Morphology Dependent Anomalous Frequency Shifts of Infrared Parallel Bands of Polymer Crystals: Spectral Changes Induced by Isotopic Dilution in H–D Cocrystals of Poly(oxymethylene) as Evidence of a Transition Dipolar Coupling Mechanism

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ABSTRACT: Morphology dependent anomalously large frequency shifts of infrared parallel absorption bands found in some crystalline polymers, including poly(oxymethylene) and poly(ethylene oxide), have been accounted for by the strong transition dipolar interactions among the molecules constructing one crystallite domain of the lamella-type.[15] In order to get conclusive evidence supporting this mechanism, infrared spectra of lamella-type mixed crystals of normal and deuterated paraformaldehydes (PFA and PFA-d_2, linear oligomers of poly(oxymethylene)) were investigated. The A_2 parallel bands due to both PFA and PFA-d_2 were found to exhibit remarkable changes in both peak position and profile with variation in the PFA/PFA-d_2 composition, whereas the E_1 perpendicular bands remained unchanged. The main feature of the observed spectral changes was interpreted in terms of the reduction of the transition dipolar interactions in the infrared-active zone-center modes (due to the in-phase oscillation of the transition dipoles) caused by the frequency mismatch between the normal and deuterated molecules. The simplest spectral change was found for the $A_2(4)$ band of PFA-d_2 which shifted from 850 cm^{-1} (in pure PFA-d_2 under the highest transition dipolar interactions) to 833 cm^{-1} (highly diluted with PFA). The observed spectral change in the 860–830 cm^{-1} range was reproduced fairly well by a Monte Carlo simulation based on the transition dipolar coupling theory. The more complicated spectral change seen for the $A_2(4)$ of PFA and $A_2(3)$ of PFA-d_2 was accounted for by the vibrational coupling between the two isotopic species generated in the mixed crystals.

Introduction

In a series of previous papers[1-10] we have demonstrated that for some crystalline polymers anomalously large and very specific infrared (IR) spectral changes are induced by changes in crystal morphology. The morphology dependent IR spectral changes are observed most significantly for the trigonal modification of poly(oxymethylene) $(-CH_2O-)_n$ (abbreviated as t-POM) which is known to construct various crystal morphologies situated between the two extreme cases of the fully extended-chain crystal (ECC) and the folded-chain or lamellar crystal (FCC). The typical ECC (micron-sized needle-like single crystals[11,12]) and FCC (lamellar crystals grown from a dilute bromobenzene solution[13,14]) samples of t-POM give rise to essentially the same X-ray diffraction pattern. Nevertheless, their IR spectra are remarkably different from each other.[2] Moreover, the difference is very specific; as the morphology of the sample goes from the ECC to the FCC type, the A_2 IR bands having the transition moment parallel to the chain axis (the parallel bands) are shifted toward the high-frequency side by as large as 100 cm^{-1}, whereas the E_1 bands having the transition moment perpendicular to the chain axis (the perpendicular bands) appear at the same position regardless of the crystal morphology. The infrared-inactive Raman bands (due to the A_1 and E_2 symmetry species) of the two samples appear at the same frequencies.

Such a specific IR spectral phenomenon is not limited to t-POM but is commonly found in other polymer crystals, including the orthorhombic modification of POM (o-POM),[3] poly(ethylene oxide) (abbreviated as PEO),[4,5] and poly(tetrafluoroethylene) (PTFE).[9,10] The morphology dependent spectral changes found in these polymers have the following common characteristics. (1) As the morphology goes from ECC to FCC, only the IR parallel bands are blue-shifted. (2) The FCC-type IR spectrum originates not from the folded-chain structure but from the lamellar-type crystal morphology.[6] (3) The magnitudes of the band shifts are proportional to the oscillator strengths of the bands. (4) The remarkable band shifts are observed only for the fundamental modes but not for the multiphonon modes (overtones and combinations). (5) The intense IR parallel bands exhibiting large frequency shifts have a rather broadened profile in contrast to the sharp Lorentzian profile of the IR perpendicular bands as well as the Raman bands. All the characteristic features were interpreted quantitatively in terms of the transition dipolar coupling theory.[15]

The theory tells us that the blue shifts of the IR parallel bands of the lamellar crystal are attributed to the in-phase oscillation of parallel transition dipoles associated with the ensemble of molecules constructing a single domain in the lamellar crystal. Therefore, the theory predicts that such a dipolar interaction is reduced to a great extent in mixed crystals of normal and deuterated molecules even though the molecules are accommodated in typical lamellar crystals, because the in-phase oscillation is distributed by the frequency mismatch between the two isotopic species. If this is confirmed experimentally, we are able to get conclusive evidence that supports our transition dipolar coupling mechanism presented as the origin of this specific spectral phenomenon.

To this end, in the present work, IR spectra of lamella-type mixed crystals of normal (H) and deuterated (D) paraformaldehyde (PFA and PFA-d_2, linear oligomers of POM and POM-d_2, respectively, consisting of about

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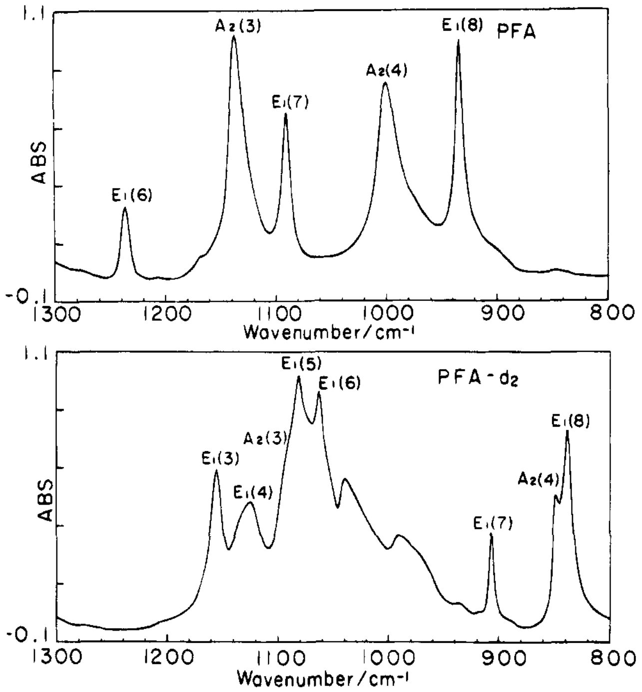

Figure 1. Infrared spectra of paraformaldehyde (PFA) and perdeuterioparaformaldehyde (PFA-d_2) measured on lamellar crystals deposited from hexafluoro-2-propanol (HFIP) solutions. The assignments of the IR-active fundamentals are indicated.

100 monomeric units) grown from dilute solutions were investigated. In the crystalline phase PFA molecules are known to be arranged in the t-POM lattice. Our attention was focused on the spectral change of the parallel bands accompanied with variation of the H/D composition. The observed spectral changes were attempted to be reproduced by a Monte Carlo simulation based on the transition dipolar coupling theory.

Experimental Section

PFA and PFA-d_2 samples used were purchased from Nakarai Chemical Ltd. (Japan) and MSD Isotopes (Canada), respectively. They were purified by reprecipitation from hexafluoro-2-propanol (HFIP) solutions with acetone. Lamellar crystals of pure PFA (or PFA-d_2) were prepared as follows. About 100 mg of PFA (or PFA-d_2) was dissolved in 5 mL of HFIP, and acetone (5 mL) was added rapidly to the solution with stirring. The gelatinous precipitate obtained was collected by filtration and washed with acetone. The wet precipitate was suspended in cyclohexane and freeze-dried, giving a white fine powder. The trigonal crystal form as well as the lamella-type crystal morphology of the samples thus obtained was confirmed by infrared spectroscopy as described below. Lamellar crystals of PFA/PFA-d_2 mixtures of various compositions covering the H/D mole ratio from 90/10 to 10/90 were prepared by the same procedure.

The fine powder samples thus obtained were mulled tenderly with liquid paraffin to be subjected to IR measurements. In the sampling process special care was taken for protecting the lamella-type crystal morphology from mechanical destruction. The PFA and PFA-d_2 samples thus prepared gave rise to IR spectra typical of the lamellar crystal of trigonal POM, as shown in Figure 1 (compare with the spectra of ECC and FCC samples of POM and POM-d_2 reproduced in Figure 2), where the parallel bands due to the $A_2(3)$ and $A_2(4)$ modes appear, respectively, at 1134 and 995 cm^{-1} for PFA and 1095 and 850 cm^{-1} for PFA-d_2.

In the spectra of the same solution-grown samples ground with KBr powder, the absorption profiles of these parallel bands are deformed to a great extent in a manner similar to the case of low-molecular-weight POM diacetate,[6] reflecting the destruction of the lamellar morphology.

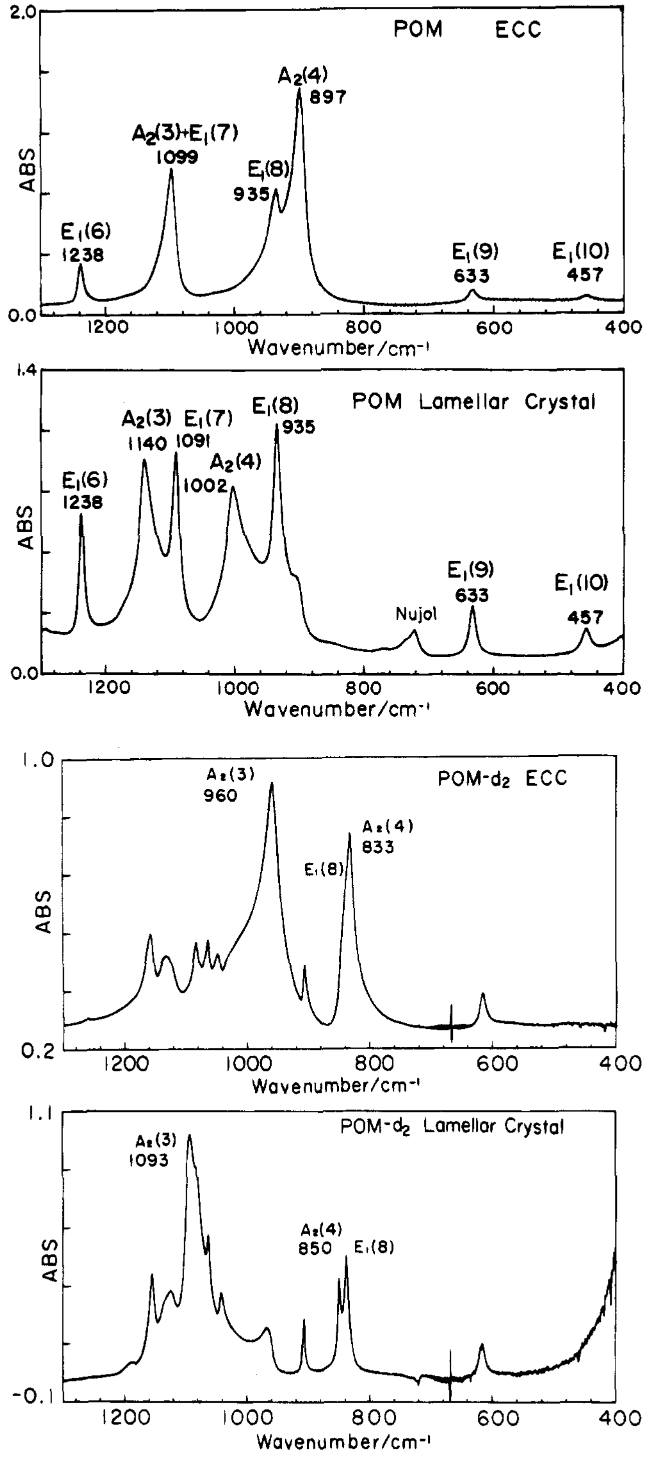

Figure 2. Infrared spectra of ECC and lamellar crystals of high-molecular-weight poly(oxymethylene) (a: upper two) and poly(oxymethylene-d_2) (b: lower two). Reproduced with permission from ref 2. Copyright 1988 Butterworth Publishers.

Results and Discussion

Infrared Spectra of Mixed Crystals of PFA and PFA-d_2. The zone-center molecular vibrations of a (9/5) uniform helix in the trigonal lattice of POM are classified into six symmetry species as $\Gamma = 5A_1 + 5A_2 + 11E_1 + 12E_2 + 12E_3 + 12E_4$. The A_1 and E_2 species are Raman-active, A_2 is IR-active giving rise to parallel bands, E_1 is active in both IR (perpendicular bands) and Raman, and the other species are optically inactive. The details of the assignment of the IR and Raman bands are given in previous papers.[2,7,15,16] In the present work

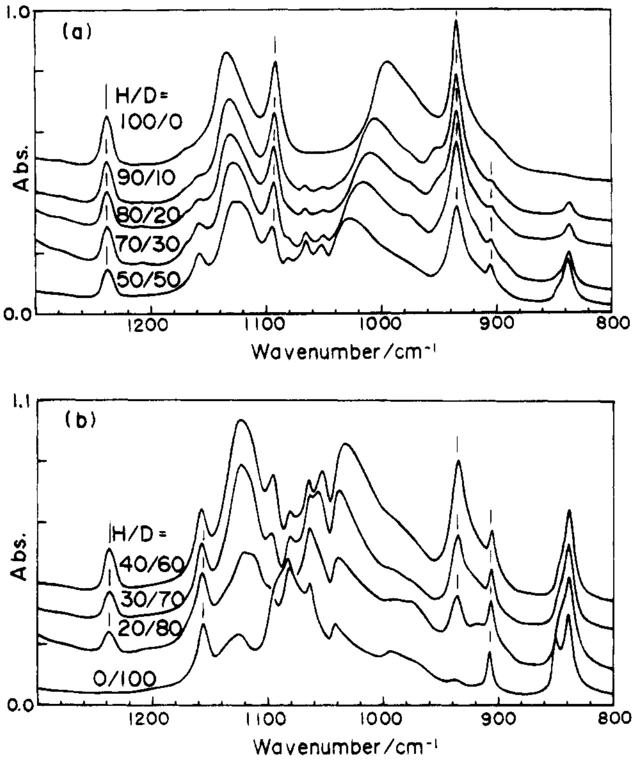

Figure 3. Infrared spectra of PFA/PFA-d_2 mixed crystals of various H/D compositions. (a) H/D = 100/0−50/50, (b) H/D = 40/60−0/100. The vertical lines indicate the peak positions of the E_1 fundamentals (associated with both PFA and PFA-d_2) whose frequencies are unaffected by the morphological change.

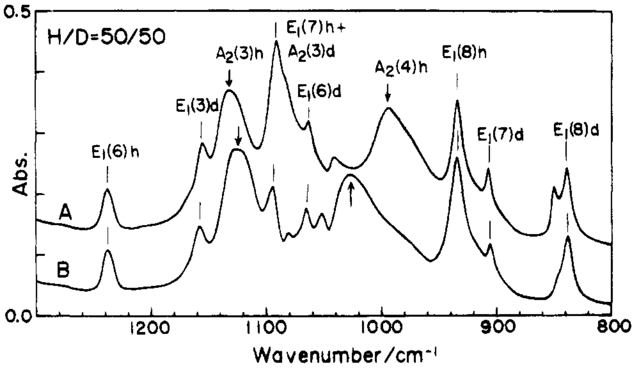

Figure 4. Comparison between the 1:1 addition of PFA and PFA-d_2 spectra (A) and the spectrum measured on the 50/50 mixed crystal (B). A significant difference between the two is seen for the A_2 bands, as indicated by arrows.

we are concerned with the A_2 and E_1 IR bands appearing in the midinfrared range.

Figure 3 shows the IR spectral change with variation in H/D composition measured on a series of PFA/PFA-d_2 mixed crystals precipitated from HFIP solutions. The sharp absorption bands marked with vertical lines are due to the E_1 fundamentals (the perpendicular bands) of the normal or deuterated poly(oxymethylene) molecules. Their frequencies remain unaltered with change in composition. On the contrary, the absorptions due to the A_2 fundamentals (the parallel bands) exhibit dramatic changes in both peak position and shape depending on H/D composition. This is demonstrated by comparing the spectrum of a 50/50 mixed crystal (B in Figure 4) with the 1:1 addition spectrum of the two components (A). The $A_2(3)$ and $A_2(4)$ bands of PFA and the $A_2(3)$ band of PFA-d_2 in the mixed crystal are quite different from those in the pure samples, as indicated by the arrows. In contrast, all the E_1 bands (marked with vertical lines) appear at the same positions in the two spectra.

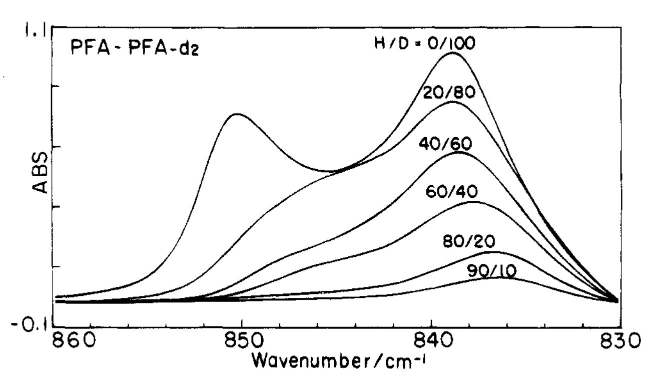

Figure 5. Infrared spectral change of the $A_2(4)$ and $E_1(8)$ bands of $(-CD_2O-)_n$ with variation in H/D composition of the PFA/PFA-d_2 mixed crystals.

The main features of the spectral change shown in Figure 3 are as follows. With decreasing H/D value the 1134 cm^{-1} $A_2(3)$ band of PFA is red-shifted to ca. 1110 cm^{-1} (the shoulder observed in the 20/80 sample). The latter frequency corresponds to that of the $A_2(3)$ mode of the ECC sample of POM (see Figure 2a) in which the effect of the transition dipolar interactions vanishes. The frequency shift can be interpreted qualitatively as being caused by the reduction of transition dipolar interactions among the neighboring PFA molecules with the increasing extent of isotopic dilution with PFA-d_2 molecules. However, quantitative analysis of the absorption profile is rather difficult because of superposition with the 1091 cm^{-1} $E_1(7)$ band of PFA and the 1095 cm^{-1} $A_2(3)$ and the 1125 cm^{-1} [presumably the $E_1(4)$] bands of PFA-d_2. The 995 cm^{-1} $A_2(4)$ band of PFA changes in a very complicated fashion; with decreasing H/D the peak position is blue-shifted continuously toward 1095 cm^{-1} of the $A_2(3)$ band of PFA-d_2. Accompanying this spectral change, a broad absorption appears in the 960−890 cm^{-1} range and gets stronger. The appearance of the latter absorption is accounted for by the red shift of the $A_2(4)$ band of PFA caused by the reduction of the transition dipolar interactions. The former noticeable spectral change is accounted for by the strong coupling between the $A_2(4)$ mode of PFA and the $A_2(3)$ mode of PFA-d_2 in the mixed crystals. The occurrence of such a vibrational coupling between H and D molecules may be possible because the $A_2(3)$ mode of PFA-d_2 molecules surrounded by PFA molecules (free from transition dipolar coupling) appears around 960 cm^{-1}, just in the frequency range where the $A_2(4)$ mode of the surrounding PFA molecules appears. However, the spectral change of such a coupled A_2 mode with H/D composition occurs in a too complicated way to be analyzed quantitatively.

Quantitative analysis of the change in absorption profile induced by isotopic dilution in the lamella-type H/D mixed crystals was performed for the $A_2(4)$ band of PFA-d_2. This band is free from the interference by the absorption associated with PFA. This band moves from 850 cm^{-1} (for the ideal lamellar crystal) to 833 cm^{-1} (for the ideal ECC) as shown in Figure 2b. In this frequency range there appears only one additional sharp band due to the $E_1(8)$ fundamental of PFA-d_2 whose position (840 cm^{-1}) remains unaffected by the isotopic dilution. The spectral change with H/D composition is reproduced in Figure 5. The $A_2(4)$ band is shifted from 850 cm^{-1} of pure PFA-d_2 to 836 cm^{-1} of the mixed crystal of H/D = 90/10.

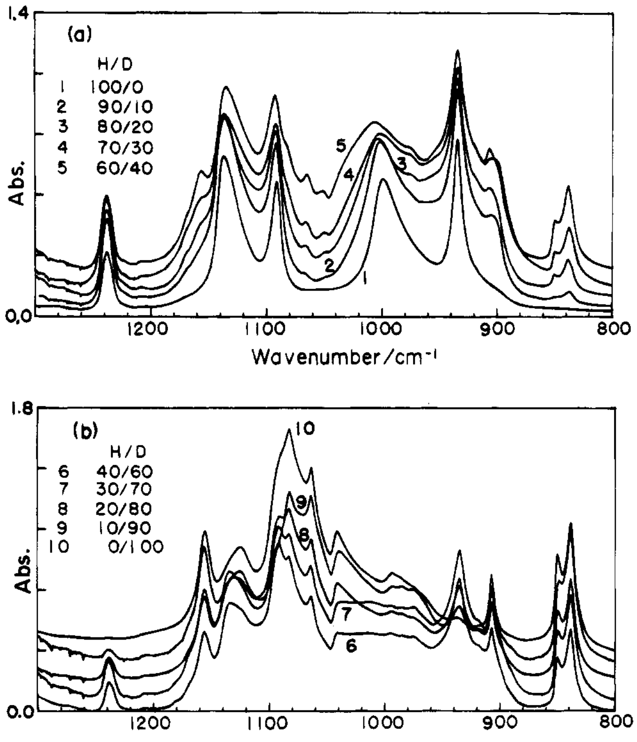

Figure 6. Infrared spectra of POM/PFA-d_2 mixed crystals (deposited from HFIP solution) of various H/D compositions: (a) H/D = 100/0–60/40; (b) H/D = 40/60–0/100.

Thus, the features of IR spectra measured for the lamella-type crystals of PFA/PFA-d_2 mixtures are in accordance with the prediction from the transition dipolar coupling theory.

Isotope Phase Separation Occurring on Crystallization. Isotopic (H/D) blends of polymers have been used for studying phase separation or segregation occurring on crystallization. In the case of PFA/PFA-d_2 mixtures mentioned in the preceding section, there is no indication of the occurrence of isotopic phase separation during the formation of lamellar crystals from HFIP solution. In contrast, the mixtures of high-molecular-weight POM ($M_w = 4 \times 10^4$) and PFA-d_2 ($M_w = 3 \times 10^3$) deposited from HFIP solutions gave rise to the IR spectra shown in Figure 6. All the spectra are approximately reproduced by the weighted superposition of the spectra of pure POM and PFA-d_2, although for some samples the absorption profiles due to the A_2 modes are deformed a little from the superposed ones. The small deformation might be caused by disturbance of the lamella-type crystal morphology that happened on mulling the polymer samples with Nujol. Figure 7 shows the spectra of the POM/PFA-d_2 mixtures in the 860–830 cm^{-1} range. Here, the intensity scale is so reduced that the absorbance of the 840 cm^{-1} $E_1(8)$ band is proportional to the mole fraction of the D species. No frequency shift is observed for the $A_2(4)$ band of PFA-d_2, indicating that one isotopic species forms crystallites segregated from the other species, in great contrast to the cocrystallization of PFA and PFA-d_2 (Figure 5).

For studying such an isotopic phase separation in polymeric systems, the neutron diffraction method has been used. For the case of some polymer crystals in which strong transition dipolar interactions act among the neighboring molecules, like in POM and PEO, the infrared method is very sensitive and powerful for the study of the aggregation state among the normal and deuterated species.

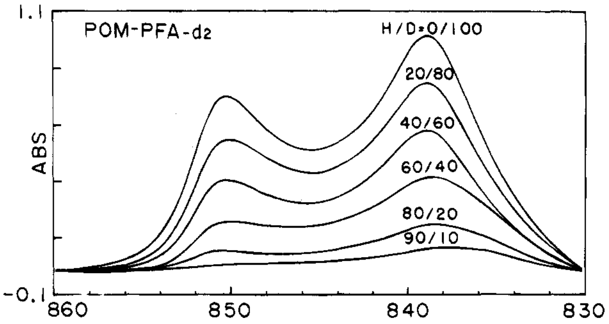

Figure 7. Infrared spectral change of $A_2(4)$ and $E_1(8)$ of $(-CD_2O-)_n$ with variation in the H/D composition of POM/PFA-d_2 mixed crystals.

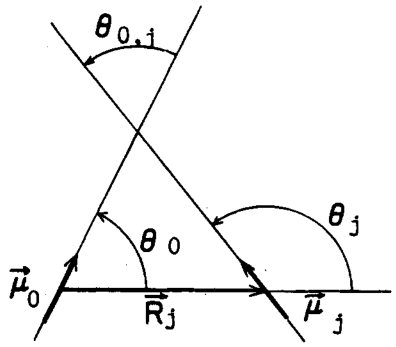

Figure 8. Transition dipolar interaction.

Transition Dipolar Interactions and Resultant Bandshifts in H/D Mixed Crystals. According to the theory developed first by Hexter,[17,18] the magnitude of the bandshift (in cm^{-1}) for the IR-active kth fundamental (due to the 0 → 1 transition) of the zone-center modes of a crystal caused by transition dipolar interactions among the oscillating molecules is expressed by the equation

$$\Delta\nu_k(0 \rightarrow 1) = (1/8\pi^2c^2\nu_k^0)(\partial\mu/\partial Q_k)^2\sum K_j/R_j^3 \qquad (1)$$

where μ denotes the dipole moment of the whole crystallite, Q_k is the normal coordinate of the kth mode, and ν_k^0 is the intrinsic frequency (in cm^{-1}) of the mode free from the transition dipolar interactions (the ν_k^0 value includes the contribution from the other short-range intermolecular interactions). $\sum(K_j/R_j^3)$ is the geometric factor (the Madelung constant) related to the spatial distribution of the transition moment within the whole crystallite. Each K_j/R_j^3 term for the interaction between the transition dipoles at the origin (the zeroth site) and the jth site is expressed by the following equation using the parameter defined in Figure 8

$$K_j/R_j^3 = (\cos\theta_{0j} - 3\cos\theta_0\cos\theta_j)/R_j^3 \qquad (2)$$

Here, we consider a crystal in which only one polymer molecule passes through the unit cell, like the case of t-POM. For the crystal consisting of H or D polymers alone, the IR-active parallel bands arise from the in-phase oscillation of the transition dipoles along the chain axis, so that the geometric factor for such an "in-phase mode" is reduced to

$$\sum(K_j/R_j^3) = \sum(1 - 3\cos^2\theta_j)/R_j^3 \qquad (3)$$

We have demonstrated in ref 15 that the magnitude of this factor is strongly dependent on the morphology

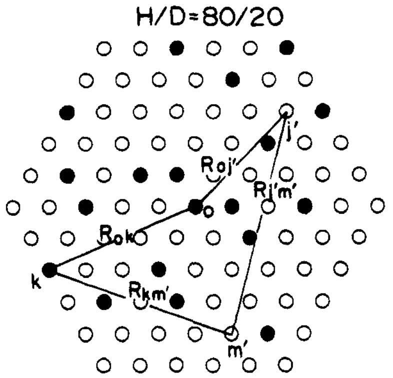

Figure 9. Model of the PFA/PFA-d_2 mixed crystal. The normal (○) and deuterated (●) poly(oxymethylene) chains are arranged randomly at the sites of the two-dimensional hexagonal lattice under the restriction of a constant preset H/D composition. The chain axes are directed normal to the lattice plane.

of the crystallite; it vanishes for the extreme case of the ideal ECC and increases monotonously as the crystal morphology goes to the lamella type (see Figure 12 in ref 15), approaching the maximum for the other extreme case of the two-dimensional lattice (the ideal lamellar crystal). For the latter case the geometric factor is simply given by $\sum R_j^{-3}$. Therefore, the frequency gap of the kth parallel band between the two extreme cases of crystal morphology, $\Delta\nu_k^{\max} = \nu_k(\text{lamella}) - \nu_k(\text{ECC})$, is expressed as

$$\Delta\nu_k^{\max}\ (\text{in cm}^{-1}) = (1/8\pi^2c^2\nu_k^0)(\partial\mu/\partial Q_k)_0^2(\textstyle\sum R_j^{-3}) \quad (4)$$

The $(\partial\mu/\partial Q_k)_0^2$ in eq 1 is expressed in terms of the integrated absorption coefficient A (in cm mol^{-1} per monomeric unit)

$$(\partial\mu/\partial Q_k)_0^2\ (\text{in cm}^3\ \text{s}^{-1}) = 3pc^2A/N_A\pi = 1.42 \times 10^{-3} \quad (5)$$

where c (cm s^{-1}) denotes the velocity of light in vacuum and N_A is the Avogadro constant. Here, we assume that p monomeric units contribute to the unit transition dipole moment along the chain axis. Thus eq 4 is reduced to

$$\Delta\nu_k^{\max} = p(1/8\pi^2c^2)(A/\nu_k^0)\ (\text{in cm}^2\ \text{mol}^{-1})\ (\textstyle\sum R_j^{-3})\ (\text{in A}^{-3}) = 2.009 \times 10^{-2}p(A/\nu_k^0)\ (\text{in cm}^2\ \text{mol}^{-1}\ \text{per monomer unit})\ (\textstyle\sum R_j^{-3})\ (\text{in A}^{-3}) \quad (6)$$

In H/D mixed crystals, the in-phase condition of the dipolar oscillation does not hold in the strict sense. In order to reproduce the observed IR spectral change with variation in H/D composition, we consider molecular vibrations in the following two-dimensional hexagonal lattice depicted in Figure 9 where the molecules are arranged with the chain axes perpendicular to the lattice plane. The central molecule is surrounded with 90 molecules positioned at the sites of the hexagonal lattice points. Firstly, a D molecule (solid circle) is put at the central site and each of the other sites is arranged so as to be occupied by an H (open circle) or D molecule (solid circle) in a random way that the overall H/D mole ratio coincides with a preset composition (Figure 9 shows the case H/D = 80/20). For one preset H/D composition, a series of such models was generated using a table of random digits.

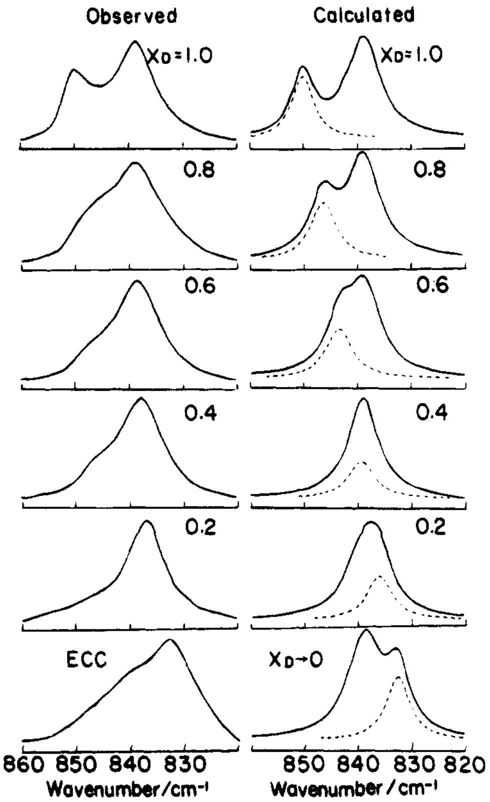

Figure 10. Change in the IR absorption profile (in the 860–830 cm^{-1} range) of PFA/PFA-d_2 mixed crystals with variation in H/D composition: (left) observed; (right) calculated by a Monte Carlo simulation. The calculated profile of the $A_2(4)$ component of $(-CD_2O-)_n$ is described with broken lines.

For a particular molecular arrangement, the dynamical matrix describing the parallel oscillations of molecules is given as

$$\begin{bmatrix}
\nu_{0D} & f_{0,1'} & f_{0,2} & f_{0,3} & \cdots & & f_{0,N-1} & f_{0,N'} \\
f_{1',0} & \nu_{0H} & f_{1',2} & f_{1',3} & \cdots & & f_{1',N-1} & f_{1',N'} \\
f_{2,0} & f_{2,1'} & \nu_{0D} & f_{2,3} & \cdots & & f_{2,N-1} & f_{2,N'} \\
f_{3,0} & f_{3,1'} & f_{3,2} & \nu_{0D} & \cdots & & f_{3,N-1} & f_{3,N'} \\
 & & & & & \cdots\cdots\cdots & & \\
f_{N-2',0} & f_{N-2',1'} & f_{N-2',2} & \cdots & \nu_{0H} & & f_{N-2',N-1} & f_{N-2'N'} \\
f_{N-1,0} & f_{N-1,1'} & f_{N-1,2} & \cdots & f_{N-1,N-2'} & & \nu_{0D} & f_{N-1,N'} \\
f_{N',0} & f_{N',1'} & & \cdots & f_{N',N-2'} & & f_{N',N-1} & \nu_{0H}
\end{bmatrix} \quad (7)$$

where $f_{j,k} = f_{k,j}$ or $f_{s,t'} = f_{t',s}$ (symmetric matrix) and the suffices with and without prime indicate that the sites are occupied by H and D molecules, respectively. The term ν_{0H} or ν_{0D} is the intrinsic A_2 mode frequency of H or D molecules free from transition dipolar interaction. If the vibrational coupling between H and D molecules is very small, the $f_{st'}$ (or $f_{t's}$) terms vanish and the dynamical matrix is diagonalized into two blocks which are associated with H and D molecules, respectively. In such a case, the frequency of the most-in-phase oscillation of the D molecules is given approximately by the equation

$$\nu_D = \nu_{0D} + F\textstyle\sum' f_{0,j} = \nu_{0D} + F\sum' R_j^{-3} \quad (8)$$

where $\sum'$ denotes that the summation covers only the terms due to the interactions between D molecules.

The $A_2(4)$ mode of PFA-d_2 in H/D mixtures can be analyzed using eq 8. In this particular case, $\nu_{0D} = 833$ cm^{-1} (the frequency of the ECC sample of POM-d_2) and the proportionality constant F is determined so that the two-dimensional lattice consisting of D molecules gives $\nu_D = 850$ cm^{-1}. The simulation of the spectral change shown in Figure 5 was performed as follows. For each model of mixed crystals generated randomly under the condition of a constant H/D composition, the ν_D value was calculated according to eq 8. All the Lorentzian functions centered at various ν_D positions thus calculated, which have the common FWHH (the full width at the half-height) of 5.2 cm^{-1} [the value of the $A_2(4)$ band of pure PFA-d_2] and the common peak height (an arbitrary value), were superposed, giving the $A_2(4)$ band profile for the preset H/D composition. By the same procedure, the $A_2(4)$ band profiles were obtained for various H/D compositions. Every $A_2(4)$ profile was superposed by a Lorentzian curve due to the $E_1(8)$ band that is centered at 840 cm^{-1} having the FWHH = 7.8 cm^{-1} and the integrated intensity 1.67 times greater than that of the $A_2(4)$ band (the experimental values evaluated from pure PFA-d_2). Thus, for PFA/PFA-d_2 mixed crystals with various H/D compositions, we simulated the absorption profiles in the 860−830 cm^{-1} range.

The result is compared with the observed spectral change in Figure 10, where the composition is represented by the mole fraction X_D of the deuterated species. In each calculated profile, the $A_2(4)$ component is described with a broken curve. The simulation reproduced fairly well the feature of the observed spectral change with X_D, although a discrepancy in shape is seen in each pair of the observed and calculated profiles. The discrepancy is mainly due to a broadened shape of the observed $A_2(4)$ component compared with the calculated one. This broadness arises presumably from the fact that in the mixed crystals even the modes other than the zone-center mode get IR activity by the breakdown of the translational symmetry. Such additional absorptions were ignored in the present calculation.

For the simulation of a very complicated spectral change in the 1100−900 cm^{-1} range (Figure 3), we need a more comprehensive normal mode analysis taking the vibrational coupling between the normal and deuterated molecules into account. This will be reported elsewhere.

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