ESR study on radical polymerization of styrene

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

Bunichiro Yamada, Masakazu Kageoka, and Takayuki Otsu*

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

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-
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-triphenyl-verdazyl(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):

\[
k_p = \frac{R_p}{[St][St.^-]}
\]

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 \( (M_n) \) calibrated with standard poly(St) was obtained by a GPC (Toso 8000 series) and \( P_n \) was calculated from \( M_n \). 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