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Measurements of Neutron Incoherent Inelastic Scattering in Solid Polymers

Part 2 Normal Vibrational Frequency Distribution in Solid Polymers

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The neutron incoherent inelastic scattering (NIIS) measurements of solid polymers have been carried out by time-of-flight (TOF) technique using thermal neutron from KUR neutron guide tube installed at Research Reactor Institute of Kyoto University. The inelastic scattering spectra were converted to density of phonon state to reveal normal vibrational frequency distribution in solid polymers. It was found that some peaks due to vibrational modes can be observed in the density of phonon state and assignment of the modes was discussed.

KEY WORDS: Neutron incoherent inelastic scattering (NIIS)/ Normal vibrational frequency distribution/ Density of phonon state/ Poly(isobutylene oxide)/ Isotactic polypropylene/ Poly(ethylene oxide)/

1. INTRODUCTION

Neutron inelastic scattering is a powerful tool for investigation of molecular vibrations in a low frequency region in solid polymers. Molecular vibrations have been traditionally studied by infrared (IR) and Raman spectroscopy. However, there are inactive modes in such spectroscopies; IR and Raman spectroscopy are inactive for modes which do not induce changes of electric dipole-moment and of polarizability, respectively. On the other hand, neutron spectroscopy is not limited by selection rules, because neutrons are scattered directly from vibrating nuclei.^{1,2)} Regardless of the utility, neutron scattering measurements of polymers have been scarcely carried out in this country, because of the lack of strong neutron sources and suitable facilities.

In this situation we started neutron scattering measurements a few years ago using a neutron spectrometer at Research Reactor Institute of Kyoto University(KUR). We have used a neutron beam having a broad distribution in wavelength to obtain sufficient

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scattering intensity for analysis. Hence, two problems have arisen; the one is the overlapping of elastic and inelastic scatterings and the other is deformation of the elastic scattering profile due to Bragg reflections from crystallites in the polymer sample. In the preceding paper³⁾, we established a method to separate the inelastic part from the elastic part in time-of-flight spectra of solid polymers. In the present paper, we analyse the inelastic scattering to reveal normal vibrational frequency distribution in solid polymers.

2. THEORETICAL

The differential cross-section of incoherent inelastic scattering is defined as the probability that an incident neutron with energy E_0 is scattered into a solid angle element $\partial\Omega$, and in an energy interval between E and $E+\partial E$. The double differential cross-section for the single-phonon process $\partial^2\sigma_{\text{incoh}}/\partial\Omega\partial E$ is given¹⁾ by

$$\frac{\partial^2\sigma_{\text{incoh}}}{\partial\Omega\partial E} = \sum_{q,j} \frac{k}{k_0} \delta(\hbar\omega \mp \hbar\omega_j(\mathbf{q})) \frac{\hbar \left(n_s + \frac{1}{2} \pm \frac{1}{2} \right)}{2\omega_j(\mathbf{q})} \times \sum_{\rho} \frac{(\langle b_{\rho}^2 \rangle - \langle b_{\rho} \rangle^2)}{M_{\rho}} |\mathbf{Q} \cdot \mathbf{U}_{\rho}^j(\mathbf{q})|^2 e^{-2W_{\rho}} \quad (1)$$

Here k_0 and k are the lengths of the wave vectors of incident and scattered neutrons \mathbf{k}_0 and \mathbf{k} , respectively. \mathbf{Q} is the scattering vector defined as $\mathbf{Q} = \mathbf{k}_0 - \mathbf{k}$. $\hbar\omega_j(\mathbf{q})$ is phonon energy of the mode j with phonon wave vector \mathbf{q} . b_{ρ} is the scattering length of the atom at the position ρ , M_{ρ} its mass and $e^{-2W_{\rho}}$ its Debye-Waller factor. \mathbf{U}_{ρ}^j is a vector which represents the displacement of the atom for the phonon of the mode j ("polarization vector"). $n_s + \frac{1}{2} \pm \frac{1}{2}$ is Bose-Einstein population factor, where

$$n_s = [\exp(\hbar\omega_j(\mathbf{q})/k_B T) - 1]^{-1}. \quad (2)$$

k_B and T are Boltzmann constant and absolute temperature, respectively. The upper sign refers to neutron energy loss and the lower sign to energy gain. The lower sign should be adopted for the present experiment, because we employed the up-scattering of neutrons.

Equation (1) informs us some important features of incoherent inelastic scattering. The differential cross-section is proportional to incoherent atomic cross-section, $4\pi(\langle b_{\rho}^2 \rangle - \langle b_{\rho} \rangle^2)$. It means that the observed differential cross-section is mainly dominated by the scattering from hydrogen atoms, because the samples used in the experiment contain only three kinds of atoms, H, C, and O, and the incoherent atomic cross-section of hydrogen atom is much larger than that of other atoms. The term $|\mathbf{Q} \cdot \mathbf{U}_{\rho}^j(\mathbf{q})|^2$ in eq. (1) also implies that maximum value of the differential cross-section is obtained when direction of momentum transfer of neutron $\hbar\mathbf{Q}$ is parallel to that of the polarization vector $\mathbf{U}_{\rho}^j(\mathbf{q})$ of hydrogen atom. Further, it suggests that modes having large vibrational amplitude give large scattering intensity. This is in contrast to IR or Raman spectroscopy, where the large intensity is obtained for the mode which induces large changes of dipole-moment or polarizability.

Incoherent inelastic neutron spectra are frequently converted to a density of phonon state which is essential for discussion of normal vibrational frequency distribution because

it corresponds to the amplitude-weighted number of energy levels in a sample per unit energy. It is given²⁾ by

$$Z(\omega) = \frac{4M\omega}{\hbar} \exp\left(\frac{\hbar\omega}{2k_B T}\right) \sinh\left(\frac{\hbar\omega}{2k_B T}\right) \frac{S_s(\mathbf{Q}, \omega)}{Q^2} \quad (3)$$

Here $S_s(\mathbf{Q}, \omega)$ is scattering law which is obtained by Fourier transform of time-space self-correlation function and can be connected with the differential cross-section through the following equations

$$S_s(\mathbf{Q}, \omega) = (\langle b^2 \rangle - \langle b \rangle^2)^{-1} \frac{\hbar_0}{\hbar} \frac{\partial^2 \sigma_{\text{incoh}}}{\partial \Omega \partial E} \quad (4)$$

and

$$\frac{\partial^2 \sigma_{\text{incoh}}}{\partial \Omega \partial \omega} = \hbar \frac{\partial^2 \sigma_{\text{incoh}}}{\partial \Omega \partial E} \quad (5)$$

The differential cross-section can be expressed by using time of flight τ of neutrons.

$$\frac{\partial^2 \sigma_{\text{incoh}}}{\partial \Omega \partial E} = \frac{\tau^3}{m_n} \frac{\partial^2 \sigma_{\text{incoh}}}{\partial \Omega |\partial \tau|} \quad (6)$$

where m_n is mass of neutron.

Then, we can calculate the phonon density $Z(\omega)$ by using eqs. (3), (4), (5) and (6) from the observed time of flight spectrum, or time-differential cross-section $\partial^2 \sigma_{\text{incoh}} / \partial \Omega |\partial \tau|$.

3. EXPERIMENTAL

Poly(isobutylene oxide) (PIBO) fibers, poly(ethylene oxide) (PEO) fibers, and uniaxially oriented isotactic polypropylene (PP) films were used as samples.

The neutron inelastic scattering measurements were carried out by time-of-flight (TOF) technique using thermal neutrons from the neutron guide tube installed at KUR.⁴⁾ The incident neutron energy (wavelength) was selected by two methods; mechanical and filter ones. In the former case, neutrons with wavelengths longer than 6.5 Å were selected by adjusting a cylindrical rotating chopper. In the latter, incident neutrons were filtered by polycrystalline beryllium (Be) to have relatively narrow energy spread of 0 to 5 meV. In this case, the chopper was used only to make neutron beam into pulses. In the present paper, we report the results of Be filter method. For detection of scattered neutrons, BF₃ counters were used. Scattering angle is set to be 90°. The polymer films and fibers were mounted on a sample holder so that momentum transfer vector of neutrons is perpendicular to the chain axis of the polymer samples. Details of the experiment were reported in the preceding paper.³⁾

4. RESULTS

The observed TOF spectrum of PIBO is shown in Fig. 1. The peak at about 1200 μ s arises from elastic scattering from the sample. The solid curve in the figure indicates pure incoherent elastic scattering profile which is determined by elastic scattering of vanadium. The elastic scattering profile of the sample is considerably deformed from the pure elastic

Normal Vibrational Frequency Distribution by Neutron Scattering

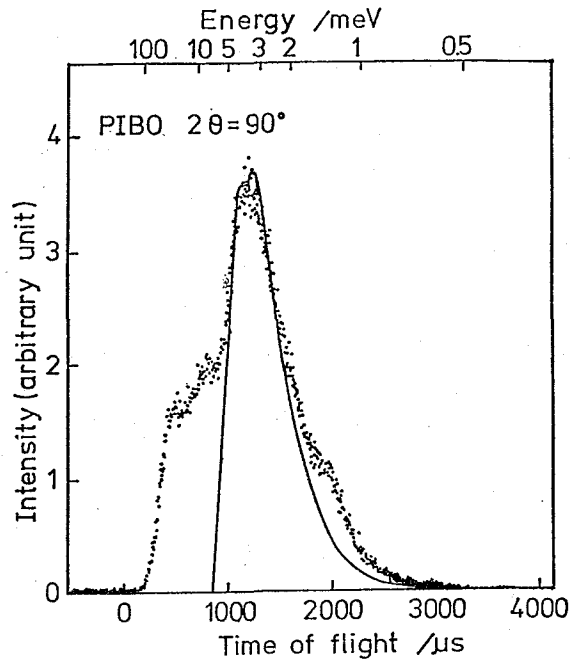


Fig. 1. TOF spectrum of PIBO fibers at a scattering angle of 90° . The direction of momentum transfer of neutrons is perpendicular to the chain axis. The solid curve indicates the pure incoherent elastic scattering profile.

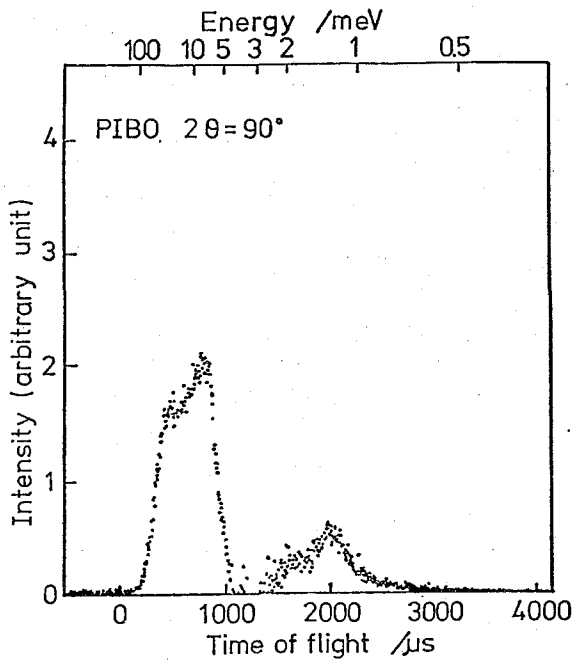


Fig. 2. TOF spectrum of PIBO obtained by subtracting the incoherent elastic scattering from the spectrum in Fig. 1. The peak remaining in the elastic scattering region is due to the 110 and 200 Bragg reflections of PIBO crystals.

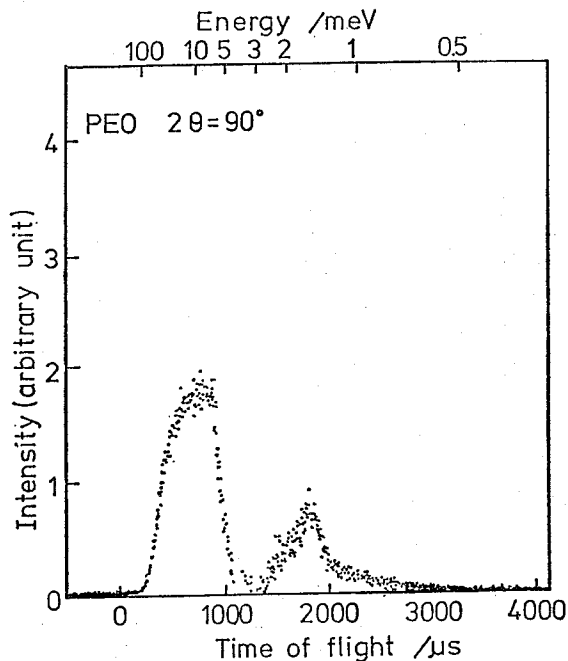


Fig. 3. TOF spectrum of PEO fibers after subtraction of the incoherent elastic scattering. The peak remaining in the elastic scattering region is due to the 120 Bragg reflection of PEO crystals.

one. As shown in the previous paper,³⁾ this deformation is due to Bragg reflections from crystallites in the polymer. According to the separation method of inelastic scattering,³⁾ we subtracted the incoherent elastic scattering from the TOF spectrum. The result is shown in Fig. 2. The incoherent inelastic scattering profile appears clearly in the TOF region shorter than 1000 μs . The remaining peaks in the elastic region have been assigned to the 110 and 200 reflections.^{3,5)} Similar measurements were carried out on PP and PEO and the inelastic scattering profiles were separated. The result for PEO is shown in Fig. 3. In this polymer, Bragg reflection from the (120) plane of crystallites appears in the elastic region.

It was found from Figs. 2 and 3 that the inelastic scattering profile of PIBO has more detailed structure compared with that of PEO. The difference may be due to methyl group vibrations in PIBO since the chemical structure of their main chains is the same.

5. DISCUSSION

The density of phonon state calculated for PP is shown in Fig. 4 where far infrared (FIR) spectrum reported by Miyazawa et al.⁶⁾ is also included. It must be noted that the intensity in spectral density below 100 cm^{-1} is overestimated because of the poor separation of elastic and inelastic peaks. Four peaks appearing in the FIR spectrum have been assigned from theoretical calculation of dispersion curve of this polymer; 106 cm^{-1} : torsional vibration of main chain, 169 and 321 cm^{-1} : C-C-C bending vibration, 251 cm^{-1} : C-C-C bending vibration and torsional vibration of methyl group. In the

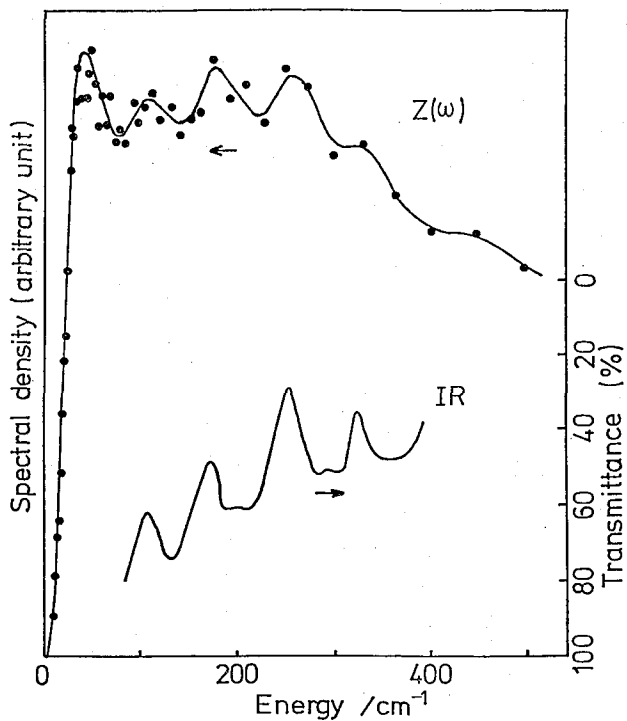


Fig. 4. Density of phonon state and FIR spectrum⁶⁾ for PP.

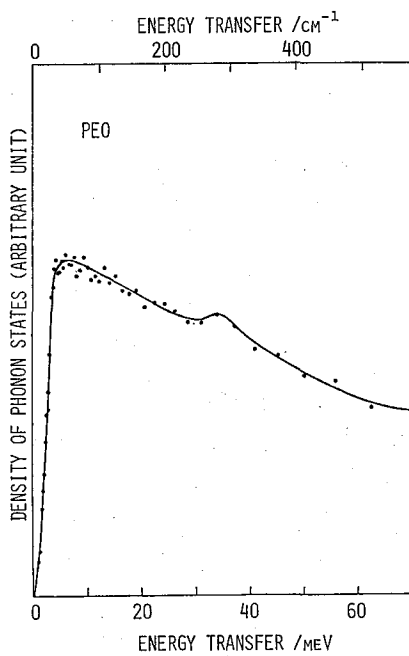


Fig. 5. Density of phonon state for PEO.

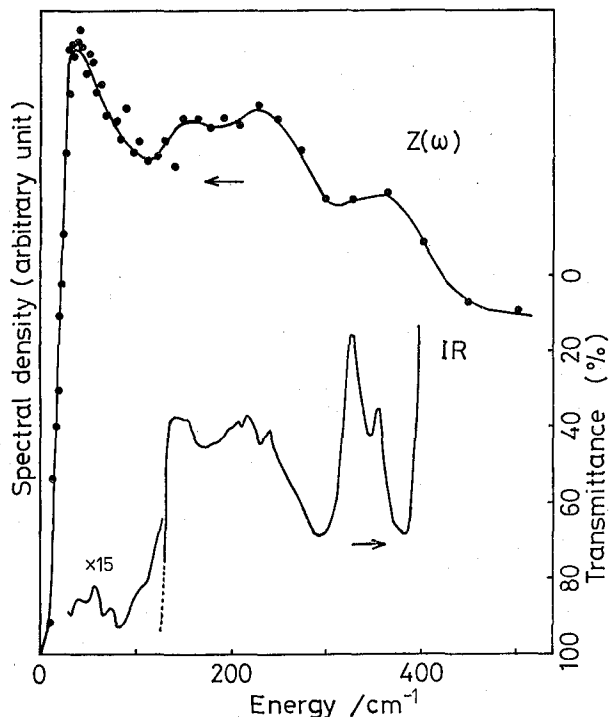


Fig. 6. Density of phonon state and FIR spectrum for PIBO.

density of phonon state, five peaks are observed at 50, 110, 180, 260 and 320 cm^{-1} and four peaks except for 50 cm^{-1} agree with the FIR results. Allen⁷⁾ have also carried out neutron inelastic scattering measurements on PP and reported that the peak at 50 cm^{-1} disappears when the scattering vector \mathbf{Q} is parallel to the molecular chain axis. It suggests that direction of the vibrational mode is perpendicular to the chain axis. However, exact assignment is in a further problem. The density of phonon state of PEO is shown in Fig. 5. Only two peaks are observed at 50 and 270 cm^{-1} . The peak at 270 cm^{-1} may correspond to phonon dispersion in crystallites of the polymer. However, other modes can not be observed in the phonon density for PEO, though many modes are detected for PP. This is considered as follows. Neutron inelastic scattering intensity is proportional to square of amplitude of atomic vibration. In PP, main chain vibration induces displacement of methyl groups and the methyl groups play a role to emphasize the amplitude of the main chain vibrations.

In Fig. 6, the density of phonon state of PIBO is shown with FIR spectrum which was measured by the present authors. In the figure, peaks appear at 50, 160, 240 and 370 cm^{-1} and the positions are in fairly good agreement with those of FIR spectrum. Unambiguous assignment of each peak is difficult because there is no theoretical calculation of dispersion curve for this polymer. In analogy with the result of PP, we can probably assign the peak at 240 cm^{-1} to torsional vibrational mode of methyl groups and the peak at 50 cm^{-1} may represent similar mode to that observed at the same position in PP. The peaks at 160 and 370 cm^{-1} may correspond to those at 180 and 320 cm^{-1} in PP. The details are now in consideration.

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