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A_2 Mode Vibration in Infrared Absorption Spectrum of Trigonal Poly(oxymethylene)

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ABSTRACT: A phenomenological model is proposed to explain the anomalous shift of the A_2 infrared absorption bands in two trigonal poly(oxymethylene) crystals (needlelike extended-chain crystal and solution-grown folded-chain crystal). For crystals with sufficiently large stem length, the large interactions among induced dipole moments yield the "dynamic ferroelectric" state, resulting in the large nonlinear lattice vibration for the A_2 mode. The nonlinear vibration causes the band shift. For small crystals, the interactions among induced dipole moments are too small to cause the nonlinear vibration, and the usual harmonic vibration approximation to the infrared absorption spectrum can be applied. The nonlinear effect is large in the C–O–C antisymmetric vibration and the internal rotation around the main-chain bonds.

Introduction

Poly(oxymethylene) (POM) is usually crystallized in a trigonal modification consisting of 9/5 (or 29/16) helical polymer chains. The two typical crystals of trigonal POM (t-POM) are known as needlelike crystals and solution-grown crystals. The needlelike crystal is a trigonal single crystal with fully extended chains, and the solution-grown crystal is a well-known lamellar crystal with folded chains.

The vibrational spectrum of t-POM shows very specific changes depending on the state and/or the processing method of the sample.[1-6] The morphology dependence of the infrared spectrum is the most characteristic feature.[5,6] Figure 1 shows the infrared spectra of t-POM for two crystals with different morphologies. Some bands assigned to the A_2 symmetry species exhibit anomalously large shifts between the needlelike crystal and the solution-grown crystal.[6] The A_2 mode is characterized to have a transition dipole moment parallel to the chain axis. The other infrared-active mode E_1 (the transition dipole moment is perpendicular to the chain axis) and the Raman-active modes (A_1, E_1, and E_2) remain at nearly the same frequencies in both crystals.[6] It should be noted that the powdered samples of these two crystals yield virtually identical wide-angle X-ray diffraction patterns. Highly drawn POM film shows essentially the same spectra as the needlelike crystal.

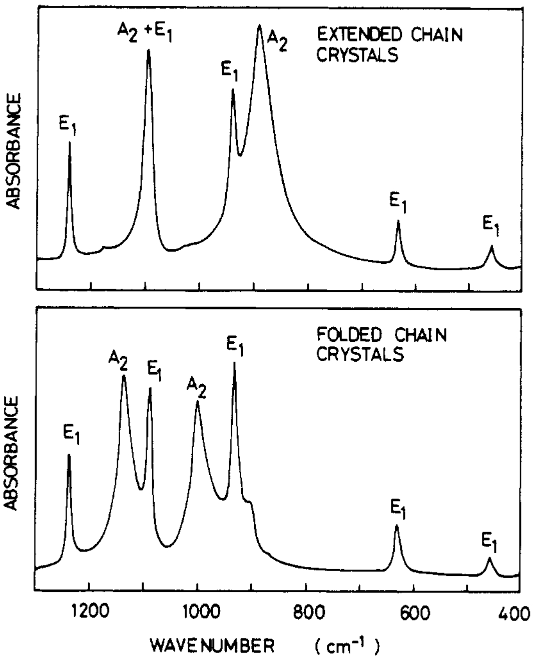

Figure 1. Infrared spectra of poly(oxymethylene) crystals. Assigned vibrational modes are shown for each crystal.

This large frequency shift for the specific infrared spectral mode is actually related to the morphological change, although it has been thought that vibrational spectra in the infrared region do not depend on the higher order structure such as the morphology. Since t-POM oligomers show nearly the same spectra as the solution-grown crystal, the frequency shift is related to the stem length in the crystal.[1,7] The other polar polymer, poly(ethylene oxide), shows a similar spectral shift between the drawn film and the solution-grown crystal.[8,9] Another modification of the POM crystal, the orthorhombic POM crystal consisting of 2/1-helical chains, exhibited the same phenomenon. That is to say, only the B_1 bands with the transition dipole moments parallel to the chain axis appear at the different frequencies between the two orthorhombic modifications generated by pressure from the trigonal needlelike and solution-grown crystals.[10] It was suggested that the strong transition dipole interactions are important for this anomalous shift of the specific infrared band.[10,11]

Model

It is assumed that the band shift of the A_2 mode in t-POM crystals is attributed to nonlinear effects caused by the induced dipole moment interactions. For crystals with sufficiently large stem length, the induced dipole moment interactions become large along the chain direction when induced dipole moments align in the same direction (A_2 mode). The "ferroelectric-like" state is assumed for each instant of vibration. This stage changes with the time variation of each induced dipole moment and can be called the "dynamic ferroelectric" state. For small crystals, the interactions among induced dipole moments are too small to realize the ferroelectric-like state even for an instant.

A one-dimensional model is adopted that has the dipole moments induced by the A_2 mode vibration arranged linearly in the chain direction (see Figure 2). As is well-known, the infrared absorption is due to the ionic polarization. The displacement at the nth repeating unit in the ith normal vibration of the A_2 mode is denoted by

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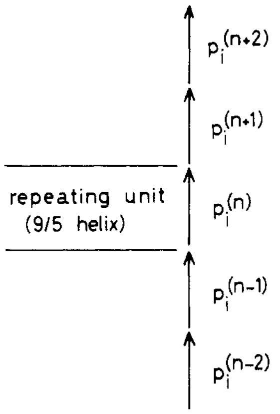

Figure 2. Linearly aligned induced polarizations for the ith A_2 mode vibration.

$Q_i^{(n)}$, where a repeating unit consists of 9 monomers in the 9/5-helical POM chain. The polarization $p_i^{(n)}$ induced at the nth repeating unit by $Q_i^{(n)}$ along the chain direction is given by $p_i^{(n)} = q_i^{(n)}Q_i^{(n)}$, where $q_i^{(n)}$ is an effective charge. If a chain stem in the crystal consists of N repeating units, the polarization along the chain stem direction per repeating unit, P_i, due to the ith A_2 normal vibration is represented by $P_i = (1/N)\sum_{n=1}^{N} p_i^{(n)}$, and the total polarization P of the t-POM crystal along the chain axis per repeating unit, which is induced by all A_2 mode vibrations, is given by $P = \sum_i P_i$.

When dipole moments align in a chain direction, the local field E_{loc} is approximated as $E_{\text{loc}} = E + \gamma_i P + \eta_i P^3$ (see Appendix 1), where E is the macroscopic electric field in the medium and γ_i and η_i are related to the dipole-dipole interactions and other multipolar interactions, respectively. The parameters γ_i and η_i are positive. Using the local field, one may also express the polarization P_i by $P_i = \alpha_i(P)E_{\text{loc}}(P)$, where α_i is a polarizability. Here, the P dependence of α_i is very important to consider for the ferroelectric-like state.

The infrared spectrum can be observed only for the vibration with no phase difference between vibrating repeating units, so only P_i need be considered hereafter and $P_i = q_iQ_i$. It is assumed for simplicity that each vibration of the A_2 species occurs independently. For a normal vibration of the A_2 species, the other vibrations act as a viscous damping force since each normal vibration has a different frequency. The ferroelectric-like state is described by the P_i dependence of α_i and E_{loc}. Since the even powers of P_i for the polarizability are effective for the antisymmetric infrared-active vibration such as the A_2 species, $\alpha_i(P_i)$ can be expanded as follows:

$$\alpha_i(P_i) = \alpha_i^{(0)} + \alpha_i^{(2)}P_i^2 + \alpha_i^{(4)}P_i^4 + \dots \qquad (1)$$

and

$$P_i = b_1E + b_3E^3 + \dots \qquad (2)$$

where

$$b_1 = \frac{\alpha_i^{(0)}}{1 - \alpha_i^{(0)}\gamma_i} \qquad (3a)$$

$$b_3 = \frac{\alpha_i^{(2)}\alpha_i^{(0)2}}{(1 - \alpha_i^{(0)}\gamma_i)^3} + \frac{(\alpha_i^{(2)}\gamma_i + \alpha_i^{(0)}\eta_i)\alpha_i^{(0)3}}{(1 - \alpha_i^{(0)}\gamma_i)^4} \qquad (3b)$$

The coefficient $\alpha_i^{(2)}$ is important for the appearance of the ferroelectric state. The internal energy of the ith vibration of the A_2 species is given by

$$U(P_i) = U(0) + (1/2b_1)P_i^2 - (b_3/4b_1^4)P_i^4 + \dots \qquad (4)$$

where $U(P_i) = \int E\, dP_i$ is used. The fourth-order term of P_i in eq 4 comes from the P_i dependence of the polarizability $\alpha_i(P_i)$, especially $\alpha_i^{(2)}$, and from the higher order term $\eta_i P^3$ in the local field. When the displacement x_i is induced by the polarization P_i, which is the variation of the minimum point of potential energy like thermal expansion and is different from the displacement of lattice vibration Q_i, the Helmholtz free energy $F(x_i,P_i)$ is given by

$$F(x_i,P_i) = F(0,0) + (k_i/2)x_i^2 + (1/2b_1)P_i^2 - (b_3/4b_1^4)P_i^4 - h_ix_iP_i^2 \qquad (5)$$

where k_i and h_i are the elastic constant for displacement x_i and the coupling constant between x_i and P_i, respectively. Only the smallest order term of coupling between x_i and P_i is retained. Higher order terms such as P_i^6 are necessary to consider the stability of the system but not important to discuss the vibrational spectrum.

Let the external force be X_i; the free energy $G(X_i,P_i)$ is represented by

$$G(X_i,P_i) = G(0,0) + a_i^{(2)}P_i^2 - a_i^{(4)}P_i^4 \qquad (6)$$

where $a_i^{(2)} = (1/2b_1) - (h_i/k_i)X_i$ and $a_i^{(4)} = (b_3/4b_1^4) + (h_i^2/2k_i)$. Here it must be noted that $a_i^{(4)}$ is positive if $h_i^2/2k_i$ is sufficiently large. This corresponds to ferroelectric substances with the first-order transition in the static case.

The additional energy term due to the interaction of induced dipole moments

$$V = a_i^{(2)}P_i^2 - a_i^{(4)}P_i^4 \qquad (7)$$

appears even at the temperature $T = 0$ (K), based upon the many-body interaction within a chain. Accordingly, the ith vibration of the A_2 species occurs in the usual harmonic field of $(1/2)(\dot{Q}_i^2 + \omega_i^{(0)2}Q_i^2)$ and additional potential field V, where the dot over Q_i denotes the time derivative and $\omega_i^{(0)}$ is a normal frequency determined by the force constant and the effective mass for the ith vibration. The Hamiltonian H_i for the ith band of the A_2 mode is given by

$$H_i = (1/2)(\dot{Q}_i^2 + \omega_i^{(0)2}Q_i^2) + V \qquad (8)$$

Using $P_i = q_iQ_i$

$$H_i = (1/2)(\dot{Q}_i^2 + \omega_i^2Q_i^2) - a_i^{(4)}q_i^4Q_i^4 \qquad (9)$$

where $\omega_i^2 = \omega_i^{(0)2} + 2a_i^{(2)}q_i^2$ and ω_i is a characteristic frequency for the ith band including the $a_i^{(2)}$ term due to the induced dipole moment interaction. This term $a_i^{(2)}$ would exist in other mode vibrations (for example, the E_1 species). The effect of $a_i^{(2)}$ can be included in the estimation of the force constant. The size effect of the A_2 mode vibration of the infrared spectra is not relatd to the $a_i^{(2)}$ term but is related to the $a_i^{(4)}$ term. The coefficient of $a_i^{(4)}$ would increase stepwise from zero to some value as the chain stem length l in crystals becomes large beyond a critical value l_0, which is shown schematically in Figure 3.

The first-order perturbation theory of semiclassical quantum mechanics (electric field described classically) for harmonic vibration gives the energy level W_{ni} for the

ith vibration.

$$W_{ni} = \hbar\omega_i(n_i + 1/2) - a_i^{(4)}q_i^4(\hbar^2/\omega_i^2) \times [(3/4)(2n_i^2 + 2n_i + 1)] \quad (10)$$

where n_i is the quantum number and $\hbar$ is Planck's constant divided by 2π.

The fundamental transition from $n_i = 0$ to $n_i = 1$, ω, is as follows:

$$\omega = \omega_i - 3a_i^{(4)}q_i^4\hbar/\omega_i^2 \quad (11)$$

The coefficient $a_i^{(4)}$ is not large for very small crystals such as solution-grown single crystals because the length along the chain axis direction is too small (usually below 10 nm for POM) to yield the ferroelectric state. In this case, the frequency of infrared absorption is given by ω_i. On the contrary, needlelike crystals of t-POM have sufficiently large crystal length along the chain axis ($\sim$10 μm), and the ferroelectric state with a large nonlinear coefficient $a_i^{(4)}$ is realized and reveals the frequency ω. As mentioned above, the nonlinear coefficient $a_i^{(4)}$ is positive and ω is smaller than ω_i as seen from eq 11. This result qualitatively coincides with the experimental result.

The wave function $\varphi_n(Q_i)$ corresponding to energy W_n is approximated by

$$H_i\varphi_n(Q_i) = W_n\varphi_n(Q_i) \quad (12)$$

$$\varphi_n(Q_i) = u_n(Q_i) - (a_i^{(4)}q_i^4\hbar^2/\omega_i^2) \times \frac{{}^1/_4[n(n-1)(n-2)(n-3)]^{1/2}}{W_n - W_{n-4}}u_{n-4}(Q_i) + \frac{{}^1/_2 n^{1/2}(n-1)^{3/2}}{W_n - W_{n-2}}u_{n-2}(Q_i) + \frac{{}^1/_2(2n+3)[(n+2)(n+1)]^{1/2}}{W_n - W_{n+2}}u_{n+2}(Q_i) + \frac{{}^1/_4[(n+4)(n+3)(n+2)(n+1)]^{1/2}}{W_n - W_{n+4}}u_{n+4}(Q_i) + \ldots \quad (13)$$

where

$$u_n(Q_i) = [\beta/\pi^{1/2}(2^n)n!]^{1/2}H_n(\beta Q_i)\exp(-{}^1/_2\beta^2Q_i^2) \quad (14)$$

with $\beta^4 = \omega_i^2/\hbar^2$. $H_n(\beta Q_i)$ is the Hermite polynomial, and the function $u_n(Q_i)$ denotes the eigenfunction of the harmonic oscillator. The correction terms in eq 13 are small and the vibration is considered as a quasi-harmonic oscillation.

The total Hamiltonian is represented as

$$H = \frac{1}{2}\sum_{i=1}^{m}(\dot{Q}_i^2 + \omega_i^2Q_i^2 - a_i^{(4)}q_i^4Q_i^4) + \frac{1}{2}\sum_{j=m+1}^{M}(\dot{Q}_j^2 + \omega_j^2Q_j^2) \quad (15)$$

where m is the total number of A_2 mode vibrations of POM and M is the total number of normal vibrations. The first term on the right-hand side of eq 15 denotes the A$_2$ mode vibrations with the large induced dipole moment interactions, and the second denotes the other normal vibrations in POM. The wave function Ψ for the total system is given by

$$\Psi = \prod_{i=1}^{m}\varphi(Q_i)\prod_{j=m+1}^{M}u(Q_j) \quad (16)$$

The A$_2$ mode vibration can be described to be quasi-harmonic, and the other mode vibrations are harmonic.

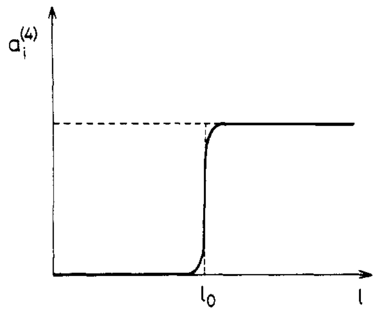

Figure 3. Schematic figure to show the dependence of the coefficient $a_i^{(4)}$ on the chain stem length l in crystals.

The effect of the dynamic ferroelectric state is very small on the absorption intensity because of the quasi-harmonic vibration. The absorption intensity can be approximated by the harmonic vibration.

Discussion

Our model can qualitatively explain the experimental results, in particular the frequency shift due to the stem length difference. However, quantitative comparison with experiments is very difficult because $a_i^{(4)}$ cannot be directly estimated. Hence we will discuss the relative values of $a_i^{(4)}$. From eq 11 the frequency difference $\Delta\omega = \omega_i - \omega$ for the ith A$_2$ band is given by

$$\Delta\omega/\omega_i = 3\hbar a_i^{(4)}q_i^4/\omega_i^3 \quad (17)$$

The fourth power of q_i is estimated from the integrated absorbance area for the ith band, Y_i, because the vibration is considered to be quasi-harmonic, and $Y_i \propto f_iq_i^2$, where f_i is the oscillator strength. The effect of f_i is small and neglected or included in the estimation of q_i. In Table I, the values of ω_i and ω are cited from ref 6, and Y_i is calculated from the data of ref 12, where Y_i is the relative value to that of the 1385-cm^{-1} absorption band. The values of $a_i^{(4)}$ in Table I are described in arbitrary units.

The coefficient $a_i^{(4)}$ of the C–O–C antisymmetric vibration is the largest (for 1138 and 1000 cm^{-1}), and the internal rotation around the main-chain bonds also gives rise to a large value of $a_i^{(4)}$ (for 236 cm^{-1}). Rocking and wagging modes of CH$_2$ do not show any large nonlinear coefficient. This result is reasonable because a large nonlinear coefficient $a_i^{(4)}$ would arise from the complex interactions among atoms and electrons within the main chain. The atomic and electronic structure in the main chain would change sensitively through the ferroelectric-like interaction of the induced dipole moments. On the other hand, rocking and wagging modes of CH$_2$ are not so sensitively influenced by the atomic and electronic structure of the main chain. To develop the detailed molecular theory of the anomalous shift of the infrared bands, one must mainly take into account the change in the atomic and electronic structure of the main chain.

In conclusion, the anomalous shift of the A$_2$ infrared bands in t-POM is based on the induced dipole moment interactions. Nonlinear lattice vibrations appear in the A$_2$ mode of large chain stem length samples (needlelike crystals and highly drawn films) under the assumption of a dynamic ferroelectric state. This rather small (quasi-harmonic oscillation) but prominent nonlinear effect is large in the C–O–C antisymmetric vibration and the internal rotation around the main-chain bonds.

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Table I
Estimation of Relative Values of Nonlinear Coefficient $a_i^{(4)}$ for Each Band of A_2 Mode in Poly(oxymethylene)

ω_i,[a] cm^{-1} soln-grown cryst	ω,[a] cm^{-1} needlelike cryst	Y_i[b] (rel values) integrated absorbance area for needlelike cryst	$\Delta\omega/\omega_i$	$a_i^{(4)}$ (rel values)	vib mode[c]
2983	2985		0		$\nu_a(CH_2)$
1385	1385	1	0	0	$w(CH_2)$
1138	1093	25	0.04	8	$\nu_a(COC)$ (77) + $r(CH_2)$ (19)
1000	895	70	0.11	2	$r(CH_2)$ (75) − $\nu_a(COC)$ (21)
236	220	4	0.07	5	$\tau_a(96)$ + $r(CH_2)$ (3)

[a] Cited from ref 6. [b] Calculated from ref 12. [c] Cited from ref 12.

also due to Dr. H. Kyotani and other members in their laboratory for important suggestions to this work.

Appendix 1. Expression for Local Electric Field

As written in various kinds of books relating to dielectricity, the local field E_{loc} in a dielectric medium is decomposed as follows:

$$E_{loc} = E_0 + E_1 + E_2 + E_3 \tag{A1}$$

where E_0 is the applied external field, $E_1 = -(L/\epsilon_0)P$ is the depolarization field depending on the shape of the medium (L is the geometrical depolarization factor, ϵ_0 is the vacuum permittivity, and P is the polarization), E_2 is the Lorentz cavity field, and E_3 is the field caused by the interactions with surrounding dipoles and multipoles in the neighborhood of the dipole at the origin. The macroscopic field E in the medium is described by $E = E_0 + E_1$. For transverse plane waves, L is equal to zero and for longitudinal plane waves, L is unity (in MKS units). In the discussion of infrared spectroscopy, we have only to consider the transverse wave. The Lorentz field is given by $E_2 = (^1/_{3\epsilon_0})P$. The field E_3 is proportional to P when the dipolar interaction is dominant, and the approximation

$$E_2 + E_3 = (^1/_{3\epsilon_0})KP \tag{A2}$$

is ordinarily used, where K is the coefficient representing the effect of dipole interactions. On the other hand, the approximation

$$E_3 = cP + dP^3 + ... \tag{A3}$$

must be used when multipolar interactions become large, where c and d are constants. The terms of odd powers of P contribute to E_3 because PE_3 has the dimension of energy and is a scalar. Accordingly, the expression

$$E_{loc} = E + \gamma P + \eta P^3 + ... \tag{A4}$$

is derived. The coefficients γ and η include the effect of dipole–dipole interactions and other multipolar interactions, respectively.

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