

Infra-red study on the conformational regularity in needle-like and other polyoxymethylene crystals

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Infra-red spectra of needle-like single-crystals and other polyoxymethylene specimens of various crystallinity were studied in 550–1300 cm^{-1} region. The absorption bands were classified into crystallinity-sensitive and crystallinity-insensitive ones and bands at 1000 and 1140 cm^{-1} which were characteristic of irregular specimens and had no theoretical assignment were assumed to have resulted from the shift of bands at 900 and 1095 cm^{-1} , respectively. Complementary relationships were obtained between the intensities of these bands and the crystalline perfection of samples, defined in terms of conformational regularity, is discussed.

Keywords Conformation; crystallinity; needle-like crystal; polyoxymethylene; infra-red bands; infra-red absorption

INTRODUCTION

Crystallinity is an important property of polymeric materials and is measured by various methods. 'Crystallinity bands', appearing on infra-red spectra, are characteristic of individual polymers and they are distinguished in polymers having relatively simple backbone structures. For this reason, the application of infra-red spectroscopy for the measurement of crystallinity lacks the generality of X-ray and density methods which are based on assuming the crystalline-amorphous, binary-phase models. Nevertheless, analysis of infra-red spectra is useful for investigating the regularity or the local disordering of molecular conformation in crystals or crystallites.

From this point of view, a vast number of studies have been published in the last two decades for various polymers. Among these, polyethylene was most rigorously studied, ever since changes in the intensity of some bands by annealing were originally pointed out by Brown¹. The analysis was applied by Koenig and Witenhafer² for the quantitative analysis of chain folds in lamellar specimens and many works followed.

For polyoxymethylene, a hexagonal crystal consisting of chains in helical conformation is common, though an orthorhombic modification is another form found in some specimens. By now, assignment of absorption bands has been almost established by reference to theoretical calculations. That the infra-red spectrum of the hexagonal form changes with crystallinity in the 900–1200 cm^{-1} region, was first reported by Zamboni and Zerbi³. Bands in this region were studied in detail by Oleinik and Enikolopyan⁴ by bringing in a series of oligomeric homologues: it was assumed that the bands at 903 and 1238 cm^{-1} were regularity bands characteristic of longer *gauche* helix, whereas 'additional' bands at 985 and 1130 cm^{-1} were affiliated to planar zig-zag chains in non-crystalline area. These assumptions were supported by

Terlemezyan *et al.*^{5,6} who studied the effect of temperature and mechanical force on the *gauche* conformation fraction of the polymer. However, results obtained in these studies were rather qualitative, partly due to the lack of standard as only pressure-crystallized highly crystalline samples were made available for the study of polyethylene.

Needle-like, hexagonal single-crystals of polyoxymethylene developed in our laboratory^{7,8} consist of extended helical chains and their perfection has been proved by X-ray and various other measurements⁹⁻¹¹. Infra-red spectroscopic study of this specimen has been of interest. As expected, preliminary experiment gave a spectrum having only five absorption bands in the 550–1300 cm^{-1} region, whereas up to seven bands were observed for conventional polyoxymethylene samples.

In this study, measurement of infra-red spectra in the 550–1300 cm^{-1} region has been made for various polyoxymethylene specimens of various structures. From their analysis, an attempt has been made to classify absorption bands into crystallinity-insensitive and crystallinity-sensitive and systematic relationships have been obtained between the intensities of the latter bands, giving a measure for the crystalline perfection defined in terms of conformational regularity.

EXPERIMENTAL

Samples

Needle-like crystals were grown in a cationic polymerization system of trioxane under similar conditions as described previously⁸ and subjected to boron trifluoride etching⁹ to disrupt the original radial assembly.

Feather-shaped crystals were prepared in a similar system during the polymerization of trioxane^{12,13}.

Fibrillar crystals were prepared by the cationic solid-state polymerization method¹⁰ and refluxed in an ethanol/water mixture containing a small amount of triethylamine to remove the traces of catalytic species.

A heterogeneous as-polymerized sample was obtained by polymerizing trioxane in nitrobenzene (3.3 mol l^{-1}) with boron trifluoride catalyst (1 mmol l^{-1})¹⁴.

A melt crystallized sample, in the form of a thin film, was prepared from polyoxymethylene diacetate (Delrin 500X from E. I. du Pont de Nemours and Co.). The polymer was dissolved in hexafluoroacetone sesquihydrate and cast on a glass plate. After washing out the solvent with acetone and drying, the polymer was melted at 180°C and allowed to cool to room temperature. The film comprised spherulites in its morphology.

A reprecipitate from Delrin 500X was obtained by dissolving 0.1 g polymer in 10 ml hexafluoroacetone sesquihydrate and pouring in a large amount of acetone. The precipitate was freeze-dried with benzene.

Lamellar crystals were prepared, with both needle-like polymer and Delrin 500X, from 0.3% bromobenzene solution containing 0.4% 2,6-di-tert-butyl-*p*-cresol at 130°C and, after filtration, freeze-dried using benzene. Since needle-like crystals were insoluble in boiling bromobenzene, they had to be dissolved in hexafluoroacetone sesquihydrate to destroy their highly crystalline structure and reprecipitated in acetone prior to the solution crystallization. The lamellar crystals also served for measurements after annealing at various temperatures, between 155° and 170°C , for 2 h.

Infra-red measurement

A diffraction grating infra-red spectrometer, Model 701G, of Japan Spectroscopic Co., Ltd., was used and spectra in the region of interest ($550\text{--}1300 \text{ cm}^{-1}$) were recorded with expanded wavenumbers. For measurement, powder samples were mullied with Nujol and sandwiched between two KBr plates. Some samples were ground and pelletized with KBr powder and served for measurement.

Data processing

FACOM/HITAC M 160-II digital computer was employed. Recorded spectra of $550\text{--}1300 \text{ cm}^{-1}$ region were manually digitized at 5 cm^{-1} intervals and, after smoothing by the seven-point cubic method¹⁵, the percent transmission was converted into the absorbance unit. For the data of the Nujol mull method, subtraction of background was based on reference to the peak at 720 cm^{-1} . All spectra were normalized based upon the height of 1240 cm^{-1} peak, which seemed to be common to and invariant for all specimens, and curves were drawn by means of an X-Y plotter.

In order to separate overlapped peaks and to measure their area intensities, a curve resolver, Model 301, of E. I. du Pont de Nemours and Co., was used.

RESULTS AND DISCUSSION

Spectra of various specimens measured by the Nujol mull method, or by the film method for film specimens, have been processed to convert the percent transmission to the absorbance unit according to the procedure described

above and typical curves between 550 and 1300 cm^{-1} are shown in Figure 1. The difference in spectra between different specimens is clearly illustrated. It is remarked that the curves from the specimens of highest crystalline perfection, i.e., needle-like and feather-shaped crystals, are rather simple with five peaks, whereas those from other specimens are more complicated, as usually observed, with up to seven peaks or shoulders in the present wavenumber region. (It has come to the authors' notice that a spectrum reported earlier by Zamboni and Zerbi³ for a crystalline sample is similar to that of needles or feathers. The sample might have been of similar perfection, although the details are not clear.) It should be noted that the curves for two solution grown crystals from different sources, Delrin and needle-like polymer, are almost identical, showing that the difference of end groups, acetyl and hydroxy, has hardly affected these spectra.

Figure 2 shows spectra of some specimens obtained by the KBr pellet method. The measurement was primarily aimed at testing the effect of sample orientation which could have been significant for the Nujol mull method sandwiching anisotropic samples in a thin layer, despite the latter method's advantage of avoiding damage to samples. This was not the case, however, and the spectra of needle-like and feather-shaped crystals, as well as of fibrillar crystal, were almost the same as those obtained by the Nujol mull method. Instead, the spectra of other specimens comprising folded-chains or more or less imperfect structures changed dramatically, reflecting the effect of mechanical deformation⁵ caused by the pelletization. The spectra of the heterogeneous polymer polymerized in nitrobenzene and the reprecipitate are found to be changed and become similar to the spectrum of the fibrillar specimen (Figure 1 (c)). The change of spectra of the solution grown and the melt recrystallized specimens are rather complicated, however.

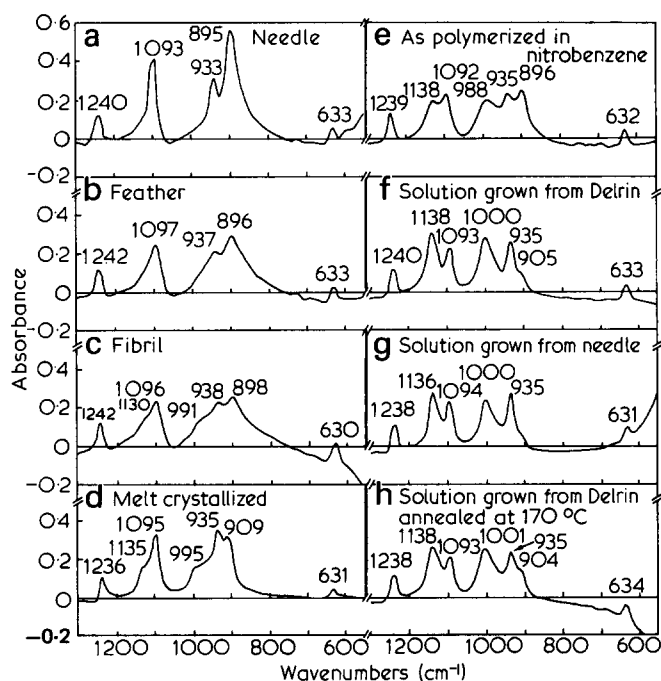


Figure 1 Infra-red spectra of various polyoxymethylene specimens. Method: (a), (b), (c), (d), (f), (g) and (h): Nujol mull method, (e): film method

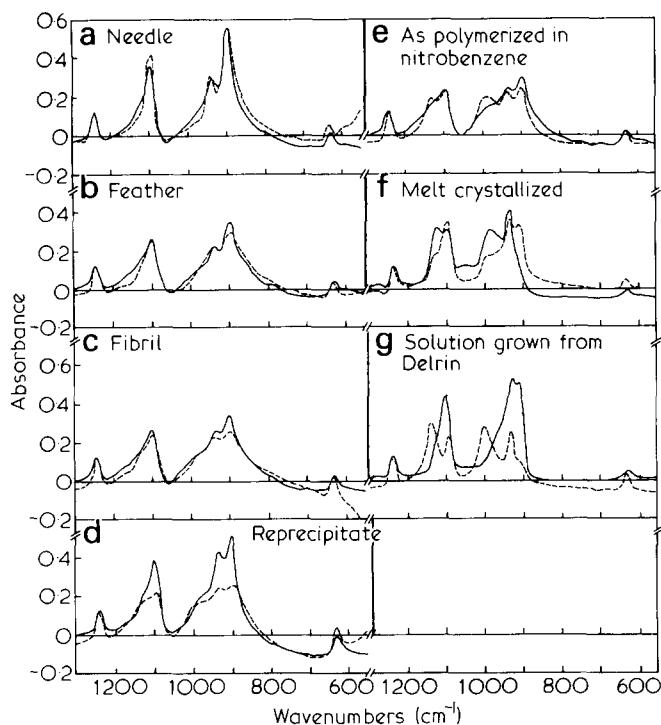


Figure 2 Infra-red spectra of various polyoxymethylene specimens measured by KBr pellet method. (Broken lines reproduce spectra by Nujol mull or film method.)

For these curves, the wavenumbers of peaks for different specimens are scanned to fall almost at the same positions, with a minor deviation, ≤ 7 wavenumbers in this region. The intensity of peaks has been classified into five levels and listed in Table 1. Three peaks at 1240, 935 and 635 cm^{-1} are present in all spectra and their intensities seem to be constant, suggesting that these bands are independent of crystallinity. The other four peaks at 1140, 1095, 1000 and 900 cm^{-1} are changeable in intensity and, in some cases, the bands at 1140 and 1000 cm^{-1} have completely disappeared from the spectra. It is certain that the band at 900 cm^{-1} is characteristic of the regular structure of helical conformation as has been concluded before⁴: the peak is outstanding for extended-chain type specimens and also it tends to increase for folded-chain type specimens in consequence of annealing. That the peak at 1095 cm^{-1} is dependent on the nature of sample, being stronger for regular specimens, is clear from the present results, though it has not been pointed out before. The peaks at 1140 and 1000 cm^{-1} are absent from the curves of highly perfect specimens and their affiliation to irregular structure, reported previously⁴, has been confirmed. Of course, the validity of these interpretations rests on the assumption that the 1240 cm^{-1} peak is consistent and useful for normalizing curves, as was actually done, but the assumption is not unreasonable in the light of a previous report⁴.

When the peaks in Figures 1 and 2 were examined carefully, it was deduced that the absorption bands at 1140 and 1000 cm^{-1} changed with proportional intensities. The relation between the peaks at 1095 and 900 cm^{-1} was not so simple but it seemed that the former band overlapped two absorptions, one variable and one constant, and the variable part was proportional to the peak of 900 cm^{-1} . In order to make it quantitative, peak areas were measured by means of a curve resolver. Plots

have been made in Figures 3 (a) and (b) and the expected linear relationships obtained. Here, the normalization of areas was carried out on the basis of the 1240 cm^{-1} peak but similar linearities were also obtained when the 935 cm^{-1} peak was adopted.

At the foot of Table 1, the assignments of infra-red absorption for hexagonal polyoxymethylene crystals given by Zerbi and Hendra¹⁶ with reference to theoretical calculation and Raman data are cited. (The interpretation is slightly different from a preceding report from Matsui *et al.*¹⁷, but the following discussion is made on the basis of the former assignments.) For seven absorption bands in the present wavenumber region, correspondence to the calculation is found for five bands observed in common with all spectra but for two bands unobserved in those of highly crystalline specimens. Four bands at 1240, 935, 900 and 635 cm^{-1} are assigned to [CH₂ rock.+COC bend.+COC sym. str.], [COC sym. str.], [COC asym. str.+CH₂ rock.] and [COC bend.], respectively. At around 1095 cm^{-1} , correspondences are found to [COC asym. str.+OCO bend.] and [CH₂ rock.+COC asym. str.]. It is recognized that the 1095 and 900 cm^{-1} bands involve [COC asym. str.] in their assignments. From the knowledge of these assignments and the results described above, it is assumed that the bands associated with [COC asym. str.] are changeable with crystallinity and the unassigned bands at 1000 and 1140 cm^{-1} have resulted from the shift of 900 and a part of 1095 cm^{-1} bands, respectively, due to the disordering of conformation. (According to Oleinik and Enikolopyan⁴, these new bands are affiliated to planar zig-zag conformation, though there has been no theoretical explanation.) If this assumption is valid, complementary relationships might

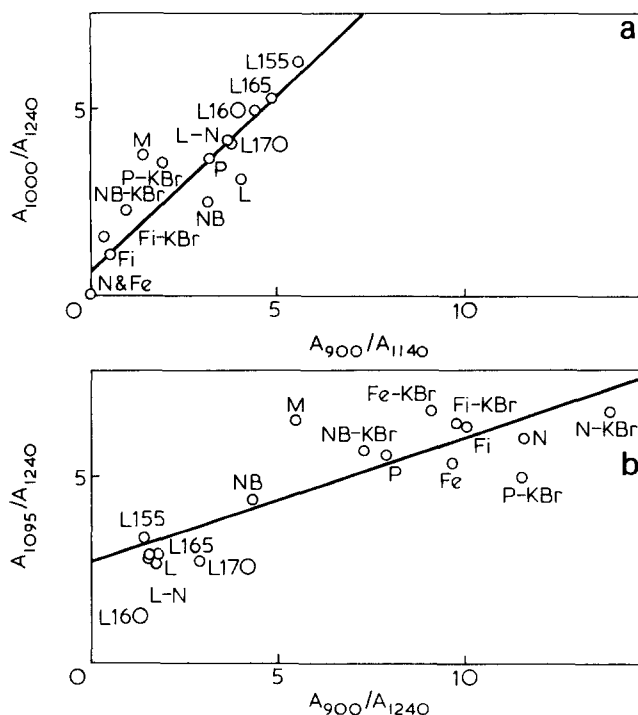


Figure 3 Plot of relative absorption intensities. (a): A_{1000}/A_{1240} vs. A_{1140}/A_{1240} . (b): A_{1095}/A_{1240} vs. A_{900}/A_{1240} . Notation: N: needle, Fe: feather, Fi: fibril, P: reprecipitate, NB: polymerized in nitrobenzene, M: melt crystallized, L: lamella, L-N: lamella from needle, Lxxx: lamella annealed at xxx°C

Table 1 Intensity of absorption bands for various polyoxymethylene specimens in 550–1300 cm⁻¹ region

Specimen	Wavenumbers (cm ⁻¹)						
	635	900	935	1000	1095	1140	1240
Needle ^a	w	vs	m	—	vs	—	m
Feather ^a	w	vs	m	—	s	—	m
Fibril ^a	w	s	m	sh	s	sh	m
As-polymerized in nitrobenzene ^a	w	m	m	m	m	m	m
Melt crystallized film ^b	w	m	s	w	s	w	m
Reprecipitate ^a	w	s	m	w	s	w	m
Solution grown from Delrin ^a	w	sh	s	s	m	s	m
Solution grown from needle ^a	w	sh	s	s	m	s	m
Solution grown from Delrin, annealed at 155°C ^a	w	sh	m	s	m	s	m
Solution grown from Delrin, annealed at 160°C ^a	w	sh	m	s	m	s	m
Solution grown from Delrin, annealed at 165°C ^a	w	w	m	s	m	s	m
Solution grown from Delrin, annealed at 170°C ^a	w	w	m	s	m	s	m
Needle (KBr) ^c	w	vs	m	—	vs	—	m
Feather (KBr) ^c	w	vs	m	—	s	—	m
Fibril (KBr) ^c	w	vs	m	sh	s	sh	m
As-polymerized in nitrobenzene (KBr) ^c	w	s	m	w	s	sh	m
Reprecipitate (KBr) ^c	w	vs	s	sh	vs	sh	m
Solution grown from Delrin (KBr) ^c	w	vs	s	—	vs	—	m
Melt crystallized (KBr) ^c	w	—	vs	s	s	s	m
Assignment ¹⁶	OCO bend.	COC asym. str. + CH ₂ rock.	COC sym. str.	—	COC asym. str. + OCO bend. and CH ₂ rock. + COC asym. str.	—	CH ₂ rock. + COC bend. + COC sym. str.

Measuring method: ^a Nujol mull method^b Film method^c KBr method

exist between the intensities of 1095 and 1140 cm⁻¹ bands and between those of 900 and 1000 cm⁻¹ bands. The plots have been made in *Figures 4 (a)* and *(b)*, respectively. Although the points are scattered considerably, it should not be unreasonable to approximate them with straight lines for both *Figures*. That the ratios of extinction coefficients for two pairs of absorptions, i.e., the slopes in *Figure 4*, are not far from unity, at least, supports the assumption of the band shift. In the course of these analyses, it became clear that the broadness as well as the shape of peaks at the same band regions were variable between samples. The reason is not clear, except that an effect by the environment surrounding any particular conformation is conceivable.

The cause of the scattering of data is not simple. Firstly, the effect of the scattering of the incident beam would not have been the same for all measurements, since it was inevitable that samples used were either in the form of

powders with different grain sizes or films. Secondly, errors are inevitably introduced during the resolving of curves, particularly for those comprising heavily overlapped peaks.

Leaving aside these problems, the way of plotting in *Figures 4 (a)* and *(b)* gives a semi-quantitative measure for the conformational regularity of helix in polyoxymethylene crystals. In general, polyoxymethylene ranks with the most highly crystalline polymers, and its degree of crystallinity, determined e.g. by the X-ray method, would not be less than 60%. In *Figures 4 (a)* and *(b)*, the plots are distributed over a wide range on the slopes, signifying that the degree of regularity, in terms of molecular conformation, is widely different between samples. It is surprising that the points for solution grown crystals, which are fine lamellae in morphology, are located far left on the slopes, indicating a rather irregular structure. It is suspected that the disordering of

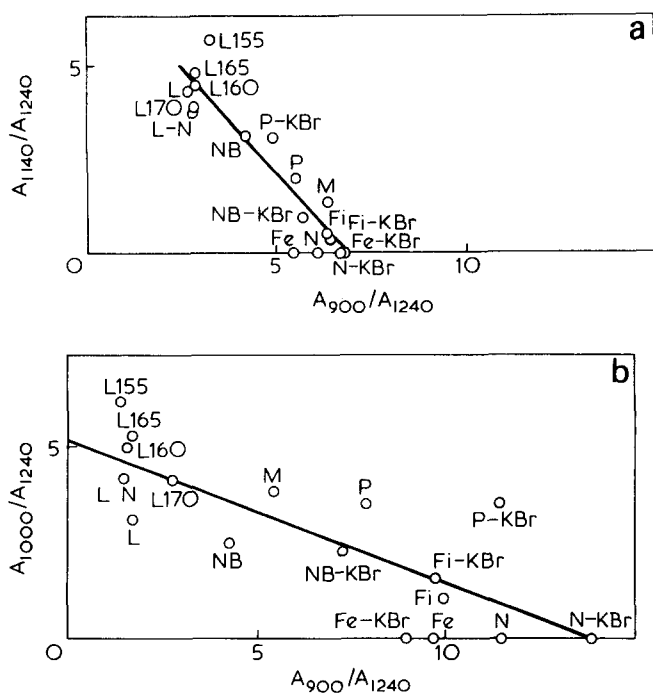


Figure 4 Plot of relative absorption intensities. (a): A_{1140}/A_{1240} vs. A_{1095}/A_{1240} . (b): A_{1000}/A_{1240} vs. A_{900}/A_{1240} . Notations are the same as in Figure 3

conformation might be penetrating, from the fold surface, deep into the crystals. The effect of annealing in increasing regularity is seen on the plots only as a trend. The points of needle-like and feather-shaped crystals lie on the horizontal axis, which indicates hundred percent regularity, and those of fibrillar crystal resulting from solid-state polymerization are found very close to the same axis. It is interesting to note that the heterogeneous polymer obtained by polymerizing trioxane in nitrobenzene increased its regularity smoothly with the mechanical force applied in the process of pelletization.

CONCLUSION

The interpretation of crystallinity depends strongly on the measuring method and, through this work, infra-red spectroscopy has proved to be useful for investigating the conformational regularity or the crystalline perfection of polyoxymethylene. Another way to demonstrate the crystalline perfection has been obtained by thermoluminescence measurements on irradiated polyoxymethylene crystals¹¹.

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