

### Crystalline Syndiotactic Polystyrene

Following the invention of isotactic polystyrene by Natta in 1955, a number of papers appeared describing the stereospecific polymerization of styrene by coordination, anionic, and radical means.<sup>1-3</sup> However, syndiotactic polystyrene with a high stereoregularity has not yet been synthesized and characterized.

We have recently succeeded in obtaining a new polystyrene which has a syndiotactic structure and a high degree of crystallinity. In this communication, we describe the determination of the stereoregularity and some other properties of the newly obtained polystyrene.

The new polymer was prepared and purified as follows: 20.8 g of styrene was polymerized with our novel catalyst system, containing a titanium compound and an organo-aluminum compound, for 2 h at 50 °C, and 20.3 g of polymer was obtained. The crude product was extracted with methyl ethyl ketone under reflux for 4 h. A total of 98 wt % of the polymer was insoluble in methyl ethyl ketone and its weight-average molecular weight was 82 000.

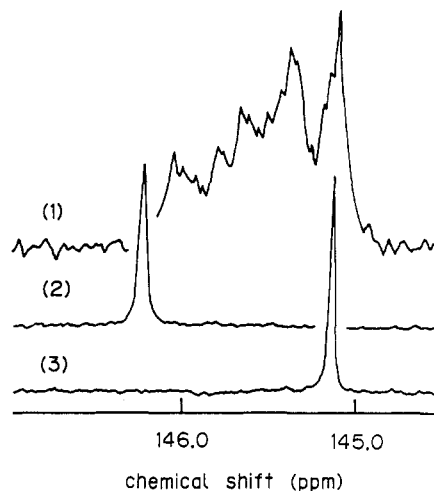
The new polymer thus obtained was examined by <sup>13</sup>C and <sup>1</sup>H NMR, IR spectroscopy, and X-ray diffraction, together with an atactic polystyrene prepared with 2,2'-azobis(isobutyronitrile) and an isotactic polystyrene prepared with a TiCl<sub>4</sub>-Al(Et)<sub>3</sub> Ziegler-Natta catalyst.

Carbon-13 NMR spectroscopy has been used extensively in recent years to obtain detailed information on the microstructure of vinyl polymers. The signals of the methylene and phenyl C-1 carbons of polystyrene were reported to be split, reflecting configurational sequences<sup>4-8</sup>. Sato et al.<sup>9</sup> reported the assignments for these signals. According to their results the most important signal for determining stereoregularity is the phenyl C-1 carbon signal.

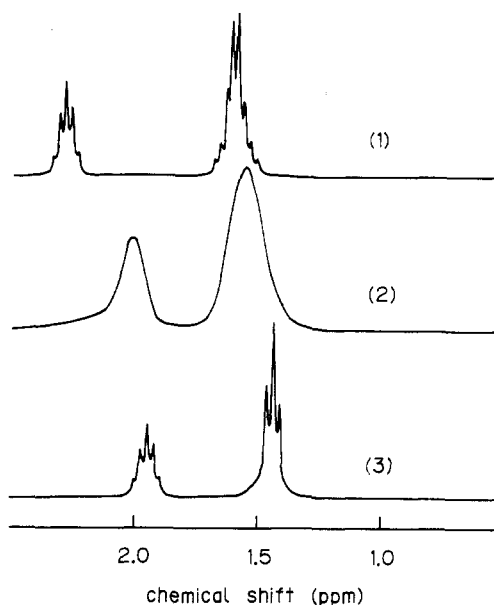
Figure 1 shows carbon-13 NMR spectra of the phenyl C-1 carbon of the three types of polystyrene measured at 67.8 MHz in 1,2,4-trichlorobenzene at 130 °C with a JNMGX-270 spectrometer. The spectrum of atactic polystyrene (Figure 1-(1)) shows five main peaks in the range 145.12-146.7 ppm, corresponding to its various configurational sequences. The spectrum of isotactic polystyrene (Figure 1-(2)) shows a single sharp peak at lower magnetic field ( $\delta$  = 146.24) corresponding to the *mmmm* pentad configuration.

In contrast, the chemical shift of the phenyl C-1 carbon in the new polymer was observed at higher magnetic field ( $\delta$  = 145.13), and the peak was single and sharp. We conclude that this peak at higher magnetic field should be assigned to the *rr* triad or *rrrr* pentad configuration. Its syndiotacticity, directly measured from the relative peak area, was greater than 98%.

Figure 2 shows the <sup>1</sup>H spectra of the methine and methylene protons of the three types of polystyrenes measured at 270.1 MHz in 1,2,4-trichlorobenzene at 130 °C with a JNMGX-270 spectrometer. Yoshino et al.<sup>10</sup> reported that the difference in chemical shift between methine and methylene protons is greater in isotactic polystyrene than in atactic polystyrene. Matsuzaki et al.<sup>11</sup> reported that the methine proton signal is shifted to higher magnetic field in the order isotactic-, atactic-, syndiotactic-rich polymer. As shown in Figure 2, the difference in chemical shift between the methine and methylene protons is less in the new polymer than in isotactic polystyrene, and the methine proton signal of the new polymer is observed at highest magnetic field. The appearance of the proton spectra of the new polymer is consistent with the results of Yoshino and Matsuzaki. In addition, referring to the splitting of the proton signal by spin-spin coupling, the methylene proton signal of the new polymer is very



**Figure 1.** <sup>13</sup>C NMR spectra of polystyrenes: (1) atactic; (2) isotactic; (3) the new polymer.



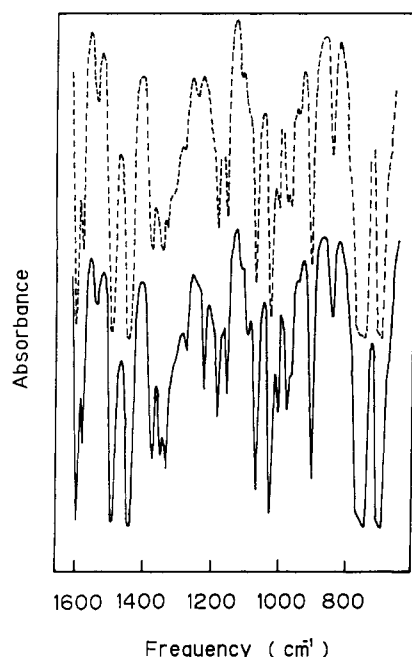
**Figure 2.** <sup>1</sup>H NMR spectra of the methine and methylene protons of polystyrenes; (1) isotactic; (2) atactic; (3) the new polymer.

different from those of the other two types of polystyrene.

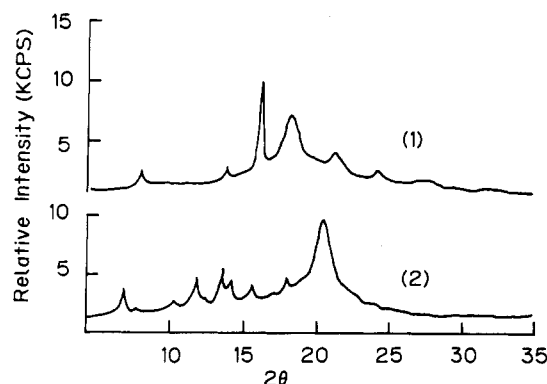
The methylene proton signal of the atactic polystyrene was only a broad resonance, as shown by Bovey et al.<sup>12</sup> (Figure 2-(2)). Heatley et al.<sup>13</sup> reported that the two methylene protons in isotactic polystyrene are nonequivalent. In agreement with this observation, the spectrum shown in Figure 2-(1) has eight peaks due to the signals of two nonequivalent methylene protons. However, as shown in Figure 2-(3), the methylene proton signal of the new polymer shows only a triplet. This suggests that the two methylene protons of the new polymer are equivalent and that the structure of the new polymer is syndiotactic. We conclude, therefore, that the new polymer is syndiotactic polystyrene.

Figure 3 shows infrared spectra (1600-700 cm<sup>-1</sup>) of the new polymer. The solid line denotes the crystallized sample and the broken line denotes the quenched sample. The absorption spectrum of isotactic polystyrene has been investigated by Tadokoro et al.<sup>14</sup> They concluded that the characteristic signals observed in the region 1450-1180 cm<sup>-1</sup> (1364, 1314, 1297, and 1185 cm<sup>-1</sup>) are to be associated with the helical structure and to originate from intermolecular interaction.

As shown in Figure 3, the absorption signals attributed



**Figure 3.** Infrared spectra of the new polymer: (—) crystallized sample; (---) quenched sample.



**Figure 4.** X-ray diffraction spectra of the crystallized sample: (1) isotactic polystyrene; (2) the new polymer.

to a helical conformation were not observed in the crystallized sample, and a new absorption signal was observed at  $1200\text{ cm}^{-1}$ . This absorption signal also disappeared in the quenched sample. Therefore, we conclude that the absorption signal at  $1220\text{ cm}^{-1}$  is closely associated with the conformation of the new polymer and that this polymer has a conformation different from the helical structure of isotactic polystyrene.

The X-ray diffraction spectra of the new polymer and isotactic polystyrene are shown in Figure 4. The well-defined X-ray diffraction pattern of the new polymer is quite different from that of isotactic polystyrene. The identity period measured from the fiber spectrum of the new polymer is about  $5.06\text{ Å}$ , which is much smaller than that of crystallized isotactic polystyrene ( $6.65\text{ Å}$ ), having a threefold helical structure. Furthermore, the identity period is twice as great as that of polyethylene and nearly equal to that of syndiotactic poly(vinyl chloride), having a planar zigzag conformation. We conclude, therefore, that the new polymer has a planar-zigzag conformation in the crystalline state.

The crystallization rate of the new polymer was extremely high in comparison with that of isotactic polystyrene, which is comparable to polyethylene. The melting point of the new polymer is about  $270\text{ °C}$ , which is higher than that of isotactic polystyrene by  $40\text{ °C}$ .

A more complete characterization and description of the method of preparation of the new polymer are in progress and will be reported shortly.

**Registry No.** Syndiotactic polystyrene, 28325-75-9.

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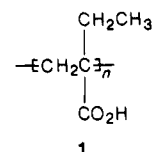
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## Glucose-Dependent Disruption of Phospholipid Vesicle Membranes†

Poly( $\alpha$ -ethylacrylic acid) (PEAA, 1) undergoes a conformational transition to a globular structure upon acidification of its aqueous solutions.<sup>1,2</sup> The globular polymer



associates strongly with bilayer vesicles prepared from phosphatidylcholines and phosphatidylglycerols, with profound disruption of bilayer organization.<sup>3,4</sup> The latter phenomenon allows the formulation of phospholipid vesicles that release their contents rapidly and quantitatively in response to small changes in environmental pH.<sup>4</sup> We show herein that this process can be combined with enzymic generation of  $\text{H}^+$  to produce vesicles sensitive to low concentrations of neutral organic solutes such as glucose.<sup>5</sup>

Hydration of L- $\alpha$ -dilauroylphosphatidylcholine (DLPC) at a concentration of  $2.4\text{ mg/mL}$  in pure water or in aqueous salt solutions affords turbid suspensions of multilamellar vesicles.<sup>6,7</sup> Addition of PEAA<sup>8</sup> and/or the enzyme glucose oxidase (GO)<sup>9</sup> to the hydration medium

†Part 11 in the series "Interactions of Synthetic Polymers with Cell Membranes and Model Membrane Systems". For Part 10, see: Ramaswami, V.; Tirrell, D. A. *J. Polym. Sci., Polym. Chem. Ed.* **1986**, *24*, 241.