

Vinyl Monomers Bearing Chromophore Moieties and Their Polymers. IX. Initiation and Photochemical Behavior of Water and Liposoluble Acrylic Monomers Having Pyrimidinyl Moiety and Their Polymers

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ABSTRACT: Two acrylic monomers bearing a pyrimidinyl moiety, *N*-acryloyl-*N'*-2-pyrimidinylpiperazine (APMP) and *N*-methacryloyl-*N'*-2-pyrimidinylpiperazine (MPMP), are prepared by reactions of *N*-2-pyrimidinylpiperazine with corresponding acryloyl chlorides in the presence of triethylamine. APMP and MPMP can be polymerized either by using radical initiators such as azobisisobutyronitrile or potassium persulfate (KPS) or by UV light irradiation without any sensitizer. APMP, MPMP, and their polymers are water soluble and liposoluble. They can act as sensitizers to initiate the photopolymerizations of acrylonitrile (AN) in DMF and acrylamide (AAM) or *N*-acryloylmorpholine (AMPL) in an aqueous medium. They can also act as one component of a redox initiation system by combining with KPS to initiate the polymerization of AAM in an aqueous medium, and a superhigh molecular weight up to 10^6 – 10^7 for P(AAM) or 10^5 – 10^6 for P(AMPL) is obtained. The above polymerizations are pursued kinetically. The mechanism of the photopolymerizations initiated by MPMP or P(MPMP) are confirmed by an electron spin resonance study. By the fluorescent analysis of PAN and P(AAM) initiated by MPMP, APMP, or their polymers we confirm that they not only initiate the polymerization but also enter the polymer chains. The fluorescence spectra of MPMP, APMP, and their polymers are recorded. A fluorescence structural self-quenching effect is also observed. The fluorescence of P(MPMP) can be quenched by adding electron-deficient unsaturated compounds such as methacrylonitrile, AN, fumaronitrile, tetracyanoethylene, methyl acrylate, and methyl methacrylate and the correlation between the Stern–Volmer constants and the electron deficiency of the quenchers is described. The fluorescence quenching of P(MPMP) by a water-soluble C₆₀ derivative is also demonstrated. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 76: 19–28, 2000

Key words: *N*-acryloyl-*N'*-2-pyrimidinylpiperazine; *N*-methacryloyl-*N'*-2-pyrimidinylpiperazine; fluorescence structural self-quenching effect; polymerizability; water soluble sensitizers; water-soluble C₆₀

INTRODUCTION

We reported on the photochemical and initiation behavior of acrylic monomers bearing electron-

donating chromophore moieties: 4-(*N,N*-dimethylamino)benzyl methacrylate,¹ *N*-(*N',N'*-dimethylaminophenyl)acrylamides,² *N*-acryloyl-*N'*-phenylpiperazines (APP),³ *N*-(4-dimethylaminophenyl) maleimide, *N*-(4-dimethylaminophenyl) itaconimide,⁴ *N*-acryloylphenothiazines,⁵ and their polymers. The fluorescence intensities of these monomers were found to always be much lower than those of their corresponding polymers at the

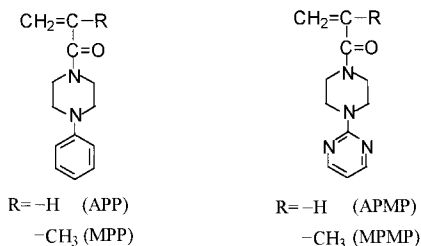
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same chromophore concentration. This may be ascribed to the inter- or intramolecular charge transfer interaction between the coexisting electron-accepting acrylic carbon-carbon double bond and the electron-donating chromophore moiety upon UV light irradiation. This phenomenon is termed the fluorescence structural self-quenching effect (SSQE) to distinguish it from the well-known fluorescence concentrational SQE. Electron-deficient unsaturated compounds such as acrylonitrile (AN) and methyl acrylate (MA) can quench the fluorescence of the above polymers in solution, but their corresponding saturated compounds such as propionitrile and methyl propionate cannot, verifying that the coexisting acrylic carbon-carbon double bond does play an important role in SSQE. The above chromophore-containing acrylic monomers not only sensitize their own photopolymerization without any other sensitizers but also sensitize the photopolymerization of some other electron-deficient monomers such as AN and methyl methacrylate (MMA), which have no chromophore moieties.³ They can also act as one component of a redox initiation system to initiate the thermal polymerization of some other vinyl monomers such as MMA and AN in organic solvents.^{3,4}

Because the pyrimidine ring occurs in the prosthetic groups of some enzymes and sulfa drugs, the understanding of the character of the pyrimidine ring in polymer chemistry, especially the initiation and photochemical behavior of acrylic monomers bearing a pyrimidinyl moiety and their polymers, is of interest. In this study two acrylic monomers bearing a pyrimidinyl moiety [*N*-acryloyl-*N'*-2-pyrimidinylpiperazine (APMP) and *N*-methacryloyl-*N'*-2-pyrimidinyl piperazine (MPMP)] and their polymers were synthesized. The structures of these monomers are similar to those of APP and *N*-methacryloyl-*N'*-phenylpiperazines (MPP), which were previously reported.³ The structural differences between them are mainly in the benzene ring and pyrimidine ring; the latter is a six-membered heterocyclic ring containing two nitrogen atoms in the 1,3 position whose electron-donating ability affects the fluorescence behavior of MPMP and APMP.



Because MPMP and APMP are water soluble, we sought to develop a novel kind of polymerizable photosensitizer that dissolves in both an aqueous medium and organic solvents. Furthermore, we were also concerned whether the SSQE occurs in these monomers (MPMP, APMP).

EXPERIMENTAL

Materials

N-2-Pyrimidinylpiperazine dihydrochloride (Aldrich) was used as received. *N*-Acryloylmorpholine (AMPL) was prepared by a reaction of morpholine with acryloyl chloride in the presence of triethylamine. The other reagents and solvents were purified by distillation or recrystallization prior to use.

Monomer Synthesis

MPMP

To a stirred solution of 3.1 g (13 mmol) of *N*-2-pyrimidinylpiperazine dihydrochloride and 2.8 g (28 mmol) of triethylamine in 40 mL of chloroform a solution of 2.9 g (29 mmol) of methacryloyl chloride in 20 mL of chloroform was added dropwise at 0–5°C. The reaction was kept at room temperature overnight. After removal of the precipitate the solution was washed with diluted potassium carbonate aqueous solution and dried over anhydrous potassium sulfate, and the solvent was evaporated. The residue was recrystallized with cyclohexane; 2.3 g of MPMP was obtained (80%). It was a hygroscopic white needle with a melting point of 111–112°C. ¹H-NMR (ppm, TMS, CDCl₃): 8.33–8.34 (d, 2H of 4, 6 position of pyrimidine ring), 6.54–6.58 (t, 1H of 5 position in pyrimidine ring), 5.02–5.26 (d, 2H, H₂C=C), 3.4–4.0 (m, 8H of piperazine ring), 1.86–2.06 [s, 3H, =C(CH₃)—]. IR(KBr, cm⁻¹): 690, 780, 1420, 1480, 1580 (pyrimidine ring); 1240 (*N,N*-dialkylamino-group); 1630 (C=C); 1750 (acrylic C=O). MS (EI): 232 (*m/e*).

ANAL. Calcd: C, 62.07%; H, 6.89%; N, 24.13%; Found: C, 62.03%; H, 6.85%; N, 24.12%.

APMP

The procedure for the synthesis of APMP was the same as for MPMP. The yield was about 65%. It is also a hygroscopic white needle with a melting point of 95–96°C. ¹H-NMR (ppm, TMS, CDCl₃): 8.33–8.34 (d, 2H of 4, 6 position of pyrimidine ring), 6.53–6.58 (t, 1H of 5 position in pyrimidine

Table I Absorption Peaks (λ_{\max}) and Extinction Coefficients (ϵ) of MPMP, APMP, and Their Polymers in Different Solvents

	λ_{\max} ($\epsilon \times 10^{-4}$) (nm)		
	H ₂ O	CHCl ₃	Cyclohexane
MPMP	250 (8.40), 310 (0.73)	250 (1.27), 310 (0.11)	250 (1.70), 305 (0.13)
P(MPMP)	245 (1.27), 308 (0.20)	245 (1.63), 305 (0.11)	
APMP	242 (2.29), 310 (0.20)	245 (2.13), 310 (0.20)	245 (1.53), 305 (0.13)
P(APMP)	237 (1.36), 310 (0.19)	245 (3.40), 302 (0.80)	

ring), 5.34–5.48 (m, 3H, H₂C=CH—), 3.21–4.15 (m, 8H of piperazine ring). IR (KBr, cm⁻¹): 700, 780, 1400, 1480, 1570 (pyrimidine ring); 1630 (amino group); 1640 (acrylic C=C); 1730 (acrylic carbonyl group). MS (EI): 218 (*m/e*).

ANAL. Calcd: C, 58.41%; H, 6.19%; N, 28.32%. Found: C, 58.34%; H, 6.21%; N, 28.26%.

Preparation of Water-Soluble C₆₀ (ws-C₆₀)

A mixture of 20 mg of C₆₀ and 20 mL of 2-aminoethanol was heated at 50°C with vigorous stirring till the solution became completely clear. Then the excess 2-aminoethanol was removed under reduced pressure. The residue was dissolved in a small amount of water and then poured into a large amount of acetone. A water-soluble adduct of C₆₀ with 2-aminoethanol, —H—NHCH₂CH₂OH, was obtained. The *n* value of the adduct was estimated to be 12, which was detected by the acylating titration method with acetic anhydride.

Polymerization of MPMP and APMP

The polymerizations of MPMP and APMP were carried out in chloroform at 60°C using AIBN as an initiator. The polymers were water soluble and were purified by dialysis against deionized water until no monomer appeared in the dialyzed water as detected by UV analysis. The polymers were characterized by the disappearance of the carbon–carbon double bond absorption at 1630 cm⁻¹ of the monomers in the IR spectra.

Kinetic Study of Polymerization of AN, Acrylamide (AAm), and AMPL

An approximate 3-mL volume dilatometer made of hard glass was used in a thermostat to pursue the polymerization. A 300-W high pressure mercury lamp was used as the light source and filtered by potassium chromate solution. The molecular weights of P(AAm) and P(AMPL) were deter-

mined by viscosity measurement. The following equations were used for the calculation for P(AAm),

$$[\eta] = 3.73 \times 10^{-4} M^{0.66}$$

(H₂O, 25°C; ref. 6) and for P(AMPL),

$$[\eta] = 6.40 \times 10^{-2} M^{0.68}$$

(H₂O, 20°C; ref. 7).

Apparatus and Spectral Measurement

The absorption spectra were recorded on a Shimadzu model UV-250 spectrophotometer at room temperature. The fluorescence spectra of the sample in solution, which was purged with nitrogen for 10 min prior to recording, were recorded on a Hitachi model M-850 fluorescence spectrophotometer at room temperature. The slit widths of the monochromometers were both 10 nm. The solvents and reagents used were purified to eliminate the interfering impurities for fluorescence. The electron spin resonance (ESR) spectrum was recorded on a Bruker ER-200D SRC ESR spectrometer using a 180-W medium pressure mercury lamp as a light source.

RESULTS AND DISCUSSION

MPMP and APMP both dissolve in water and common organic solvents. Table I lists the absorption peaks (λ_{\max}) and the corresponding extinction coefficients (ϵ) of APMP, MPMP, and their polymers in different solvents. MPMP and APMP showed similar absorption peaks in organic solvents and water. The strong absorption of these monomers at 305–310 nm in organic solvents and water makes them good candidates as sensitizers

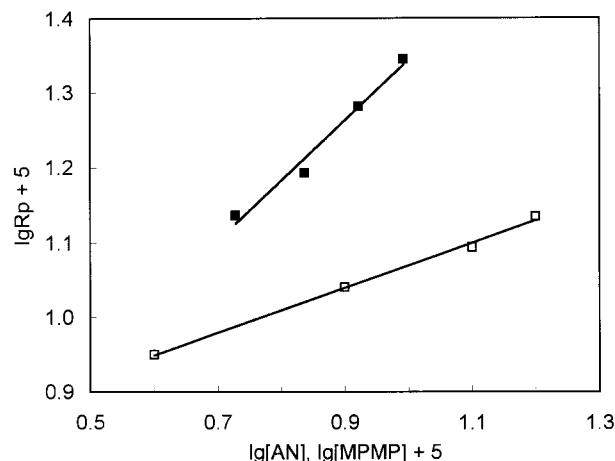


Figure 1 The dependence of the R_p on the AN and MPMP concentrations for the photopolymerization of AN sensitized by MPMP in DMF at 25°C: (■) $\lg R_p$ vs. $\lg [AN]$, $[MPMP] = 1.59 \times 10^{-4}$ mol/L; (□) $\lg R_p$ vs. $\lg [MPMP]$, $[AN] = 3.8$ mol/L.

for photopolymerizations of liposoluble or water-soluble vinyl monomers.

Initiation Behavior of MPMP and Its Polymer P(MPMP)

MPMP and P(MPMP) Act as Sensitizers for Photopolymerization of AN in DMF

To pursue the photopolymerization of AN in a homogeneous system, the photopolymerization of AN sensitized by MPMP or P(MPMP) was carried out in DMF. By changing one of the concentrations of AN and MPMP or P(MPMP), the photopolymerization rates (R_p) were obtained as shown in Figures 1 and 2. For the photopolymerization of AN sensitized by MPMP the R_p is proportional to the 0.35th power of the MPMP concentration and the 0.85th power of the AN concentration. The overall activation energy (E_a) of the polymerization was obtained from the slope of the straight line of the $\lg R_p$ versus $1/T$ plot and calculated by the Arrhenius equation to be 4.71 kcal/mol. In the AN photopolymerization sensitized by P(MPMP) the R_p is proportional to the 0.30th power of the P(MPMP) concentration and the 1.0th power of the AN concentration. The E_a was 4.58 kcal/mol. Thus, the rate equations can be expressed as follows:

$$R_p \propto [AN]^{0.85}[MPMP]^{0.35}, \quad E_a = 4.71 \text{ kcal/mol}$$

$$R_p \propto [AN]^{1.0}[P(MPMP)]^{0.30}, \quad E_a = 4.58 \text{ kcal/mol}$$

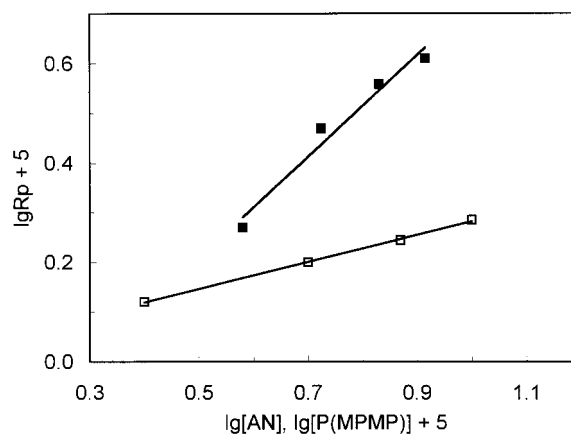


Figure 2 The dependence of the R_p on the AN and P(MPMP) concentrations for the photopolymerization of AN sensitized by P(MPMP) in DMF at 25°C: (■) $\lg R_p$ vs. $\lg [AN]$, $[P(MPMP)] = 1.01 \times 10^{-4}$ mol/L; (□) $\lg R_p$ vs. $\lg [P(MPMP)]$, $[AN] = 3.8$ mol/L.

The obtained E_a values are close to that of the ordinary photopolymerization of vinyl monomers.

MPMP Acts as Water-Soluble Sensitizer for Photopolymerization of AAm and AMPL in Aqueous Medium

Shown in Figures 3 and 4 are the plots of $\lg R_p$ versus $\lg [AAm]$ or $\lg [MPMP]$ and $\lg R_p$ versus $[AMPL]$ or $[MPMP]$, respectively. According to the above method, the rate equations of the photopolymerization of AAm and AMPL are expressed as follows:

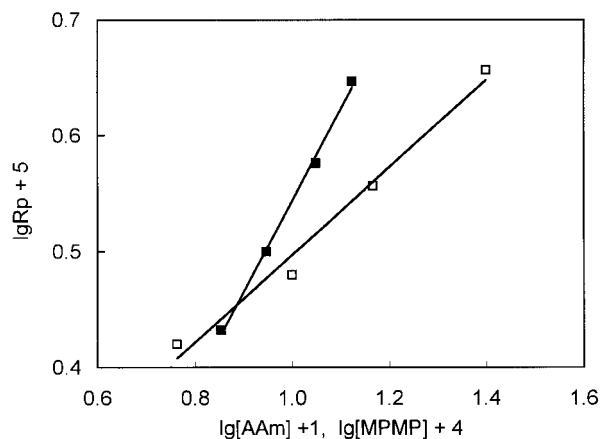


Figure 3 The dependence of the R_p on the AAm and MPMP concentrations for the photopolymerization of AAm sensitized by MPMP in H_2O at 30°C: (■) $\lg R_p$ vs. $\lg [AAm]$, $[MPMP] = 1.0 \times 10^{-4}$ mol/L; (□) $\lg R_p$ vs. $\lg [MPMP]$, $[AAm] = 1.0$ mol/L.

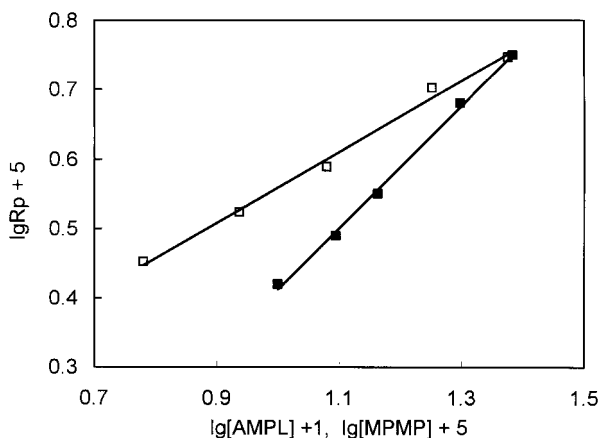
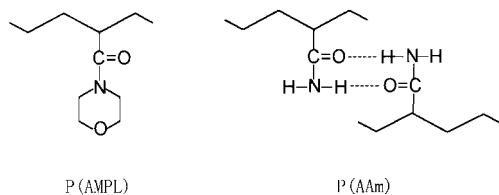


Figure 4 The dependence of the R_p on the AMPL and MPMP concentrations for the photopolymerization of AMPL sensitized by MPMP in H_2O at $25^\circ C$: (■) $\lg R_p$ vs. $\lg [AMPL]$, $[MPMP] = 1.66 \times 10^{-4}$ mol/L; (□) $\lg R_p$ vs. $\lg [MPMP]$, $[AMPL] = 2.0$ mol/L.

$$R_p \propto [AAm]^{0.88}[MPMP]^{0.36}, \quad E_a = 5.02 \text{ kcal/mol}$$

$$R_p \propto [AMPL]^{1.0}[MPMP]^{0.45}, \quad E_a = 5.07 \text{ kcal/mol}$$

The influence of the photopolymerization conditions on the molecular weights of P(AAm) and P(AMPL) is listed in Table II. High molecular weights of up to 10^6 for P(AAm) or 10^5 for P(AMPL) were obtained. The molecular weights decreased with the increase of MPMP concentration and the polymerization temperature and increased with the increase of the concentrations of the monomers. Note that the molecular weight of P(AMPL) is lower than that of P(AAm), even though the polymerizations were performed under the same conditions. This may be attributed to the formation of an interchain hydrogen bond of P(AAm), leading to the increase of the inherent viscosity of the polymer in solution. On the other hand, P(AMPL) does not have a hydrogen atom directly connecting with the nitrogen atom of amide group, which does not cause the formation of an interchain hydrogen bond as shown in the following structures:



MPMP Acts as One of Components of Redox Initiation System

MPMP has a 2-(*N,N*-dialkylamino)pyrimidine moiety. It can combine with water-soluble peroxy-

Table II Influence of Photopolymerization Conditions on Molecular Weights of P(AAm) and P(AMPL) Sensitized by MPMP

[AAm] (mol/L)	[AMPL] (mol/L)	[MPMP] $\times 10^4$ (mol/L)	Temp. ($^\circ C$)	$M_n \times 10^{-6}$
		1.0	30.0	0.28
		1.0	30.0	0.23
		1.0	30.0	0.21
		1.0	30.0	0.15
		0.5	30.0	0.09
		1.0	30.0	0.23
		1.5	30.0	0.37
		2.0	30.0	0.42
		1.0	25.0	0.31
		1.0	30.0	0.23
		1.0	35.0	0.19
		1.0	40.0	0.15
1.0		0.5	30.0	4.97
1.0		1.0	30.0	3.65
1.0		1.5	30.0	2.84
1.0		2.0	30.0	2.47
0.5		1.0	30.0	2.30
1.0		1.0	30.0	3.65
1.5		1.0	30.0	4.52
2.0		1.0	30.0	5.44
1.0		1.0	25.0	4.89
1.0		1.0	30.0	3.65
1.0		1.0	35.0	2.97
1.0		1.0	40.0	2.66

ides such as potassium persulfate (KPS) to form water-soluble redox initiation systems to initiate the aqueous polymerization of water-soluble

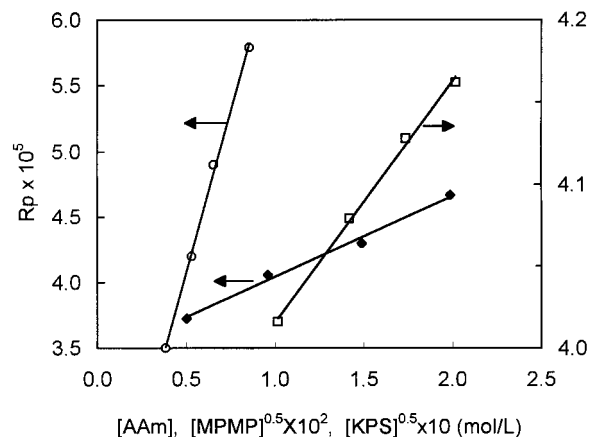


Figure 5 The dependence of the R_p on the AAm, KPS, and MPMP concentrations for the polymerization of AAm initiated by the MPMP-KPS redox system in H_2O at $30^\circ C$: (■) R_p vs. $[AAm]$, $[MPMP] = 1.66 \times 10^{-4}$ mol/L; (□) $\lg R_p$ vs. $\lg [MPMP]$, $[AMPL] = 2.0$ mol/L.

Table III E_a Values of AAm Aqueous Polymerization Initiated by Polymerizable Tertiary Amines Combining with KPS

Polymerizable Amines	Chemical Structure	E_a (Kcal/mol)	Ref
N,N-dimethylaminoethyl methacrylate (DMAEMA)		9.2	8
N-(N',N'-dimethylaminomethyl) methacrylamide (DMAMMA)		8.7	8
N-morpholinylisopropanyl methacrylate (MPIPMA)		11.1	9
N-morpholinylethyl methacrylate (MPEMA)		13.6	9
N-morpholinylmethyl acrylate (MMMA)		13.4 ^a	10
N-morpholinylmethyl acrylamide (MMAA)		9.2 ^a	10
N-methacryloyl-N'-2-pyrimidinylpiperazine (MPMP)		10.1	ER

ER, experimental result.

^a Combined with lauloyl peroxide.

monomers such as AAm, AMPL, and so forth. Figure 5 shows the relationships between R_p and $[AAm]$, $[MPMP]^{0.5}$, or $[KPS]^{0.5}$. The good linearity of the plots reveals that the R_p is proportional to the 0.5th power of $[MPMP]$ and $[KPS]$, and the 1.0th power of $[AAm]$. Thus, the rate equation can be presented as follows:

$$R_p = K_p [KPS]^{0.5} [MPMP]^{0.5} [AAm]^{1.0}$$

The overall activation energy for the polymerization was obtained from the slope of $\lg R_p$ versus the $1/T$ plot and was calculated by the Arrhenius equation to be 10.1 kcal/mol. This is close to that of the ordinary redox system. It is also close to those of the aqueous polymerizations of AAm initiated by redox initiation systems consisting of polymerizable tertiary amines and KPS as summarized in Table III.⁸⁻¹⁰ The influence of the

polymerization condition on the molecular weights of P(AAm) and P(AMPL) initiated by the MPMP-KPS initiation system was also explored. The results are listed in Table IV. A superhigh molecular weight up to 10^7 for P(AAm) or 10^6 for P(AMPL) was obtained. The molecular weights of the polymers increased with increasing concentrations of AAm and AMPL, as well as with decreasing the polymerization temperature. The result is similar to that of the photopolymerization of AAm or AMPL sensitized by MPMP as described above.

Fluorescent Analysis of Polymers Sensitized by MPMP and P(MPMP)

P(MPMP) and the copolymers of MPMP with other vinyl monomers such as MMA, AN, and AAm display fluorescence peaks at 400 nm with

Table IV Influence of Polymerization Condition on Molecular Weights of P(AAm) and P(AMPL) Initiated by MPMP-KPS System

[AAm] (mol/L)	[AMPL] (mol/L)	[MPMP] $\times 10^4$ (mol/L)	[KPS] $\times 10^3$ (mol/L)	Temp. (°C)	$M_\eta \times 10^{-7}$
	1.00	2.40	1.00	40.0	0.136
	1.00	4.80	1.00	40.0	0.122
	1.00	7.20	1.00	40.0	0.106
	1.00	9.60	1.00	40.0	0.092
	0.50	4.80	1.00	40.0	0.083
	1.00	4.80	1.00	40.0	0.122
	2.00	4.80	1.00	40.0	0.199
	1.00	4.80	1.00	30.0	0.150
	1.00	4.80	1.00	40.0	0.122
	1.00	4.80	1.00	50.0	0.074
1.00		2.40	1.00	40.0	1.26
1.00		4.80	1.00	40.0	1.14
1.00		7.20	1.00	40.0	0.73
1.00		9.60	1.00	40.0	0.55
0.50		4.80	1.00	40.0	0.92
1.00		4.80	1.00	40.0	1.14
2.00		4.80	1.00	40.0	1.43
1.00		4.80	1.00	30.0	1.21
1.00		4.80	1.00	40.0	1.14
1.00		4.80	1.00	50.0	0.74

an exciting wavelength at 340 nm as shown in Figure 6. Because MPMP is a polymerizable photosensitizer, it is incorporated into the polymer chains and the resulting polymers show the same fluorescence spectrum in solution as P(MPMP) does. This was proved by fluorescent analysis of PAN sensitized by MPMP and P(MPMP). As shown in Figure 7, after removal of the homopoly-

mer P(MPMP) by several extractions with chloroform till no fluorescence of P(MPMP) appears in the extracting solution, the fluorescence intensity at 400 nm remains unchanged for the PAN sensitized by MPMP or P(MPMP), which indicates that MPMP or P(MPMP) not only acts as a photosensitizer to initiate the polymerization but also enters the PAN chains.

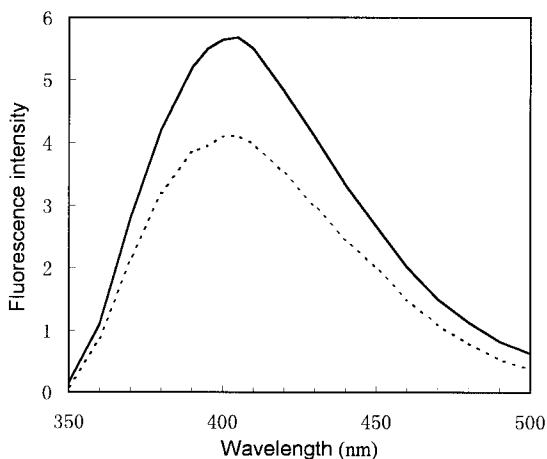


Figure 6 The fluorescence emission spectra of MPMP and P(MPMP) in DMF at the same chromophore concentration of 2.5×10^{-4} mol/L; $\lambda_{\text{ex}} = 340$ nm: (—) P(MPMP); (---) MPMP.

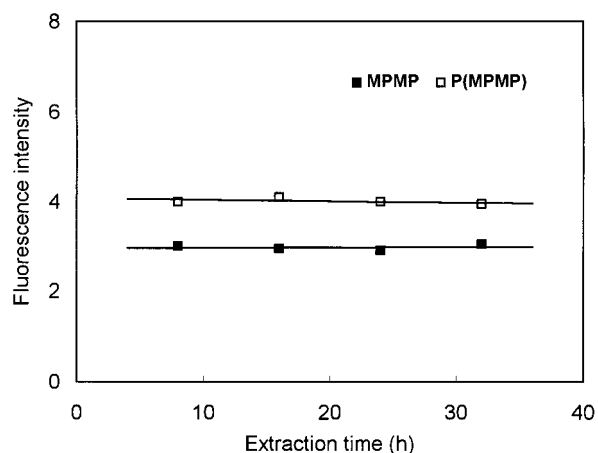


Figure 7 The relationship between the extraction time and relative intensity of PAN sensitized by MPMP and P(MPMP); solvent, DMF; $\lambda_{\text{ex}} = 340$ nm; $\lambda_{\text{em}} = 400$ nm.

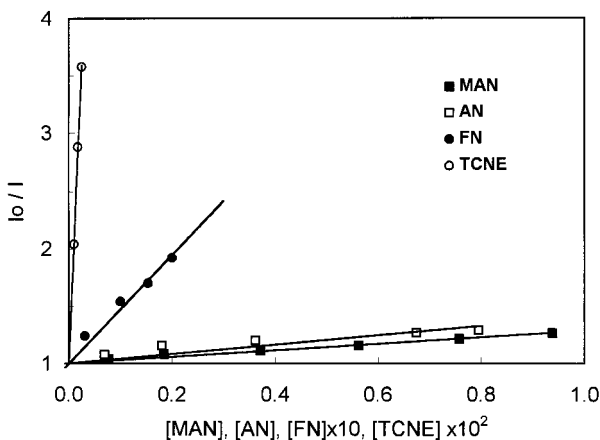


Figure 8 The Stern–Volmer plots for the fluorescence quenching of P(MPMP) by TCNE, FN, AN, and MAN. $[P(MPMP)] = 2.2 \times 10^{-4}$ mol/L, solvent, DMF; $\lambda_{\text{ex}} = 340$ nm; $\lambda_{\text{em}} = 400$ nm.

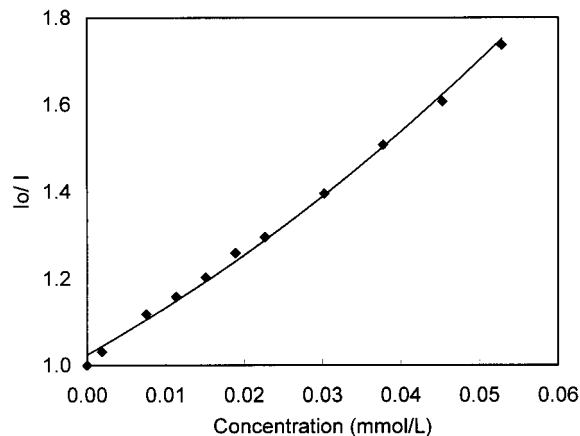


Figure 9 The Stern–Volmer plot for the fluorescence quenching of P(MPMP) by ws- C_{60} . $[P(MPMP)] = 2.2 \times 10^{-4}$ mol/L; solvent, water; $\lambda_{\text{ex}} = 340$ nm; $\lambda_{\text{em}} = 400$ nm.

Fluorescence Behavior of MPMP and P(MPMP)

We reported that the fluorescence intensities of a series of acrylic monomers bearing electron-donating chromophore moieties are always much lower than those of their corresponding polymers at the same chromophore concentration. A similar phenomenon was also observed for MPMP and P(MPMP). Figure 6 shows the fluorescence intensities of MPMP and P(MPMP) at the same chromophore concentration. The fluorescence intensity of MPMP is lower than that of its polymer P(MPMP), which indicates that a fluorescence SSQE occurs for MPMP. In order to verify that the electron-deficient carbon–carbon double bond does play an important role in the SSQE, the unsaturated nitriles methacrylonitrile (MAN), AN, fumaronitrile (FN), and tetracyanoethylene (TCNE), and the unsaturated esters MA and MMA were chosen to quench the fluorescence of P(MPMP) in the DMF solution. The results show that all the electron-deficient unsaturated compounds can quench the fluorescence of P(MPMP), but the corresponding saturated compounds such as propionitrile and methyl acetate do not. Figure 8 shows the Stern–Volmer plots of the fluores-

cence of P(MPMP) quenched by some of the above quenchers. The resulting Stern–Volmer constants are listed in Table V. It is obvious that the quenching ability of the quenchers is directly related to their electron deficiency represented by e . The larger the e value, the stronger the quenching ability of the quenchers. APMP and its polymer also display similar fluorescence properties.

It is reported that C_{60} can act as a powerful electron acceptor to quench the fluorescence of polymers having electron-donating chromophore moieties.¹¹ However, it is not clear whether the modified C_{60} does the same. The ws- C_{60} derivative modified by 2-aminoethanol (ws- C_{60}) was chosen as a quencher. Shown in Figure 9 is the Stern–Volmer plot of P(MPMP) quenched by ws- C_{60} . It can be seen that the fluorescence of P(MPMP) is strongly quenched by ws- C_{60} , which implies that the water-soluble C_{60} still possesses powerful electron-accepting ability. An upward deviation from the linearity of the Stern–Volmer plot indicates that a charge-transfer interaction between the fluorescent chromophore and ws- C_{60} may occur in the ground state and the excited state.

Table V Correlation between e Values and Stern–Volmer Constants

Quenchers	Nitriles				Esters	
	TCNE	FN	AN	MAN	MA	MMA
$K_q \tau$ (mol ⁻¹ L)	10.1×10^3	46.4	0.32	0.17	0.16	0.16
e Values	2.3	1.96	1.20	0.40	0.60	0.40

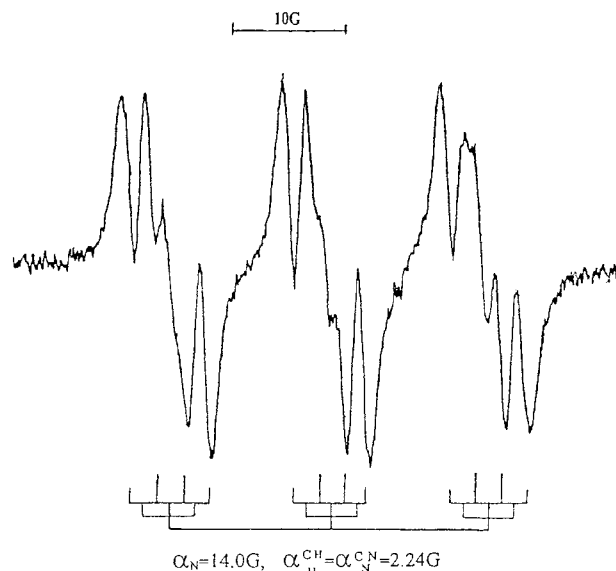
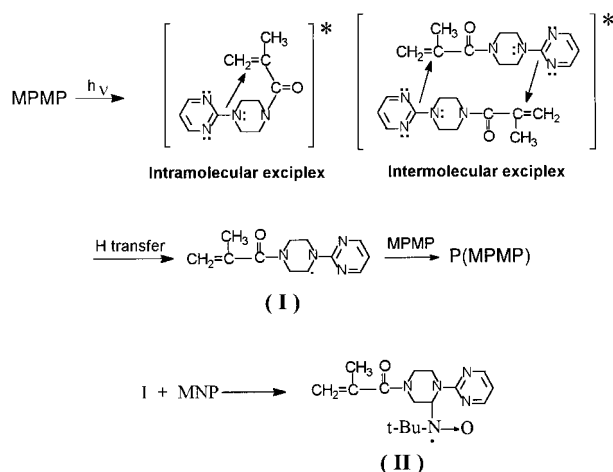


Figure 10 The ESR spectrum of MPMP and MNP in benzene irradiated by UV light. [MPMP] = 1.26×10^{-2} mol/L, [MNP] = 5.9×10^{-3} mol/L.

Mechanism of Vinyl Polymerizations Initiated by MPMP and P(MPMP)

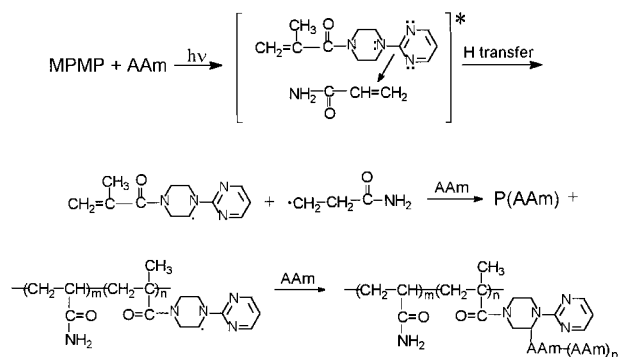
Because MPMP can be photopolymerized without any sensitizer upon UV light irradiation and it possesses an SSQE, the mechanism of the photopolymerization of MPMP itself is deduced as follows:



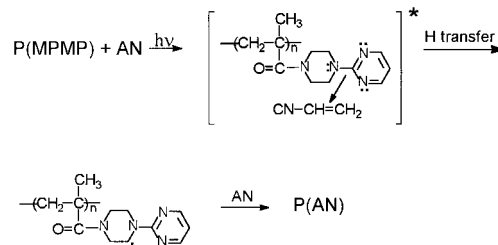
The above mechanism was also confirmed by the ESR study. Figure 10 shows the ESR spectrum of the free radical of MPMP trapped by 2-methyl-2-nitritopropane (MNP) (II) in benzene under UV light irradiation. From the spectrum it can be seen that the resulting radical of MPMP under UV light irradiation is (I) as schemed above.

Photopolymerization of AN and AAm Sensitized by MPMP

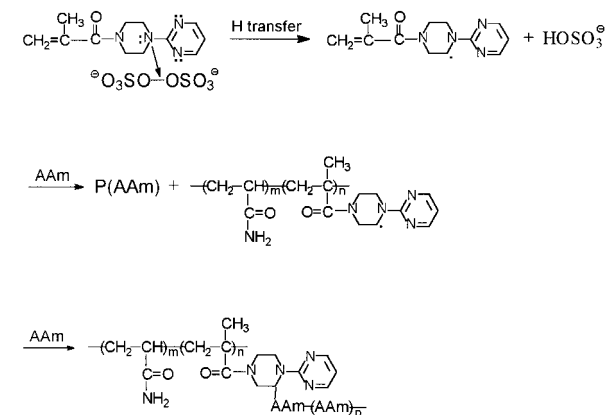
AN and AAm can be photopolymerized by sensitization of MPMP and P(MPMP) in DMF and an aqueous medium, respectively. The fluorescence of P(MPMP) can be quenched by electron-deficient monomers such as AN, and the sensitizers MPMP and P(MPMP) can be incorporated into the AN and AAm polymer chains. Considering AAm as an example, the mechanism would be tentatively deduced as follows:



Photopolymerization of AN Sensitized by P(MPMP)



Polymerization of AAm and AMPL Initiated by MPMP-KPS Initiation System



CONCLUSION

Two acrylic monomers bearing a pyrimidinyl moiety, APMP and MPMP, and their polymers were

prepared. The monomers and their polymers dissolve well in common organic solvents and in water. Thus, they can act as water-soluble sensitizers for the photopolymerization of water-soluble monomers. They can also act as one component of a redox initiation system combined with inorganic persulfate for the polymerization of water-soluble vinyl monomers such as AAm and AMPL in an aqueous medium.

APMP and MPMP can act as polymerizable photosensitizers: they not only initiate the polymerization of vinyl monomers such as AAm and AN, but also incorporate into the polymer chains. A superhigh molecular weight of 10^6 – 10^7 of P(AAm) or 10^5 – 10^6 of P(AMPL) was obtained by initiation of the MPMP-KPS redox system. The molecular weight of P(AMPL) was lower than that of P(AAm), even though the polymerizations were performed under the same conditions, which might be explained by the interaction of the PAAm chains via the hydrogen bond formation in the aqueous medium. The fluorescence intensities of MPMP and APMP were lower than those of their polymers at the same chromophore concentration, indicating that SSQE occurred for these two monomers. The fluorescence of these polymers can be quenched by electron-deficient compounds. We revealed that the higher the electron deficiency of the quencher, the larger the Stern–

Volmer constants. Furthermore, the fluorescence of P(MPMP) is strongly quenched by a water-soluble C_{60} derivative in an aqueous medium. This means that the modified C_{60} still possesses powerful electron-accepting ability.

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