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Radical Polymerization of 5-(4-Acrylamido)-phenyl-10,15,20-triphenylporphyrin

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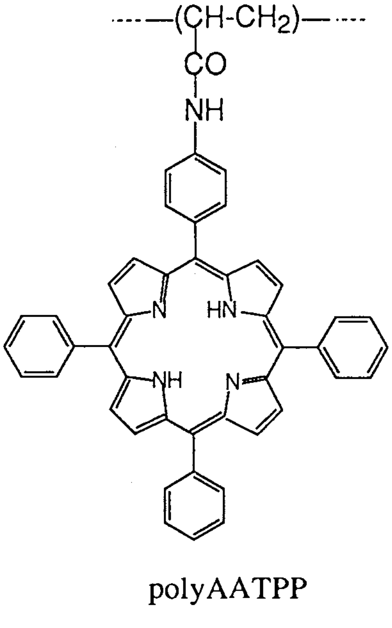
Polyacrylamide having tetraphenylporphyrin rings in its side chain was prepared by radical polymerization of 5-(4-acrylamido)-phenyl-10,15,20-triphenylporphyrin (AATPP) by using AIBN at 60 °C in benzonitrile.

It is well known that porphyrin derivatives play an important role in photosynthesis and oxygen-transportation in living systems. Polymers containing porphyrin moieties in their side chains are of interst as functional polymers which mimic a living system.1-4) Accordingly, polymers containing porphyrins in their side chains have been prepared by the reaction of prepolymers with porphyrin derivatives, and the copolymerization of vinyl monomers with vinyl monomers containing porphyrin derivatives.5)

Previously, we synthesized high polymers of 5-(4-acryloyloxy)-phenyl-10,15, 20-triphenylporphyrin (AOTPP)6) and 5-(4-methacryloyloxy)-phenyl-10,15,20-triphenylporphyrin (MAOTPP)7) by radical polymerization and investigated physicochemical properties of their metal complexes.

In this communication, we report the radical polymerization of 5-(4-acrylamido)-phenyl-10,15,20-triphenylporphyrin (AATPP) initiated by AIBN in benzonitrile. Since a bulky tetraphenylporphyrin (TPP) group is attached to the vinyl residue by the amide bond in AATPP, the restricted rotation of the bulky substituent group may impose greater steric hindrance on the propagation step than in the case of AOTPP, in which the



polyAATPP

Table 1. Radical Polymerization of AATPP[a)]

AATPP (M)	Conv. /%	$\overline{M}_w$[b)]	$\overline{M}_w/\overline{M}_n$[b)]
0.55	99.8	$2.88\text{x}10^4$	1.79
0.59	100	$2.83\text{x}10^4$	1.80

a) 60 °C, 60 h. AIBN 1 mol%, in benzonitrile.
b) $\overline{M}_w$, $\overline{M}_n$; by GPC, calibrated by standard polystyrene.

TPP group is attached to the vinyl residue by a flexible ester linkage. Therefore, it is interesting to examine the polymerizability of AATPP in comparison with AOTPP.

AATPP was prepared by reaction of 5-(4-amino)-10,15,20-triphenylporphyrin (1.09 g, 26.0 mmol) with acryloylchloride (1.57 g, 17.3 mmol) in the presence of triethylamine (2.53 g, 26.0 mmol) in toluene at 0 °C. The monomer was purified on a silicagel column using toluene/THF (9/1:v/v) as eluent. Yield 0.716 g, 60.7%, purple crystal, E. A., Found: C;82.17, H;5.00, N;10.02%, Calcd for $C_{47}H_{33}N_5O$: C;82.55, H;4.86, N;10.24%. MS(FD), Found 683.5, Calcd 683. Mp >300 °C.

Polymerizations of AATPP were carried out in benzonitrile at 60 °C in the presence of AIBN. Polymers obtained were purified by successive reprecipitation

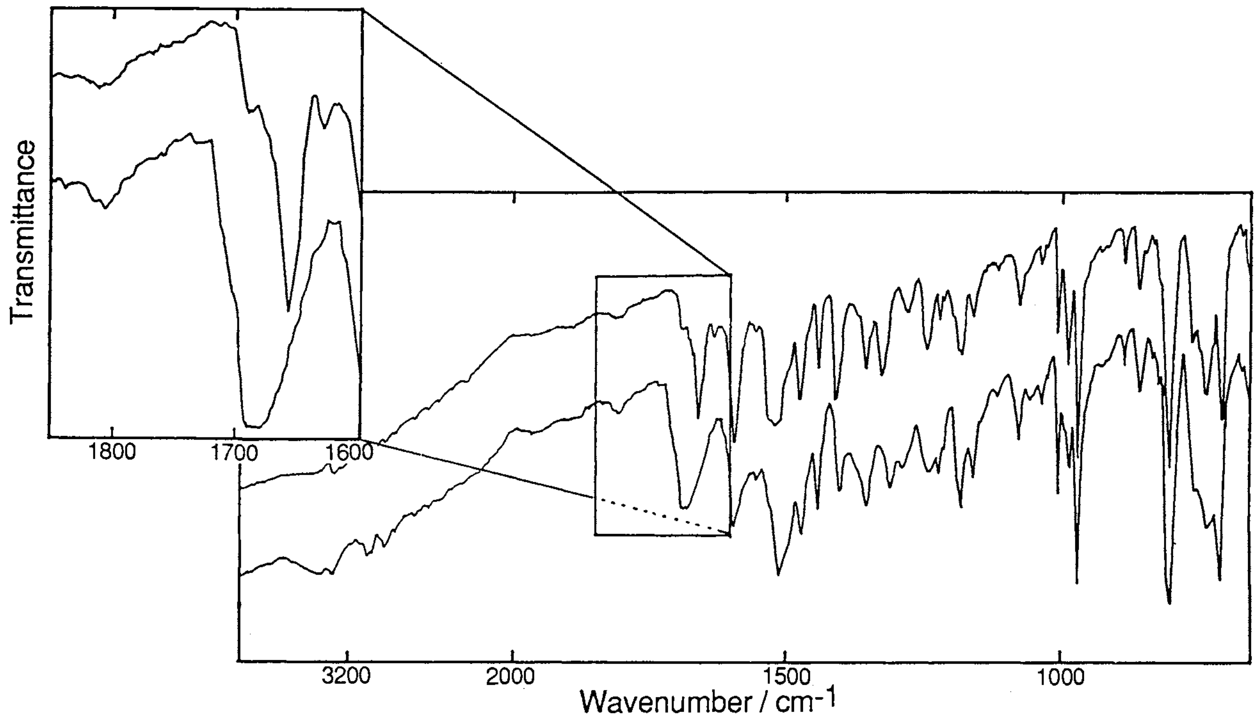


Fig. 1. IR spectra of AATPP (upper) and polyAATPP (lower) (KBr).

from THF solution into acetone. Molecular weights of the polymers were determined using GPC. Results of the polymerization are shown in Table 1. Despite the bulky TPP group is linked by the rigid amide bond, AATPP was found to give high polymers. Observed molecular weights of 2.88×10^4 and 2.83×10^4 for the polymers correspond to the degrees of polymerization of 42 and 41, respectively. In comparison with AOTPP,[6,7] AATPP showed comparable or even higher polymerizability under the similar polymerization conditions. These results may imply that other factors such as solubility of the monomers and the polymers in the solvents for the polymerization, and stability of propagating radicals have larger effects on the polymerizability of such sterically hindered monomers than does the rigidity of the spacer bond between the substituent porphyrin moiety and the vinyl group.

Comparison of the IR spectra of AATPP and polyAATPP indicates that addition polymerization occurred through the vinyl bonds (Fig. 1). The IR bands of the monomer at 1630 and 1660 cm^{-1} are assignable to ν(C=C) and ν(C=O) in unsaturated amide, respectively. On polymerization, the former band disappeared while the latter shifted to 1685 cm^{-1} and broadened. The 1685 cm^{-1} band can be assigned to ν(C=O) in saturated amide.[8] Other absorption bands characteristic of the porphyrin ring remained unchanged after the polymerization.

The UV-visible absorption spectra of polyAATPP in chloroform implied a strong electronic interaction among the TPP moieties (Fig. 2). The monomer showed a Soret band at 419.5 nm (absorption coefficient $\varepsilon = 4.35 \times 10^5$) and Q

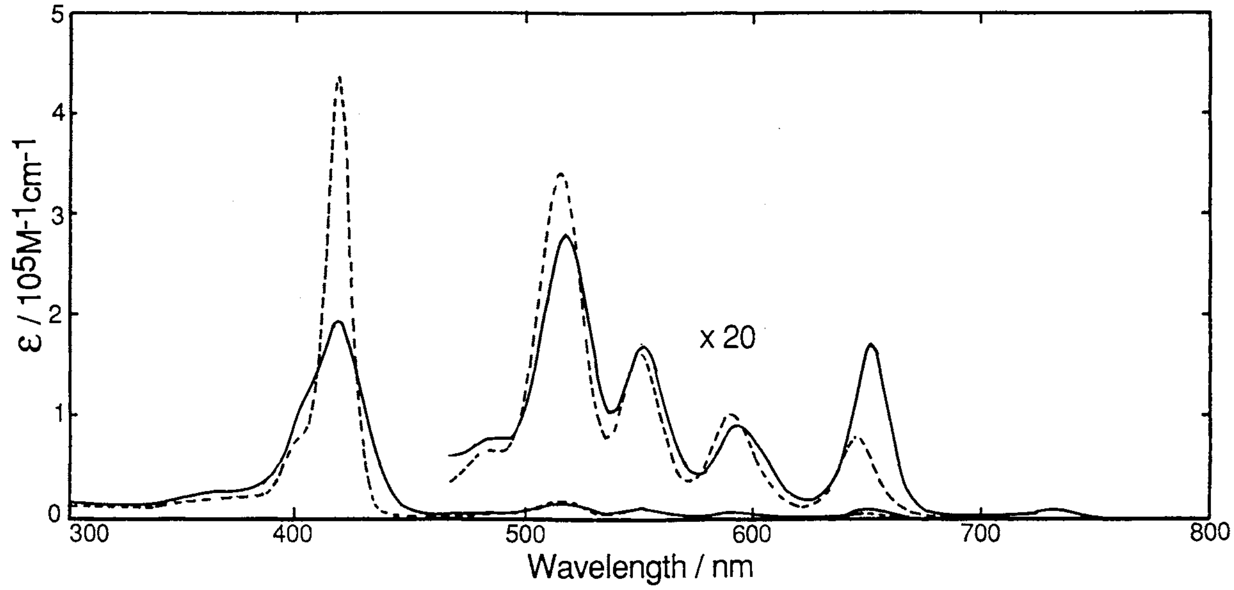


Fig. 2. Absorption spectra of AATPP (----) and polyAATPP (———) in chloroform.

bands at 515.5(ε = 1.70×10^4), 551.0(ε = 8.02×10^3), 590.5(ε = 5.06×10^3), and 646.5 nm (ε = 3.95×10^3). PolyAATPP exhibited a Soret band at 418.5 nm (ε = 1.93×10^5) and Q bands at 517.5 (ε = 1.39×10^4), 552.5 (ε = 8.38×10^3), 594.0 (ε = 4.51×10^3), and 652.5 nm (ε = 8.50×10^3). The molar extinction coefficient of the Soret band of AATPP was markedly decreased upon polymerization. Similar phenomena have been observed in other porphyrin-containing polymers4) and in porphyrin dimers9) in organic solution. These phenomena may be explained on the basis of an exciton coupling model due to a close approach of two porphyrin rings.10)

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