Polymer Bulletin 6, 189–194 (1981)

Polymer Bulletin

Kinetic Study on Radical Polymerization with Consideration of Reversibility of Propagation Reaction

Polymerizations of Phenyl Methacrylate and *o-sec*-Butylphenyl Methacrylate

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Summary

Kinetic equation of radical polymerization was derived by considering reversibility of propagation reaction. After polymerization for a certain polymerization time, the concentration of the monomer remained, $[M]_t$, was found to be expressed by the initial monomer concentration, $[M]_0$, and the equilibrium monomer concentration, $[M]_e$;

$$[M]_t = [M]_0\exp(-ABt) + [M]_e(1 - \exp(-ABt))$$

Where t denotes the polymerization time, and A and B are constants depending on polymerization conditions. The kinetic equation derived was applied to radical polymerizations of phenyl methacrylate and o-sec-butylphenyl methacrylate.

Introduction

Radical polymerization is a typical chain reaction consisting of initiation, propagation, and termination reactions. Because propagtion reaction is addition of a polymer radical to the carbon-carbon double bond of a monomer, decreases in enthalpy and entropy are caused by proceeding of the reaction. The free energy change of polymerization, ΔG, is determined by the enthalpy change, ΔH, and the entropy change, ΔS;

$$\Delta G = \Delta H - T\Delta S$$

and will only be negative when ΔH is negative and $|\Delta H| > |T\Delta S|$. Therefore, there must be a temperature when ΔG will become to zero. Above this temperature, addition of the monomer unit to a polymer chain involves positive ΔG, whereas elimination of the monomer unit from the chain would lower the free energy (IVIN 1973).

This critical temperature corresponds to the ceiling temperature (T_c), and polymer formation is thermodynamically prohibited at temperatures above it. Kinetically, T_c is understood as the temperature at which the rate of propagation is equal to that of depropagation. In vinyl polymerization, the concept of T_c has been established and applied to explain the polymerization behavior of some monomers (IVIN 1973; LÜSSI 1966). However, short lifetime and extremely low concentration of the growing polymer radical make difficult to study directly on reversibility of propagation reaction in radical polymerization.

Recently, we have reported determination of T_c for some ortho-

0170-0839/81/0006/0189/$01.20

substituted phenyl methacrylates using eq. (1) (OTSU, et al. 1980; YAMADA, et al. 1981a).

$$\frac{d(\ln k_p'/k_t^{0.5})}{d(1/T)} = \frac{(k_d E_d/R[M] - k_p E_p/R)}{(k_p - k_d[M])/k_t^{0.5}}$$

and

$$\lim_{T \to T_c} \frac{d(\ln k_p'/k_t^{0.5})}{d(1/T)} = \infty \qquad (1)$$

Where k_p', k_p, k_d, and k_t denote the rate constants for apparent propagation, propagation, depropagation, and termination reactions, respectively. E_p and E_d are the activation energies of the propagation and depropagation reactions. Experimentally, T_c can be determined as the temperature at which $k_p'/k_t^{0.5}$ is equal to zero or infinitely small. The ratio of rate constants increases with increasing in temperature at temperatures enough lower than T_c. As polymerization temperature raised further, at a temperature close to T_c, $k_p'/k_t^{0.5}$ passes through a maximum and then decreases with increasing in temperature. Because depropagation reaction rate is comparable to propagation reaction rate in such a temperature range, polymerization rate could be adequately expressed by consideration of propagation and depropagation reactions.

In this article, derivation of the kinetic equation with consideration of the reversibility of propagation and application of the equation to radical polymerizations of phenyl methacrylate (PMA) and o-sec-butylphenyl methacrylate (SBPMA) are described.

Experimental

Polymerizations were carried out in sealed tubes and p-xylene was used as the solvent. 2, 2'-Azobisisobutyronitrile (AIBN), 1, 1'-azobiscyclohexane-1-carbonitrile (ACN), and tert-butyl peroxide (TBP) were chosen as the initiators, depending on the polymerization temperature. Decomposition rate constants of the initiators were calculated from the Arrhenius equations (MASSON 1975). The efficiencies of initiation were assumed to be 0.5 and 1.0 for the azo-initiators and TBP, respectively. PMA and SBPMA prepared by the reactions of methacryloyl chloride with the corresponding phenols were distilled under reduced pressure before use. The concentration of the unchanged monomer was calculated from the weight of the polymer formed.

Results and Discussion

Introducing depropagation reaction into the usual scheme of radical polymerization, for long chain, polymerization rate is given by the following equation.

$$M_n\cdot \; + \; M \; \underset{k_d}{\overset{k_p}{\rightleftharpoons}} \; M_{n+1}\cdot$$

$$-d[M]/dt = k_p[M][M\cdot] - k_d[M\cdot]$$

At T_c, $k_p/k_d = 1/[M]_e$. Where $[M]_e$ is the equilibrium monomer concentration.

During the polymerization for t, the monomer concentration decreases from $[M]_0$ to $[M]_t$. Integrating the above equation from $[M]_0$ to $[M]_t$ under the conditions of constant $[M\cdot]$, the following equations are obtained. Such conditions are attainable when the polymerization time is so short that the decrease in the initiator concentration is negligible.

$$\int_{[M]_0}^{[M]_t} \frac{d[M]}{k_d[M\cdot] - k_p[M\cdot][M]} = \int_0^t dt$$

$$\int_{[M]_0}^{[M]_t} \frac{d[M]}{k_d[M\cdot] - k_p[M\cdot][M]} = \frac{1}{k_p[M\cdot]} \Big[\ln\ (k_p[M\cdot][M] - k_d[M\cdot]) \Big]_{[M]_0}^{[M]_t}$$

$$= \frac{1}{k_p[M\cdot]} \left(\ln \frac{[M]_0 - k_d/k_p}{[M]_t - k_d k_p} \right)$$

Under the steady state conditions,

$$[M\cdot] = (2fk_{dec}[I]/k_t)^{0.5} = (R_i/k_t)^{0.5}$$

Therefore,

$$\ln \frac{[M]_0 - k_d/k_p}{[M]_t - k_d/k_p} = R_i^{0.5}(k_p/k_t^{0.5})t$$

Substituting $R_i^{0.5} = A$, $k_p/k_t^{0.5} = B$, and $k_d/k_p = [M]_e$ in the above equation yields the following expression.

$$[M]_t = \frac{[M]_0}{e^{ABt}} + [M]_e(1 - \frac{1}{e^{ABt}}) \qquad (2)$$

Without consideration of the reversibility of propagation reaction, eq. (3) is derived.

$$[M]_t = [M]_0/e^{ABt} \qquad (3)$$

Under the conditions of constant A, B, and t, the plot of $[M]_t$ against $[M]_0$ is expected to give a straight line which intersects with the straight line showing $[M]_t = [M]_0$ at $[M]_0 = [M]_e$. Figs. 1 and 2 show the plots of $[M]_t$ against $[M]_0$ on the basis of the data from the polymerizations of PMA and SBPMA at various temperatures. In these figures, all the straight lines intersect with the line of $[M]_t = [M]_0$, except for the line of PMA at 90°C. In these cases, the plot of $[M]_t$ against $[M]_0$ according to eq. (3) would draw erroneous conclusion about the polymerization, because the straight line given by eq. (3) should pass through the origin.

Eq. (2) can be rewritten as the expression of the conversion;

$$([M]_0 - [M]_t)/[M]_0 = [M]_e(e^{-ABt} - 1)/[M]_0 - (e^{-ABt} - 1) \qquad (4)$$

Although the conversion should be independent of the monomer concentration for the polymerization of irreversible propagation owing to

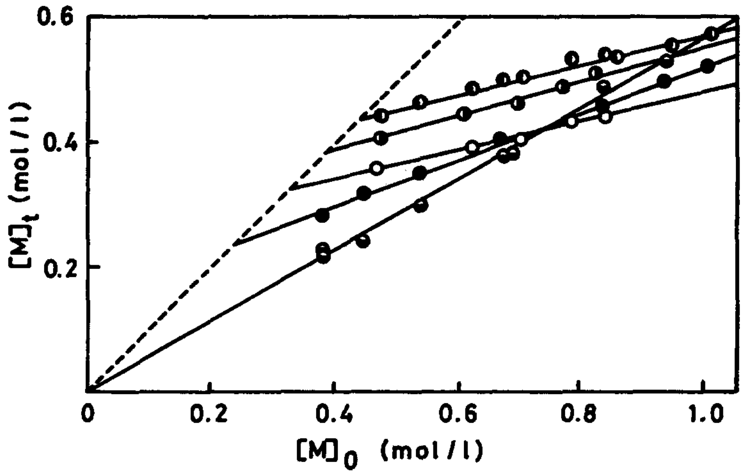

FIGURE 1. Determination of $[M]_e$ in PMA polymerization: [TBP] = 0.017 mol/l: ◒ , 90°C, 11.5 hr; ● , 115°C, 100 min; ○ , 120°C, 100 min; ◑ , 125°C, 1 hr; ◐ , 130°C, 50 min

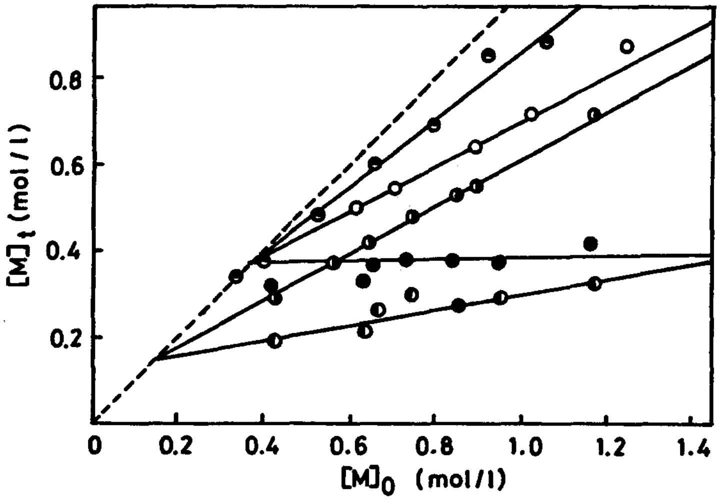

FIGURE 2. Determination of $[M]_e$ in SBPMA polymerization: ◓ , [ACN] = 0.023 mol/l, 50 min, 90°C; ○ , [ACN] = 0.018 mol/l, 1 hr, 90°C; ● , [ACN] = 0.019 mol/l, 6 hr, 90°C; ◑, [AIBN] = 0.023 mol/l, 2.5 hr, 60°C; ◐, [AIBN] = 0.023 mol/l, 6 hr, 60°C

first order with respect to the monomer concentration, eq. (4) indicates that the conversion at a certain polymerization time is proportional to $1/[M]_0$. Fig. 3 shows the plot of eq. (4). While at 90°C, the conversion was kept constant consistent with $[M]_e = 0$, at 130°C, the plot gives a straight line with the intercept equal to $[M]_e$ on the ordinate.

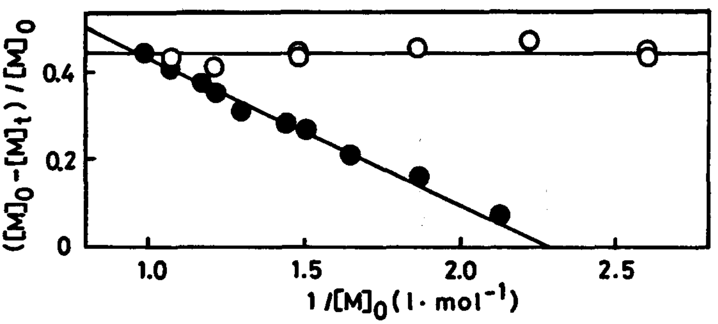

FIGURE 3. Dependency of conversion of PMA polymerization on $[M]_0$: ○, 90°C; ●, 130°C

The equilibrium monomer concentrations determined are summarized in Table 1, and those are plotted against $1/T_c$ in Fig. 4, according to the equation;

$$\ln\,[M]_e = \frac{\Delta H_{ss}}{RT_c} + \frac{\Delta S_{ss}^0}{R}$$

Where the suffix "ss" denotes polymerization of a monomer in solution to a polymer dissolved in the same solvent including of the monomer, and ΔS_{ss}^0 is the entropy change at the monomer concentration of 1 mol/l.

TABLE 1

Equilibrium monomer concentration in p-xylene determined by eq. (2)

Temp.(°C)	$[M]_e$ of PMA(mol/l)	Temp.(°C)	$[M]_e$ of SBPMA(mol/l)
90	0	50	0.10
95	0.02	60	0.14
100	0.09	70	0.18
110	0.20	86	0.32(b)
115	0.24	90	0.37, 0.37(b)
120	0.32	97	0.42(b)
125	0.38	101	0.67(b)
130	0.43, 0.43(a)	115	1.05(b)
131	0.43(b)	130	1.58(b)

a) Determined by eq. (4). b) Determined by eq. (1).

The equilibrium monomer concentrations of some ortho-substituted phenyl methacrylates have been determined by eq. (1) at various temperatures (YAMADA, et al. 1981b). In Fig. 4, the plots of $\ln\,[M]_e$ against $1/T_c$ for PMA and the substituted PMA's are shown. For the substituted PMA's, straight lines parallel to one another are obtained, indicating that the bulkiness of the ortho-substituent affects only ΔS_{ss}^0; ΔS_{ss}^0 for o-tert-butyl PMA and 2, 6-dimethyl PMA, and o-isopropyl PMA obtained are -25.4 and -22.7 e.u., respectively. The values of ΔH_{ss} and ΔS_{ss}^0 for SBPMA obtained are -9.06 kcal/mol and -23.3 e.u., respectively. While the temperature range of the experimental data for PMA is relatively narrow, the straight line parallel to the others seems to be drawn; ΔH_{ss} = -9.06 kcal/mol and ΔS_{ss}^0 = -20.8 e.u. As expected from Fig. 1,

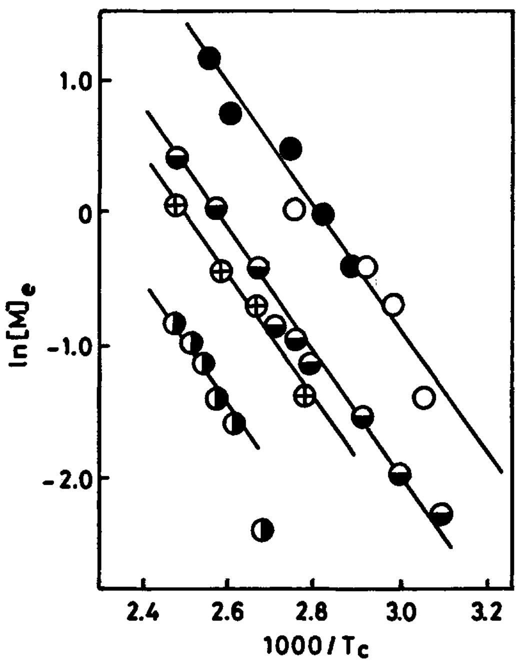

FIGURE 4. Plot of ln $[M]_e$ versus $1/T_c$: ◑ , PMA; ⊕ , o-isopropyl PMA; ◓ , SBPMA; ○ , o-tert-butyl PMA; ● , 2, 6-dimethyl PMA

the lower equilibrium monomer concentration involves larger experimental error, and the experimental points of PMA at $[M]_e = 0.02$ and 0.09 mol/l deviate from the straight line.

It seems that the values of T_c for the ortho-substituted PMA including of PMA itself are dependent on ΔS^0_{ss} and that ΔH_{ss} is kept constant regardless of the bulkiness of the substituent. Therefore, we will be able to prepare PMA of desired T_c or the equilibrium monomer concentration adjusting the size of the substituent.

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Received October 26, 1981
Accepted November 17,1981

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