Vibrational spectroscopic study on low-molecular-weight polyoxymethylene diacetate

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Infra-red and Raman spectra of low-molecular-weight polyoxymethylene diacetates are investigated and compared with those of the extended- and folded-chain crystals of high-molecular weight trigonal polyoxymethylene. Some bands assignable to the A_2 symmetry species shift towards the high-frequency side, as was found in the folded-chain crystal. The infra-red spectral changes for the extended-chain crystal, folded-chain crystal and low-molecular-weight polyoxymethylene diacetates that occur on mechanical deformation and melt crystallization are also discussed. A minor shift of Raman bands of the low-molecular-weight polyoxymethylene diacetates was also found and discussed.

(Keywords: trigonal polyoxymethylene; polyoxymethylene diacetates; low-molecular-weight polyoxymethylene; infra-red spectra; Raman spectra)

INTRODUCTION

Polyoxymethylene (POM) is known as a typical crystalline polymer and appears in two crystal modifications, the stable trigonal form consisting of chains in the 9/5 (or more exactly 29/16) helical conformation[1–3] and the metastable orthorhombic form of a 2/1 helix[4,5]. Vibrational spectra of both modifications, especially of the trigonal form, have been the subject of many studies for years[6–12]. The extended-chain crystal of orthorhombic form was found as a by-product of the synthesis of needle-like crystals of trigonal POM[5,13]. Using the newly found orthorhombic single crystal, vibrational spectroscopic studies have been performed on the molecular aggregation state and the solid-state phase transition[14,15]. For the trigonal crystal, assignment of the infra-red absorption bands and the Raman scattering lines has been established with reference to the normal-mode calculation of an infinitely extended polymer chain[16]. Zamboni and Zerbi[6] first reported that the infra-red spectrum in the 1200–900 cm^{-1} region of the trigonal POM changes with processing of the specimens. Infra-red spectral differences among various specimens of trigonal POM, different in origin and/or processing history, were also investigated by Shimomura and Iguchi[11].

In a previous paper, the vibrational spectra of two typical single crystals of trigonal POM were examined and discussed in relation to their morphological structure[17]. One typical crystal is the needle-like crystal[18,19], which is known as the polymer whisker. It consists of fully extended molecular chains, and its high crystalline perfection has been proved by various measurements, such as wide-angle X-ray diffraction, d.s.c. and thermoluminescence[20–22]. The other typical trigonal crystal is the lamellar crystal, crystallized isothermally from dilute solution, in which molecular chains are folded periodically[23,24]. The infra-red spectra of these two single crystals are quite different from each other and the infra-red spectra of the other trigonal POM specimens could be explained as the superposition of these two extreme spectra[11,17]. Though the molecular mechanism was not clear, it was concluded phenomenologically that the spectral difference between the extended-chain crystal (ECC) and the folded-chain crystal (FCC) results from the anomalously large shifts of the bands assigned to the infra-red-active A_2 symmetry species towards the high-frequency side in the FCC (solution-grown crystal). On the other hand, the vibrations assigned to the other species, Raman-active A_1 and E_2 and infra-red- and Raman-active E_1, show no significant shift among various samples of trigonal POM. Thus, significant frequency shifts take place only in the infra-red bands with the transition dipole parallel to the chain axis. The wide-angle X-ray diffraction patterns of the two crystals were identical, indicating that these trigonal single crystals had the same unit-cell structure.

In this paper, the infra-red and Raman spectra of low-molecular-weight POM diacetates (LMW-POM) are presented and discussed in comparison with those of the ECC and FCC of high-molecular-weight POM. The molecular-weight dependence of the spectra of the LMW-POM was examined. Spectral changes during mechanical deformation of the samples by milling with KBr and during melt crystallization were also examined.

EXPERIMENTAL

Samples

The needle-like crystal was synthesized in a cationic

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polymerization system of trioxane[19]. The solution-grown crystal was prepared under similar conditions to those published previously[17].

The LMW-POM were prepared from paraformaldehyde[25]. A mixture of commercial paraformaldehyde and acetic anhydride was heated in an autoclave and acetylated low-molecular-weight POM was extracted and crystallized using ether, chloroform, benzene or xylene.

As some oligomers are soluble in $CDCl_3$, n.m.r. spectra were measured and the degrees of polymerization were determined from the signal intensities due to the methyl protons of the acetyl end-groups and the methylene protons in the main chain. The degrees of polymerization of the LMW-POM with rather than molecular weight were determined from the intensities of the Raman bands and the infra-red absorption bands due to the acetyl end-groups. The degrees of polymerization of the LMW–POM were determined as 12 to 30 in (CH_2O) units, which were in good accordance with the literature[25].

Infra-red absorption spectrum

A Jasco model 701G diffraction grating infra-red spectrometer was used. Sampling methods used were the Nujol mull and the KBr pellet methods. Since the solution-grown crystal of POM transforms very easily to another crystal form and/or another morphology, giving rise to a significant change in the infra-red spectrum, all samples were mixed carefully with Nujol to avoid mechanical deformation and subjected to the measurement. The background due to the mulling reagent was removed by a subtraction technique. Some sample powders were also ground well with KBr, pelletized and measured. The KBr pellets were heated at about 200°C on a hot plate and measured again after cooling.

Raman scattering spectrum

For the Raman measurement, the samples were sealed in glass ampoules and measured with a Jasco model R-500. The 514.5 nm line of an Ar^+ laser was used as the excitation source.

X-ray diffraction and d.s.c. measurement

A Philips model PW1700 system with a graphite monochromator was used for wide-angle X-ray diffraction measurements. D.s.c. curves were measured by a Perkin–Elmer model DSC-2.

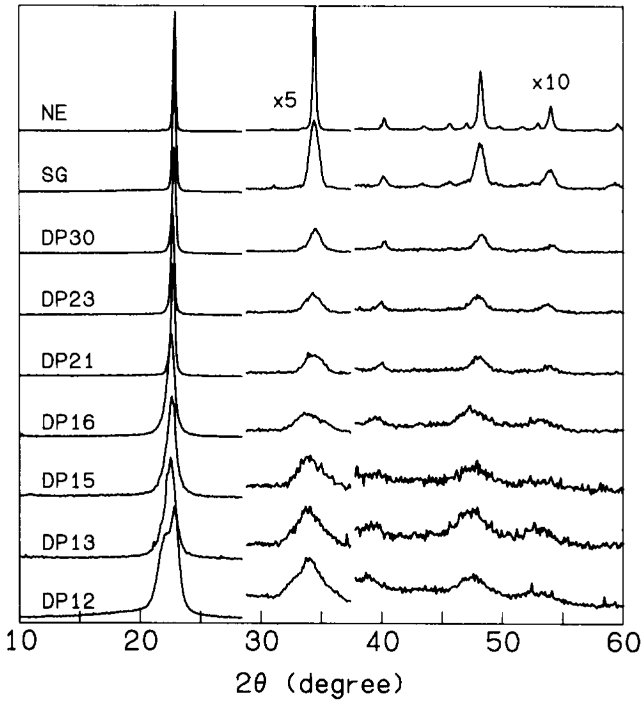

Figure 1 X-ray diffraction of various polyoxymethylene specimens: NE, needle-like crystals; SG, solution-grown crystals; *DP*, denotes degree of polymerization

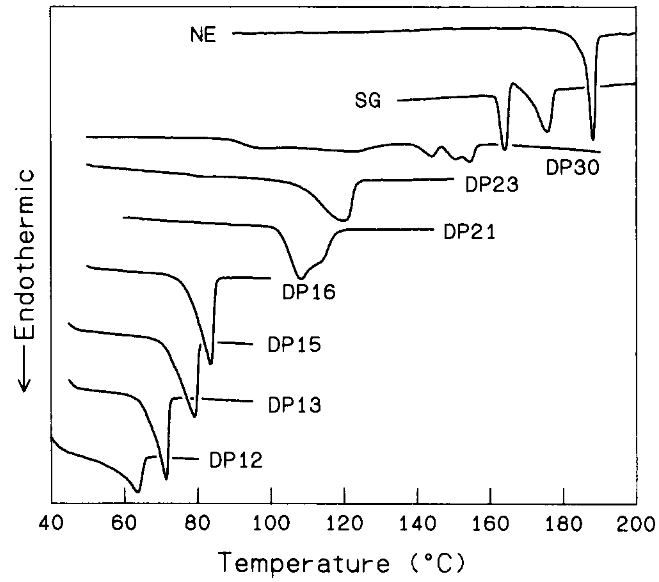

Figure 2 D.s.c. curves of various polyoxymethylene specimens (notations are same as in *Figure 1*)

RESULTS AND DISCUSSION

Figure 1 shows the wide-angle X-ray diffraction patterns of the needle-like crystal, the solution-grown crystal and the LMW-POM (*DP* denotes the degree of polymerization). It is evident that all oligomeric samples were crystalline as well as the high-molecular-weight POM samples, though the widths of diffraction peaks, which reflect their crystal perfection, etc., were different from each other. It could be said that the unit-cell structure of the LMW-POM was very close to that of the needle-like crystal and the solution-grown crystal, i.e. the trigonal modification consisting of basically 9/5 helical molecules. The Bragg angles of the diffraction peaks of the LMW-POM, especially of lower degree of polymerization, were a little smaller than those of the high-molecular-weight POM crystals and the LMW-POM might have a larger unit-cell dimension.

D.s.c. curves of the low- and high-molecular-weight POM crystals are reproduced in *Figure 2*. Melting points of the LMW-POM specimens were, qualitatively at least, in good accordance with the degree of polymerization determined by n.m.r. and vibrational spectra. This also indicated that all samples were more or less crystalline, as was found by wide-angle X-ray diffraction. The curve of *DP*30 showed that this sample had a wide molecular-weight distribution compared with the other LMW-POM specimens.

In a previous paper[17], the changes in the vibrational spectra of the trigonal POM crystals were summarized as follows. Only bands assigned to the A_2 symmetry species of the ECC shift towards the high-frequency side in the FCC. Namely, the bands at around 895 and 220 cm^{-1} and one of the overlapping components at 1093 cm^{-1} of the ECC shifted to 1000, 234 and 1138 cm^{-1}, respectively, and the other bands, assigned to the A_1, E_1 and E_2 symmetry species, appeared at the same wavenumbers in both crystals. The spectral change was once ascribed to the effect of chain folding[11], i.e. molecular distortion caused by the chain folding penetrates deep into the crystallite and, as a result, disturbs the molecular as well as crystalline structure. It was difficult, however, to explain the spectral change in terms of disorders or defects[17]. In order to obtain more spectral data, the vibrational spectra of the LMW-POM specimens were measured.

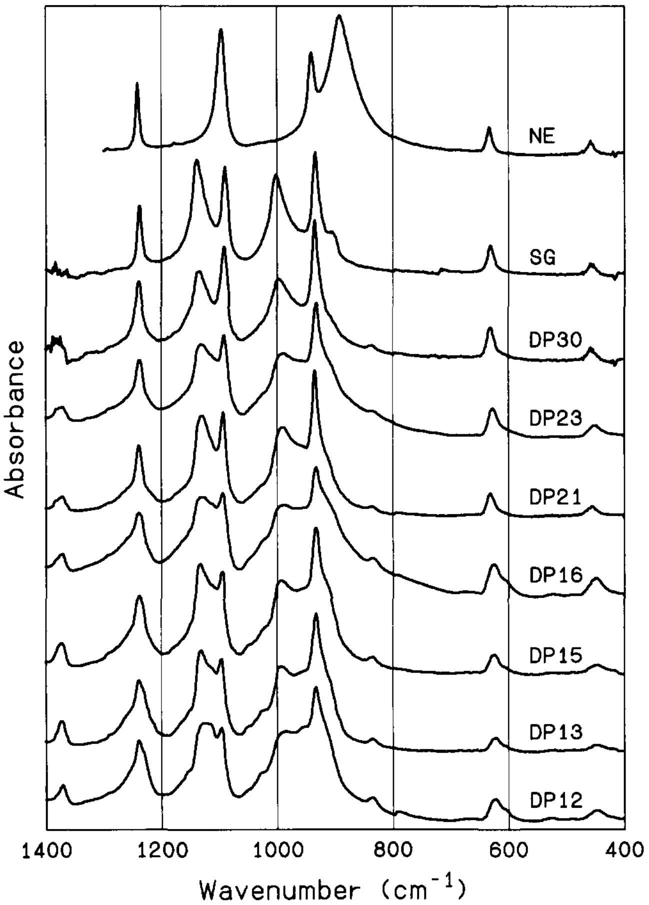

Figure 3 Infra-red spectra of various polyoxymethylene specimens (notations are same as in *Figure 1*)

In *Figure 3*, the infra-red spectra of the LMW-POM specimens measured by the Nujol mull method are compared with those of the two extreme crystals of high-molecular-weight POM. The spectral change between the ECC (needle-like crystal) and the FCC (solution-grown crystal) is very clear. The infra-red spectra of the LMW-POM were quite different from that of the ECC, which is thought to be the 'normal' or 'standard' crystal, and resembled that of the FCC, though some minor discrepancies exist. In fear of mechanical deformation, the samples were not ground well with mulling reagent and the dispersion of the sample powder in Nujol was not so good. Thus, the infra-red spectra of the LMW-POM were not clear enough to be discussed in detail.

The Raman spectra of the high- and low-molecular-weight POM specimens are shown in *Figure 4*. As mechanical deformation can be avoided easily during sample preparation, the Raman spectra of the LMW-POM were clearer than the infra-red spectra. In *Figure 4*, lines at 2948 and 841 cm^{-1} are due to the acetyl end-group and the other lines, assigned to the A_1, E_1 and E_2 species, were basically the same as those of the high-molecular-weight POM crystals.

The infra-red and Raman spectra of the LMW-POM samples (*DP*12–30) were essentially the same as those of the FCC of high-molecular-weight POM, i.e. only the bands assigned to A_2 species exhibited a large shift towards the high-frequency side. The estimated length of the LMW-POM chain was less than 5 nm, while the thickness of the solution-grown crystal, the period of the

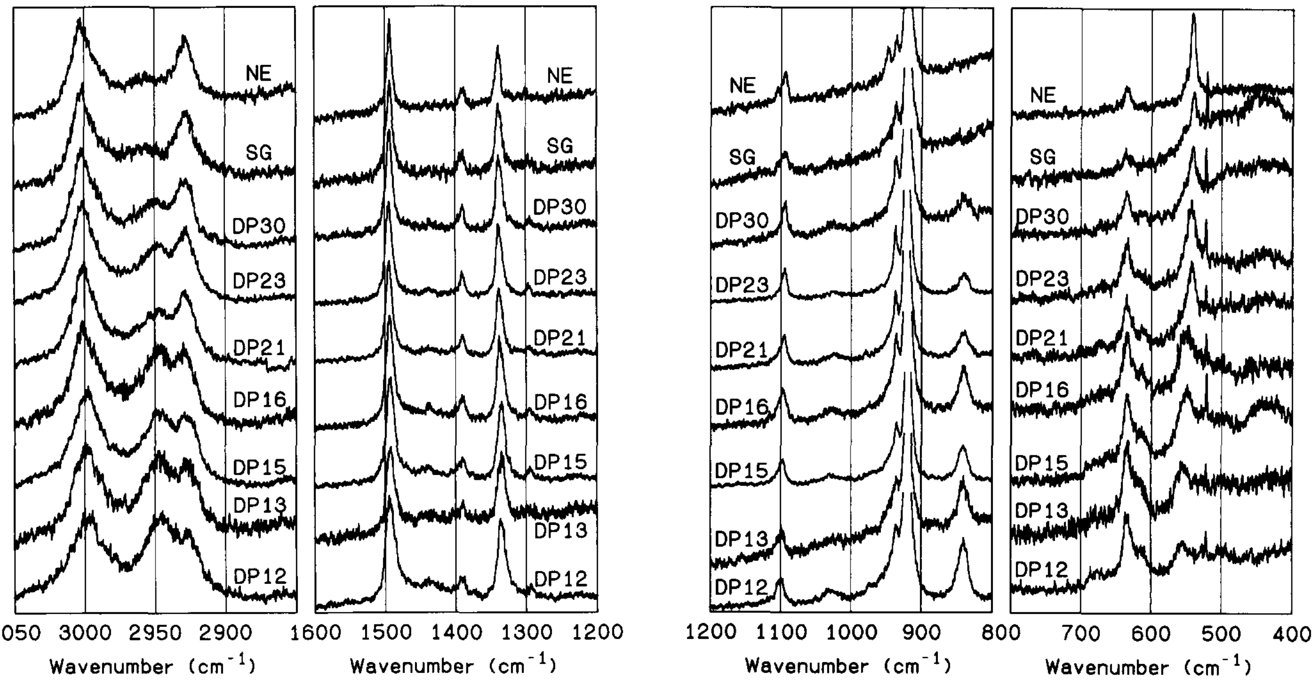

Figure 4 Raman spectra of various polyoxymethylene specimens (notations are same as in *Figure 1*)

Table 1 Raman bands of various polyoxymethylene specimens (notations are same as in *Figure 1*)

	Observed wavenumbers (cm^{-1})								
Species	NE	SG	*DP*30	*DP*23	*DP*21	*DP*16	*DP*15	*DP*13	*DP*12
E_1	3004	3003	3002	3002	3001	3002	2999	2999	2999
A_1	2929	2928	2929	2929	2930	2030	2030	2927	2928
A_1	1494	1495	1494	1496	1495	1494	1494	1494	1495
E_2	1391	1392	1391	1392	1392	1391	1391	1392	1392
A_2	1340	1340	1339	1340	1340	1339	1337	1336	1337
E_2	1106								
E_1	1096	1096	1096	1096	1097	1099	1099	1101	1102
E_2	949								
E_1	938	938	937	938	938	938	937	936	937
A_1	921	922	921	922	922	921	921	921	921
E_1	637	637	636	636	637	636	636	636	636
A_1	542	541	542	544	543	552	550	557	557

chain folding measured by small-angle X-ray diffraction, was about 9 nm. Such short molecules as LMW-POM might be extended in a crystal as was found with n-alkane crystals. On the other hand, the vibrational spectra of the LMW-POM were basically the same as those of the FCC. This result suggests that the infra-red spectral change between the ECC and FCC is related to the crystallite size along the *c* axis.

In the Raman spectra of the LMW-POM, minor variations in wavenumber and in relative intensity were observed among the samples. The wavenumber of the Raman bands, with their symmetry species, are listed in *Table 1* (bands due to the end-group are omitted here). For bands at 3004, 1340, 1096 and 542 cm^{-1} of the needle-like crystal, small frequency shifts among the LMW-POM specimens were found. The symmetry species of these shifted bands are both E_1 and A_1. The directions of the shifts were both to higher- and lower-frequency sides, as was predicted by the dispersion curves of trigonal POM[26]. The amount of the shifts changed continuously with the molecular weight, and the maximum value of the shift was only 15 cm^{-1} for the 542 cm^{-1} band. The shifts in the Raman spectra of the LMW-POM might be due to the molecular weight and/or a small difference in the conformation (unit-cell size), as was detected by the wide-angle X-ray diffraction measurements.

The behaviour of the shifts observed in the Raman spectra of the LMW-POM were quite different from that of the infra-red bands of the ECC and FCC. In the infra-red spectra, the symmetry species of the shifted bands was limited to A_2, the direction of the shifts was always towards the high-frequency side on going from the ECC to the FCC and also the band shifts occur discretely. The behaviour of both types of shifts showed that the mechanism of the large shifts of the A_2 bands is quite different from that of the minor shifts found in the Raman spectra of the LMW-POM. The shifts in the Raman spectra of the LMW-POM samples might be interpreted as minor deviations in the conformation and/or effects of the finite length of the molecular chain. In contrast, the small difference in the conformations of chains cannot explain such a large shift of the A_2 bands between the ECC and the FCC.

It is known that the infra-red spectra of the needle-like crystal taken with the Nujol mull and the KBr pellet methods show no significant difference. In contrast, the spectrum of the solution-grown crystal taken with the KBr pellet method was much different from that measured with the Nujol mull method and is rather similar to that of the needle-like crystal[11]. *Figure 5* shows the infra-red spectra of the LMW-POM specimens and the solution-grown crystal measured by the Nujol mull method (A) and the KBr method (B). The difference between the spectra of the solution-grown crystal measured by both methods was evident, namely the intensities of the bands at around 1095 and 900 cm^{-1} in the spectrum measured with the KBr pellet method became much larger than those found with the Nujol mull method. The spectrum measured by the KBr pellet method was like that of the needle-like crystal. On the other hand, the infra-red spectra of the LMW-POM measured by both methods showed no significant difference. The spectrum of *DP*30, a specimen with a wide distribution of the chain lengths and rather high molecular weight, showed minor changes like that of the solution-grown crystal with mechanical treatment during pelletization.

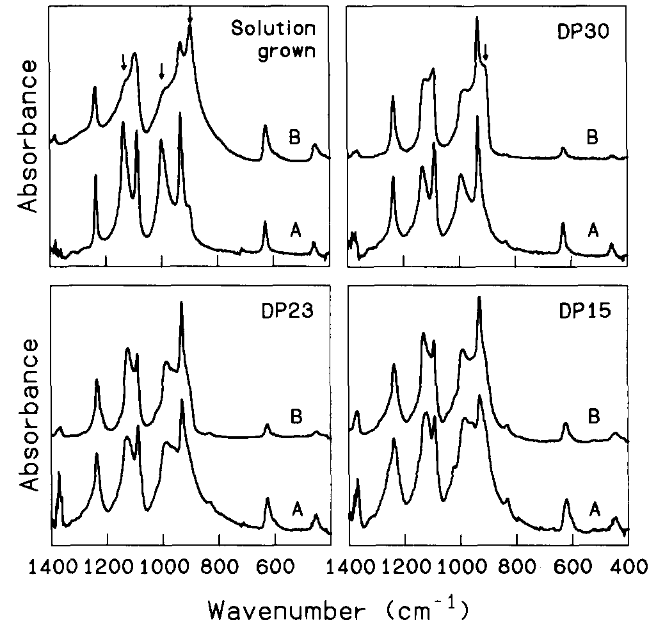

Figure 5 Infra-red spectra of solution-grown crystals of polyoxymethylene and low-molecular-weight polyoxymethylene diacetates: A, Nujol mull method; B, KBr pellet method

In *Figure 6*, the infra-red spectra of POM specimens before (A) and after (B) melt crystallization, heated up to 200°C and cooled, are shown. Though the spectral change of the solution-grown crystal was not so drastic as was found in *Figure 5*, the spectrum after melt

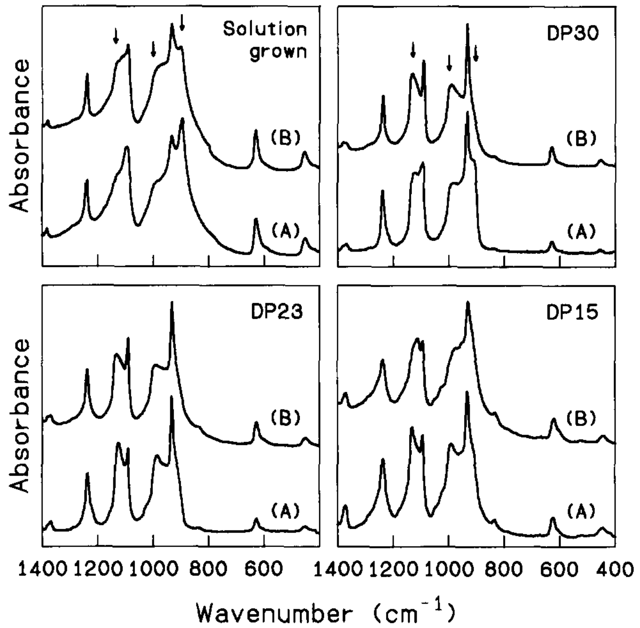

Figure 6 Infra-red spectra of solution-grown crystals of polyoxymethylene and low-molecular-weight polyoxymethylene diacetates: A, before melt crystallization; B, after melt crystallization

crystallization was like the spectrum of a melt-crystallized film[11] and could be considered as the superposition of the spectrum of the ECC and the original spectrum of the FCC. For the LMW-POM, basically the same spectra were obtained before and after melt crystallization.

These behaviours of the infra-red spectra of the LMW-POM with KBr pelletization and subsequent melt crystallization could be summarized as follows. The infra-red spectrum of the solution-grown crystal of high-molecular-weight POM changes very easily with treatments that affect the morphology, while the infra-red spectra of the LMW-POM showed no significant change with those treatments. Also LMW-POM containing long molecular chains (*DP*30) showed the same tendency as the solution-grown crystal of high-molecular-weight POM.

These phenomena could be interpreted in terms of the new hypothesis as follows, though theoretical explanations could not yet be given. Through the milling of the sample, the long molecular chains of the solution-grown crystal were extended with shear stress and the spectrum changes to that of the extended-chain crystal. In the course of subsequent melt crystallization, long molecular chains could not fold regularly and both long extended and folded parts would coexist. The resulting infra-red spectrum could be thought of as the superposition of those of the ECC and FCC. On the contrary, molecular chains in the LMW-POM specimens are too short to have a long extended part and the spectra remain unchanged through the milling and subsequent melt crystallization.

Another interpretation of the large anomalous high-frequency shifts of the A_2 bands could be that the shifts are related to the crystallite size along the *c* axis, though theoretical explanations cannot yet be given.

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