# Long period measurement of isotactic poly(4-methyl-1-pentene) by small angle X-ray scattering in conjunction with selective staining

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*(Received 12 November 1991)*

The long period of poly(4-methyl-1-pentene) was measured at room temperature by small angle X-ray scattering (SAXS) in conjunction with a selective staining technique. Since the unit cell structure and crystallinity were not influenced by staining, as shown by the wide-angle X-ray diffraction pattern, the long period of poly(4-methyl-1-pentene) was estimated to be 335 Å from the peak maximum in SAXS.

**(Keywords: poly(4-methyl-1-pentene); long period; SAXS; staining; $OsO_4$)**

*Introduction*

Poly(4-methyl-1-pentene) (P4MP) prepared with a Ziegler catalyst system has a predominantly isotactic structure, which forms a $7_2$ helix conformation in the crystal structure[1,2], and shows high heat resistance. It is well known that the crystal phase is less dense at room temperature than the amorphous phase ($d_c$ = 0.828 g cm$^{-3}$, $d_a$ = 0.838 g cm$^{-3}$) unlike ordinary crystalline polymers. The high transparency of P4MP is derived from the similar densities of the crystalline and amorphous regions. However, this small density difference makes it difficult to study the fine structure of P4MP by small angle X-ray scattering (SAXS). Tanigami and Miyasaka[3] reported that heating, which increases the density difference, was effective in making the SAXS peak due to the long period measurable and they applied this method to study the effect of annealing on the fine structure of P4MP.

In this paper, we propose a method to measure the long period of P4MP at room temperature by SAXS in conjunction with a selective staining technique[4,5] which enhances the density difference between the crystalline and amorphous parts.

*Experimental*

*Polymerization.* Into a 500 ml glass flask were added 250 ml of 4-methyl-1-pentene, 0.5 ml of triethylaluminium, 0.5 mmol of trimethylmethoxysilane, 0.005 mmol of titanium catalyst and 500 ml of $H_2$. Polymerization was then carried out at 50°C for 30 min. The polymerization was terminated by addition of methanol, and the polymer was precipitated in excess methanol and separated by filtering, followed by vacuum-drying.

*Staining procedure.* P4MP sheets (0.4 mm thick) were made between heated plates in a moulding press at ~250°C. One of the sheets was immersed in 1-dodecene at room temperature for 3 h, and then stained by $OsO_4$ vapour at room temperature for 2 days. The sheet impregnated with 1-dodecene was selectively stained through the reaction of the double bond and $OsO_4$.

*Wide angle X-ray diffraction.* The X-ray diffraction patterns of sheets with and without stain were measured using a Rigaku RU-300 X-ray diffractometer. The instrumental conditions were as follows: Ni-filtered Cu K$\alpha$ radiation 50 kV, 300 mA; divergence slit 1/2°; receiving slit 0.15 mm; scatter slit 1/2°; scanning speed 2° min$^{-1}$; measurement angle 5–35°.

*Small angle X-ray scattering.* SAXS measurements were carried out using a rotating anode X-ray generator (RU-200A, Rigaku). The incident beam was Cu radiation generated at 50 kV and 200 mA. The scattered intensity was measured by a position-sensitive proportional counter.

*Results and discussion*

A vertical section of the stained sample observed by an optical microscope showed that the internal and

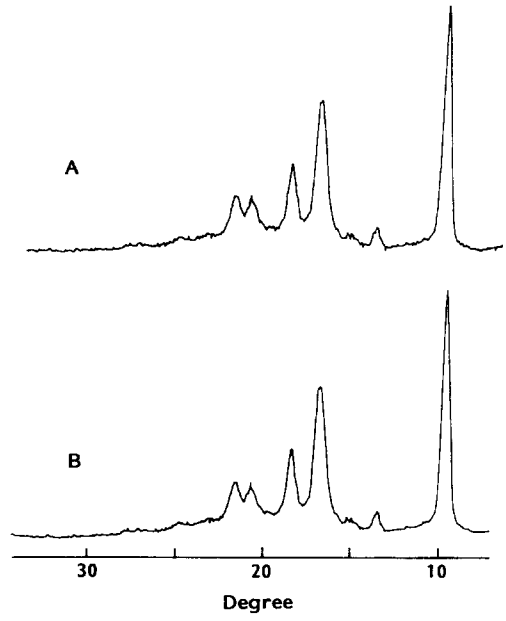


**Figure 1** Wide-angle X-ray diffraction patterns of P4MP (A) with and (B) without staining

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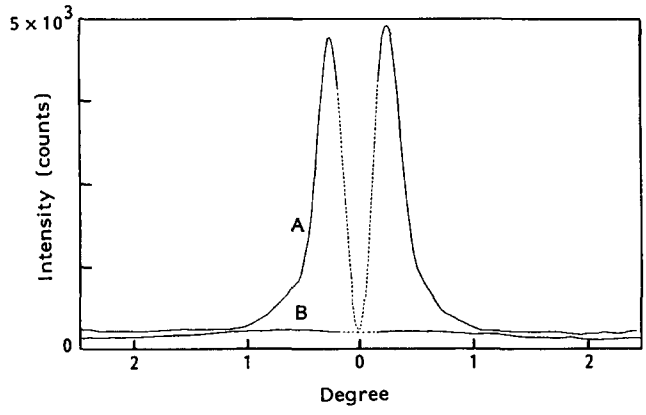


**Figure 2** SAXS intensity curves of P4MP (A) with and (B) without staining

external phases were uniformly stained with $OsO_4$. However, no practical change in thickness was observed after staining.

*Figure 1* shows the X-ray diffraction patterns of the samples with and without staining, showing that the diffraction positions and intensities are not influenced by staining. This means that the unit cell structure is not distorted by introduction of $OsO_4$ and that the crystallinity (54–55%) remains unchanged after staining. Therefore, the amorphous region of P4MP might be selectively impregnated with 1-dodecene and stained with $OsO_4$.

Since the present level of staining has practically no effect on the crystallinity, the unit cell structure and the sheet thickness of P4MP, SAXS measurements were conducted on samples with and without staining. *Figure 2* presents SAXS intensity curves for two samples, where the scattered intensity of the sample without staining is too weak to detect while the peak intensity of the stained sample remarkably increases and the position of the peak maximum gives a long period of 335 Å.

Our present data show that staining is quite effective for the observation of the SAXS peak of P4MP at room temperature and may be useful for studying, for example, annealing effects.

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