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Absolute Rate Constants in Free-Radical Polymerization. III.* Determination of Propagation and Termination Rate Constants for Styrene and Methyl Methacrylate

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ABSTRACT

A spatially intermittent polymerization (SIP) reactor has been used for determination of absolute rate constants in photo-initiated, free-radical polymerization of styrene (STY) and methyl methacrylate (MMA). Experimental data are reported in the temperature range 15-30°C and in the high molecular weight region for MMA and STY. Additional experimental data are reported at 30°C and various lower molecular weights for STY which indicate that the propagation rate constant K_p is independent of polymer molecular weight, and K_t is dependent on molecular weight, especially at low molecular weight, approaching an approximately constant value at high molecular weight.

*For Part II see Mahabadi and O'Driscoll [1].

INTRODUCTION

In a recent paper [1] we derived an expression for the rate constant of the termination reaction between two radicals, K_t , which permits an a priori calculation of it based on experimentally accessible physical parameters. We have shown that K_t may be represented by

$$K_t = F_1(\zeta, T) F_2(\alpha, N) \quad (1)$$

where F_1 is a function only of temperature and the segmental frictional coefficient ζ , and F_2 is a function of the chain expansion coefficient α of the reacting polymer radicals and of their chain length N . The value of F_2 for reacting polymer radicals A and B is given by Eq. (2):

$$F_2 = (\alpha_A \alpha_B)^{-1.3} \{ 1 - 0.37 (\alpha_A \alpha_B)^{0.37} [1 - (32N_0/3\pi)^{1/2} (N_A N_B)^{-1/4} / (\alpha_A \alpha_B)^{1/2}] \} \quad (2)$$

where N_0 is the number of monomer units in a segment.

The experimentally determined values of the termination rate constant \bar{K}_t in free-radical polymerization is the average rate constant for reaction between all possible pairs of radicals existing in the radical population and can be expressed [2] by Eq. (3).

$$\bar{K}_t = \frac{\sum_{N_A} \sum_{N_B} K_t(N_A, N_B) P_{N_A} \cdot P_{N_B} \cdot}{\sum_{N_A} \sum_{N_B} P_{N_A} \cdot P_{N_B} \cdot} \quad (3)$$

where $P_{N_A} \cdot$ is the concentration of radicals of size N_A and $K_t(N_A, N_B)$ is the actual value of K_t for radicals of length N_A and N_B .

In free-radical polymerization the deviation between the measured value of \bar{K}_t (at a given average degree of polymerization, \bar{X}_n) and

$K_t(N_A, N_B)$ when $N_A = N_B = \bar{X}_n$ can be significant when K_t is a strong function of chain length and/or when the polydispersity ratio \bar{X}_w/\bar{X}_n is high. We have found [1] that letting $N_A = \bar{X}_n = N_B/2$ serves as a good approximation in Eq. (2) for calculation of \bar{K}_t . Equation (2) and existing experimental data [3, 4] indicate that K_t for a given polymer-solvent system decreases as the chain length increases and approaches a constant value at high chain length. Therefore, for a polymerization which is carried out at high \bar{X}_n ($\bar{X}_n > 1000$), $K_t(N_A, N_B)$ can be equated to the experimentally measurable \bar{K}_t . Therefore Eq. (1) for the high molecular weight region can be written as

$$\bar{K}_t = F_1 F_2 \quad \text{For } N > 1000 \quad (4)$$

In Eq. (4), F_2 is nearly constant, being only a weak function of molecular weight for $N > 1000$ and can be calculated from Eq. (2).

Equation (4) permits the estimation of F_1 by using the calculated value of F_2 and the experimentally measured value of \bar{K}_t at a high, measured molecular weight.

The values of F_1 can be obtained at various temperatures and then can be used along with Eqs. (1) and (2) to predict K_t for a given polymer-solvent system at any temperature and for any chain length of reacting polymer radicals.

In a previous paper [3] we used a spatially intermittent polymerization (SIP) reactor to determine the propagation rate constant K_p and average termination rate constant \bar{K}_t in the photoinitiated polymerization of methyl methacrylate (MMA) at 25°C. We found that \bar{K}_t in the bulk polymerization of MMA at 25°C is a strong function of chain length at low molecular weight and a much weaker function at $\bar{X}_n > 1000$.

The K_p and \bar{K}_t values reported below have been obtained in the nonstationary state, for low conversion polymerization, utilizing [3] Eqs. (5) and (6)

$$K_p = \frac{\bar{R}_p / R_{ps}}{2\tau_s M [(\bar{X}_n)^{-1} - C_{try} (y/M)]} \quad (5)$$

$$\bar{K}_t = \frac{\bar{R}_p / R_{ps}^2}{2\tau_s^2 [(\bar{X}_n)^{-1} - C_{try}(y/M)]} \quad (6)$$

where \bar{R}_p and \bar{X}_n are the average rate and the average degree of polymerization for the nonstationary state condition, R_{ps} is the rate for stationary-state polymerization, M is monomer concentration, and C_{try} is the constant for chain transfer to species Y . τ_s is the mean radical lifetime under steady illumination. This method for determination of τ_s , by analyzing the nonstationary-state data, has been described in detail [3]. Equations (5) and (6) have been derived based on the assumption that the termination is by combination and the average square of the radical concentration is equal to the square of the average radical concentration:

$$(\overline{P\cdot})^2 = (\bar{P\cdot})^2 \quad (7)$$

If a fraction X of the termination occurs by disproportionation, then the rate constants in Eqs. (5) and (6) must be multiplied by the quantity $(1 + X)$.

In this paper, K_p and \bar{K}_t for bulk polymerization of STY and MMA at high molecular weight and various temperature are reported. The temperature dependence of K_p and \bar{K}_t for STY and MMA are presented.

EXPERIMENTAL

Materials

Monomer, purified by distillation is mixed with initiator after deaeration by several freeze-thaw cycles. The monomer-initiator solution is stored in the dark under nitrogen at 0°C in a vessel which serves as a reservoir for a syringe sump (SIP reactor feed pump, sage model 335). Initiator, azobisisobutyronitrile (AIBN), was recrystallized from acetone, dried under vacuum at room temperature, and stored in the dark in a freezer.

Apparatus and Procedure

Apparatus (SIP reactor) and procedure have been previously described [3]. The rate of polymerization was obtained by measuring the concentration of polymer in the effluent from the SIP reactor by using a chromatographic column packed with deactivated 75-125 μm Porasil particles. The molecular weight of the polymer in the SIP effluent was determined by using a Waters Associates, Model ALC-301 gel-permeation chromatograph. Necessary values were taken from the literature for monomer densities [5, 6] and $C_{t,m}$ [7, 8] as a function of temperature.

RESULTS

The kinetic studies were carried out for initiator concentrations between 0.015 and 0.075 mole/liter and at temperatures of 15-30°C. All of the data were obtained for conversions less than 1%.

The values of K_p and \bar{K}_t obtained by the procedure based on Eqs. (5) and (6) for STY and MMA are given in Tables 1 and 2, respectively. It is clear that, for styrene at 30°C, K_p is independent of \bar{X}_n over a wide range, while \bar{K}_t is a strong function of \bar{X}_n at low molecular weight and a much weaker function at $\bar{X}_n > 2000$. An identical situation was previously established for MMA [3].

Values of K_p and \bar{K}_t from Tables 1 and 2 are plotted against $1/T$ in Fig. 1; for STY, only the data for $\bar{X}_n = 2400$ were used. The Arrhenius relationships calculated by least-square analysis are as follows ($RT = \text{cal/mole}$):

MMA ($\bar{X}_n = 10^4$):

$$K_p = 4.92 \times 10^5 \exp \{-4353/RT\} \quad (8)$$

$$\bar{K}_t = 9.80 \times 10^7 \exp \{-701/RT\} \quad (9)$$

STY ($\bar{X}_n = 2.5 \times 10^3$):

$$K_p = 1.09 \times 10^7 \exp \{-7051/RT\} \quad (10)$$

$$\bar{K}_t = 1.703 \times 10^9 \exp \{-2268/RT\} \quad (11)$$

TABLE 1. Values of K_p and \bar{K}_t for Styrene

| T (°C) | [AIBN] ₀ (mole/liter) | \bar{X}_n | K_p (liter/mole-sec) | $\bar{K}_t \times 10^{-6}$ (liter/mole-sec) |
|-----------------|-------------------------------------|-------------|---------------------------|--|
| 15 | 0.075 | 2705 | 48.7 | 32.4 |
| 20 | 0.045 | 2686 | 60. | 34.6 |
| 25 ^a | 0.03 | 2600 | 73.6 | 37. |
| 30 | 0.015 | 2770 | 89.4 | 39. |
| 30 | 0.02 | 2400 | 89.6 | 39.4 |
| 30 | 0.03 | 1650 | 89.8 | 44.2 |
| 30 | 0.045 | 1300 | 89.6 | 47. |
| 30 | 0.075 | 950 | 89.7 | 50. |
| 30 | 0.095 | 780 | 90. | 53. |

^aData of O'Driscoll and Mahabadi [3].

TABLE 2. Values of K_p and \bar{K}_t for Methyl Methacrylate

| T (°C) | [AIBN] ₀ mole/liter | $\bar{X}_n \times 10^{-3}$ | K_p (liter/mole-sec) | $K_t \times 10^{-6}$ (liter/mole-sec) |
|-----------------|-----------------------------------|----------------------------|---------------------------|--|
| 15 | 0.05 | 14.95 | 244.1 | 28.8 |
| 20 | 0.04 | 13.0 | 278.5 | 29.4 |
| 25 ^a | 0.03 | 13.91 | 315.0 | 30. |
| 30 | 0.025 | 10.62 | 356.0 | 30.6 |

^aData of O'Driscoll and Mahabadi [3].

Values of \bar{K}_t for STY at 30°C are plotted as a function of \bar{X}_n in Fig. 2.

DISCUSSION

The activation energies in Eqs. (8)-(11) are consistent with those tabulated in the literature [9]. They are expected to be nearly independent of chain length at high \bar{X}_n . The absolute values of K_p and \bar{K}_t are subject

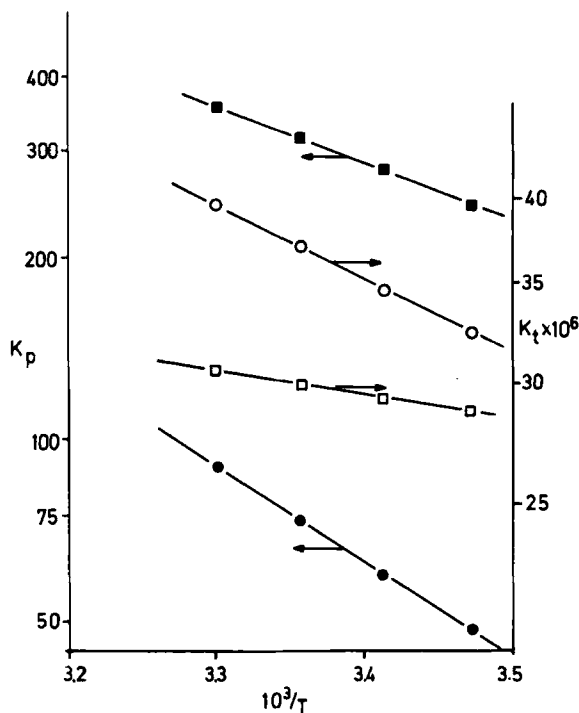


FIG. 1. K_p for MMA (■) and STY (●) and \bar{K}_t for MMA (□) and STY (○) as a function of temperature.

to correction for the occurrence of termination by disproportionation as mentioned above. However, the exact amount of disproportionation, if any, must be regarded as unknown at present since previous workers, who have dealt with this, have not acknowledged the existence of a chain-length dependence of K_t . It is probable that styrene terminates exclusively by combination while MMA has significant combination [10].

Because the \bar{K}_t values in Eqs. (9) and (11) are for moderately high molecular weight, they may also be used, with minor corrections, for higher molecular weights. Furthermore, from Eq. (2), we can calculate the temperature-independent values of F_2 at the high molecular weights where \bar{K}_t was measured and, using Eq. (4), calculate F_1 , at various temperatures.

To utilize Eq. (2) we must have a relation between the chain

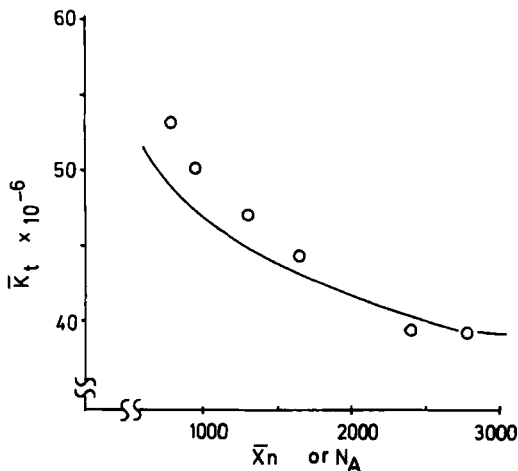


FIG. 2. \bar{K}_t for STY at 30°C as a function of \bar{X}_n . Solid line calculated from Eqs. (1), (2), and (13) as described in text.

expansion coefficient α and chain length N . As we have previously shown [1] this is $\alpha = .857 N^{0.0473}$ for poly(MMA) dissolved in its monomer. Using Ito's data [11] we find $\alpha = 0.831 N^{0.067}$ for poly(STY) in its monomer. As before [1], we take $N_0 = 4.84$ for MMA and 6.0 for STY. Thus we calculate

$$F_1 (\text{MMA}) = 3.1 \times 10^8 \exp \{-695/RT\} \quad (12)$$

$$F_1 (\text{STY}) = 6.0 \times 10^9 \exp \{-2268/RT\} \quad (13)$$

Equation (13) with Eqs. (1) and (2) now permits us to calculate the solid line shown in Fig. 2 for comparison with experimentally measured \bar{K}_t values. The agreement is reasonable, but not exact. As noted above, deviation between the experimentally measured \bar{K}_t and that calculated for \bar{X}_n is to be expected when \bar{K}_t is a strong function of chain length.

Some comment should be made concerning the approximation that $(\bar{P}^2) = (P \cdot)^2$ when conversion in SIP reactor is less than 1%; this was used for estimation of K_p and K_t in Eq. (5) and (6). The

exact value of the ratio $(\overline{P \cdot^2})/(\overline{P \cdot})^2$ can be calculated by using the average initiation rate in the SIP reactor which can be written as

$$\frac{\overline{P \cdot^2}}{(\overline{P \cdot})^2} = [(rz^2 + 1)/(r + 1)] (R_{ps}/\overline{R_p})^2 \quad (7)$$

where $r = 6.98$ is the ratio of dark to light length in our SIP reactor, and z is the fraction of thermal polymerization, $\overline{R_p}/R_{ps}$ is a complex function of r , z , and flow rate [3]. For conversion less than 1% and $z \leq 0.2$ the maximum error of approximating $(\overline{P \cdot^2})$ by $(\overline{P \cdot})^2$ is calculated to be less than 8%.

Since the initiator concentrations were low and monomer concentrations were high (bulk polymerization in the high molecular weight region) the effect of primary radical termination on the estimated values of K_p and $\overline{K_t}$ is negligible.

The simultaneous determination of \overline{X}_n and $\overline{R_p}$ under intermittent illumination at very low conversion and high molecular weight enables us to see the effect of chain length dependence on $\overline{K_t}$ and eliminate it from the derived values of the activation energies of propagation and termination.

The calculation of K_t for MMA or STY by Eq. (1), (2), and (12) or (13) is possible now for any solvent-polymer system where the solvent viscosity η_0 and the dependence of α on N are known. The latter can be obtained from intrinsic viscosity-molecular weight relations [1]. An a priori estimate of F_1 can be done by using the previously derived [1] relation:

$$F_1 = \frac{4}{3} \times 10^{-3} N_{av} k_B TR/a_m N_0 \eta_0 (\zeta_0/\zeta_{sp}) \quad (14)$$

Using the data previously given [1] we find at 25°C

$$F_1 (\text{MMA}) = 1.15 \times 10^8$$

compared to the value of 0.96×10^8 from Eq. (12) and

$$F_1 (\text{STY}) = 1.38 \times 10^8$$

compared to the value of 1.30×10^8 from Eq. (13).

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