

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

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ABSTRACT

The photopolymerization of acrylonitrile and methyl methacrylate initiated by condensed aromatic hydrocarbon-aniline systems was studied at 25°C under irradiation of 365 nm wavelength light. From kinetic data the monomer exponent has been measured to be 1.1. Within the concentration of 10^{-4} — $10^{-2}M$, the aromatic hydrocarbon exponents changed from 0.30 to 0.40, depending on the values of molar extinction coefficient of the hydrocarbons at 365 nm (ϵ_{365}). The greater the ϵ_{365} , the lower the exponents. The aniline exponents were measured to be in the range of 0.30—0.45. The aromatic hydrocarbon-aniline systems with the lower aniline exponent showed a lower ratio of the fluorescence quenching of the hydrocarbon by aniline and by the monomer.

INTRODUCTION

Condensed aromatic hydrocarbon (CAH) are known as the photoinitiator for vinyl polymerization^[1-4]. Barton et al.^[3,4] studied the photopolymerization of acrylonitrile (AN) initiated by naphthalene and other CAH. Based on the fluorescence quenching of CAH by AN, they proposed the initiation mechanism involving the formation of the exciplex from the excited state CAH and the ground state AN. It is also well known that CAH also form exciplexes with amines^[5]. Recently Kubota et al.^[6] reported the photopolymerization initiated by naphthalene-tertiary amines system, that in the presence of CAH such as naphthalene, aniline and N-methylaniline exhibited inhibition effect on the polymerization. But in our study, aniline was found to enhance the vinyl photopolymerization with CAH, such as anthracene, pyrene, chrysene and 1,2-benzoanthracene. In this paper we report the kinetics of such polymerization.

EXPERIMENTAL

1. Materials

AN was dried with anhydrous CaCl_2 and CaH_2 and then distilled under N_2 before use. Methyl methacrylate (MMA) was dried with CaH_2 and distilled under N_2 .

Anthracene, pyrene, chrysene and phenanthrene were purified by recrystallization. 1,2-benzoanthracene was a commercial reagent from Switzerland.

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Aniline was twice distilled under reduced pressure in a stream of N_2 . Other amines and dimethylformamide (DMF) were purified by distillation and their physical constants were consistent with literature values.

2. Methods

The rate of photopolymerization was measured dilatometrically at 25°C . A 300W high-pressure mercury lamp was served as the radiation source, and a CuSO_4 solution filter ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ 250 g/l $1\text{H}_2\text{O}$, 1cm) was used to cut out the light above 365 nm wavelengths^[7]. The polymerization were carried out in DMF solution. $[\text{AN}] = 3.8\text{ M}$, $[\text{MMA}] = 4.7\text{ M}$. The absorption spectra were recorded with Specord UV-VIS Spectrophotometer.

RESULTS AND DISCUSSION

1. The reaction of photopolymerization

Aniline does not initiate the polymerization under 365 nm wavelength in the concentration range used ($< 2 \times 10^{-2}\text{ M}$) because of no light absorption at this wavelength. But CAH, such as anthracene, pyrene and chrysene, which absorb the light of 365 nm, are able to initiate the polymerization of AN or MMA, and the polymerization rate will further increase by adding some aniline or its derivatives. As shown in Fig. 1, in adding $5 \times 10^{-3}\text{ M}$ aniline into $2.5 \times 10^{-3}\text{ M}$ pyrene, the rates of polymerization (R_p) of AN and MMA were increased from 0.21 and 0.16 to 0.60 and 0.53% min^{-1} respectively. Such enhancement effect should be ascribed to the interaction between CAH and aniline.

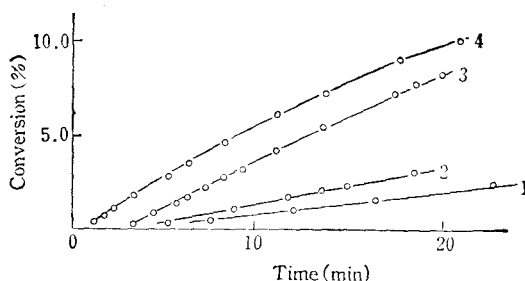


Fig. 1 Conversion-time plots of photopolymerization of AN and MMA
 1 $[\text{Pyrene}] = 2.5 \times 10^{-3}\text{ M}$, Monomer: MMA
 2 $[\text{Pyrene}] = 2.5 \times 10^{-3}\text{ M}$, Monomer: AN
 3 $[\text{Pyrene}] = 2.5 \times 10^{-3}\text{ M}$, $[\text{Aniline}] = 5 \times 10^{-3}\text{ M}$, Monomer: MMA
 4 $[\text{Pyrene}] = 2.5 \times 10^{-3}\text{ M}$, $[\text{Aniline}] = 5 \times 10^{-3}\text{ M}$, Monomer: AN

Naphthalene does not absorb the light of 365 nm so it will not initiate the polymerization of AN and MMA under 365 nm wavelength, even in the presence of aniline (up to the concentration of $2 \times 10^{-2}\text{ M}$).

Trace of 2,2,6,6-tetramethyl-piperidol nitroxyl radical (TMPN), a well known radical scavenger, will clearly inhibit the polymerization. Oxygen also inhibits the polymerization remarkably. So it is reasonable to consider that such a polymerization will follow the radical mechanism.

Fig. 2 presents the conversion-time relationship of MMA photopolymerization initiated by the combination of pyrene and different amines. The rates of polymerization as calculated from the slopes of the straight lines are arranged in the following sequence: N,N-dimethylaniline (DMA) > triethylamine (TEA) > N-methylaniline (NMA) > aniline. It is interesting to notice that the rate of polymerization by pyrene-DMA system ($1.63\% \text{ min}^{-1}$) is nearly twice of that by benzoin initiator ($0.8\% \text{ min}^{-1}$).

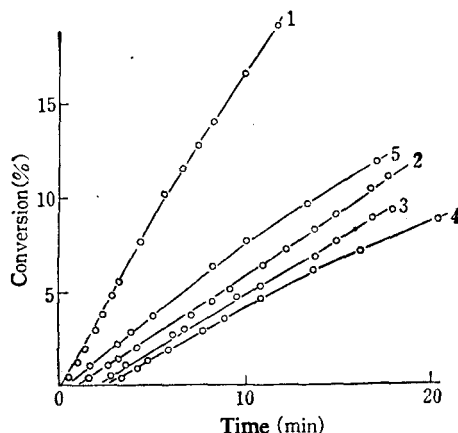


Fig. 2 Conversion-time plots of photopolymerization of MMA initiated by pyrene ($2.5 \times 10^{-3} M$)–aniline ($5 \times 10^{-3} M$) systems

- | | |
|------------------------------------|-------------------|
| 1 Pyrene-DMA; | 2 Pyrene-TEA; |
| 3 Pyrene-NMA; | 4 Pyrene-aniline; |
| 5 Benzoin ($5 \times 10^{-3} M$) | |

2. The relationship between R_p and concentration of CAH

For naphthalene-TEA system, Kubota et al.^[6] reported 0.5 exponent of naphthalene merely from a plot of R_p vs. $[\text{naphthalene}]^{\frac{1}{2}}$. It seems that a precise relationship between R_p and the concentration of CAH should be calculated from the plots of $\log R_p \sim \log [\text{CAH}]$, as shown in Fig. 3, which reveals that in a wide concentration range $\log R_p$ vs. $\log [\text{CAH}]$ does not show strict linear relationship. The slopes of the curves become smaller as the concentra-

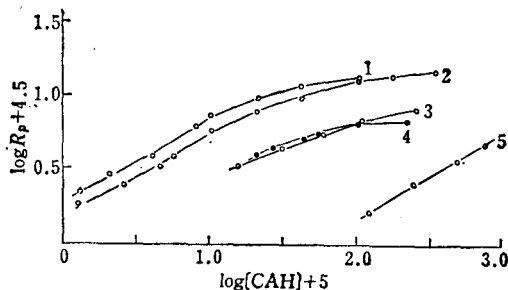


Fig. 3 Plots of $\log R_p \sim \log [\text{CAH}]$ in the photopolymerization of AN initiated by CAH-aniline systems ($[\text{Aniline}] = 10^{-2} M$)

- | | | |
|------------------------|----------------|-------------|
| 1 1,2-benzoanthracene; | 2 Pyrene; | 3 Chrysene; |
| 4 Anthracene; | 5 Phenanthrene | |

tion increases. This phenomenon may be explained as follows:

It is known that I_a , the moles (einstains) of light absorbed, may be expressed as

$$I_a = I_0(1 - 10^{-\epsilon[S]l}) \quad (1)$$

where I_0 represents the intensity of incident light, ϵ is the molar extinction coefficient of the initiator at the light wavelength employed, $[S]$ is the initiator concentration and l is the light path length.

From eq. (1) and $R_p \propto I_a^{1/2}$ the relationship between R_p and $[S]$ will be different in the different concentration range of initiator. In the quite low concentration of initiator, i.e. $\epsilon[S]l < 0.1$, $1 - 10^{-\epsilon[S]l}$ is practically equal to $2.303 \epsilon[S]l$, so $R_p \propto [S]^{1/2}$. At very high $[S]$, $\epsilon[S]l > 2$, $I_a \approx I_0$, i.e. all the incident light is absorbed by the sample, so that I_a practically does not depend on $[S]$. In this case the initiator exponent will be near zero. Therefore, in case of $0.1 < \epsilon[S]l < 2$, the initiator exponent must lie between 0.5 and 0.

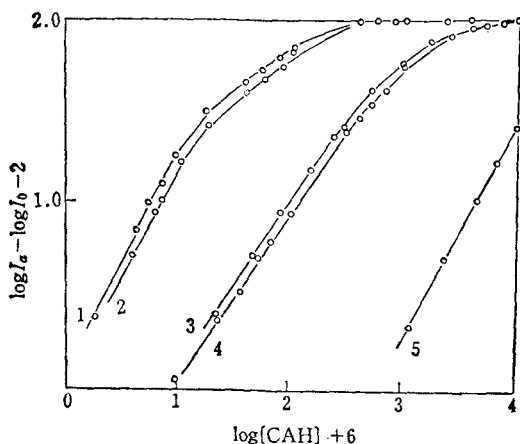


Fig. 4 The relationship between $\log I_a$ and $\log [CAH]$ ($l = 1$ cm)

- | | |
|---------------|------------------------|
| 1 Anthracene; | 2 1,2-benzoanthracene; |
| 3 Chrysene; | 4 Pyrene; |
| | 5 Phenanthrene |

Fig. 4 present the relationship between I_a and $[S]$ for different CAH, where I_a was calculated according to $I_a = I_0(1 - I/I_0)$ (I is the intensity of the transmitted light) and $\log I_0/I$ (absorbance) was measured experimentally. It reveals that I_a is proportional to $[S]$ only in the low concentration of CAH, and $\log I_a \sim \log [S]$ becomes nonlinear in higher $[S]$. This makes the nonlinear relationship between $\log R_p$ and $\log [CAH]$ when $[CAH]$ increases.

For different CAH, the concentration in which the condition $\epsilon[S]l = 0.1$ was fulfilled depends on their different ϵ_{365} values. If $l = 0.5$ cm (the internal diameter of the dilatometer was 0.8 cm), the required concentration of 1,2-benzoanthracene ($\epsilon_{365} = 7200$) and pyrene ($\epsilon_{365} = 410$) should be lower than $2 \times 10^{-5} M$ and $5 \times 10^{-4} M$ respectively. Fig. 3 shows that the slopes of curve 1 and curve 2 are 0.54 and 0.52 respectively when the concentration is lower than $10^{-4} M$, which suggests that the initiator exponents are near to the expected value 0.5 in this concentration range.

From Fig. 3 the CAH exponents for pyrene, chrysene, anthracene and 1,2-benzo-

anthracene were calculated to be 0.40, 0.40, 0.30 and 0.30 respectively in the concentration $10^{-4}M-10^{-3}M$. The difference of the exponents is ascribed to the different ϵ_{365} for different CAH used. In the same range of concentration, the CAH with greater absorbance showed greater ϵ_{365} value, which caused more deviation from $\epsilon[S]I < 0.1$ and thus led to lower CAH exponent. The ϵ_{365} value of phenanthrene is very small (4.7) and the condition of $\epsilon[S]I < 0.1$ is fulfilled in the concentration range $10^{-3}M-10^{-2}M$, so its exponent 0.55 is roughly in accordance with the expected value 0.1.

From above derivation, as [CAH] continually increases to a certain value, the I_a value will not change much and R_p might asymptotically approach a constant value. In fact, however, a decreasing of R_p was observed above a certain concentration ($[CAH]_{max}^p$) for anthracene, pyrene, chrysene and 1,2-benzoanthracene-aniline systems (Fig. 5B). Table 1 shows that the greater the ϵ_{365} for the CAH, the lower the $[CAH]_{max}^p$ will be, i.e. anthracene $\sim$ 1, 2-benzoanthracene $<$ chrysene $<$ pyrene $<$ phenanthrene. This sequence is in accordance with that of ϵ_{365} of CAH (in inverse order). The decreasing of R_p may be ascribed to (1) the cage effect occurred among the radicals which were produced by the photoreaction at high CAH concen-

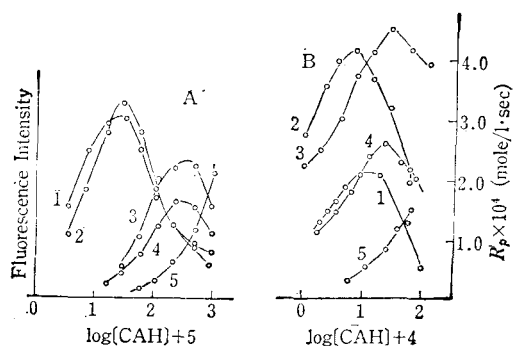


Fig. 5 A. The relationship between fluorescence intensity of CAH and [CAH];
B. The relationship between rate of polymerization of AN initiated by CAH-aniline ($10^{-2}M$) and [CAH]

1 Anthracene; 2 1,2-benzoanthracene;
3 Pyrene; 4 Chrysene; 5 Phenanthrene

Table 1 Relationship between photopolymerization of AN and ϵ_{365} of CAH

CAH	$\epsilon_{365}^a)$	$[CAH]_{max}^F)^b)$	$[CAH]_{max}^p)^c)$	Exponent of CAH ^{d)}
Anthracene	7500	$2.0 \times 10^{-4}M$	$1.0 \times 10^{-3}M$	0.30
1,2-benzoanthracene	7300	$2.0 \times 10^{-4}M$	$1.0 \times 10^{-3}M$	0.30
Chrysene	430	$2.5 \times 10^{-3}M$	$2.4 \times 10^{-3}M$	0.40
Pyrene	410	$4.0 \times 10^{-3}M$	$3.0 \times 10^{-3}M$	0.40
Phenanthrene	4.7	/	/	0.55

a) Molar extinction coefficient of CAH at 365 nm in benzene

b) Concentration of CAH at the maximum of the curves presented in Fig. 5A

c) Concentration of CAH at the maximum of the curves presented in Fig. 5B

d) $[CAH] = 10^{-4}M-10^{-3}M$ ([Phenanthrene] = $10^{-3}M-10^{-4}M$), [Aniline] = $10^{-2}M$, AN polymerization

tration and crowded in a thin layer of solution faced to the incident light and (2) the self-quenching of the excited state of the CAH at high concentration.

Fig. 5A shows the relationship between fluorescence intensity of CAH and $[CAH]$. A maximum of fluorescence was observed for anthracene, pyrene, chrysene and 1,2-benzoanthracene. This may be ascribed to the self-quenching of the excited state of the CAH at high concentration. The greater the ε_{365} value of the CAH, the lower the concentration at which the maximum appeared (Table 1). The sequence of CAH was similar with that shown in Fig. 5B.

Phenanthrene did not show any decrease of fluorescence intensity as well as R_p in a concentration range of $10^{-3} M$ — $10^{-2} M$ because of its low ε_{365} value (4.7) and, therefore, also very low absorbance in this concentration.

3. The relationship between R_p and aniline concentration

Fig. 6 presents the relationship between R_p and aniline concentration for the photopolymerization of AN initiated with CAH-aniline systems. The aniline exponent, calculated from the slopes of the straight lines, varied from 0.30 to 0.45 (Table 2) for different CAH-aniline systems.

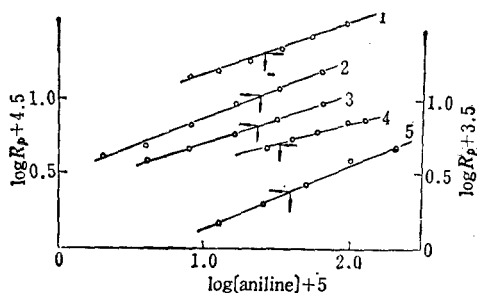


Fig. 6 Dependence of R_p of AN polymerization on $[aniline]$ ($[CAH] = 3 \times 10^{-3} M$ except $[phenanthrene] = 5 \times 10^{-3} M$)

1 1,2-benzoanthracene; 2 Pyrene; 3 Chrysene;
4 Phenanthrene; 5 Anthracene

Table 2 Relationship between aniline exponent and $k_q(A) / k_q(AN)^a$

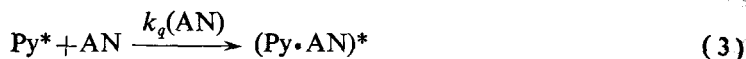
CAH	$k_q\tau(A)^b$	$k_q\tau(AN)^b$	$k_q(A)/k_q(AN)$	Aniline exponent ^c
Anthracene	30	0.026	115	0.45
Pyrene	115	0.105	110	0.41
1,2-benzoanthracene	70	0.081	86	0.35
Chrysene	60	0.085	70.5	0.35
Phenanthrene	10	2.2	4.5	0.30

a) $k_q(A)$ and $k_q(AN)$ represent the quenching rate constants of CAH by aniline and by AN respectively

b) Stern-Volmer quenching constants of CAH measured in DMF

c) Polymerization of AN initiated by CAH-aniline. $[CAH] = 3 \times 10^{-3} M$ with the exception $[phenanthrene] = 5 \times 10^{-3} M$

In the system composed of CAH-aniline-AN, CAH can form exciplexes not only with aniline, but also with AN. For example:



where Py^* represents the excited state of pyrene, "A" represents aniline, $k_q(\text{A})$ and $k_q(\text{AN})$ refer to the quenching rate constants of aniline and AN and $(\text{Py} \cdot \text{A})^*$, $(\text{Py} \cdot \text{AN})^*$ refer to the exciplexes respectively. Both routes can lead to initiation of polymerization. So the lower aniline exponent may be ascribed to the presence of such polymerization caused by the interaction between CAH and the monomer.

Fig. 7 shows the Stern-volmer plots for the fluorescence quenching of pyrene by aniline, AN and MMA respectively. Table 2 presents the $k_q\tau$ values for other CAH.

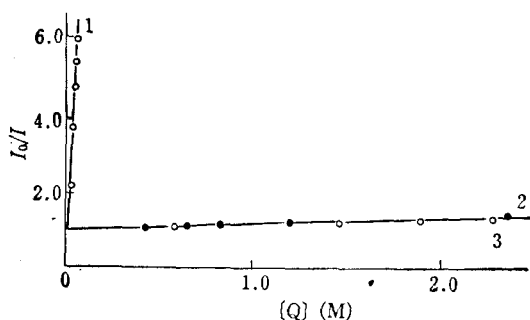


Fig. 7 Stern-volmer plots for the fluorescence quenching of pyrene ($[\text{Pyrene}] = 2 \times 10^{-4} \text{M}$, in DMF)
 1 aniline (115); 2 MMA (0.14); 3 AN (0.105)
 (The numbers in the brackets represent the $k_q\tau$ values calculated from Stern-Volmer equation $I_0/I = 1 + k_q\tau[Q]$)

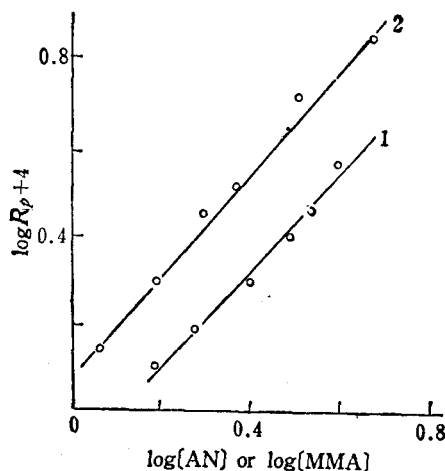


Fig. 8 $\log R_p \sim \log [\text{monomer}]$ plots
 ($[\text{Pyrene}] = 3 \times 10^{-3} \text{M}$, $[\text{Aniline}] = 10^{-3} \text{M}$, in DMF)
 1 AN; 2 MMA

From Table 2 one can see the relationship between aniline exponent and the ratio of the two quenching rate constants ($k_q(A)$ and $k_q(AN)$). The greater the ratio $k_q(A) / k_q(AN)$, i.e. the more important role the interaction between CAH and aniline plays, the higher the aniline exponent will be.

4. The relationship between R_p and monomer concentration

Fig. 8 shows the relationship between R_p and monomer concentration in the photopolymerization of AN and MMA initiated by pyrene-aniline system. The slopes of the plots, showing the monomer exponent, are all of the same value 1.1. The small deviation near to the expected value of 1.0 could be explained by the participation of some monomer molecules in the initiation reaction, as shown in expression (7).

In summary, the kinetic equation of the photopolymerization of AN initiated with CAH-aniline system is given by

$$R_p \propto [CAH]^{0.30-0.40} [Aniline]^{0.30-0.45} [AN]^{1.1}$$

1. The CAH exponent will vary with different concentrations of CAH. The exponent decreases with the increasing of the concentration and approaches 0.5 only at quite low absorbance. In the concentration range of $10^{-4}M$ — $10^{-3}M$ the exponent values are within the range of 0.30—0.40.

2. The exponent for various CAH depends on their molar extinction coefficient ϵ_{365} . The CAH with lower ϵ_{365} will show higher CAH exponent.

3. For different CAH-aniline systems, the aniline exponent depends on the $k_q(A)/k_q(AN)$ ratio. The higher the ratio, the higher the aniline exponent will be.

REFERENCES

- [1] Andersen, V.S. and Norrish, R.G.W., *Proc. Roy. Soc. London A*, **1959**, 251, 1.
- [2] Norrish, R.G.W. and Simons, I.P., *Proc. Roy. Soc. London A*, **1959**, 251, 4.
- [3] Barton, J. and Capek, I., *J. Polym. Sci. Polym. Lett. Ed.*, **1974**, 12, 327.
- [4] Barton, J., Capek, I. and Hrdlovic, P., *J. Polym. Sci. Polym. Chem. Ed.*, **1975**, 13, 2671.
- [5] Mataga, N., Okada, T. and Oohari, H., *Bull. Chem. Soc. Japan*, **1966**, 39, 2563.
- [6] Kubota, N. and Ogiwara, Y., *J. Appl. Polym. Sci.*, **1983**, 28, 2425.
- [7] 李 潼、曹维孝、冯新德, 高分子通讯, **1983**, (4) 260.