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Measurements of Neutron Incoherent Inelastic Scattering in Solid Polymers

Part 1 A Separation Method of Inelastic Scattering in Time-of-Flight Spectrum

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The neutron incoherent inelastic scattering (NIIS) measurements of polymers have been carried out by time-of-flight (TOF) technique using thermal neutrons from the KUR neutron guide tube installed at Research Reactor Institute of Kyoto University. In this paper a separation method of inelastic scattering from elastic scattering in TOF spectrum is reported. It is found that deformation of the elastic scattering profile from the pure incoherent elastic one is caused by Bragg reflections of polymer crystals.

KEY WORDS: Neutron incoherent inelastic scattering (NIIS)/ Time-of-flight (TOF) measurements/ Separation of inelastic scattering/ Poly(isobutylene oxide)/ Isotactic polypropylene/ Poly(ethylene oxide)/

1. INTRODUCTION

The molecular vibrations of polymers in a low frequency region corresponding to far-infrared (FIR) and Raman spectroscopies are of great importance to understand the macroscopic dynamic properties. However, the FIR and Raman spectroscopies do not always detect all molecular vibrations because of the selection rules to these spectroscopies. On the other hand, there is no such inactive mode in neutron scattering because neutrons are scattered directly from vibrating nuclei,[1-2] so that the neutron inelastic scattering technique can be an effective probe for studying the molecular vibration. The neutron scattering measurements of polymers have scarcely carried out in this country, because of the lack of strong neutron sources and suitable facilities. The purpose of this work is to establish an analytical method of the inelastic scattering data obtained with a neutron source and a spectrometer available.

We have used a neutron beam having a broad distribution in wavelength to

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obtain sufficient scattering intensity for analysis. Hence, two problems have arised; the one is the overlapping of elastic and inelastic scatterings and the second is deformation of the elastic scattering profile due to the Bragg reflections from crystallites in the polymer sample. In this paper we report a method to separate the inelastic part from the elastic part in time-of-flight spectra of solid polymers.

2. EXPERIMENTAL

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

The neutron inelastic scattering measurements were carried out by time-of-flight(TOF) technique using thermal neutrons from the KUR neutron guide tube installed at Research Reactor Institute of Kyoto University. The energy spectrum of neutrons is distributed over the range of wavelength from 1 to 20Å, having a maximum intensity at the wavelength of about 2Å. The details are reported in the literature.[4] In the measurements, the up-scattering of neutrons was employed. The incident neutron-energy (wavelength) selection was made by two methods; mechanical and filter ones. In the former case, neutrons with wavelengths longer than 6.5Å were selected by adjusting a cylindrical rotating chopper,[4] by which neutrons were pulsed at the same time. In the latter, incident neutrons filtered by polycrystalline beryllium used, having relatively narrow energy spread of 0 to 5 meV. In this case the chopper was used only to make neutron beam into pulses.

The experimental arrangement is schematically shown in Fig. 1, where the scattering angle is 90°. When the chopper was used to cut off the shorter wavelength neutrons than 6.5Å, the Be-filter was removed. The chopper was operated at a speed of rotation 60 rps and the flight distance from sample to detector 1 m. The neutrons were collimated with a pair of line-slits 4 and 2 mm wide and 100 mm in

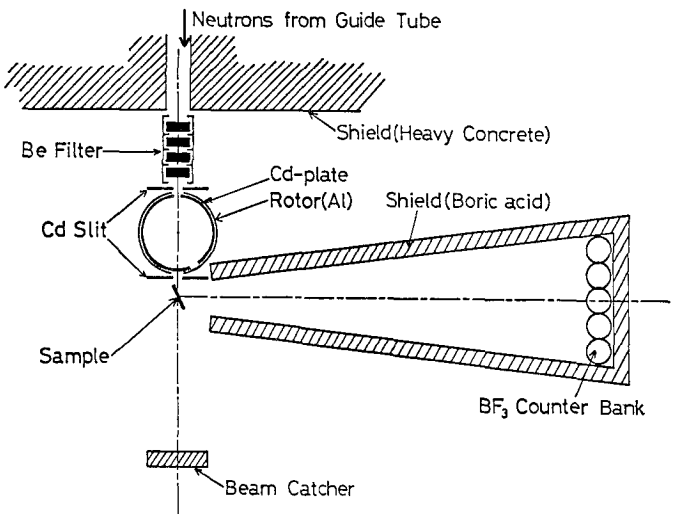

Fig. 1. Schematic diagram of the arrangement for the time-of-flight measurement at KUR Neutron Guide Tube.

height at the entrance and the exit of chopper, respectively. As detectors, five BF_3 proportional counters set-up vertically were arranged horizontally as shown in the figure. The time resolution was consequently about 4%.

3. SEPARATION OF THE INELASTIC SCATTERING SPECTRUM

The purpose of this study is to find a separation procedure of the inelastic part from the elastic part in the observed TOF spectrum. Here we will discuss the two cases in which the wavelengths of incident neutrons are 6.5 and 4.0Å.

3.1 TOF spectra measured with use of incident neutrons of 6.5Å

Figure 2 shows the TOF spectrum of the direct neutron beam in the case of incident neutrons of 6.5Å. The abscissa designates the time of flight per meter of neutrons and the ordinate the relative intensity (counts per channel or per 5.12μs).

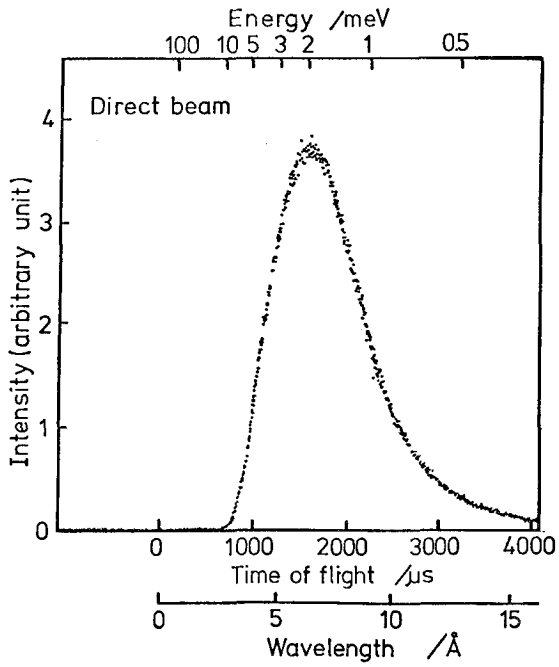

Fig. 2. Time-of-flight (TOF) spectrum of the direct beam of mechanically monochromatized neutrons. The cut-off wavelength 6.5 Å.

The time of flight at the maximum of this spectrum corresponds to a wavelength of 6.5Å. In order to determine the profile of the pure incoherent elastic scattering in the experimental system, the TOF spectrum of vanadium was measured. Figure 3 is the spectrum at a scattering angle of 90°; the strong peak at about 1640 μs is the elastic scattering and the small one at about 500 μs is the inelastic scattering owing to the crystalline dispersion. The pure incoherent elastic profile in the experimental system is therefore obtained from the profile of vanadium by reference to the profile of direct beam.

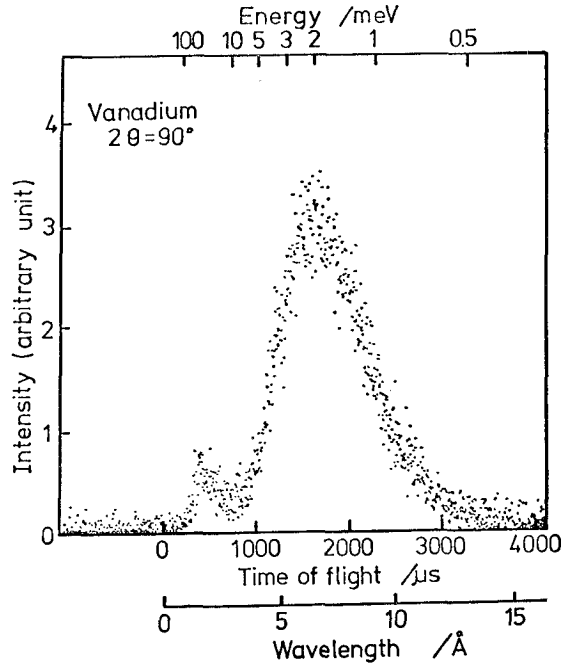

Fig. 3. TOF spectrum of vanadium at a scattering angle of 90°.

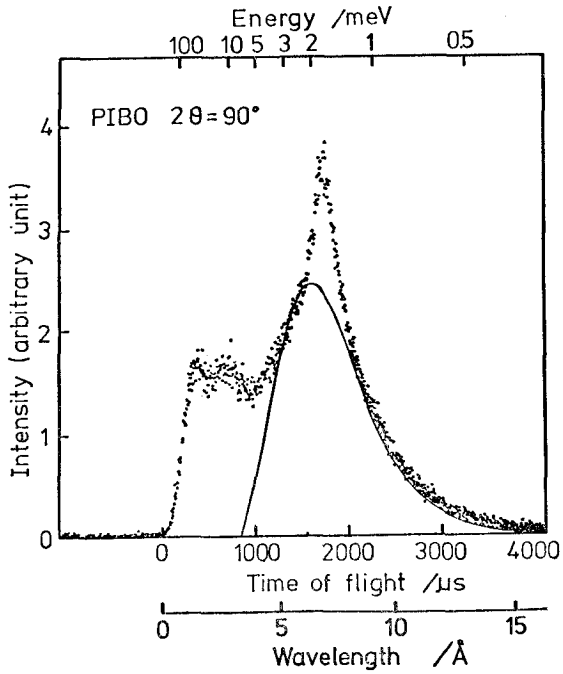

Fig. 4. TOF spectrum of poly(isobutylene oxide) fibers at a scattering angle of 90°. The direction of momentum transfer of neutrons is perpendicular to the chain axis. The solid curve indicates the incoherent scattering profile.

Figure 4 shows the observed TOF spectrum of PIBO fibers at a scattering angle of 90°. The fibers were mounted on the sample holder so that the fiber axis would be parallel to the beam line-slit and perpendicular to the beam direction. Therefore, the momentum transfer vector Q of neutrons is nearly perpendicular to the fiber axis or chain axis of the polymer molecules. As can be seen from the figure, the elastic peak is greatly deformed. In order to find out the origin of such a phemomenon, we tried to subtract the pure incoherent elastic profile determined above from the spectrum. This treatment was carried out on the graphic display; first the pure incoherent elastic profile was fitted to the observed spectrum by changing the ordinate of the elastic profile as is shown by a solid line in Fig. 4. Then, the fitted elastic profile was subtracted; Fig. 5 shows the result. In the region of elastic scattering a sharp strong peak remains, which may be considered due to Bragg reflections since the sample used is semicrystalline and contains carbon and oxygen atoms with considerable coherent scattering lengths.

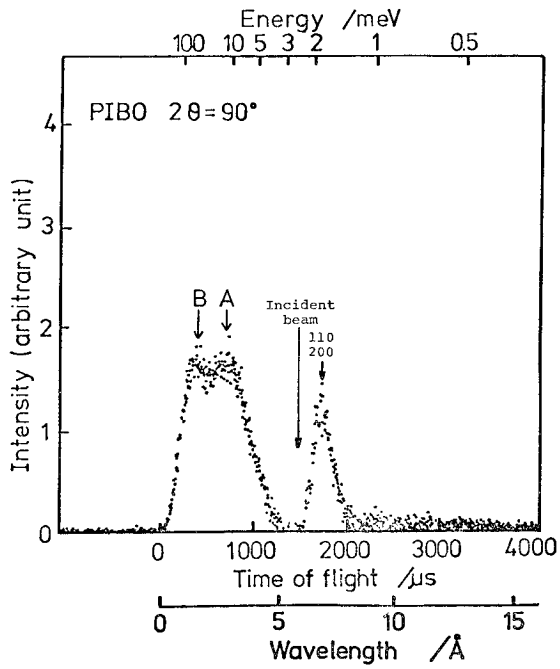

Fig. 5. TOF spectrum obtained by subtracting the incoherent elastic scattering from the spectrum in Fig. 4. The peak remaining in the elastic scattering region is due to the 110 and 200 Bragg reflections of poly(isobutylene oxide) crystals.

The crystal structure of PIBO assumes orthorhombic with parameters a=10.76Å, b=5.76Å, and c=7.00Å (chain axis).[5] From this structure, the very strong reflections from (200) and (110) planes with the lattice spacings of 5.38 and 5.08Å, respectively, are expected. For the scattering angle of 90°, the wavelengths which fulfil the Bragg conditions for these lattice planes are 7.61 and 7.18Å, respectively. The wavelength at the maximum position of the remaining peak in the elastic region

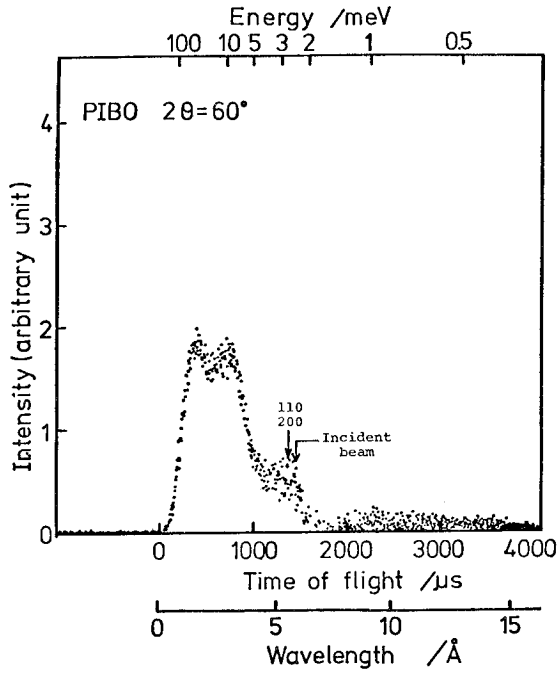

Fig. 6. TOF spectrum of poly (isobutylene oxide) fibers at a scattering angle of 60° after subtraction of the incoherent elastic scattering. Also see the legend of Fig. 5.

in Fig. 5 is between these two values. Hence, this peak can be regarded as the superposition of the 200 and 110 reflections. In order to confirm this the scattering angle was changed from 90° to 60°; the resulting spectrum is shown in Fig. 6 after subtracting the incoherent elastic profile. As was presumed, the maximum position shifts to a value between calculated values of 5.38 and 5.08Å. The decrease in intensity of this peak is caused by the decrement in intensity of the incident neutron beam in the corresponding region of wavelength. More direct evidence for this conclusion is obtained by an experiment with the sample rotated by 90° around the axis perpendicular to the fiber axis. In this case it is presumed that no lateral reflections such as 200 and 110 appear in the detector direction. The experimental result is shown in Fig. 7, where no Bragg reflections are seen in the elastic region.

Similar experiments were carried out also for oriented isotactic polypropylene film and poly(ethylene oxide) fibers. The results are shown in Fig. 8 and 9, respectively. In both cases the remaining Bragg reflections are seen; 040, 130, and 110 reflections for isotactic polypropylene[6] and 120 reflection for poly (ethylene oxide).[7]

It has become apparent from the above experiments that the Bragg reflection is responsible for the deformation of the elastic scattering profile. The inelastic part can be separated from the incoherent elastic part. However, it is noted that the effect of Bragg reflection cannot be removed completely as far as the incident beam of the shorter wavelength than 6.5Å is used. Although the cut-off at a longer

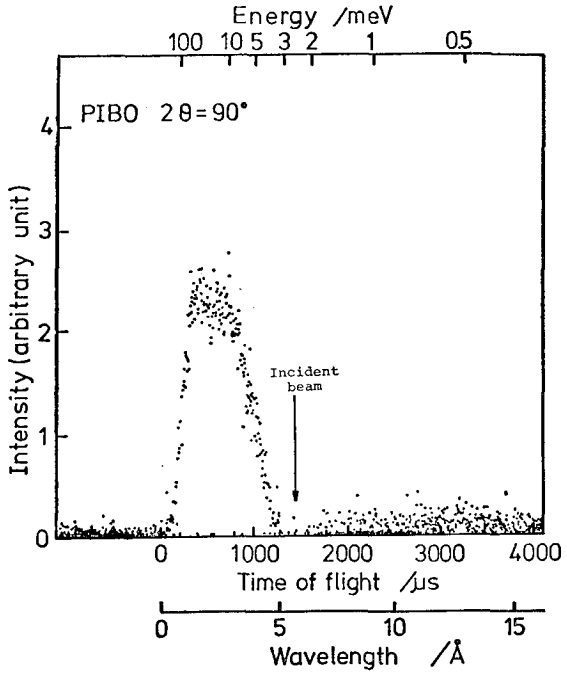

Fig. 7. TOF spectrum of poly(isobutylene oxide) fibers at a scattering angle of 90° after subtraction of the incoherent elastic scattering. The direction of momentum transfer of neutrons is parallel to the chain axis.

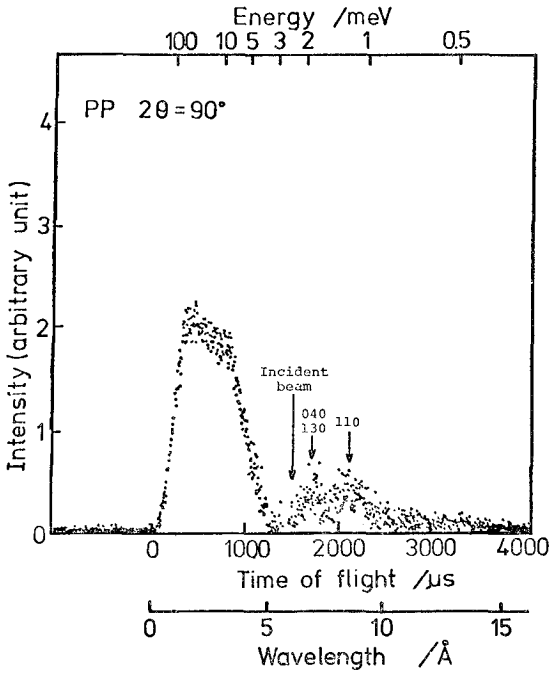

Fig. 8. TOF spectrum of oriented isotactic polypropylene film after subtraction of the incoherent elastic scattering. The peaks remaining in the elastic scattering region are due to the 110, 040, and 130 Bragg reflections of polypropylene crystals.

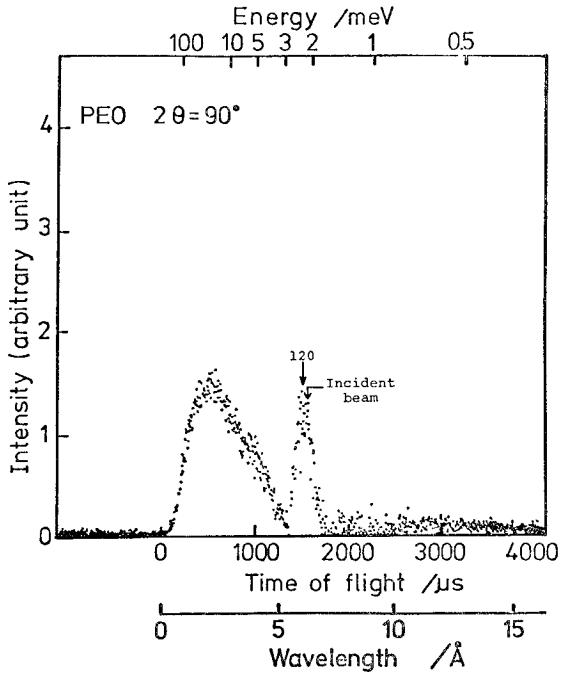

Fig. 9. TOF spectrum of poly(ethylene oxide) fibers after subtraction of the incoherent elastic scattering. The peak remaining in the elastic scatetring region is due to the 120 Bragg reflection of poly(ethylene oxide) crystal.

wavelength would avoid the problem of Bragg reflections, it will greatly decrease intensity, so that it is not desirable in practice. Therefore, the experiments must be carried out under the condition in which inseparable Bragg reflections can be neglected.

3.2 TOF spectra with use of the Be-filtered neutrons of 4.0Å

As described above, the problem of Bragg reflections can be neglected in the time-of-flight spectrum at large scattering angles when the neutrons of 6.5Å are used. In that case, however, we cannot obtain sufficient intensity to give a statistically significant spectral density. Therefore, we have examined whether the separation of inelastic and elastic scatterings is possible or not also in the TOF spectra obtained by Be-filtered neutrons with shorter wavelengths.

The 99.9% neutrons with wavelengths shorter than 4.0Å were removed with use of the Be-filter of the total thickness 120 mm. The chopper was used only for the time-of-flight measurements. The other conditions were the same as in the section 3.1. Figure 10 and 11 show the TOF spectra of the direct beam and the neutrons scattered by vanadium, respectively, when the Be-filtered neutrons were used. From these spectra the profile of incoherent elactic scattering was determined in a similar manner as in the previous section. The TOF spectrum of PIBO fibers is shown in Fig. 12; the solid curve designates the incoherent elastic scattering profile determined above. The subtraction of incoherent elastic scattering gives Fig. 13. Bragg reflections also remain in the elastic scattering region. Comparison of Fig. 5 and Fig. 13

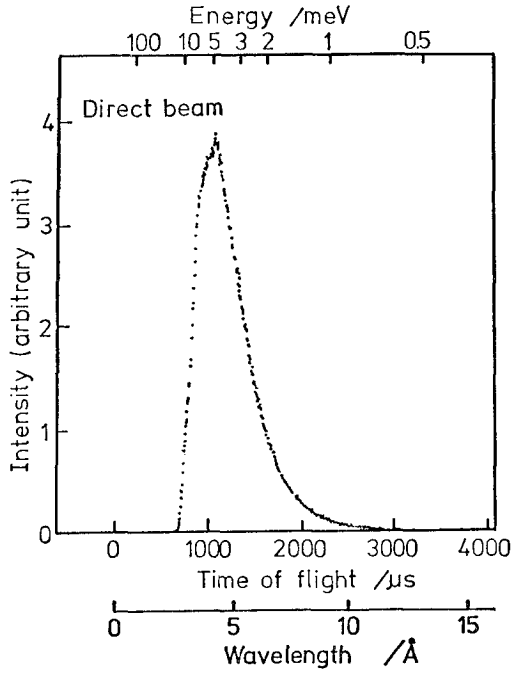

Fig. 10. TOF spectrum of the direct beam of Be-filtered neutrons. The cut-off wavelength 3.96 Å.

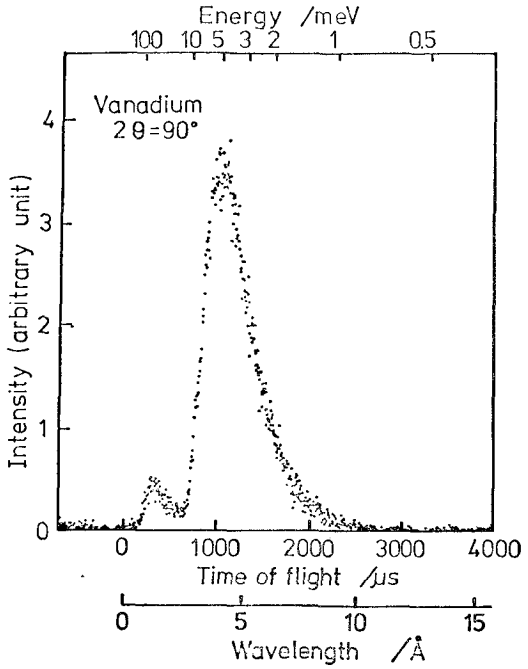

Fig. 11. TOF spectrum of vanadium at a scattering angle of 90°. Be-filtered neutron beam used.

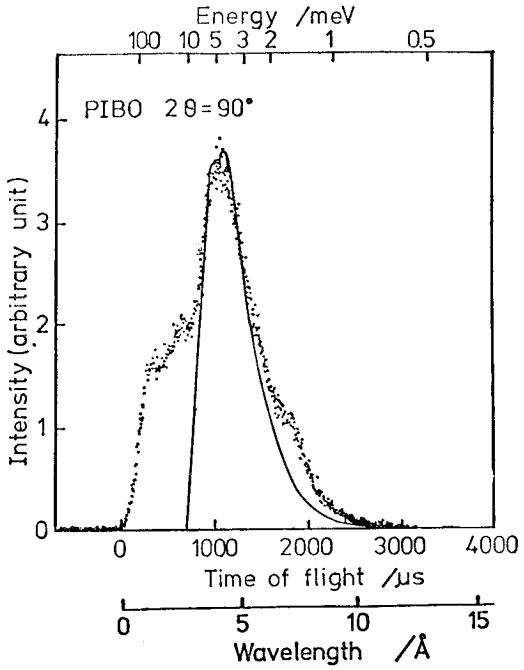

Fig. 12. TOF spectrum of poly(isobutylene oxide) fibers at a scattering angle of 90°. Be-filtered neutron beam used. See the legend of Fig. 4.

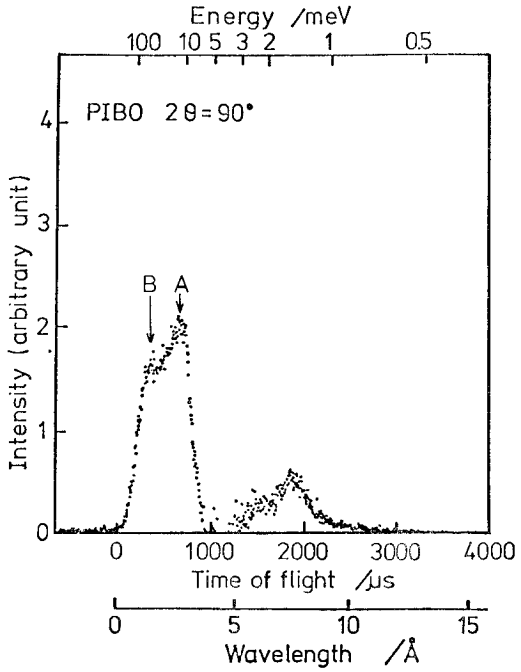

Fig. 13. TOF spectrum obtained by subtracting the incoherent elastic scatterig from the spectrum in Fig. 12. See the legend of Fig. 5.

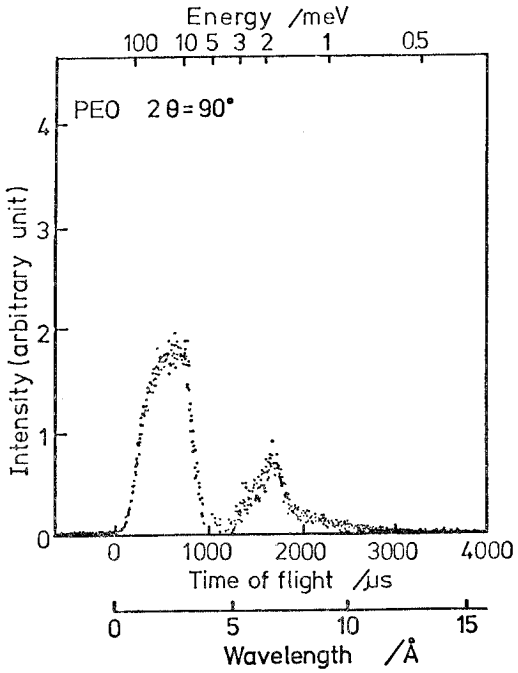

Fig. 14. TOF spectrum of poly(ethylene oxide) fibers after subtraction of the incoherent elastic scattering. Be-filtered neutron beam used. See the legend of Fig. 9.

shows that the intensity of peak A in Fig. 13 is higher than that in Fig. 5. This may be caused by the fact that the inelastic scattering spectrum is contracted in the scale of time of flight when the neutrons with shorter wavelengths are used; the smaller the energy shift, the more the spectrum contractes. Another cause may be the error when the incoherent elastic profile is subtracted. Figure 14 shows the TOF spectrum of PEO fibers corresponding to Fig. 9.

It is concluded from the results discussed in sections 3.1 and 3.2 that the usage of Be-filtered neutrons is more advantageous in comparison with the usage of mechanically cut-off neutrons.

In data analyses the FACOM M160-AD at the computer center of the Institute for Chemical Research, Kyoto University, was used.

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