Recognition of High Sensitivity of Vibrational Spectroscopy in Study of Higher-Order Structure of Polymers

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Abstract: Vibrational spectroscopy had been for a long time believed to be sensitive to only the local structure of polymers. But this technique has been found to be powerful in the study of higher-order structure of polymers. Concrete examples were presented in this review, including the morphology-dependent infrared spectra of polyoxymethylene and their application to the study of crystallization process, the intimate relationship between stress-induced Raman spectral change and stress distribution in bulk polyoxymethylene samples and poly-*p*-phenylene benzobisoxazole fibers, and the chain folding mode in crystalline lamellae of polyethylene.

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1. Introduction

In the long history of polymer science, people have been utilizing vibrational spectroscopy as a tool useful for the characterization of polymers [1]. For example, the so-called crystallization-sensitive infrared/Raman bands are well known, by which the degree of crystallinity can be evaluated quantitatively. By utilizing polarization character of infrared/Raman bands, we can get information on molecular chain orientation in the crystalline or amorphous region. In this way infrared/Raman spectroscopy gives us much information on structure of polymers. But it might be a general recognition that the vibrational spectroscopy is sensitive to only the local structure of polymers but is quite weak for the study of structure of larger scale. That is to say, most people had not believed so far that the vibrational spectroscopy can give us much valuable information on the higher-order structure of polymers. If this is true, the infrared/Raman spectroscopy can become a quite useful tool for clarifying both the local structure (chain conformation, configuration, etc.) and the higher-order structure or morphology of polymers. In the present paper, several concrete examples are reviewed to show the powerfulness of vibrational spectroscopy in the study of complicated higher-order structure of semicrystalline polymer materials.

crystallize in various shapes or morphologies. For example, cationic polymerization of trioxane gives a whisker of POM [2]. As shown in Fig. 1(a), this whisker has a size of several tens μm in length and several μm in radius. The whisker consists of fully extended chains and forms an extended-chain crystal (ECC). POM can be crystallized also from the solution to give a so-called folded-chain crystal (FCC) in which the chains are packed in a crystal lamella with a finite thickness by a folding mode [Fig. 1(b)]. As shown in Fig. 2, Shimomura and Iguchi [3] found that the infrared spectra of these two types of crystal (FCC and ECC) are quite different from each other as if the spectra of different chemical compounds are measured. X-ray diffraction patterns of these samples are essentially the same, indicating that the molecular conformation and the chain packing mode in the crystal lattice are almost the same. In other words, it is just the difference in morphology, ECC and FCC, that gives such remarkably

Fig. 1 Illustration of (a) extended-chain crystal (ECC) and (b) folded-chain crystal (FCC) of polyoxymethylene.

2. Morphology-sensitive infrared spectra

2.1 Infrared spectra of POM

As well known, polyoxymethylene (POM) can

Fig. 2 Infrared spectra of (upper) ECC and (lower) FCC samples of polyoxymethylene. [Reprinted from M. Kobayashi and Y. Matsumoto, *Macromolecules*, **28**, 1580 (1995).]

different infrared spectra. This was a discovery which might explode such a longtime-believed commonsense that the infrared spectra are insensitive to the morphology of a polymer material. By investigating the spectra in detail, Shimomura et al. [4] extracted the various characteristic features of the spectra: (i) among various vibrational modes, only the A_2 modes with transition dipoles parallel to the chain axis show remarkable frequency shift, (ii) the E_1 modes with transition dipoles perpendicular to the chain axis do not change their frequencies in both the ECC and FCC, (iii) the shift value of the A_2 band depends on the vibrational mode and is in proportion to the oscillator strength (= absorbance/frequency), and (iv) such a curious phenomenon is not observed in the Raman spectra. Kobayashi et al. developed a theory with taking the dipole-dipole interactions into account and succeeded to explain these experimental data of (i) – (iv) [5]. As shown in Fig. 3, the crystal is assumed to have a cylindrical shape of height H and radius R . By summing up all the interactions between transition dipole moments, the shift of vibrational frequency $\Delta\nu$, which is defined as a difference in vibrational frequency between with (ν) and without dipole-dipole interactions (ν_0), is expressed in the following equation.

Fig. 3 (upper) A cylindrical model of a crystallite and (lower) a dipole-dipole interaction term in equation 1 of the text plotted against the ratio R/H . [Reprinted from M. Kobayashi and M. Sakashita, *J. Chem. Phys.*, **96**, 748 (1992).]

$$\Delta\nu = \nu - \nu_0 \propto \Sigma(K_j/R_j^3) \cdot (\partial\mu/\partial Q)^2 / \nu_0 \quad (1)$$

Here $(\partial\mu/\partial Q)$ is the transition dipole for the normal mode Q , R_j is the distance between these dipoles, and $K_j = \cos\theta_{0j} - 3\cos\theta_0\cos\theta_j$ where θ_j is the angle between dipole j and cylindrical axis, θ_{0j} is the angle between the central dipole (0) and j -th dipole. The second term in equation 1, $(\partial\mu/\partial Q)^2 / \nu_0$, is the so-called oscillator strength. The first term in equation 1, $\Sigma(K_j/R_j^3)$, is a total sum of interactions between dipoles included in the cylinder and is a function of shape parameters H and R . In Fig. 3 is plotted this term as a function of R/H . As seen here, this term is remarkably dependent on the ratio R/H . The limiting state at zero R/H ratio corresponds to an ECC or whisker and the state of infinitely high R/H ratio corresponds to an FCC or solution-grown single crystal. The vibrational frequency of FCC is predicted to appear at a higher frequency position than that of ECC. For

Fig. 4 Infrared spectra of polyoxymethylene samples prepared by various methods. (a) Solution grown, (b) cast from the solution, (c) melt-quenched, and (d) whisker [8].

the degenerated E_1 modes, the first term in equation 1 becomes 0. In this way the position of A_2 modes changes remarkably depending on the ratio R/H . Therefore, the infrared spectral pattern of POM is predicted to change sensitively depending on the crystal morphology or the sample preparation condition. In fact, as seen in Fig. 4, the infrared spectral pattern of POM is different between the whisker, solution-cast film, solution-grown single crystal, melt-cooled sample, and so on. In other words, it may be possible to estimate the morphology of the sample by analyzing the infrared spectral profile.

Such a phenomenon of morphology-dependent infrared spectra is seen also for polytetrafluoroethylene [6] and poly(ethylene oxide) [7]. The observation is not limited to these special polymers but should be made in principle for any polymer with large oscillator strength and large dipole-dipole interactions as well understood from equation 1.

2.2 Structural change in crystallization of POM

By utilizing this characteristic feature of infrared spectra of POM, the morphological change in the

Fig. 5 Infrared spectral change of polyoxymethylene measured in the cooling process from the melt [8].

Fig. 6 Temperature dependence of infrared absorbance estimated for the bands characteristic of ECC and FCC of polyoxymethylene in the cooling process from the melt [8]. The upper curve is the DSC thermogram.

crystallization process can be speculated by measuring the infrared spectral change. As the first trial we carried out the measurement of infrared spectra of POM

Fig. 7 An illustration of structural change of polyoxymethylene in the crystallization process from the melt [8].

in the cooling process from the molten state [8]. Fig. 5 shows the temperature dependence of the thus measured infrared spectra. In the vicinity of 155°C the crystallization-sensitive bands started to appear and increased in intensity. These bands were found to be those characteristic of FCC. Around 140°C the bands characteristic of ECC, for example the A_2 band at 902 cm^{-1} , appeared and increased in intensity gradually as seen in Fig. 6. When the sample was reheated after being cooled down to room temperature, the bands of ECC decreased in intensity gradually in a wide temperature region and disappeared around 130°C . Above 165°C , the FCC bands also disappeared steeply. The similar measurement was made for a whisker of ECC. The bands disappeared at much higher temperature of about 190°C . Since the above-mentioned ECC bands disappeared around $130 - 140^{\circ}\text{C}$, much lower than the melting point of the whisker, the structure giving the infrared bands of ECC is considered to be small in size. In parallel to this infrared spectral measurement, the

temperature dependence of small-angle X-ray scattering (SAXS) was measured in the cooling process from the melt. At about 155°C the peak corresponding to the long period of ca. $140\text{ \AA}$ ($= 14\text{ nm}$) started to appear and increased in intensity. As the temperature approached 140°C , the second peak began to appear, the long period of which was ca. $70\text{ \AA}$, a half the long period of $140\text{ \AA}$ observed in the first crystallization stage [8].

By combining all these infrared and SAXS data, the following structural model may be deduced for the crystallization process of POM. As shown in Fig. 7, when the sample is cooled from the melt, the lamellae with chain folding structure start to generate and increase in their number. The long period of these stacked lamellae is about $140\text{ \AA}$. Some of the chains are considered to pass through the neighboring lamellae as seen in Fig. 7(b). When the temperature approaches 140°C , the amorphous part existing between the two adjacent lamellae changes into a new lamella and the long period becomes about $70\text{ \AA}$ as a result. In this secondary crystallization, some of the molecular chains passing through the original two lamellae are extended to cover the several continuous lamellae, as shown in Fig. 7 (c). The length of this extended-chain stem is $150 - 200\text{ \AA}$, which is detected as the infrared bands intrinsic of ECC. This fully-extended stem is considered to correspond to the so-called taut tie chain and significantly affects the mechanical property of the sample. Utilization of morphology-dependent infrared bands makes it possible to detect tie chains in a concrete manner.

3. Vibrational spectra and stress distribution in the bulk sample

Fig. 8 Raman spectral changes measured for polyoxymethylene samples subjected to a tensile force: (left) draw ratio (λ) 34 and (right) draw ratio 7.3. [Reprinted from K. Tashiro, G. Wu, and M. Kobayashi, *Polymer*, 29, 1768 (1988).]

Fig. 9 Apparent crystallite modulus E_c^{app} and bulk modulus E_{bulk} measured for polyoxymethylene samples with various draw ratios. [Reprinted from K. Tashiro, G. Wu, and M. Kobayashi, *Polymer*, **29**, 1768 (1988).]

When a polymer sample is tensioned, the molecular chains are deformed. In order to clarify the details of the molecular deformation mechanism, the infrared and Raman spectra are sometimes employed as a useful tool [9]. A slight change in molecular geometry and intra- (and inter-) molecular interactions results in a detectable change in the vibrational spectra. One example is shown in Fig. 8. This is the Raman spectral change observed for a uniaxially-oriented POM sample subjected to a tensile force [10]. With increasing tensile stress, the peak position of the Raman band (COC angle deformation mode) shifts toward lower frequency side. Magnitude of frequency shift per 1 GPa stress is called a shift factor. When this type of experiment was made for various kinds of POM samples with different preparation conditions, the shift factor was found to be smaller for the sample with a higher draw ratio. The measurement of crystallite modulus E_c or the Young's modulus along the chain axis in the crystal lattice was made for these POM samples by the X-ray diffraction method. As shown in Fig. 9, the E_c was different depending on the sample preparation condition or the draw ratio. In some case E_c was lower than the Young's modulus of the bulk sample (E_{bulk})! This is quite curious. The E_c is assumed to be a limiting modulus of the semicrystalline samples, which can not be different depending on the sample preparation condition and should not be lower than E_{bulk} as long as the stress is distributed homogeneously in the sample. In other words, these Raman and X-ray data indicate that the stress distribution in the sample is not necessarily homogeneous. If the stress is distributed

Fig. 10 Various mechanical models. In the analysis of the data shown in Figs. 8 and 9, the model b was actually used.

homogeneously, the crystallite modulus should be the same independently of the sample preparation condition. But the heterogeneous stress distribution may give the different values to the crystallite modulus depending on the sample history. In order to interpret these data systematically, a quantitative analysis was made on the basis of a heterogeneous stress distribution model. Fig. 10(b) is the model used in this analysis. The parallel part of crystalline (C2) and amorphous (A) regions is connected to the crystalline region (C1) in a series manner. The Young's modulus of the bulk sample (E_{bulk}) and that of the crystalline region (E_c^{app}) can be expressed in terms of a true Young's modulus of the crystalline region (E_c^{true}) and a modulus of the amorphous region (E_a) as given in the following equations.

$$E_{\text{bulk}} = 1 / [(1-a)/E_c^{\text{true}} + a/(bE_c^{\text{true}} + (1-b)E_a)] \quad (2)$$

$$E_c^{\text{app}} = E_c^{\text{true}} x / [1 - a + ab/\{b + (1-b)E_a/E_c^{\text{true}}\}] \quad (3)$$

where a and b are the parameters denoting the fractions of the crystalline and amorphous regions (refer to Fig. 10). The degree of crystallinity is given by $x = 1 - a(1-b)$. The apparent shift factor of the Raman band α^{app} is given by the following equations.

$$\langle v \rangle = v_0 - \alpha^{\text{app}} \sigma_{\text{bulk}} \quad (4)$$

$$\alpha^{\text{app}} = \alpha^{\text{true}} (E_c^{\text{true}} / E_c^{\text{app}}) \quad (5)$$

where $\langle v \rangle$ is an observed Raman frequency, v_0 is a Raman frequency of free tension, σ_{bulk} is a stress of the bulk sample, and α^{true} is a true shift factor of this band. The parameters a and b , the moduli E_c^{true} and E_a , and the shift factor α^{true} were determined in such a way that all the experimental data shown in Figs. 8 and 9 could be reproduced as reasonably as possible. The thus evaluated E_c^{true} is about 75 GPa. The modulus 58 GPa,

Fig. 11 Mechanical models estimated for various types of polyoxymethylene samples.

which was estimated at room temperature by carrying out the molecular dynamics calculation, corresponds relatively well to this E_c^{true} [11]. The fractions of C1, C2, and A regions defined in Fig. 10 were estimated as shown in Fig. 11. In the sample with a low draw ratio ($\lambda = 7$), the size of parallel component C2 is small but cannot be ignored. When the tension is applied to this sample, the stress is concentrated to the small C2 region and the strain of this region becomes quite large. The actually observed strain is an average between the strains generated in the C1 and C2 regions. Therefore a stress concentration in the C2 region makes an apparently observed strain larger, resulting in lower E_c^{app} . The Raman shift factor α^{app} is also larger. For the sample with a higher draw ratio ($\lambda = 34$), the fraction of C2 region is larger and the stress concentration is reduced, resulting in higher E_c^{app} and smaller α^{app} .

This type of analysis was made also for several other polymers. For example, the Raman spectra of uniaxially-oriented polyethylene samples were measured under tension, from which the E_c^{true} of ca. 260 GPa was estimated [10]. This value is higher than the apparent crystallite modulus measured by X-ray method (235 GPa) [12, 13] and is rather closer to the Young's modulus 280 GPa estimated from the experimental data of longitudinal acoustic mode observed in the Raman spectra [14, 15]. The molecular dynamics calculation gave the modulus 280 GPa at room temperature, consistent also with E_c^{true} [11]. The similar treatment was made for fibers of rigid-rod polymer, poly-*p*-phenylene benzobisoxazole [16]. In this case the mechanical series was found to be reasonably applicable in the interpretation of Raman band shifts observed for the samples with different preparation conditions. In fact the E_c^{true} is almost constant, about 460 GPa, while E_{bulk} changes from 187 to 352 GPa depending on the preparation condition of the fiber.

4. Chain folding structure in crystalline lamella

As well known, flexible polymer chains are folded many times to form a crystalline lamella from the solution or from the melt. In order to clarify a trace of a whole chain in the lamella or the chain folding mode, various models have been proposed so far [17]. But a definite answer has not yet been established. Here we will see the usefulness of vibrational spectroscopy for this chain folding problem.

4.1 LAM band and lamellar thickness

The thickness of lamella or the length of stem (extended part of the chain) is evaluated by measuring the so-called accordion mode or longitudinal acoustic mode (LAM) of a chain. This band was originally discovered for a series of *n*-alkane molecules, where the vibrational frequency was inversely proportional to the chain length [18, 19]. The frequency ν is approximately expressed by the following equation.

$$\nu = (1/2L)(E_c/\rho)^{1/2} \quad (6)$$

where L is the stem length, E_c is the Young's modulus of the stem, and ρ is the density of the sample. Therefore, the length of the stem can be evaluated from the observed LAM frequency if the E_c and ρ are known. In fact the lamellar thickness was estimated for polyethylene (PE) samples treated at the various conditions and was compared with the result by small-angle X-ray scattering measurement [20]. The LAM band can be observed also for a random coil, by which the chain structure in the melt may be investigated, for example [21].

4.2 Chain folding mode

Infrared spectroscopy is useful as a method to investigate the chain folding mode in the lamella. Let us see the case of PE lamella as an example. PE takes an orthorhombic unit cell in which two fully-extended chains are packed with a herringbone mode. For the infrared-active vibrational modes, these two chains vibrate at two different phase relations (phase angles) of 0 and π . Therefore the infrared bands are expected to split into two, being called the correlation splitting. Krimm et al. measured the infrared spectra for a blend sample between homogeneous (CH_2) and deuterated (CD_2) species and interpreted the spectra from the viewpoint of correlation splitting [22, 23]. If the H and D chains in the blend sample are assumed to cocrystallize

Fig. 12 (a) and (b) Packing structures of H and D chains in the crystal lattice of polyethylene, and the corresponding infrared spectra. (c) A model to show an array of H and D chain stems along the [110] direction. [Reprinted from S. Sasaki, K. Tashiro, N. Gose, K. Imanishi, M. Izuchi, M. Kobayashi, M. Imai, M. Ohashi, Y. Yamaguchi, and K. Ohyama, *Polym. J.*, **31**, 677 (1999).]

in the same crystalline lattice, there should be such a probability that one H chain-stem is surrounded by the D chains (see Fig. 12(b)). Because the vibrational frequencies of the CH_2 and CD_2 modes are largely different, the vibrational coupling is cut between the CH_2 and CD_2 modes. Therefore the correlation splitting of the CH_2 band, which should occur due to the coupling between the adjacent CH_2 stems, does not occur any more and the band becomes singlet. This situation changes sensitively depending on the fraction of the H and D chains in the blend or the spatial distribution of the H and D chain-stems in the lamella. Before the infrared spectral data are interpreted along this idea, however, it must be noticed that the H and D chains in the blend might be segregated from each other when the samples are cooled slowly from the melt. This phenomenon was actually observed for the blend between fully-deuterated high-density PE (DHDPE) and normal

Fig. 13 A series of infrared spectra measured for DHDPE/LLDPE blend samples with different D/H ratios. [Reprinted from K. Tashiro, *Acta Polym.*, **46**, 100 (1995).]

high-density PE (HDPE) [24]. Then people had to use the melt-quenched samples to realize the situation of homogeneously-mixed D and H chains. Therefore it is difficult to assume that the blend samples of HDPE and DHDPE are good candidates for the purpose to investigate the spatial distribution of the D and H chain-stems in the lamella. Tashiro et al. found the blend of DHDPE with linear low-density PE (LLDPE) with about 17 ethyl branches per 1000 carbon atoms shows almost perfect mixing of the D and H species even when the blend sample is crystallized slowly from the melt [25]. In other words the D and H species show almost perfect cocrystallization in the crystalline region. Infrared spectra of these blend samples with different D/H ratios are shown in Fig. 13. As the fraction of D species increases, the splitting width of CH_2 rocking bands decreases gradually, and the band becomes singlet for the blend with a low H fraction and then the band disappears for the pure D sample. The CD_2 rocking bands behave in an opposite way. The splitting width and singlet component fraction were quantitatively analyzed and were interpreted reasonably by assuming a random distribution of the D and H stems in the crystalline lattice [26]. As shown in Fig. 12(c), the CH_2 stems are assumed to be arrayed along the [110] direction in the lattice and this array is interrupted by an invasion of D chain stems (... D-H-H-H-...-H-H-D-...). If the D and H stems are distributed randomly obeying the so-called Markov statistics, then the splitting width $\Delta\nu$ and the fraction of singlet band component (f_{singlet}) are expressed in the following equations under the

Fig. 14 Dependencies of (a) splitting width and (b) singlet fraction of the CH_2 rocking bands on the H species fraction in the blends: (○) DHDPE/LLDPE and (●) $n\text{-C}_{30}\text{H}_{62}/n\text{-C}_{30}\text{D}_{62}$. The solid lines are the theoretically calculated results under the assumption of random distribution of H and D stems in the crystal lattice.

assumption of a simply-coupled oscillator model.

$$\Delta\nu = \Delta\nu_0 \cos[\pi(1-X)/(2-X)] \quad (7)$$

$$f_{\text{singlet}} = (\text{singlet})/(\text{singlet}+\text{doublet})$$

$$= \epsilon_{\text{singlet}}(1-X)/[\epsilon_{\text{singlet}}(1-X) + \epsilon_{\text{doublet}}X] \quad (8)$$

where X is the fraction of H species, $\Delta\nu_0$ is the band splitting width for the pure H sample ($X = 1$), and ϵ is an extinction coefficient of the corresponding infrared band. The solid lines shown in Fig. 14 are the thus calculated results, fitting well the actually observed data indicated by open circles. A similar treatment could be made also for the thermal data. The melting and crystallization temperatures of these samples also change systematically depending on the D/H blend ratio, and these data could be interpreted on the basis of the above-mentioned structure model.

The small-angle neutron scattering (SANS) experiment was made also for these blend samples,

giving us such information that the D and H chains are homogeneously mixed in the molten state and that the radii of gyration (R_g) of the D and H chains in the molten state do not change even when the blend sample is cooled down slowly to an ambient temperature. The wide-angle neutron scattering (WANS) data collected for a series of D/H blend samples told us that these samples show diffuse scatterings in the low-angle regions, indicating that the D and H species are homogeneously and randomly mixed in the crystalline and amorphous regions as supported by a computer simulation [26].

In this way, the various kinds of experimental data collected for a series of blend samples between DHDPE and LLDPE supported the random distribution of the D and H species in the crystalline lamella grown from the melt. This image of random distribution of stems leads us naturally to the folding model of random reentry of the D and H chains, as shown in Fig. 15(b). The regular adjacent reentry model is impossible at least for the D/H blend samples crystallized from the melt.

Fig. 15 Illustration of various types of chain folding structure. (a) Regular adjacent reentry, (b) random reentry, and (c) cluster model consisting of the mixture of (a) and (b).

By combining the above-mentioned various kinds of experimental data with the other data of time-resolved infrared and X-ray scattering measurements [27, 28], the crystallization behavior of a chain could be described concretely. In the molten state the chains are gathered together randomly and homogeneously. When the sample is cooled from the melt, the random coils are regularized partially and these regular parts change into extended stems to form a lamella with random-reentry folding mode. During this process there occurs no change in R_g . As the crystallization proceeds furthermore, the long period of the stacked lamellae changes from 800 Å to 400 Å because of an occurrence of the secondary crystallization in the amorphous region sandwiched between the neighboring two lamellae.

5. Concluding remarks

For a long time vibrational spectroscopy has been believed to be sensitive to only the local structure of polymers and is utilized as a useful tool for characterizing the chain conformation, configuration, crystallinity, chain orientation, and so on. But, as reviewed in this article, vibrational spectroscopy is powerful also for the investigation of aggregation structure of chains or the morphology of polymer solids. By combining this spectroscopic technique with other methods such as X-ray diffraction, electron diffraction, neutron scattering, solid-state nmr, computer simulation, etc., we may be able to obtain more useful information concerning the morphology of polymers from both the microscopic and macroscopic points of view.

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