Molecular Configuration of Poly(m-methylstyrene) and Poly(p-trimethylsilylstyrene)

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Syntheses and infrared studies of poly(*m*-methylstyrene) (PMMS) and poly(*p*-trimethylsilylstyrene) (PPTMSS) have already been reported by Murahashi, Nozakura and Tadokoro¹⁾. In this communication, molecular configuration of these polymers will be reported on the basis of X-ray diffraction evidence.

The fiber period calculated from the layer line spacing is 57.1 Å for PMMS and 60.6 Å for PPTMSS. And by taking photographs of tilted specimens, axial maximum intensity on the 29th layer line was observed (see Fig. 1). The repeat distance of successive monomers along the fiber axis (1.97 Å for PMMS and 2.09 Å for PPTMSS) is much shorter than 2.53 Å found in the case of fully extended chain of singly linked carbon atoms. Therefore, it would be appropriate to conclude that these polymers construct uniform helices in their crystalline regions, indicating one of characteristic features of isotacticity.

To analyze further the helical structure, the authors used the method of Cochran

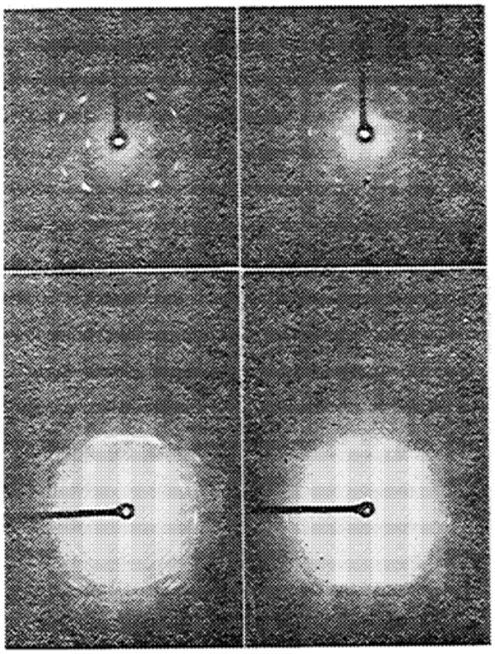

Fig. 1. Fiber diagrams of X-ray diffraction patterns.
Left: Poly(*m*-methylstyrene)
Right: Poly(*p*-trimethylsilylstyrene)
Upper: The axis of specimen is vertical.
Lower: The axis of specimen is inclined at about 23° to the vertical.

TABLE I

(PMMS)			(PPTMSS)		
l*	I**	$\|n\|$***	l	I	$\|n\|$
0	*s*	0	0	*s*	0
1	—	11	1	—	13
2	—	7	2	*mw*	3
3	*m*	4	3	—	10
4	—	14	4	*w*	6
5	*ms*	3	5	—	7
6	—	8	6	—	9
7	—	10	7	*ms*	4
8	*s*	1	8	—	12
9	—	12	9	*s*	1
10	*mw*	6	10	—	14
11	—	5	11	*s*	2
12	—	13	12	—	11
13	*ms*	2	13	—	5
14	—	9	14	—	8
15	—	9	15	—	8
16	—	2	16	—	5
17	—	13	17	—	11
18	—	5	18	*vw*	2
19	—	6	19	—	14
20	—	12	20	*w*	1
21	*w*	1	21	—	12
22	—	10	22	—	4
23	—	8	23	—	9
24	—	3	24	—	7
25	—	14	25	—	6
26	—	4	26	—	10
27	—	7	27	—	3
28	—	11	28	—	13
29	*m*	0	29	*m*	0
30	—	11	30	—	13
31	—	7	31	—	3
32	—	4	32	—	10
33	—	14	33	—	6
34	—	3	34	—	7
35	—	8	35	—	9
36	—	10	36	—	4
37	*vw*	1	37	—	12
38	—	12	38	*w*	1
39	—	6	39	—	14
40	—	5	40	—	2

* Index of the layer.
** Estimated average intensity of the layer.
*** Order of the Bessel function.

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1) S. Murahashi, S. Nozakura and H. Tadokoro, This Bulletin, **32**, 534 (1959).

and others[2]. Taking the fiber axis as the c axis and using cylindrical coordinates $R, \psi, l/c$ in the reciprocal space, the structure factor of a helical molecule can be given as follows:

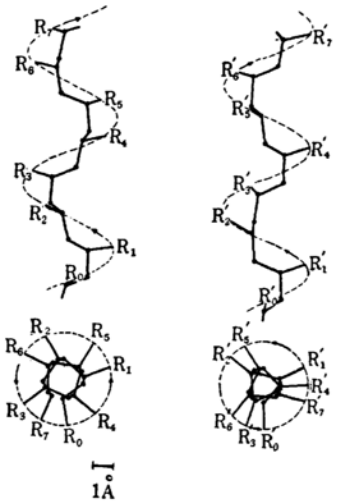
$$F(R, \psi, l/c) = \sum_j \sum_n f_j J_n(2\pi R r_j) \times \exp\left\{i\left[n\left(\psi - \varphi_j + \frac{\pi}{2}\right) + 2\pi l z_j/c\right]\right\} \quad (1)$$

where r_j, φ_j, z_j represent the cylindrical coordinates of the j-th atom of a monomer, and J_n's are Bessel functions, the order n of which are to be obtained properly for the reflexions on each layer line l by solving the equation;

$$l = un + vm \quad (n, m; \text{ integers}) \quad (2)$$

where u and v are, respectively, the number of turns and that of monomers in the repeat distance.

Trial consideration** on various possibe types of helices shows that the helix of 8 turns ($u=8$, $v=29$) for PMMS and 9 turns ($u=9$, $v=29$) for PPTMSS will be taken as to account qualitatively for average intensity of each layer line (see Table I). The helical model thus obtained seems to be quite reasonable, because, from the observed value of fiber period and the assumed 1.54 Å of the C-C single bond length, the standard tetrahedral angle (109.5°) comes out in the permissible region of C-C-C bond angle calculated for the C helix. Moreover, the region of intense reflexions conforms to the properties of the selected Bessel function for each layer line. After all such considerations the authors are led to the probable configuration shown in Fig. 2. Although precise orientations of side groups have not been determined from such considerations alone, it would be imagined reasonable that the plane of phenyl radical is so inclined as to be influenced by steric hindrances of neighboring hydrogen atoms.



a) b)

Fig. 2. Chain configuration of the molecule (side and end views of right-handed helix only two turns drawn).

a) Poly(*m*-methylstyrene), $R = C_6H_4CH_3$

b) Poly(*p*-trimethylsilylstyrene), $R' = C_6H_4Si(CH_3)_3$

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[2] W. Cochran, F. H. C. Crick and V. Vand, *Acta Cryst.*, **5**, 581 (1952).

** From Eq. 1, it is shown that on a particular layer line a strong reflexion can occur in a region where R is small only if the corresponding Bessel function is of a low order, so long as a helix dose not take too large a value of any r_j.