Structural change of st-PMMA on drawing, absorption and desorption of solvents

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Well-oriented crystalline samples of syndiotactic poly(methylmethacrylate) (st-PMMA) could be prepared from stretched non-crystalline samples on solvent-induced crystallization using chloroacetone, diethyl ketone, etc. as the solvent. X-ray fibre diagrams of these samples usually show period of 35.4Å and also suggest that the st-PMMA chains have a helical conformation of large radius and small axial pitch along the original stretched direction. Inversion of dichroism for most infra-red absorption bands during the crystallization, which is an indication of a wide variation in the orientation of the chains, again supports the large helical conformation. It was also confirmed that the solvents are necessary in maintaining the crystlalinity as the samples lose crystallinity on desorption of the solvents. From these results, it is conceivable that st-PMMA forms a complex with the solvents similar to the well-known amylose–iodine complex.

Keywords Solvent-induced crystallization; syndiotactic poly(methylmethacrylate); X-ray; infra-red; orientation

Introduction

The structures of poly(methylmethacrylate) (PMMA) in both crystalline[1–7] and non-crystalline states[8–10] have been much investigated by X-ray diffraction. A crystal model of the stereocomplex was also proposed by Liquori *et al.*[2]. For it-PMMA, it was determined, after much investigation[3–6], that the polymer chains form double-strand helices in the crystalline phase[7]. So far as we are aware, however, there has been no literature published on the preparation of oriented crystalline st-PMMA samples, and hence the crystal structure is still unresolved. Recently, we succeeded in preparing well-oriented crystalline samples of st-PMMA by solvent-induced crystallization for oriented non-crystalline samples[11–13]. In this communication, the crystallization mechanism and the crystal model of st-PMMA will be proposed on the basis of X-ray and infra-red data for the oriented and non-crystalline and crystalline samples.

Experimental

The triad tacticities of st-PMMA used in this study were estimated by proton n.m.r. to be S(91%), H(7%) and I(2%). Uniaxially-oriented crystalline samples were prepared as follows. st-PMMA films cast from a chloroform solution were stretched in hot water at *ca.* 75°C to about four times the original length. Subsequently, these films were crystallized on the absorption of vapour of several solvents. As a result of examination with many solvents, some ketonic solvents such as chloroacetone and diethyl ketone were found to induce the crystallization well[11,12]. Chloroacetone was the most effective solvent on both the crystallization and orientation. In practice, both chloroacetone and diethyl ketone were absorbed at room temperature for 1 to 2 h, and these samples were sealed off in thin-walled Lindeman glass capillaries. Conversely, desorption of the solvents was achieved on heating the crystalline samples at *ca.* 120°C *in vacuo* for 10 h.

X-ray photographs were taken using CuKα radiation monochromatized with a graphite crystal. A cylindrical vacuum-camera with a radius 10 cm was used to obtain high resolution of the reflections. *Figure 1* shows X-ray patterns of the selfsame oriented sample through a series of treatments; (a) cast from chloroform, (b) absorb chloroacetone, and (c) remove chloroacetone, respectively. Polarized infra-red spectra in *Figures 2* (*A*), (*B*) and (*C*) correspond to *Figures 1* (*a*), (*b*) and (*c*), respectively.

Results and Discussion

X-ray photographs. The light and shade in the most intense halo in *Figure 1*(*a*) indicates that a preferred orientation of polymer chains is already achieved in the stretched non-crystalline state. By absorbing chloroacetone, the polymer chains crystallize and give the fibre pattern as shown in *Figure 1*(*b*). A feature of this pattern is that all the $4n$th($n = 1 \sim 4$) layer lines, which can be explained in terms of a period of 8.85 Å, are strong. In addition, the 2nd, 3rd and 5th layer lines can be observed, therefore the fibre period is determined to be $8.85 \times 4 = 35.4$ Å. Furthermore, due to the appearance of a reflection having *d*-spacing of 20 Å on the equator, a large unit cell should be adopted. It seems that the broad reflections split into several sharp reflections with the advance of crystallization. About 50 independent reflections are observed for the highest crystalline sample, as shown in *Figure 1*(*b*). *Figure 1*(*c*) taken after the desorption of chloroacetone exhibits essentially the same halo as *Figure 1*(*a*), but the orientation is not so definite. Again the oriented crystalline sample can be obtained from sample (*c*) by absorbing chloroacetone once again.

When the crystalline sample is allowed to stand for a long time at room temperature, instead of heating, again the crystallinity is diminished. In any event, the special solvents, such as chloroacetone, diethyl ketone, are indispensable in maintaining the crystallinity.

Polarized infra-red spectra. The polarized infra-red spectra of *Figures 2*(*A*) and (*C*) are for the non-crystalline state, while the spectra of *Figure 2*(*B*) are for the crystalline

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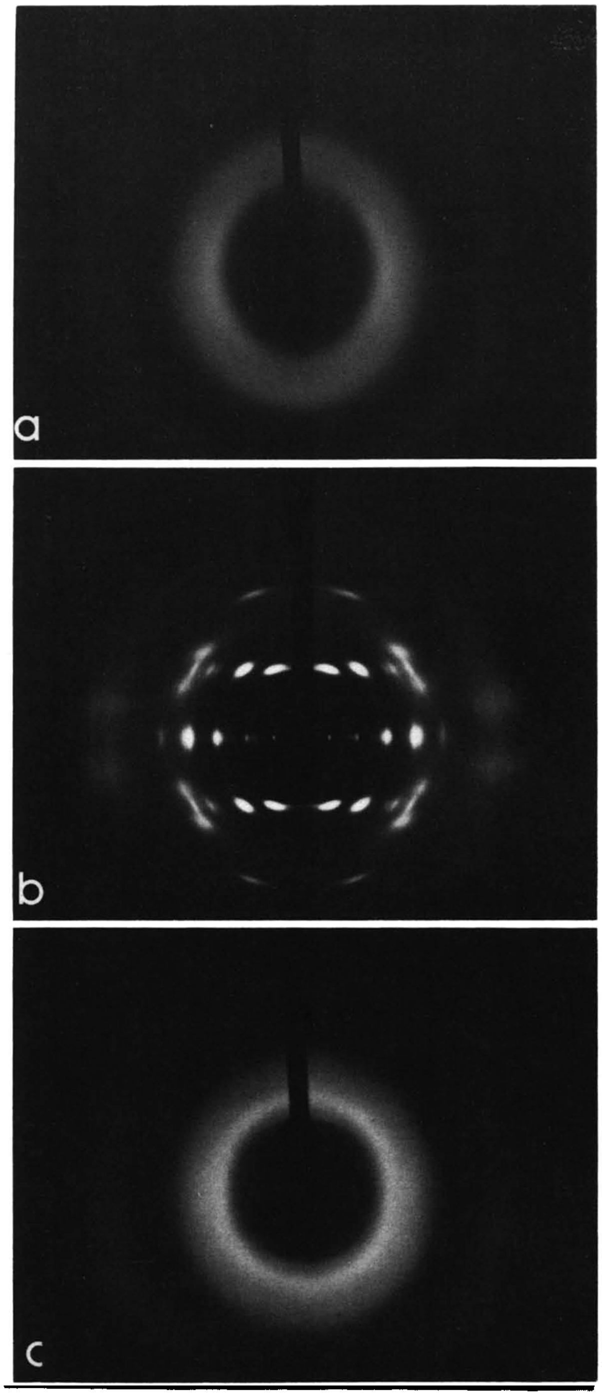

Figure 1 X-ray photographs of a stretched st-PMMA sample; (a) cast from chloroform, (b) absorb chloroacetone, and (c) remove chloroacetone

state. *Figure 2*(*A*) exhibits the dichroism, so the polymer chains are oriented, and this feature coincides well with the X-ray evidence mentioned above. The dichroism of most bands associated with the polymer reverses with the crystallization on the absorption of chloroacetone: some perpendicular bands change to parallel bands, and *vice versa*. Since rotation of the bulky side chains of PMMA are restricted, the reversal of dichroism can be ascribed to a large variation in the orientation of the polymer chains themselves. Two parallel bands at 858 and 1401 cm^{-1} observed in *Figure 2*(*B*), are assigned to crystalline bands and appear in the spectra of st-PMMA crystallized by diethyl ketone instead of chloroacetone[11-13]. The two crystalline bands decrease the intensities remarkably from *Figure 2* (*B*) to (*C*), while the dichroism for most bands does not vary much so as to revert to the variation from *Figure 2* (*A*) to (*B*). Therefore, the structures of both (*A*) and (*C*) are non-crystalline alike, but differ from each other with respect to the orientation of the polymer chains.

The 667 cm^{-1} band in *Figure 2* (*A*) and the 569 cm^{-1} band in *Figure 2* (*B*) arise from chloroform and chloroacetone, respectively. From *Figures 2* (*A*) and (*B*), it is found that chloroform is replaced by chloroacetone during the absorption of chloroacetone. The ~755 cm^{-1} band in *Figure 2* (*A*) is an overlapping band from chloroform and PMMA. Besides the 569 cm^{-1} band, weak bands arise from chloroacetone at 732, 1024 and 1362 cm^{-1} and can be observed in *Figure 2* (*B*). Since all of the bands from the solvent disappear in *Figure 2* (*C*), it is clear that chloroacetone is removed.

As a result of elementary analysis, the films exhibiting *Figure 2* (*A*), contain chloroform at a MMA/chloroform mole ratio of *ca.* 5:1, whilst for the films absorbing chloroacetone sufficient to correspond to *Figure 2* (*B*), the MMA/chloroacetone mole ratios are *ca.* 2:1.

Orientation of polymer chains. Figure 3 shows schematically the variations in the orientation of polymer chains on various treatments. In the stretched non-

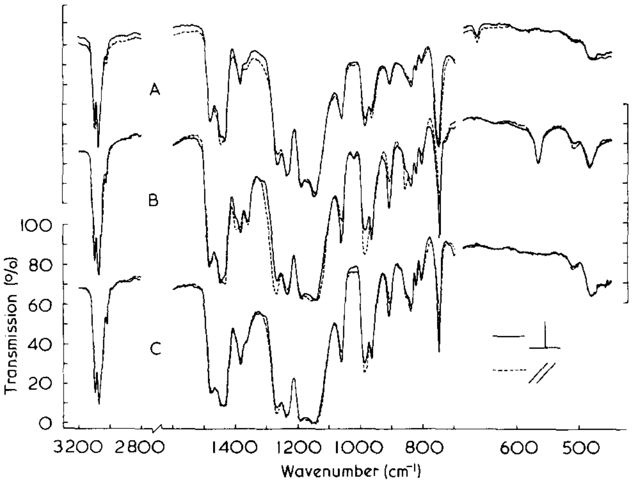

Figure 2 Polarized infra-red spectra of st-PMMA; (A) cast from chloroform, (B) absorb chloroacetone, and (C) remove chloroacetone. (——) Electric vector perpendicular to elongation (⊥). (– – –) Electric vector parallel to elongation (||)

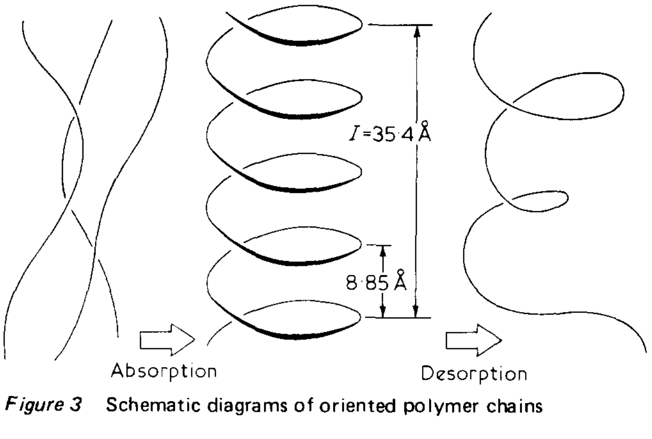

Figure 3 Schematic diagrams of oriented polymer chains

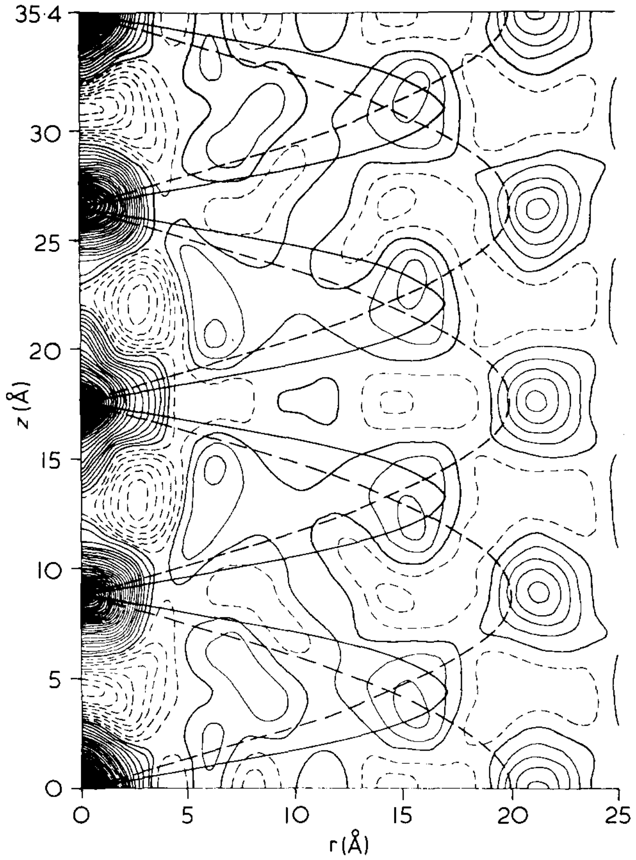

Figure 4 Cylindrical Patterson map of the st-PMMA–chloroacetone system

crystalline sample cast from a chloroform solution, the polymer chains tend to orient along the stretching direction. This feature is supported by, not only the infra-red dichroism shown in *Figure 2* (*A*), but also the analysis of the wide angle X-ray scattering for the oriented non-crystalline sample[8,9]. Taking into account the reversal of infra-red dichroism due to crystallization, it is considered that the polymer chains incline widely out of the stretching direction on crystallization. Considering the X-ray data, which suggests a large unit cell, together with the infra-red dichroism, a helical chain structure which has a sufficiently large radius as compared with the axial pitch may be reasonable for the crystalline phase. Although the polymer chains lose the order of conformation on the desorption of the solvent, the orientation of polymer chains appears not to vary from that for the crystalline state where the infra-red results show that the dichroism of most bands in the crystalline state is retained.

Crystal model. Detailed structure analysis of st-PMMA crystallized by solvents seems difficult at the present stage, for the following reasons: (1) large cell dimensions (c (fibre axis) = 35.4 Å and probably 20 Å or more both for a and b axes); (2) a large number of monomeric units in the fibre identity period (perhaps, to the extent of 100 monomeric units); (3) a possibility of multiple stranded helices and (4) a possibility of formation of a complex with the absorbed solvent, and if this is the case, the mole ratio of solvent to MMA.

Figure 4 shows the cylindrical Patterson map of the st-PMMA–chloroacetone system calculated from the fibre pattern in *Figure 1*(*b*). Since *Figure 4* consists approximately of a repeat of the pattern in a quarter of the fibre period along the z-axis, a four-fold helix shown by the solid lines can be considered. Besides the single four-fold helix, a double-strand which is composed of two two-fold helices related azimuthally by a rotation π may also be possible, as shown by the broken lines. In either case, a hole through the helical chains of st-PMMA appears to be large enough to admit chloroacetone molecules. It should be noted that the solvent is indispensable to give the crystalline X-ray pattern. Therefore it is most probable that a st-PMMA–chloroacetone complex like the well-known amylose–iodine complex is appropriate for the crystal model. Such a complex model gives a suggestion for the structure of the stereocomplex of PMMA.

A more detailed analysis of the crystal structure is in progress.

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