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New Polymers Containing Pendant Metalloporphyrins. Radical Polymerization of 2-Acryloyloxymethylene-5,10,15,20-tetraphenylporphinatometals

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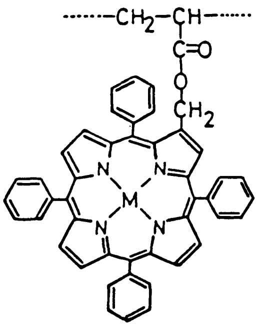
Polyacrylates having tetraphenylporphinatocopper(II) or tetraphenylporphinatovanadyl(II) as their pendant groups have been prepared by the radical polymerization of the corresponding acrylates. The decrease in the molar extinction coefficient of the Soret band and Q-band was observed, and in addition, new absorption band at 638 nm appeared in the visible spectra of the polymers. This shows that porphyrin moieties bound to a polymer chain are probably forced to make some electronic interactions due to their connection with a polyacrylate chain.

Various kinds of polymers containing metalloporphyrins in their side chains have been prepared because of their characteristic photochemical and photophysical properties and in relation to the formation of biologically and biomimetically important substances.[1-3] Since aggregation of porphyrin moieties plays an important role in the photosynthesis, special physicochemical properties seem to be expected in polymers obtained from vinyl monomers containing pendant porphyrins. To our knowledge, no homopolymerization of vinyl compounds containing porphyrin moieties has been reported except for our papers.[4-7] We previously succeeded in the preparation of polymers containing porphyrin and metalloporphyrin moieties by the radical polymerization of acrylates and methacrylates containing tetraphenylporphyrin(TPP) and



polyAOMTPPM M:Cu,VO

Fig.1. Polymer structure.

paramagnetic metallotetraphenylporphyrin in their side chains,$^{4-7)}$ and found that magnetic interaction takes place between paramagnetic species in the polymers containing paramagnetic metalloporphyrins. In the extension of the study of the magnetism, we intended to prepare vinyl polymers in which pendant porphyrin moieties are closer than those in polymers obtained so far. In this paper, we report the radical polymerization of 2-acryloyloxymethylene-5,10,15,20-tetraphenylporphinatoparamagnetic metal ions (AOMTPPM: M=Cu(II) and VO(II)), in which the distance between main chain and porphyrin ring is considered to be closer than those in the polymers reported previously.$^{4-7)}$

2-Formyl-5,10,15,20-tetraphenylporphinatovanadyl(II) (FTPPVO(II)) was prepared using Vilsmeier reaction.$^{8)}$ Yield 60%. Found: C, 76.05; H, 4.05; N, 7.88%. Calcd for $C_{45}H_{28}N_4O_2V$: C, 76.38; H, 3.99; N, 7.92%.

2-Hydroxymethyl-5,10,15,20-tetraphenylporphinatovanadyl(II) (HOMTPPVO(II)) was prepared by the reduction of FTPPVO(II) with sodium borohydride. FTPPVO(II)(6.0 g) was dissolved in 1.0 l of chloroform. Sodium borohydride(2.0 g) suspended in 150 ml of ethanol was added into the chloroform solution with stirring at room temperature. After 10 minutes, the reaction mixture was filtered to remove excess sodium borohydride. The filtrate was washed with water and dried by magnesium sulfate. HOMTPPVO(II) was quantitatively isolated by removal of solvent.

2-Acryloyloxymethylene-5,10,15,20-tetraphenylporphinatovanadyl(II) (AOMTPPVO(II)) was prepared from acryloylchloride and HOMTPPVO(II) by the Schotten-Baumann reaction. Acryloyl chloride(10 ml) was added to a solution of HOMTPPVO(II)(6.0 g) and triethylamine(20 ml) in 300 ml of benzene. After 1 h, the reaction mixture was filtered to remove triethylammonium chloride. Removal of the solvent afforded a crude product which was dissolved in benzene and chromatographed on a silica gel column(20 cm length and 5 cm diameter) using benzene as an eluent. AOMTPPVO(II) was isolated by removal of the solvent from the second fraction, and recrystallized from benzene-hexane. Yield 60%. Found: C, 75.23; H, 4.31; N, 7.30; V, 6.54%. Calcd for $C_{48}H_{32}N_4O_3V$: C, 75.49; H, 4.22; N, 7.34; V ,6.67%.

2-Acryloyloxymethylene-5,10,15,20-tetraphenylporphinatocopper(II) (AOMTPPCu(II)) was prepared by a similar method. Yield 65%. Found: C, 76.11; H, 4.41; N, 7.23; Cu, 8.16%. Calcd for $C_{48}H_{32}N_4O_2Cu$: C, 75.82; H, 4.24; N, 7.37; Cu, 8.36%.

Polymers were prepared as follows: 0.5 g of AOMTPPVO(II) or -Cu(II) and 1.1 mg of 2,2'-azobis(isobutyronitrile)(AIBN) were put into an ampoule, and then dissolved in benzonitrile. The solution was degassed under high vacuum, and polymerization was carried out at 60 °C for 50-100 h. The polymers were isolated by three dissolution-precipitation-separation steps from benzene-acetone. polyAOMTPPVO(II), Found: C, 75.36; H, 4.43; N, 7.07; V, 6.65%. Calcd for $C_{48}H_{32}N_4O_3V$: C, 75.49; H, 4.22; N, 7.34; V, 6.67%. polyAOMTPPCu(II), Found: C, 75.98; H, 4.38; N, 7.10; Cu, 8.16%. Calcd for $C_{48}H_{32}N_4O_2Cu$: C, 75.82; H, 4.24; N, 7.37; Cu, 8.36%. Molecular weights of the polymers were determined by GPC measurements using THF as an eluent. The molecular weight was calibrated by a standard polystyrene.

Results of the radical polymerization of the monomers are shown in Table 1. These polymers were soluble in benzene, benzonitrile, THF, DMF and chloroform; and insoluble in methanol, hexane, acetone, and water.

Table 1. Radical polymerization of AOMTPPM[a)]

Monomer	Volume of solvent/ml	Time/h	Conversion/%	Mw[b)]	Mw/Mn[b)]
AOMTPPCu	2.0	50	35	12000	1.89
	1.0	50	27	18000	1.98
	0.5	50	26	21000	2.48
	2.0	100	35	14000	1.54
AOMTPPVO	2.0	50	25	7800	1.49
	1.0	50	34	11000	1.49
	0.5	50	40	15000	1.56
	2.0	100	28	7900	1.28

a) Monomer, 0.50 g (0.66 mmol); AIBN, 6.8×10^{-3} mmol; solvent, benzonitrile; 60 °C.

b) GPC method(THF); calibrated by standard polystyrene.

In the IR spectra of AOMTPPVO(II) and polyAOMTPPVO(II), the IR bands of the monomer at 1630 and 1730 cm^{-1} are assignable to absorptions due to olefinic and carbonyl bonds of unsaturated ester, respectively. In polyAOMTPPVO(II), the former disappeared and the latter shifted to 1733 cm^{-1}, which indicates that carbonyl bond of unsaturated ester changed to that of saturated ester. No change was found in absorption bands due to the porphyrin ring about 700-800 cm^{-1} after polymerization. Similar change was observed in comparison with IR spectra of AOMTPPCu(II) and polyAOMTPPCu(II). These findings show that the polymerization takes place through the C=C bond of the monomers. Elemental analysis of the polymers obtained was consistent with the results of the corresponding monomers, indicating that addition polymerizations took place.

The visible spectra of polyAOMTPPVO(II) and AOMTPPVO(II) are shown in Fig. 2. AOMTPPVO(II) has Soret band at 425 nm and Q band at 548 nm, while polyAOMTPPVO(II) has Soret band at 422 nm, Q band at 549 nm, and a new absorption band at 638 nm. The Soret band of polyAOMTPPVO(II) at 422 nm is much weaker and broader than that of the monomer. The new absorption band at 638 nm did not appeared by the reaction of TPPVO(II) with AIBN in benzonitrile.

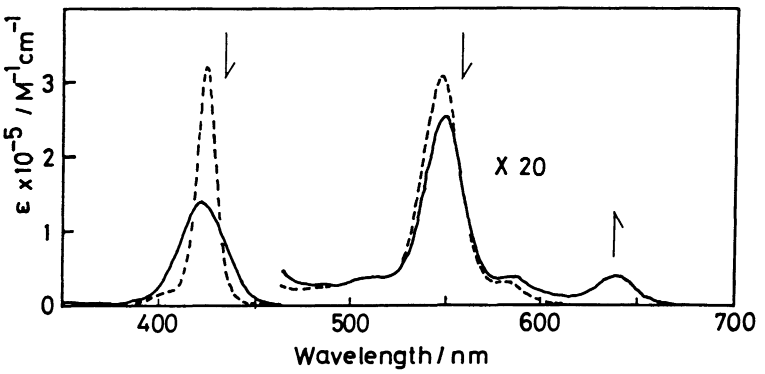


Fig.2. Visible spectra of AOMTPPVO(II)(----) and polyAOMTPPVO(II)(——) in benzene.

The decrease in the intensity at 422 nm and appearance of new absorption band at 638 nm is probably due to some electronic interactions between the porphyrin moieties caused by their connection with a polyacrylate chain. Similar changes in all absorption bands were also observed in comparison with visible spectra of AOMTPPCu(II) and polyAOMTPPCu(II). Further studies are underway on microstructures and physicochemical properties of the polymers.

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References

1) W. Lautsch, W. Broser, W. Biedermann, and H. Gnichtel, J. Polym. Sci., 17, 479 (1955).
2) H. Kamogawa, J. Polym. Sci., B, 10, 711 (1972); J. Polym. Sci., 12, 2317 (1974).
3) E. Tsuchida, H. Nishide, M. Yuasa, T. Baba, and M. Fukuzumi, Macromolecules, 22, 66 (1989).
4) M. Kamachi, X. S. Cheng, T. Kida, A. Kajiwara, and S. Nagata, Macromolecules, 20, 2665 (1987).
5) M. Kamachi, H. Akimoto, and S. Nozakura, J. Polym. Sci., Polym. Lett. 13, 693 (1983).
6) M. Kamachi, X. S. Cheng, H. Aota, W. Mori, and M. Kishita, Chem. Lett., 1987, 2331.
7) N. Watanabe, X. S. Cheng, A. Harada, M. Kamachi, H. Nakayama, W. Mori, and M. Kishita, Polym., J., 21, 633 (1989).
8) H. J. Callot, Tetrahedron, 29, 899 (1973).

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