

Radical Polymerization of 5-(4'-Acrylamidophenyl)-10,15,20-triphenylporphine and 5-(4'-Methacrylamidophenyl)-10,15,20-triphenylporphine

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ABSTRACT: High polymers were obtained by the radical polymerization of 5-(4'-acrylamidophenyl)-10,15,20-triphenylporphine (AATPP) and 5-(4'-methacrylamidophenyl)-10,15,20-triphenylporphine (MATPP) in which vinyl groups bind to a tetraphenylporphyrin (TPP) with amide linkage, using 2,2'-azobis(isobutyronitrile) as an initiator at 60°C. Monomer reactivity ratios were determined by the copolymerization of AATPP or MATPP (M_1) with styrene (M_2) as $r_1 = 0.065 \pm 0.045$ and $r_2 = 0.67 \pm 0.07$, or $r_1 = 0.14 \pm 0.01$ and $r_2 = 0.72 \pm 0.01$, respectively. Q and e were 0.28 and 1.41 for AATPP and 0.39 and 0.79 for MATPP, respectively based on r_1 and r_2 values. Rate constants of the addition of diphenylphosphinoyl radicals ($\text{Ph}_2\dot{\text{P}}=\text{O}$), generated by the photolysis of 2,4,6-trimethylbenzoyl diphenylphosphine oxide (TMDPO), to amide-TPP monomers were determined by time-resolved electron spin resonance (ESR) spectroscopy. The rate constants of the reaction of the amide-TPP monomers ($\sim 1.3 \times 10^6 \text{ s}^{-1} \text{ M}^{-1}$ for AATPP and $\sim 0.5 \times 10^6 \text{ s}^{-1} \text{ M}^{-1}$ for MATPP) were much smaller than that of *N*-phenylacrylamide ($\sim 4.2 \times 10^7 \text{ s}^{-1} \text{ M}^{-1}$) or *N*-phenylmethacrylamide ($\sim 1.4 \times 10^8 \text{ s}^{-1} \text{ M}^{-1}$), probably due to decrease in resonance stabilization due to a steric hindrance of bulky TPP moiety.

KEY WORDS Tetraphenylporphyrin / Radical Polymerization / Copolymerization / Q , e Values / Monomer Reactivity Ratio / Time-Resolved Electron Spin Resonance / Initiation Rate Constant /

Kamachi *et al.* have paid attention to the preparation of magnetically-interaction polymers.^{1–4} To obtain polymers which have magnetic activity, they have also prepared vinyl polymers containing paramagnetic metal complexes of porphyrins in the side chains and their magnetic behavior was investigated by magnetic susceptibility and ESR spectroscopy.^{5–12} The synthesis of polymers in which porphyrin moieties bind to a polymer chain with amide group is necessary for understanding of the magnetic behavior of polymers, because superexchange interaction of paramagnetic species through carbonyl group and their mobility is important for the molecular design for magnetism.⁵ Although copolymers of acrylamide and methacrylamide having porphyrin moieties in the side chain have been prepared for the design of functional polymers, no homopolymer was reported^{13–16} prior to our preliminary report on polymer formation.¹⁷ Since bulky substituted methacrylamide do not homopolymerize under usual radical polymerization,¹⁸ polymer formation was considered difficult from these amide monomers having much bulky porphyrin moieties. Recently, radical homopolymerizations of AATPP¹⁶ and MATPP were conducted, although polymerization rates of AATPP and MATPP were lower compared with those of the corresponding *N*-phenylacrylamide (*N*-phAA) and *N*-phenylmethacrylamide (*N*-phMA), respectively. To our knowledge, radical polymerizabilities of vinyl monomers having TPP moieties in their side groups have not been studied systematically so far. Accordingly, we investigated the radical polymerizabilities of AATPP and MATPP by determination of copolymerization parameters, estimation of the addition rate constants of di-

phenylphosphinoyl radical to them, and comparison of these data with those of *N*-phAA and *N*-phMA.

EXPERIMENTAL

Materials

Benzonitrile was purified by distillation according to the usual method.¹⁹ 2,2'-Azobis(isobutyronitrile) (AIBN) was recrystallized from diethyl ether. Styrene was purified in the usual manner and distilled under reduced pressure over BaO just before use. Other materials were used as received.

Syntheses of monomers (AATPP and MATPP) are summarized in Scheme 1.

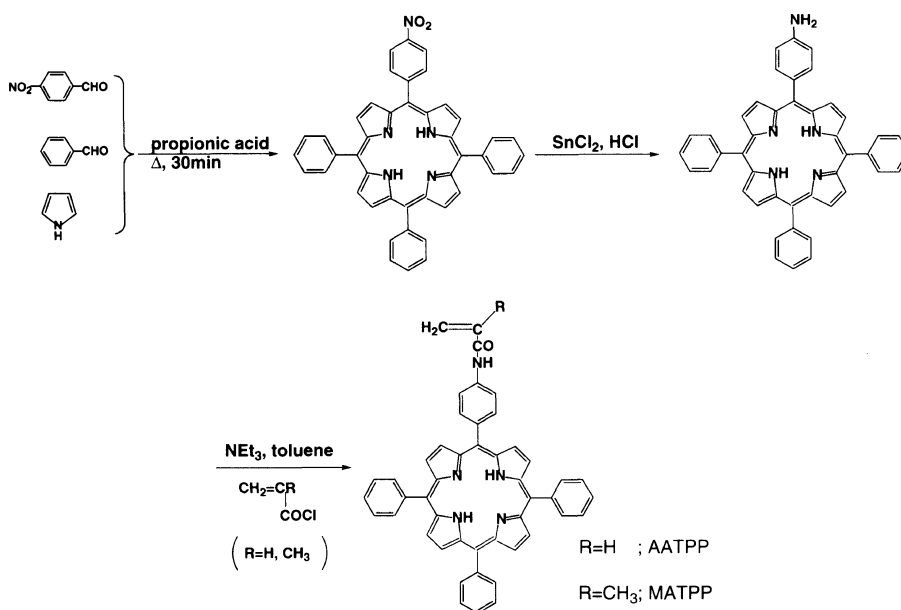
5-(4'-Acrylamidophenyl)-10,15,20-triphenylporphine (AATPP). AATPP was synthesized according to the literature²⁰ and purified by column chromatography over silica gel (Wakogel C-200). As the eluent in chromatography, a mixed solvent, tetrahydrofuran (THF)/toluene (1:9, v/v) was used. AATPP thus obtained was recrystallized from toluene to be purple microcrystals. Total yield was 2.2%. IR (KBr) 1630 cm^{-1} , ν (C=C), 1660 cm^{-1} , ν (C=O); ¹H NMR (CDCl₃, 270 MHz) δ -2.75 (s, 2H), δ 5.88, 5.91 (d, 1H), δ 6.34–6.44 (q, 1H), δ 6.56–6.62 (d, 1H), δ 7.53 (s, 1H), δ 7.71–7.81 (m, 9H), δ 7.95 (d, 2H), δ 8.16–8.24 (m, 8H), δ 8.85–8.88 (m, 8H). *Anal.* Calcd for C₄₇H₃₃N₅O: C, 82.55; H, 4.86; N, 10.24. Found: C, 82.04; H, 4.85; N, 10.11. FD-MS Calcd [M] m/z : 683. Found [M] m/z : 683.5. mp > 300°C.

5-(4'-Methacrylamidophenyl)-10,15,20-triphenylporphine (MATPP). MATPP was synthesized according to the literature²¹ and obtained as purple microcrystals. Total yield was 1.2%. IR (KBr) 1630 cm^{-1} , ν (C=

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C), $1670\text{--}1690\text{ cm}^{-1}$, ν (C=O); $^1\text{H NMR}$ (CDCl_3 , 270 MHz) δ -2.75 (s, 2H), δ 2.18 (s, 3H), δ 5.60 (s, 1H), δ 5.97 (s, 1H), δ $7.72\text{--}7.78$ (m, 9H), δ 7.84 (s, 1H), δ $8.19\text{--}8.24$ (m, 8H), δ $8.84\text{--}8.88$ (m, 8H). *Anal.* Calcd for $\text{C}_{48}\text{H}_{35}\text{N}_5\text{O}\cdot\text{H}_2\text{O}$: C, 80.54; H, 5.21; N, 9.78. Found: C, 80.43; H, 4.98; N, 9.76. FAB-MS Calcd. [M] m/z : 697. Found [M+1] m/z : 698.5. mp $>300^\circ\text{C}$.

N-Phenylacrylamide (*N*-phAA) and *N*-phenylmethacrylamide (*N*-phMA). *N*-phAA and *N*-phMA were prepared according to the literature.²²

Radical Polymerization

Homopolymerization: The general procedure is described for the polymerization of AATPP.¹⁷ AATPP (127.3 mg, 1.86×10^{-1} mmol) and AIBN (1 mol% of the monomer) were dissolved in benzonitrile (0.34 ml). The solution was placed in a glass ampoule, degassed three times with an oil diffusion pump after three times with a rotary pump, sealed under high vacuum and polymerized at 60°C for 60 h. The solution was poured into acetone and the precipitated polymer was separated by centrifugation. The polymer was dissolved in THF and this dissolution–precipitation–separation process was repeated three times to purify the polymer. The obtained polymer was dried with heating *in vacuo*. The polymer was purple solid. *Anal.* Calcd for $(\text{C}_{47}\text{H}_{33}\text{N}_5\text{O}\cdot\text{H}_2\text{O})_n$: C, 80.44; H, 5.03; N, 9.80. Found: C, 80.45; H, 5.26; N, 9.76. PolyMATPP was obtained by radical polymerization following the same procedure for polyAATPP synthesis. For polyMATPP, *Anal.* Calcd for $(\text{C}_{48}\text{H}_{35}\text{N}_5\text{O}\cdot 2\text{H}_2\text{O})_n$: C, 79.54; H, 5.28; N, 9.66. Found: C, 79.24; H, 5.08; N, 9.52. For these polymers, M_w and M_n were determined by GPC calibrated by standard polystyrenes. Results of homopolymerization are summarized in Table I.

Copolymerization: Copolymerizations of AATPP and MATPP with styrene were performed with AIBN at 60°C in benzonitrile. Total molar concentrations of amide-TPP monomer and styrene was 0.5 M, and AIBN was 1 mol% of the monomer concentration. Purification of the copolymers and estimation of the molecular weights were performed as described in the experimental section of

homopolymerization. Copolymer compositions were estimated by elemental analysis. Monomer reactivity ratios were evaluated by fitting the copolymer composition curves.

Measurements

UV-Vis spectra were measured in CHCl_3 with a Shimadzu spectrophotometer UV-2100. IR spectra were recorded in KBr disks with a JASCO FT/IR-3 infrared spectrophotometer. GPC analysis was carried out by a TOSOH CCP & 8010 series high-speed liquid chromatograph system by using TSK gel and THF as an eluent. As detectors, TOSOH UV-8010 and TOSOH RI-8012 were used. Molecular weights of the polymers were estimated using calibration curves from standard polystyrene. $^1\text{H NMR}$ spectra were obtained in CDCl_3 on a JEOL JNM-EX 270 (at 30°C). Mass spectra were taken on a JEOL JMS SX-102 mass spectrometer by fast atom bombardment (FAB). The sample was dissolved in CHCl_3 and mass number was calibrated using cesium iodide (CsI). Time-resolved ESR experiments were performed on a JEOL JES-FE1X spectrometer operated without magnetic field modulation. Laser pulses were irradiated using a Q-switched Nd:YAG laser (Quantaray DCR-2) operated at the third harmonic (54 mJ per flash at 355-nm with a 6-ns fwhm). ESR spectra of transient diphenylphosphonyl radicals in liquid solution were taken as done previously.²³

RESULTS AND DISCUSSION

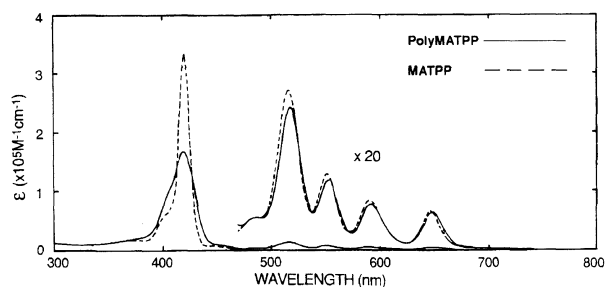
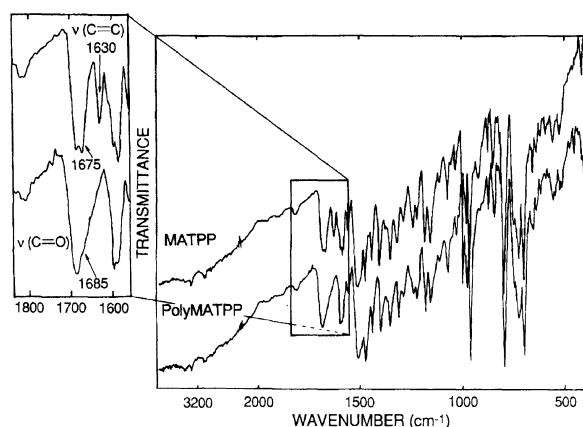
Radical Homopolymerization

Radical polymerizations of AATPP and MATPP were homogeneous in benzonitrile. Although the methacrylamide has bulky TPP moieties, homopolymerization proceeded. The polymerized products were purified by repeated reprecipitation from THF–acetone. Polymers were obtained as deep purple powders. The results of the radical polymerization of AATPP and MATPP are summarized in Table I along with those of other vinyl monomers having TPP moieties. Monomer concentration

Table I. Radical polymerizations of porphyrin monomers

Monomer	Concn	[AIBN]	Yield	M_w^c	
	M	mM	%		
AATPP ^a	0.59	5.9	100	28000	ref 17
MAATPP ^a	0.60	6.0	81.1	58000	This work
VTPP ^a	0.65	6.5	71.9	107000	ref 9
MAOTPP ^b	0.11	0.2	36.7	83000	ref 8
AOTPP ^b	0.11	1.5	49.7	10000	ref 8

^a 60°C, 60 h, in benzonitrile. ^b 60°C, 50 h, in benzonitrile. ^c GPC, calibrated with polystyrene standards.

**Figure 1.** Infrared spectra for MATPP and polyMATPP (KBr).**Figure 2.** UV-Vis absorption spectra for MATPP (---) and polyMATPP (-----) in chloroform.

was restricted by the low solubility of these monomers. PolyAATPP and polyMATPP were soluble in chloroform, dichloromethane, benzene, toluene, DMF, THF, and benzonitrile and insoluble in hexane, acetone, ethanol, methanol, diethyl ether, and water.

The IR spectrum of polyMATPP is shown in Figure 1 along with that of monomer. In the case of MATPP, IR bands at 1630 cm^{-1} and 1675 cm^{-1} are assignable to the stretching vibration mode of C=C and C=O bonds of vinyl and unsaturated amide, respectively. The C=C bond disappeared and the C=O bond shifted to 1685 cm^{-1} , which is assignable to the C=O bonds of the saturated amide.²⁴ The same was observed in the case of AATPP and polyAATPP as reported previously.¹⁷ In both amide-TPP polymers, absorption bands characteristic of the porphyrin ring remained unchanged after polymerization. This indicates that polymerization occurred though C=C double bonds of the vinyl group.

Visible spectra of MATPP and polyMATPP are shown in Figure 2. MATPP has a Soret band at 420.0 nm and

Table II. Results for AATPP-styrene copolymerization

No.	x_{AATPP}	x_{AATPP} in polymer ^b	Polymerization time ^a /h	M_w^c	Conversion
					%
1	0.80	0.55	8.8	20000	3.5
2	0.65	0.40	8.8	35000	6.2
3	0.50	0.39	7.3	46000	3.7
4	0.35	0.32	5.0	33000	4.1
5	0.20	0.23	5.0	59000	5.4

^a Total monomer concentration $[M_0]=0.45\text{ M}$. Polymerized in benzonitrile, 1 mol% AIBN, 60°C. ^b Estimated from C/N ratio measured by elemental analysis. ^c GPC, calibrated with polystyrene standards.

Table III. Results for MATPP-styrene copolymerization

No.	x_{MATPP}	x_{MATPP} in polymer ^b	Polymerization time ^a /h	M_w^c	Conversion
					%
1	0.80	0.57	8.8	48000	6.6
2	0.65	0.47	8.8	64000	6.3
3	0.50	0.40	7.3	63000	10.0
4	0.35	0.32	5.0	63000	4.1
5	0.20	0.21	5.0	53000	5.9

^a Total monomer concentration $[M_0]=0.45\text{ M}$. Polymerized in benzonitrile, 1 mol% AIBN, 60°C. ^b Estimated from C/N ratio measured by elemental analysis. ^c GPC, calibrated with standard polystyrene.

Q bands at 516.0, 551.5, 590.5, and 646.5 nm. Comparison of this spectrum to that of TPP²⁵ indicates that the *Q* band peak at the lowest energy is *ca.* 20 nm lower than that of TPP.^{25,26} Other peaks of MATPP appear at similar wavelength as the case of TPP. This shows that there is inductive effect by the amide group. PolyMATPP exhibits a Soret band at 419.0 nm, and the *Q* bands at 517.5, 553.0, 591.5, and 647.5 nm. Detailed examination of these spectra showed that the Soret band of polyMATPP is weaker and broader than that of MATPP, indicating that the molecular extinction coefficient markedly decreases in the polymer. These results indicate that electronic interactions occur among porphyrin moieties in the polymer. This hypochromism at the Soret band has been also observed for polyAATPP comparing to AATPP.¹⁶ These observations are similar to those for the other porphyrin containing polymers we have reported.^{6,8,9,12} 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.^{26,27}

Radical Polymerizability

To understand the effects of the bulkyness of TPP on the radical reactivity of the vinyl monomers, copolymerizations of amide-TPP monomer (M_1) with styrene (M_2) were performed in benzonitrile at 60°C with AIBN as an initiator (Tables II and III). Copolymer composition plots of AATPP and MATPP and curves obtained by fitting are shown in Figures 3(a) and (b), respectively. Monomer reactivity ratios were determined from these composition curves to be $r_1=0.065\pm 0.045$ and $r_2=0.67\pm 0.07$ for AATPP and $r_1=0.14\pm 0.01$ and $r_2=0.72\pm 0.01$ for MATPP. In all cases, r was smaller than

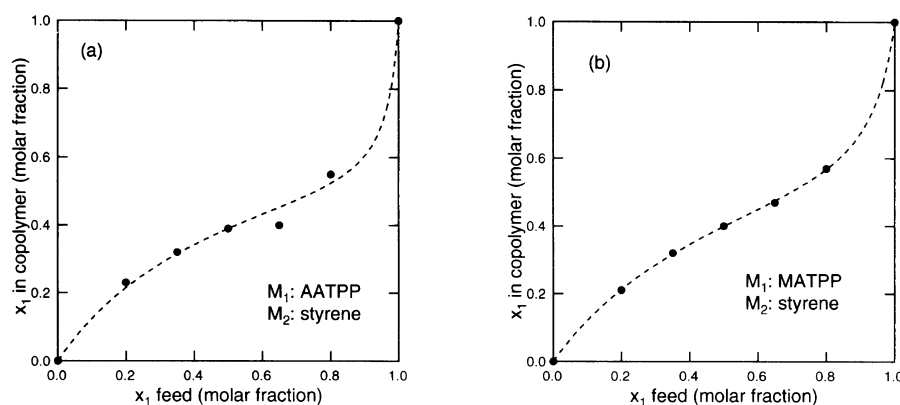


Figure 3. (a) Copolymer composition plots for AATPP (M_1) with styrene (M_2) and copolymer composition curve obtained by fitting. (b) Copolymer composition plot for MATPP (M_1) with styrene (M_2) and copolymer composition curve obtained by fitting.

Table IV. Results for *N*-phenyl acrylamide(*N*-phAA)-styrene copolymerization

No.	$x_{N\text{-phAA}}$	$x_{N\text{-phAA}}$ in polymer ^b	Polymerization time ^a /min	M_w ^c	Conversion %
1	0.80	0.73	15	44000	2.8
2	0.65	0.61	30	27000	2.4
3	0.52	0.48	30	38000	2.4
4	0.35	0.37	50	31000	2.7
5	0.20	0.22	130	21000	3.1

^aTotal monomer concentration $[M_0]=1.5$ M. Polymerized in benzonitrile, 1 mol% AIBN, 60°C. ^bEstimated from C/N ratio measured by elemental analysis. ^cGPC, calibrated with polystyrene standards.

Table V. Results for *N*-phenyl methacrylamide(*N*-phMA)-styrene copolymerization

No.	$x_{N\text{-phMA}}$	$x_{N\text{-phMA}}$ in polymer ^b	Polymerization time ^a /min	M_w ^c	Conversion %
1	0.80	0.73	30	27000	1.3
2	0.65	0.58	50	23000	2.4
3	0.50	0.44	50	20000	1.6
4	0.35	0.33	80	24000	1.5
5	0.20	0.20	215	17000	9.2

^aTotal monomer concentration $[M_0]=1.5$ M. Polymerized in benzonitrile, 1 mol% AIBN, 60°C. ^bEstimated from C/N ratio measured by elemental analysis. ^cGPC, calibrated with polystyrene standards.

unity. The propagating radical of each amide-TPP monomers is thus more reactive toward styrene, and styrene radical is somewhat more reactive toward amide-TPP monomers than styrene. The copolymers thus have relatively alternate sequence distribution.

To examine the effects of bulky TPP attached to amide group, we examined the radical polymerizability of acrylamide and methacrylamide monomers with smaller side chain such as *N*-phAA and *N*-phMA. We investigated the copolymerization of *N*-phAA (or *N*-phMA) (M_1) with styrene (M_2). Total monomer concentration $[M_0]$ was 1.5 M and $[AIBN]$ was 1.5×10^{-2} M. The polymerizations were performed in benzonitrile at 60°C. The results of the copolymerization are summarized in Tables IV and V. Monomer reactivity ratios were $r_1 = 0.58 \pm 0.03$ and

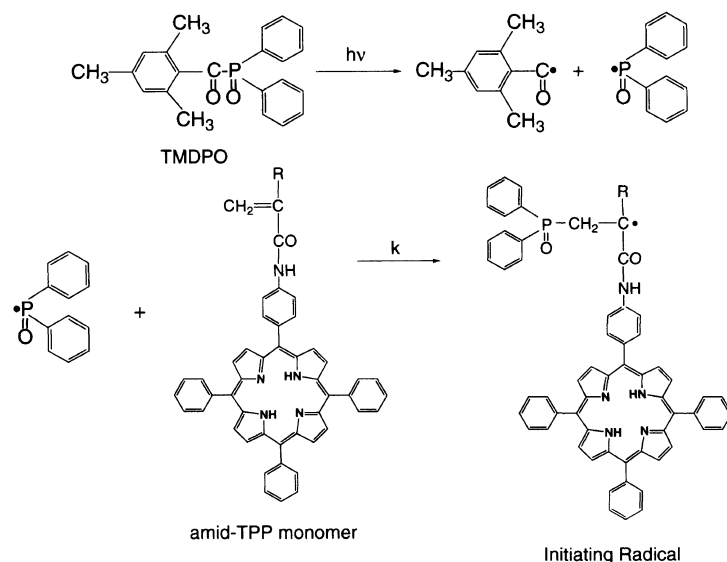
Table VI. Q - e Data for monomers

Monomer	Q	e	
AATPP	0.36	0.97	This work
MATPP	0.41	0.72	This work
<i>N</i> -phAA	0.44	0.15	This work
<i>N</i> -phMA	0.55	0.02	This work
VTPP	0.85	0.24	ref 9
Styrene	1	-0.80	ref 27

$r_2 = 0.68 \pm 0.02$ for *N*-phAA and $r_1 = 0.54 \pm 0.08$ and $r_2 = 0.94 \pm 0.10$ for *N*-phMA from the composition curves.

Q and e for TPP monomers are summarized in Table VI along with those for methyl methacrylate, styrene, methacrylate type TPP monomer (MAOTPP), and TPP monomer, 5-(4-vinylphenyl)-10,15,20-triphenylporphyrin (VTPP), in which vinyl group bound directly to TPP just like as styrene. Q and e were estimated to be 0.36 and 0.97 for AATPP, 0.41 and 0.72 for MATPP, 0.44 and 0.15 for *N*-phAA, and 0.55 and 0.02 for *N*-phMA, respectively based on r_1 and r_2 . e for AATPP is larger than that for *N*-phAA by 0.82. Q for AATPP is smaller than that for *N*-phAA by 0.08. Almost the same was observed in MATPP and *N*-phMA. That is, in amide case, AATPP and MATPP have larger e and smaller Q s than the corresponding *N*-phenylamides. The porphyrin moiety is thus a more electron withdrawing substituent than a phenyl group, and resonance stabilization by TPP moiety is smaller than that by the phenyl group. Since bulky TPP is linked to the vinyl group *via* stiff amide linkage, the TPP moiety may not be at the position where resonance effect of TPP expands to the vinyl group. By comparison of AATPP and MATPP or *N*-phAA and *N*-phMA, when a methyl group is bound to the vinyl group, the e becomes smaller and Q becomes larger. Smaller Q in methacrylamide derivatives is deduced from the hyperconjugation of the methyl group. Q of VTPP was also smaller than that of styrene. Since the vinyl group binds directly to TPP in VTPP, the resonance stabilization between the vinyl group and TPP might be ascribable to steric repulsion between the vinyl group and bulky TPP.

To examine the effects of bulkiness of side chain on the rate of radical polymerization, AATPP, MATPP, *N*-phAA, and *N*-phMA were homopolymerized under the same conditions; *i.e.*, $[M]=0.55$ M and AIBN was 1 mol% of $[M]$ in benzonitrile at 60°C 10.5 h under high



Scheme 2.

Table VII. Radical polymerization ratios of amide monomers

	Conversion/% ^a	
	Run 1	Run 2
AATPP	10	9
MATPP	25	38
<i>N</i> -phAA	100	100
<i>N</i> -phMA	46	71

^a Determined by GPC.

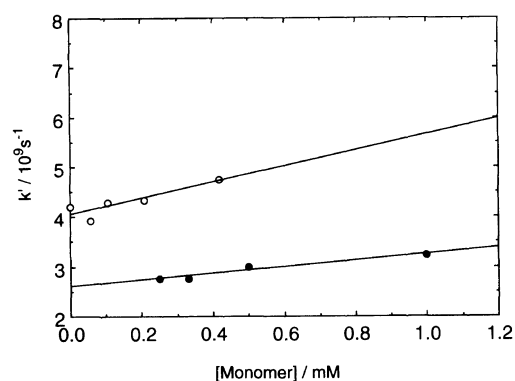
Table VIII. Rate constants for addition reactions of the diphenylphosphinoyl radical to vinyl monomers.

Monomer	k' ($s^{-1} M^{-1}$)	
AATPP	$(1.3 \pm 0.3) \times 10^6$	ref 23
MATPP	$(1.4 \pm 0.5) \times 10^6$	This work
VTPP	$(0.54 \pm 0.5) \times 10^6$	ref 9
<i>N</i> -phAA	$(4.2 \pm 0.1) \times 10^7$	This work
<i>N</i> -phMA	$(1.38 \pm 0.01) \times 10^8$	This work
Styrene	$(1.1 \pm 0.2) \times 10^7$	ref 23

vacuum. The results are summarized in Table VII. In the case of vinyl monomers with TPP, the polymerization rates were always smaller than the corresponding monomers with phenyl group, due to the presence of bulky side chain. The polymerization rate of MATPP was larger than that of AATPP, while that of *N*-phMA was smaller than that of *N*-phAA. The reverse trend in the polymerization rates might be due to decrease in termination rate owing to the steric repulsion between the propagation radicals of MATPP.

Time-Resolved ESR Study

We reported a time-resolved ESR study on the initiation step of the photoinitiation of various monomers with TMDPO, whose photodissociation yielded the 2,4,6-trimethylbenzoyl radical and diphenylphosphinoyl radical.²³ To evaluate the radical reactivity of amide-TPP monomers, rate constants of the addition of diphenylphosphinoyl radical ($\text{Ph}_2\text{P}=\text{O}$), generated by the photolysis of 2,4,6-trimethylbenzoyl TMDPO, to AATPP and

Figure 4. Plots of k' vs. concentration of added monomer (O, AATPP; ●, MATPP).

MATPP were determined by time-resolved ESR spectroscopy (Scheme 2). We also measured rate constants for the radical addition to *N*-phAA and *N*-phMA and these results are listed in Table VIII along with those for VTPP and styrene.

The decay rate of diphenylphosphinoyl radical increased with concentrations of monomers and followed first order kinetics even in the presence of monomers. The initiation rate constants for the addition of the diphenyl phosphinoyl radical to AATPP and MATPP were estimated from the relation between the concentrations and decay rates (Figure 4). The initiation rate constant for AATPP²³ was $(1.3 \pm 0.3) \times 10^6 s^{-1} M^{-1}$ and for MATPP was $(0.54 \pm 0.5) \times 10^6 s^{-1} M^{-1}$. The rate constant of MATPP was two orders of magnitude smaller than that of *N*-phMA ($(1.38 \pm 0.01) \times 10^8 s^{-1} M^{-1}$). That of AATPP was one order of magnitude smaller than that of *N*-phAA ($(4.2 \pm 0.1) \times 10^7 s^{-1} M^{-1}$). The steric bulkiness of TPP moiety decreases the resonance stabilization of the vinyl group in AATPP and MATPP, and as a result, the rate constants of TPP monomers are much smaller than those of *N*-phAA and *N*-phMA. The same was noted for VTPP and styrene.⁹ These results are consistent with the small Q values for TPP monomers obtained from the copolymerization of TPP monomers with styrene.

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REFERENCES

1. Y. Tamaki, Master Thesis, Osaka University (1981).
2. M. Kamachi, Y. Tamaki, Y. Morishima, S. Nozakura, W. Mori, and M. Kishita, *Polym. J.*, **14**, 363 (1982).
3. M. Kamachi, H. Enomoto, M. Shibasaka, W. Mori, and M. Kishita, *Polym. J.*, **18**, 439 (1986).
4. M. Kamachi, H. Sugimoto, A. Kajiwara, A. Harada, Y. Morishima, W. Mori, N. Omac, M. Nakano, M. Sorai, T. Kobayashi, and K. Amaya, *Mol. Cryst. Liq. Cryst.*, **232**, 53 (1993).
5. M. Kamachi, H. Akimoto, W. Mori, and M. Kishita, *Polym. J.*, **16**, 23 (1984).
6. S. Nozakura and M. Kamachi, *Makromol. Chem. Suppl.*, **12**, 255 (1985).
7. M. Kamachi, H. Akimoto, and S. Nozakura, *J. Polym. Sci., Polym. Lett. Ed.*, **21**, 693 (1983).
8. M. Kamachi, X. S. Cheng, T. Kida, A. Kajiwara, M. Shibasaka, and S. Nagata, *Macromolecules*, **20**, 2665 (1987).
9. A. Kajiwara, K. Aramata, M. Kamachi, and K. Sumi, *Polym. J.*, **26**, 215, (1994).
10. M. Kamachi, M. Shibasaka, A. Kajiwara, W. Mori, and M. Kishita, *Bull. Chem. Soc. Jpn.*, **62**, 2465 (1989).
11. M. Kamachi, X. S. Cheng, H. Aota, W. Mori, and M. Kishita, *Chem. Lett.*, 2231 (1987).
12. M. Kamachi, X. S. Cheng, and S. Nozakura, Fifth Rare Earth Symposium (Tokyo, 1987), Preprints, 2B05.
13. W. Lautch, W. Broser, W. Rothkegel, W. Biedermann, U. Doering, and H. Zoschke, *J. Polym. Sci.*, **8**, 191 (1952).
14. W. Lautch, W. Broser, W. Biedermann, and H. Gnichel, *J. Polym. Sci.*, **17**, 479 (1955).
15. M. Kamogawa, *J. Polym. Sci. B*, **10**, 711 (1972).
16. M. Kamogawa, *J. Polym. Sci., Polym. Chem. Ed.*, **12**, 2317 (1972).
17. A. Kajiwara, K. Aramata, S. Nomura, Y. Morishima, and M. Kamachi, *Chem. Lett.*, 95, (1992).
18. W. C. Wooten, R. B. Blanton, and H. W. Coover, Jr., *J. Polym. Sci.*, **25**, 403 (1957).
19. D. D. Perrin and W. L. F. Armarego, "Purification of Laboratory Chemicals," 3rd ed., Pergamon Press, Oxford, England, 1988.
20. E. Hasegawa, J. Nemoto, T. Kanayama, and E. Tsuchida, *Eur. Polym. J.*, **14**, 123 (1978).
21. G-X Wan, K. Shigehara, E. Tsuchida, and F. C. Anson, *J. Electroanal. Chem.*, **179**, 239 (1984).
22. K. Bulter, P. R. Thomas, and G. J. Tyler, *J. Polym. Sci.*, **48**, 357 (1960).
23. A. Kajiwara, Y. Konishi, Y. Morishima, W. Schnabel, K. Kuwata, and M. Kamachi, *Macromolecules*, **26**, 1656 (1993).
24. L. J. Belami, "The Infrared Spectra of Complex Molecules," Methuen, London, 1985, p 179.
25. I. W. White, "Porphyrins," M. Dolphin, Ed., Vol. 4, Academic Press, New York, N.Y., 1973, pp 306—325.
26. M. Goutermann, D. Holten, and D. Libermann, *Chem. Phys.*, **25**, 139 (1977).
27. J. Brandrup and E. H. Immergut, Ed., "Polymer Handbook," 3rd ed, John-Wiley & Sons, New York, N.Y., 1989, pp II/268—269.