

ESR study on radical polymerization of styrene

2. Propagation rate constant of polystyrene radical with different molecular weights

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Summary

Propagation rate constant (k_p) for styrene was evaluated at different chain lengths of the polymer radical based on the steady-state concentration of the polymer radical determined by means of ESR spectroscopy at 70°C. Over a range of degree of polymerization of the polymer radical from 40 to 410, the value of k_p , 480 ± 10 L/mol·s, remained constant. A considerable increase in viscosity of the polymerization mixture did not affect this value.

Introduction

Radical polymerization is an useful method to produce polymers from a wide variety of monomers, and is a typical chain reaction. Usually the steady-state concentration of propagating radical which is the chain carrier is too low to be determined and removed from the standard kinetic equation for radical polymerization. However, if concentration of the radical can directly be determined by ESR spectroscopy, the elementary reactions including propagation and termination reactions could be discussed quantitatively and separately.

Recently, the steady-state concentration of the polymer radical from methyl methacrylate (MMA) has been determined by means of ESR spectroscopy over a wide conversion range (1-3). A significant increase in the concentration of the polymer radical caused by a decrease in the termination rate constant has been shown during the period of gel effect. At higher conversions, a further decrease in the termination rate caused by restricted mobility of segment and entanglement of the polymer chain has also been emphasized.

On the basis of the following aspects, we have anticipated that styrene (St) is one of the most suitable monomers for the ESR study on its radical polymerization. Non-polar nature of St could allow us to detect the spectrum of poly-(St) radical with a high sensitivity and the sensitivity of ESR spectrometer could remain constant throughout the polymerization irrespective of the conversion. Furthermore, a precise determination of the molecular weight of poly(St) by GPC is also advantageous over other polymers.

From such a point of view, we have determined the absolute rate constants of St up to a high conversion, and dependence of the absolute rate constants on conversion has been described in our preceding paper(4). The rate con-

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stant of propagation (k_p) remained constant for the whole range of conversion and the termination rate constant was found to decrease to 1/2000 of the initial value at 97% conversion. Since the constant k_p up to the high conversion also suggests the insensitivity of k_p to a change in viscosity of polymerization mixture, combination of the k_p determined by the ESR method with the molecular weight of the polymer radical or polymer could reveal a dependency of k_p on the chain length of poly(St) radical.

In the present communication, we have described the determination of the molecular weight of poly(St) formed within narrow conversion ranges throughout the polymerization in relation to the change in the k_p value. Furthermore, k_p of poly(St) with different chain lengths was evaluated at different concentrations of the initiator used.

Experimental

St was distilled under reduced pressure before use. Commercially available dimethyl 2,2'-azobisisobutyrate (MAIB) (Wako) was recrystallized from n-hexane. ESR spectra of the polymer radical were obtained by a Bruker ESP 300 spectrometer with a 5 mm-o.d. sample tube sealed under vacuum. Sensitivity of the spectrometer at each conversion was examined on the basis of intensity of spectrum of manganese oxide, which was sealed in a quartz capillary tubing (1 mm-o.d.) attached to the ESR tube containing the polymerization mixture. Polymerization in the cavity of the ESR spectrometer was initiated with MAIB at 70°C.

Concentration of the radical was determined by using a calibration line between concentration of 1,3,5-triphenylverdazyl(6) and the intensity of its integrated spectrum. The k_p value was calculated from the overall rate of polymerization (R_p) by using the following equation(4):

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

where [St] and [St·] stand for the concentrations of St and of poly(St) radical, respectively. R_p was calculated from the slope of conversion versus time plot, and the polymerization for determination of R_p was conducted in sealed tubes with MAIB at 70°C.

Viscosity of the polymerization mixture at different conversion was measured by an Ostwald viscometer (< 40 % conversion) or E type viscometer (Tokyou Keiki Visconic EMD) (> 40 % conversion). Number average molecular weight (\bar{M}_n) calibrated with standard poly(St) was obtained by a GPC (Toso 8000 series) and \bar{P}_n was calculated from \bar{M}_n . The polymer samples for the molecular weight measurements were also prepared by the polymerization in the sealed tubes.

Results and Discussion

The ESR spectrum of poly(St) radical observed at an initial stage of the polymerization is illustrated in Fig. 1 together with the simulated spectrum based on the coupling constants reported by Smith and coworkers(7) with an increased line width. Similarity of these spectra evidences

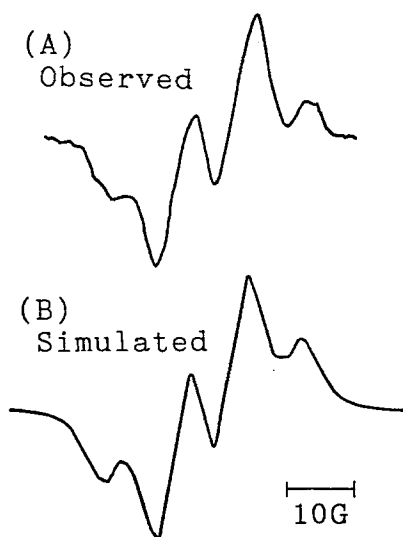


Fig. 1. ESR spectrum of poly(St) radical (A) and the simulated spectrum (B)

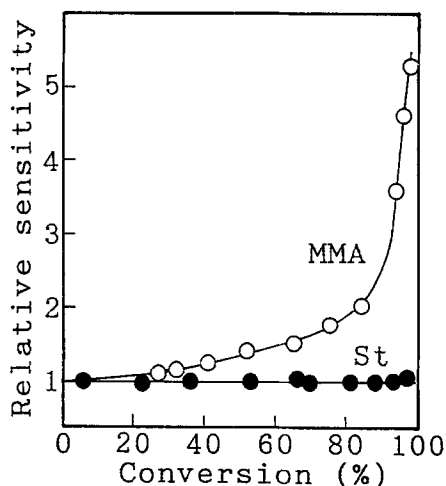


Fig. 2. Changes in the sensitivity of ESR spectrometer with proceeding of bulk polymerization of St at 70°C (●) and polymerization of MMA (7 mol/L) in benzene at 40°C (○)

detection of the propagating radical of St. Since we preferred to determine the concentration of poly(St) radical precisely, the spectrum consisting of broad lines caused by a relatively high modulation amplitude, 10 G, was recorded.

Fig. 2 shows the change in the sensitivity of the ESR spectrometer with proceeding of the polymerization. As expected from the non-polar nature of St, the sensitivity of the spectrometer remained constant unlikely to MMA polymerization. Therefore, the concentration of poly(St) radical could directly be determined on the basis of the double integrated value of the ESR spectrum without correction for the sensitivity change.

We have previously reported the detection of poly(St) radical and determination of the steady-state concentration of the radical using ESR spectroscopy(4). To determine the k_p value for the polymer radical with different \bar{P}_n , we employed two procedures, viz. one is the k_p determination at different stages of the polymerization, since \bar{M}_n changes with conversion, and another consists of evaluation of k_p at various concentrations of MAIB; an increase in MAIB concentration should result in a reduced kinetic chain length at the initial stages of the polymerization.

Instantaneous \bar{P}_n is thought to change with conversion because \bar{P}_n of the polymer is influenced by the instantaneous rates of propagation and termination. Fig. 3 shows the GPC elution curves of the polymers isolated at various conversions. In this figure, the peak area is normalized as to correspond to the conversion. The elution curve slightly

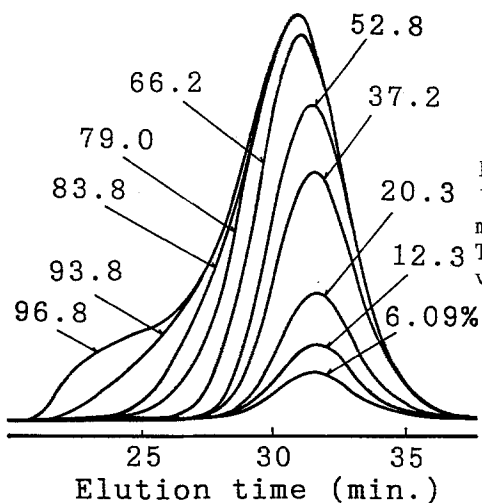


Fig. 3. Normalized GPC elution curves of the St polymers at different conversions. The figures denote the % conversion

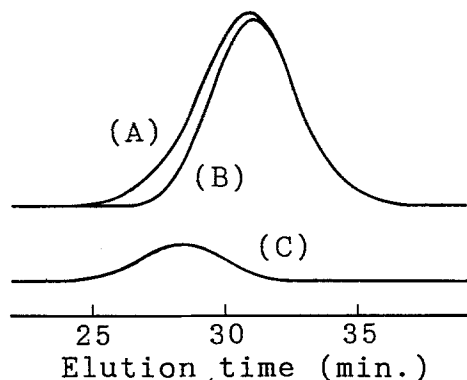


Fig. 4. GPC elution curves for poly(St) at 66.2 % (A) and 79.0 % conversions (B), and curve obtained by subtraction of A from B (C)

shifts to lower molecular weight at the initial stage of the polymerization up to ca. 20 % conversion, because of a decrease in St concentration. From the middle to final stages of the polymerization, a decrease in the termination rate predominantly contributes to an increase in \bar{P}_n with conversion(4).

The \bar{P}_n of poly(St) instantaneously formed in a narrow conversion range can be estimated by subtraction of an elution curve at a lower conversion from that at a higher conversion. For example as shown in Fig. 4, the elution curve for the polymer formed during the period of 66.2-79.0 % conversion ($\bar{P}_n = 309$, $\bar{M}_w/\bar{M}_n = 1.84$) was obtained by subtraction of the curve for the polymer at 66.2 % conversion ($\bar{P}_n = 111$ and $\bar{M}_w/\bar{M}_n = 1.97$) from the curve for the polymer at 79.0 % conversion ($\bar{P}_n = 125$ and $\bar{M}_w/\bar{M}_n = 2.32$).

Fig. 5 shows the variations in the values of \bar{P}_n obtained in the cumulative and instantaneous manners with conversion. Apparently the cumulative \bar{P}_n changed to a smaller

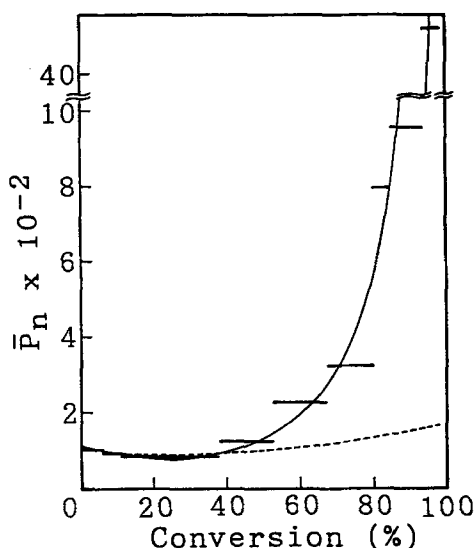


Fig. 5. Changes in cumulative (---) and instantaneous \bar{P}_n 's (—) with conversion for St polymerization. Horizontal lines show the ranges of conversion for determination of instantaneous \bar{P}_n

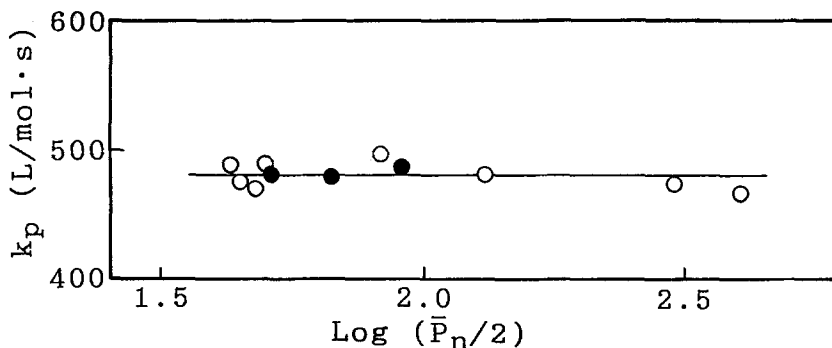


Fig. 6. Plot of k_p versus $\text{Log}(\bar{P}_n/2)$ from instantaneous \bar{M}_n (O) and \bar{M}_n of poly(St) obtained at different initiator concentrations (●)

extent than the instantaneous \bar{P}_n as a consequence of the considerable change in the termination rate with an increase in the viscosity of the polymerization mixture at the final stages.

The kinetic chain length which is the chain length of the polymer radical participating to termination can be estimated as a half of \bar{P}_n in the St polymerization, since poly(St) radical has been known to terminate mainly by combination(7). We preferred to use $\bar{P}_n/2$ for expression of the chain length of the polymer radical for consideration of a relationship between k_p and the chain length of the polymer radical. If the k_p value was dependent on the chain length, we could observe the average of the rate constants

up to the instantaneous $\bar{P}_n/2$. Then the k_p value is plotted against logarithm of $\bar{P}_n/2$ as depicted in Fig. 6; k_p remains constant, 480 ± 10 L/mol·s at 70°C. During the k_p determination over the wide conversion range, the viscosity of the polymerization mixture changed from 0.51 cp for the neat St to 117 cp at 60 % conversion.

In the same figure, the k_p values for poly(St) radicals prepared by using different amounts of MAIB are also plotted. The polymerization at the MAIB concentration of 2.00, 1.00, and 0.50×10^{-1} mol/L gave poly(St) samples having different \bar{P}_n , 115, 133, and 182, at 70°C, respectively. However, the k_p value, 480 ± 10 L/mol·s, under these polymerization conditions again remained constant.

The constant k_p over the range of $\bar{P}_n/2$ from 40 to 410 which was confirmed by the two procedures, can exclude the possibility that diffusion of the polymer radical could affect the propagation rate. A considerable change in the viscosity of the polymerization mixture also did not affect the k_p value supporting the conclusion obtained.

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References

1. Carswell, T. G., Hill, D. J. T., Hunter, D. S., Pomery, R. J., O'Donnell, J. H., and Winzor, C. L., *Europ. Polym. J.*, 1991, 26, 541
2. Garrett, R. W., Hill, D. J. T., O'Donnell, J. H., Pomery, R. J., and Winzor, C. L., *Polym. Bull.*, 1989, 22, 611
3. Zhu, S., Tian, Y., Hamielec, A. E., and Eaton, D. R., *Macromolecules*, 1991, 23, 1144
4. Yamada, B., Kageoka, M., and Otsu, T., *Macromolecules*, 1991, 24, 5234
5. Kuhn, R. and Trischmann, H., *Monatsch. Chem.*, 1964, 95, 457
6. Smith, P., Gilman, L. B., Stevens, R. D., and de Hargrave, C. V., *J. Magn. Reson.*, 1978, 29, 545
7. Hatada, K., Kitayama, T., Masuda, E., *Polym. J.*, 1985, 17, 985