Electron Spin Resonance Estimation of Propagation Rate Constants of Radical Polymerization of Benzyl Methacrylate

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Introduction

Much attention has been paid to electron spin resonance (ESR) studies on the radical polymerization of vinyl or diene compounds because ESR spectroscopy can, in principle, provide direct information on the structure, properties, and concentration of free radicals.[1,2] Recently, we found that the well-resolved ESR spectra of the propagating radicals of vinyl and diene compounds could be observed by a conventional ESR spectrometry[3−8] without the aid of the computer accumulation and that ESR signals can be observed at the steady-state concentration of the propagating radicals if the optimum conditions are chosen mainly in the initiator concentration and irradiation light intensity.[3−8] When the radical concentration in the steady-state can be measured by ESR spectroscopy, the propagation rate constant (k_p) of radical polymerization can be determined directly from

$$R_p = -d[M]/dt = k_p[P_n^*][M] \quad (1)$$

or its integrated form,

$$\ln([M]_1/[M]_2) = k_p[P_n^*](t_2 - t_1) \quad (2)$$

where R_p and $[P_n^*]$ are the rate of polymerization and the concentration of the propagating radical, respectively, and $[M]_1$ and $[M]_2$ are the monomer concentrations at time t_1 and t_2, respectively.

Accordingly, we determined propagation rate constants of vinyl and diene compounds by the ESR method.[3−8] Since ESR spectroscopy is the only model-independent experimental method for measuring k_p, it seems to be advantageous to use ESR spectroscopy for the determination of k_p. However, because of the experimental limitation, ESR spectroscopy is a difficult technique to acquire accurate kinetic data for some systems. To get information on the reliability of the obtained k_p values, the rate constants for styrene[7] and dodecyl methacrylate (DMA)[8] were respectively compared with ones determined by pulsed laser polymerization (PLP) methods, which constitutes the IUPAC-recommended procedure for reliable k_p measurements.[9,10] Although we came across the fact that there was a difference in k_p for styrene between the ESR method and PLP method, the k_p values for DMA from the ESR method are in fair agreement with the corresponding data obtained by the PLP method. Very recently, Zammit et al.[11a] and Hutchinson et al.[11b] have reported k_p and its Arrhenius parameters for the radical polymerization of benzyl methacrylate (BzMA) by the PLP method. In the extension of the ESR estimation of k_p, we also paid attention to the ESR estimation of k_p values for the radical polymerization of benzyl methacrylate because BzMA is a monomer which has necessary conditions for the accurate determination of k_p by ESR spectroscopy.[7] Comparison of the PLP-estimated k_p values and Arrhenius parameters with the corresponding data obtained by the ESR method will be quite significant from the point of further development of the accurate estimation of k_p values.

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Experimental Section

Benzyl methacrylate (BzMA) was purified by passing through an activated alumina column twice. Di-*tert*-butyl peroxide (DtBPO) was used after distillation under reduced pressure. Toluene was purified by distillation over benzophenone ketyl.

A toluene solution of BzMA (2.0 M) and initiator (10 mol % with respect to BzMA) was put into a sample tube (outer diameter: 5 mm), and the solution was purged using argon gas. Photoinitiated polymerizations were carried out with DtBPO under UV irradiation in an ESR spectrometer at a controlled temperature. The equipments and other conditions were the same as reported previously.[3−8]

The rate of polymerization, R_p, was estimated as the rate of consumption of the monomer. A very small amount of the polymerization mixture was sampled out from the ESR tube irradiated at a given temperature and time. Decreases in the amount of the monomer in the sample were checked by gel permeation chromatography (GPC) measurements in THF with a TOSOH CCP & 8010 series GPC system equipped with UV (254 nm) and refractive index detectors.

The steady-state concentration of the propagating radical in each polymerization system was measured by the double integration of the ESR spectrum at a given temperature and calibration curve from the use of 4-hydroxy-2,2,6,6,-tetramethyl-1-piperidinyloxy (TEMPOL) in the same media. The k_p values were determined by eq 2.

Results and Discussion

ESR measurements of radical polymerization systems of BzMA were performed in the temperature region between 0.0 and 60.0 °C. An ESR spectrum of the propagating radical of BzMA initiated with DtBPO (0.2 M) under UV irradiation at 30.0 °C is shown in Figure 1. The ESR spectrum consists of well-resolved 13 lines, and it could be assigned to the spectrum of the propagating radical of BzMA. Similar spectra were observed at other temperatures. In these measurements, we used an initiator concentration in which only a well-resolved ESR spectrum of the propagating radical was clearly observed under steady state and also the molecular weight of the obtained polymer is large enough to be recognized as a polymer by GPC. A typical example of the confirmation of the steady state is shown in Figure 2 as a time dependence of the signal intensity during irradiation. An example of a GPC pattern of the polymerization system (50.1 °C, 5 min later) is shown in Figure 3. This pattern shows that other reactions except for polymerization can be negligible in this system, although initiator concentration is 1 order of

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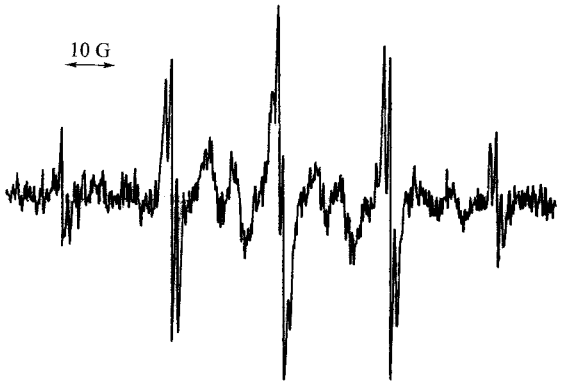

Figure 1. ESR spectrum of the propagating radical of BzMA in toluene (2.0 M) initiated with DtBPO (0.2 M) under irradiation at 30.0 °C. (0.1 mT modulation; time constant, 0.1 s; sweep time, 16 min).

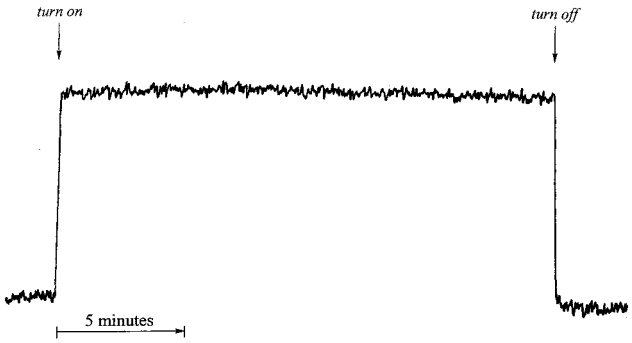

Figure 2. Time dependence of the signal intensity in the ESR spectrum of BzMA in toluene at a constant magnetic field.

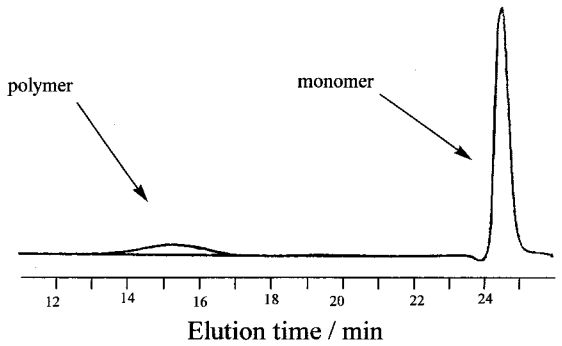

Figure 3. GPC elution diagram of the polymerization mixture sampled out after irradiation at 50.1 °C for 5 min.

magnitude larger than the usual concentration of radical polymerization. The steady-state radical concentration was estimated to be about $(8.87 \pm 0.21) \times 10^{-7}$ M at 30.0 °C by the double integration of this spectrum and calibration curve obtained from the TEMPOL radical in the same media. The rate of polymerization was estimated by GPC as the rate of the consumption of the monomer. The first-order plots for the rate of the consumption of the monomer are shown in Figure 4. The k_p value for the radical polymerization of BzMA was determined to be (608 ± 59) M^{-1} s^{-1} at 30.0 °C by using eq 2. The other k_p values similarly obtained at various temperatures are shown in Table 1[1]. The Arrhenius plot of k_p for the radical polymerization of BzMA in toluene is shown in Figure 5. From the slope and the intercept of these plots, the activation energy (E_a) and preexponential factor (A) for the photoinitiated radical polymerization of BzMA were estimated to be about 19.0 kJ/mol and 1.42×10^6 M^{-1} s^{-1}, respectively.

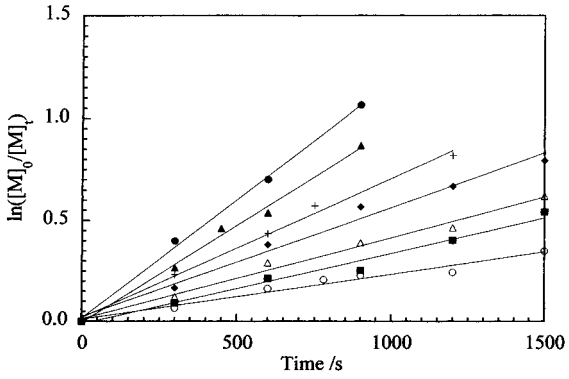

Figure 4. The first-order plots of the rate of consumption of BzMA during radical polymerizations at various temperatures. ○, 0.0 °C; ■, 10.0 °C; △, 20.0 °C; ◆, 30.0 °C; +, 40.1 °C; ▲, 50.1 °C; ●, 60.0 °C.

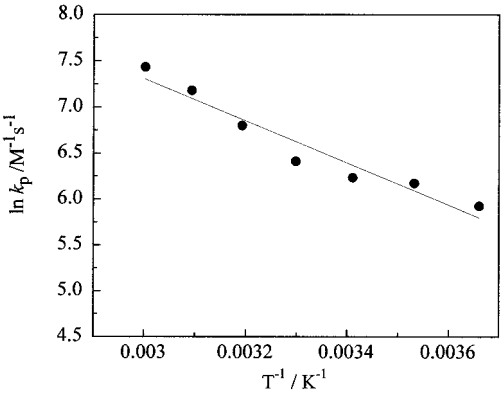

Figure 5. The Arrhenius plot of k_p for the polymerization of BzMA in toluene solution (2.0 M) determined in the temperature range 0.0−60.0 °C.

Table 1. Kinetic Data for the Radical Polymerization of BzMA in Toluene (2.0 M) at Various Temperatures

temperature/°C	$k_p[P^*]/(s^{-1} \times 10^4)$	$[P^*]/(M \times 10^7)$	$k_p/(M^{-1}\ s^{-1})$
0.0	2.23 ± 0.24	5.94 ± 0.20	375 ± 55
10.0	3.50 ± 0.43	7.29 ± 0.36	480 ± 87
20.0	4.02 ± 0.45	7.89 ± 0.13	510 ± 66
30.0	5.39 ± 0.39	8.87 ± 0.21	608 ± 59
40.1	6.88 ± 0.36	7.65 ± 0.03	899 ± 51
50.1	9.60 ± 0.72	7.29 ± 0.04	1317 ± 106
60.0	11.7 ± 1.20	6.90 ± 0.07	1696 ± 193

Very recently, Zammit et al.[11a] and Hutchinson et al.[11b] independently reported k_p values of BzMA in a bulk system by using the PLP method and estimated that A and E_a for the k_p value were about 8.50×10^6 M^{-1} s^{-1} and 23.2 kJ/mol, and about 3.61×10^6 M^{-1} s^{-1} and 21.5 kJ/mol, respectively. These values of A and E_a are larger as compared with our values. A long time ago, the k_p values for BzMA had been estimated by the rotating sector method.[12,13] Mayer and Schulz[12] have estimated the values to be 1.26×10^6 M^{-1} s^{-1} and 18.8 kJ/mol for the polymerization of BzMA in bulk or in ethyl phthalate by the rotating sector method, which are in agreement within the experimental error with our data, respectively. Since each method for k_p measurements has its own factors which lead to experimental error, we cannot conclude which value is the most precise k_p. Two reasons will be considered as an origin of the difference in k_p values between ESR and PLP methods. One of them may be due to the chain-length dependence of k_p values because ESR measurements were performed in 1 order of higher concentration of the initiator. GPC data show that the molecular weight of

polymers produced in ESR measurements is smaller than that of polymers in the PLP method. The other might be due to the presence of solvent, which led to the decrease in the preexponential factor.

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