# Proton Magnetic Resonance Study of Poly(*p*-chlorostyrene) of Low Molecular Weight

Yoshiyuki HIRAI, Yoshio NUNOMURA, and Yoshio IMAMURA

*Department of Chemistry, Faculty of Science, Science University of Tokyo, Kagurazaka, Shinjuku-ku, Tokyo 162*

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Poly(*p*-chlorostyrne) samples of relatively low molecular weight (average degrees of polymerization($\overline{\text{DP}}$): 15, 24, and 46) were prepared by radical polymerization and their PMR spectra were observed in the temperature range 5—88 °C. When the temperature was elevated, the absorption of the methyne proton moved to lower field and the half height width for the absorption of the *ortho* proton decreased more remarkably than that of the *meta* proton. The absorption of the *ortho* proton of one polymer sample ($\overline{\text{DP}}$: 15) showed an anomalous broadening. These features of the observed spectra were interpreted in terms of ring current shielding by aromatic side groups, and the conformations of the polymer are discussed.

Many studies of proton magnetic resonance (PMR) spectra and proton relaxation times of polymers of low molecular weight have been made by various authors.[1-4] In many cases reported in the literature, the spectral patterns or spin-lattice relaxation times change with chain length in the region of short chains, and they become less sensitive to chain length as the chain becomes longer (*e.g.* average degrees of polymerization ($\overline{\text{DP}}$) : 20 for polystyrene).[2,5] These observations have been interpreted in terms of a so-called "polymeric effect". However, more precise discussion based on the viewpoint of conformations or internal motions of polymer chains has not been sufficiently developed. The present paper is concerned with the discussion of the conformations of polymers (poly(*p*-chlorostyrene)) of such low degrees of polymerization.

PMR spectra of polymers which contain aromatic side groups are always deformed by the ring current effect of the side groups. The extent of the ring current effect on each proton of the polymer would be influenced by the polymer conformation. Therefore, the PMR spectra of these polymers are accessible for conformational consideration. Poly(*p*-chlorostyrene) is one of the most favorable samples to this purpose, because this polymer gives well-resolved spectra in comparison with other polymers containing aromatic side groups, such as polystyrene and its *ortho* or *meta* derivatives.

The PMR spectra of poly(*p*-chlorostyrne)s ($\overline{\text{DP}}$ : 15, 24, and 46) were observed in the temperature range 5—88 °C. The observed spectra were compared with each other in chemical shifts and in half height width, and the conformations are discussed in terms of the ring current shielding.

## Experimental

*p*-Chlorostyrene was prepared by the procedure described in "Organic Syntheses".[6] Samples of poly(*p*-chlorostyrene) were obtained by polymerization of 10 ml of monomer in 50 ml of carbon tetrachloride for 5 h at 80 °C, using $\alpha,\alpha'$-azobisisobutyronitrile as an initiator. To obtain polymer samples of various molecular weights, the amount of the initiator was changed over the range from 0.5 g to 3 g. The polymers were precipitated in about 10 volumes of methanol in order to free them from any residual monomer and initiator, and were dried *in vacuo*. The number-average molecular weights of these polymers were determined using "KUNAUAR's Vapor Pressure Osmometer" in chloroform solution at 37 °C. The average degrees of polymerization of polymer samples were 14.8, 24.0, and 46.4 (they are denoted as 15-, 24-, and 46-polymer).

Polymer solutions for PMR spectral measurements were prepared by dissolving 0.1 g of the polymer in 1.0 ml carbon tetrachloride (spectral grade). Tetramethylsilane was added to each solution as an internal reference. The polymer solutions were transferred to 5 mm o.d. NMR tubes, which were sealed after the atmosphere was replaced with nitrogen gas. The PMR spectra of each polymer were observed over the range from 5 °C to 88 °C. These spectra were measured using a Japan Electric Optics Laboratory "JNM PS-100 Spectrometer" operated at 100 MHz.

## Results and Discussion

*Temperature Dependence of Chemical Shift.* Figure 1 shows the PMR spectra of the phenyl protons of 24-polymer in carbon tetrachloride at 5 and 70 °C. The peaks at 2.95 $\tau$ and 3.59 $\tau$ are assigned to *meta* protons (*m*-H) and *ortho* protons (*o*-H) respectively. Figure 2 shows the spectra of aliphatic protons at various temperatures. The weak absorption near 7 $\tau$ corresponds

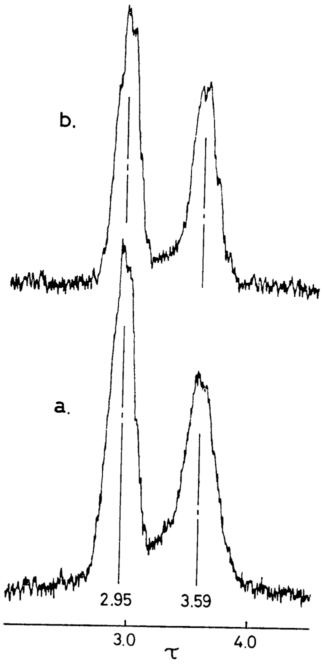

Fig. 1. PMR spectra of phenyl protons of poly(*p*-chlorostyrene) in carbon tetrachloride(0.1 g/ml). (a) 5 °C, (b) 70 °C.

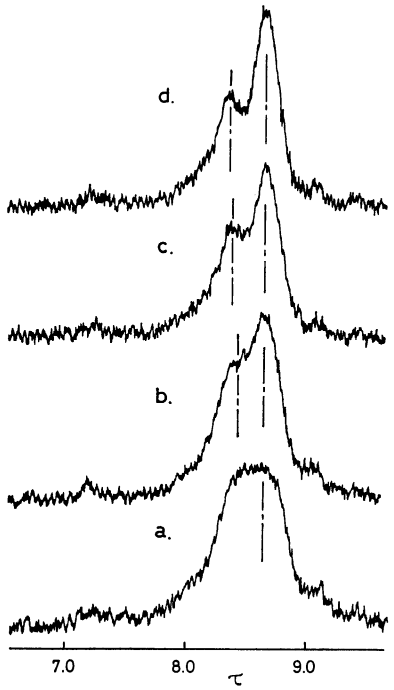

Fig. 2. PMR spectra of aliphatic protons of poly-($p$-chlorostyrene) in carbon tetrachloride(0.1 g/ml). (a) 5 °C, (b) 30 °C, (c) 50 °C, (d) 70 °C.

to the protons in terminal monomer units. The absorptions of the methyne proton (CH) and the methylene proton($CH_2$) in nonterminal monomer units appear at about 8—9 $\tau$. Figures 1 and 2 show that the peaks of the absorption of $o$-H, $m$-H, and $CH_2$ do not move, while that of CH moves to lower field as the temperature is raised.

The movement of peaks suggests a change of conformations. Indeed, chemical shifts are often influenced by conformations: for a change of conformations causes a change of environment at the position of the resonating proton, while the environment is governed by the effects of magnetic anisotropy or of electric field, *etc.* For poly($p$-chlorostyrene), the effect of magnetic anisotropy is the most important factor. The magnetic anisotropy of the phenyl ring is significantly larger than that of the carbon–carbon (C–C) or carbon–chlorine (C–Cl) bond ($\chi_{//}-\chi_{\perp}$ : $3.3\times10^{-6}$ cm$^3$ mol$^{-1}$ for C–C,[7] $3\times10^{-7}$ cm$^3$ mol$^{-1}$ for C–Cl[8] bond). Therefore, in this case, the changes of chemical shift caused by the conformational changes should be mainly governed by the effect of magnetic anisotropy (ring current effect) of the phenyl rings.

The extent of ring current shielding produced at the positions of $CH_2$, CH, $o$-H, and $m$-H was calculated for preferred conformations. The effects from the phenyl rings on either side of these protons were taken into account in this calculation. Phenyl-ring planes are assumed to be perpendicular to the plane defined by adjoining skeletal bonds. This assumption seems to be reasonable, as reported by Abe *et al.*[9,10] The ring current shieldings were estimated by the following equation:[11]

$$\Delta\sigma = \frac{\chi_{//}-\chi_{\perp}}{3R^3}(1-3\cos^2\theta)$$

where $\chi_{//}-\chi_{\perp}$ is the anisotropy of the magnetic susceptibility, $R$ is the distance of the resonating proton from the center of the phenyl ring, and $\theta$ is the angular displacement from the symmetry axis. The bond length and bond angle are shown in Fig. 3. The value of $\chi_{//}-\chi_{\perp}$ for a $p$-chlorophenyl group would be somewhat different from the value for benzene. However, only a qualitative estimation is required in the present case: we used $-59.7\times10^{-6}$ cm$^3$ mol$^{-1}$ [12] (benzene) as the value of $\chi_{//}-\chi_{\perp}$ for the $p$-chlorophenyl ring.

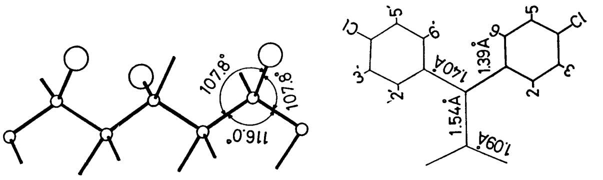

Fig. 3. Conformation and projection along the longitudinal axis of all-*trans* hypothetical syndiotactic poly($p$-chlorostyrene).

TABLE 1. COMFORMATIONS AND RING CURRENT SHIELDING (ppm unit)

| Chain conform. | | $\Delta E$[a] | $CH_2$ | CH | $o$-H | $m$-H |
|---|---|---|---|---|---|---|
| Meso | TG | | −0.58 | | | |
| | GT | | −0.67 | | | |
| Racemic | TT | 0 | −0.67 | | | |
| | GG | 1.66 | −0.38 | | | |
| Iso | TGTG | 0 | | 0.50 | 0.04 | 0.03 |
| | GTGT | | | 0.87 | 0.30 | −0.07 |
| | GTTG | 1.06 | | 0.48 | −0.23 | −0.16 |
| Hetero | TTTG | 0 | | 1.45 | 0.33 | −0.08 |
| | TTGT | 0.23 | | 1.47 | 0.60 | 0.11 |
| | GGTG | 1.54 | | 0.43 | −0.17 | −0.05 |
| Syndio | TTTT | 0 | | 1.45 | 0.33 | −0.08 |
| | GGTT | 1.10 | | 0.58 | 0.51 | 0.09 |
| | TTGG | | | 0.43 | −0.17 | −0.05 |

a) Conformational energies (kcal/mol): Ref. 17.

The calculated results are given in Table 1, where the minus and plus signs represent paramagnetic and diamagnetic shielding, respectively. The results obtained from Table 1 follow: (a) Methylene protons experience approximately constant paramagnetic shelding, and *meta* protons experience only small paramagnetic shielding. (b) *Ortho* protons experience and indefinite amount of shielding, and the correlation to conformations is found to be irregular. (c) A methyne proton experiences diamagnetic shielding in any conformation, and the shielding was remarkably effective in the stable conformations in syndiotactic and heterotactic sequences (TTTT, GTTT, and TGTT).

Evidently, polymer chains occupy more stable conformations at low temperatures, and the rise of the temperature enables polymer chains to occupy conformations of higher energy. Table 1 demonstrates that such changes in conformations reduced the diamagnetic shielding produced at the position of CH in syndiotactic and heterotactic sequences, and cause the downfield shift of the peak of the methyne proton. Polystyrene or ring-substituted polystyrene by radical polymerization is known from NMR studies[13-15] to be syndiorich. Therefore, the spectra of samples examined in this investigation should also reflect the characteristics of the ring current effect in syndiotactic and heterotactic sequences.

On the basis of a comparison of the observed results with the calculated ones, the following reasonable conclusions are drawn: (a) When the temperature is elevated, the fractions of the stable conformations (TTTT, GTTT, and TGTT) decrease. That decrease results in the decrease of diamagnetic shelding at the position of CH; consequently, the peak of CH moves to lower field. (b) The shielding produced at the positions of $CH_2$, *o*-H, and *m*-H is less sensitive to conformations, and the peaks of these protons do not move, even though the temperature is elevated and the fractions of stable conformations decrease.

*Temperature Dependence of Half Height Width.* Table 2 represents half height widths ($\Delta H_{1/2}$) for the absorptions of *o*-H and *m*-H of 24-polymer at various temperatures.

TABLE 2. HALF HEIGHT WIDTHS OF PMR PEAKS OF PHENYL PROTONS

| Temp (°C) | | 5 | 20 | 30 | 40 |
|---|---|---|---|---|---|
| $\Delta H_{1/2}$ (Hz) | *o*-H | 31.3 | 29.3 | 28.3 | 27.3 |
| | *m*-H | 23.7 | 22.5 | 22.5 | 21.8 |
| **Temp (°C)** | | **50** | **60** | **70** | **88** |
| $\Delta H_{1/2}$ (Hz) | *o*-H | 25.3 | 25.3 | 24.8 | 25.3 |
| | *m*-H | 21.5 | 21.3 | 20.5 | 20.0 |

The temperature dependence of the $\Delta H_{1/2}$ is shown in Fig. 4, together with those of 15- and 46-polymer. The $\Delta H_{1/2}$ for *o*-H absorption is apparently large at low temperatures, and decreases sharply up to 50 °C, and then decreases gradually with further rise in temperature. The abrupt small decrease between 40 °C and 50 °C may reflect an increase of the tortional oscillation of nonrotating phenyl rings, as Liu *et al.*[16] pointed out in the study of polystyrene. The $\Delta H_{1/2}$ for *m*-H absorption is small at low temperatures, and decreases gradually with the rise of temperature.

In general, the widths of spectra of polymers are caused by unresolved spin-spin splitting and by the time dependence of magnetic dipole interaction. However, this strong broadening observed only in *o*-H absorption at low temperatures cannot be interpreted in terms of these factors.

Table 3 represents the differences ($\Delta\sigma'$) of the ring current shielding on ortho protons and on meta protons: $\Delta\sigma' = |\Delta\sigma(H_2) - \Delta\sigma(H_6)|$ or $|\Delta\sigma(H_3) - \Delta\sigma(H_5)|$. The differences indicate the degree of difference in the chemical shifts of *ortho* protons or *meta* protons. The $\Delta\sigma'$ for *o*-H is great in any conformation, and it is particularly great at stable conformations (TTTT in syndiotactic, GTTT and TGTT in heterotactic sequence). On the other hand, the $\Delta\sigma'$ for *m*-H is relatively small in any conformation, and is less sensitive to conformations. The $\Delta\sigma'$ for *o*-H indicates that the *o*-H spectra consist of two absorptions (absorptions of $H_2$ and $H_6$) with different chemical shifts as the chains occupy the stable conformations.

TABLE 3. CONFORMATIONS AND DIFFERENCES ($\Delta\sigma'$) OF RING CURRENT SHIELDING (ppm unit)

| Chain conform | | $\Delta\sigma'$ | |
|---|---|---|---|
| | | $\lvert\Delta\sigma_{H_2} - \Delta\sigma_{H_6}\rvert$ | $\lvert\Delta\sigma_{H_3} - \Delta\sigma_{H_5}\rvert$ |
| Iso | TGTG | 0.18 | 0.01 |
| | GTGT | 0.81 | 0.08 |
| | GTTG | 0.46 | 0.12 |
| Betero | TTTG | 1.03 | 0.03 |
| | TTGT | 1.30 | 0.16 |
| | GGTG | 0.11 | 0.24 |
| Syndio | TTTT | 1.03 | 0.03 |
| | GGTT | 0.78 | 0.04 |
| | TTGG | 0.11 | 0.24 |

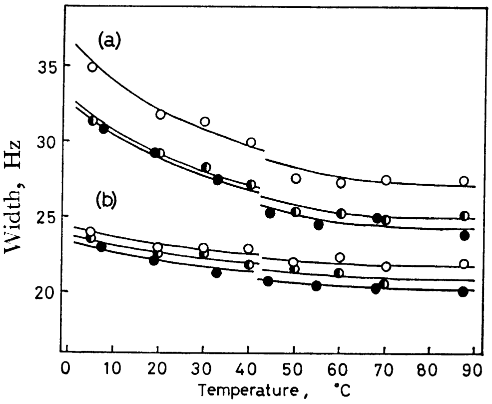

Fig. 4. Half height widths of Peaks of *ortho* protons(a) and *meta* protons(b) as a function of temperature. ○: 15-Polymer, ◐: 24-polymer, ●: 46-polymer.

From the above considerations, some interpretations for the temperature dependence of the width for phenyl absorptions can be drawn: (a) The polymer chains occupy stable conformations (TTTT, GTTT, and TGTT) at low temperatures; in these conformations the proton ($H_2$) has a different chemical shift from that of the proton ($H_6$). The overlap of the absorptions of $H_2$ and $H_6$ results in a broader absorption. (b) When the temperature is raised, the fractions of these conformations decrease, and the line widths decrease steeply. (c) The difference in the chemical shifts of *m*-H in any conformation is small, and such strong broadening as appeared in *o*-H is not observed.

These interpretations for the temperature dependence of the width are compatible with the conclusions drawn from the temperature dependence of chemical shifts.

*Line Width and Molecular Weight.* Figure 4 shows $\Delta H_{1/2}$ for phenyl absorptions of 15-, 24-, and 46-polymer as a function of temperature. The molecular weight dependence of $\Delta H_{1/2}$ for *m*-H absorption is small. While the $\Delta H_{1/2}$ values for *o*-H absorption of 24-polymer are similar to those of 46-polymer, those of 15-polymer are considerably different from those of 24- and 46-polymer and are anomalously large (the anomalous broadening was also observed in spectra of a polymer of lower molecular weight, $\overline{DP}$ : 9.9). This phenomenon is contrary to the well-known fact that line widths of spectra of polymers generally increase with the increase of molecular weights.

If the molecular weight distribution of 15-polymer sample is assumed to be broader than those of other samples, the sample would give a broader absorption. As shown in the absorption of aliphatic protons, if the chemical shift of phenyl protons in terminal monomer units differs from that of nonterminal monomer units and if these absorptions overlap, then the absorption of aromatic protons may become broad. This effect would be effective in the sample of low molecular weight (15-polymer). However, the anomalous broadening cannot be attributed to such effects as described above, because the anomalous broadening is observed only in *o*-H absorption and is not observed in *m*-H absorption.

As described in preceding sections, the ring current effect played an important role in understanding the PMR spectra of poly(*p*-chlorostyrene). The anomalous broadening observed in 15-polymer may also be related to the shielding effect. The temperature dependence of the chemical shift and the half height width was interpreted in terms of the preferred conformations listed in Table 1. The molecular weight dependence of the widths (the anomalous broadening) cannot be interpreted in terms of these conformations. The conformations listed in Table 1 are preferred conformations for polymers of low or high molecular weight; however, short chains could also occupy other conformations than these. For example, in shoft chains side groups are able to escape from each other, whereas in long chains such conformations are limited by steric restrictions. Since shielding is a function of conformations, the conformations which are permissible only in short chains ("permissible conformation"), produce somewhat different shielding from the shielding for the conformations listed in Table 1, and the existence of the permissible conformations must result in a broadening of spectra. As described in the preceding section, the ring current effect is effective for *o*-H and almost without effect for *m*-H; therefore, the broadening should be observed in the absorption of *o*-H.

On the basis of the above considerations, we can draw some reasonable interpretations for the PMR spectra of 15-, 24-, and 46-polymer. (a) The 15-polymer can occupy some conformations which are not permissible in polymers of higher molecular weight, and its *o*-H absorption shows the anomalous broadening owing to the absorptions arising from the so-called "permissible conformations"; the anomalous broadening can be interpreted only by the assumption of such conformations. (b) On the other hand, in the cases of 24- and 46-polymer, the conformations of the chains are just about limited to those listed in Table 1, and the anomalous broadening is not observed in the spectra of these polymers. The limitation of conformations in polymer chains might correspond to the phenomena called the "polymeric effect" cited at the beginning of this paper.

The assumption of permissible conformations does not disturb the interpretations for the temperature dependence of chemical shifts and half height widths given in preceding sections.

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