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ESR study of the radical polymerization of styrene

5. Temperature dependence of propagation and termination rate constants over a wide temperature range

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Summary

The absolute rate constant of propagation (k_p) in styrene polymerization was determined on the basis of ESR detection of the polymer radical in the temperature range of 0 to 130°C. The Arrhenius plot of k_p gave a good linear relationship and the activation energy of the propagation was evaluated to be 39.7 KJ/mol. The termination rate constants over the same temperature range were also obtained by using the k_p values according to the standard kinetics of radical polymerization. Apparent activation energy of the termination was estimated to be 15.6 KJ/mol.

Introduction

Polymerization of styrene (St) by radical chain mechanism has been studied extensively and absolute rate constants for individual elementary reactions have been evaluated mainly at initial stages of polymerization by various techniques [1]. Since the radical polymerization is a typical chain reaction, the determination of the rate constants, especially propagation and termination rate constants (k_p and k_t), is required for quantitative discussion on polymer formation. The kinetic equations for the techniques used to evaluate the rate constants are mathematically derived by using assumptions [2] which could sometimes be responsible for discrepancy of the rate constants among those determined by the different techniques. Evaluation of the rate constants based on direct determination of concentration of polymer radical by means of ESR spectroscopy with fewer assumptions has been considered to be advantageous over the other techniques [3,4], and quantitative information about the elementary reaction obtained by the ESR method seems to be preferable for better understanding of radical polymerization.

St polymerization has been study by only a few groups using ESR spectroscopy. Bresler and coworkers [5] evaluated k_p and k_t based on determination of the steady state concentration of poly(St) radical employing a specially designed ESR spectrometer. Recently, we have studied on radical polymerization of St at 70°C using ESR spectroscopy. We have determined the steady-state concentration of the polymer radical during St polymerization over a wide conversion range up to 97% despite a considerable increase in

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viscosity of the polymerization mixture with progress of polymerization [6,7].

Although the ESR spectrum observed consisted of broad lines, as a result of a search of suitable conditions for obtaining a well-resolved spectra, we have reported the spectra of poly(St) radical consisting of more than 18 lines at room temperature (ca. 22°C). The hyperfine coupling constants for all the hydrogens have been evaluated by computer simulation [8]. The ESR spectra detected during the polymerizations of St and the substituted St have been unambiguously assigned to the corresponding polymer radicals which participate in the propagation and termination [6,8], whereas recently, the presence of inactive polymer radical called "trapped radical" in the polymerization of methyl methacrylate has been proposed [9].

Although the k_p and k_t values for St have also been determined at different temperatures as compiled [1], the Arrhenius plots of k_p and k_t are given overe a relatively narrow temtemperature range in the literature. However, because of considerable scatter of k_p value and the narrow temperature range arising from a lack of the data at the temperatures above 100°C, the reliability of the activation parameters for the elementary reactions of the St polymerization is not so high. We though that determination of the rate constants by the ESR technique which is not disturbed by an increase in viscosity of the polymerization mixture with conversion nor decreases in monomer and initiator concentrations by progress of polymerization can be applied to the St polymerization over a wide temperature range including the high temperatures.

In this article, we describe monitoring the St polymerization over the temperature range from 0 to 130°C by means of ESR spectroscopy, and the k_p values at different temperatures were determined by combination of the overall rate of polymerization and the concentration of the polymer radical. Moreover, the temperature dependence of k_t was also estimated.

Experimental

Commercial St was distilled under reduced pressure before use. Methyl 2,2'-azobisisobutyrate (MAIB) was recrytallized from n-hexane. 2,2'-Azobis-2,4-dimethylvaleronitrile (AVN) and 1,1'-azobis-1-cyanocyclohexane (ACN) were recrystallized from methanol. tert-Butyl peroxide (TBP) was distilled under reduced pressure. The polymerization of St at 0°C was initiated with ACN under irradiation by a 500 W xenon lamp in the cavity of an ESR spectrometer. Decomposition of ACN under the UV irradiation in the cavity at 0°C was monitored by recording the absorbance at 360 nm on a Shimadzu UV-160 spectrophotometer, and the polymerization initiated with ACN/UV was also carried out in the cavity at 0°C. The polymerizations at 50, 70, 100, and 130°C for determination of the overall rates of polymerization (R_p's) were run in sealed ampoules and poly(St) was isolated using methanol as precipitant. R_p's were obtained from the slopes of the conversion-time plots at the respective temperatures.

ESR spectra of poly(St) radical were recorded on a Bruker ESP 300 spectrometer operated at X band with 100 kHz field modulation at the microwave power of 20 mW using a 0.5 cm outer diameter quartz tube and the modulation amplitude was 10 G. The spectra were recorded over a magnetic field of 150 G width divided into 1024 points and the conversion time of each point was 40.96 ms. The time required for each scan was ca. 42 s and most of the spectra were recorded by a single scan. The concentration of poly(St) radical was determined from the intensity of the spectrum obtained by double integration and calibrated with the intensity of the spectrum of 1,3,5-triphenylverdazyl [10] as described before [6].

Results and Discussion

Since concentration of the polymer radical can be measured by ESR spectroscopy, the absolute value of k_p was calculated from the following equation:

$$k_p = R_p/([St\cdot][St])$$

where [St·] and [St] stand for the concentrations of poly(St) radical and monomeric St, respectively. The polymerizations of St were initiated with different initiators depending on the polymerization temperature as summarized in Table 1.

Figure 1 illustrates the ESR spectra of poly(St) radical recorded at the bigining of the polymerizations at 0, 70, and 130°C. Since accurate determination of the intensity of the spectra was preferred over well resolved spectra, 4-line spectra with broad line-width were recorded. The 4-line spectra can be accounted for by splitting of the α- and two of β-hydrogens of poly(St) radical, because difference in the hyperfine splitting constant between two types of the hydrogens is comparable or less than the line width.

To obtain the ESR spectra of poly(St) radical, all the polymerizations were initiated with relatively high concentrations of the initiators. Since the half life-time of MAIB at 100°C is estimated to be 10.7 min, the conversion of St reached to 49% after the polymerization for 10 min with

Table 1. Initiation of St polymerization at different temperatures

Temp. (°C)	Initiation	[I] (mol/L)	$k_d \times 10^5$ (s^{-1})
0	ACN/UV	0.05	4.00
50	AVN	0.5	2.05 a)
70	MAIB	0.2	3.20 a)
100	MAIB	0.1	108 a)
130	TBP	0.5	2.92 a)

a) Ref. 11.

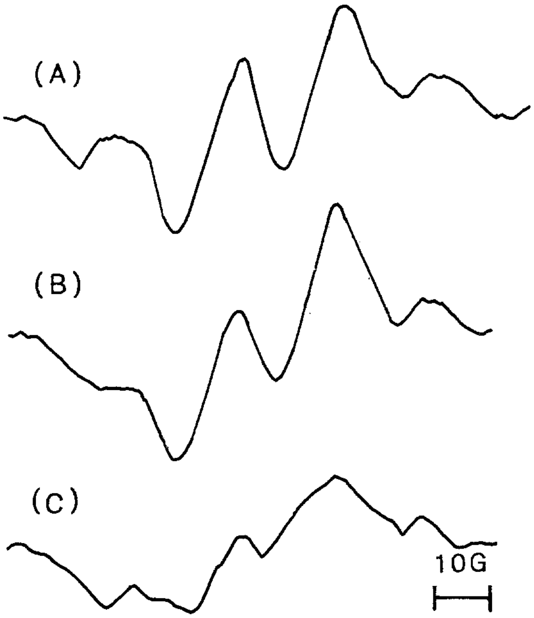

Fig. 1. ESR spectra of poly(St) radical observed at low conversions (< 5%) of bulk polymerizations at 0 (A), 70(B), and 130°C (C)

0.1 mol/L of MAIB at this temperature accompanying the rapid decrease in concentration of MAIB. However the spectrum was taken within 42 s, and the measurement of the polymer radical concentration was accomplished under the conditions of such fast decomposition of MAIB, because calculation of k_p from R_p requires the instantaneous radical concentration. In our previous papers [6,7], we confirmed that the k_p value for St remains constant irrespective of conversion and molecular weight of the polymer radical. Therefore, the k_p value determined at any stage of the polymerization can be used for the Arrhenius plot.

Figure 2 shows the conversion-time and radical concentration-time plots at 50°C. The ESR spectrum became more intense with conversion, and the radical concentrations were determined in the range of 20 to 30% conversion. Since the slope of the plot of the conversion versus time corresponds to R_p, the k_p value can be obtained straightforwardly using the radical concentration. The k_p values calculated are summarized in Table 2 in which the conversion ranges for conversion-time plots are also given. The Arrhenius plot of k_p based on the values in Table 2 is depicted in Fig. 3, and the activation energy of propagation (E_p) is obtained from the slope of the linear relationship:

$$E_p = 39.7 \text{ KJ/mol}$$

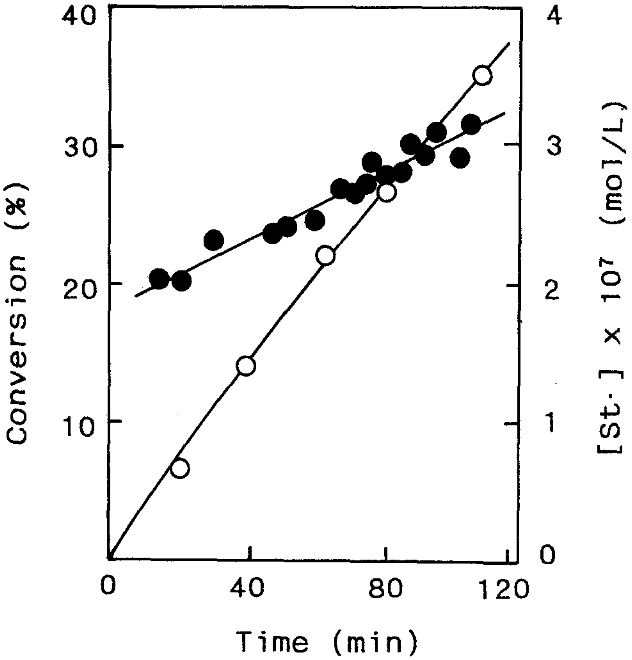

Fig. 2. Variation of conversion (○) and concentration of poly(St) radical (●) with time during St polymerization in bulk at 50°C

The Arrhenius equation is obtained as

$$k_p \text{ (L/mol·s)} = 5.50 \times 10^8 \exp[-39.7(\text{KJ/mol})/RT]$$

An international group of polymer chemists has reported the consistent value of k_p for St determined by a spatially intermittent polymerization and emulsion polymerization, and the Arrhenius equations for k_p in the range of 45 to 65°C have been given [3]:

$$k_p \text{ (L/mol·s)} = 10^{7.04} \exp[-29.5(\text{KJ/mol})/RT]$$

and

$$k_p \text{ (L/mol·s)} = 10^{(7.1 \pm 0.5)} \exp[-(29 \pm 3)(\text{KJ/mol})/RT]$$

Bresler et al. [5] have derived the following equation based on the k_p values determined by the ESR method from 50 to 90°C:

$$k_p \text{ (L/mol·s)} = 2.4 \times 10^8 \exp[-(37.5 \pm 1.6)(\text{KJ/mol})/RT]$$

It is found that the activation energy evaluated in the present study is greater than those in the literature calcu-

Table 2. k_p values for St at different temperatures

Temp (°C)	Conversion range (%)	R_{p0} x 10^4 a) (mol/L·s)	k_p (L/mol·s)
0	0-6	0.177	12.3
50	0-35	4.51	256
70	0-85	8.77	481
100	0-40	68.0	1620
130	0-50	54.0	3350

a) R_p estimated at 0% conversion obtained from the slope of the conversion-time plot.

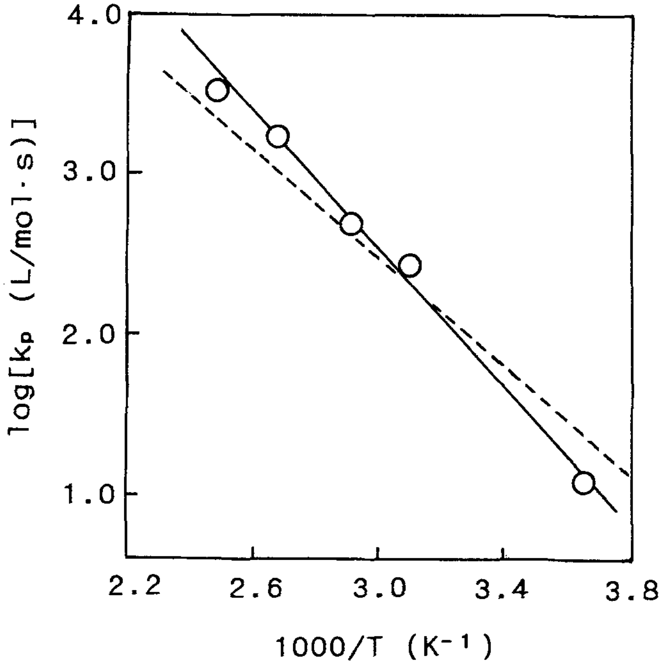

Fig. 3. Arrhenius plot of k_p for bulk polymerizations of St in the temperature range of 0 to 130°C. Dotted line is drawn according to the Arrhenius equation from ref. 3 (A = $10^{7.04}$ and E = 29.5 KJ/mol)

lated from the k_p values in the narrow temperature ranges [3,5]. Although, in addition to these, the Arrhenius plots based on the absolute k_p values of St compiled in the temperature range of 40 to 70°C have also been shown, considerable scatter of the values of k_p did not allow to determine E_p definitely [1].

The k_t values could be obtained by monitoring the decay of the ESR signal at individual temperatures. Since k_t value has been shown to vary with conversion [6] and molecular weight of the polymer radical [12], the determination of k_t under the comparable conditions at different temperature is almost impossible. Alternatively, we estimated the k_t values at the initial stages of the polymerization from R_{p0}'s based on the standard kinetics of radical polymerization:

$$R_{p0} = (R_i/k_t)^{0.5} k_p [St]$$

Table 3 summarizes the kinetic data of the St polymerization used for calculation of k_t and the k_t values obtained.

Although the primary radical termination might be involved in termination of the polymerization initiated with a high concentration of MAIB at 100°C, the Arrhenius plot in Fig. 4 shows a satisfactorily good linear relationship. The apparent value of E_t is estimated to be 15.6 KJ/mol. In contrast to insignificant E_t for vinyl acetate and methyl methacrylate obtained by the ESR method [13], we recognized acceleration of the termination with an increase in the tem-

Table 3. Kinetic data and k_t values at different temperatures

Temp. (°C)	$[St]_0$ (mol/L)	$R_{p0} \times 10^{4\,a)}$ (mol/L·s)	$R_i \times 10^{5\,b)}$ (mol/L·s)	$k_t \times 10^{-8}$ (L/mol·s)
0	8.54	0.177	0.20	0.704
50	7.56	4.51	1.03	1.90
70	8.29	8.77	0.64	1.32
100	8.50	68.0	10.8	4.43
130	7.83	54.0	2.92	6.90

a) R_p at 0% conversion estimated from the slope of the conversion-time plot.

b) Initiation efficiencies of the azo initiators and TBP were assumed to be 0.5 and 1.0, respectively.

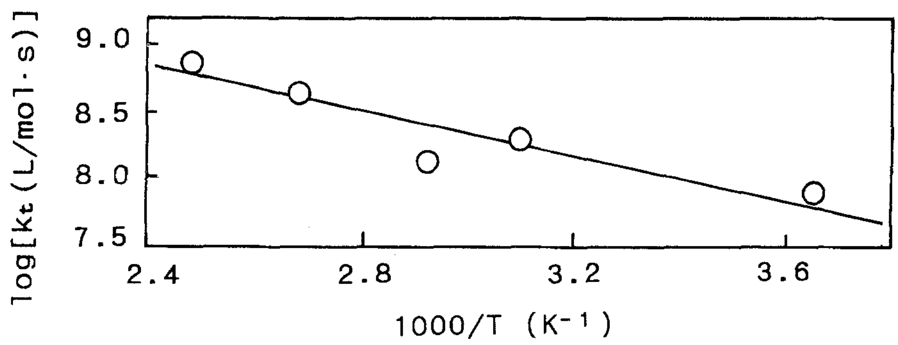

Fig. 4. Arrhenius plot of k_t for bulk polymerization of St in the temperature range of 0 to 130°C

perature during the experiments of the present work. As a consequence, relatively large amounts of the initiators were used to attain the sufficiently high concentrations of the polymer radical at 100 and 130°C.

The E_p value obtained in the present study together with the E_t value estimated can offer the basis of consideration on the polymerization of St over a wide temperature range. Furthermore, utility of the ESR method for kinetic analysis of radical polymerization has been exemplified.

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