Photopolymerization Using Sensitizers of Binary System of Aromatic Hydrocarbon and Amine

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Synopsis

Photopolymerizations of acrylonitrile and methyl methacrylate, using binary sensitizers of aromatic hydrocarbon and amine, were investigated at 30°C in *N,N*-dimethylformamide under the irradiation with a light of λ > 300 nm. Naphthalene, anthracene, and phenanthrene were employed as aromatic hydrocarbons in the experiment. The binary system was effective for the initiation of the monomers. The combinations of naphthalene with tertiary amines, triethylamine and *N,N*-dimethylaniline, were remarkably effective among various combinations. The rate of polymerization with naphthalene–triethylamine sensitizer was observed to be proportional to the first, $1/2$, and $1/2$ powers of monomer, naphthalene, and triethylamine concentrations, respectively. The kinetics of the photopolymerization are proposed, and the initiation schemes are discussed, comparing them with those in the system sensitized by aromatic ketone–amine reported previously.

INTRODUCTION

This paper deals with the combination effect of sensitizers of photopolymerizations of acrylonitrile (AN) and methyl methacrylate (MMA), using a binary system of aromatic hydrocarbon and amine.

In a previous paper[1] the combination of aromatic ketone, such as benzophenone and fluorenone, and amine was noticed to have a remarkable effect initiating the photopolymerization of AN, in which both radicals from ketone and amine are produced. The aromatic ketone is photoreduced[2] by amine in the process, resulting in the formation of amine radical, which are supposed to contribute to the initiation. Moreover, the initiation system was characterized by an elevated susceptibility of the primary radical termination, which was studied by the kinetics of polymerization.

Aromatic hydrocarbons as well as aromatic ketone sensitizers are known to undergo a photoreduction[2] due to amines so that the combination of aromatic hydrocarbon and amine is expected to initiate the photopolymerization of vinyl monomers.

EXPERIMENTAL

Aromatic hydrocarbons, naphthalene, anthracene, phenanthrene, and amines, triethylamine (TEA), diethylamine (DEA), *N,N*-dimethylaniline (DMA), *N*-methylaniline (NMA), and aniline, were of all reagent grades and used without further purification. AN, MMA, and *N,N*-dimethylformamide (DMF) were purified by distillation.

A Pyrex glass tube containing 6 mL of DMF, in which known quantities of sensitizer, amine, and monomer were dissolved, was filled with nitrogen. Then,
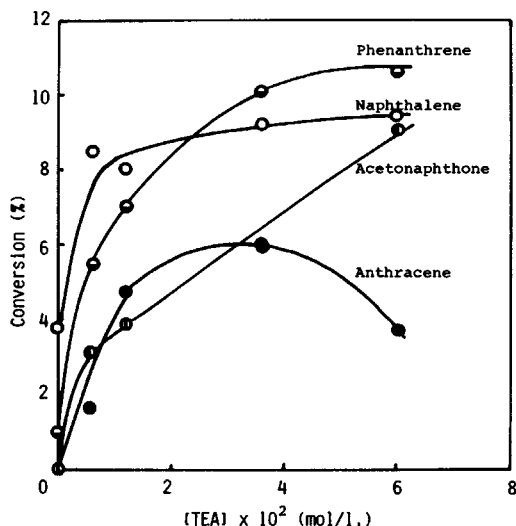
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Fig. 1. Photopolymerization of AN sensitized by a combination of sensitizer and TEA: [sensitizer] = 1.1×10^{-2} mol/L; [AN] = 2.53 mol/L; time = 60 min; temp = 30°C.

polymerization was carried out by keeping the system at 30°C for a given duration under irradiation. The homogeneity of the system continued till the end of polymerization under the conditions employed in this study. The irradiation was conducted in a Riko Rotary Photochemical Reactor RH 400-10 W with a high-pressure mercury lamp (400 W) around which the glass tubes were set to rotate. Conversion was determined gravimetrically.

Absorption spectra were recorded with a Hitachi spectrophotometer 124 type.

RESULTS AND DISCUSSION

Figure 1 shows the photopolymerization of AN sensitized by a combination of aromatic hydrocarbon and TEA. The polymerization was easily initiated by the combination of anthracene and TEA, while no initiation was observed for the system using anthracene alone. On the other hand, naphthalene and phenanthrene had an ability of initiating the photopolymerization without amine. However, the conversions were surely increased by adding TEA to the system. Figure 2 shows the results of MMA monomer. Naphthalene, phenanthrene, and anthracene also proved to become effective by the use of TEA in the photopolymerization of MMA.

Aromatic hydrocarbons are known to have an ability to initiate photopolymerizations of styrene[3] and AN.[4,5] Naphthalene and phenanthrene were confirmed in this study to initiate photopolymerizations of AN and MMA even in the system without amine. However, TEA was noticed to enhance the ability of aromatic hydrocarbons to perform photopolymerization more effectively. Figures 1 and 2 also include the results of 2-acetonaphthone as aromatic ketone sensitizer. Conversions by naphthalene and phenanthrene were found to be higher than that of 2-acetonaphthone.
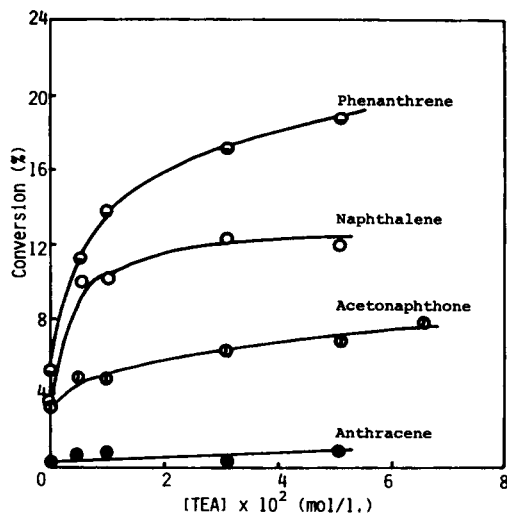
Fig. 2. Photopolymerization of MMA sensitized by a combination of sensitizer and TEA: [sensitizer] = 1.1×10^{-2} mol/L; [MMA] = 2.69 mol/L; time = 60 min; temp = 40°C.
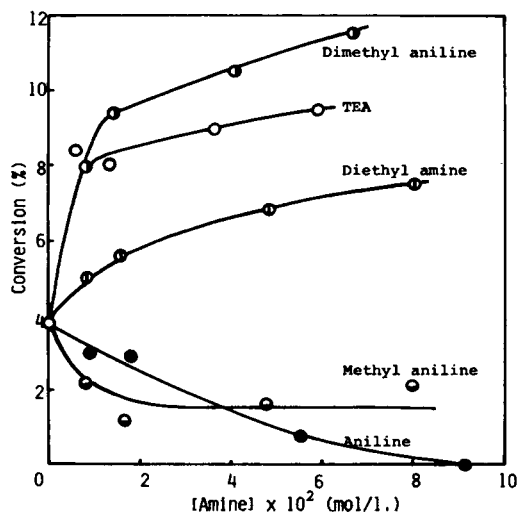

Fig. 3. Photopolymerization of AN sensitized by a combination of naphthalene and amine: [naphthalene] = 1.1×10^{-2} mol/L; [AN] = 2.53 mol/L; time = 60 min; temp = 30°C.

Figure 3 presents photopolymerization of AN sensitized by a combination of naphthalene and amine. The combination effect was recognized for only DEA, TEA, and DMA among aliphatic and aromatic amines examined here. Namely, tertiary amines, TEA and DMA, were found to be highly effective in the naphthalene-sensitized system. The result of 2-acetonaphthone-sensitized system is shown in Figure 4. Aromatic amines, aniline and NMA, were noticed to be effective in this system, indicating a somewhat different tendency from that in the naphthalene-sensitized system shown in Figure 3. It has been observed in the photopolymerization[6] of MMA sensitized by benzophenone that the mag-
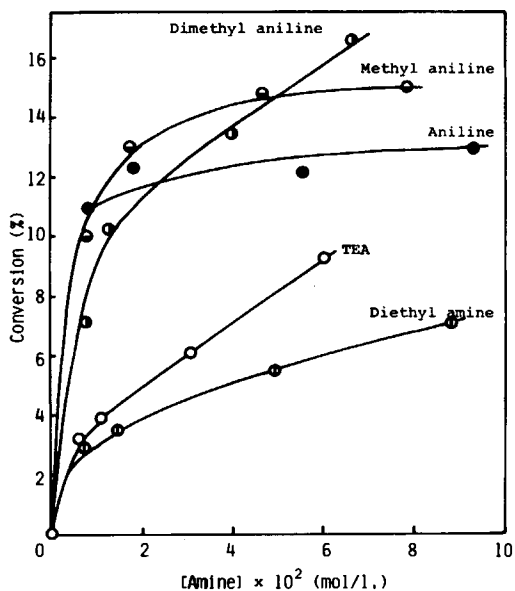
Fig. 4. Photopolymerization of AN sensitized by a combination of 2-acetonaphthone and amine: [2-acetonaphthone] = 1.1×10^{-2} mol/L; [AN] = 2.53 mol/L; time = 60 min; temp = 30°C.
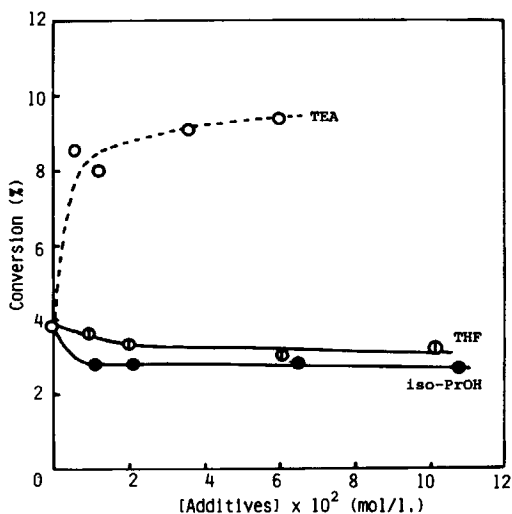

Fig. 5. Photopolymerization of AN sensitized by a combination of naphthalene and additives: [naphthalene] = 1.1×10^{-2} mol/L; [AN] = 2.53 mol/L; time = 60 min; temp = 30°C.

nitude of effect of aromatic amine is in the order DMA > NMA > aniline. It is not clear why the negative effect is recorded for aniline and NMA in the naphthalene-sensitized system.

Figure 5 shows photopolymerization of AN sensitized by a combination of naphthalene and hydrogen donors, tetrahydrofurane (THF) and isopropanol (iso-PrOH). Almost no change in the conversion was brought by the use of hydrogen donors in the system sensitized by naphthalene. Thus, amines have a
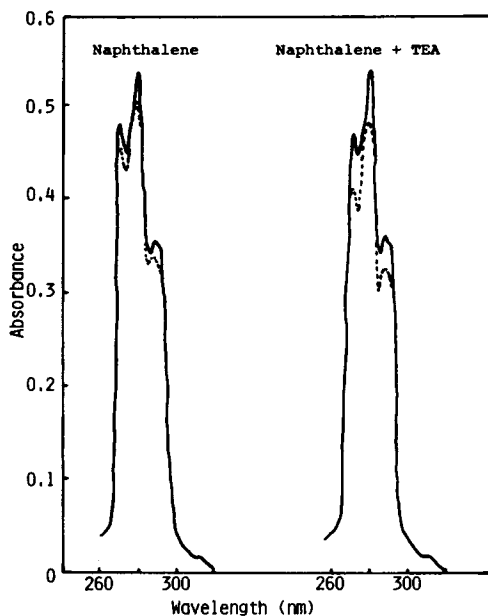
Fig. 6. UV spectra of naphthalene in DMF: (—) without irradiation; (- - - -) with irradiation at 30°C for 60 min; [naphthalene] = 2.0 × 10⁻⁴ mol/L; [TEA] = 2.0 × 10⁻³ mol/L.

large effect on the naphthalene-sensitized system, proving a different activity from those of hydrogen donors, such as THF and iso-PrOH. In a previous paper,[1] the hydrogen donors had no effect on systems sensitized by benzophenone and fluorenone. This phenomenon was ascribed to the quenching rate constant[2,7] of the excited triplet sensitizer with AN, which is greater than those with THF and iso-PrOH. The quenching rate constant[5] of the excited singlet naphthalene with AN is known as 1.44×10^7 mol⁻¹·s⁻¹. Unfortunately, the values with THF and iso-PrOH are not available in the literature. However, the values are expected to be smaller than that with AN the same as in the case of aromatic ketone sensitizer so that the effects of iso-PrOH and THF on the naphthalene-sensitized system are so difficult to be detected. On the other hand, the quenching rate constant of the excited singlet naphthalene with amine may be somewhat higher than that with AN, since an increased conversion is observed by the addition of TEA to the naphthalene-sensitized system as shown in Figures 1 and 2. The reaction of excited naphthalene with TEA will be discussed later.

Figure 6 shows the absorption spectra of naphthalene in DMF solution. No change in the spectrum was observed by adding TEA to the solution. This suggests that no formation of charge transfer complex between naphthalene and TEA at their ground states is plausible. By adding TEA, the spectrum of naphthalene solution after irradiation was decreased sharply in its strength. This seems to be the effect of contribution of TEA to the photoreduction of naphthalene.

Kuzmin and Guseva[8] measured emission spectra of naphthalene and amine in n-heptane solution and observed the formation of charge transfer complex between the excited singlet naphthalene and TEA at the ground state. It has
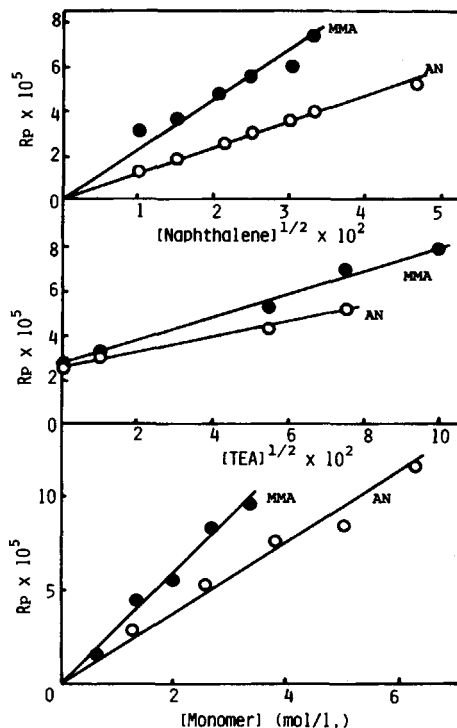
Fig. 7. Photopolymerizations of AN and MMA sensitized by a combination of naphthalene and TEA: [MMA] = 2.69 mol/L, temperature = 40°C; [AN] = 2.53 mol/L, temperature = 30°C; [TEA] = 1.0 × 10^{-2} mol/L; [naphthalene] = 1.1 × 10^{-2} mol/L.

also been reported that 1,4-dihydronaphthalene[2] is a major product in the sample of photoirradiation of naphthalene and TEA in acetonitrile. Accordingly, it is conceivable that the photoreduction of naphthalene proceeds through eq. (1),
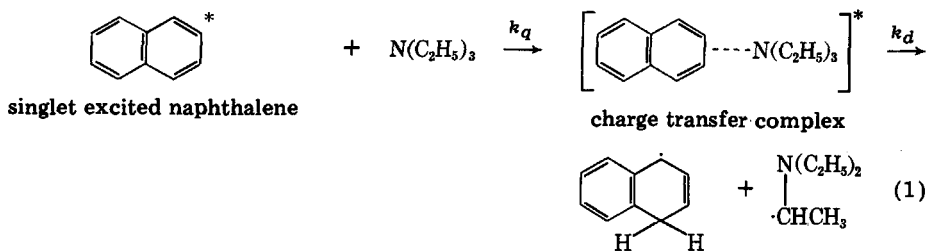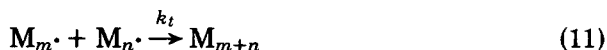

in the system sensitized by a combination of naphthalene and TEA. This reaction is essentially the same as the photoreduction[2] of aromatic ketone sensitizer by amine.

Relationships between the rate of polymerization (R_p) and the concentrations of naphthalene, TEA, and monomer in the system sensitized by naphthalene–TEA are shown in Figure 7. The rate equation obtained for AN and MMA monomers is represented as

$$R_p = K[\text{naphthalene}]^{1/2}[\text{TEA}]^{1/2}[\text{monomer}]^{1.0} \qquad (2)$$

Based on the above investigations, the kinetic schemes of the photopolymerization sensitized by a combination of naphthalene and TEA are proposed as follows:

$$S \xrightarrow[k_\epsilon I]{h\nu} S^* \tag{3}$$

$$S^* \xrightarrow{k_f} S + h\nu \tag{4}$$

$$S^* \xrightarrow{k_{IC}} S \tag{5}$$

$$S^* + TEA \xrightarrow{k_q} [S \text{ - - - - } TEA]^* \tag{6}$$

$$[S \text{ - - - - } TEA]^* \xrightarrow{k_{f'}} S + TEA \tag{7}$$

$$[S \text{ - - - - } TEA]^* \xrightarrow{k_d} R\cdot \tag{8}$$

$$R\cdot + M \xrightarrow{k_i} M\cdot \tag{9}$$

$$M\cdot + M \xrightarrow{k_p} M_m\cdot \tag{10}$$

$$M_m\cdot + M_n\cdot \xrightarrow{k_t} M_{m+n} \tag{11}$$
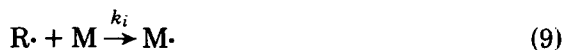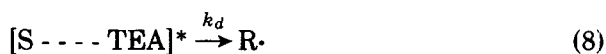
The first step involves the excitation of naphthalene by light as eq. (3), where S, I, and k_ϵ denote naphthalene, light intensity, and light absorption fraction, respectively. The excited naphthalene (S^*) is deactivated by fluorescence of eq. (4) or nonradiative decay of eq. (5). Equation (6) presents the quenching reaction of S^* with TEA, resulting in the formation of complex. Equation (7) presents the deactivation of complex to the ground state of each component. Radicals $R\cdot$ are generated by the decomposition of complex according to eq. (8). The radicals are supposed to be those originated from naphthalene and TEA, as shown in eq. (1). Initiation, propagation, and termination are presented as eqs. (9)–(11), respectively, where M denotes AN and MMA.

Applying the steady-state assumption to both $[S^*]$ and $[M\cdot]$, the following is derived as the rate expression:

$$R_p = K' \frac{[TEA]^{1/2}[S]^{1/2}[M]^{1.0}}{(k_f + k_{IC} + k_q[TEA])^{1/2}} \tag{12}$$

where $K' = k_p(k_d/k_t)^{1/2}(k_\epsilon k_q I)^{1/2}/(k_{f'} + k_d)^{1/2}$.

If $k_f + k_{IC} \gg k_q[TEA]$ is assumed, then eq. (12) is simplified to

$$R_p = K''[TEA]^{1/2}[S]^{1/2}[M]^{1.0}$$

where $K'' = k_p(k_d/k_t)^{1/2}(k_\epsilon k_q I)^{1/2}/(k_{f'} + k_d)^{1/2}(k_f + k_{IC})^{1/2}$

The kinetics seem to coinside with the experimental results of Figure 7 explained by eq. (2). In the range of low TEA concentration, therefore, radicals

are supposed to be generated by eqs. (6) and (8), and the polymerization is supposed to proceed by eqs. (9)–(11).

As above, it was confirmed that the polymerization sensitized by a combination of aromatic hydrocarbon and amine is subjected to the mechanisms, in which the radicals are generated by the photoreduction of sensitizer with amine, leading to the initiation of vinyl polymerization. These mechanisms seem to be almost similar to those in the system sensitized by aromatic ketone–amine.[1] In a previous paper,[1] however, the primary radicals were confirmed to participate in the termination of polymer radicals. So that, the rate equation was shown quite different from those familiar to general radical polymerization. The kinetic exponents of sensitizer and monomer concentrations were recorded as less than 0.5 and more than unity, respectively, at that time. To make explanation of the experimental results of eq. (2) in this study, it is necessary to consider the mutual termination between polymer radicals following to eq. (11). This may suggest that the termination by primary radicals does not easily go on in the system sensitized by aromatic hydrocarbon–amine.

References

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