*Crystalline Polymers of Some Nuclear-substituted Styrenes**

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In the preceding paper we pointed out the possible crystallization of poly(*p*-methylstyrene) and poly(*m*-methylstyrene) prepared by Ziegler's catalyst from the observation of infrared spectra and density-measurements[1]. In the present communication, we wish to report that this expectation has been realized by the suitable heat-treatment in both cases and also a newly prepared poly(*p*-trimethylsilylstyrene) has been found to crystallize easily by the same treatment.

These results stand in contrast with the recent observation by Natta that the polymers of *p*-substituted styrene obtained with Ziegler's catalysts are generally amorphous, except for *p*-fluorostyrene, because of a steric hindrance caused by the *p*-substituent in crystallization[2].

TABLE I. POLYMERIZATION OF NUCLEAR-SUBSTITUTED STYRENES WITH ZIEGLER'S CATALYST AT 70°C IN 20 ML. OF *n*-HEPTANE

Monomer g.	$TiCl_4$ mmol.	$AlEt_3$ mmol.	$AlEt_3$ added after washing mmol.	Time hr.	Conversion %	$[\eta]$[a]	Softening point °C[b]
p-Methylstyrene, 3.7 g.	2.2	2.3	2.5	3.6	43	2.61	130
m-Methylstyrene[c], 3.3 g.	3.2	3.4	3.4	3.5	21	2.52	90
p-Trimethylsilylstyrene[d], 4.3 g.	3.3	3.4	3.4	4.3	13	See Table II	

a) Intrinsic viscosity in toluene at 30°C.
b) Softening points were observed under a microscope.
c) *m*-Methylstyrene was supplied from the Research Laboratory of Dainihon Celluloid Co.
d) *p*-Trimethylsilylstyrene was supplied from the Engineering Laboratory of Mitsubishi Electric Manufacturing Co.

TABLE II. FRACTIONAL EXTRACTION OF THE CRUDE POLY(*p*-TRIMETHYLSILYLSTYRENE)[a]

Solvent for extraction	Fraction %	$[\eta]$	Softening p. or m. p. °C[b]	X-ray evidence
Acetone	19	0.35	s. p. 125	Amorphous
Ether	11	0.61	s. p. 145	Partially crystalline
Benzene	70	2.49	m. p. 284	Highly crystalline

a) Hot extraction was carried out using a modified Soxhlet's extractor.
b) Softening points and melting points were observed under a polarized microscope.

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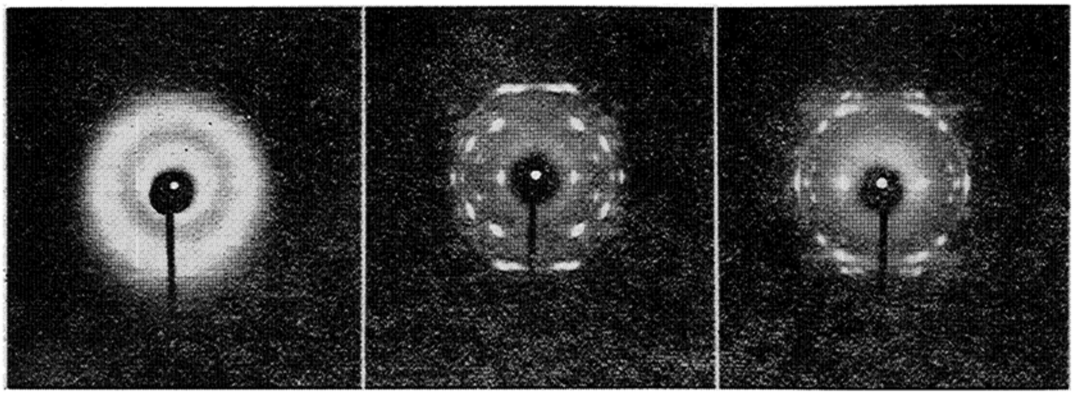
[1] H. Tadokoro, S. Nozakura, T. Kitazawa, Y. Yasuhara and S. Murahashi, This Bulletin, 32, 313 (1959).

[2] G. Natta, F. Danusso and D. Sianesi, *Makromol. Chem.*, 28, 253 (1958).



(a) (b) (c)

Fig. 1. Fiber diagrams of X-ray diffraction patterns.

(a) Poly(p-methylstyrene). An extruded filament was drawn at 135°C to about 20 times of the original length and heated for 6 hr. at the same temperature.

(b) Poly(m-methylstyrene). Drawn at 90°C to about 20 times and heated for 3 hr. at 100°C.

(c) Poly(p-trimethylsilylstyrene). Drawn at 150°C to about 20 times and heated for 0.5 hr. at 200°C.

All the polymerization procedure in this paper was performed by the use of Ziegler's catalysts according to the modified method described in the previous paper[3], i. e., the catalystic solid mass was washed with n-heptane prior to polymerization (Table I). The fractional extraction of the crude polymer was carried out in the case of poly(p-trimethylsilylstyrene) as shown in Table II.

The fiber diagrams of X-ray diffraction patterns with these polymers are shown in Fig. 1. Poly(p-methylstyrene) could be crystallized by the heat-treatment in a stretched state, although its crystallinity was rather low as shown in Fig. 1 (a). On the contrary, the benzene-fraction (Table II) of poly(p-trimethylsilylstyrene) was found to be crystallized easily and highly crystalline even in an unoriented state. Poly(m-methylstyrene) was more reluctant to crystallize than poly(p-trimethylsilylstyrene) in an unoriented sample.

Fiber periods observed are 12.9, 57.0 and 60.4 Å for the polymers of p-methyl-, m-methyl- and p-trimethylsilyl-styrene, respectively. The large values of identity periods of these polymers suggest some complicated nature of the helical structures of these isotactic polymers. The detailed X-ray analysis will be published elsewhere by Nitta and others.

These three polymers are all considered to be isotactic and to have the helical structure of trans-gauche alternate sequence from the inspection of the following infrared data. (1) The 2849 $\mathrm{cm^{-1}}$ CH_2 symmetric stretching band has almost no dichroism (or rather weak parallel dichroism), though the 2924 $\mathrm{cm^{-1}}$ CH_2 antisymmetric stretching band shows distinguished perpendicular nature, as is in the case of isotactic polystyrene[4]. This dichroic behavior indicates such an inclination of the triangle of the methylene group that the direction of H—H is nearly perpendicular to the fiber axis and the angle between the bisector of the angle H—C—H and the fiber axis is about 54°44′. (2) The four bands in the region of 1400~1100 $\mathrm{cm^{-1}}$, which are considered to be closely associated with the helical structure in the previous paper[1], are also found in the polarized spectra of these three polymers, showing the same dichroic natures as the corresponding bands of the oriented isotactic polystyrene: 1364 ($\perp$), 1314 ($\perp$), 1297 ($\parallel$) and 1185 $\mathrm{cm^{-1}}$ ($\parallel$).

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[3] S. Murahashi, S. Nozakura, M. Sumi and K. Hatada, to be published in this Bulletin.

[4] H. Tadokoro, N. Nishiyama, S. Nozakura and S. Murahashi, *J. Polymer Sci.*, in press.