

STUDIES ON THE MECHANISM OF VINYL PHOTOPOLYMERIZATION INITIATED BY CONDENSED AROMATIC HYDROCARBON-ANILINE SYSTEMS*

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ABSTRACT

Initiation mechanism of the photopolymerization of acrylonitrile and methyl methacrylate, using binary condensed aromatic hydrocarbon (CAH)-aniline systems as initiator, was studied. The stronger the electron-donating ability of the aniline derivatives, the faster the rate of photopolymerization will be. The radical intermediates produced by photoreaction between anthracene and aniline were detected with ESR spectra. The initiation scheme involves the formation of exciplex between the excited singlet state of CAH and the ground state of aniline as the first step, and then followed by proton transfer, leading to the generation of two kinds of radicals. From the end-group analysis of the polymers obtained, it is suggested that both kinds of radicals are involved in the initiation.

The binary system of benzophenone(BP)-amine is well known in the photoinitiation of vinyl polymerization^[1,2], in which the $n\pi^*$ excited triplet BP molecule forms an exciplex with amine, leading to the generation of radicals for initiation. Condensed aromatic hydrocarbon (CAH) in the excited singlet of $\pi\pi^*$ transition is also known to form exciplex with amine^[3]. However, while some authors have reported the polymerization using CAH alone as photoinitiator^[4,5], less attention was paid to the polymerization initiated by CAH-amine systems. In our previous paper^[6] we studied the kinetics of the vinyl photopolymerization initiated by the binary system of CAH and aniline. This paper will deal with its initiation mechanism.

EXPERIMENTAL

1. Materials

Acrylonitrile (AN), methyl methacrylate (MMA), CAH, aniline and other aromatic amines were purified as previous report^[6]. 2-methyl-2-nitroso-propane (MNP) was prepared as described in reference [7].

2. Methods

The photopolymerization was carried out as the procedure in previous paper^[6]. The polymers were purified repeatedly with solution-precipitation method until no absorption of initiators in the discard solution and then used for detecting the end-group in fluorescence spectrophotometry.

Fluorescence spectra were recorded with Hitachi-850 Fluorescence spectrophotometer. ESR spectra were measured with X-band 100KHz modulation ESR spectrometer. Before

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the ESR spectra recording, the reagent solution was bubbled with purified nitrogen and irradiated with GCQ200 super-high pressure mercury lamp, with QB24 glass as filter.

RESULTS AND DISCUSSION

1. The formation of exciplex

No change in the absorption spectra of CAH in solution was observed by adding aniline. It shows no interaction takes place between aniline and CAH in the ground state. Under irradiation, however, the exciplex will be formed between the $\pi\pi^*$ excited CAH and the ground state aniline, which was confirmed by the fluorescence quenching of CAH by aniline and its derivatives. Fig. 1 shows the Stern-Volmer plots for the fluorescence quenching of anthracene by aniline and its derivatives.

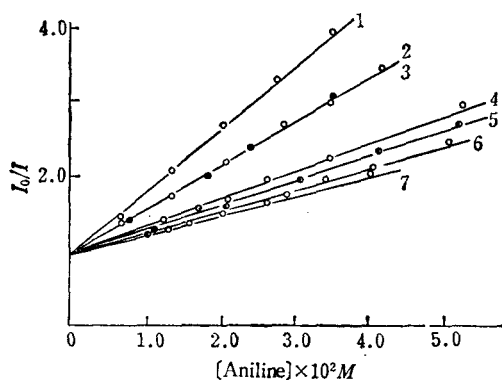


Fig. 1 Stern-Volmer plots for the fluorescence quenching of anthracene ($10^{-3}M$) by amines in AN
 1. $C_6H_5N(CH_3)_2$; 2. $C_6H_5NHCH_3$; 3. $C_6H_5NHC_6H_5$; 4. $p-CH_3C_6H_4NH_2$;
 5. $C_6H_5NH_2$; 6. $p-ClC_6H_4NH_2$; 7. $p-BrC_6H_4NH_2$.

Although no exciplex fluorescence was observed in the fluorescence quenching of CAH by primary and secondary aromatic amines, the quenching increased with the increasing of the electron-donating ability of the amines and the increasing of $k_q\tau$ values, calculated from the slope of the line shown in Fig. 1, is in accordance with the increasing of the ionization potential (I.P.) values of the amines. This suggests that the fluorescence quenching was caused by a charge-transfer process.

Table 1 shows the role of the exciplex played in the initiation. The electron-drawing substituents on the aniline nucleus will make the exciplex formation less favorable and, therefore, decrease the rate of polymerization, while the electron-donating substituents on the nitrogen atom will enhance the exciplex formation as well as the rate of photopolymerization. The order of the rate of polymerization (R_p) for anthracene-aromatic amine system is in accordance with the order of $k_q\tau$ values for the fluorescence quenching of anthracene by amines.

Acetanilide and N-methyl-acetanilide could not quench the fluorescence of CAH and therefore no exciplex was formed between them. So no enhancement of R_p was observed by adding acetanilide or N-methyl-acetanilide to anthracene in spite of the presence of abstract-

able hydrogen atom in their molecules. On the other hand, although triphenylamine forms exciplex with CAH, it will not act as an initiation system with CAH because of the absence of abstractable hydrogen atom. Therefore, both the formation of exciplex and the presence of abstractable hydrogen atom in the amine molecule are necessary for the initiation.

Diphenylamine (I.P. 7.7eV), a stronger donor as well as a powerful quencher for anthracene, shows much lower ability for initiation than aniline (I.P. 7.7eV) (Table 1). This may be ascribed to the stability of its radical $C_6H_5-\dot{N}-C_6H_5$ formed.

Table 1 The photopolymerization of AN initiated by anthracene ($2 \times 10^{-3}M$)—aromatic amine ($10^{-3}M$) system

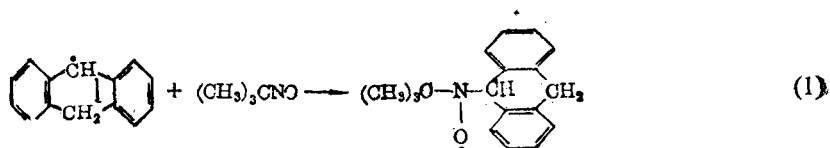
Amine	I.P.(eV)[7a]	$k_q\tau$ (a)	R_p (mol/l.s.)	M_w (b)
$C_6H_5N(CH_3)_2$	7.10	76.3	2.2×10^{-4}	0.84×10^4
$C_6H_5NHC_6H_5$	7.24	57.1	0.58×10^{-4}	0.73×10^4
$C_6H_5NHCH_3$	7.30	57.1	1.0×10^{-4}	1.0×10^4
$p-CH_3C_6H_4NH_2$	7.5	47.0	0.84×10^{-4}	1.1×10^4
$C_6H_5NH_2$	7.7	35.8	0.78×10^{-4}	1.1×10^4
$p-ClC_6H_4NH_2$	—	32.0	0.60×10^{-4}	1.3×10^4
$p-BrC_6H_4NH_2$	7.8[8]	28.0	0.54×10^{-4}	1.7×10^4

a) Calculated by Stern-Volmer equation $I_0/I = 1 + k_q\tau(\text{amine})$ in Fig. 1;

b) Measured with viscosimetry at 25°C and calculated by $[\eta] = 5.74 \times 10^{-4}M^{0.78}$ [9].

2. ESR spectra of anthracene-amine system

Okada et al.^[10] studied the photoreaction of pyrene-aniline and pyrenediphenylamine systems with flash photolysis technique and observed the instantaneous absorption of pyrenyl radical and diphenylamine radical. They proposed a fast proton transfer reaction in the encounter complex of pyrene-aromatic primary or secondary amines, which led to produce two corresponding radicals species. But such intermediates in other CAH-aniline systems have not been proved. We investigated the ESR spectra of anthracene-aniline system and anthracene-N-methylaniline system with spin trapping technique, as shown in Fig. 2 and Fig. 3 respectively. The signals are assigned to be the ESR spectrum of radical (I) (eq. (1)) $a_N = 14.5G$, $a_H = 0.87G$, somewhat overlapped by another signal ($a_N = 15.2G$), ascribed to the product (II) of photolysis of MNP (eq. (2)).



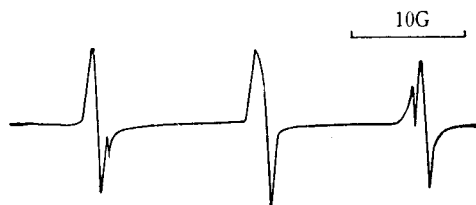


Fig. 2 ESR plot of anthracene ($2 \times 10^{-3}M$)-aniline ($2 \times 10^{-2}M$)-MNP ($1.3 \times 10^{-2}M$) after irradiation 80 seconds (in benzene)

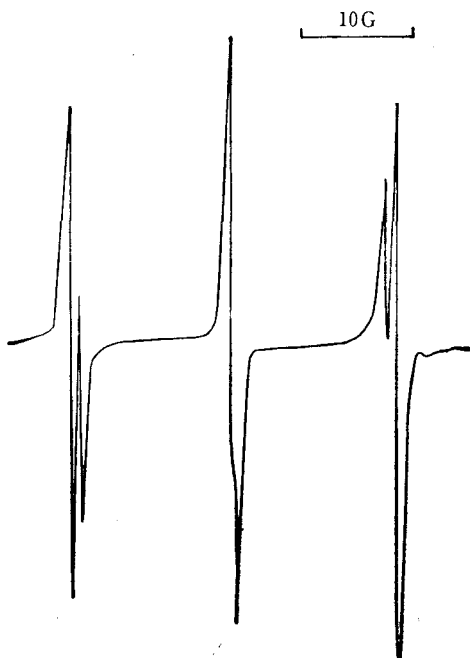
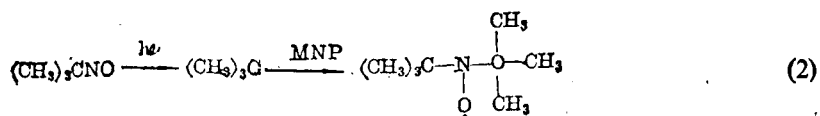


Fig. 3 ESR plot of anthracene ($2 \times 10^{-2}M$)-NMA ($2 \times 10^{-2}M$)-MNP ($1.3 \times 10^{-2}M$) after irradiation 90 seconds (in benzene)



No signal corresponding to the radical formed by trapping of anilino or N-methylanilino radical by MNP was observed. This may be ascribed to the unstable linkage of $\text{>N}-\text{N}-\text{O}^\bullet$.

3. The influence of solvent polarity on the polymerization rate

Okada et al.^[10] observed a strong absorption of ion-radicals in pyrene-aniline-acetonitrile system with the flash photolysis technique and suggested that the exciplex between pyrene and aniline would be dissociated into solvated ion-radicals in high polar solvents. In order

to clarify whether the proton transfer takes place within the exciplex or between solvated ion-radicals, we investigated the influence of solvent polarity on the polymerization rate (Table 2). The results shows that for MMA, a lower polar monomer, R_p increases with the increasing

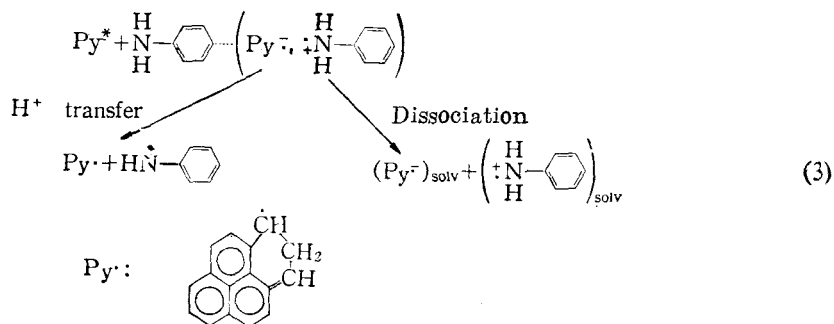
Table 2 R_p (conversion %min.⁻¹) of photopolymerization of AN and MMA initiated with pyrene-aniline in various solvents

Solvent	Dielectric constant ^[7b]	R_p (MMA) ^{a)}	R_p (AN) ^{b)}
Cyclohexane	2.023	0.054	0.191
Benzene	2.275	0.056	0.218
Ethanol	24.58	0.158	0.379
Methanol	32.70	0.276	0.250
Acetonitrile	37.5	0.284	0.209

a) [Pyrene]= $2.5 \times 10^{-3}M$, [Aniline]= $7 \times 10^{-3}M$, [MMA]= $4.7M$

b) [Pyrene]= $2.0 \times 10^{-3}M$, [Aniline]= $1.0 \times 10^{-3}M$, [AN]= $7.6M$

of the polarity of solvents (monomer:solvent=1:1) because it favored the exciplex formation, while for the higher polar monomer AN R_p shows a maximum value in medium polar solvent ethanol and will decrease in high polar solvent methanol and acetonitrile because the exciplex will be dissociated into solvated ion-radicals in such high polar media. These results suggest that the dissociation of exciplex into solvated ion-radicals will hinder the proton transfer and then hinder the polymerization, as illustrated with pyrene (Py)-aniline as follows:



4. The role of the excited triplet state of CAH in the initiation of polymerization

The excited singlet state of CAH could transfer to the triplet state through the inter-system crossing. The quantum yield of intersystem crossing (ϕ_{ISC}) for anthracene and pyrene is 0.75 and 0.27–0.38 respectively^[4]. In studying of the photopolymerization of AN initiated by naphthalene, Barton et al.^[11] proposed that both of the excited singlet state and the triplet state were responsible for the initiation. For CAH-aniline system, however, we assumed that the proton transfer took place in the excited singlet state of CAH as in the above description. To clarify the role of the triplet state in the initiation we have investigated the influence of the heavy atom on the photopolymerization (Table 3). The data shows that R_p decreases

in the following sequence, i.e. in benzene $>$ in $C_2H_5Br >$ in $C_2H_4Br_2$. In C_2H_5Br and $C_2H_4Br_2$ the yield of the excited singlet state will decrease and the yield of the excited triplet state will increase because of the heavy atom effect.

Table 3 R_p (conversion % min^{-1}) of photopolymerization of AN initiated with anthracene-aniline and pyrene-aniline systems in some solvents*

Initiator system \ Solvent	Benzene	C_2H_5Br	$C_2H_4Br_2$
Anthracene-aniline	0.096	0.039	0.020
Pyrene-aniline	0.218	0.120	0.048

* $[CAH]=2 \times 10^{-3}M$, $[aniline]=10^{-2}M$, $[AN]=7.5M$.

In addition, when 9, 10-dibromoanthracene ($\phi_{ISC}=0.9^{[12]}$) was used in stead of anthracene, R_p will decrease sharply because of the intra-molecular heavy atom effect. For example, R_p of AN were $0.36\% \text{ min}^{-1}$ and $0.04\% \text{ min}^{-1}$ for anthracene ($10^{-3}M$)-aniline ($10^{-2}M$) system and 9, 10-dibromoanthracene ($10^{-3}M$)-aniline ($10^{-2}M$) system, respectively. These results indicate that proton transfer in CAH-aniline system takes place favorably in the singlet excited state rather than in the triplet state.

5. The end-group of the formed polymer

In order to evaluate the contribution of the two kinds of radicals produced from the photoreaction of CAH and aniline in the polymerization, the end-groups of the formed polymers were examined.

Fig. 4 shows the fluorescence spectra of PMMA initiated by anthracene-aniline and by

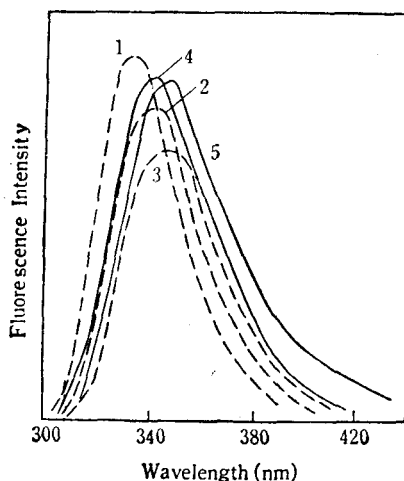
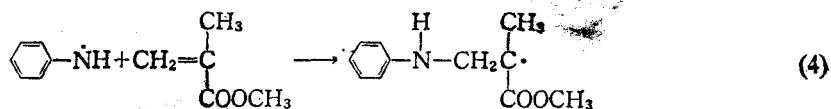
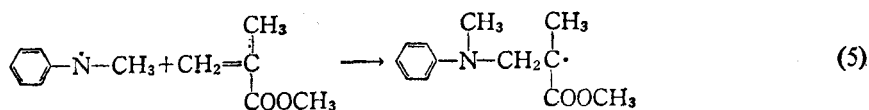


Fig. 4 Fluorescence spectra (in THF, $\lambda_{ex}=300nm$)
 1. Aniline (333nm); 2. NMA (340nm); 3. DMA (345nm);
 4. PMMA initiated with anthracene-aniline system (340nm);
 5. PMMA initiated with anthracene-NMA system (345nm).
 (The numbers in the brackets represent the values of $F\lambda_{max}$)

anthracene-N-methylaniline (NMA) in tetrahydrofuran (THF). In THF, with the excitation light at 300nm, the wavelengths at which the fluorescence maximum ($F\lambda_{\max}$) appears are located at 333nm, 340nm and 345nm for aniline, NMA and N,N-dimethylaniline (DMA), respectively. The $F\lambda_{\max}$ of PMMA initiated with anthracene-aniline system was observed at 340nm, the same as that of NMA, while the $F\lambda_{\max}$ of PMMA initiated with anthracene-NMA system was at 345nm, the same as that of DMA. These results suggest that the anilino radicals initiate the vinyl polymerization and the corresponding secondary amino end-group is formed as follows:



and the N-methylanilino radicals initiate the vinyl polymerization and a tertiary amino end-group is formed as follows:



Similar results have been obtained from the fluorescence spectra of PAN initiated by anthracene-aniline system and anthracene-NMA system, as shown in Fig. 5. In dimethyl-

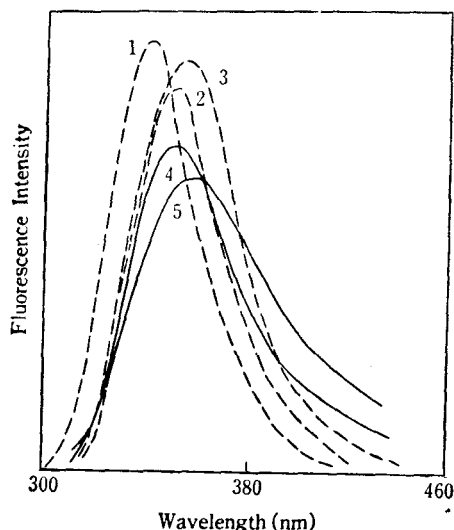


Fig. 5 Fluorescence spectra (in DMF, $\lambda_{\text{ex}}=300\text{nm}$)
 1. Aniline (339nm); 2. NMA (347nm); 3. DMA (352nm);
 4. PAN initiated with anthracene-aniline system (349nm);
 5. PAN initiated with anthracene-NMA system (352nm).
 (The numbers in the brackets represent the values of $F\lambda_{\max}$)

formamide (DMF), with the excitation light at 300nm, the $F\lambda_{\max}$ for aniline, NMA and DMA were observed at 339nm, 347nm and 353nm, respectively. The fluorescence emission ($F\lambda_{\max}=349\text{nm}$) of PAN obtained from anthracene-aniline system shows the presence of NMA end-group, and the fluorescence emission ($F\lambda_{\max}=352\text{nm}$) of PAN obtained from anthracene-NMA system shows the presence of DMA end-group.

We could not detect the fluorescence spectrum of the anthracene end-group probably because this group (see (I) in eq. (1)) does not consist of condensed aromatic hydrocarbon structure so no fluorescence will be emitted with the excitation light at 300nm. However, when pyrene-aniline system was used, the pyrenyl radical (see eq. (3)) would be produced through the photoreaction, which still has the condensed aromatic hydrocarbon structure. In benzene the fluorescence spectra of PMMA obtained with pyrene-aniline as initiator (Fig. 6) shows

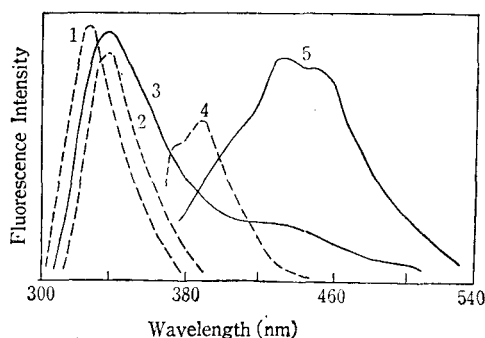
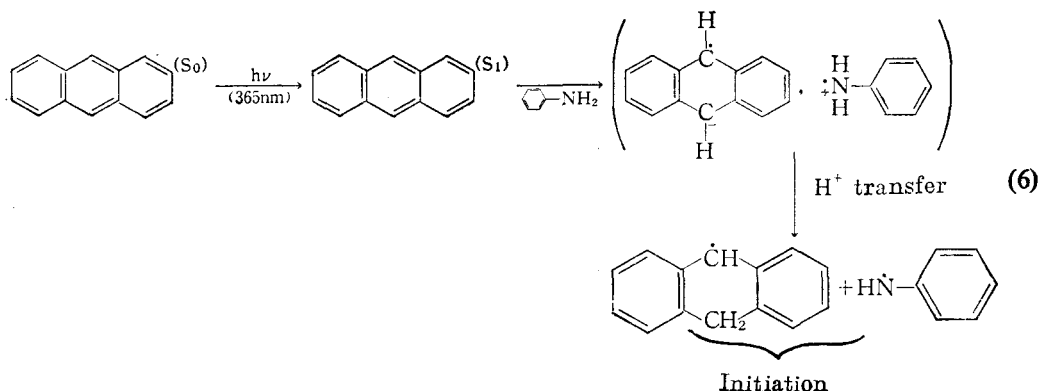


Fig. 6 Fluorescence spectra (in benzene)

1. Aniline (325nm); 2. NMA (335nm);
 3. PMMA initiated with pyrene-aniline system (335nm); 4. Pyrene (395nm);
 5. PMMA initiated with pyrene-aniline system (420nm).
- ($\lambda_{\text{ex}}=300\text{nm}$ for 1,2,3 and $\lambda_{\text{ex}}=360\text{nm}$ for 4,5. The numbers in the brackets represent the values of $F\lambda_{\max}$)

not only the fluorescence assigned to amino group ($F\lambda_{\max}=335\text{nm}$ with the excitation light at 300nm) but also another fluorescence at 420nm with the excitation light at 360nm, which may be assigned to the pyrenyl end-group. So the CAH radicals were proposed to initiate the polymerization.

Thus the initiation scheme of CAH-aniline system could be represented as follows using anthracene for illustration:



i.e. the excited anthracene (singlet state) forms exciplex with the ground state aniline. It is then followed by a proton transfer to produce two kinds of radicals. From the end-group analysis of the polymers we propose that both radicals are involved in the initiation of polymerization. The contribution of each for the initiation deserves further study.

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