

Photopolymerization of Acrylonitrile Sensitized with a Combination of Aromatic Ketone and Amine

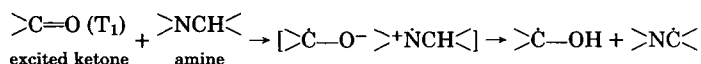
HITOSHI KUBOTA and YOSHITAKA OGIWARA, *Department of Chemistry, Gunma University, Kiryu, Gunma 376, Japan*

Synopsis

Effect of amines on photopolymerization of acrylonitrile sensitized with various sensitizers was investigated in *N,N*-dimethylformamide at 30°C. Photopolymerizations sensitized with aromatic ketones such as benzophenone (BP), fluorenone (Fl), acetophenone, and Michler's ketone were noticed to be activated by triethylamine (TEA). Diethylamine, tri-*n*-butylamine, di-*n*-butylamine, and *n*-butylamine besides TEA also proved to be effective for the system sensitized with BP or Fl. On the other hand, TEA indicated a negative effect for systems sensitized with α,α' -azobisisobutyronitrile (AIBN), benzoyl peroxide (BPO), benzoin, and 2-*tert*-butylanthraquinone. Characteristics of the BP— and Fl—amine-sensitized systems were compared with the systems sensitized with AIBN, BPO, and benzoin with respect to kinetics. Contrary to the latter polymerizations following the general kinetics, including the termination of growing chains by mutual deactivation, the former polymerizations were characterized by an elevated susceptibility of the primary radical termination.

INTRODUCTION

Photoreduction¹ of aromatic ketones by amines is known to proceed through a formation of complex between the both followed by a generation of radicals as in the following equations:



Leaver and Ramsay² observed in ESR studies on photoreduction of benzophenone (BP) that the radicals are formed on amines at the carbon atom next to nitrogen atom by the hydrogen abstraction. The resultant amine radicals are believed to be capable of initiating polymerizations of vinyl monomers. Photopolymerizations^{3,4} of acrylate monomers sensitized with a combination of BP and triethylamine (TEA) have been reported.

In this paper, the effect of amines on the photopolymerization of acrylonitrile (AN) with various sensitizers was investigated to hunt for an effective photoinitiation system. Among sensitizing systems, the combination of aromatic ketone and amine was found to be effective for accelerating the photopolymerization. Lastly, characteristics of the systems of combined sensitizer were discussed with respect to kinetics comparing with systems sensitized with other types of sensitizers.

EXPERIMENTAL

Sensitizers, BP, fluorenone (Fl), acetophenone, *p,p'*-tetramethyldiaminobenzophenone (Michler's ketone), α,α' -azobisisobutyronitrile (AIBN), benzoyl peroxide (BPO), benzoin, and 2-*tert*-butylanthraquinone (*t*-BAQ), and amines, TEA, diethylamine (DEA), *n*-butylamine (*n*-BA), di-*n*-butylamine (DBA), and tri-*n*-butylamine (TBA) were of all reagent grades and used without further purification. AN, *N,N*-dimethylformamide (DMF), and benzene were purified by distillation.

A Pyrex glass tube containing 6 mL of DMF, in which known concentrations of sensitizer, amine, and AN were dissolved, was filled with nitrogen. Then, polymerization was carried out by keeping the system at 30°C for a given time under irradiation. The irradiation was conducted in a Riko rotary photochemical reactor RH400-10W with a high-pressure mercury lamp (400 W), around which the glass tubes were set to rotate. Polymerization solution was poured into an excess methanol to precipitate the polymer, filtered, washed with methanol, and then dried under reduced pressure. Conversion was determined gravimetrically.

The intrinsic viscosities of polymer were determined using an Ubbelohde type viscometer at 25°C in DMF. Absorption spectra were recorded with a Hitachi spectrophotometer 124 type.

RESULTS AND DISCUSSION

Effect of Amines

The effect of TEA on photopolymerization of AN sensitized with various sensitizers was examined, and the results are presented in Table I. TEA has been known to have an ability to initiate photopolymerizations of methyl methacrylate⁵ and styrene.⁶ As clearly seen in the table, however, no photopolymerization of AN initiated in the system with TEA alone and free from sensitizer under the present irradiation conditions. The conversions were observed to be increased by the activation with TEA in polymerization system sensitized with BP, Michler's ketone, acetophenone, and Fl, in which DMF was used as a solvent. On the other hand, the conversions were decreased in systems sensitized with *t*-BAQ, benzoin, BPO, and AIBN by the addition of TEA. The same phenomena were also observed in heterogeneous systems using benzene solvent. Thus, the accelerating effect of photopolymerization of AN due to TEA was conceived peculiar to the systems sensitized with aromatic ketones.

Figure 1 shows the effect of various amines on the BP-sensitized system. TBA, DBA, and *n*-BA besides TEA also activated the photopolymerization of AN and the conversions increased with increasing the amine concentration. On the other hand, no change in the conversion was observed by the addition of hydrogen donors, such as tetrahydrofuran (THF) and isopropanol (iso-PrOH), in place of amines. Block et al.⁷ reported the BP-sensitized photopolymerization of methyl methacrylate in benzene, in which an enhanced polymerization was observed by the addition of THF or iso-PrOH. Lower concentrations of THF and iso-PrOH in our study might be one of the causes of the obscure effects of the hydrogen donors. However, amines activated the BP-sensitized photopolymerization of AN at the same level of concentration as THF or iso-PrOH. This

TABLE I
Effect of Triethylamine on Photopolymerization^a of Acrylonitrile

Sensitizer ^b	TEA ^c	Conversion (%)	
		DMF	Benzene
None	Yes	0	0
BP	None	8.2	0
	Yes	11.1	10.7
Michler's ketone	None	0.4	—
	Yes	8.2	—
Acetophenone	None	1.7	—
	Yes	5.1	—
Fl	None	0	0
	Yes	12.4	4.1
<i>t</i> -BAQ	None	19.5	0.9
	Yes	13.0	0
Benzoin	None	40.0	32.9
	Yes	18.4	14.6
BPO	None	13.5	19.9
	Yes	12.6	14.9
AIBN	None	24.5	—
	Yes	19.8	—

^a Photoirradiation was carried out at 30°C for 60 min. Concentration of AN was 2.53 mol/L.

^b Concentration of sensitizer was $7\text{--}12 \times 10^{-3}$ mol/L.

^c Concentration of TEA was 1.43×10^{-2} mol/L.

may suggest that amines work not only as a mere hydrogen donor, but also interact specially with BP as mentioned in the "Introduction."

On the other hand, the quenching rate constants of the excited triplet BP with TEA¹ and AN⁸ are known as $2.3 \times 10^9 \text{ mol}^{-1}\cdot\text{s}^{-1}$ and $3.4 \pm 0.3 \times 10^7 \text{ mol}^{-1}\cdot\text{s}^{-1}$, respectively. These values are greater by 1 or 3 orders of magnitude than the rate constants for the excited triplet BP abstracting hydrogen from iso-PrOH¹ and THF⁸ with $1.8 \times 10^6 \text{ mol}^{-1}\cdot\text{s}^{-1}$ and $3 \pm 1 \times 10^6 \text{ mol}^{-1}\cdot\text{s}^{-1}$, respectively. Taking into consideration the above rate constants, which are smaller compared to those for amine and AN, the obscure effects of iso-PrOH and THF on BP-

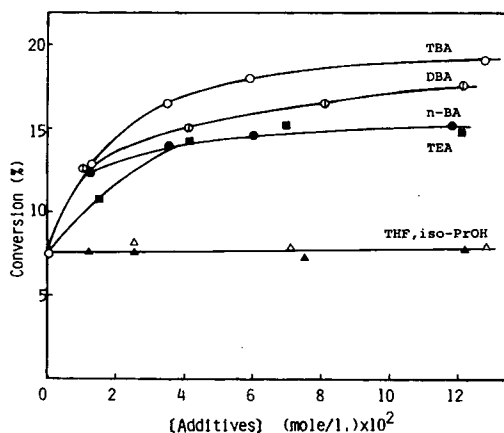


Fig. 1. Effect of amines on BP-sensitized photopolymerization of AN in DMF. Concentrations of BP and AN were 1.1×10^{-2} mol/L and 2.53 mol/L, respectively. Photoirradiation was carried out at 30°C for 60 min.

sensitized photopolymerization of AN may be understandable. In these systems, energy transfer of the excited triplet BP to AN will overcome the transfer to iso-PrOH or THF.

Figure 2 shows results of the FI-sensitized system. No polymerization of AN was initiated in the system with FI alone, but it was promoted by the aid of amines such as TEA, DEA, TBA, DBA, and nBA. Such systems marked a maximum conversion at a certain concentration of amine, and the conversion decreased gradually in the range of higher concentration. Despite the high activation effect on the BP-sensitized system, TBA was scarcely effective for FI sensitizer, which may suggest a different mechanism of interaction between amine and sensitizer of a different kind. As for the hydrogen donors, THF initiated appreciably the polymerization, while iso-PrOH did not at all. Thus, amines were available for the systems sensitized with FI as well as BP. Ledwith and Purbrick⁹ reported that the FI-sensitized photopolymerization of methyl methacrylate was activated by *N,N*-dimethylethanolamine.

Figure 3 shows the relationship between intrinsic viscosity and TEA concentration for polymers obtained in the BP- and FI-sensitized systems. The number-average molecular weights calculated following the equation proposed by Onyon¹⁰ were in the range of about 3000–10,000. The molecular weights of the polymers were known to be relatively low and to decrease with increasing the TEA concentration.

Absorption spectra of FI in DMF solution are shown in Figure 4. No change in the spectrum by the irradiation at 30°C for 60 min indicated that no photo-reduction of FI was induced under such irradiation. The spectrum of FI was also unchanged by TEA. The absorption of the TEA-containing solution was sharply decreased in its intensity at about 400 nm by the irradiation. This phenomenon may be ascribed to $n-\pi^*$ transition of the carbonyl group of FI molecule. Accordingly, photoreduction of FI was sure to occur in the TEA-containing system. No spectrum change in the system, to which iso-PrOH was added instead of TEA, was observed after the photoirradiation.

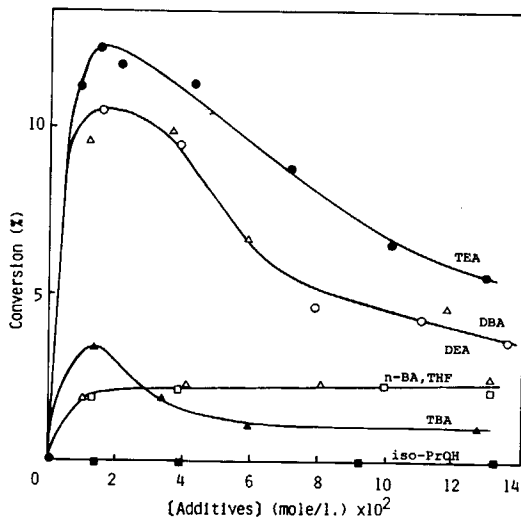


Fig. 2. Effect of amines on FI-sensitized photopolymerization of AN in DMF. Concentrations of FI and AN were 1.1×10^{-2} mol/L and 2.53 mol/L, respectively. Photoirradiation was carried out at 30°C for 60 min.

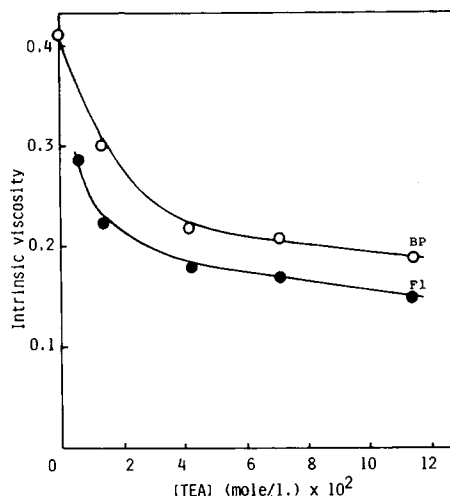
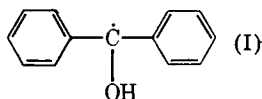
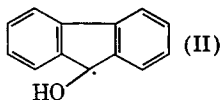


Fig. 3. Intrinsic viscosities of polyacrylonitrile obtained in BP- and FI-sensitized systems. Concentrations of sensitizer and AN were 1.1×10^{-2} mol/L and 2.53 mol/L, respectively. Photoirradiation was carried out at 30° for 60 min.

Thus, it was confirmed that photopolymerization of AN was initiated in the TEA-containing system where FI was reduced by the photoirradiation, while no initiation resulted in the system without photoreduction of FI. Therefore, the polymerization seems to be initiated by radicals formed during the process of photoreduction of FI due to TEA. The radicals may be two, amine and sensitizer radicals, as shown in the Introduction section. The sensitizer radicals may be



and



in the BP- and FI-sensitized systems, respectively. Ledwith and Purbrick⁹ observed in the BP-sensitized photopolymerization of methyl methacrylate that the ketyl radical of BP (I) participates in termination, but it is unable to initiate polymerization at 30°C . Therefore, the amine radical is considered to play a role of initiation of the polymerization at 30°C .

Based on the above investigations, it was confirmed that photopolymerizations of AN sensitized with BP and FI are activated by amines. As a conclusion, amines do not work only as hydrogen donors, but they may interact with sensitizers resulting in a high activity of polymerization.

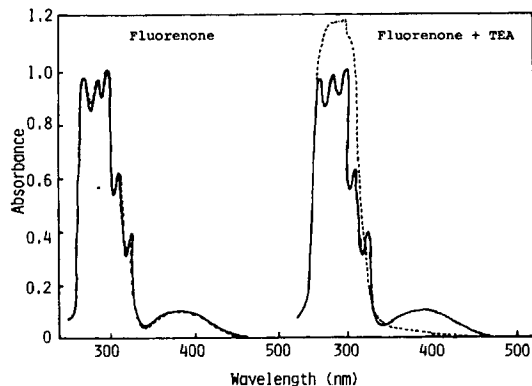


Fig. 4. Absorption spectra of Fl in DMF. Concentrations of Fl and TEA were 6.7×10^{-4} mol/L and 2.86×10^{-2} mol/L, respectively. Solid and dotted lines represent spectra before and after photoirradiation at 30°C for 60 min, respectively.

Characteristics of BP— and Fl—Amine Systems

In order to reveal the characteristics of sensitizers with combinations of BP or Fl and amines, they were compared with BPO, AIBN, benzoin, and *t*-BAQ initiators. BPO, AIBN, and benzoin sensitizers¹¹⁻¹⁵ are known to be photodecomposed to yield their fragment radicals capable of initiating polymerization. On the other hand, *t*-BAQ^{16,17} is believed to have an ability to abstract hydrogen atom at its excited state, by which polymerization can be initiated.

Figure 5 presents the relationship between the rate of polymerization (R_p) and the concentration of sensitizer. The R_p in the system with AIBN was proportional to the $1/2$ power of the AIBN concentration, while the sensitizer exponents in the systems with BP— and Fl—amine were lower than $1/2$. Still lower exponents were observed in the range of concentration over about 10^{-3} mol/L.

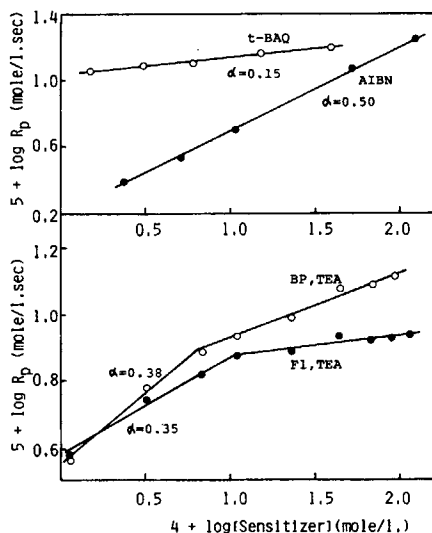


Fig. 5. Effect of sensitizer concentration on R_p in DMF at 30°C . Concentrations of AN and TEA were 2.53 mol/L and 1.4×10^{-2} mol/L, respectively.

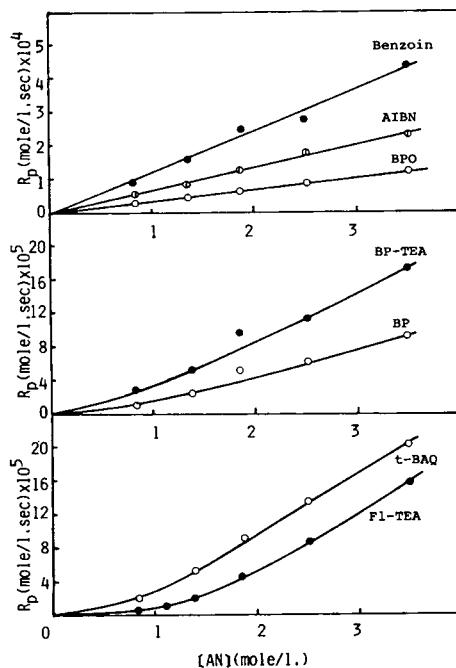


Fig. 6. Effect of AN concentration on R_p in DMF at 30°C. Concentrations of sensitizer and TEA were $0.7\text{--}1.1 \times 10^{-2}$ mol/L and 1.4×10^{-2} mol/L, respectively.

Figure 6 shows the relationship between the R_p and the concentration of AN. The R_p in the systems with BPO, AIBN, and benzoin increased linearly with the concentration of AN. On the other hand, the relations of R_p and AN concentration in the systems with BP— and Fl—amine were indicated as curves, in which the exponents of AN concentration were given higher than unity.

The results are summarized in Table II. The R_p 's in the system with BPO, AIBN, and benzoin are proportional to the first power of AN concentration and to the $1/2$ power of sensitizer concentration. Accordingly, the photopolymerization of AN with such initiators is considered to proceed following the general kinetics of radical polymerization. At the systems with combinations of BP or Fl and amines, on the other hand, the exponents of AN concentration were higher than unity, while those of sensitizer concentration recorded lower than $1/2$. The system with *t*-BAQ showed the same result as the systems with BP— and Fl—amines. The system with AIBN, which follows the usual kinetics of radical polymerization, changed the exponents of AN and AIBN concentrations to 1.5 and 0.45, respectively, by the addition of TEA. Thus, the relations of R_p to concentrations of monomer and sensitizer in the system with amines proved to deviate from the general kinetics of radical polymerization.

The causes of deviation from unity in monomer concentration dependence are considered as (1) cage effect,¹⁸ (2) complex formation between initiator and monomer,¹⁸ (3) primary radical termination,^{19,20} (4) degradative chain transfer,^{19,21-23} and (5) diffusion-controlled termination.²⁴ In this study, the conversion was observed to decrease with the concentration of TEA in the higher range in the Fl-sensitized system (Fig. 2). And, the molecular weights of polymer reduced with increasing the concentration of TEA, as shown in Figure 3. On

TABLE II
Dependence of R_p on Concentrations of Monomer and Sensitizer in Various Sensitized Systems at 30°C

Sensitizer	Monomer exponent ^a	Sensitizer exponent ^b
AIBN	1.0	0.50 ($1.0 \times 10^{-4} \sim 4.9 \times 10^{-3}$)
AIBN—TEA ^c	1.5	0.45 ($1.0 \times 10^{-4} \sim 4.9 \times 10^{-3}$)
BPO	1.0	0.50 ($1.0 \times 10^{-4} \sim 5.0 \times 10^{-3}$)
Benzoin	1.0	—
<i>t</i> -BAQ	1.6	0.15 ($1.5 \times 10^{-4} \sim 3.8 \times 10^{-3}$)
FI—TEA ^c	2.2	0.35 ($1.1 \times 10^{-4} \sim 1.1 \times 10^{-3}$)
		0.10 ($2.2 \times 10^{-3} \sim 8.9 \times 10^{-3}$)
FI—DEA ^c	2.0	—
FI—DBA ^c	1.9	—
BP	1.3	0.32 ($1.1 \times 10^{-4} \sim 2.2 \times 10^{-3}$)
BP—TEA ^c	1.3	0.38 ($1.1 \times 10^{-4} \sim 6.7 \times 10^{-4}$)
		0.20 ($1.1 \times 10^{-3} \sim 8.9 \times 10^{-3}$)
BP—DEA ^c	1.2	—
BP—TEA ^c	1.2	—

^a Concentration of AN was varied from 0.86 mol/L to 3.50 mol/L. Concentration of sensitizer was $7\text{--}12 \times 10^{-3}$ mol/L.

^b Values in parentheses were range of sensitizer concentration (mol/L).

^c Concentration of amine was $1\text{--}2 \times 10^{-2}$ mol/L.

the other hand, R_p in the BP- and FI-sensitized systems decreased sharply in the range of sensitizer concentration higher than 10^{-2} mol/L in Figure 5. These results suggest that primary radicals produced in the system with the combination of BP or FI and amines are sure to participate in the termination reaction. From the dependence of R_p on monomer concentration in Table II, the FI-sensitized system is believed to be more susceptible to the primary radical termination than the BP-sensitized system.

In case of the system with AIBN containing TEA, some fragment radicals of AIBN may transfer to amine molecule, which perhaps makes deviation from the general kinetics of radical polymerization. Thus, the characteristics of initiation systems with amines seem to be explained by a relatively high susceptibility to the primary radical termination.

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