

DYNAMIC MODELS AND COMPUTER SIMULATION OF LOCAL MOTIONS SHOWN
IN POLARIZED LUMINESCENCE OF LABELED POLYMERS

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Abstract - Theoretical approach to the relationships of molecular mobility manifested in the polarized luminescence involves several problems. (1) The investigation of the mobility of a given chain element unperturbed by a marker ("phantom" marker). (2) The study of heterogeneous dynamic chain models in which the differences between the statistic and dynamic parameters of the labeled element and those of a standard chain element are taken into account. (3) The computer simulation of the rotational mobility of chains containing phantom or real markers. (4) The introducing of the concept of kinetic segment based on the specific features of the kinetics of longitudinal relaxation processes in polymer chains. The experimentally observed relationships of polarized luminescence of labeled macromolecules in solutions and those of some other local relaxation properties are discussed in terms of theoretical treatments mentioned above.

INTRODUCTION

Theoretical analysis of the relationships of molecular mobility manifested in the polarized luminescence of labeled macromolecules in solution involves several problems some of which will be considered in this lecture. (1) The investigation of the mobility of a selected chain element unperturbed by a marker into which a marker is subsequently incorporated. This investigation is carried out with the aid of an analytical theory for viscoelastic dynamic chain models or models consisting of rigid elements. In a given element the direction is selected in which the oscillator of the luminescent marker will be subsequently oriented. In other words, a chain containing a "phantom" marker is considered. (2) The use of heterogeneous dynamic viscoelastic or other "solvable" chain models in which the difference between the statistic and dynamic parameters of the "labeled" element and the parameters of a standard chain element is taken into account. (3) The application of the methods of computer simulation including the methods of molecular and Brownian dynamics to the establishment of relationships of the rotational mobility of chains containing "phantom" and "loading" markers.

SOME PROBLEMS OF THE THEORY OF POLARIZED LUMINESCENCE FOR
DYNAMIC MODELS OF CHAINS CONTAINING "PHANTOM" MARKERS

In the processes of polarized luminescence (PL) the micro-Brownian motion changes the distribution of emission oscillators with respect to the electric vector and the direction of incident light of the exciting emission from the moment of excitation to that of observation (or the emission of the absorbed quantum). If the selected chain element is a three-dimensional body, its orientation in space is determined by three independent angular variables (e.g. three Euler angles). Anisotropic volume element is characterized by the anisotropic tensor of rotational diffusion (with a tri- or biaxial ellipsoid of the diffusion tensor: with the three or two principal values characterizing the diffusion around the three main axes). In the most general case, the anisotropic rotational diffusion of a three-dimensional body (including the selected chain element) is determined by five independent spherical harmonics of the second order. In papers by Dale-Favro, Chuang and Eisenthal, and Woessner et al. a rigorous mathematical theory of this anisotropic diffusion has been developed, in particular, for NMR and polarized luminescence. The theory of rotational diffusion has been developed in connection with the problems of

polarized luminescence for small molecules (mainly axially or spherically symmetrical molecules) in the classical papers by Levshin and Vavilov, Perrin, Weber, Yablonsky, Memming, etc. Wahl and Gotlib have analyzed in detail the manifestation of the Brownian motion in the PL of small molecules containing groups with internal rotation. Subsequently the theory of NMR and polarized luminescence in polymer chains has been developed by many authors (Ullman, Khazanovich, Anufrieva, Gotlib, Torchinskii, Dubois-Violette, Monnerie et al., Wahl et al. (Refs. 1-6) and the bibliography in these Refs.). In recent papers by Yamakawa et al. (Ref. 7) a similar theory has been developed for a polymer chain in which the selected element (subbody) is a three-dimensional body. However, a correct dynamic description is still rather complex and considerable simplifying assumptions are required. Hence, in the subsequent discussion of the dynamics of the polymer chain only simpler dynamic models with an axially symmetrical "linear" chain element (longitudinal or transverse element) will be considered.

In the case of PL the observed value is the inverse degree of polarization of luminescence, $1/P$. The degree of polarization occurring upon the irradiation by natural light is determined by the equation

$$P = (I_z - I_x) / (I_z + I_x) \quad (1)$$

where I_x is the component of intensity of luminescent light observed along the y axis normally to the direction of incident light (axis x) polarized along this direction and I_z is the intensity of luminescent light polarized in the plane normal to the direction of the exciting beam and normally to the direction of observation of luminescence. Sometimes the degree of polarization is introduced according to Tao. For the natural light this degree of polarization is given by

$$r = (I_z - I_x) / (2I_z + I_x) = (2/3) [(1/P) + (1/3)]^{-1} \quad (2)$$

where $2I_z + I_x$ is proportional to the total intensity of luminescent light and also to that of incident light. For irradiation by the light polarized along the z axis the values of P_p and r_p are introduced and it is found that

$$P = P_p / (2 - P_p) \quad \text{and} \quad r_p = (I_z - I_x) / (I_z + 2I_x) \quad (3)$$

Then

$$r_p \text{ (or } r) = (2/3) [(1/P) \pm (1/3)]^{-1} \quad (4)$$

The choice of the values of r and r_p (and not of P and P_p) depends on physical rather than formal considerations since these values are additive if several types of luminescent markers are present or if the markers luminescent in the same spectral region exhibit different value of luminescence parameters (different lifetimes of excitation of the marker and different times of rotational diffusion if the markers are in different dynamic environments). When PL is observed in the simplest case of axially symmetrical (with respect to the initial state) rotational Brownian motion of the emitting oscillator and under steady-state radiation the following simple relationship exists between the PL parameters and the parameters of rotational Brownian motion:

$$Y = (1/P + 1/3) / (1/P_0 + 1/3) = (r_0/r) \quad (5)$$

where the signs \pm correspond to P or P_p , respectively, and

$$(r/r_0) = (3/2\tau_f) \int_0^\infty [\langle \cos^2 \theta \rangle - (1/3)] \exp(-t/\tau_f) dt \quad (6)$$

where τ_f is the lifetime of the luminescent marker in the excited state for the exponential law of emission, $\langle \cos^2 \theta \rangle$ is the mean square cosine of the angle of rotation of the emitting oscillator during the time t from the moment of excitation.

The values of r_0 or P_0 characterize the so-called limiting depolarization of luminescence due to "instantaneous" intramolecular transfer of excitation from absorbing oscillators to emitting oscillators, the value of P_0 appearing for the frozen Brownian motion in glassy state or at a high solvent viscosity. The value of P_0 is determined by the chemical structure of the luminescent group, by its environment and the mutual arrangement of absorbing and emitting oscillators. For the pulsed excitation of luminescence it is possible to observe the evolution with time of individual components of luminescent light $I_x(t)$ (or $I_z(t)$) where t is counted from the moment of switching off of the pulse. In this case the time dependences of decay in the components $I_{x,z}(t)$

are determined by the time dependences of various spherical harmonics of the second order and not only by $P_2(\cos \theta)$.

For relatively simple dynamic models of small molecules (dumbbell, spherical, ellipsoidal or rodlike models for continuous rotational diffusion, hopping-type diffusion and discrete lattice models), the correlation functions for the second harmonics including the simplest harmonic $(2/3)[\langle \cos^2 \theta \rangle - (1/3)]$ for particles with an axial symmetry are directly obtained from the diffusion or kinetic equations. Unfortunately, for most relatively simply solved and analyzed models of a polymer chain, linearized equations only for the average projections of chain units and the corresponding correlators related to $P_1 = \langle \cos \theta \rangle$ have been obtained (Refs. 3,9). The correlation functions of the second order P_2 have been directly determined for chains only in a discrete tetrahedral lattice model by Monnerie et al. (Ref. 10), in which they were found to coincide with P_1 and for Yamakawa's model (Ref. 7), i.e., for a model chain without internal viscosity but exhibiting flexural and torsional rigidity. For this dynamic model (Ref. 7) the solution is possible at certain simplifying assumptions and the qualitative analysis based on this model is difficult.

Hence, as yet we will deal only with an analysis of the relationship between $\langle P_1 \rangle$ and $\langle P_2 \rangle$ and the comparison of results for simpler models and the discussion of simple limiting cases for long and short times. Thus, for a discrete tetrahedral lattice (Monnerie's) chain model the simplest equation is obeyed

$$\langle P_1(\cos \theta) \rangle = \langle P_2(\cos \theta) \rangle \quad (7)$$

For any chain model with a continuous mechanism of motion at small variations of $\delta \langle P_1 \rangle$ and $\delta \langle P_2 \rangle$ for any rigid chain element we have

$$\delta \langle P_1 \rangle = 1/3 \delta \langle P_2 \rangle \quad (7A)$$

Eq. (7A) is obtained by using the expansion

$$\begin{aligned} \langle P_1 \rangle &= 1 - \langle \delta \theta^2 \rangle / 2 + O(\delta \theta^4) \\ \langle P_2 \rangle &= 1 - (3/2) \langle \delta \theta^2 \rangle + O(\delta \theta^4) \end{aligned} \quad (8)$$

at such small δt values for which $O(\delta \theta^4) \ll \langle \delta \theta^2 \rangle$. For diffusion-type motions (when $\delta \theta^2 \sim t$), in contrast to inertial motions for which $\delta \theta^2 \sim t^2$, it is possible to consider the relationship of initial slopes

$$(d \langle P_1 \rangle / dt) = (1/3) (d \langle P_2 \rangle / dt) \quad (9)$$

For a spherically symmetrical particle or a rigid dumbbell isotropic diffusion eqs. (7A) and (9) are obeyed at all t : $\langle P_1 \rangle = \exp[-(t/\tau)]$, $\langle P_2 \rangle = \exp[-(3t/\tau)]$ and

$$\langle P_2(t) \rangle = \langle P_1(t) \rangle^3 \quad (10)$$

According to Wahl and Ullman (Ref. 11), the correlator

$$[\langle (\vec{b}_j(0), \vec{b}_j(t)) \rangle^2 / b^4] = \langle [u_j(0)u_j(t) + v_j(0)v_j(t) + w_j(0)w_j(t)] \rangle^2 / b^4$$

(where u_j, w_j, v_j are the projections of unit vector \vec{b}_j on the Cartesian coordinate axis) is taken as the measure of the value $\langle \cos^2 \theta \rangle$. Then, owing to the specific properties of the chain model consisting of quasi-elastic elements we have $\langle P_2 \rangle \sim \langle u_j(0)u_j(t) \rangle^2 / b^4$ or

$$\langle P_2(\cos \theta) \rangle = \langle P_1(\cos \theta) \rangle^2 \quad (11)$$

This result remains valid under the condition $\langle \cos^2 \theta \rangle \sim \langle u_j(0)u_j(t) \rangle^2$ for any models in which the viscoelastic approximation is introduced for the dissipative function and the potential V_{eff} , and may be obtained by a transition to normal coordinates. This result is also valid for dynamic models with internal viscosity and thermodynamic rigidity. Khazanovich (Ref. 12) also considers the model for quasi-elastic subchain but, in contrast to Ref. 11, the value of $\cos \theta$ for a deformed subchain element is rigorously defined as

$$\cos^2 \theta_j = \langle (\vec{b}_j(0), \vec{b}_j(t)) \rangle^2 / b_j^2(0)b_j^2(t) \quad (12)$$

For this definition of $\cos \theta$ the values of $\langle P_1 \rangle$ and $\langle P_2 \rangle$ are very complex functions of $\langle u_j(0)u_j(t) \rangle$. However, in this case, even at $t \rightarrow 0$, we have

$$(\langle P_1 \rangle / dt) = (1/3) (\langle P_2 \rangle / dt) \quad (13)$$

and only at high t

$$\langle P_2 \rangle \sim C \langle P_1 \rangle^2 \quad (13A)$$

(where $C \sim 0.6$), i.e., the result is again close to that of Wahl-Ullman. Here $C < 1$, which is due to a steeper initial increase in $\langle P_2(t) \rangle$.

Recently Balabaev, Darinskii, Neelov and the present author (Refs. 16,17) have carried out computer simulations of molecular motion by the method of molecular dynamics for the model of a polymer chain consisting of particles bonded by rigid links. The interaction between these particles is described by the Lennard-Jones potential. It was found that in this case also we have $P_2 \sim P_1^3$ up to a decrease in P_2 by a factor of e . Hence, for dynamic models of a chain with a continuous mechanism of motion for short times ($t < t^*$) the relationship between $\langle P_1(t) \rangle$ and $\langle P_2(t) \rangle$ is similar to that for small *rigid* axially symmetrical particles $\langle P_2 \rangle \sim \langle P_1 \rangle^3$. For long times, $t > t^*$, when the rigid element is dragged as a result of motions of large chain parts to which the quasi-elastic approximation is adequately applicable, it may be expected that the relationship $P_2 \sim P_1^2$ is obeyed. The time t^* is of the order of relaxation time for the equilibration between the rigid element and a quasi-elastic chain segment (Gaussian subchain). The dependence $\langle P_2(t) \rangle$ may conveniently be represented over the entire range of t in the form of the empirical equation

$$\langle P_2 \rangle = [A + B \exp(-t/\tau^*)] \langle P_1 \rangle^2 \quad (14)$$

where the values of A , B and t are chosen in such a manner as to satisfy eqs. (10,11,13) taking into account that for long times eq. (13A) should also be obeyed for chains with short-range interaction. Then, we have $A + B = 1$, $A \sim 0.6$ (in a more precise theory may be regarded as a parameter) and

$$\tau_{\text{init}}^{-1}(P_1) \equiv \left. \frac{d\langle P_1 \rangle}{dt} \right|_{t \rightarrow 0} \quad t^* = 0.4 \tau_{\text{init}}(\langle P_1 \rangle)$$

In discussing the relationship between $\langle P_1 \rangle$ and $\langle P_2 \rangle$ it should be borne in mind that for a hopping type diffusion (for the times $t \sim 10^{-8} - 10^{-9}$ s in which we are interested) the relationship between $\langle P_1 \rangle$ and $\langle P_2 \rangle$ ($\tau_{\text{init}}(P_1)$ and $\tau_{\text{init}}(P_2)$) is slightly different compared with eq. (13). Weber (Ref. 18) has considered a cubic discrete model in which a particle has six orientational states along three mutually perpendicular directions. He has used these results for an approximate qualitative modelling and for the description of the diffusion for a particle: a three-axial ellipsoid. Then for a discrete cubic model for isotropic rotational diffusion with a jump by 90° a simple exponential law is valid

$$\langle P_2 \rangle = \exp(-6Wt) = \exp(-t/\tau_2) \quad (15)$$

where $\tau_0 = (1/W)$ is the average time for the expectation of a jump from a initial state into the neighbouring state. It is of interest that for the same model

$$\langle P_1 \rangle = \exp(-4Wt) = \exp(-t/\tau_1) \quad (16)$$

For a discrete hopping-type diffusion cubic model the relative difference between τ_2 and τ_1 , $(\tau_2/\tau_1) = (2/3)$, is less than for continuous rotational diffusion. It is noteworthy that for particles located in a cubic lattice (the case considered above) jumps of $\delta\theta = \theta(t) - \theta(0)$ by angles $\pi/2$ and π are possible. In this case the time evolution of the initial state occurs as a result of changes in two independent functions of time with different relaxation times, one of which determines the time changes in P_1 and the other controls the time dependence of P_2 .

In the statistical physics and in the kinetics of macromolecules the most realistic of possible discrete lattice models is the tetrahedral lattice chain model. A specific feature of the tetrahedral model with *one* value of rotation angle for each hop is the coincidence of time dependences $\langle P_1(\cos \theta) \rangle$ and $\langle P_2(\cos \theta) \rangle$ for both an individual particle and a chain unit. For discrete rotational diffusion of a single element in four "tetrahedral" orientations (e.g., along the directions of four diagonals in a cube) we have

$$\langle \cos \theta \rangle = (3/2) [\langle \cos^2 \theta \rangle - 1/3] = \exp(-4Wt) \quad (17)$$

where W is the average hopping frequency of a particle by a tetrahedral angle. In the general case it may be said that the larger the number of various orientations and the set of hopping angles $\delta\theta = \theta(t) - \theta(0)$ in the system, the greater the difference between the time behaviour of P_1 and P_2 . For continuous diffusion this is the greatest difference as compared to discrete diffusion models for the same spatial dimensionality (planar or three-dimensional models). The dynamics of real chains in solution is characterized by the quasi-continuous mechanism of mobility rather than by a discrete mechanism with multibarrier jumps. Hence, eqs.(10,11) will be mainly used. It is possible that in some cases (or in concentrated systems) discrete jumps can also occur.

The relaxation spectra for $\langle P_2 \rangle \sim \langle P_1 \rangle^2$ (and, even to a greater extent, for $\langle P_2 \rangle \sim \langle P_1 \rangle^3$) are more narrow than for $\langle P_1 \rangle$ and their asymptotic behaviour at $t \rightarrow \infty$ for draining chains is given by $\langle P_1 \rangle^2 \sim t^{-1}$ and $\langle P_1 \rangle^3 \sim t^{-3/2}$, respectively. It should be noted that the corresponding distribution densities $L(\tau)$ of relaxation times (on the $\ln \tau$ scale) behave at $\tau \rightarrow \infty$ as τ^{-1} and $\tau^{-3/2}$ (Refs. 8,28-30). For non-draining polymer chains or chains with volume effects a slightly different behaviour of P_1 (and P_2) at long times is also observed as a result of another dependence $\tau(k)$ at $k \rightarrow 0$ (where k is a wave number of the normal mode). In order to evaluate P_1 and P_2 at high t the relationships $P_1 \sim [\delta r^2 / L^2(\delta r)]$ and $P_2 \sim P_1^2$ are used. Here δr^2 is the mean square displacement of a chain element during the time t and $L(\delta r)$ is the mean contour length of a chain part be carried away during this time so that $\delta r^2 \sim L(\delta r) \lambda_{\text{segment}}$. In the general case of partially or completely non-draining chains with volume effects we have (at $t \rightarrow \infty$)

$$\langle P_1(t) \rangle \sim t^{-\gamma} \quad \text{and} \quad \langle P_2 \rangle \sim t^{-2\gamma}$$

where $\gamma = (2/3)$ for ideal non-draining chains and $\gamma = (4/9)$ for non-draining chains with volume effects. However, in PL (at $\tau_f \sim 10^{-8} - 10^{-9}$ s) the main effects are determined by the behaviour of $\langle P_2 \rangle$ at small t .

The behaviour of $\langle P_1(t) \rangle$ and of polarization of luminescence has been analyzed for chains with different stiffness and internal viscosities (Refs. 13-15) and for dynamic lattice models (Refs. 20,14) by computer simulation including the methods of molecular (Ref. 16,17) and Brownian dynamics (Ref. 19) and by the Monte-Carlo method (Ref. 20). In particular, the results (Refs. 16,17,19) confirm the validity of the expressions $\langle P_2 \rangle \sim \langle P_1 \rangle^3$ and $\tau_{PL} \sim 1/3 \tau_{\text{diel.relax}}$ and the existence of a narrow relaxation spectrum in PL.

The fact following from the theory for the case of high friction and experimentally confirmed is generally applied to the analysis of PL data for the steady-state radiation: all relaxation times τ in the relaxation spectrum for $P_2(t)$ are proportional to solvent viscosity η (at each temperature). For usual experiments, mixed solvents with different η but the same thermodynamic strength are used and the dependence $Y(T/\eta)$ is studied. In some cases, however, quenchers (or polymers with different markers) are used and $Y(\tau_f)$ is studied. The following equation resulting from eqs.(5) and (6) is used:

$$Y = \frac{(1/P) \pm (1/3)}{(1/P_0) \pm (1/3)} = Y(\tau_f T / \eta) \quad (18)$$

The initial slope Y as a function of T/η can be related to the initial relaxation time $\tau_{\text{init}} = \langle 1/\tau \rangle^{-1}$, and the asymptotical slope (at $\tau_f T / \eta \rightarrow \infty$) can be related to the weight-average relaxation time

$$\tau_w = \langle \tau^2 \rangle / \langle \tau \rangle$$

Analysis of experimental data (see, e.g., Refs. 1,2,4,21,22) shows that good agreement between the values of the times of labeled polymers determined by PL and dielectric relaxation times for the same (or similar: poly(styrene) (PS)-poly(p-chloro styrene) (PPChS)) systems reduced to the same solvent viscosity is not always observed. A certain discrepancy between the results and interpretations of various authors is also observed (Refs. 1,2,4). However, for all types of local relaxation times (dielectric, luminescent, NMR and EPR relaxation times) a distinct dependence of relaxation times on solvent strength was observed. When the solvent strength decreases, relaxation times increase ($\tau \sim [\eta]^{-1}$), which is due to an increase in local concentration and the kinetic effect of intermolecular contacts (see Refs. 20,23). The theoretical calculations carried out in Ref. 20 for the lattice chain model by the Monte-Carlo

method have also led to an increase in $\tau(P_1)$ and $\tau(P_2)$ when the solvent strength decreases.

In recent years, in connection with the study of DNA and other relatively stiff biopolymers with the torsional-vibrational flexibility mechanism, several theoretical dynamics in the polarized luminescence of a dye bonded to DNA have been published (Refs. 24,25). The theory for purely transverse torsional vibrations has been developed (Refs. 26,27). In this case, if the accumulation of transverse torsional vibration is taken into account, relatively narrow relaxation spectra rapidly decreasing at $t \rightarrow \infty$ ($P_2 \sim \exp[-\sqrt{t/\tau}]$) are obtained.

The evaluation of longitudinal flexural rigidity at relatively small times (but exceeding the range of initial slope) leads to the dependence $\langle P_2(t) \rangle \sim \exp[-(t/\tau)^{1/4}]$ (compare Refs. 24,8). However, for long times and for long chains the usual power dependence for $P_1 \sim t^{-1/2}$ appears again. For $P_2(t)$ this dependence gives $P_2(t) \sim (1/t)$ for long times.

LOCAL RELAXATION PROPERTIES OF POLYMER CHAINS CONTAINING MARKERS DIFFERING FROM STANDARD SEGMENT

In the study of dynamic properties of the chain by methods using markers (polarized luminescence and EPR) it is necessary to take into account the specific features of dynamic behaviour of the selected chain segment containing a marker and differing from other, i.e., standard segments. For cross-linked or branched polymer systems it is necessary to analyze the motion of a "crosslink" bonding neighbouring chains and adjoining chain units of the same chain. As has been shown (Refs. 29,30), the dynamic problems for simple models of two physically different systems (a "labeled" segment in a homogeneous chain (chain with an "inclusion") and a bridge bonding two long homogeneous chains) are identical and can be considered together. The method of finding the Fourier-transform of $P(t)$ and the Laplace transformation for $P(t)$ for the given element has been considered and the effect of the inclusion parameters on the dynamic properties manifesting in polarized luminescence the simplest case, $P_2 = P_1$, was considered in details. This relationship was used for the qualitative evaluation of the effect of changes in inclusion parameters. A direct calculation of P_1 and P_2 for finite chains containing an inclusion showed that the relative effect of changes in the inclusion parameters on the time behaviour of the values of $P_1(t)$ and $P_2(t)$ is similar. In accordance with the theory developed by the authors of Ref. 30, the inverse polarization of luminescence for a system characterized by the relaxation spectrum as a function of τ_f , the lifetime of an emitting oscillator of the luminescent marker in the excited state, can be obtained if the reduced complex compliance $\chi(i\omega)$ of a system with the same relaxation spectrum is known. On the other hand, $\chi(i\omega)$ is calculated directly from the reaction of the system to a periodical external field $F \exp(i\omega t)$ for which $u_j \equiv u$ is the conjugated coordinate. Then we have

$$[\chi(i\omega)/\chi(0)] = [u(i\omega)/F]/[u(0)/F] \quad (19)$$

Hence, the problem is to find the frequency dependence $u(i\omega)$ where $u(i\omega)$ is the projection of the inclusion segment.

The relationship between $\chi(i\omega)$ and the reduced inverse polarization of luminescence Y characterized by the same spectrum of relaxation times is established in Refs. 29,30

$$Y = \frac{(1/P) + (1/3)}{(1/P_0) + (1/3)} = \left(1 - \frac{\chi(i\omega = 1/\tau_f)}{\chi(0)} \right)^{-1} \quad (20)$$

where P is the polarization of luminescence, P_0 is the limiting polarization and τ_f is the lifetime of a luminescent marker in the excited state. Substitution of the solution for $\chi(i\omega)$ obtained for the corresponding dynamic problem (Ref. 29) into eq.(20) gives

$$Y = 1 + \frac{(2K_1/\zeta_1)\tau_f}{1 + (\zeta/2\zeta_1) [\sqrt{1 + (4K\tau_f/\zeta)} - 1]} \quad (21)$$

where $K_\alpha = (3kT/\ell_\alpha^2)$, ℓ_α is the length of a chain element or a marker and ζ_α is

the friction coefficient (K, ζ for a chain element and K_1, ζ_1 for the marker).

In experiments the dependence of Y on the T/η ratio (where T is the temperature and η is the solvent viscosity) is usually studied. Theoretically the shape of the dependence of Y on T/η is determined by the shape and width of the entire relaxation spectrum assuming that $\tau \sim (\eta/T)$. Figure 1 shows the dependences $Y(x)$ for an infinite chain with an inclusion at various values of the ζ_1/ζ and K_1/K ratios. Here $x = (2K_1/\zeta_1)\tau_f$. In the framework of the sub-

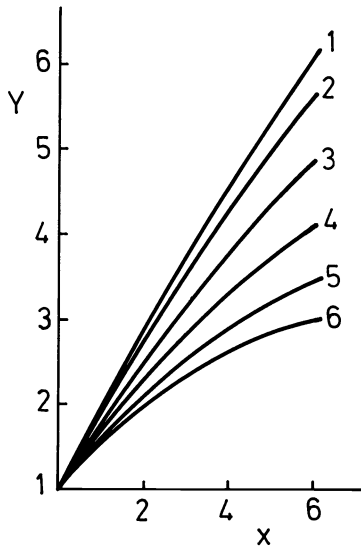


Fig.1. Relative inverse polarization of luminescence Y vs $x = (2K_1/\zeta_1)\tau_f$ for chains containing an inclusion: (1) $K_1/K = 10$, $\zeta_1/\zeta = 10$; (2) $K_1/K = 10$, $\zeta_1/\zeta = 1$; (3) $K_1/K = 1$, $\zeta_1/\zeta = 10$; (4) $K_1/K = 1$, $\zeta_1/\zeta = 3$; (5) $K_1/K = 1$, $\zeta_1/\zeta = 1$; (6) $K_1/K = 1$, $\zeta_1/\zeta = 1/3$.

chain model considered here it is assumed that ζ and $\zeta_1 \sim \eta/T$ and hence $x \sim T/\eta$. It follows from the theory that the initial slope of $Y(x)$ is determined only by the value of K_1/ζ_1 and therefore for this choice of the $Y(x)$ coordinates all dependences $Y(x)$ reduce to the same initial slope. This reduction makes it possible to compare easily the shape of dependences $Y(x)$ at various ζ_1/ζ and K_1/K ratios.

When the hydrodynamic thicknesses of a standard chain element and an inclusion are equal, the only parameter of the problem remains - the ℓ_1/ℓ ratio. In this case the initial slope $Y(\tau_f)$ (or the initial relaxation time) varies monotonically with increasing ℓ (at $\ell_1 = \text{const}$) as a result of additional loading of the marker by the nearest chain units. However, at the fixed finite values of the parameter τ_f/τ_M (where τ_M is the characteristic time of inclusion: $\tau_M = 6kT/\zeta_1\ell_1^2$) a dependence of Y on ℓ/ℓ_1 having a maximum exists. The highest value of Y at a given value of (τ_f/τ_M) is observed at $(\ell/\ell_1)^* = (\tau_f/\tau_M)^{1/3}$. This effect reveals for draining chains and is due to the retardation of diffusion of a chain element at a given δr value with decreasing ℓ (at high t) in accordance with the de Gennes equation

$$\delta r^2(t) \sim \sqrt{\ell}t$$

At high t the following asymptotic relationship is obeyed for the marker

$$P_1 \sim (\ell_1/\ell)^2 [\delta r^2(t)/L^2(\delta r)] \sim (\ell_1^2/\delta r^2)$$

Eq.(21) may be generalized for the case of dynamic models of chains with internal friction. It is relatively easy to obtain the result for a model with short-range internal friction. In this case we have

$$Y = 1 + \frac{(2K_1/\zeta_1)\tau_f}{1 + (2\zeta_1 \int_0^t \tau_f / \zeta_1) + (\zeta/2\zeta_1) [\sqrt{1 + (4\hat{R}\tau_f/\zeta)} - 1]} \quad (22)$$

where ζ_{int} is the internal friction coefficient in a standard chain element, ζ_{int}^* is this coefficient in an element containing a marker and $\hat{K} = K + [\zeta_{int}^* / \tau_f]$. The existence of internal friction greatly increases the degree of involvement of the marker in the chain motion.

INVESTIGATION OF MOBILITY OF A CHAIN CONTAINING A MARKER BY THE BROWNIAN DYNAMICS STUDY

Balabaev, Darinskii, Neelov and the author (Ref. 17) have established by the method of molecular dynamics that the relationship $P_2 = P_1^3$ is adequate for the units of a chain consisting of particles attached to each other by rigid bonds and interacting with each other according to the Lennard-Jones potential. Recently Darinskii, Klushin, Neelov and the author (Ref. 31) have considered the orientational mobility of a chain with hindered internal rotation by the method of Brownian dynamics. Numerical experiments were carried out for a chain consisting of 16 units at fixed valence angles and bonds, and at the symmetrical potential of hindered internal rotation with the barriers $U/kT \sim 0-6$. It was established that even at hindered internal rotation the expression $P_2 = P_1^3$ is still obeyed for both longitudinal and transverse emitting oscillators with relaxation times $\tau_{||}$ and τ_{\perp} , respectively (for the time during which P_2 decreases by a factor of e). The effective activation energy for relaxation times for P_1 and P_2 corresponded to single-barrier transitions and was close to the values obtained directly for the frequencies of corresponding conformational rearrangements (transitions over the single barrier). The increase in the barrier to internal rotation led to a decrease in the anisotropy of relaxation times of local motions, i.e., to a decrease in the $\tau_{||}/\tau_{\perp}$ ratios to the values of $\sim 1.3-1.5$. Previously this effect of internal viscosity has been supposed on the basis of analysis of the properties of viscoelastic models. For chains with hindered internal rotation a marked difference in the mobility of the terminal and inner units (by a factor of ~ 4) was also found, which is in good agreement with the experimental data for polystyrene (Ref. 32) obtained by the methods of polarized luminescence.

KINETIC SEGMENT OF A POLYMER CHAIN IN SOLUTION

The above dynamic models for a polymer chain, the results of computer simulation by the method of Brownian dynamics and the conclusions of the experimental investigations may serve as a basis for introducing the concept of a "kinetic segment" (KS) of a chain in solution. In the statistical physics of macromolecules a "statistical Kuhn's segment" implies a chain segment that may be oriented independently of the orientation of the preceding chain segment. Along the length of the statistical segment the orientational "memory" of the preceding segment is lost. Then it would be natural to define the kinetic segment as a minimum chain fragment which can change its spatial orientation *with time* and make jumps or local bending independently of the neighbouring fragments. This kind of definition of a kinetic segment would be a natural sequence (or condition) of using the lattice rotational-isomeric dynamic chain models. Kinetic segments (or, more precisely, minimum mobile segments) were assumed to be such minimum conformers in which discrete jumps (or hopping rearrangements) were possible from the initial into the final conformation of a chain part. These jumps are compatible with the geometry of the lattice, do not require great stresses of valence angles in KS and are compatible with the fixing of the adjoining chain "tails". In the simplest KS the end bonds were assumed to be coaxial and the jump reduced to the rotation of a kinetic unit as a whole about these bonds. For more complex KS it was assumed that rotations are possible when terminal bond are not necessarily coaxial and these rotations are accompanied by deformation of valence bonds and angles inside the units. In this case only the final and the initial states should be compatible with the lattice (Ref. 33).

Similar definitions have also been introduced for non-discrete or non-lattice dynamic chain models. In Ref. 34 a concept has been introduced of a kinetic segment as a minimum chain fragment for which internal rearrangement of conformation was assumed to be possible as a result of the accumulation of torsional-vibrational displacements with superposed constraints. These constraints included the fixation of the positions and orientations of terminal bonds and the fixation of valence angles and bonds. These conditions directly led to the minimum mobile unit containing five bonds (on the background of an arbitrary chain conformation). The development of the concept of single-barrier transitions (Refs. 35-37) has changed somewhat the approach to the definition of the kinetic segment. For the single-barrier transition the value

of KS may be defined as the minimum length of a chain fragment in which, at the transition of the first unit over the potential barriers, the displacement of the unit in space at the end of the fragment should be less than a definite value ($\sim 1/10$ of the unit size). If this definition is used, a direct experimental detection of KS is difficult but possible, e.g., by studying changes in the mobility of a flexible fragment of a non-homogeneous chain "squeezed" between bulky groups which are not very mobile in a given time interval (see Ref. 38). These above mentioned definitions of KS are kinematic rather than dynamic and do not take into account (with the exception of the last definition) the real dynamic interactions between the neighbouring KS at any types of motion. The a priori possibility of independent rearrangement of neighbouring KS does not imply their dynamic independence. In the real chain kinetics in each normal mode a cooperative motion of a large number of units (and hence of KS) always occurs within the scale fixed by the spatial periodicity $\exp(ijk)$ of a given normal mode $\Lambda \sim (\ell\pi/k)$ units. Alternatively, in each normal mode the "kinetic memory" extends at a distance of the order of magnitude of the wavelength Λ of this mode ($\Lambda \sim (\ell\pi/k)$). Here ℓ is the length of the chain unit.

However, for a dynamically cooperative polymer chain the introduction of the KS concept is possible and useful. This concept may be based on the experimentally observed or theoretically predicted different dependences of relaxation times $\tau(k)$ on external friction (solvent viscosity) and barriers to internal rotation for different normal modes on passing from short modes to longer modes. This definition may be related to other characteristic statistical and kinetic chain scales. As has been shown in Refs. 28,39 the times of cooperative single-barrier transitions are presented to a good approximation for every normal mode with a wave number k in the form corresponding to successive transition over the potential barrier at a local hopping-type motion with the time τ_{loc} and to the overcoming of the external viscous friction drag with the time $\tau_{visc}(k)$

$$\tau(k) \approx \tau_{loc} + \tau_{visc}(k) \quad (24)$$

To a first approximation the value of τ_{loc} is independent of k .

Two ranges of the dependence of $\tau(k)$ follow from Eq.(24). (1) The range of large-scale motions (low k) when $\tau_{loc} \ll \tau_{visc}(k)$. In this range we have $k \ll 1$ and

$$\tau_{visc} \sim [2\tau_{min}/(1-\cos k)](A/\ell) \quad (25)$$

where A is the length of the statistical segment and ℓ is the length of a rigid element in a given dynamic model (e.g., a monomer unit). This range may be called the range of segmental motion controlled by the viscosity of the external medium (solvent). The thermodynamic stiffness of the chain is contained in τ_{visc} in the form of the factor (A/ℓ) . (2) The range of local motions in which $\tau_{loc} > \tau_{visc}$. Relaxation times in this range are controlled by the height of barriers to internal rotation and by external viscosity in the form of the pre-exponential factor in τ_{loc} (in the case of high external friction). The values of τ_{min} calculated per a monomer unit for common carbon chain polymers poly(methyl methacrylate) (PMMA), poly(styrene) (PS), poly(*p*-chloro styrene) (PPChS) may be estimated either from the effective size of the unit and the local viscosity of solution ($\tau_{min} \sim 3\eta V_{unit}/kT$) where V_{unit} is the hydrodynamic volume of the unit, or from the data on dielectric relaxation of hydrogenated monomers. The values of A/ℓ are estimated from the data on conformational statistics (from dimensions, optical anisotropy and dipole moments). Finally, the values of τ_{loc} are manifested in dielectric relaxation, polarized luminescence, EPR (with the correction for the effect of the marker) and in NMR. The typical values, for example for PS (or its dielectrically active analogue, PPChS) at $\eta=0.6$ cp, are given by

$$\tau_{min} \sim 10^{-11} \text{ to } 10^{-10} \text{ s}; \tau_{loc} \sim 4 \times 10^{-9} \text{ s}; (A/\ell) \sim 8 \text{ to } 10 \quad (26)$$

It follows from Eq.(26) that, when k changes, τ_{visc} is varied from the values of $\tau_{min} \ll \tau_{loc}$ to

$$\tau_{max}(Z) \sim \tau_{min} Z^\alpha \gg \tau_{loc}$$

Here Z is the degree of polymerization. In the first range, the times $\tau(k) \sim \tau_{loc}$ and weakly depend on k and, in the second range, they strongly depend

on k ($\sim k^{-2}$ for draining chains or $k^{-\alpha}$ in other cases ($1.5 < \alpha < 2.2$)). The condition of transition from the first to the second range may be written as

$$\tau_{\text{visc}}(k^*) \approx \tau_{\text{loc}} \quad (27)$$

when the evaluations in Eq.(26) are valid; $k^* \ll \ell$ and at $k < k^* < \ell$, we have

$$\tau \approx (4\tau_{\text{min}}/k^2)(A/\ell) \quad (28)$$

For chains with non-screened hydrodynamic and volume interactions at low k we have $\tau \sim k^{-\alpha}$ and all subsequent considerations may also be extended to this case in which the numerical evaluations will change slightly. Now it is convenient to introduce the concept of KS assuming KS to be a minimum chain segment of such length A^* or with such number of units s^* that for normal modes with the $s^* \sim (\pi/k^*)$ relaxation times are described by the same dependence on k as for a chain consisting of freely-jointed elements (or Gaussian subchains) and are controlled *only* by the external viscosity of the medium. If the phase shift $\Psi = s^*k$ between neighbouring KS is introduced, then eq.(28) is given by

$$\tau \approx (4\tau_{\text{min}}/\Psi^2)s^{*2}(A/\ell) = [4\tau(s^*)/\Psi^2](A/\ell) \quad (29)$$

In Ref. 31 a definition of KS similar in the physical meaning has been introduced: a real chain was represented from the very beginning by a sequence of freely-jointed rigid three-dimensional ellipsoids or rods. This definition made it possible to take into account local hydrodynamic effects. Then the lengths of chain portions corresponding to the length of KS were evaluated from the comparison of calculated and experimental local relaxation times. The principles and results of this method are close to those of the foregoing method. Similar reasoning was also used in some experimental papers. The evaluations made by Klushin and the author give for carbon chain polymers the values of $A^* = 10-15$ monomer units. This is the order of magnitude of the length of a statistical segment for these polymers. Only in such a kinetically and statistically flexible polymer as polyoxyethylene, KS is shorter than the statistical segment. Alternatively, common carbon chain polymers in solution should be regarded as polymers with considerable local internal viscosity and characteristic length of KS of the order of magnitude of the length of the statistical segment.

The above definition of a kinetic segment is based on the specific features of the kinetics of longitudinal relaxational processes manifested in the factor $2(1-\cos k)$ (eq.(25)). In contrast, for transverse relaxation processes, if internal viscosity (high barriers to internal rotation) and thermodynamic rigidity exist and if the accumulation of rotational or vibrational displacements are taken into accounts a relatively narrow relaxation spectrum is exhibited for long chains. If the barriers to internal rotation are high, then for transverse processes even for the longest modes ($k \rightarrow 0$) relaxation times are also controlled mainly by internal friction (jumps over the barriers) and are controlled by the external friction only in the form of the pre-exponential factor. This difference between transverse and longitudinal relaxation processes may be responsible for certain experimental facts which have not yet been adequately explained. The processes of dielectric relaxation observed in carbon chain polymers (e.g., in PPChS) in solution should be treated as transverse relaxation processes. These dielectric relaxation processes are characterized by the values of activation energy (21-29 kJ/mol) exceeding those for viscous flow. However, for the processes occurring in the same time interval (10^{-8} to 10^{-9} s) observed by polarized luminescence in the same (or similar) polymers with luminescent markers, relaxation times are characterized by the activation energy close to that for viscous flow. This effect has been studied in detail for PMMA (Refs. 1,2). A possible simple explanation for this effect is that the presence of the marker prevents rotational isomerization in the adjoining chain part, and in the experimental range of values of inverse polarization, only torsional-vibrational relaxation is observed. Another most probable reason may lie in the fact that if a bulky marker is incorporated in the chain the longitudinal relaxation spectrum of the adjoining chain parts is excited. The larger-scale motions arise comparable in the length to the kinetic and statistical segments. In this case the relaxation times are to a greater extent controlled by solvent viscosity and are less sensitive to small-scale hoppings. Additional loading and increasing rigidity of a chain segment by a marker may lead to an increase in the contribution of larger-scale modes and to a lower value of the effective activation energy of the local process.

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