# Vibrational spectroscopic study on poly(ethylene oxide) crystals

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It has been found for polyoxymethylene that differences in morphological structure cause remarkable frequency changes for some infra-red-active vibrational modes. In relation to this phenomenon, the vibrational spectra of poly(ethylene oxide) were investigated on two samples with different morphologies, a well drawn film and a solution-grown lamellar crystal. The $A_2$ bands of the solution-grown crystal shifted towards the high-frequency side, while the other bands, $A_1$ and $E_1$, remained at the same positions as those of the drawn film. It was concluded that the spectral change is due to the same mechanism as in polyoxymethylene.

## INTRODUCTION

The vibrational spectra of trigonal polyoxymethylene (t-POM) crystals[1-3] have been of interest as well as those of another modificiation, the metastable orthorhombic form (o-POM)[4,5], and a number of studies have been published[6-15]. It has been found that the infra-red spectra of t-POM are very dependent on the state and/or the route of processing of the specimens measured[13]. Though the absorption profiles are rather complicated, the infra-red spectra of some t-POM specimens could be reproduced by the superposition of the spectra of two extreme samples. One is a needle-like crystal known as a polymer whisker[16,17], in which the molecular chains are thought to be fully extended and are arranged in completely high perfection[18-20]. The other is a lamellar crystal grown isothermally from dilute solution, with molecular chains folded periodically[21,22]. The infra-red spectra of these two extreme crystals are quite different, though both crystals show the same wide-angle X-ray diffraction pattern, i.e. both crystals have the same unit-cell structure. The infra-red spectrum of the needle-like crystal is very close to that of a well oriented and highly crystalline film sample and the assignment of the bands has been established by normal-mode analysis[6]. On the contrary, some bands of the solution-grown crystal shifted substantially from the positions of the corresponding bands of the needle-like crystal. In previous work[23,24], the symmetry species of the shifted bands of the solution-grown crystal was determined to be $A_2$, which has transition moment parallel to the $c$ axis. In

clear contrast, the bands of the other symmetry species, infra-red- and Raman-active $E_1$ and Raman-active $A_1$ and $E_2$, showed no frequency difference between these two extreme crystals. The same phenomenon was also observed with deuterated samples of trigonal polyoxymethylene (t-POM-$d_2$)[23].

Recently, an extended-chain crystal of o-POM was obtained in a cationic polymerization system of trioxane as a by-product of needle-like crystal synthesis[25,26], and spectroscopic studies have been performed[27,28]. A folded-chain crystal of o-POM was obtained by a pressure-induced solid-state phase transition[29,30]. These o-POM crystals exhibited the same spectral change caused by the difference in morphology. In this case, only the bands assigned to the $B_1$ species with transition moment parallel to the molecular axis shift towards the high-frequency side in the spectrum of the folded-chain crystal.

In this work, another polar polymer, the monoclinic form of poly(ethylene oxide) (PEO), was investigated in order to obtain more experimental information on the anomalous behaviour of the vibrational spectra of POM crystals. PEO is a crystalline polymer with 7/2 helical conformation[31,32] and contains oxygen atoms in the main chain as well as POM. Unfortunately, a PEO crystal consisting of fully extended-chain structure like the needle-like crystal of t-POM cannot be obtained at the moment. A well drawn film of PEO was used in this study, because the drawn film of t-POM shows nearly the same type of infra-red spectrum as the extended-chain needle-like crystal. The infra-red and Raman spectra of the solution-grown (folded-chain) crystal and drawn film of PEO were measured and the difference was considered in relation to the cases of t-POM and o-POM.

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## EXPERIMENTAL

### Samples

Commercial PEO with average molecular weight about $3 \times 10^5 \text{g mol}^{-1}$ was used. Film samples with appropriate thickness for the infra-red measurement were cast from methanol solution. After drying in air, the film was drawn eight times at room temperature.

The solution-grown crystal was prepared from the same resin. The folded-chain crystal was crystallized from dilute (0.5 wt%) xylene solution[33,34] at room temperature. After filtration, the crystals were dispersed in benzene and freeze-dried. To avoid the effect of water, the solvents were dried with calcium sulphate before the crystallization or freeze-drying operations.

### Infra-red absorption spectrum

A Fourier-transform infra-red spectrometer, Perkin–Elmer model 1800, was used. Sampling for the solution-grown crystal was performed by the Nujol (liquid paraffin) mull method in order to avoid mechanical deformation, since the folded-chain structure is destroyed very easily by grinding with KBr powder, causing a significant spectral change just like the t-POM solution-grown crystal. Measurements on KBr pellets of the same sample were also performed for comparison. The bands due to water in the atmosphere were carefully subtracted. In the case of the Nujol mull method, the background due to the mulling reagent was also subtracted.

### Raman scattering spectrum

A Jasco model R-800S spectrometer was used. Samples were rotated during the measurements to avoid damage (melting) caused by the laser light. The 488 nm line of an $Ar^+$ laser was used as the excitation source.

### X-ray diffraction measurement

A Philips model PW1700 system with a graphite monochromator was used for the powder pattern measurement.

## RESULTS AND DISCUSSION

*Figure 1* shows the wide-angle X-ray diffraction patterns of the PEO samples. The drawn film was cut into small pieces and a randomly oriented sample was prepared and measured (upper panel in *Figure 1*). Both patterns of the drawn film and the solution-grown crystal (lower panel in *Figure 1*) were identical. This means that these samples have the same unit-cell structure.

Infra-red spectra of the PEO drawn film and the solution-grown crystal were measured. It was confirmed that the effect of humidity in the air can be ignored in this work. Though the difference in the spectrum between the two samples was not so significant, a small difference was found. In order to clarify the difference and determine the symmetry species of the infra-red bands, polarization measurements were made. On the drawn film, spectra were measured with parallel and perpendicular polarized light. The result was in good accordance with the literature[35,36] and the symmetry species, infra-red-active $A_2$ and $E_1$, could be determined easily. The spectra of $A_2$ and $E_1$ were separated by the subtraction method. For the solution-grown crystal, random and semi-plane-oriented samples were prepared. When the sample
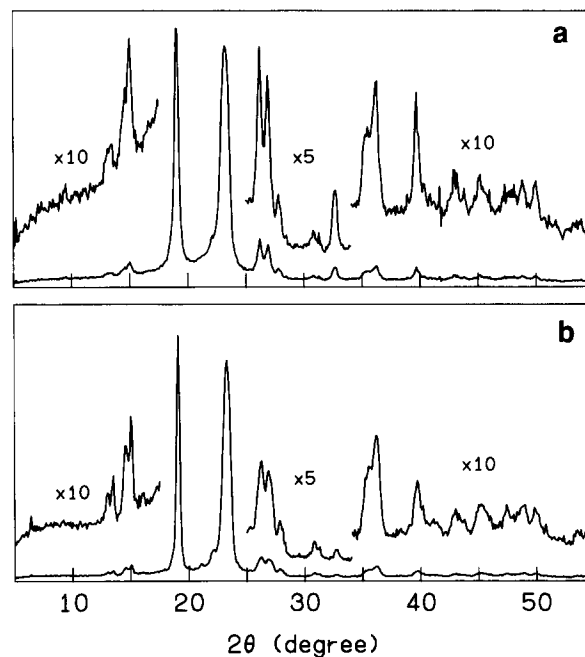


**Figure 1** X-ray diffraction patterns of poly(ethylene oxide) crystals. (a) Drawn film (random); (b) solution grown crystal

powder, mixed with a small amount of liquid paraffin, was sandwiched between the two KBr windows without a spacer, the lamellar crystals were partly oriented with their $c$ axis directed normal to the window surface. On measuring the transmission spectrum of this sample, with the infra-red incidence nearly perpendicular to the window surface, the $c$-polarized $A_2$ bands should diminish in intensity compared with a spectrum measured on a randomly oriented sample[23]. By insertion of a spacer of sufficient thickness, randomly oriented solution-grown crystals could be prepared. After elimination of the background due to the liquid paraffin, subtraction between the spectra of the random and the plane-oriented samples was performed, and well separated infra-red spectra of the $A_2$ bands and $E_1$ bands were obtained. The $E_1$ bands of the drawn film and those of the solution-grown crystal are compared in *Figure 2* (upper panel), which showed no significant difference. On the contrary, in the spectra of the $A_2$ bands (*Figure 2*, lower panel), shifts were clearly found, i.e. 1341.6, 1241.4, 1099.4 and 961.8 cm$^{-1}$ bands of the drawn film shifted to 1344.8, 1242.8, 1118.4 and 966.0 cm$^{-1}$, respectively, in the spectrum of the solution-grown crystal.

The observed frequencies of the infra-red bands of PEO specimens are listed in *Table 1* along with their symmetry species and the frequency gaps between two specimens. It was clear that no meaningful shift was found in the bands assigned to the $E_1$ species. It was also clear that the $A_2$ bands of the solution-grown crystal shifted to the high-frequency side compared with those of the drawn film, though the magnitudes of the shifts were not so large as were observed in the case of the t-POM crystals. It has also been noticed by the authors that the amount of the shifts might have some relation with the band intensity, i.e. the stronger band showed the larger shift.

*Figure 3* shows Raman scattering spectra of the PEO samples, in which the bands assigned to the Raman-active $A_1$ and $E_1$ species were observed. In the Raman spectra, no significant difference was found, i.e. the $A_1$ bands and $E_1$ bands appeared at the same positions.
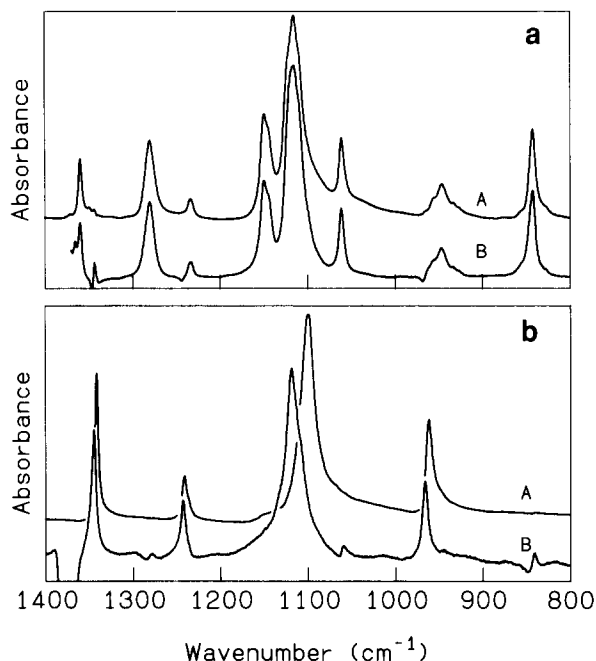
**Figure 2** (a) $E_1$ and (b) $A_2$ bands in infra-red spectra of poly(ethylene oxide) obtained by a subtraction method. Curve A, drawn film; curve B, solution grown crystal

**Table 1** Infra-red bands of poly(ethylene oxide)

| | Wavenumber (cm⁻¹) | | |
| --- | --- | --- | --- |
| Species | Solution grown, $\gamma_A$ | Drawn film, $\gamma_B$ | $\gamma_A - \gamma_B$ |
| $E_1$ | 1359.6 | 1359.6 | 0.0 |
| $A_2$ | 1344.8 | 1341.6 | 3.2 |
| $E_1$ | 1280.2 | 1280.2 | 0.0 |
| $A_2$ | 1242.8 | 1241.4 | 1.4 |
| $E_1$ | 1234.2 | 1234.2 | 0.0 |
| $E_1$ | 1149.2 | 1149.4 | −0.2 |
| $E_1$ | 1116.0 | 1115.6 | −0.4 |
| $A_2$ | 1118.4 | 1099.4 | 19.0 |
| $E_1$ | 1061.0 | 1061.0 | 0.0 |
| $A_2$ | 966.0 | 961.8 | 4.2 |
| $E_1$ | 946.6 | 946.6 | 0.0 |
| $E_1$ | 842.4 | 842.6 | −0.2 |

These observations could be summed up as follows. The wide-angle X-ray diffraction patterns of the PEO drawn film and the PEO solution-grown crystal were identical, i.e. both samples have the same unit-cell structure. The bands assigned to the $A_2$ symmetry species, whose transition moments were parallel to the $c$ axis, shifted towards the high-frequency region in the vibrational spectra of the solution-grown crystal, while the other bands, assigned to the $A_1$ and $E_1$ species, appeared at the same frequency in the two different specimens. The results mentioned above are just the same as those found in t-POM and t-POM-$d_2$ crystals[23].

The folded-chain structure in the solution-grown crystal of t-POM varies very easily by mechanical stress. The infra-red spectrum of the t-POM solution-grown crystal measured by the KBr pellet method changes to that of the extended-chain needle-like crystals[24]. *Figure 4* (trace B) shows the infra-red spectrum of the PEO solution-grown crystal measured by the KBr pellet method. The spectrum measured with the Nujol mull method and those of the drawn film are also reproduced

(*Figure 4*, traces A and C) for comparison. The change in the spectrum of the solution-grown crystal with mechanical deformation was clear. Though polarization data could not be obtained by the KBr pellet method, it could be concluded that the $A_2$ bands measured with the KBr method appear at the same wavenumber as those of the drawn film. *Figure 5* shows the infra-red spectra of a KBr pellet of the PEO solution-grown crystal before (A) and after (B) melt crystallization. The spectrum changed again after melt crystallization and was like the spectrum measured with the Nujol mull method.

These spectral behaviours of the PEO solution-grown crystal have also been observed for the t-POM solution-grown crystals[24]. These facts might be interpreted as follows. The folded-chain (solution-grown) crystal was
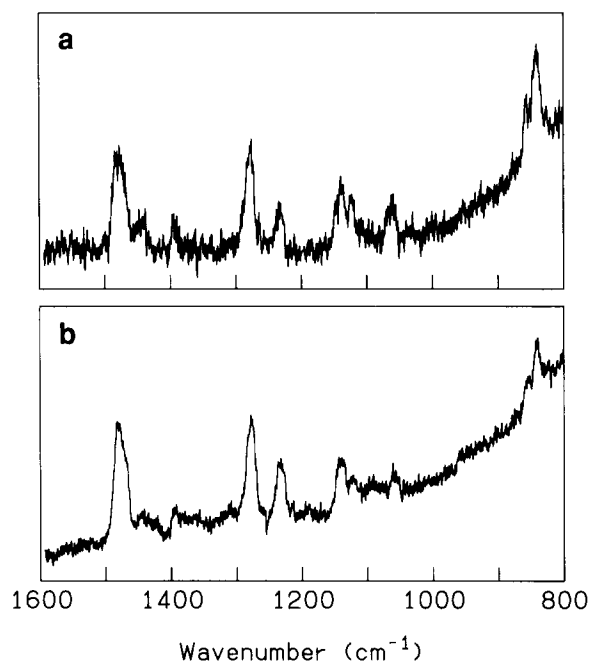


**Figure 3** Raman spectra of poly(ethylene oxide) crystals. (a) Drawn film; (b) solution grown crystal
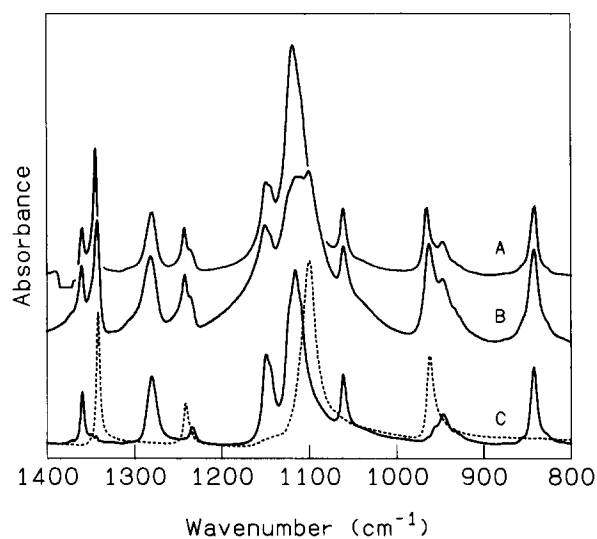


**Figure 4** Infra-red spectra of poly(ethylene oxide): A, solution-grown crystal (Nujol); B, solution-grown crystal (KBr pellet); C, drawn film, $E_1$ bands (——) and $A_2$ bands (······)
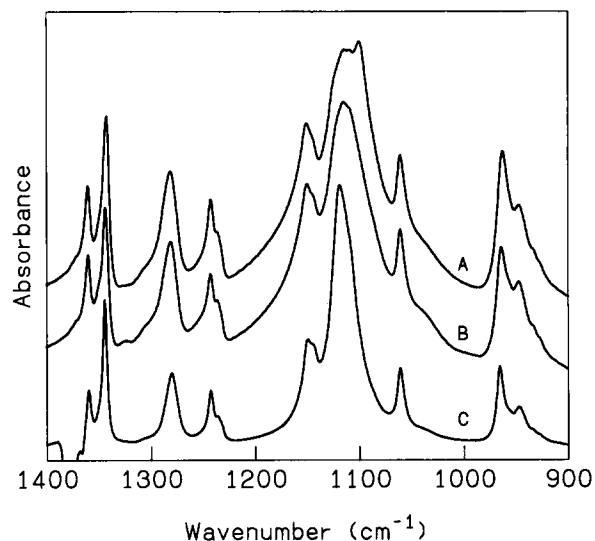
**Figure 5** Infra-red spectra of poly(ethylene oxide) solution-grown crystal: A, KBr, before melt crystallization; B, KBr, after subsequent melt crystallization; C, Nujol mull method

destroyed and molecular chains were stretched by the shear stress during pelletization and the stretched chains gave the infra-red spectrum of the extended-chain crystal type. By the subsequent melt crystallization, the stretched chains folded again, though some parts remained extended, and the spectrum became the superposition of the spectra of the folded-chain type and the extended-chain type.

## CONCLUSIONS

The drawn film and the solution-grown crystal of PEO, which give the same wide-angle X-ray diffraction patterns, showed different infra-red spectra. In the vibrational spectra of the solution-grown crystal, only the $A_2$ bands shifted towards the high-frequency side, while the other bands, $A_1$ and $E_1$, remained unshifted. The infra-red spectrum of the solution-grown crystal changed to the drawn-film type spectrum by application of mechanical deformation. By subsequent melt crystallization, the spectrum again changed into the solution-grown crystal type. This behaviour of the infra-red spectra of the PEO crystals was just the same as was observed with t-POM crystals and was considered to have the same origin.

Though the mechanism is not fully understood, this behaviour, i.e. only the bands with transition moment parallel to the $c$ axis shift towards the high-frequency side, is common with t-POM, t-POM-$d_2$, o-POM and PEO crystals.

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