Determination of Kinetic Parameters of Ethyl Methacrylate Polymerization Initiated by the Redox Pair SO$_2$-*tert*-Butyl Hydroperoxide

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DETERMINATION OF KINETIC PARAMETERS OF ETHYL METHACRYLATE POLYMERIZATION INITIATED BY THE REDOX PAIR SO$_2$-*tert*-BUTYL HYDROPEROXIDE

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ABSTRACT

In the bulk polymerization of ethyl methacrylate with the redox initiator pair sulfur dioxide-*tert*-butyl hydroperoxide (SO$_2$–TBHP), the kinetic parameters were determined by the dead-end polymerization technique using the dilatometric method. Polymerization was conducted with various initiator pair compositions in the temperature interval of 12–35°C. An activation energy of 14.1 kJ/mol for [SO$_2$]/[TBHP] = 0.44 was determined for this temperature range. The values of k_p^2/k_t obtained in this study were in the interval 1.34 × 10^{-4} to 1.11 × 10^{-3} L/mol·s. The f/k_d ratios for the redox pair at different temperatures and for different initiator ratios were also calculated. The f/k_d ratios of the initiator pair changed between 15.1 and 187.6 seconds. The wide variations in these kinetic parameters were explained on the basis of competitive reactions between the redox pair and their reaction products.

INTRODUCTION

Compared to thermal initiation, redox initiation has some advantages such as shorter induction time, lower values of activation energy, and higher yield of products in relatively short time periods. A low activation energy value permits the redox polymerization reaction to proceed at lower temperatures. At low temperatures, the possibility of side reactions decreases, and it becomes easier to control the properties of the resulting polymer. The active species which initiate redox polymerization are produced by reactions between redox pairs. Among a wide variety of redox pairs investigated in redox polymerization systems, little attention was devoted to those using SO_2 as a constituent of a redox pair.

It is known that liquid SO_2 in the presence of vinyl compounds causes the formation of polysulfonates and copolymers with bicyclic olefines [1]. It has also been shown that aqueous SO_2, i.e., sulfurous acid, can initiate vinyl polymerization [2]. It is also known that SO_2 under appropriate conditions at very low concentrations initiates the polymerization of some vinyl monomers [3]. In their study with methyl acrylate and methyl methacrylate, Ghosh and O'Driscoll used t-butyl hydroperoxide in a redox pair with SO_2 [4].

In the present study ethyl methacrylate was polymerized under dead-end polymerization conditions. By following the polymerization of ethyl methacrylate via the dilatometric technique, f/k_d ratios of the initiator pair were determined. Kinetic parameters relevant to the polymerization of ethyl methacrylate, namely k_p^2/k_t and the activation energy of polymerization, were also determined.

EXPERIMENTAL PROCEDURE

Ethyl methacrylate (EMA), supplied by Janssen Chimica Co., stabilized with 15 ppm hydroquinone methyl ether, was vacuum distilled to remove the polymerization inhibitor. An 80% solution of TBHP in di-$tert$-butyl peroxide was used. SO_2 was freshly produced by the reaction of $NaHSO_3$ with H_2SO_4, dried, and stored in stainless steel cylinders.

The conversion curves were constructed by using the dilatometric method at different temperatures and molar ratios of the initiator pair. The dilatometric results were also checked by parallel gravimetric measurements. The amount of SO_2 dissolved in monomer was determined by using the standard iodometric method.

The number-average molecular weights of the polymers were determined by using GPC (Waters Associates Model 244, GPC/ALC). The separation unit of GPC consisted of a series of ultrastyragel (Waters Associates) columns with porosities of 10^4, 10^5, and 10^6 Å . Tetrahydrofuran (Janssen Co., HPLC quality), after being degassed in an ultrasound bath, was used as the eluting solvent. The flow rate of the solvent was 1 mL/min.

The number- and weight-average molecular weights of polymer samples obtained at different experimental conditions were determined by using the Cohn-Ginsberg technique [5] after the transformation of the primary calibration curve of

PS standards having $M_w/M_n < 1.1$ to the universal calibration curve using the KMHS equation given for PS in THF, $[\eta] = 6.09 \times 10^{-5} M^{0.79}$ dL/g [6]. For the conversion of universal calibration values into those of PEMA, the following KMHS equation was used [6]:

$$[\eta] = 15.49 \times 10^{-5} M^{0.679} \text{ dL/g}$$

RESULTS AND DISCUSSION

In this study the conversion curves were obtained by the dilatometric method and the results were also occasionally checked by gravimetry. Figure 1 shows the typical curves constructed for the polymerization of EMA at 12°C for a fixed SO_2 and varying TBHP concentration. The conversion of monomer to polymer was observed to increase with increasing TBHP concentration until the ratio reached 0.22 and then decreased after reaching a certain TBHP concentration. The decrease in conversion for the bulk polymerization of EMA with the redox initiator pair SO_2–TBHP started at a higher concentration of TBHP at 12°C. When the temperature was raised to 35°C, the decrease in conversion started at a lower TBHP concentration.

It was generally observed that conversion increased with increasing SO_2 concentration at a fixed temperature and fixed TBHP concentration. At 12°C, 5% conversion was reached in 20 minutes for $[SO_2]/[TBHP] = 0.10$. The amount of product obtained in the same time interval was doubled when the ratio was 0.44 and exceeded 20% for a ratio of 2.09 (Fig. 2).

The initial rate of polymerization and the polymer yield increased with increasing temperature. When the temperature was raised from 12 to 35°C for the same ratio of initiator pair at a fixed TBHP concentration, the conversions increased from 10 to 35% (Fig. 3).
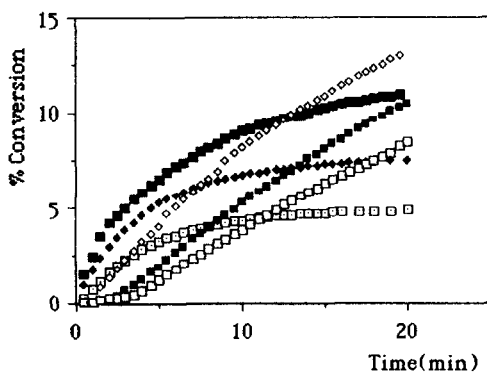

FIG. 1.   Change of conversion with time for various initiator compositions at 12°C. $[SO_2] = 0.01$ M [TBHP] = varies. $[SO_2]/[TBHP]$: (▣) 0.07, (◆) 0.08, (■) 0.10, (◇) 0.22, (■) 1.20, (□) 8.43.
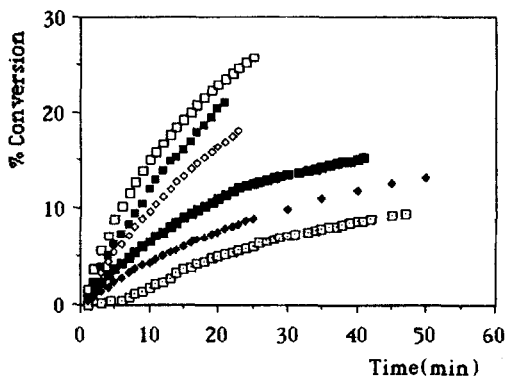
FIG. 2. Change of conversion with time for various initiator compositions at 12°C. [SO₂] = varies, [TBHP] = 0.02 M. [SO₂]/[TBHP]: ($\boxdot$) 0.10, ($\blacklozenge$) 0.16, ($\blacksquare$) 0.44, ($\lozenge$) 0.82, ($\blacksquare$) 1.17, ($\square$) 2.09.

In redox polymerization induced by radical initiation, the initiation of polymerization by free radicals depends upon the relative concentrations of monomer and activator. In the case of a relatively low concentration of monomer and a high concentration of the activator, nonradical species are produced by side redox reactions or the primary radicals are removed by mutual combinations. Such side reactions were observed in polymerization systems using the redox initiator pairs dimethyl aniline–benzoyl peroxide [7] and potassium persulfate–tyomalic acid [8]. A similar type of side reactions may also be expected for the redox pair SO_2–TBHP. A variety of reactions can be proposed in the redox reaction of this pair [9]:
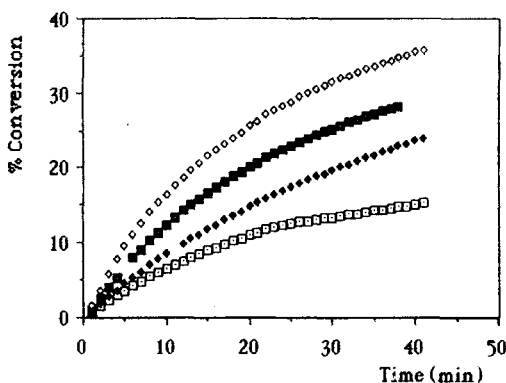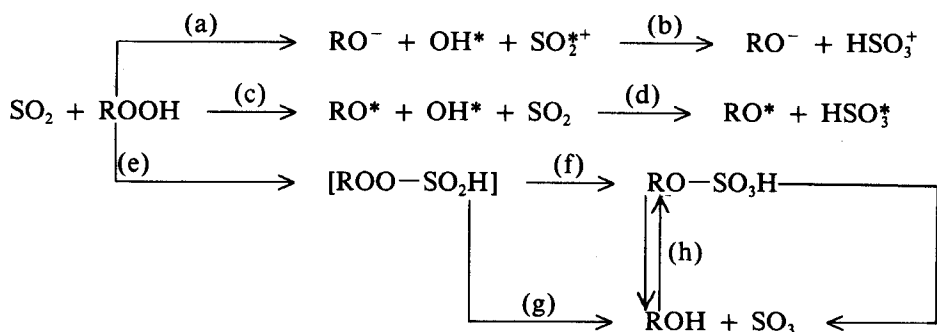

FIG. 3. Change of conversion with time for various temperatures. [TBHP] = 0.02 M. [SO₂]/[TBHP] = 0.44. T: ($\boxdot$) 12°C, ($\blacklozenge$) 18°C, ($\blacksquare$) 25°C, ($\lozenge$) 35°C.

$$\begin{array}{c} \text{(a)} \longrightarrow \; RO^- + OH* + SO_2^{*+} \; \xrightarrow{\text{(b)}} \; RO^- + HSO_3^+ \\[1mm] SO_2 + ROOH \; \xrightarrow{\text{(c)}} \; RO* + OH* + SO_2 \; \xrightarrow{\text{(d)}} \; RO* + HSO_3^* \\[1mm] \text{(e)} \longrightarrow \; [ROO-SO_2H] \; \xrightarrow{\text{(f)}} \; RO-SO_3H \\[1mm] \text{(g)} \longrightarrow \; ROH + SO_3 \; (\text{h}) \end{array}$$

In Reaction c the radicals obtained by the homolytic decomposition of hydroperoxide produce new radical species by combining with SO_2. Reaction (a) produces ionic species. If ionic species produced in Reaction (b) initiate the polymerization, the polymerization must be of an ionic nature, but it is known that methacrylates are not generally polymerized by ionic processes. In the bulk polymerization of EMA with the redox pair SO_2–TBHP, the establishment of a constant conversion at high TBHP concentrations can be explained by the formation of ionic species and the production of side redox reactions (Reactions f and g).

The k_p^2/k_t values for a monomer were obtained by using the number-average molecular weights found by GPC of polymer samples obtained at different polymerization times:

$$DP_n = \frac{k_p^2[M]^2}{(2k_{td} + k_{tc})R_p} \tag{1}$$

where DP_n is the number-average degree of polymerization, k_p is the propagation rate constant, and k_{td} and k_{tc} are the rate constants for termination by disproportionation and combination, respectively. Since a disproportionation type of termination is generally observed at relatively high polymerization temperatures, we may assume that termination is predominantly by combination. R_p and [M] correspond to the rate of polymerization and monomer concentration at any time, t. These last two values were directly determined from the conversion curves. By determining the DP_n, [M], and R_p values simultaneously, k_p^2/k_t values were calculated from Eq. (1) and are listed in Table 1.

In the kinetic analysis of polymerization reactions, the most widely used method for the simultaneous determination of the decomposition constant (k_d) and the efficiency factor of the initiator is the dead-end polymerization technique [10]. In the case of a system such as SO_2–TBHP it is necessary to follow the conversion as a function of time to the limiting values. Then the f/k_d ratios for the redox pair at different temperatures and for different initiator ratios can be calculated by using the k_p^2/k_t ratios determined from Eq. (1) and the following equation [11]:

$$\frac{[M]_0}{[M]_\infty} = \left[\frac{(a_0/b_0)^{1/2} + 1}{(a_0/b_0)^{1/2} - 1} \right] (fk_p^2/k_tk_d)^{1/2} \tag{2}$$

TABLE 1. f/k_d of the Redox Initiator Pair SO_2–TBHP and k_p^2/k_t Values of Monomer at Different Temperatures and Initiator Compositions.

T, °C	$[SO_2]/[TBHP]$	% Conversion	$M_n \times 10^{-3}$	$k_p^2/k_t \times 10^4$, L/mol·s	f/k_d, seconds
12	0.08	3.85	7.2	1.66	147.7
	0.08	6.71	8.2	1.89	129.6
	0.08	8.14	11.3	2.61	93.9
	0.10	4.82	9.1	1.94	187.6
	0.10	11.88	12.3	2.61	139.5
18	0.07	1.87	8.3	1.41	51.2
	0.07	3.88	10.5	1.80	40.1
	0.07	4.46	16.4	2.81	25.7
	0.08	2.23	8.8	1.34	42.0
	0.08	4.40	17.7	2.70	20.8
	0.10	7.22	12.2	2.85	62.1
	0.10	8.42	11.5	2.68	66.0
	0.16	5.58	11.0	2.67	114.7
	0.16	9.78	13.8	3.36	91.1
	0.16	13.83	30.5	7.44	41.2
	0.22	15.92	12.5	2.91	97.0
25	0.07	3.68	24.5	4.10	17.6
	0.07	4.46	24.9	4.20	17.2
	0.08	5.19	17.3	4.50	48.0
	0.08	6.94	21.2	5.50	39.3
	0.08	8.31	38.5	10.00	21.6
	0.10	7.31	18.0	4.50	41.1
	0.10	8.62	28.0	7.00	26.4
	0.16	6.24	13.8	5.50	48.9
	0.16	9.59	14.9	4.60	58.5
	0.16	12.74	12.5	8.60	31.3
	0.22	7.02	10.4	3.20	110.4
	0.22	11.32	13.0	4.00	88.4
	0.22	17.64	15.0	4.70	75.2
35	0.07	5.32	22.9	4.50	23.1
	0.08	3.78	21.8	5.60	20.8
	0.08	6.30	30.2	7.70	15.1
	0.10	3.15	15.9	3.70	37.0
	0.10	6.37	20.7	5.10	26.8
	0.10	7.42	22.7	7.10	19.3
	0.16	11.05	27.5	11.10	17.2
	0.22	12.59	20.0	8.20	34.8
	0.22	15.95	27.2	11.10	25.7

where $[M]_0$ = the initial concentration of monomer
  $[M]_\infty$ = the concentration of monomer at t_∞
  a_0 = the initial concentration of the reducing agent
  b_0 = the initial concentration of the oxidant

According to Eq. (2), conversion in redox initiator systems is controlled by the ratio a_0/b_0 and the maximum limiting conversion should be obtained when $a_0 = b_0$.

The initial rate and maximum conversion values rise with an increase in the initial concentration of the reducing agent (a_0: TBHP) up to 0.050 M. Above this concentration the maximum conversion starts to fall.

$$ROOH + OR^* \longrightarrow ROH + ROO^*$$
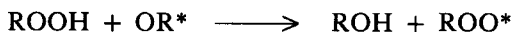
According to the above reaction scheme, reactive alkoxy radicals which initiate polymerization are converted into unreactive peroxy radicals. This can explain the decrease in conversion with increasing TBHP concentration.

In Fig. 4 the maximum conversions are plotted against the mole fraction of TBHP for polymerizations conducted at 25°C. The maximum in the experimental plot corresponds to $a_0 = b_0$. Similar results were obtained at 12, 18, and 35°C. If the appearance of a maximum in the experimental plot does not correspond to $a_0 = b_0$, then Eq. (2) has to be modified [12].

As can be observed from Table 1, the k_p^2/k_t ratios of ethyl methacrylate increased steadily with increasing % conversion for a fixed TBHP concentration. Since the viscosity of the polymerization mixture increases with increasing conversion of monomer to polymer, the rise in k_p^2/k_t values can be explained by diffusion-controlled termination. It is very well known that the apparent termination rate constant is inversely proportional to the viscosity of the polymerization mixture, and the propagation stage of polymerization involves the reaction of small molecules which may not be adversely affected by diffusional effects. As a result, k_p^2/k_t values also increase with increasing viscosity of the reaction mixture. The values obtained in this study were in the interval 1.3×10^{-4} to 1.11×10^{-3}. The k_p^2/k_t
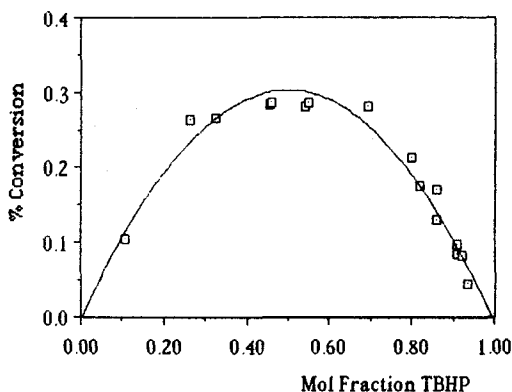

FIG. 4. Relationship between molar fraction of TBHP and limiting conversion of EMA in SO_2–TBHP redox system at 25°C.
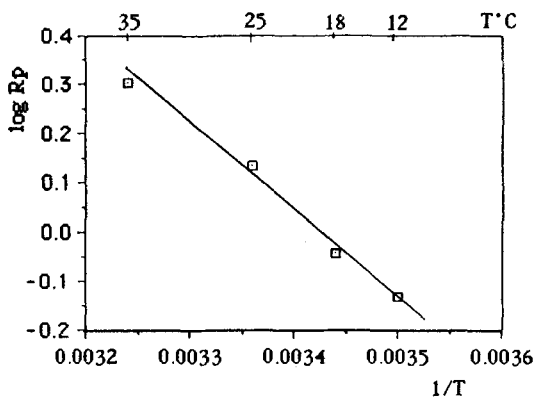
FIG. 5. Arrhenius plot of bulk polymerization of EMA initiated by SO_2-TBHP. $[SO_2/[TBHP] = 0.44$.

ratio for the bulk polymerization of ethyl methacrylate initiated by azobisisobutyronitrile in the 60 to 90°C temperature interval was reported to change from 1.4×10^{-2} to 5.2×10^{-2} [13]. The difference observed in these two studies is mainly due to wide differences in temperature intervals.

The overall activation energy of polymerization calculated from the Arrhenius plot is 14.1 kJ/mol for $[SO_2]/[TBHP] = 0.44$, as shown in Fig. 5. This value agrees well with the values found in other redox systems [4,14].

In conclusion, it was determined that the SO_2-TBHP redox pair can effectively initiate the polymerization of EMA in ambient and subambient temperatures. The results of preliminary studies on various properties of PEMA synthesized by this redox pair showed that it possesses better properties than those prepared by other conventional initiators. The most interesting scientific and technical impact of this work is the possibility of using the notorious pollutant SO_2 in the in-situ polymerization of EMA. The initial results of our work on this possibility will be published soon [15].

ACKNOWLEDGMENT

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