

Preparation of ^{13}C -Poly(*p*-phenylene). IR, ^{13}C -NMR, and ESR Spectra of the Polymer

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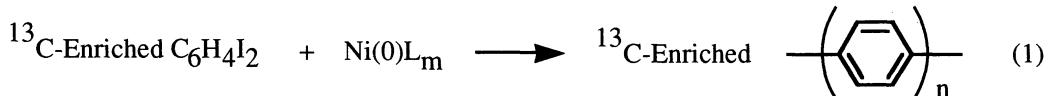
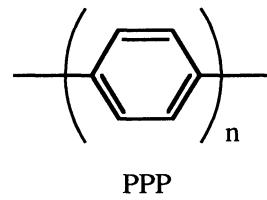
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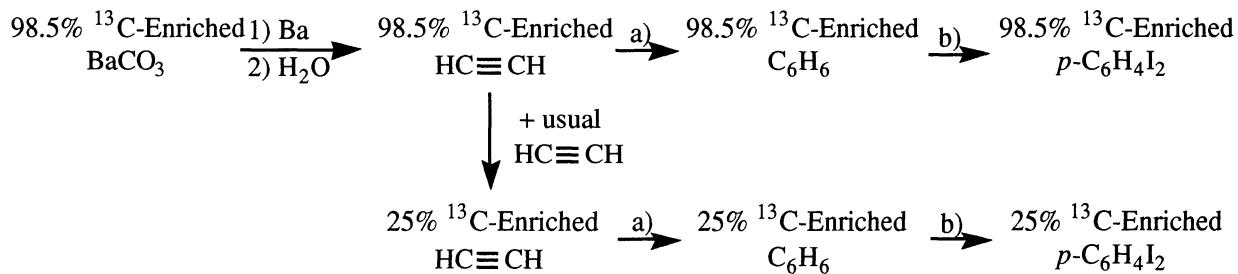
^{13}C -Enriched poly(*p*-phenylene) PPP prepared by dehalogenation polycondensation of ^{13}C -enriched *p*-diiodobenzene with Ni(0) complex gives basic data for assignment of the IR vibration modes of PPP, reveals the magnitude of magnetic dipole interaction in the NMR spectrum, and indicates considerably small coupling of spin with ^{13}C -nuclei in the ESR spectrum presumably due to rapid movement of electrons.

Preparation of electrically conducting π -conjugated polymers and revealing their chemical and physical properties are subjects of recent interest. Among the π -conjugated polymers, poly(*p*-phenylene) PPP has a simple and rigidly linear structure and attracted attentions of many research groups.¹⁾ We have prepared ^{13}C -enriched PPP for further understanding of the properties of PPP and now report IR, ^{13}C -NMR, and ESR data of the ^{13}C -enriched PPP.

The ^{13}C -enriched PPP was synthesized by dehalogenation polycondensation of ^{13}C -enriched *p*-diiodobenzene $p\text{-C}_6\text{H}_4\text{I}_2$ with zero-valent nickel complex (a mixture of bis(1, 5-cyclooctadiene)nickel $\text{Ni}(\text{cod})_2$ and 2, 2'-bipyridine bpy).²⁾



The monomer with 25% or 98.5% enrichment was prepared according to the following procedure.



a) Treated on Cr/Al₂O₃ catalyst.³⁾
 b) Treated with I₂ in the presence of Tl(OCOCF₃)₃.⁴⁾

Figure 1 shows comparison of IR spectra of non-enriched PPP and 98.5% enriched PPP, and Table 1 summarizes the data.

Table 1. IR data of PPP and 98.5% ¹³C-enriched PPP

PPP	¹³ C-Enriched PPP	
ν_1 / cm ⁻¹	ν_2 / cm ⁻¹	ν_1 / ν_2
1908	1886	1.012
1596	1543	1.034
1479	1449	1.021
1398	1361	1.027
999	964	1.036
811	799	1.015
763	749	1.019
692	676	1.024

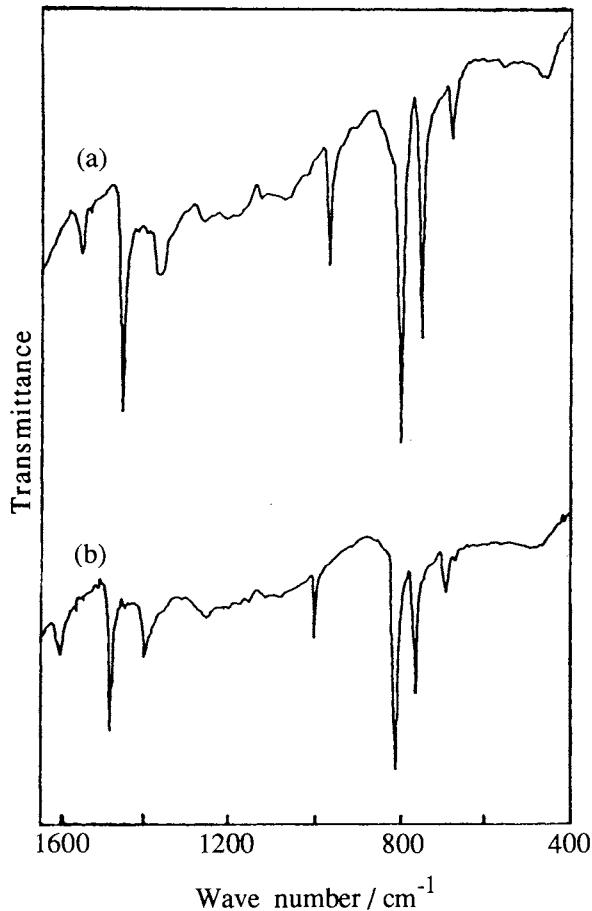


Fig. 1. IR spectra of (a) 98.5% ¹³C-enriched PPP and (b) PPP.

The absorption bands of PPP observed at 1596 and 1479 cm⁻¹ are considered to be mainly related to ring deformation of the phenylene ring.⁵⁾ However, as shown in Table 1, the observed ν_1 / ν_2 ratios for the absorption bands are considerably smaller than the value calculated by assuming simple mass effect for a C-C vibration suggesting participation of hydrogen in their normal vibrations; the calculated ν_1 / ν_2 value = $\sqrt{13/12} = 1.041$. Similar smaller ν_1 / ν_2 values (1.008-1.020) for the ring deformation vibrations were also observed for the monomer $p\text{-C}_6\text{H}_4\text{I}_2$.

Figure 2 shows CP/MAS ^{13}C -NMR spectra of PPP, 25% enriched PPP, and 98.5% enriched PPP. The half width of both α - and β -carbons of PPP becomes larger with increase in the extent of the ^{13}C -enrichment presumably due to magnetic dipole interactions between ^{13}C -nuclei; the half width of the β -carbon signals of PPP, 25% enriched PPP, and 98.5% enriched PPP are 160 Hz, 330 Hz, and 675 Hz, respectively.

Figure 3 shows ESR spectra of PPP, Na-doped PPP, 98.5% enriched PPP and Na-doped 98.5% enriched PPP. The doping was carried out with excess sodium naphthalide in THF.⁶⁾ The spin concentration increases markedly on the Na- doping.⁶⁾

As shown in Fig. 3, the ESR signals are relatively sharp probably due to rapid movement of electrons in the polymer chain and/or between the polymer chains.⁷⁾ The increase in the line width of the signal (peak-to-peak width ΔH_{pp} in Fig. 3) due to the ^{13}C -enrichment ($\Delta\Delta H_{pp} = 0.27$ mT and 0.13 mT for the undoped and Na-doped samples, respectively) is considerably small (less than about half) compared with the reported ^{13}C -hyperfine coupling constants.⁸⁾ This indicates that the coupling of electron spin with ^{13}C -nuclei is also affected by the assumed rapid movement of electrons along the polymer chain or between the polymer chains.

All the above described data reveal interesting effects of the ^{13}C -enrichment on the IR, NMR and ESR spectra, and further detailed analysis of the effect is expected to provide bases for understanding chemical and physical properties of PPP.

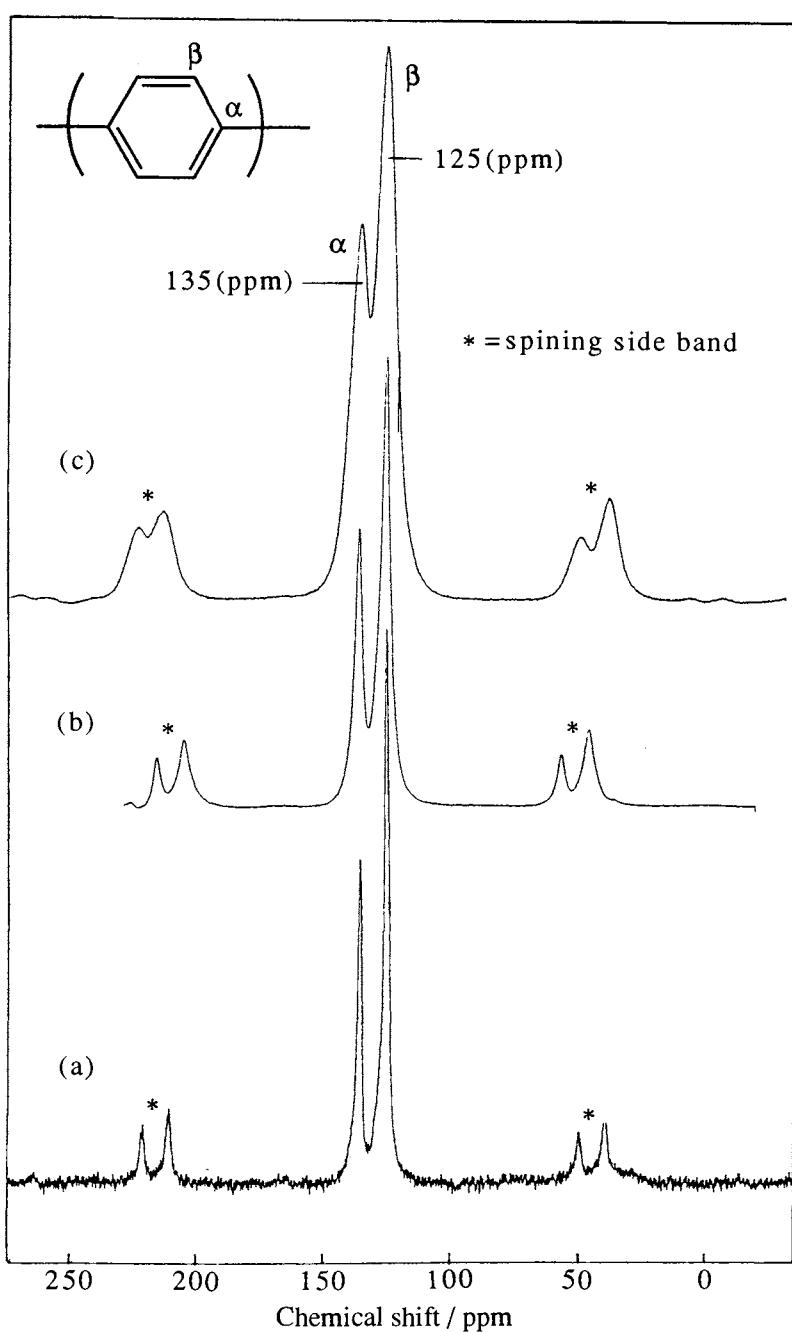


Fig. 2. CP/MAS ^{13}C -NMR spectra of (a) PPP, (b) 25% enriched PPP, and (c) 98.5% enriched PPP.

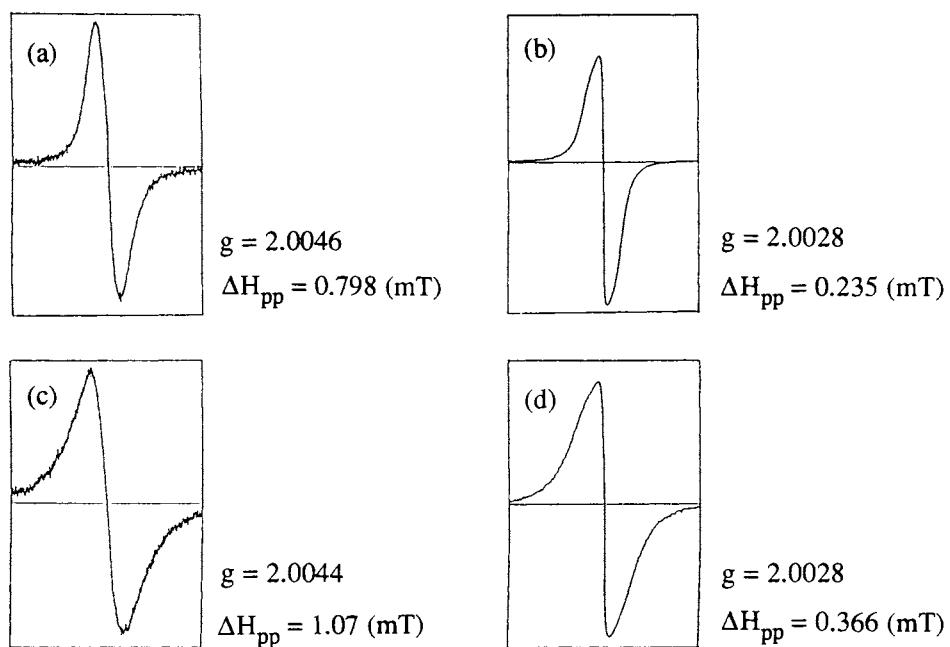


Fig. 3. ESR spectra of (a) PPP, (b) Na-doped PPP, (c) 98.5% enriched PPP, and (d) Na-doped 98.5% enriched PPP.

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References

- 1) R. L. Elsenbaumer and L. W. Shacklette, "Handbook of Conductive Polymers," ed by T. A. Skotheim, Marcel Dekker, New York (1986), Vol. 1, p. 213.
- 2) T. Yamamoto, A. Morita, Y. Miyazaki, T. Maruyama, H. Wakayama, Z. -H. Zhou, Y. Nakamura, T. Kanbara, S. Sasaki, and K. Kubota, *Macromolecules*, **25**, 1214 (1992).
- 3) F. Pietig and H. W. Scharpenseel, *Proc. Int. Conf. Methods Prep. Stor. Label. Compounds*, **2**, 57 (1966).
- 4) A. McKillop, J. S. Fowler, M. J. Zelesko, and J. D. Hunt, *Tetrahedron Lett.*, **29**, 2423 (1969); N. Ishikawa and A. Sekiya, *Bull. Chem. Soc. Jpn.*, **47**, 1680 (1974).
- 5) R. M. Silverstein, C. G. Bassler, and T. C. Morrill, "Spectroscopic Identification of Organic Compounds," 3rd ed, John Wiley, New York (1974), p. 90.
- 6) Similar doping of PPP with sodium and potassium naphthalide has been reported : L. W. Shacklette, R. R. Chance, D. M. Ivory, G. G. Miller, and R. H. Baughman, *Synth. Metals*, **1**, 307 (1979) ; E. E. Havinga and L. W. Van Horssen, *ibid.*, **16**, 55 (1986). Peak height of the ESR signals in Fig. 3a and Fig. 3c is comparable to that of MnO used as the reference (peak height ratio = ca. 2 : 1). On the other hand, peak height of ESR signals in Fig. 3b and Fig. 3d is much larger than that of MnO (the ratio between the two signals > 80).
- 7) P. Bernier, "Handbook of Conductive Polymers," ed by T. A. Skotheim, Marcel Dekker, New York (1986), Vol. 2, p. 1099
- 8) M. Karplus and G. K. Frankel, *J. Chem. Phys.*, **35**, 1312 (1961); E. De Boer, *ibid.*, **25**, 190 (1956).

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