

THE PHOTOPOLYMERIZATION KINETICS OF PHOTSENSITIZED ACRYLAMIDE SYSTEM INDUCED BY He-Ne LASER

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ABSTRACT

The kinetics of the photopolymerization of sensitized acrylamide (AM) system induced by He-Ne laser has been investigated. Using methylene blue (MB)-triethanolamine (TEOA) as the photosensitive system, the photopolymerization followed a nonsteady-state kinetic scheme in the initial period of polymerization (the monomer conversion $C\% < 2\%$) and then followed a steady-state kinetic scheme ($5\% > C\% > 2\%$). According to the steady-state hypothesis, the mechanism of photopolymerization was proposed. The deduced kinetic equation of the photopolymerization of AM is in good coincidence with the experimental results.

INTRODUCTION

With the rapid development of laser technology, much attention has been paid to the application of the technology in the field of polymer photochemistry. Study on the laser induced polymerization has been developed quite actively. The aspects of the mechanisms of initiation and polymerization and the effects of several factors have been investigated. Many highly active systems of photopolymerization have been found^[1-10].

This paper reports the kinetics of the photopolymerization of sensitized AM system induced by He-Ne laser. Using the methylene blue (MB)-triethanolamine (TEOA) as the photo-sensitive system, the photopolymerization was found to follow a nonsteady-state kinetic scheme in the initial stage of polymerization (monomer conversion $C\% < 2\%$), characterized by the variation of polymerization rate with the exposure time. Thereafter the photopolymerization ($5\% > C\% > 2\%$) obeyed a steady-state kinetic scheme, the rate of polymerization did not change with the exposure time. The relation between polymerization rate and such factors as reactant concentrations was studied with a recording dilatometer. The experimental kinetic equation of photopolymerization at 25 °C under constant laser intensity was obtained. According to the steady-state hypothesis, the mechanism of photopolymerization was theoretically proposed. The deduced kinetic equation of polymerization is in good agreement with the experimental results.

EXPERIMENTAL

Materials

Acrylamide (AM) was recrystallized twice from benzene-methanol (10:1

$v/v)^{[11]}$ and vacuum dried, m.p. = 84 — 85 °C .

Triethanolamine (TEOA) and methylene blue (MB) were analytical reagents and used without further purification .

Polymerization

Aqueous acrylamide solutions of definite concentrations were prepared in volumetric flasks in the dark .

The polymerization reaction was carried out in a recording dilatometer^[12] . The dilatometer was placed 20 cm from the exit of a He-Ne laser . The diameter of the light spot was 5 mm . The output of laser was 5 mW .

The molecular weight of the polymer was determined by measuring the intrinsic viscosities of the polymer in 1N NaCl solution at 30 °C . Number-average molecular weight ($\overline{Mn}$) was calculated from the following equation : ^[13]

$$[\eta] = 6.8 \times 10^{-4} \overline{Mn}^{0.66}$$

Quantum yield for monomer consumption (ϕ_m) is calculated from

$$\phi_m = NC / Ia$$

where $N = 6.02 \times 10^{23}$, C = the monomer conversion, Ia = the initiating energy quanta absorbed by the sample .

Quantum yield for polymer formation (ϕ_p) was actually obtained from

$$\phi_p = \phi_m / \overline{Mn}$$

RESULTS AND DISCUSSION

Spectral characteristics of photosensitized acrylamide system

The UV-visible absorption spectra of aqueous AM, TEOA and MB solutions were respectively measured with a Shimadzu UV-240 UV-Visible spectrophotometer. The wavelength at maximum absorption (λ_{max}) of AM was 198nm and the maximum molar extinction coefficient (ϵ_{max}) was approximately 10^4 . The λ_{max} of TEOA was 194nm with $\epsilon_{max} = 600$. There appeared three maximum at 661, 290 and 246nm in the absorption spectrum of aqueous MB solution. The molar extinction coefficient of MB was 3.6×10^4 at 632.8nm which is the wavelength of He-Ne laser emission. Fig. 1 shows the absorption spectrum of aqueous photosensitized AM solution containing AM, TEOA and MB. The system of aqueous photosensitized AM solution could strong absorb the laser light .

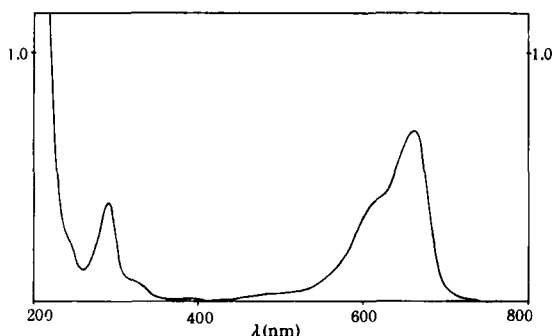


Fig.1 The absorption spectrum of photosensitized acrylamide system
 $[M] = 1.0 \times 10^{-2} M$; $[TEOA] = 2.6 \times 10^{-4} M$; $[MB] = 1.0 \times 10^{-5} M$

Characteristics of a nonsteady-state and a steady-state in the polymerization

MB-TEOA, as a sensitizing system, could initiate the polymerization of AM monomer induced by He-Ne laser. The conversion of monomer versus time during the photopolymerization was recorded as shown in Fig. 2, which demonstrated that the photopolymerization proceeded through a complicated kinetic scheme. The initial nonlinear portion (dotted lines) of the curves in Fig. 2 changed to linear when the complete fading of MB had occurred. It should be noted that before the fading of MB, the rate of polymerization actually increased with time. It is a nonsteady-state kinetic scheme because the active free radicals of polymerization were continuously increasing.

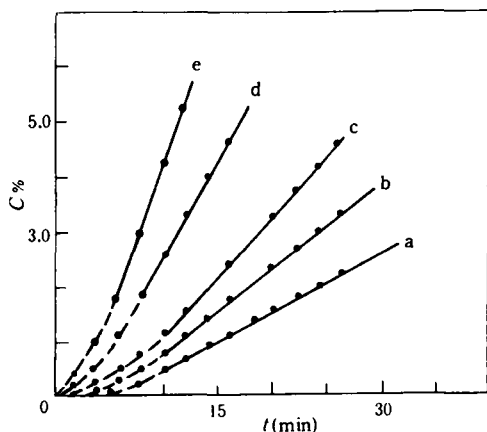


Fig. 2 Monomer conversion with exposure times (t) of polymerization induced by He-Ne laser
 $[MB] = 2.0 \times 10^{-4} M$, $[TEOA] = 4.28 \times 10^{-2} M$
 $[M] = a) 1.0 M$, $b) 1.5 M$, $c) 2.0 M$,
 $d) 3.0 M$, $e) 4.0 M$

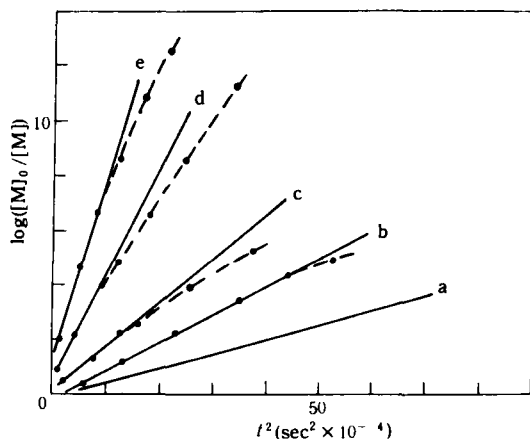


Fig. 3 Relation between $\log([M]_0/[M])$ and t^2 at different monomer concentrations
 $[MB] = 2.0 \times 10^{-4} M$, $[TEOA] = 4.28 \times 10^{-2} M$

In the rate expression:

$$R_p = -d[M]/dt = k_p [R \cdot] [M]$$

where $[M]$ is the monomer concentration, $[R \cdot]$ is the radical concentration and k_p is the rate constant for propagation, if k_p is constant, the increase in rate with time could only be attributed to an increase in $[R \cdot]$. Thus, if $[R \cdot] \propto t$, the rate can be expressed as the following:

$$R_p = -d[M]/dt = K [M] t$$

then

$$\log [M]_0/[M] = K' t^2$$

where $[M]_0$ is the initial monomer concentration, t is the time of polymerization, and K' is a proportionate constant relating to initiation, propagation, MB concentration and laser light intensity. When the nonlinear portions of the curves in Fig. 2 were replotted as $\log [M]_0/[M]$ against t^2 . Straight lines were obtained as shown in Fig. 3 and dotted lines were corresponding to the linear portions of Fig. 2. It showed that the photopolymerization of AM sensitized solution systems induced by He-Ne laser underwent a nonsteady-state kinetic scheme in the initial period of polymerization^[14], then the rate did not vary with

time and followed a steady-state kinetic scheme. The rate of polymerization (R_p) could be obtained from the slopes of linear portions in Fig. 2.

Kinetics of polymerization

The relation between R_p and the concentrations of reagents including AM, TEOA and MB was obtained in Fig. 4 under a constant laser intensity. From Fig. 4, the observed kinetics of photopolymerization at 25 °C can be expressed by the following equation :

$$R_p = K [M]^{1.4} [\text{TEOA}]^{0.41} [\text{MB}]^{0.37}$$

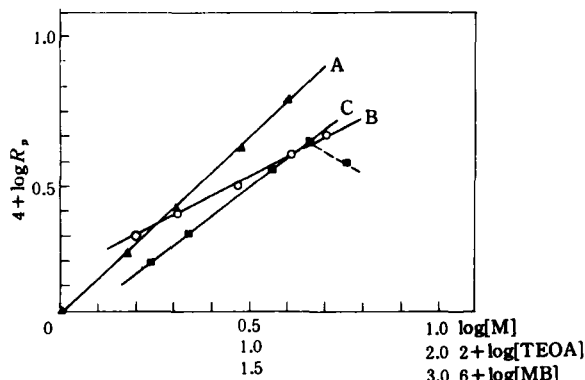


Fig. 4 Dependence of R_p on the concentration of AM, TEOA or MB

A. $[\text{TEOA}] = 4.28 \times 10^{-2} M$, $[\text{MB}] = 2.0 \times 10^{-4} M$

B. $[M] = 2.0 M$, $[\text{MB}] = 2.0 \times 10^{-4} M$

C. $[M] = 2.0 M$, $[\text{TEOA}] = 4.28 \times 10^{-2} M$

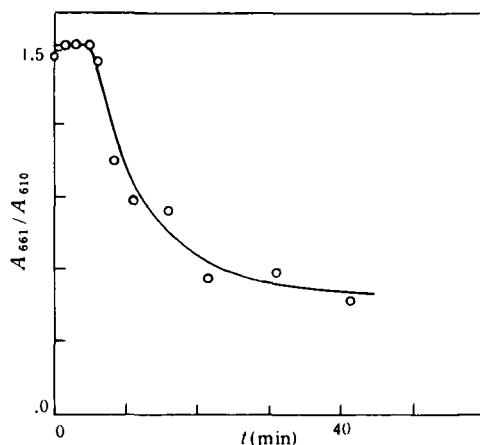


Fig. 5 Changes of A_{661}/A_{610} with time
 $[M] = 1.0 M$, $[\text{TEOA}] = 8.55 \times 10^{-2} M$,
 $[\text{MB}] = 4.0 \times 10^{-5} M$
 at room temperature

The role of dye MB was rather complicated during the polymerization. From the absorption spectrum of MB aqueous solution shown in Fig. 1, two overlapping peaks in the visible region were observed at $\lambda = 661$ and 610 nm. This has been explained by the existence of two forms of the dye molecules.^[14] The peak at the higher wavelength ($\lambda = 661$ nm) was the absorption of the monomeric dye molecules while that at the lower wavelength ($\lambda = 610$ nm) represented the absorption of the associated dye molecules. Both spectroscopic and photopolymerization behaviors suggested that the monomeric form of MB was a photosensitizer of sensitized AM system while the associated form was a chain terminator or chain-transfer agent. The polymerization rate changed with the concentration of the monomeric form of MB. When the concentration of MB was changed in the ranges of $10^{-6} - 2.0 \times 10^{-4} M$, a maximum rate of polymerization was observed (Fig. 4C) when MB concentration was $1.0 \times 10^{-4} M$.

Furthermore, the variety of the absorption spectrum of sensitized AM system with irradiation time was observed. The relative abundance of the monomeric and the associated form of MB was estimated from the ratio A_{661}/A_{610} . Result shown in Fig. 5 indicated that A_{661}/A_{610} decreased with prolonged irradiation. This implied that the monomeric form of dye consumed more quickly than the associated form did in the polymerization (at conversion $< 5\%$), therefore it could be

inferred that the monomeric form of MB consumed in the initiation process.

Quantum yields

The quantum yields of the photopolymerization of sensitized AM system irradiated by a constant laser intensity at 30 °C were calculated in Tab. 1. The results showed that the quantum yields increased with reaction time until the dye completely faded. The energy absorbed here was calculated on the initial dye concentration. Because the actual dye concentration decreased with exposure time, the actual energy absorbed decreased with exposure time. The actual quantum yields increased rapidly with the time of exposure.

Table 1 Photopolymerization of AM induced by He-Ne Laser

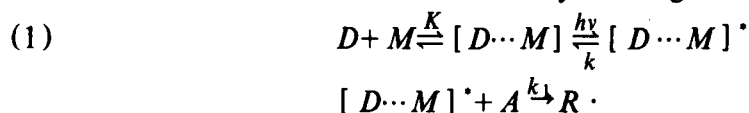
Time of exposure (min.)	Energy absorbed (quanta)	Monomer conv. (%)	Monomer molecules polymd.	[η] (dl/g)	$\overline{Mn} \times 10^{-4}$	Quantum yields	
						Monomer ϕ_M	Polymer ϕ_P
2	1.18×10^{18}	0.33	8.02×10^{21}	1.14	7.68	6.80×10^3	0.0885
6	3.55×10^{18}	1.56	3.76×10^{22}			1.06×10^4	0.138
10	5.92×10^{18}	3.79	9.13×10^{22}			1.54×10^4	0.201

$$I_a = 3.1 \text{ mV}$$

Mechanism of the polymerization

From the result of kinetic study, it has been suggested that: (1) the monomer, TEOA, MB all participate in the formation of the initial free radicals; (2) the growing chain radicals are mainly terminated by mutual termination. The mechanism of photopolymerization of sensitized AM system is proposed as the following:

The formation of initial radicals induced by laser light

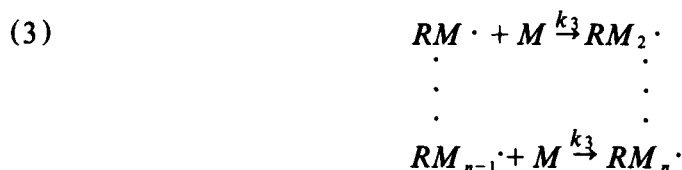


where D , A denote MB, TEOA, respectively.

Initiation of the chain



Propagation steps (each with the same rate constant)



Termination of the chain



Applying the steady-state hypothesis and assuming that the polymer is mainly formed by mutual termination, we may obtain

$$\frac{d[R\cdot]}{dt} = k_1[D\cdots M]^*[A] - k_2[R\cdot][M] = 0$$

$$[R\cdot] = \frac{k_1[D\cdots M]^*[A]}{k_2[M]}$$

From the equilibrium of the reaction (1):

$$[D\cdots M]^* = K_1 K_2 [D][M] = K [D][M]$$

$$[R\cdot] = \frac{k_1 K}{k_2} [D][A]$$

$$\frac{d[RM\cdot]}{dt} = k_2[R\cdot][M] - k_4[RM\cdot]^2 = 0$$

$$[RM\cdot] = \left(\frac{k_2}{k_4} [R\cdot][M] \right)^{\frac{1}{2}} = \left(\frac{k_1 K}{k_4} [D][A][M] \right)^{\frac{1}{2}}$$

thus

$$\begin{aligned} R_p &= -\frac{d[M]}{dt} = k_3[RM\cdot][M] = k_3[M] \left(\frac{k_1 K}{k_4} [D][A][M] \right)^{\frac{1}{2}} \\ &= K [M]^{\frac{3}{2}} [D]^{\frac{1}{2}} [A]^{\frac{1}{2}} \end{aligned}$$

The somewhat lowering in the order of reaction for MB (0.37) and TEOA (0.41) is attributable to the probable transfer to termination of the chain radicals to MB and TEOA, respectively. The reactivities of the radicals formed by chain transfer are proposed to be the same as the chain radicals.

Keywords :

He-Ne Laser ; Photopolymerization ; Photosensitive system ; Quantum yield

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