field orientation M_e depends on the distribution of the dipole moments for the chain units and boils down to the relaxation of linear combinations of $\cos \theta_j$ of the respective dipoles with the external field, $M_e = \sum_j \mu_j \cos \theta_j$, in which M_j —dipole moments pointing in the direction of, or lateral to, the chain units.

The dynamics of dielectric relaxation will be given by the correlation functions of the type $\langle \cos \theta_j(0) \cos \theta_p(t) \rangle$. Only in some specific dipole moment distributions can one express the dielectric relaxation through $P_1(t)$. This will be the case for isolated dipoles remote from each other in the chain (copolymers with a small admixture of a polar component). This situation will also be realized where there is a random alternation of negative and positive μ_j -values along

the chain (one of the "lateral" branches of relaxation movement for polar, atactic polymers). The differences between typical periods (and relaxation spectra of dielectric relaxation and polarized luminescence will depend on differing behaviour in time of $\langle \cos \theta_j \rangle$ and $\langle \cos^2 \theta_j \rangle$, μ_j distributions and dipole moment orientations, as well as luminescence oscillators with respect to the chain axis, i.e. on the actual chemical composition of the main chain, the branch radicals and the labels. Table 3 contains as example the comparison of the polarized luminescence periods for several types of light oscillator orientations and dielectric relaxation times for isolated dipoles orientated in the same way respectively, but also for the dielectric relaxation times $\tau(\pi)$ (eqn. (7)), which is equivalent to an alternation of the signs in front of the longitudinal components μ_j (e.g. for CH_2-CHCl type of chains [14]).

The "standard" $\tau_1/\tau_2=3$ for the rigid, spherical particle or the rigid dumb-bells ((17) and [9, 10]). The results of the numerical experiments given in Table 3 make it clear that identical oscillator orientations (in polarized light—PL) and dipole moments (in dielectric relaxation—DR) will have a $\tau_{\text{DR}}/\tau_{\text{PL}}=\tau_1/\tau_2$ varying within the limits 2–3, i.e. will be slightly smaller on average than the standard. The $\tau(\pi)$ values however will be smaller than any of the examined time types τ_{PL} . The found τ_{DR} and τ_{PL} can be compared with those calculated for the Hearst–Harris model. The correlations of the monotypical τ_1 and τ_2 {(15) and (16)} had been evaluated earlier; as to the correlations of type $\tau_2/\tau(\pi)$, for the oscillators pointing in chain direction for example, this value will be 4 in the case of the Hearst–Harris model for the tetrahedral angle between the units ($\theta=109^\circ 30'$) and 10·8 ($\theta=120^\circ$). The $\tau_2/\tau(\pi)$ ratio got from the numerical experiment was found to be close to that calculated for the Hearst–Harris model with $\theta=109^\circ 30'$ (i.e. 4 at $T=1\cdot2$), but any temperature elevation caused it to drop slightly (to about 3 at $T=2\cdot0$ and about 2·5 at $T=3\cdot3$).

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THE HYDRODYNAMIC AND CONFORMATIONAL PROPERTIES OF POLY-*p*-PHENYLENEOXADIAZOLE IN SOLUTIONS*

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The diffusion coefficients D and intrinsic viscosities $[\eta]$ have been measured for 23 poly-*p*-phenyleneoxadiazole specimens in sulphuric acid. Molecular weights of the specimens have been calculated from the experimental values of D and $[\eta]$ for different theoretically possible values of the hydrodynamic parameter A_0 . It is shown that the experimental data agree well with theories of translational friction and intrinsic viscosity of vermicular chains when values of the molecular parameters are as follows: $A_0 = 3.6 \times 10^{-10}$ erg/deg, monomer unit length $\lambda = 7.2$ Å, Kuhn segment length $A \approx 100$ Å, hydrodynamic diameter of the molecular chain $d \approx 6$ Å. Relationships determining the dependence of D on M_D , and of $[\eta]$ on M_D , are adduced.

POLYPHENYLENEOXADIAZOLES [1-3] are materials that have good thermomechanical properties and are accordingly widely used for the preparation of heat stable synthetic fibres.

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