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### Relaxation Studies of Emulsion Polymerization of Styrene Initiated by Ultraviolet Light (using $\alpha$ -sodium anthraquinone sulfonate/triethyl amine as photosensitizer)

Shoukuan Fu<sup>a</sup>; Yu Qian<sup>a</sup>; Qun Wang<sup>a</sup>; Lei Xu<sup>a</sup>

<sup>a</sup> Department of Materials Science, Fudan University, Shanghai, Peoples Republic of China

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## RELAXATION STUDIES OF EMULSION POLYMERIZATION OF STYRENE INITIATED BY ULTRAVIOLET LIGHT (USING $\alpha$ -SODIUM ANTHRAQUINONE SULFONATE/TRIETHYL AMINE AS PHOTSENSITIZER)\*

SHOUKUAN FU, YU QIAN, QUN WANG, and LEI XU

Department of Materials Science  
Fudan University  
Shanghai, 200433 Peoples Republic of China

### ABSTRACT

This paper presents the results of relaxation studies of the seeded emulsion polymerization of styrene initiated by UV-light with a water-soluble photosensitizer. The relaxation kinetic runs were performed at 45, 50, 55, and 60°C using a small diameter rotary dilatometer with an inner magnetic agitator. The entry rate coefficient of thermally induced free radicals into the latex particles,  $\rho_0$ ; the exit rate coefficient of free radicals from latex particles,  $k$ ; and the average number of free radicals per particle in the thermally induced background polymerization,  $n_{ss(\text{thermal})}$  were determined. The propagating rate coefficient  $k_p$  was determined with the data of monomer concentration in a particle,  $C_M$ , obtained from experiments with chemical initiation. The Arrhenius formula with  $\rho_0$ ,  $k$ , and  $k_p$  was also obtained.

### INTRODUCTION

Lansdowne et al. reported the method of  $\gamma$ -ray-induced seeded emulsion polymerization of styrene in a dilatometer [1]. After a steady-state polymerization rate was reached, the irradiation source was removed and the relaxation process of

\*Dedicated to Otto Vogl on the occasion of his 65th birthday.

the polymerization rate was observed. Through such experiments the entry rate coefficient of thermally induced free radicals,  $\rho_0$ , and the exit rate coefficient of free radicals,  $k$ , were obtained and compared with the results of kinetic studies with chemical initiation [2], and the results agreed with each other. It was also reported that  $\gamma$ -ray initiation enables relaxation studies under different temperatures, and the activation energies of the rate coefficients  $\rho_0$ ,  $k$ , and  $k_p$  could be determined.

UV-initiation has the same advantages as  $\gamma$ -initiation. In addition, UV-light is safer and can be cut off more easily and quickly, so that the relaxation process can be observed at once. The problem is that styrene alone cannot be effectively initiated by UV-light, and the steady-state polymerization rate cannot be reached quickly, so a water-soluble photosensitizer ( $\alpha$ -sodium anthraquinone sulfonate/triethyl amine system) was added. Moreover, the emulsion systems have poor transparency, so UV-initiation may cause unevenness in polymerization. To solve this problem, a small diameter rotary dilatometer with an inner magnetic agitator was used (see Fig. 1). With such an approach the steady-state polymerization rate was reached quickly, and this polymerization rate was quite similar to that found with a high concentration chemical initiator. Furthermore, the results showed excellent reproducibility and thus suggested that the attempt to study the relaxation process by the UV-initiated seeded emulsion polymerization of styrene was a success.

### THEORETICAL TREATMENT

The theoretical treatment of this study is similar to that of Ref. 1, and the derivation of the equations in the current section is quoted from Ref. 1 to make the following sections more convenient to comprehend. The method of seeded emulsion

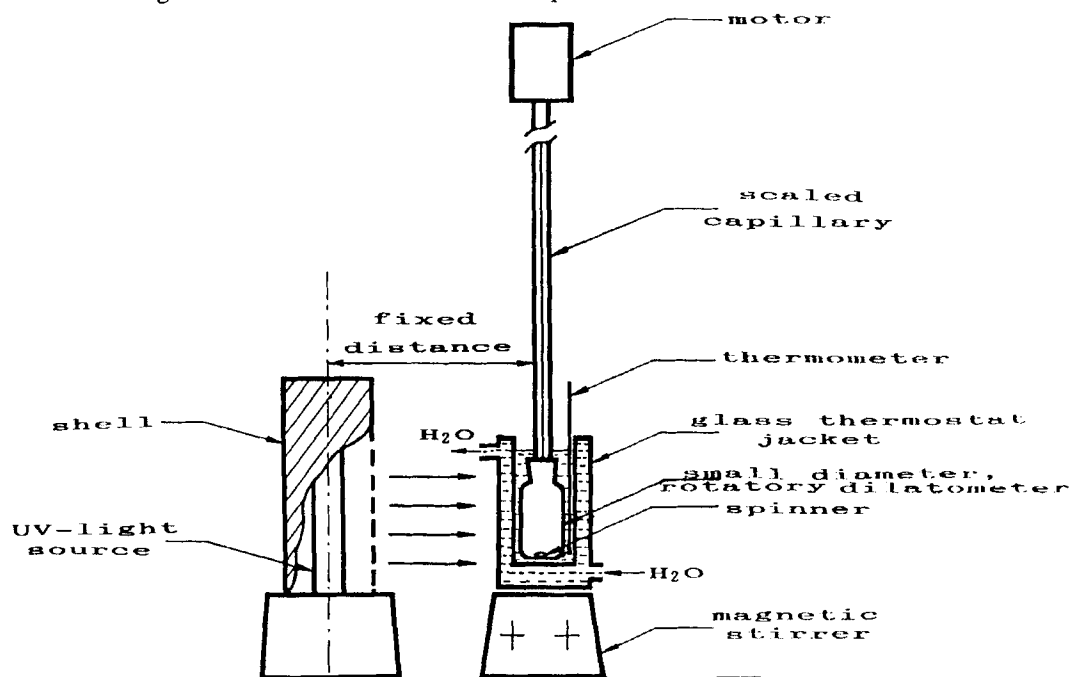


FIG. 1. Experimental scheme.

polymerization obviates the complicated nucleation process in Interval I of emulsion polymerization because the reaction starts in Interval II, in which the number of latex particles present in the system remains constant. So the time evolution of  $N_n$ , the fraction of particles containing  $n$  free radicals, can be given by the Smith-Ewart equations:

$$dN_n/dt = \rho(N_{n-1} - N_n) + k[(n+1)N_{n+1} - nN_n] + c[(n+2)(n+1)N_{n+2} - n(n-1)N_n], \quad n = 0, 1, 2, 3, \dots \quad (1)$$

where  $\rho$  is the entry rate coefficient of free radicals into the latex particles,  $k$  is the exit rate coefficient of free radicals from latex particles, and  $c$  is the rate coefficient of bimolecular termination.

As in the case of the small radius seeded emulsion polymerization of styrene,  $c \gg \rho, k$ , it can be assumed that  $N_i = 0$  when  $i > 3$ , so, Eq. (1) can be derived into Eq. (2) by making a steady-state approximation and ignoring the high-order term  $\rho/c$  and  $k/c$ .

$$\frac{d}{dt} \begin{pmatrix} N_0 \\ N_1 \end{pmatrix} = \begin{pmatrix} -\rho(k + \rho) \\ \rho - (k + \rho) \end{pmatrix} \begin{pmatrix} N_0 \\ N_1 \end{pmatrix} \quad (2)$$

The general solution of Eqs. (1) and (2) is

$$N(t) = \sum_i \exp(\lambda_i t) [{}^L e_i \cdot N_{(t=0)}] \cdot {}^R e_i \quad (3)$$

where  $\lambda_i$ ,  ${}^L e_i$ , and  ${}^R e_i$  are, respectively, the  $i$ th eigenvalue and the corresponding left and right eigenvectors of the matrix defined by Eqs. (1) and (2).

In the Interval II of emulsion polymerization, fractional conversion of monomer to polymer,  $x$ , at time,  $t$ , is given by

$$x = A \int_0^t \sum_n n N_n(t) dt = A \int_0^t n(t) dt \quad (4)$$

with  $A = k_p N_c C_M / n_M^0 N_A$ , where  $k_p$  is the propagation rate coefficient,  $N_c$  is the number of latex particles present in the system,  $C_M$  is the concentration of monomer within the latex particles,  $n_M^0$  is the number of moles of monomer initially present,  $n$  is the average number of free radicals in each particle, and  $N_A$  is Avogadro's constant.

The experimental process of relaxation study can be divided into two stages: the radiation stage and the postradiation stage. In the radiation stage, i.e., under the UV-light radiation, the steady-state polymerization rate is reached rapidly. In this stage,  $N_1 = \rho/(k + 2\rho)$  and  $N_0 = 1 - N_1$ , when  $\rho \gg k$  (which can be expected in the case of high free-radical concentration). These are simplified as  $N_0 = N_1 = n_{SS} = 0.5$ , and thus

$$\frac{dx}{dt} = k_p C_M \left( \frac{N_c}{n_M^0 N_A} \right) n_{SS} = \frac{1}{2} A \quad (5)$$

In the postradiation stage, i.e., after the UV-light is cut off, the polymerization rate gradually decays to the equilibrated rate of thermally induced background polymerization. Here,  $\rho$  is denoted by  $\rho_0$ , which is the entry rate coefficient of

thermally generated free radicals. The initial condition of this stage is  $N_{1(t=0)} = N_{0(t=0)} = n_{SS} = 0.5$ . When the solution of Eq. (3) is substituted into Eq. (4), we have

$$x = A\lambda^{-1}[\lambda\Omega t + (0.5 - \Omega)(1 - e^{-\lambda t})] \quad (6)$$

where  $\lambda = k + \rho_0$  and  $\Omega = \rho_0/\lambda$ .

At long times, Eq. (6) becomes Eq. (7):

$$x(t \rightarrow \infty) = at + b \quad (7)$$

where  $a = A\Omega$  and  $b = A(0.5 - \Omega)/\lambda$ .

When  $A$ ,  $a$ , and  $b$  are determined from Eqs. (5) and (7), the values of  $\rho_0$  and  $k$  can be directly calculated, even without knowledge of  $k_p$  and  $C_M$ .

From Eqs. (4) and (7) it can be derived that

$$n_{\text{thermal}} = a/A = \Omega = \rho_0/(k + 2\rho_0) \quad (8)$$

Here,  $n_{\text{thermal}}$  refers to the average number of free radicals per particle in the equilibrated thermally induced background polymerization.

With the value of  $C_M$  determined in the kinetic study of emulsion polymerization with chemical initiation [3], the value of  $k_p$  can be calculated from the value of  $A$ , which is a convenient way to determine  $k_p$ .

## EXPERIMENTAL

The seed latex used in this study was prepared by emulsion polymerization at 90°C, with styrene (Gao-Qiao Chemical Inc., and distilled under reduced pressure prior to use) as monomer, Aerosol MA (prepared and purified by the authors) as emulsifier, and KPS (A.R. Grade and recrystallized before use) as initiator. The radius of the resulting latex was 40.2 nm as determined by TEM. Details of the preparation and characterization of this seed latex were described elsewhere [4].

The water-soluble 2-sodium anthraquinone sulfonate/triethyl amine system was selected as the photosensitizer system of UV-light. The concentration of both was 0.001 mol/dm<sup>3</sup>, which was just sufficient to let the reaction system reach steady state rapidly, but with the least effect which might occur because of the addition of the photosensitizer to the reaction system. The steady-state polymerization rate of this system was equal to that of systems with chemical initiation.

The recipe for the kinetic study was: seed latex 0.50 g (with a solid content of 29.8%), styrene monomer 0.70 g, SDS 0.03 g, and deionized water 15.0 g. These were stirred for approximately 24 h, deaerated, and injected into the above-described dilatometer together with the photosensitizer (with a total volume of 5 cm<sup>3</sup>).

The UV-light source was a mercury-arc lamp with a power of 500 W. The distance from the center of the dilatometer to the lamp was fixed at 65 mm. The system was exposed to UV-light for 5–7 min (time region  $T_1$  in Fig. 2). Then the UV-light was cut off, and the relaxation process was observed. Polymerization was controlled to take place in Interval II for all the kinetic runs, i.e.,  $C_M$  was constant; the particle density,  $N_c$ , of all the systems was fixed at  $7 \times 10^{16}$  dm<sup>-3</sup>; and the temperatures were fixed within  $\pm 0.05^\circ\text{C}$ . After all the kinetic runs were completed, the resulting lattices were checked by TEM, and no renucleation was spotted.

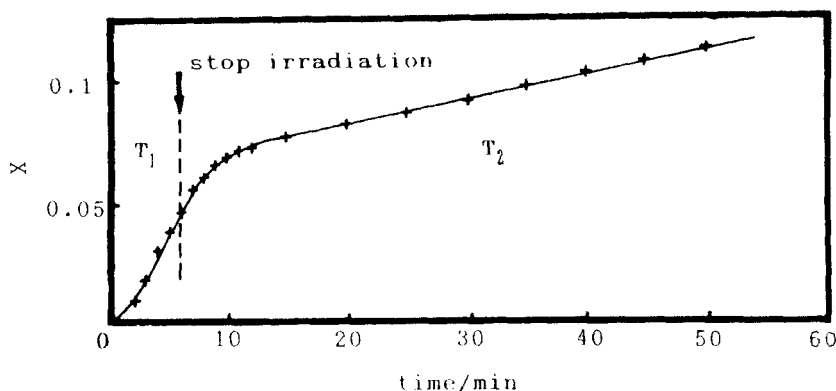


FIG. 2. Plot of fraction conversion as a function of time (55°C).

## RESULTS AND DISCUSSIONS

### 1. Polymerization Rate

The polymerization rates of the steady state under UV-irradiation and the equilibrated thermally induced background polymerization rates can be observed from the plot of fractional conversion versus time, as shown in Fig. 2. After about 2 min' UV exposure, the polymerization rate reached the steady-state value, with the average number of monomer molecules converted to polymer in each particle per second,  $R_{SS}$ , being  $836 \text{ s}^{-1}$ . This value agreed well with the results reported by Hawket et al. [2],  $R_{SS} = 737 \text{ s}^{-1}$ , which was observed in a similar system but with a high concentration of chemical initiator (yielding  $n_{SS} = 0.5$ ) and a seed radius of 47.0 nm. Therefore, it is deduced that the steady-state polymerization rate of UV-initiated and chemical-initiated emulsion polymerization can be very similar, at least in the above-mentioned cases.

When the UV-light was cut off, the polymerization rate gradually decayed, and finally reached the value of equilibrated thermally induced background polymerization, which was 350 times larger than that of the bulk system. This was because the compartmentalization effect of emulsion polymerization systems reduced the opportunities of binary termination between free radicals and thus prolonged the average lifetimes of the free radicals.

TABLE 1. The Results of Relaxation Kinetics Initiated by UV-Light

$t$ , °C	$(dx/dt)_t \times 10^3$ min <sup>-1</sup>	$(V_{SS})_{It}$ , <sup>a</sup> molecules/s <sup>-1</sup>	$n_{SS}$	$\rho_0 \times 10^4$ s <sup>-1</sup>	$k \times 10^3$ s <sup>-1</sup>	$k_p$ , dm <sup>3</sup> ·mol <sup>-1</sup> ·s <sup>-1</sup>
60	8.69	127	0.056	1.67	2.68	387
55	7.40	105	0.054	1.21	2.00	327
50	6.40	91	0.054	1.09	1.80	283
45	5.30	45	0.032	0.63	1.35	233

<sup>a</sup>Unit of rate in relaxation period  $T_2$ , reacted molecules per particle per second.

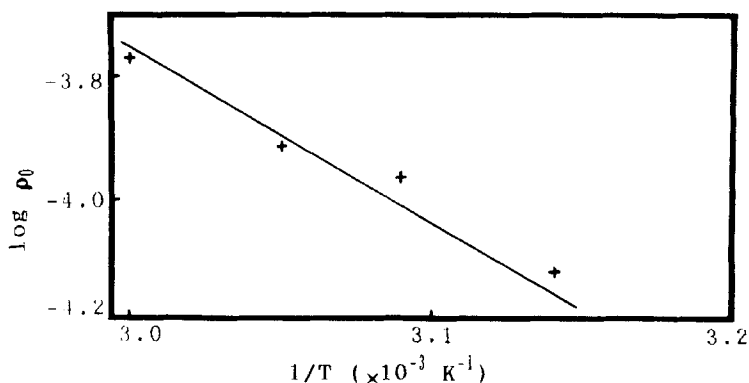


FIG. 3. Plot of  $\log \rho_0$  as a function of  $1/T$ .

## 2. Kinetic Parameters: $\rho_0$ , $k$ , $k_p$ , and $n_{\text{thermal}}$

The values of  $\rho_0$ ,  $k$ ,  $k_p$ , and  $n_{\text{thermal}}$  at four different temperatures are listed in Table 1. Figures 3–5 are plots of  $\log \rho_0$ ,  $\log k$ , and  $\log k_p$  versus  $1/T$ , through which the Arrhenius formula of these rate coefficients were derived (see Eqs. 9–11).

$$\lg \rho_0 = (4.86 \pm 0.6) - (55 \pm 1.5) \text{ kJ} \cdot \text{mol}^{-1} / 2.303RT \quad (9)$$

$$\lg k = (3.61 \pm 0.3) - (39.5 \pm 0.8) \text{ kJ} \cdot \text{mol}^{-1} / 2.303RT \quad (10)$$

$$\lg k_p = (7.29 \pm 0.3) - (30.0 \pm 0.3) \text{ kJ} \cdot \text{mol}^{-1} / 2.303RT \quad (11)$$

These formulas were compared with the results of the  $\gamma$ -initiated kinetic studies by Lansdowne et al. [1]. It was found that our results are quite similar to theirs, and it was also found that because of the advantages of the UV method, e.g., it can be cut off quickly and the relaxation process can be observed at once, the UV method had a smaller deviation than the  $\gamma$ -method.

The value of  $C_M$  was quoted from studies of a similar system with a chemical initiation of  $C_M = 5.78 \text{ mol/dm}^3$  [3] in order to calculate the value of  $k_p$ . The value

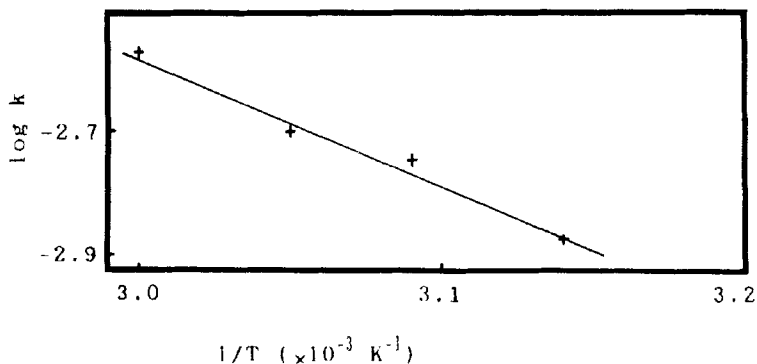


FIG. 4. Plot of  $\log k$  as a function of  $1/T$ .

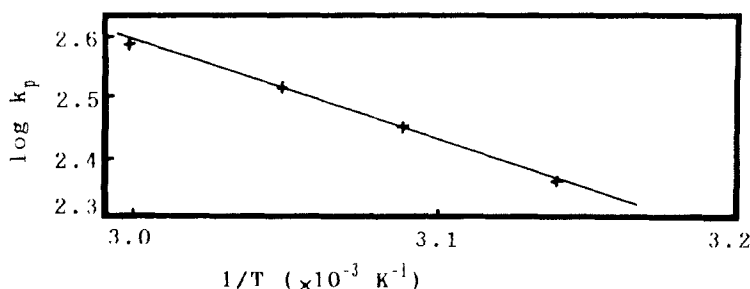


FIG. 5. Plot of  $\log k_p$  as a function of  $1/T$ .

of  $k_p$ , thus obtained was  $283 \text{ dm}^3 \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$  at  $50^\circ\text{C}$ , which agrees with the literature value ( $240 \pm 90 \text{ dm}^3 \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$ ) [5]. The activation energy obtained from Fig. 5 was  $30.0 \text{ kJ/mol}$ , which lay in the range ( $25\text{--}50 \text{ kJ/mol}$ ) of the literature value [5].

The Arrhenius formula for  $\rho_0$  in our result is quite different from that in the literature [1]. This might be due to the difference in the property of the particle surface caused by the addition of water-soluble photosensitizer in our experiments. However, because the nature of the activation energy of  $\rho_0$  is still quite vague and the surface condition of latex particles is complicated, a definite explanation of the difference will be investigated by further study.

The average number of free radicals per particle in thermally induced background polymerization,  $n_{\text{thermal}}$ , which was calculated by Eq. (8), is consistent with published results. This is also because of the compartmentalization effect.

The above discussions also show that the UV-method described in this work is a convenient and feasible method for the study of the relaxation kinetics in emulsion polymerization.

### ACKNOWLEDGMENT

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