Dependence of Propagation and Termination Rate Constants on Conversion for the Radical Polymerization of Styrene in Bulk As Studied by ESR Spectroscopy

Radical polymerization, a typical chain reaction, has been utilized for the preparation of polymers from a wide variety of monomers. The rate constants for the individual elementary reactions have been indirectly evaluated by analysis of the nonsteady or quasi-steady state,[1] because of the extremely low concentration of the chain carrier. If the polymer radical was detected by spectroscopy, particularly ESR spectroscopy, instantaneous propagation and termination rate constants (k_p and k_t, respectively) could be directly determined. Among the unsolved problems in radical polymerization, the dependence of k_p and k_t on conversion can be straightforwardly examined by using this approach.

Detection of the propagating radical in a homogeneous system has not been an easy task even with ESR spectroscopy. However, the spectra of the propagating radicals from styrene (St), methyl methacrylate (MMA), and vinyl acetate have been recorded by an ESR instrument equipped with a balance resonator during their polymerizations.[2,3] Kamachi and his co-workers[4] enhanced the sensitivity by using a TM_{110} mode cavity and obtained the spectra of the propagating radicals of several monomers including MMA. The k_p values for these monomers have been calculated by using the determined concentration of the polymer radicals and the overall rate of polymerization (R_p). Computer control of an ESR spectrometer has made it possible to observe polymer radicals present in 10^{-7}–10^{-6} mol dm^{-3} without difficulty.

Recently, determination of k_t based on the decay curve of the ESR signal of a poly(MMA) radical has confirmed the decrease in k_t with conversion.[5,6] Hamielec and co-workers[7] have proposed the existence of a trapped poly(MMA) radical, of which appearance coincided with merging of the gel effect. They have suggested that a poly(MMA) radical with a certain chain length or above forms an entanglement resulting in the trapped radical and that the shorter polymer radical terminates faster without suppression by the entrapment. Furthermore, dependence of k_p on the chain length has been speculated, because the trapped radicals might not readily have access to the monomers.

Similar tendencies observed in the rate constants for MMA have been confirmed by a rotating sector method at low conversions and by analysis of the aftereffect at high conversions.[8] Beyond the conversion at which T_g of a poly(MMA)/MMA mixture reaches its polymerization temperature, k_t is abruptly reduced by restricted segmental movement of the polymer radical. While a change from a purely chemical control to diffusion control of the propagation has been considered to cause the dependence of k_p on conversion, k_p also decreased abruptly at a high conversion, leading to a T_g higher than the polymerization temperature. Moreover, a slight decrease in k_p with an increase in chain length was shown to be plausible. Thus, the effect of changes in the physical situation of the polymerization system on the rate constants has been emphasized in MMA polymerization.

The ESR spectrum of the propagating radical during St polymerization has been recorded by a flow technique, and hyperfine splitting constants for the α, β, meta, ortho, and para hydrogens have been evaluated.[9] As already mentioned, Bresler et al. have succeeded in determining the steady-state concentration, and they obtained k_p values at different temperatures.[2]

St, as well as MMA, is a typical radically polymerizable monomer, and the kinetic parameters for St have been evaluated by a rotating-sector method and other techniques.[1] However, the absolute rate constants for St polymerization over a wide conversion range have not been determined. Soh and Sundberg have noted on the basis of their theory that the gel effect in St polymerization is mild until the conversion reaches about 50% and that the effect of polymer chain entanglement appears in the final stages of polymerization.[10]

We thought that St has advantages over MMA for monitoring the polymerization by ESR spectroscopy. Considering the less polar nature of St compared to MMA, we can detect the poly(St) radical with a higher sensitivity. A change in the polarity of the polymerization mixture with the conversion is likely to be less than that of MMA. Furthermore, the degree of polymerization, which is closely related to the rates of the elementary reactions, can be precisely determined by gel permeation chromatography (GPC) using the standard poly(St).

In this article, St polymerization was followed by ESR spectroscopy over a wide range of conversion in order to examine the conversion dependencies of k_p and k_t. The concentration of the poly(St) radical, R_p, and the molecular weight of poly(St) were determined throughout the polymerization.

Commercially available St was distilled under reduced pressure before use. Dimethyl 2,2′-azobis(isobutyrate) (MAIB) was recrystallized from *n*-hexane. *tert*-Butyl peroxide (TBP) was distilled under reduced pressure.

To determine R_p, St polymerization was carried out in sealed tubes and the conversion of St was calculated from the weight of isolated poly(St). ESR spectra of the poly(St) radical were measured by a Brüker ESP 300 spectrometer with a 5-mm-o.d. sample tube. Polymerization in the cavity was initiated by irradiation with a 500-W xenon lamp (Ushio) or by heating at a specified temperature. The spectra of the poly(St) radical at different conversions were taken by the accumulation of 20 scans. The steady-state concentration of the poly(St) radical, averaged over the period for the scan, was determined by a calibration line between the concentration of 1,3,5-triphenylverdazyl (TPV)[11] and the double-integrated intensity of its ESR spectrum with an accuracy of better than ±10%.

Number- and weight-average molecular weights ($\bar{M}_n$ and $\bar{M}_w$, respectively) calibrated with the standard poly(St) were obtained by a Toso 8000 series HPLC equipped with columns of G2000HXL, G4000HXL, G4000HXL, and G6000HXL, connected in this order. Tetrahydrofuran was used as an eluent.

Figure 1 shows the spectra of the propagating radical at different polymerization times, indicating that the observed four-line spectrum first becomes broader and larger with an increase in conversion. The four-line spectrum can be simulated by the ESR parameters reported by Smith and co-workers[9] with an increased line width.

According to the calibration relation using TPV, the concentration of the poly(St) radical was found to increase from the order of 10^{-7} to 10^{-6} mol dm^{-3} with conversion under the present conditions as shown in Figure 2. During the final stages, the polymerization mixture solidified and the radical concentration reached the maximum value at a conversion very close to 100%. After completion of the polymerization, the poly(St) radical still survived, indicating that the radical lost its activity by a slow reaction.

0024-9297/91/2224-5234$02.50/0

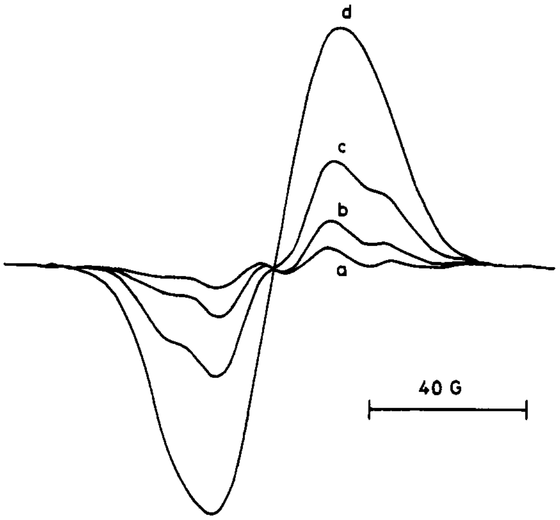

Figure 1. ESR spectra of the poly(St) radical presenting in bulk polymerization initiated with MAIB after polymerization for 11 (a), 142 (b), 171 (c), and 186 min (d) at 70 °C. [MAIB] = 0.2 mol dm^{-3}.

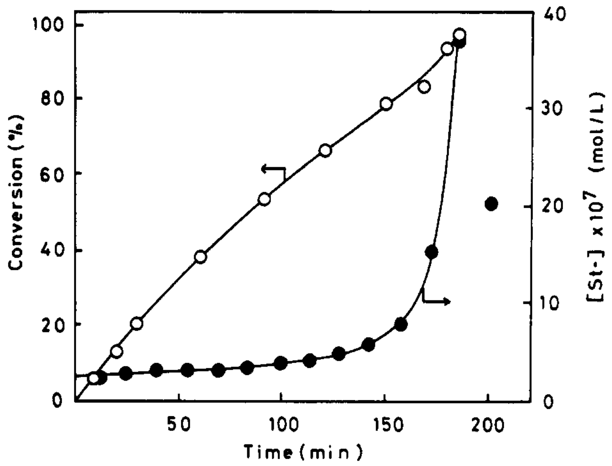

Figure 2. Plots of conversion and concentration of the poly(St) radical versus polymerization time using the same concentration of MAIB as in Figure 1.

Proceedings of the St polymerization bring about changes in the $\bar{M}_n$ of poly(St). A gradual decrease in the cumulative $\bar{M}_n$ from 13 800 ($\bar{M}_w/\bar{M}_n$ = 1.61) to 12 000 ($\bar{M}_w/\bar{M}_n$ = 1.75) with conversion ascribable to a decrease in the St concentration was observed below 30% conversion. After that period, $\bar{M}_n$ increased to 23 400 ($\bar{M}_w/\bar{M}_n$ = 4.43) at 96.7% conversion.

Since the slope of the conversion-time plot allows us to estimate R_p, k_p values at different conversions were calculated from

$$R_p = k_p[\mathrm{St}][\mathrm{St}^{\bullet}]$$

where [St] and [St$^{\bullet}$] denote concentrations of monomeric St and the poly(St) radical, respectively. The k_p value at a conversion very close to 0% was calculated from the radical concentration given as the intercept on the ordinate of Figure 2. It should be noted that the values of k_p shown in Figure 3 remain constant up to a high conversion: k_p = 480 ± 10 dm^3 mol^{-1} s^{-1}. The constant k_p throughout the polymerization signifies that St propagation is chemically controlled irrespective of conversion.

Consistent values of the rate constants for radical polymerization have been extensively discussed by an IUPAC Working Party on "Modeling of Free Radical Polymerization Kinetics and Processing". They have quoted the reliable Arrhenius equations for k_p; eqs 1 and 2 have been obtained by spatially intermittent polymerization and emulsion polymerization, respectively:[12]

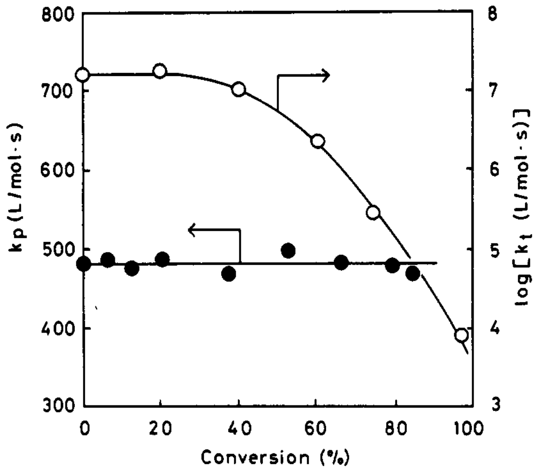

Figure 3. Decreases in k_p (●) and k_t (○) for the bulk polymerization of St with an increase in conversion.

$$k_p\,(\mathrm{dm^3\,mol^{-1}\,s^{-1}}) = 10^{7.04}\exp[-29.5\,(\mathrm{kJ\,mol^{-1}})/RT] \quad (1)$$

$$k_p\,(\mathrm{dm^3\,mol^{-1}\,s^{-1}}) = 10^{7.1\pm0.5}\exp[-(29\pm3)\,(\mathrm{kJ\,mol^{-1}})/RT] \quad (2)$$

The estimates of k_p at 70 °C are 350 dm^3 mol^{-1} s^{-1} from eq 1 and 480 dm^3 mol^{-1} s^{-1} from eq 2. The absolute value of k_p at 70 °C is also calculated from the Arrhenius equation derived by Bresler et al.[1,2] as 442 dm^3 mol^{-1} s^{-1}:

$$k_p\,(\mathrm{dm^3\,mol^{-1}\,s^{-1}}) = 2.4\times10^{8}\exp[-(37.5\pm1.6)\,(\mathrm{kJ\,mol^{-1}})/RT] \quad (3)$$

The k_p determined in the present study seems to agree with those estimated from the Arrhenius equations.

The k_t value was evaluated from the decay curve of the spectrum in the presence of poly(St). The St polymerization was initiated with TBP at 100 °C, and at a certain conversion the polymerization mixture was cooled to 70 °C. GPC measurement of poly(St) formed at 100 °C exhibited $\bar{M}_n$ = 102 000 and 103 000 at 14 and 69%, respectively, and the $\bar{M}_n$ would increase further with an increase in conversion. The poly(St) radical was formed by UV irradiation in the presence of the polymer matrix at 70 °C, and the decay curve for k_t determination was obtained by interruption of the irradiation. Since no initiation with TBP occurred in the dark, a decrease in the radical concentration was caused solely by a mutual reaction of the poly(St) radical.

The k_t value was determined according to second-order kinetics. The change in the k_t value with conversion is also shown in Figure 3. For determination of k_t at 0% conversion, the polymerization was initiated by the irradiation for a certain period to attain the stationary state of the spectrum, and the lamp was turned off to record the decay curve. Since the $\bar{M}_n$ of poly(St) obtained at 70 °C in the absence of the polymer was 14 800, the $\bar{M}_n$ of poly(St) could increase with an increase in the amount of the polymer used as the matrix. Note that the $\bar{M}_n$ of the poly(St) radical for the k_t determination is likely to be that of the polymer radical formed during the k_p determination.

Over the conversion range from 0 to 20% or above, k_t changed from 1.66 × 10^7 to 1.70 × 10^7 dm^3 mol^{-1} s^{-1}. Above

40% conversion, k_t began to decrease rapidly toward 7.94 × 10^3 $dm^3\,mol^{-1}\,s^{-1}$ at 93.8% conversion, which is less than the k_t at 6.1% conversion by a factor of 2 × 10^3. The steep decrease in k_t corresponded to an increase in the viscosity of the polymerization mixture.

Thus, the present study revealed that the concentration of the poly(St) radical gradually increased to 30% conversion with small changes in the rate constants. The abrupt decrease in k_t arising from an enhanced viscosity of the polymerization system results in acceleration of the polymerization and an increase in $\bar{M}_n$ of the polymer at high conversions. As a distinction from MMA polymerization,[6,7] the present polymerization yielded a poly(St) much shorter than poly(MMA). The chain length of the poly(St) radical was probably too short to suppress diffusion, forming an entanglement.[13] Therefore, acceleration of polymerization caused by a considerable decrease in k_t is observed in the final stages of St polymerization and the conversion reaches almost 100%. While the change in k_p with conversion to MMA polymerization has been interpreted by the restricted diffusion of the polymer radical and monomer arising from lowering the T_g,[7,8] k_p remained constant from the initial to final stages of St polymerization.

Buback and Schweer have concluded that k_p for ethylene is identical with the rate constant for addition of the C_{10} radical or above to ethylene irrespective of chain length.[14] However, if a slower diffusion of the poly(St) radical, which is less reactive than the poly(ethylene) radical, could differentiate from a low molecular weight homologue, the k_p and k_t values at the low-conversion range would exhibit dependencies on chain length.

References and Notes

(1) Berger, K. C.; Meyerhoff, G. In *Polymer Handbook*, 3rd ed.; Brandrup, J., Immergut, E. H., Eds.: Wiley: New York, 1989; p II/6.
(2) Bresler, S. E.; Kazbekov, E. N.; Fomichev, V. N.; Shadrin, V. N. *Makromol. Chem.* **1972**, *157*, 167.
(3) Brelser, S. E.; Karzbekov, E. N.; Shadrin, V. N. *Makromol. Chem.* **1974**, *175*, 2875.
(4) Kamachi, M. *Adv. Polym. Sci.* **1987**, *82*, 207.
(5) Carswell, T. G.; Hill, D. J. T.; Hunter, D. S.; Pomery, R. J.; O'Donnell, J. H.; Windor, C. L. *Eur. Polym. J.* **1990**, *26*, 541.
(6) Garrett, R. W.; Hill, D. J. T.; O'Donnell, J. H.; Pomery, P. J.; Winzor, C. L. *Polym. Bull.* **1989**, *22*, 611.
(7) Zhu, S.; Tian, Y.; Hamielec, A. E.; Eaton, D. R. *Macromolecules* **1990**, *23*, 1144.
(8) Sack, R.; Schulz, G. V.; Meyerhoff, G. *Macromolecules* **1988**, *21*, 3345.
(9) Smith, P.; Gilman, L. B.; Stevens, R. D.; de Hargrave, C. V. *J. Magn. Reson.* **1978**, *29*, 545.
(10) Soh, S. K.; Sundberg, D. C. *J. Polym. Sci.: Polym. Chem. Ed.* **1982**, *20*, 1345.
(11) Kuhn, R.; Trischmann, H. *Monatsch. Chem.* **1964**, *95*, 457.
(12) Buback, M.; Garcia-Rubio, L. H.; Gilbert, R. G.; Napper, D. H.; Guillot, J.; Hamielec, A. E.; Hill, D.; O'Diriscoll, K. F.; Olaj, O. F.; Shen, J.; Solomon, D.; Moad, G.; Stickler, M.; Tirrell, M.; Winnik, M. A. *J. Polym. Sci., Part C: Polym. Lett.* **1988**, *26*, 293.
(13) Mita, I.; Horie, K. *J. Macromol. Sci.* **1987**, *C27*, 91.
(14) Buback, M.; Schweer, J. *Z. Phys. Chem. (Neue Folge)* **1989**, *161*, 153.

Bunichiro Yamada, Masakazu Kageoka, and Takayuki Otsu*

Department of Applied Chemistry
Faculty of Engineering, Osaka City University
Sugimoto, Sumiyoshi-ku, Osaka 558, Japan

Received April 29, 1991
Revised Manuscript Received July 2, 1991

CORRECTIONS

Satoshi Koizumi, Hirokazu Hasegawa, and Takeji Hashimoto*: Mutual Diffusion of Block Copolymer and Homopolymer. Visualization Using Microdomains as a Probe. Volume 23, Number 11, May 28, 1990, p 2955.

An error in computation was pointed out by Dr. Karen I. Winey, AT&T, Bell Laboratories, Murray Hill, NJ. The numerical values of Ψ_{PI} (SC) in Table II should read 0.1911 for B2 and 0.0806 for B2:H6 = 1:1, instead of 0.0678 and 0.0284, respectively, which suggests that the spheres are packed in a SC lattice rather than a BCC lattice for B2:H6 = 1:1. The packing symmetry of spheres in B2 cannot be uniquely determined by the volumetric consideration of this kind. This change does not alter the conclusions of the article.