Poly-p-halostyrenes. I. Preparation of Crystalline Poly-p-chlorostyrene

Kazuo NAGAI, Masamichi KOBAYASHI
and Eiichi NAGAI

(Received May 12, 1959)

Recently Natta et al. reported[1] that while some substituted polystyrenes prepared by Ziegler catalyst were crystalline, others were amorphous. To the contrary of Natta et al.'s results that poly-*p*-chlorostyrene is not crystalline, we find that a small part of poly-*p*-chlorostyrene prepared by Ziegler catalyst is crystalline.

p-Chlorostyrene (4.4 g.) prepared by an usual method[2], enclosed in a glass tube with $Al(C_2H_5)_3$ (0.53 g.), $TiCl_4$ (0.18 g.) and *n*-heptane (20 cc.) is polymerized at 70°C

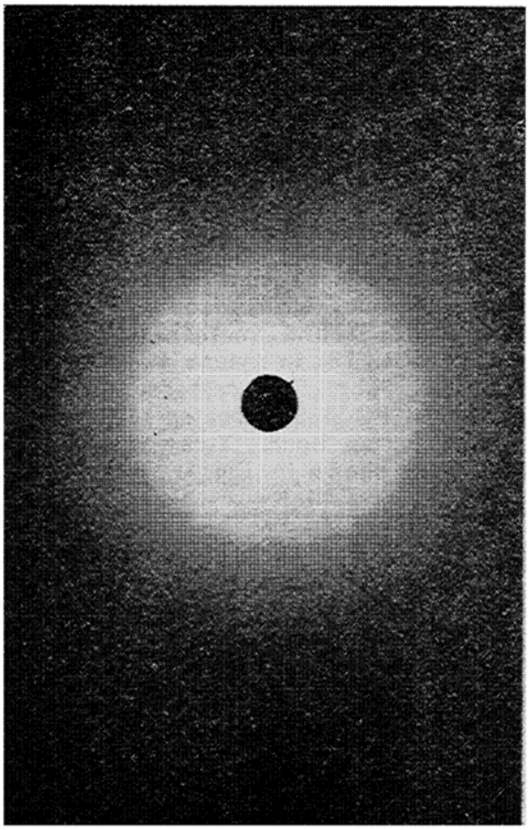

Fig. 1. X-ray diagram of poly-*p*-chlorostyrene (PClS-IS)

---

[1] G. Natta, F. Danusso and D. Sianesi, *Makro. Mol. Chem.*, **28**, 253 (1958).

[2] R. Adams and C. R. Noller, "Organic Syntheses", Vol. 5, John Wiley & Sons, New York (1925), p. 17; W. Kern and D. Braun, *Makro. Mol. Chem.*, **27**, 23 (1958).

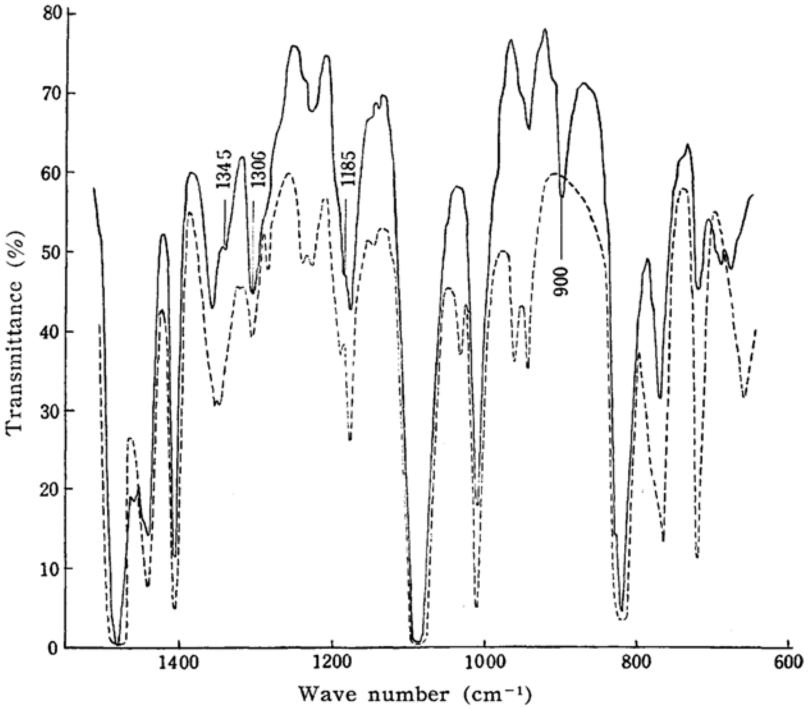

Fig. 2.

for about 10 hr. The product washed by hot ethanol and then boiled in water is dissolved in boiling xylene and the solution is filtered to separate from titanium oxide. By centrifuging this solution kept at room temperature the polymer is devided into two parts; one (2.20 g.) soluble (refered as to PClS–S) and another (0.13 g.) insoluble (PClS–IS) in xylene at room temperature. The film cast from toluene solution of PClS–IS is heated in silicon oil at 160°C for an hour. X-ray diagram of this film is shown in Fig. 1, manifesting moderate crystallinity of this sample.

In Fig. 2 are shown the infrared spectroscopic data of PClS–IS (full line) and radically polymerized poly-*p*-chlorostyrene (PClS–At) (dashed line), both previously heated at 160°C for an hour. It is expected that in the crystalline region and in the amorphous region, so far as the short portion of the polymer chain is concerned, the skeletal chain of PClS–IS has a helical structure, although whether 3-fold helix as in the case of polystyrene is still kept or not is not obvious, owing to the steric effects of chlorine atoms. Recently Tadokoro et al.[3,4] showed that the absorption bands ascribed to deformation vibrations of CH_2 and CH groups of the skeletal carbon chain, and to C–C stretching vibration were affected by the configurations of the skeletal chain, and bands at 1364, 1314, 1297 and 1185 cm^{-1} of isotactic polystyrene and *p*-deuterostyrene were assumed to be characteristic to 3-fold helical structure. Moreover, in our investigations on the infrared spectroscopy of the crystalline poly-*p*-fluorostyrene, we found[5] the bands at 1330 and 1302 cm^{-1} as to be charasteristic to the helical structure of the skeletal chain. From these results, the bands 1345, 1306 and 1185 cm^{-1} of PClS–IS are assumed to be characteristic to the helical structure. A band at 900 cm^{-1} probably corresponds to crystallization sensitive band. The spectroscopic data of PClS–S are almost similar to those of PClS–At. Investigations are in progress on the bands appearing at near 700 cm^{-1} and longer wavelength region.

We thank Mr. S. Kuribayashi for his preparation of X-ray diagram.

The Osaka Industrial Research Institute
Daini-Nishi 2-Chome, Oyodo-ku, Osaka

---

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

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

[5] K. Nagai, M. Kobayashi and E. Nagai, Presented at the 8th Annual Meeting of the Society of Polymer Science of Japan, held in Tokyo, May, 1959.