Polymerization of an Acetylene Derivative Containing Tetraphenylporphyrin in Its Side Chain: 5-(4-Ethynylphenyl)-10,15,20-triphenylporphyrin

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With the aim of the preparation of a magnetically interacting polymer, we have prepared several types of polymers containing paramagnetic metalloporphyrins in their side chains[1−6] and investigated their magnetic behavior by measurements of magnetic susceptibility and by ESR spectroscopy.[7−9] Conjugated polymers containing paramagnetic species in their side chains have been given much attention as new magnetic materials.[10−12]

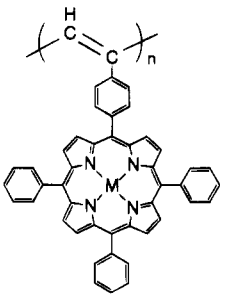
In the extension of our study, if conjugated polymers containing paramagnetic metalloporphyrins are prepared, magnetic interaction of the polymer might be enhanced owing to the π-electron on the unsaturated main chain. To our knowledge, however, no paper has been published so far on the preparation of polyenes containing metalloporphyrins in their side chains. Accordingly, we tried to prepare such polymers by the polymerization of acetylene derivatives.

In this paper, polymerizations of 5-(4-ethynylphenyl)-10,15,20-triphenylporphyrin (ETPP) and its silver(II) complex are described. Although monomers have bulky substituents, polymerization occurred and formation of polymer was confirmed spectroscopically.

Synthesis of ETPP was carried out as follows.[13] (4-Formylphenyl)acetylene[14] (316 mg, 2.4 mmol), benzaldehyde (790 mg, 7.5 mmol), and pyrrole (6.6 mg, 9.8 mmol) were stirred in distilled CH_2Cl_2 under argon in the presence of anhydrous trifluoroacetic acid (1.17 mg, 10.2 mmol, 10^{-2} M), and the reaction vessel was covered with aluminum foil to be shielded from ambient light. Then, crude porphyrinogens obtained as intermediate were oxidized by addition of *p*-chloranil (1.92 g, 7.8 mmol, 3 equiv per porphyrinogen). The products were purified by repeating column chromatography on an alumina column using CH_2Cl_2 as an eluent. The second band was collected and concentrated to afford a crude product, which was purified by recrystallization from THF−methanol to yield 92.0 mg of ETPP (6% yield overall). Anal. Calcd for $C_{46}H_{30}N_4$: C, 86.50; H, 4.73; N, 8.77. Found: C, 86.20; H, 4.60; N, 8.75. FAB-MS. Calcd: [M] = 638. Found: $[MH]^+$ = 639.[15] After successive purification, bis-, tris-, and tetrakisethynyl-substituted compounds are completely removed. The silver(II) complex of ETPP (ETPP-Ag^{II}) was synthesized under reflux with silver(I) acetate in acetic acid. Crude products were purified on column chromatography. Recrystallization from $CHCl_3$−methanol gave a dark red powder in 16% yield. Anal. Calcd for $C_{46}H_{28}N_4Ag$: C, 74.20; H, 3.79; N, 7.52. Found: C, 73.86; H, 3.68; N, 7.55. FAB-MS: Calcd: [M(Ag = 109)] = 745. Found: $[M]^+$ = 745.1.

A homopolymerization of ETPP (Chart 1) was carried out in $CHCl_3$ or THF using a commercially available (bicyclo[2,2,1]hepta-2,5-diene)rhodium(I) dimer (norbornadienerhodium(I) dimer, $[Rh(NBD)Cl]_2$) (Fluka) as

Chart 1



poly ETPP (M = 2H or Ag)

catalyst.[16] Monomer concentrations were restricted by low solubility of the monomer. ETPP (83.0 mg, 0.130 mmol) was dissolved in solvent (THF or chloroform, 1.0 mL) and stirred at 30 °C. $[Rh(NBD)Cl]_2$ (8.8 mg, 0.019 mmol) and triethylamine (196.0 mg, 1.90 mmol, 100 equiv) were dissolved in chloroform (0.46 mL) under argon, and then the solution was maintained at 30 °C for 30 min. After that, the catalyst solution was added to the above solution via a syringe at once, and then precipitates immediately formed. A small amount of THF-soluble and a large amount of THF-insoluble polymers were obtained. The crude THF-soluble polymers were purified by reprecipitation from THF−acetone several times. The THF-insoluble polymers were washed with THF several times and dried *in vacuo*. Both THF-soluble and -insoluble poly(ETPP)s were deep purple solids. The total yield was 81 mg (97%). Anal. Calcd for $(C_{46}H_{30}N_4(H_2O)_{0.5})_n$: C, 85.29; H, 4.82; N, 8.65. Found: C, 85.07; H, 4.74; N, 8.52. Molecular weights of THF-soluble polymer were roughly estimated by GPC on the basis of standard polystyrene. The elution diagram of GPC of the soluble part of this polymer showed a unimodal pattern. The results of the polymerization of ETPP are summarized in Table 1. Since the IR spectrum and elemental analysis of the THF-soluble polymer are the same as those of the THF-insoluble polymer, the difference in the solubility in THF between these polymers is possibly due to that in the degree of polymerization. In spite of the bulky side group, the C≡C triple bond in ETPP was polymerized to a high molecular weight polymer. Poly(ETPP) was allowed to be soluble in part in chloroform, CH_2Cl_2, benzene, toluene, DMF, THF, and benzonitrile and insoluble in hexane, acetone, ethanol, methanol, diethyl ether, and water.

The IR band of the monomer at 2110 cm^{-1} assignable to the stretching vibration mode of the C≡C triple bond disappeared on a polymerization. Absorption bands characteristic of the porphyrin ring remained unchanged after the polymerization. This finding indicated that the polymerization occurred through the C≡C triple bond of the ethynyl group. IR-absorption bands due to conjugated C=C double bonds of the main chain were not clearly distinguished, because these overlapped on absorption due to the tetraphenylporphyrin ring.

In Raman spectroscopy, deformation of the C≡C triple bond of ETPP was observed at 322 cm^{-1}. After polymerization, the deformation band disappeared and other bands did not changed. In ^{13}C NMR spectroscopy, ^{13}C NMR signals due to the C≡C triple bond were observed at 83.7 and 78.3 ppm in the spectrum of ETPP in $CDCl_3$. These signals obviously disappeared in the spectrum of poly(ETPP). These results also support the polymerization through the C≡C triple bond.

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Table 1. Results of Polymerization of ETPP[a]

[ETPP], mM	[Initiator], mM	solvent	conv, %	THF-insoluble part, %	THF-soluble part, %	THF-soluble polymer $\bar{M}_w$[b]	THF-soluble polymer $\bar{M}_w/\bar{M}_n$[b]
200	2	$CHCl_3$	98	97	1.0	3.0×10^4	2.5
200	2	THF	85	78	7.2	4.9×10^4	2.1
10	1	THF	96	61	29	2.5×10^3	1.2
5	1	THF	95	55	36	2.3×10^3	1.1
2	1	THF	95	trace	89	1.8×10^3	1.1

[a] [Triethylamine]/[Rh complex] = 100, 1 h, at 30 °C. [b] GPC (calibrated by a standard polystyrene).

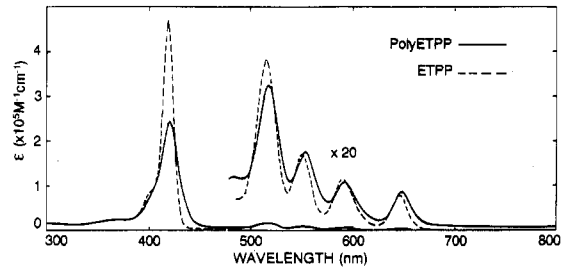

Figure 1. Absorption spectra of ETPP (- - -) and poly(ETPP) (—) in THF.

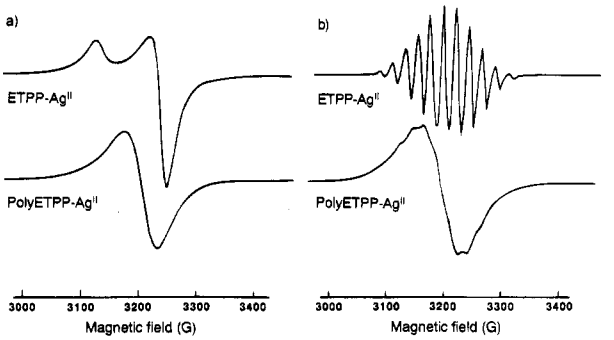

Figure 2. ESR spectra of ETPP-Ag^{II} (upper) and poly(ETPP)-Ag^{II} (lower): (a) in the solid state and (b) in a toluene solution (2 mM) at 20 °C.

Visible spectra of ETPP and poly(ETPP) are shown in Figure 1. ETPP has a Soret band at 420 nm and Q bands at 510, 550, 590, and 650 nm. The spectrum of ETPP is similar to that of TPP, indicating that the presence of the ethynyl group has little influence on the absorption of the porphyrin ring. Poly(ETPP) exhibits a Soret band at 420 nm, with the Q bands at 510, 550, 590, and 650 nm. Close examination of these spectra shows that the Soret band of poly(ETPP) is weaker and broader than that of ETPP, indicating that the molecular extinction coefficient markedly decreases in the polymer. The molecular extinction coefficients of all the Q bands of poly(ETPP) are almost comparable to those of the monomer. These results indicated that the hypochromism due to some electronic interactions occurred among porphyrin moieties in the polymer. Similar phenomena have been observed for porphyrin dimers in organic solvents and explained in terms of an exciton coupling model due to the close approach of the two porphyrin rings.[17] The differences in the spectra between poly(ETPP) and ETPP suggest that the TPP moieties bound to this polymer are forced to interact due to their proximity. Although absorption bands due to the conjugated main chains of poly(ETPP) are expected to be observed in the range of 250–400 nm,[18,19] the bands could not be distinguished from absorption bands due to the tetraphenylporphyrin ring. This finding indicates that the conjugation in the main chain of poly(ETPP) is small as compared to that of unsubstituted polyacetylenes.[19] This is reasonably ascribable to the bulkiness of the porphyrin ring.

The Ag^{II} complex of poly(ETPP) (poly(ETPP)-Ag^{II}) was also prepared by polymerization of the Ag^{II} complex of ETPP (ETPP-Ag^{II}) with a rhodium catalyst. A large amount of THF-insoluble polymer (ca. 80% in yield) and a small amount of THF-soluble polymer (ca. 20% in yield) were obtained. Anal. Calcd for $(C_{46}H_{28}N_4Ag \cdot CHCl_3)_n$: C, 74.20; H, 3.79; N, 7.52. Found: C, 73.86; H, 3.68; N, 7.55. The $\bar{M}_w$ of the soluble part was up to $\sim 10^5$ (by GPC, calibrated by a standard polystyrene). The feature of the absorption spectra of ETPP-Ag^{II} and poly(ETPP)-Ag^{II} was similar to that of these metal-free compounds. ESR spectra of ETPP-Ag^{II} and poly(ETPP)-Ag^{II} are shown in Figure 2. Measurements were carried out both in the solid and in the solution state. In the powder state, the spectrum of ETPP-Ag^{II} showed a typical anisotropic pattern, while that of the polymer showed an isotropic signal, indicating that an exchange interaction was caused among TPP-Ag^{II} moieties. Similar phenomena were also observed between the solution spectra of ETPP-Ag^{II} and poly(ETPP)-Ag^{II}. The ESR spectrum of ETPP-Ag^{II} in toluene split 11 lines due to four nitrogen nuclear spin ($I = 1$, $A_N = 22$ G) and one Ag nuclear spin ($I = 1/2$, $A_{Ag} = 44$ G), while in the toluene solution of poly(ETPP)-Ag^{II}, each split signal is broadened by electron exchange. The poly(ETPP)-Ag^{II} is likely to be expected as a magnetic material because of the presence of an exchange interaction.

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References and Notes

(1) Kamachi, M.; Akimoto, H.; Mori, W.; Kishita, M. *Polym. J.* **1984**, *16*, 23.
(2) Nozakura, S.; Kamachi, M. *Makromol. Chem. Suppl.* **1985**, *12*, 255.
(3) Kamachi, M.; Akimoto, H.; Nozakura, S. *J. Polym. Sci., Polym. Lett. Ed.* **1983**, *21*, 693.
(4) Kamachi, M.; Cheng, X. S.; Kida, T.; Kajiwara, A.; Shibasaka, M.; Nagata, S. *Macromolecules* **1987**, *20*, 2665.
(5) Kajiwara, A.; Aramata, K.; Nomura, S.; Morishima, Y.; Kamachi, M. *Chem. Lett.* **1992**, 95.
(6) Kajiwara, A.; Aramata, K.; Kamachi, M.; Sumi, K. *Polym. J.* **1994**, *26*, 215.
(7) Kamachi, M.; Shibasaka, M.; Kajiwara, A.; Mori, W.; Kishita, M. *Bull. Chem. Soc. Jpn.* **1989**, *62*, 2465.
(8) Kamachi, M.; Cheng, X. S.; Aota, H.; Mori, W.; Kishita, M. *Chem. Lett.* **1987**, 2231.
(9) Kamachi, M.; Cheng, X. S.; Nozakura, S. Preprints of the Fifth Rare Earth Symposium, Tokyo, Japan, 1987, 2B05.
(10) (a) Nishide, H.; Kaneko, T.; Yoshioka, N.; Akiyama, H.; Igarashi, M.; Tsuchida, E. *Macromolecules* **1993**, *26*, 4567. (b) Nishide, H.; Yoshioka, N.; Saitoh, Y.; Gotoh, R.; Miyakawa, T.; Tsuchida, E. *J. Macromol. Sci., Pure Appl. Chem.* **1992**, *A29*, 775. (c) Yoshioka, N.; Nishide, H.; Kaneko, T.; Yoshiki, H.; Tsuchida, E. *Macromolecules* **1992**, *25*, 3838.
(11) Fujii, A.; Ishida, T.; Koga, N.; Iwamura, H. *Macromolecules* **1992**, *25*, 1077.

(12) (a) Miura, Y.; Ushitani, Y.; Inui, K.; Teki, Y.; Takui, T.; Itoh, K. *Macromolecules* **1993**, *26*, 3698. (b) Miure, Y.; Matsumoto, M.; Ushitani, Y. *Macromolecules* **1993**, *26*, 2628. (c) Miura, Y.; Inui, K.; Yamaguchi, F.; Inoue, M.; Teki, Y.; Takui, T.; Ito, K. *J. Polym. Sci., Polym. Chem. Ed.* **1992**, *30*, 959.

(13) Formation of a porphyrin ring was carried out according to the procedure of the following paper: Linsey, J. S.; Schreiman, I. C.; Hsu, H. C.; Kearney, P. C.; Marguerettaz, A. M. *J. Org. Chem.* **1987**, *52*, 827.

(14) Kamitori, Y.; Hojo, M.; Masuda, R.; Yoshida, T. *Tetrahedron Lett.* **1985**, *26*, 4647.

(15) ETPP: mp >300 °C; ^{1}H-NMR ($CDCl_3$) δ 2.77 (s, 2H), 3.30 (s, 1H), 7.71–7.77 (m, 9H), 7.88 (d, 2H), 8.17–8.22 (m, 8H), 8.80–8.86 (m, 8H); IR (KBr) 2110 cm^{-1} (νC≡C).

(16) (a) Tabata, M.; Yang, W.; Yokota, K. *Polym. J.* **1990**, *22*, 1105. (b) Yang, W.; Tabata, M.; Kobayashi, S.; Yokota, K.; Shimizu, S. *Polym. J.* **1991**, *23*, 1135. (c) Tabata, M.; Kumagai, J.; Yokota, K. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1991**, *40*, 1040.

(17) (a) White, I. W. *Porphyrins*; Dolphin, M., Ed.; Academic Press: New York, 1973; Vol. 4, pp 306–325. (b) Goutermann, M.; Holten, D.; Libermann, D. *Chem. Phys.* **1977**, *25*, 139.

(18) Masuda, T.; Higashimura, T. *Adv. Polym. Sci.* **1987**, *81*, 121.

(19) Sondheimer, F.; Ben-Efraim, D. A.; Wolovsky, R. *J. Am. Chem. Soc.* **1961**, *83*, 1675.

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