Synthesis and Photochemical Behavior of 2-(N-acridonyl)ethyl Methacrylate and Its Polymer

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SYNOPSIS

A polymerizable photosensitizer, 2-(N-acridonyl)ethyl methacrylate (AEMA), containing both aromatic ketone and aromatic tertiary amine moieties in the same molecule, was prepared by reaction of N-hydroxyethyl acridone (HEA) and methacryloyl chloride in the presence of triethylamine (TEA). HEA was obtained by reaction of acridone with ethylene carbonate. The photochemical behavior including photoinitiation and fluorescence properties of AEMA and its polymer P(AEMA) were studied. It was found that the photoinitiation efficiency of monomeric AEMA is lower than that of its polymer for the photopolymerization of acrylonitrile (AN) in DMF. By the kinetic study and the analysis of recorded electron spin resonance spectra of the photoinitiation systems of AEMA or AEMA-dimethylaminoethyl methacrylate (DMAEMA) trapped by 2-methyl-2-nitritopropane (MNP), the mechanism is deduced to be similar to that of the benzophenone-TEA system. The recorded fluorescence spectra show that AEMA and P(AEMA) possess a strong fluorescence emission peak at 410 and 439 nm, respectively. The concentration self-quenching effect was observed with maximum intensities at a concentration of 8.6×10^{-5} mol/L in DMF for both AEMA and P(AEMA). Even though AEMA has a tertiary amino group and an electron-deficient acrylic double bond in the same molecule, it did not display structural self-quenching effect as we reported previously. This may be due to the two benzene rings in acridone that lessen the electron-donating ability of the N atom. The fluorescence quenching of AEMA and P(AEMA) by electron-donating and electron-accepting compounds was also investigated. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

With the widening applications of photosensitive polymers, the innovation of novel photosensitizers, especially polymeric or polymerizable sensitizers, becomes feasibly scheduled in order to avoid or reduce the sweating or migration of sensitizers from the photocured polymers. As effective and popular photosensitizers, benzophenone and its derivatives combined with tertiary amines were extensively studied and widely utilized.[1-5] 4-Vinylbenzophenone, a polymerizable photosensitizer derived from benzophenone, was prepared and combined with compounds having tertiary amino group or some other hydrogen-donating group such as triethylamine

(TEA), N,N-dimethylaminoethyl methacrylate (DMAEMA), or tetrahydrofuran (THF) as photoredox systems for the vinyl photopolymerization.[6,7] We reported on the polymerizable photoredox system consisting of 4-methacryloxybenzophenone (MABP) and the polymerizable amine, DMAEMA, used for the photopolymerization of acrylonitrile (AN), in which both MABP and DMAEMA are incorporated into the poly-AN (PAN) chain.[8] In this article, a polymerizable acrylic monomer bearing acridone residue that contains aromatic ketone and aromatic tertiary amine moieties in the same molecule [i.e., 2-(N-acridonyl)ethyl methacrylate (AEMA)] was synthesized and the photochemical behavior including fluorescence and photoinitiation properties of AEMA and its polymer or combination with DMAEMA were studied to evaluate their initiation ability.

The fluorescence behavior of acrylic monomers bearing electron-donatable chromophores and their

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polymers is of interest. We found that the fluorescence intensities of these monomers are always dramatically lower than those of their polymers at the same chromophore concentration and termed this phenomenon as "structural self-quenching effect," which differs from the concentration self-quenching effect caused by concentration factor.[9] This effect may be due to the occurrence of intra- or intermolecular charge transfer upon UV irradiation between the coexisting electron-donating chromophore and electron-accepting carbon–carbon double bond in one molecule. As regards the fluorescence behavior of AEMA, a monomer having benzophenone moiety and aromatic tertiary amine moiety in the same molecule and its polymer have not been reported. Because it is well known that benzophenone does not display fluorescence at room temperature, the influence of the diphenylamino group in the acridone moiety of AEMA on its fluorescence behavior attracted much of our interest. Also, because Michler's ketone, a compound having both benzophenone moiety and a tertiary amino group in the same molecule, is a sensitizer that can increase the absorption intensity within a wide range of wavelengths,[10] it is of interest to study the photoinitiation behavior of AEMA and its polymer P(AEMA) alone or in combination with DMAEMA for vinyl photopolymerization.

EXPERIMENTAL

Materials

Acridone and ethylene carbonate were purchased from Aldrich Co. and Fluka Co., respectively, and used without any purification. Methacryloyl chloride and 2-methyl-2-nitritopropane (MNP) were prepared by the methods as described in the literature.[11] DMF was dried over CaH_2 and distilled under reduced pressure. DMAEMA was redistilled under reduced pressure in the presence of zinc powder before use. AN and the other fluorescence quenchers such as α-methacrylonitrile (MAN), methyl acrylate (MA), methyl methacrylate (MMA), fumaronitrile (FN), dimethyl fumarate (DF), tetracyanoethylene (TCNE), aniline (Ani), N,N-dimethylaniline (DMA), and p-N,N-dimethyltoluidine (DMT) were redistilled or recrystallized before use.

Preparation of AEMA

N-Hydroxyethyl acridone (HEA)

HEA was prepared by reaction of thoroughly mixed acridone and ethylene carbonate at 200°C for 1.5 h.

The crude product was purified by the chromatographic method. The purified product is a yellow crystal with mp 231–233°C.

AEMA

AEMA was prepared by reaction of HEA with methacryloyl chloride in the presence of TEA in chloroform. The crude product was purified by a silica-gel chromatographic column and then recrystallized from chloroform. The purified product is a yellowish crystal with mp 180–182°C.

ANAL. Calcd: C, 74.23%; H, 5.40%; N, 4.45%. Found: C, 74.30%; H, 5.54%; N, 4.56%. ^{1}H-NMR (δ, ppm, $CDCl_3$, 80 MHz): 1.92 (3H, s), 4.64–4.73 (4H, m), 5.61–6.10 (2H, t), 7.30–8.60 (8H, m). FTIR (KBr, cm^{-1}): 1720 (ester group), 1630 (alkene C=C stretch), 1450, 1500, 1600, 3100 (aromatic ring). MS (EI): Found: 307 (M+/e); calcd: 307.17 ($C_{19}H_{17}NO_3$).

Polymerization

The photopolymerization of AN in DMF was carried out in a dilatometer made of hard glass with a volume of approximately 6 mL at 30°C. The light source was a 300-W high-pressure mercury lamp, filtered with potassium chromate solution. The polymerization system was purged with nitrogen for 20 min. P(AEMA) was prepared by polymerization of
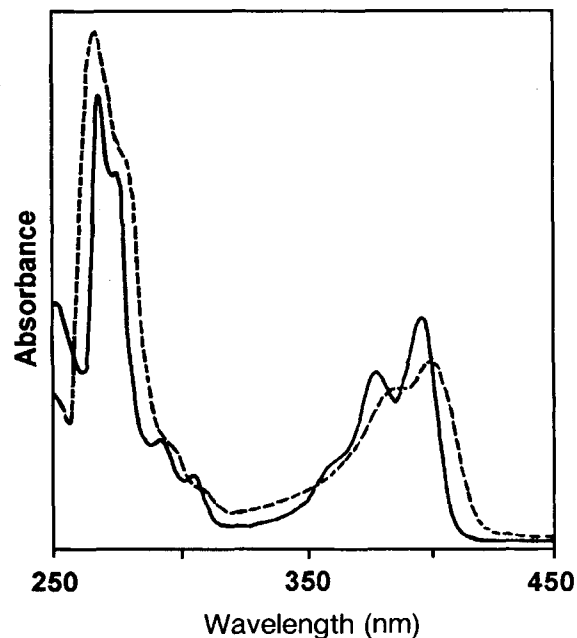

Figure 1 Absorption spectra of AEMA in (---) 1,1,2,2-tetrachloroethane and (—) DMF.

Table I Extinction Coefficients of AEMA in DMF and TCE

ε (mol^{-1} cm^{-1} L)	
DMF	TCE
2.3×10^4 ($\lambda_{max} = 268$ nm)	2.6×10^4 ($\lambda_{max} = 266$ nm)
1.2×10^4 ($\lambda_{max} = 397$ nm)	0.94×10^4 ($\lambda_{max} = 402$ nm)

AEMA in DMF, using AIBN as an initiator, and purified by reprecipitation from methanol.

Absorption, Fluorescence, and Electron Spin Resonance (ESR) Spectral Analysis

The absorption spectra were recorded on a Shimadzu model UV-250 spectrophotometer at room temperature. The fluorescence spectra of the sample solutions, purged with nitrogen for 10 min prior recording, were recorded on a Hitachi model M850 fluorescence spectrophotometer at room temperature. The slit widths of both monochromators were 10 nm. All the solvents used were purified to eliminate interfering impurities for fluorescence. ESR spectra were recorded on a Bruker ER-200D SRC ESR spectrometer, and the light source for the exciting of the photoinitiation systems was a 180-W medium-pressure mercury lamp.

RESULTS AND DISCUSSION

Initiation Behavior of AEMA and Its Polymer

Photopolymerization of AN Initiated by AEMA and P(AEMA)

The functional monomer AEMA is an MA with an acridone moiety that contains benzophenone and aromatic tertiary amine groups in the same molecule. The absorption spectra of AEMA in DMF and 1,1,2,2-tetrachloroethane (TCE) are shown in Figure 1, which are similar to that of acridone. The extinction coefficients of AEMA in DMF and in TCE are listed in Table I. Due to the aromatic ketone and tertiary amine groups in one molecule, AEMA itself may act as both a hydrogen acceptor and hydrogen donor, leading to the intermolecular hydrogen-abstracting reaction of the carbonyl group and the amino group. In order to evaluate the photoinitiation behavior of AEMA, the photopolymerization of AN in DMF with AEMA alone as a photoinitiator was conducted. Shown in Figure 2 are the relation-

ships between the photopolymerization rate (R_p) of AN and the concentrations of AN and AEMA, as well as the polymerization temperature. It is seen that the polymerization rate is proportional to the 0.96th power of the concentration of AN and the 0.74th power of the concentration of AEMA, respectively; the overall activation energy of the photopolymerization is 25.3 kJ/mol. The exponent of the concentration of AEMA is 0.74, which is larger than 0.5. This means that AEMA acts as not only a photooxidant but also as a photoreductant in the polymerization. This indicates that the initiation mechanism of AEMA is probably similar to that of a BP-TEA system; that is, the excited aromatic ketone group in the AEMA molecule draws the hydrogen atom from the methylene group linked to the nitrogen atom of another AEMA molecule, thus inducing the radical polymerization. This was confirmed by the ESR spectrum of the AEMA initiation system. Shown in Figure 3 is the ESR spectrum of excited AEMA trapped by 2-methyl-2-nitritopropane (MNP) in DMF. It reveals that the methylene radical ($>$N—$\dot{C}$H—CH$_2$—) is an active species for the photopolymerization.

P(AEMA) contains acridone as a side group. It can also act as a photoinitiator for the polymerization of vinyl monomers. To compare the initiation efficiency of AEMA and its polymer P(AEMA), the photopolymerizations of AN initiated by AEMA and P(AEMA) in the presence or absence of DMAEMA were carried out. Figure 4 shows the relationships between the conversion and the polymerization time in the absence of DMAEMA. There was no obvious difference between the two polymerization rates at
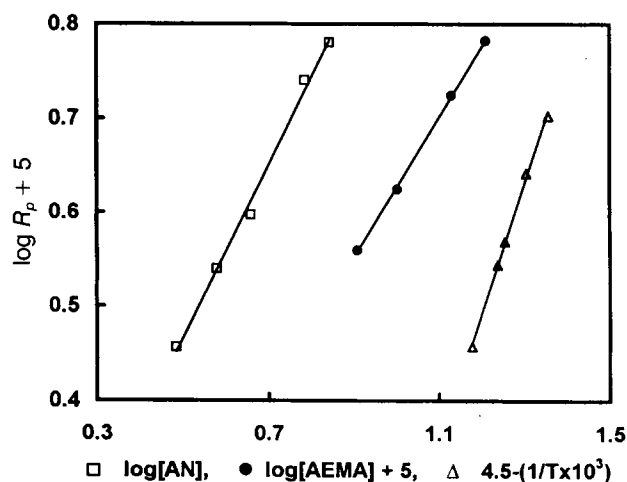
Figure 2 The relationships between R_p and the concentrations of AN, AEMA, and the polymerization temperature.
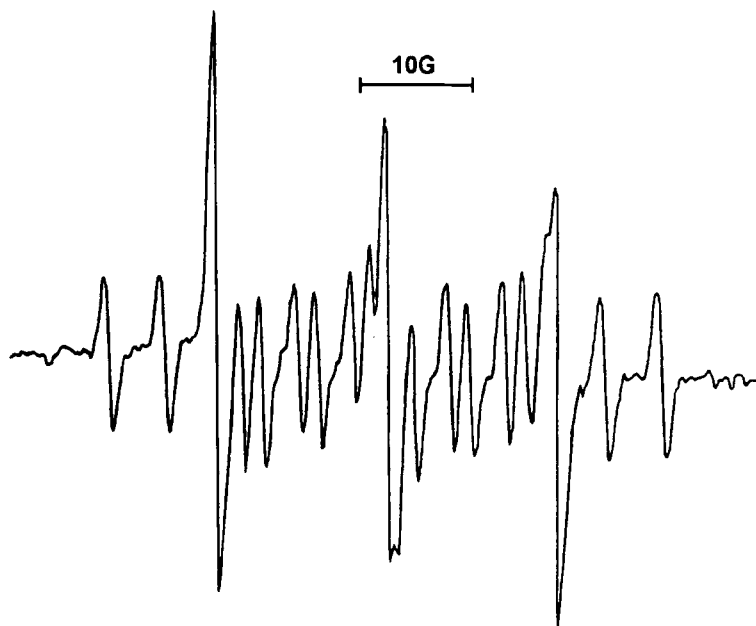
Figure 3 ESR spectrum of AEMA-MNP in benzene irradiated by UV light for 6 min:
[AEMA] = 1×10^{-2} mol/L, [MNP] = 5×10^{-3} mol/L.

the initial stage. Then the polymerization rate of AN initiated by P(AEMA) is faster than that initiated by AEMA. A similar result was also obtained in the presence of DMAEMA. This may be attributed to the energy migration of excited chromophores along the polymer chain or between the polymer chains as reported in the literature.[6,12,13]
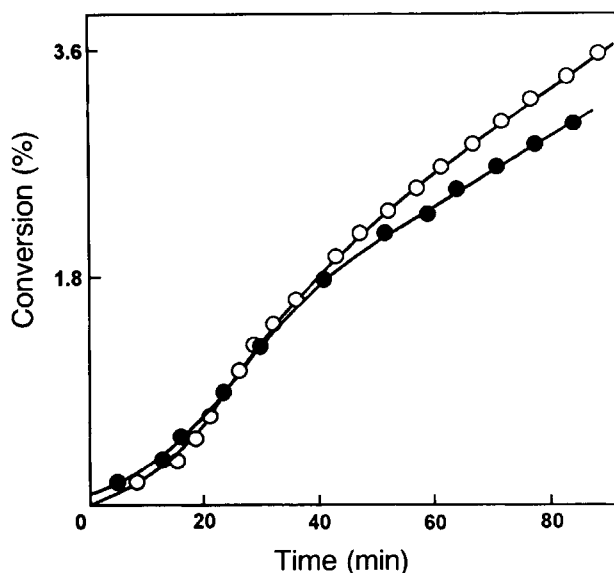
Effects of Aliphatic Tertiary Amine and Oxygen on Photopolymerization of AN Initiated by AEMA or P(AEMA)

The tertiary amine moiety in the AEMA molecule is an aromatic amine. It is known that due to the electron-drawing effect of the aromatic rings bridged by the electron-drawing carbonyl group, the reaction activity of the methylene group linked to the nitrogen atom is reduced and its proton-donating ability is
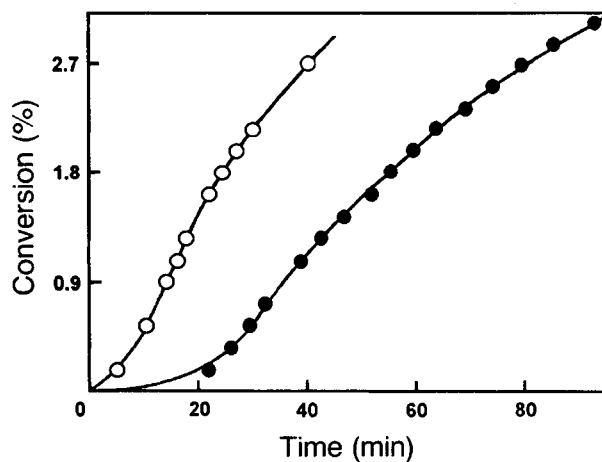

Figure 4 Conversion vs. time plots of photopolymerization of AN initiated by (●) AEMA and (○) P(AEMA). [AEMA] = [P(AEMA)] = 2.21×10^{-4} mol/L, [AN] = 3.81 mol/L.

Figure 5 Influence of DMAEMA on the photopolymerization of AN initiated by AEMA. [AN] = 3.81 mol/ L, [AEMA] = 1.36×10^{-4} mol/L, T = 30°C; purged with nitrogen for 40 min. (●) [DMAEMA] = 0; (○) DMAEMA] = 8.1×10^{-3} mol/L.
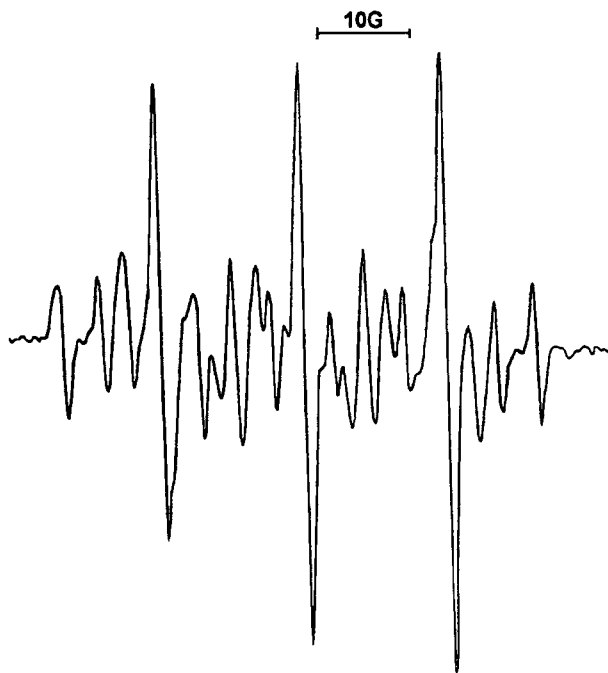
Figure 6 ESR spectrum of AEMA-DMAEMA-MNP in benzene irradiated by UV light for 1.5 min. [AEMA] = [DMAEMA] = 1 × 10⁻⁴ mol/L, [MNP] = 5 × 10⁻⁴ mol/L.

Figure 8 Fluorescence emission spectra of AEMA and P(AEMA) in DMF and 1,1,2,2-tetrachloroethane. [AEMA] = [P(AEMA)] = 1.12 × 10⁻⁴ mol/L, λ_{ex} = 275 nm. (1) AEMA, (2) P(AEMA) in DMF, (3) AEMA, and (4) P(AEMA) in tetrachloroethane.

weaker than that of ordinary aliphatic tertiary amine. Figure 5 shows the effect of DMAEMA on the photopolymerization of AN initiated by AEMA. The result indicates that the addition of aliphatic tertiary amine
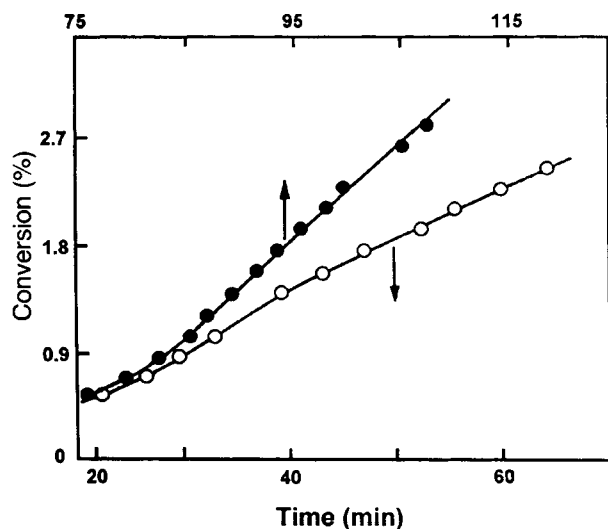
accelerates the photopolymerization rate of AN remarkably, and shortens the "induction period" of the polymerization obviously. This reveals that the excited aromatic ketone group withdraws a proton from more active DMAEMA rather than from the aromatic amine of AEMA itself, and the hydrogen-abstracting reaction proceeds more easily between the excited

Figure 7 Influence of oxygen on the photopolymerization of AN initiated by AEMA. [AN] = 3.81 mol/L, [AEMA] = 1.36 × 10⁻⁴ mol/L. (●) Not purged with nitrogen, induction period 80 min; (○) purged with nitrogen, induction period 25 min.
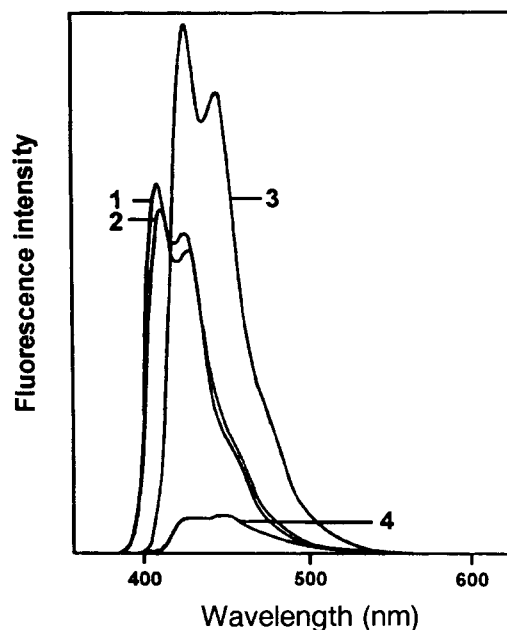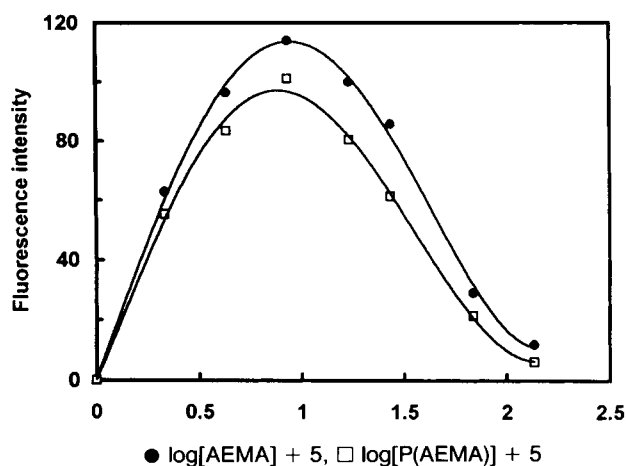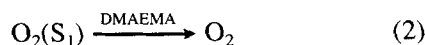

Figure 9 The relationships between fluorescence intensities and concentrations of AEMA and P(AEMA) in DMF. λ_{ex} = 275 nm, λ_{fl} = 409 nm. (●) AEMA and (□) P(AEMA).
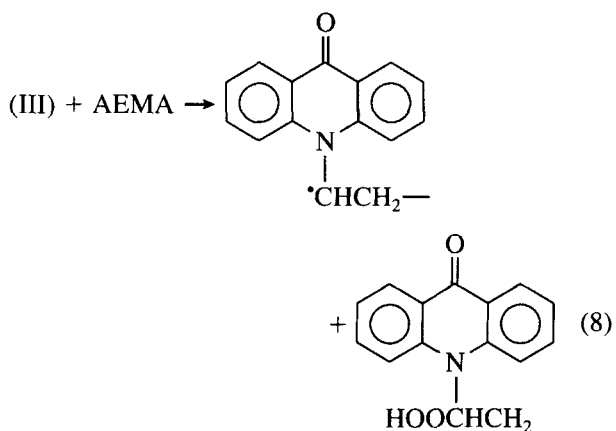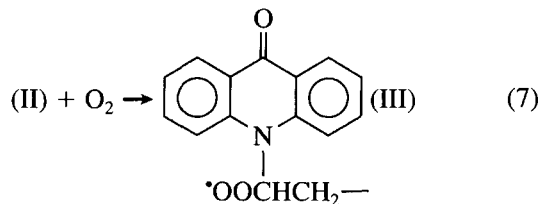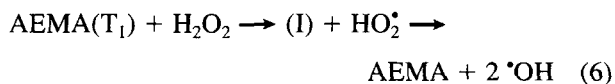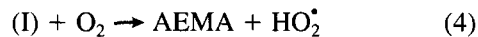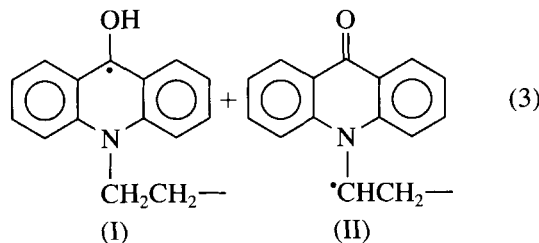
AEMA molecule and the DMAEMA molecule. Figure 6 is the ESR spectrum of the excited AEMA-DMAEMA initiation system trapped by MNP. This spectrum is similar to that of the MABP-DMAEMA system,[8] but not to that of the AEMA alone. This means that $\cdot CH_2N(CH_3)-CH_2CH_2-$ is an active species for the polymerization.

Generally, oxygen inhibits the radical polymerization of vinyl monomers. But in the photoinitiation systems consisting of BP and its derivatives combined with tertiary amines, oxygen exhibits an accelerative effect at the appropriate concentration of amines. There have been several reports about the effect of oxygen on the photopolymerization of vinyl monomers.[14,15] AEMA is a photosensitizer with an aromatic ketone group and an aromatic tertiary amine group, and it is of interest to understand the effect of oxygen on the initiation of AEMA. Figure 7 shows the effect of oxygen on the photopolymerization of AN initiated by AEMA. At higher concentration of oxygen (not purged with nitrogen), the polymerization rate of AN is greater than that at a lower concentration of oxygen. But the induction period of the former is about 80 min, which is much longer than that of the latter which is about 25 min. The same result is also observed for the AEMA-DMAEMA binary initiation system. The effects of organic amines and oxygen on the photopolymerization may be explained by the following structures:

Quenching effect of oxygen

$$AEMA(T_1) + O_2 \longrightarrow AEMA + O_2(S_1) \quad (1)$$

$$O_2(S_1) \xrightarrow{DMAEMA} O_2 \quad (2)$$

Hydrogen-abstracting reaction

$$AEMA(T_1) + AEMA(S_0) \longrightarrow$$

(3)

$$(I) + O_2 \longrightarrow AEMA + HO_2^\bullet \quad (4)$$

$$HO_2^\bullet + (I) \longrightarrow AEMA + H_2O_2 \quad (5)$$

$$AEMA(T_1) + H_2O_2 \longrightarrow (I) + HO_2^\bullet \longrightarrow$$

$$AEMA + 2\,{}^\bullet OH \quad (6)$$

In reactions (1) and (2), oxygen quenches the excited triplet state of AEMA, which displays the inhibition effect on the polymerization. But, as shown in reactions (4)-(6), oxygen is converted to active peroxide, which decomposes to an active initiating radical by photosensitization of the excited triplet AEMA. Thus, the amounts of initiating radicals increased and the polymerization rate accelerated. In general, oxygen reacts with active initiating radicals, forming the less active radical ROO$^\bullet$, which cannot initiate the polymerization of vinyl monomers. Reactions (7) and (8) show that increasing the concentration of tertiary amine can accelerate the consuming rate of oxygen in the polymerization system. Therefore, the addition of DMAEMA to the polymerization system not only accelerates the polymerization rate, but also shortens the induction period.

Table II Stern–Volmer Constants (kq τ: mol^{-1} L) of AEMA and P(AEMA) by Various Quenchers

Quenchers[a]	AN(MAN)	MMA	MA	FN	DF	TCNE	Ani	DMA	DMT
AEMA	0	5.6	6.6	181		6900			
P(AEMA)	0	5.9	7.6	183	225	7091	458	600	1300

[a] AN, acrylonitrile; MAN, methacrylonitrile; MA, methyl acrylate; MMA, methyl methacrylate; FN, fumaronitrile; DF, dimethyl fumarate; TCNE, 1,1,2,2-tetracyanoethylene; Ani, aniline; DMA, N,N-dimethylaniline; DMT, p-N,N-dimethyltoluidine.

Table III Stern–Volmer Constants (kq τ: mol^{-1} L) of Carbozole, AEMA, HEA, and Acridone Quenched by AN and MA

	Carbozole	HEA	AEMA	Acridone
AN	13.1	0	0	0
MA	55.3	7.5	6.6	5.0
N atomic net charge[a]	-4.78×10^{-2}			-3.83×10^{-3}

[a] Calculated approximately by quantum chemistry.

Fluorescence Behaviors of AEMA and Its Polymer

We reported the fluorescence behavior of acrylates having electron-donatable chromophore moieties such as p-(N,N-dimethylamino)benzyl methacrylate,[16] N,N-dimethyl-aminophenyl acrylamides,[17] 8-acryloyloxyquinolines,[18] N-acryloyl-N'-phenylpiperazines,[19] N-methyl-N-(2-methylacryloyloxyethyl) aniline,[20] and their polymers. According to our previous results, we found that for an acrylic monomer containing an electron-accepting double bond and an electron-donating chromophore moiety in the same molecule, the fluorescence intensities of monomers are always much lower than that of their polymers at the same chromophore concentration. This may be due to the formation of intra- or intermolecular by excited complexes between the electron-donating and electron-accepting groups of the monomer molecules. Such a phenomenon has been termed the "structure self-quenching phenomenon" in order to differentiate it from the concentration self-quenching effect caused by concentration factor.

AEMA is a derivative of acridone. Both AEMA and its polymer P(AEMA) display fluorescence emission as shown in Figure 8, but the fluorescent characteristics are solvent dependent. In the polar solvent DMF, AEMA and P(AEMA) show similar fluorescence spectra; in the weaker polar solvent TCE, a poor solvent for P(AEMA), they display different spectra. In TCE the intensity of AEMA is much higher than that of P(AEMA). This may be attributed to the difference in solubility and conformation of P(AEMA) in the two kinds of solvents. In the latter solvent, the chains of P(AEMA) are coiled, which causes the local high concentration of acridonylchromophores and leads to the concentration self-quenching, even though in the polar solvent DMF, AEMA and P(AEMA) display the concentration self-quenching effect at higher concentration as other organic fluorophores do. Figure 9 shows the relationships between fluorescence emission intensities of AEMA and P(AEMA) and their concentrations in DMF. It can be seen that the intensity of AEMA is slightly higher than that of P(AEMA). In other words, there is no structure self-quenching as we mentioned above. This may be attributed to the weaker electron-donating ability of the N atom of the acridonyl group in the AEMA molecule, caused by the stronger electron-drawing property of the carbonyl group between the two aromatic rings.

It is well known that the quenching ability of a quencher is mainly relevant to its electron-accepting or electron-donating ability against fluorophores. To understand the fluorescence quenching behavior of AEMA and P(AEMA), the fluorescence quenching test by different kinds of quenchers was carried out in DMF. Listed in Table II are the quenching constants of various quenchers, calculated according to the Stern–Volmer equation. The result indicates that the fluorescence of AEMA and P(AEMA) can be quenched by both electron-accepting quenchers and electron-donating quenchers, but the weaker electron-accepting quenchers against AEMA and P(AEMA), such as AN and α-methacrylonitrile (MAN), cannot quench the fluorescences of AEMA and P(AEMA). It may be due to the very weak electron-donating property of the acridonyl group. Table III shows the Stern–Volmer constants of carbozole, acridone, HEA, and AEMA quenched by AN and MA. The order of Stern–Volmer constants for MA is carbozole $\gg$ HEA > AEMA > acridone, in accordance with their electron-donating ability. It indicates that the fluorescence quenching efficiency of quenchers is dramatically affected by their electron-accepting or electron-donating ability, as well as the electron property of fluorophores. As shown in Table III, due to the absence of the electron-drawing carbonyl group within the carbozole molecule, the net charge of the nitrogen atom is much more than that within the acridone molecule.

CONCLUSION

A polymerizable photosensitizer, AEMA, and its polymer P(AEMA) were prepared. Their photo-

chemical behavior, consisting of photoinitiation and fluorescence properties, was investigated. The results of photopolymerization kinetics and the recorded ESR spectra showed that the photoinitiation mechanism of AEMA is similar to that of the BP-TEA system, that is, by the intermolecular hydrogen-abstracting reaction. Also, P(AEMA) is a polymeric photoinitiator that displayed greater initiation efficiency than the monomeric AEMA. Aliphatic tertiary amines such as DMAEMA showed an acceleration effect on the photopolymerization due to the presence of a more active methylene group linked to the nitrogen atom; oxygen displayed two kinds of effects: prolonging the induction period and increasing the polymerization rate.

The concentration self-quenching phenomenon was observed for AEMA and P(AEMA) in DMF, with maximum fluorescence intensities at the concentration of 8.6×10^{-5} mol/L. The results of fluorescence quenching indicate that the fluorescence of AEMA or P(AEMA) can be quenched by either electron-donating quenchers or electron-drawing quenchers. The quenching ability of quenchers was found to be affected by their electron-drawing or electron-donating ability, and the electron property of the fluorophores is also an important factor.

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