

SHORT COMMUNICATIONS

Synthesis and Radical Polymerization of Vinyl Monomers Containing Octaalkylporphyrins

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Polymers containing paramagnetic species in their side chains are potentially new magnetic materials, because magnetic ordering of the paramagnetic species through exchange interactions among unpaired electrons is possible in the polymers.^{1,2} We found that polyacrylates containing tetraphenylporphyrinato-silver(II) (TPP-Ag(II)) have strong antiferromagnetic interactions.³ Polymers containing metal complexes of octaalkylporphyrins (OAP: octaethylporphyrin (OEP) and etio-porphyrin (Etio)) might have closer metal-metal distances than those with TPP-metal and show stronger interactions among metal ions. In this paper, we report a preparation of acrylates containing OEP or Etio, and the radical polymerization of the acrylates.

meso-Hydroxymethyl-OEP (HOM-OEP) was prepared according to the methods described by Inhoffen *et al.*⁴ The vinyl monomer, *meso*-Acryloyloxymethyl-OEP (AOM-

OEP) was synthesized by Schotten-Baumann reaction as follows: HOM-OEP (0.20 g, 0.35 mmol) was dissolved in THF-chloroform (1 : 1 (v/v), 100 ml) containing triethylamine (0.70 ml, 5.00 mmol) and a small amount of hydroquinone. To this solution, acryloyl chloride (0.32 ml, 3.5 mmol) was added dropwise with stirring at 0°C. After 24 h, the crude product was purified by chromatography on a silicagel column (Wakogel C-200, 5 × 15 cm) using chloroform as eluent. Red-purple powder was obtained (80 mg, yield, 36%). IR (KBr) $\nu = 1720 \text{ cm}^{-1}$, (C=O); $\nu = 1630 \text{ cm}^{-1}$, (C=C). *Anal.* Calcd for AOM-OEP·CHCl₃; C₄₁H₅₁O₂N₄Cl₃: C, 66.71%; H, 6.96%; N, 7.58%. Found: C, 67.55%; H, 6.28%; N, 7.07%.

Homopolymerizations of AOM-OEP and AOM-Etio were carried out in THF, DMF, and THF-DMF mixed solution (0.1 M). Oligomers were obtained by the radical poly-

Table I. Radical polymerization of monomers containing octaalkylporphyrins^a

Monomer	Solvent	Conv./%	Time/h	\bar{M}_w	\bar{M}_n	\bar{M}_w/\bar{M}_n
AOM-OEP	DMF	15	50	2000	1600	1.31
	THF	10	50	2900	1700	1.72 ^b
AOM-Etio	DMF-THF	10	50	2600	1500	1.77 ^b

^a [Monomer] = 60 mM; AIBN = 6×10^{-4} M.

^b Measured by Kuraray Co., Ltd.

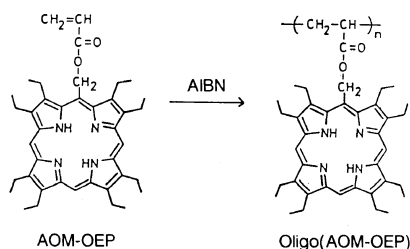


Figure 1. AOM-OEP and its radical oligomerization.

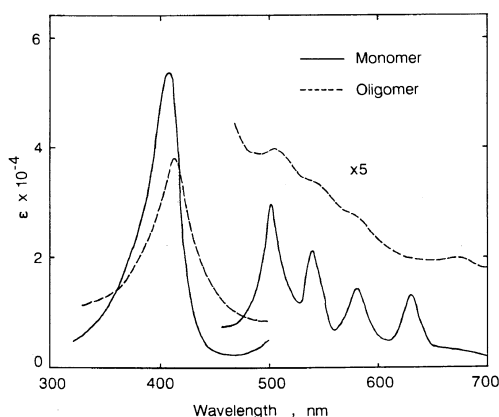


Figure 2. Absorption spectra of AOM-OEP (—) and oligo(AOM-OEP) (----) in CHCl_3 (10^{-5} M).

merization using AIBN at 60°C (Table I). Products were purified by repeated reprecipitation from THF-*n*-hexane. Molecular weights of the polymerized products were determined using GPC.

The monomer concentrations used here were one order of magnitude lower than those used in the radical polymerizations of conventional monomers,⁵ because the concentration was limited by their low solubility. The radical polymerization of AOM-OEP and AOM-Etio occurred homogeneously in THF, while a dispersed precipitate appeared during polymerization in DMF. Although the monomers were more soluble in THF than in DMF, the molecular weights of the polymers were not influenced by polymerization solvents.

The UV-visible spectra of AOM-OEP and oligo(AOM-OEP) showed specific features of

stacked porphyrin rings (Figure 2).^{6,7} The Soret band of oligo(AOM-OEP) (413 nm) shifted to a longer wavelength by 6 nm and became weaker and broader than that of AOM-OEP, indicating that its molar extinction coefficient markedly decreases with polymer formation. The molar extinction coefficients of all the Q bands of oligo(AOM-OEP) were a little larger than those of monomers. Similar phenomena have been observed in porphyrin dimers in organic solvents.⁶ These phenomena might be explained on the basis of an exciton coupling model due to the close approach of two porphyrin rings.⁷ The differences in the spectra between oligo(AOM-OEP) and AOM-OEP showed that OEP moieties bound to oligomer are forced to interact due to their close approach. We reported that polymers containing TPP in their side chains showed specific features in the absorption spectra only at high molecular weights.^{8,9} In the case of OAP, oligomers showed features similar to those of the high molecular weight polymer containing TPP, suggesting that aggregation is easier in OAP moieties than in TPP ones.

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