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Torsional Vibrations of Ester Groups as a Mechanism of Dielectric Relaxation of Poly(*p*-hydroxybenzoic Acid)

Marina G. Saphiannikova,* Natalia V. Lukasheva, Anatolii A. Darinskii, and Yulii Ya. Gotlib

Institute of Macromolecular Compounds, Russian Academy of Sciences, Bol'shoi pr. 31, 199004 St. Petersburg, Russia

Jürgen Brickmann

Institut für Physikalische Chemie I and Darmstädter Zentrum für Wissenschaftliches Rechnen, Technische Hochschule Darmstadt, Petersenstrasse 20, D-64287 Darmstadt, Germany

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ABSTRACT: Dielectric relaxation of poly(*p*-hydroxybenzoic acid) (PHBA) due to torsional vibrations of the dipoles of ester groups in the main chain is considered. A dynamic model of elastically coupled rotators interacting with the crystal lattice is applied. The model is characterized by two sets of force constants which determine intrachain correlations between rotators along a given chain and interchain interactions in the crystal lattice. Correlation functions for the cosines of the rotation angles of different rotators in a chain are calculated. Fluctuations of the components of dipole moments normal to the chain axis (transverse components) and fluctuations of the components along the chain axis (longitudinal components) are considered. The transverse component is connected with the previously considered crank-shaft type of internal rotational motions of ester groups. The origin of the longitudinal component is ascribed to a complicated superposition of internal rotations and bending vibrations. The fluctuations of the transverse and longitudinal components depend on intrachain and interchain interactions, and their contributions to the dielectric relaxation of PHBA are comparable in magnitude. The thermal averaged magnitude of fluctuations of the total dipole moment is calculated. The calculated results are compared with experimental data on the dielectric relaxation of PHBA and also with predictions based on previous molecular mechanics calculations. It is concluded that consideration of only transverse fluctuations of the dipole moment does not provide an adequate description of the experimentally observed dielectric relaxation of PHBA. On the contrary, consideration of a superposition of both transverse and longitudinal contributions results in good agreement with experiment using force constants estimated from torsional potentials (calculated by the AM1 method) and from the experimental activation energy. The activation energy corresponding to dipolar motions in noncrystalline regions of a PHBA bulk sample is obtained from the experimental dielectric relaxation.

1. Introduction

The homopolyester of 4-hydroxybenzoic acid (PHBA) is a polar macromolecule which according to X-ray data[1−4] can exist in two conformations. We will refer to them as cis and trans. In the cis-conformation the oxygen atoms of neighboring carbonyl groups are found to be at opposite sides of the main chain; in the trans-conformation these atoms are located at the same side.[5] The trans-conformation is observed only in homopolymers with low degrees of polymerization at room temperature (phase II).[1,2] In all other phases—the low-temperature phase I and two high-temperature phases III and IV—the PHBA chains exist in the cis-conformation.[1,3,4] In the cis-conformation the signs of the transverse projections of the dipole moments normal to the main chain alternate along the chain (Figure 1). Therefore, the transverse projection of the total dipole moment **M** of the PHBA chain is equal to zero in a regular chain conformation. The directions of the longitudinal projections of all the dipoles coincide; therefore, every chain has a considerable longitudinal component of **M** which is proportional to the degree of polymerization. However, in a highly ordered crystalline sample, the chain cannot reorient as a whole and the total dielectric relaxation is related only to small fluctuations of dipole moments near their equilibrium positions. Thus, the contributions from both transverse and longitudinal components of the total dipole moment may be important.

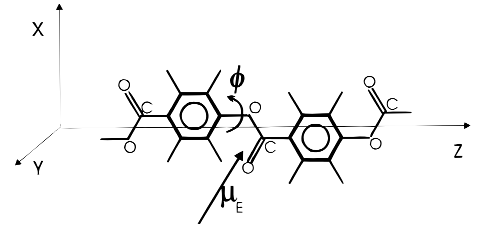

Figure 1. PHBA chain in the cis-conformation. The rotation of the ester group around a long bond of the main chain is shown by a curved arrow.

Kalika and Yoon[6] studied the dielectric relaxation of PHBA near the transition from the crystal phase to the smectic−E −like phase beginning at 325 °C. They measured the dielectric susceptibility as a function of frequency and found the value of the dielectric strength $\Delta\epsilon = \epsilon_0 - \epsilon_\infty$. Here, ϵ_0 is the static susceptibility, and ϵ_∞ is the infinite frequency limit. The measured value of the dielectric strength was found to be between 0.7 and 1.0 for different samples. It was compared to that calculated using Onsager's formula[7] for an isotropic system of freely rotating dipoles with each dipole

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moment equal to the transverse projection of the dipole moment of an ester group. Kalika and Yoon[6] interpreted the calculated result using an approximate model where some of the dipoles were assumed to perform free unhindered rotation and the others were completely fixed. From this comparison the effective fraction of freely rotating dipoles was found to be between 0.18 and 0.25 for different samples.

It is known, however, that bulk PHBA is a rather highly ordered crystal at the temperatures considered[1,4] and the existence of a significant fraction of freely rotating groups seems questionable. Therefore, we wish to consider in this work a more realistic dynamic model which assumes a superposition of different types of vibrations compatible with the crystal lattice.

In this paper we calculate the contribution to the dielectric strength $\Delta\epsilon$ from a single long PHBA chain embedded in a crystalline environment. A simplified approach based on a model of elastically coupled rotators interacting with an external molecular field (i.e., with the crystalline environment) will be applied to describe the motions of the ester groups. This approach enables us to estimate the contribution of different types of vibrations of ester groups both to the transverse and longitudinal fluctuations of the total dipole moment of a PHBA chain. If carbonyl groups are only allowed to change their orientations due to rotation around the $C_{AR}-O$ bonds, where C_{AR} is the carbon atom of a benzene ring, then only fluctuations of the transverse component of the total dipole moment are allowed (Figure 1), since the longitudinal projections of ester groups do not vary during rotational motions of this type. Actually, there are also fluctuations of the longitudinal component of $\mathbf{M}$ which should be taken into account. These can occur if rotation around the (CO)−O bond is also considered. According to semiemperical calculations of the intramolecular energy of PHBA, these ester motions should lead to vibrations with only very small amplitudes.[8] However, the contributions of these ester vibrations to the dielectric relaxation of PHBA can be substantial.

The paper is organized as follows. The model is described in section 2. Sections 3 and 4 contain general formulas for fluctuations of the transverse and longitudinal components, respectively. The evaluation of average correlation functions is performed in section 5. In sections 6 and 7 the results are discussed and some conclusions are made.

2. Model

The well-known Onsager theory (valid for isotropic systems composed of molecules with free unhindered rotation) leads to the relation between the dielectric strength $\Delta\epsilon$ and the dipole moment μ_E of a given group (under vacuum):

$$\Delta\epsilon = \frac{4\pi N}{3k_B T}\frac{3\epsilon_0}{2\epsilon_0 + \epsilon_\infty}\left(\frac{\epsilon_\infty + 2}{3}\right)^2 {\mu_E}^2 \tag{1}$$

where N is the number of dipole groups per unit volume, k_B is the Boltzmann constant, T is the absolute temperature, ϵ_0 is the static susceptibility and ϵ_∞ is that at an infinitely high frequency.

According to the more rigorous Kirkwood−Fröhlich approaches,[7] which take into account intermolecular interactions and hindered rotation, the ratio of the measured value of the dielectric strength to that calculated using the Onsager formula (eq 1) gives the value of the correlation factor g which depends on the polymer structure and the type of ordering:

$$g = \frac{\langle\delta\mathbf{M}^2\rangle}{N{\mu_E}^2},\quad \langle\delta\mathbf{M}^2\rangle = \langle\mathbf{M}^2\rangle - \langle\mathbf{M}\rangle^2 \tag{2}$$

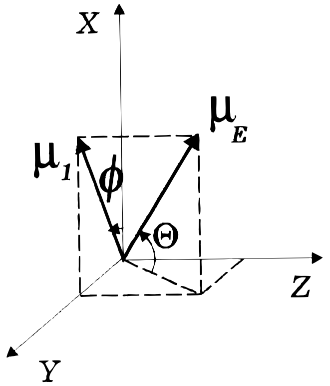

Figure 2. Dipole moment of an ester group μ_E and its transverse projection μ_1 onto the XY plane.

Here, $\langle\delta\mathbf{M}^2\rangle$ represents fluctuations of the total dipole moment $\mathbf{M}$ of the real chain (the angular brackets denote the ensemble average), and $N{\mu_E}^2$ is the value of $\langle\delta\mathbf{M}^2\rangle$ for a long chain without statistical correlations between dipoles, i.e., for freely rotating dipoles.

We consider the possible types of local motions of a given ester group. A Cartesian coordinate system is introduced with a Z axis which coincides with the chain axis (Figure 1). At equilibrium the dipole moment vector of every ester group lies in the XZ plane and makes a polar angle $\Theta = \pm\Theta_0$ with the Z axis. The direction of the Z axis is chosen in such a way that dipole moment projection onto this axis is positive and the sign of the dipole moment projection onto the X axis alternates for neighboring ester groups in the chain. If the dipole moment vector deviates from the XZ plane, its projection on the XY plane makes an azimuthal rotation angle $\phi \in [0,2\pi]$ with the X axis (Figure 2). We assume that the polar angle Θ and rotation angle ϕ only slightly deviate from their equilibrium values $\pm\Theta_0$ and $\phi_0 = 0$ (or π), respectively. Then, the motion of an ester group can be separated into two independent motions: rotation around the Z axis connected with the variation of rotation angle ϕ at Θ = constant and vibrations in the XZ plane with slight variations of the polar angle Θ. These motions will be referred to as the transverse and longitudinal motions, respectively. Note that these terms are somewhat conditional, since changing Θ leads to variations in both the longitudinal and the X-component of the dipole moment of the ester group. In this approach fluctuations of the transverse component of the chain dipole moment $\delta\mathbf{M}_T$ are a function of all $\delta\phi_j$, where $\delta\phi_j$ is a small deviation of the rotation angle, ϕ_j, from its equilibrium value ϕ_0 for the jth ester group. Fluctuations of the longitudinal component $\delta\mathbf{M}_L$ are a function of all $\delta\theta_i$, where $\delta\theta_i$ is a small deviation of the polar angle, Θ_i, from its equilibrium value $\pm\Theta_0$ for the ith ester group.

We assume in this approach that torsional vibrations governing the variations of ϕ and bending motions governing the variations of Θ are independent in the first approximation, so that the potential energy of the chain can be written as

$$U(\delta\phi,\delta\theta) = U_1(\delta\phi) + U_2(\delta\theta) \quad (3)$$

and therefore does not depend on cross-terms such as $\delta\phi_j\delta\theta_i$.

We consider only small torsional vibrations of ester groups; then the potential energy $U_1(\delta\phi)$ can be represented in a quadratic form:

$$U_1(\delta\phi) = \frac{1}{2}K_1\sum_{j=1}^{N}(\delta\phi_j - \delta\phi_{j-1})^2 + \frac{1}{2}K_2\sum_{j=1}^{N}\delta\phi_j^{\,2} \quad (4)$$

where the force constant K_1 defines the interactions between elastically coupled rotators along the PHBA main chain and the force constant K_2 defines the interactions of dipoles of a given chain with the crystalline environment.

Correspondingly, the potential energy $U_2(\delta\theta)$ is assumed to be given by a similar expression:

$$U_2(\delta\theta) = \frac{1}{2}K_1'\sum_{j=1}^{N}(\delta\theta_j - \delta\theta_{j-1})^2 + \frac{1}{2}K_2'\sum_{j=1}^{N}\delta\theta_j^{\,2} \quad (5)$$

where the force constant K_1' defines the interactions between elastically coupled rotators along the chain and the force constant K_2' defines the interactions of dipoles of this chain with the crystalline environment.

Therefore, in this linear one-dimensional approximation the hypothetical dynamic model is described by four force constants: K_1, K_1' and K_2, K_2'.

3. Fluctuations of the Transverse Component of the Chain Dipole Moment

In this case, the polar angles, Θ_i, are fixed and only the rotation angles $\phi_j \in [0,2\pi]$ vary. They are measured with respect to their equilibrium states which for even ester groups coincide with the positive direction of the X axis and for odd groups with the negative direction of the X axis (Figure 3). We consider an even number of ester groups in the chain, so that $N = 2k$, and we can write for the X- and Y-projections of the total dipole moment

$$M_x = \mu_1\sum_{j=1}^{k}(\cos\,\delta\phi_{2j} - \cos\,\delta\phi_{2j-1}),$$

$$M_y = \mu_1\sum_{j=1}^{N}(\sin\,\delta\phi_{2j} - \sin\,\delta\phi_{2j-1}) \quad (6)$$

where $\mu_1 = \mu_E \sin\Theta_0$ is the transverse projection of the dipole moment vector of an ester group, i.e., the component lying in the XY plane.

The symmetry of the considered distribution of dipole moments leads to $\langle M_x\rangle = \langle M_y\rangle = 0$ and, consequently,

$$\langle\delta\mathbf{M}^2\rangle_T = \langle\mathbf{M}^2\rangle_T = \langle M_x^{\,2}\rangle + \langle M_y^{\,2}\rangle \quad (7)$$

Then, fluctuations of the transverse component of the total dipole moment $\langle\delta\mathbf{M}^2\rangle_T$ are equal to

$$\langle\delta\mathbf{M}^2\rangle_T/\mu_1^{\,2} = N + 2\sum_{j=1}^{k}\sum_{l>j}^{k}\{\langle\cos(\delta\phi_{2j} - \delta\phi_{2l})\rangle + \langle\cos(\delta\phi_{2j-1} - \delta\phi_{2l-1})\rangle\} - 2\sum_{j=1}^{k}\sum_{l=1}^{k}\langle\cos(\delta\phi_{2j} - \delta\phi_{2l-1})\rangle \quad (8)$$

4. Fluctuations of the Longitudinal Component of the Chain Dipole Moment

In this case, the rotation angles, ϕ_j, do not change and only the polar angles, Θ_i, deviate from their equilibrium values, $\pm\Theta_0$. As above, we consider an even number of ester groups in the chain (Figure 4). Thus, we obtain for the X- and Z-projections of the total dipole moment

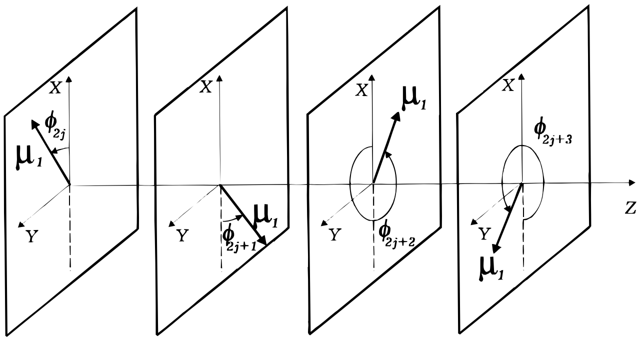

Figure 3. Schematic diagram of transverse vibrations in a PHBA chain.

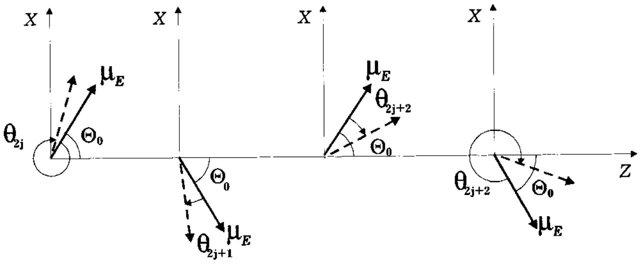

Figure 4. Schematic diagram of longitudinal vibrations in a PHBA chain.

$$M_x = \mu_E\sum_{j=1}^{k}[\sin(\Theta_0 - \delta\theta_{2j}) - \sin(\Theta_0 + \delta\theta_{2j-1})] \quad (9)$$

$$M_z = \mu_E\sum_{j=1}^{k}[\cos(\Theta_0 - \delta\theta_{2j}) + \cos(\Theta_0 + \delta\theta_{2j-1})] \quad (10)$$

The symmetry of the distribution of dipole moments leads to $\langle M_x\rangle = 0$, and, consequently,

$$\langle\delta\mathbf{M}^2\rangle_L = \langle M_x^{\,2}\rangle + \langle M_z^{\,2}\rangle - \langle\mathbf{M}\rangle_L^{\,2} \quad (11)$$

where

$$\langle\mathbf{M}\rangle_L = \mu_E \cos\Theta_0 \sum_{j=1}^{N}\langle\cos\,\delta\theta_j\rangle \quad (12)$$

In the case of a long chain, $\langle\cos\,\delta\theta_j\rangle$ does not depend on j and

$$\langle\mathbf{M}\rangle_L = N\mu_E \cos\Theta_0\,\langle\cos\,\delta\theta_j\rangle \quad (13)$$

Therefore, using eqs 11 and 13, we obtain the following expression for fluctuations of the longitudinal component of the total dipole moment:

$$\langle\delta\mathbf{M}^2\rangle_L/\mu_E^{\,2} = N + 2\sum_{j=1}^{k}\sum_{l>j}^{k}\{\langle\cos(\delta\theta_{2j} - \delta\theta_{2l})\rangle + \langle\cos(\delta\theta_{2j-1} - \delta\theta_{2l-1})\rangle\} + 2\cos 2\Theta_0\sum_{j=1}^{k}\sum_{l=1}^{k}\langle\cos(\delta\theta_{2j} - \delta\theta_{2l-1})\rangle - [N\cos\Theta_0\,\langle\cos\,\delta\theta_j\rangle]^2 \quad (14)$$

5. Correlation Functions for a Sequence of Coupled Rotators

As follows from eqs 8 and 14, to derive $\langle\delta\mathbf{M}^2\rangle_T$ and $\langle\delta\mathbf{M}^2\rangle_L$, one should know the values of $\langle\cos\,\delta\phi_j\rangle$, $\langle\cos(\delta\phi_j$

$- \delta\phi_l)\rangle$ and $\langle\cos\delta\theta_j\rangle$, $\langle\cos(\delta\theta_j - \delta\theta_l)\rangle$. They can be obtained using the distribution functions $\Phi_1(\delta\phi) = \exp(-U_1(\delta\phi)/k_BT)$ and $\Phi_2(\delta\phi) = \exp(-U_2(\delta\theta)/k_BT)$, respectively. We put detailed calculations into the Appendix, presenting here only final expressions for $\langle\cos\delta\phi_j\rangle$ and $\langle\cos(\delta\phi_j - \delta\phi_l)\rangle$:

$$\langle\cos\delta\phi_j\rangle = \exp\left(-\frac{\alpha}{2N}\right)\exp\left(-\frac{\beta}{2}[\gamma^2 + 2\gamma]^{-1/2}\right) \quad (15)$$

$$\langle\cos(\delta\phi_j - \delta\phi_l)\rangle = \exp\left\{-\beta\frac{1 - [1 + \gamma - (\gamma^2 + 2\gamma)^{1/2}]^{|j-l|}}{(\gamma^2 + 2\gamma)^{1/2}}\right\} \quad (16)$$

The dimensionless parameters α, β, and γ are given by

$$\alpha = k_BT/K_2, \quad \beta = k_BT/2K_1, \quad \gamma = \beta/\alpha = K_2/2K_1 \quad (17)$$

We consider some limiting cases.

(1) Coupled rotators of a given chain do not interact with a crystalline environment; i.e., $\alpha \to \infty$ ($\gamma \to 0$). Then

$$\langle\cos\delta\phi_j\rangle \to 0 \quad (18)$$

$$\langle\cos(\delta\phi_j - \delta\phi_l)\rangle \to \exp(-|j - l|\beta) \quad (19)$$

This result coincides with the exact solution for the system of coupled rotators with the potential energy

$$U_1(\delta\phi) = \frac{1}{2}K_1\sum_{j=1}^{N}(\delta\phi_j - \delta\phi_{j-1})^2$$

which depends only on the angles between neighboring rotators.[9] In this case, $\langle\cos(\delta\phi_j - \delta\phi_l)\rangle$ yields $\zeta^{|j-l|}$, where $\zeta = \langle\cos(\delta\phi_j - \delta\phi_{j-1})\rangle$ is the average cosine of the angle between neighboring rotators.

(2) Rotators are not coupled and interact only with the crystalline environment; i.e., $\beta \to \infty$ ($\gamma \to \infty$). Then

$$\langle\cos\delta\phi_j\rangle \to \exp(-\alpha/2) \quad (20)$$

$$\langle\cos(\delta\phi_j - \delta\phi_l)\rangle \to \langle\cos\delta\phi_j\rangle\langle\cos\delta\phi_l\rangle \to \exp(-\alpha) \quad (21)$$

i.e., $\langle\cos(\delta\phi_j - \delta\phi_l)\rangle$ does not depend on $|j - l|$.

Equation 20 coincides with the exact solution for the system of noncoupled rotators interacting with the crystalline environment. For such a system, $K_1 = 0$ and the potential energy is represented in the form

$$U_1(\delta\phi) = \frac{1}{2}K_2\sum_{j=1}^{N}\delta\phi_j^{\,2} \quad (22)$$

To derive the average correlation functions for the deviations $\delta\theta_j$ of the longitudinal components of dipole moments, it is necessary to repeat the procedure shown in the Appendix.

Finally, we obtain expressions which are similar to those derived for the deviations of rotation angles $\delta\phi_j$ (eqs 15 and 16) with the only difference being that the force constants K_1 and K_2 are replaced on the constants K_1' and K_2'.

6. Calculation of Fluctuations of the Total Chain Dipole Moment

To calculate $\langle\delta\mathbf{M}^2\rangle_T$ and $\langle\delta\mathbf{M}^2\rangle_L$, an approximation can be used which allows us to simplify the summation in eqs 8 and 14. This approximation is valid when the exponential index in eq 23 is much less than 1 at $|j - l| = 1$:

$$\exp\left\{\frac{[1 + \gamma - (\gamma^2 + 2\gamma)^{1/2}]^{|j-l|}}{(\gamma^2 + 2\gamma)^{1/2}}\beta\right\} \approx 1 + \frac{[1 + \gamma - (\gamma^2 + 2\gamma)^{1/2}]^{|j-l|}}{(\gamma^2 + 2\gamma)^{1/2}}\beta \quad (23)$$

For sufficiently large values of the force constant K_2 such that $K_2 \gg K_BT$ (this is the very estimation of K_2 value which will be obtained below), the exponential index is really small and turns out to be less than 0.1. Since $0 \le 1 + \gamma - (\gamma^2 + 2\gamma)^{1/2} \le 1$, the approximation (eq 23) will be valid for every $|j - l| > 1$.

Then, from eq 8 using eq 23, we obtain

$$\frac{\langle\delta\mathbf{M}^2\rangle_T}{\mu_1^{\,2}} \approx N + 4\sum_{j=1}^{k}\sum_{l>j}^{k}(a + b\eta^{2(l-j)}) - 2\sum_{j=1}^{k}\sum_{l=1}^{k}(a + b\eta^{|2(j-l)+1|}) \quad (24)$$

where

$$a = \exp(-\beta[\gamma^2 + 2\gamma]^{-1/2}), \quad b = a\beta[\gamma^2 + 2\gamma]^{-1/2}, \quad \eta = 1 + \gamma - [\gamma^2 + 2\gamma]^{1/2}$$

An expression for infinite regression can be used if the chain is sufficiently long. Neglecting small components, we obtain finally for fluctuations of the transverse chain dipole moment component

$$\frac{\langle\delta\mathbf{M}^2\rangle_T}{N\mu_1^{\,2}} \approx 1 - \exp(-\beta[\gamma^2 + 2\gamma]^{-1/2})\left(1 + \beta[\gamma^2 + 2\gamma]^{-1/2}\frac{2\eta}{1 + \eta}\right) \quad (25)$$

Assuming that $K_2' \gg k_BT$ and hence eq 23 is valid, we obtain from eq 14 the corresponding expression for the longitudinal component:

$$\frac{\langle\delta\mathbf{M}^2\rangle_L}{\mu_E^{\,2}} \approx N - N^2\cos^2\Theta_0\exp\left(-\frac{\alpha'}{N}\right)\alpha' + 4\sum_{j=1}^{k}\sum_{l>j}^{k}(a' + b'(\eta')^{2(l-j)}) + 2\cos 2\Theta_0\sum_{j=1}^{k}\sum_{l=1}^{k}(a' + b'(\eta')^{|2(j-l)+1|}) \quad (26)$$

where

$$a' = \exp(-\beta'[(\gamma')^2 + 2\gamma']^{-1/2}), \quad b' = a'\beta'[(\gamma')^2 + 2\gamma']^{-1/2}, \quad \eta' = 1 + \gamma' - [(\gamma')^2 + 2\gamma']^{1/2}$$

$$\alpha' = k_BT/K_2', \quad \beta' = k_BT/2K_1', \quad \gamma' = \beta'/\alpha' = K_2'/2K_1'$$

The appearance of an additional term containing $\exp(-\alpha'/N)$ in eq 26 (compare with eq 24 for the transverse component) is due to the presence of a zero normal mode, which describes rotation of the chain as a whole. Calculating the fluctuations of the transverse chain dipole moment component, the contribution from this mode vanishes due to the mutual compensation of the transverse projections of the dipole moments of ester groups. When the chain has a considerable longitudinal projection of **M**, the contribution from a zero normal mode into $\langle \delta \mathbf{M}^2 \rangle_L$ is essential.

If the chain is sufficiently long, we obtain for the fluctuations of the longitudinal chain dipole moment component

$$\frac{\langle \delta \mathbf{M}^2 \rangle_L}{N{\mu_E}^2} \approx 1 - \exp(-\beta'[(\gamma')^2 + 2\gamma]^{-1/2})\left(1 - \beta'[(\gamma')^2 + 2\gamma']^{-1/2}\frac{2\eta'(\eta' + \cos 2\Theta_0)}{1 - (\eta')^2} - \cos^2 \Theta_0 \alpha'\right) \quad (27)$$

In deriving this equation we also used the condition

$$\exp(-\alpha_2'/N) \approx 1 - \alpha_2'/N$$

which is valid for sufficiently long chains.

7. Discussion

It is necessary to recalculate a value of the dielectric strength to compare our results with experimental data using eqs 1 and 2. For this purpose the value of the total dipole moment of the ester group $\mu_E = 1.7$ D should be taken instead of its transverse projection $\mu_1 = 1.43$ D. We found that the correlation parameter g [7] is equal to 0.15 ± 0.03, i.e., less than the value obtained in ref 6. (We remind the reader that parameter g in ref 6 has the physical meaning of a fraction of freely rotating dipoles.)

To compare $\langle \delta \mathbf{M}^2 \rangle$ values and fluctuations of the rotation angles with $\Delta\epsilon$ values obtained from the experimental data[6] and also with the results of molecular mechanics calculations,[10] we should estimate the force constants K_1, K_2, and K_1', K_2'. An estimation of the magnitudes of K_1 and K_1' can be obtained from the dependencies of the torsional energy on the rotation angle. These dependencies were previously calculated using the AM1 method of quantum chemistry for the torsion motions around the $C_{AR}-O$ bonds of the PHBA main chain and ester bonds, respectively.[8] The results of this calculation show that deviations of the rotation angles of 15° from their equilibrium values correspond to an increase of the torsional energies of about 0.2–0.25k_BT. This gives values of K_1 and $K_1' \sim 5-7k_BT$ (or β and $\beta' \sim 0.1$).

An estimation of the magnitudes of K_2 and K_2' can be obtained from the experimental data on dielectric relaxation,[6] i.e., from the value of an activation energy corresponding to dipolar motions occurring in noncrystalline regions of the PHBA low-temperature phase.[6] We assume that the local structure in the high-temperature ordered phase is similar to that of the noncrystalline regions of the PHBA low-temperature phase. The activation energy is found to be approximately 14 kcal/mol. Using a simple dependency between the potential energy and the rotation angle or polar angle (for example, $U_1(\delta\phi) \sim \sin^2(\delta\phi)$ or $U_2(\delta\theta) \sim \sin^2(\delta\theta)$), we obtained the approximate relations between the height of potential barrier and K_2 or K_2' values. Such an estimation gives the values of K_2 and $K_2' \sim 10k_BT$ (α and $\alpha' \sim 0.1$).

First we consider the contribution of only transverse torsional vibrations of ester groups to the fluctuations of the chain dipole moment. The correlation parameter $g = g_T$ for transverse torsional vibrations can be calculated as

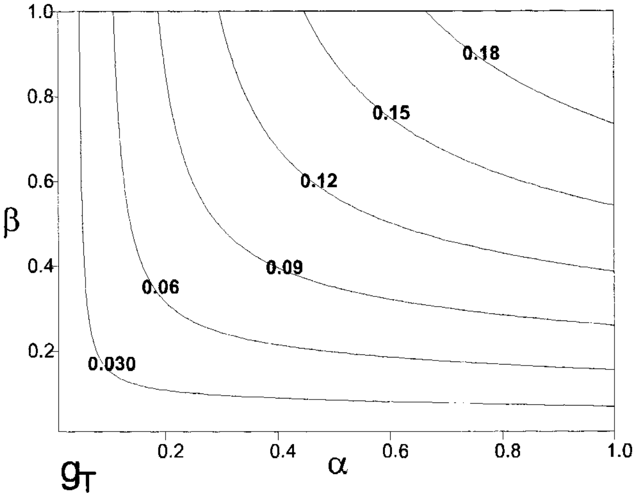

Figure 5. Contour map displaying dependence of the correlation parameter g_T on α and β.

$$g_T = \left(\frac{\langle \delta \mathbf{M}^2 \rangle_T}{N{\mu_1}^2}\right)\left(\frac{{\mu_1}^2}{{\mu_E}^2}\right) \quad (28)$$

where $\langle \delta \mathbf{M}^2 \rangle_T/(N{\mu_1}^2)$ is given by eq 25. It is necessary to take into account that the dipole moment vector of an ester group forms the angle $\Theta_0 = 57°$ with the chain axis Z;[11] thus, $\mu_1 = \sin(57°)\mu_E$. The dependence of the correlation parameter g_T on the dimensionless parameters α and β is represented in Figure 5. Fluctuations of the transverse projection of the chain dipole moment increase with the increase in α and β, i.e., with a decrease of the interactions of both types. The above-mentioned value of $g = 0.15 \pm 0.3$ obtained from the experimental data on dielectric relaxation[6] corresponds to the values of α and β greater than 0.3, whereas the values of α and β obtained from our estimations correspond to a lower value of $g \sim 0.03$. Therefore, the study of fluctuations of the transverse component of the chain dipole moment alone is not sufficient for the description of the PHBA dielectric relaxation experimentally observed by Kalika and Yoon.[6]

A certain type of the transverse torsional vibrations was considered for a polyester model used in the molecular mechanics calculations.[10] In that study rotations around the $C_{AR}-O$ bonds of the PHBA main chain were allowed (Figure 1). The authors found that the mean-square deviations of rotation angles $\delta\phi$ from their mean values were about 15–20°.

The mean-square deviation of the rotation angle ϕ from its equilibrium value (equal to 0 or π)

$$\langle \Delta\phi^2 \rangle^{1/2} = [2(1 - \cos\phi)]^{1/2}\frac{180}{\pi}$$

can be also calculated in the frame of our model with the help of eq 15. The estimated values of α and β correspond to $\langle \Delta\phi^2 \rangle^{1/2} \approx 14°$. This result is in a good agreement with the values of $\langle \Delta\phi^2 \rangle^{1/2}$ obtained in ref 10. Thus, the estimations used for the force constants K_1 and K_2 are in good accordance with the description of

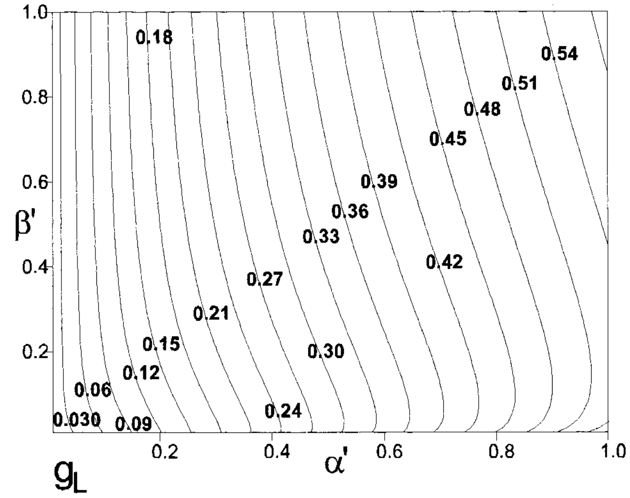

Figure 6. Contour map displaying dependence of the correlation parameter g_L on α′ and β'.

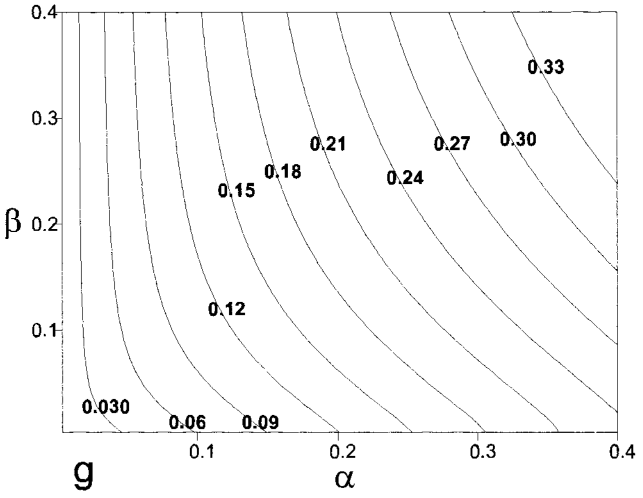

Figure 7. Contour map displaying dependence of the correlation parameter g on α and β.

transverse torsional vibrations of ester groups in the PHBA chain. However, the value of $\langle \delta \mathbf{M}^2 \rangle$ corresponding to the experimental data could be only obtained if we take into account also the longitudinal torsional and bending vibrations.

The contribution of only longitudinal vibrations of ester groups to fluctuations of the chain dipole moment is presented in Figure 6. In this case the correlation parameter $g = g_L$

$$g_L = \langle \delta \mathbf{M}^2 \rangle_L / N \mu_E^{\ 2} \tag{29}$$

can be obtained from eq 27. Figure 6 shows that fluctuations of the longitudinal component of the chain dipole moment increase with the increase in α′, i.e. with a decrease of the interactions with the crystalline environment. The dependence of these fluctuations on β' is more complicated. They almost do not depend on β' for α′ < 0.2, increase with the increase in β' for 0.2 < α′ < 0.5, for α′ > 0.5 first slightly decrease with the increase in β', and after achieving the minimum value begin to increase again. The dependence $g_L(\beta')$ qualitatively distinguishes from the dependence $g_T(\beta')$ due to different symmetry types of the distributions of dipole moment projections of ester groups participating in the transverse and longitudinal vibrations. The values of α′ and β' estimated above correspond to $g \sim 0.09$. Essentially, fluctuations of the longitudinal component are found to be not only comparable in magnitude with fluctuations of the transverse component but also approximately three times greater. Thus, fluctuations of the longitudinal component cannot be neglected in description of the dielectric relaxation of the PHBA.

In the case when both mechanisms—transverse and longitudinal vibrations—contribute to fluctuations of the dipole moment of the PHBA chain, the correlation parameter g is equal to $g_T + g_L$ (eqs 28 and 29). The dependence of g on the dimensionless parameters α and β is presented in Figure 7. The estimated values of α and β correspond to $g \sim 0.11$, which is close enough to the value of $g = 0.15 \pm 0.3$ obtained from the dielectric relaxation study.[6] Therefore, to describe the dielectric relaxation in the PHBA bulk sample, it is sufficient to consider only the mechanisms of torsional and bending vibrations of ester groups compatible with the ordered crystalline structure of PHBA. The estimated values of the force constants correspond to mean-square deviations of the rotation and polar angles of about 13−14°. These angles are slightly smaller than those corresponding to the experimental value of the correlation parameter. However, a slight increase in the amplitudes of vibrations of both types (on 2−4°) already gives the desired value of g.

Finally, we showed in this work that small torsional and bending vibrations of ester groups can result in considerable fluctuations of the total dipole moment of a PHBA chain. The experimentally observed dielectric relaxation of a PHBA chain can be described as a superposition of contributions from transverse and longitudinal vibrations of ester groups away from their equilibrium positions in the ordered crystalline lattice.

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Appendix

For a chain with free ends the linear transformation from the coordinates $\delta\phi_j$ to normal coordinates q_s is

$$\delta\phi_j = \frac{q_0}{N^{1/2}} + \left(\frac{2}{N}\right)^{1/2} \sum_{s=1}^{N-1} \cos\left(\frac{(2j+1)\pi s}{2N}\right) q_s \tag{A1}$$

Here the normal coordinate q_0 describes rotation of the chain as a whole.

Following this transformation the potential energy $U_1(\delta\phi)$ given by eq 4 is reduced to the diagonal form:

$$U(q) = {}^1/_2 \sum_{s=0}^{N-1} \lambda_s q_s^{\ 2} \tag{A2}$$

where

$$\lambda_s = 4K_1 \sin^2(\pi s/2N) + K_2 \tag{A3}$$

are the eigenvalues of the potential function.

Then

$$\langle \cos \delta\phi_j \rangle = \langle \exp(i\delta\phi_j) \rangle = I^{-1} \int_{-\infty}^{+\infty} \dots \int_{-\infty}^{+\infty} \exp\left\{ i\left[\frac{q_0}{N^{1/2}} + \left(\frac{2}{N}\right)^{1/2} \sum_{s=1}^{N-1} \cos\left(\frac{(2j+1)\pi s}{2N}\right) q_s \right]\right\} \times \exp\left\{ -\frac{1}{2k_B T}[K_2 {q_0}^2 + \sum_{s=1}^{N-1} \lambda_s {q_s}^2] \right\} \prod_{s=0}^{N-1} \mathrm{d}q_s \quad \text{(A4)}$$

where I is the normalization constant. Taking into account that the potential energy (eq A2) has a quadratic Gaussian form and that only small relative vibrations are considered (because $K_1 \gg k_B T$ and $K_2 \gg k_B T$), we can extend the integration with respect to q over the whole range from $-\infty$ to $+\infty$.

In this case, we obtain

$$\langle \cos \delta\phi_j \rangle = \exp\left(-\frac{k_B T}{2NK_2} \right) \times \exp\left(-\frac{k_B T}{2N} \sum_{s=1}^{N-1} \frac{\cos^2((2j+1)\pi s)/2N}{2K_1 \sin^2(\pi s/2N) + {}^1/_2 K_2} \right) \quad \text{(A5)}$$

Simplifying this equation further, we pass for a sufficiently long chain from a sum $\sum_{s=1}^{N-1}$ to an integral $(N/\pi)\int_0^{\pi} \mathrm{d}x$, $x = \pi s/N$, and obtain finally for $\langle \cos \delta\phi_j \rangle$

$$\langle \cos \delta\phi_j \rangle = \exp\left(-\frac{k_B T}{2NK_2} \right) \exp\left(-\frac{k_B T}{4K_1} \left[\left(\frac{K_2}{2K_1} \right)^2 + 2\left(\frac{K_2}{2K_1} \right) \right]^{-1/2} \right) \quad \text{(A6)}$$

The averaging of $\langle \cos(\delta\phi_j - \delta\phi_l) \rangle$ is performed in a similar way.

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