KINETICS OF RADICAL POLYMERIZATION OF STYRENE AT HIGH CONCENTRATION OF DIISOPROPYL DICARBONATE

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Abstract—Styrene was polymerized at 20° at high concentration of diisopropyl dicarbonate (DIPDC). When [DIPDC] = 0.55 mol l^{-1}, transfer to DIPDC predominates at almost all stages of conversion. The average chain length (≤ 90) of the polymers is less than 300, the value at which polymer molecules entangle in undiluted polymer solution. Thus, the termination rate can be treated by considering only the free volume theory. The value of γv^* (γ = overlap factor and v^* = critical free volume to permit a segment to jump) is found to be 0.39, in good agreement with the value 0.37 estimated previously from data obtained under conditions such that the termination rate depends on both entanglement and free volume. These values may be reasonable, because they yield the magnitude of 10^{-5} cm^2 sec^{-1} as the diffusion constant of monomer at low conversion. In spite of the absence of entanglement, the polymerization changes abruptly at about 70% conversion. Thus, the previous definition should be modified so that the onset of the gel effect is the point at which the termination rate changes abruptly as a result of the decrease of the free volume when the entanglement is absent, or at a critical chain length of polymers when entangling occurs.

INTRODUCTION

In radical bulk polymerization at high conversion, termination is diffusion-controlled. Thus, it depends on entanglement between polymers so changing the mobility of the polymers and the free volume which changes the mobility of the segments [1, 2]. During polymerization when transfer is predominant, chain length distribution of polymer radicals is simple, therefore the kinetics become easy [1, 3]. Thus, it was shown that the kinetic data in terms of termination rate could be treated by the simple equation [1]. An important result was obtained that, when polymer radicals are so small that they do not entangle with the surrounding polymer molecules or they do not move by reptation, the termination rate does not depend on chain lengths, but on the free volume. Theoretically, the rate can be expressed as [1, 3, 4]:

$$\bar{k}_t \, (= 4\pi DR) \propto \exp\left(-\gamma v^*/v_f\right) \qquad (1)$$

where $D \propto g(n) \exp\left(-\gamma v^*/v_f\right)$ and $R \propto 1/g(n)$. However, the previous experimental results [1] were obtained when the rate depends on both entanglement and free volume. In the present paper, equation (1) is examined, using data obtained when the rate depends on only the free volume. To do this, styrene was polymerized at high concentration of diisopropyl dicarbonate (DIPDC) at 20°.

EXPERIMENTAL

Commercial styrene was washed three times with 5% aq. NaOH and twice with water. It was dried over anhydrous MgSO$_4$ and distilled. After prepolymerization in the absence of initiator, it was again distilled under reduced pressure (43.5–44.0° at 20 mmHg). Pure DIPDC was supplied by Nippon Oils and Fats Co., Ltd. Commercial 2,2'-azobisisobutyronitrile (AIBN) was recrystallized three times from methanol.

Initiator and monomer in an ampoule (diameter = 4–8 mm) were degassed by a successive freezing and melting procedure, and the ampoule was sealed at a vacuum of about 10^{-3} mmHg. The bulk polymerization was carried out by maintaining the ampoule at 20.0 ± 0.05° for given time. When [DIPDC] ≤ 0.14 mol l^{-1} or AIBN was used, the contents of the ampoule were diluted with tetrahydrofuran. Methanol was poured into the solution to precipitate polymers. The polymers were isolated, dried and weighed. When [DIPDC] > 0.14 mol l^{-1}, conversion was estimated by liquid chromatography, because the weight loss of polymers during precipitation was not negligible. The molecular weight was measured by light scattering and gel permeation chromatography, using a Toyosoda LS 8 and HLC-8024.

RESULTS AND DISCUSSION

The relationship between $\bar{p}_n$, R_p and [C] is given by [5]:

$$\frac{1}{\bar{p}_n} = C_{trM} + C_{trC} \cdot \frac{[C]}{[M]} + f\, k_d \cdot \frac{[C]}{R_p} \qquad (2)$$

which can be rewritten as:

$$\frac{[M]}{[C]}\left(1/\bar{p}_n - C_{trM}\right) = C_{trC} + f\, k_d \cdot \frac{[M]}{R_p}. \qquad (3)$$

Equation (2) is applied to the data (Table 1) obtained in the initial stage of polymerization ($x < 0.1$). In the polymerization initiated by AIBN, a linear relationship is obtained between $1/\bar{p}_{n0}$ and $[C]_0/R_{p0}$ (Fig. 1). Thus, $C_{trAIBN} = 0$ and $f\, k_d$ and C_{trM} are found to be 1.18×10^{-8} sec^{-1} and 2.0×10^{-5}, respectively. This value of C_{trM} is in good agreement with 1.09×10^{-5} (3.58×10^{-5}) at 0° (or 30)° [6]. In the polymerization initiated by DIPDC, C_{trC} is not zero, because there is no linear relationship between $1/\bar{p}_{n0}$ and $[C]_0/R_{p0}$ (Fig. 1). Thus, equation (3) is used for the analysis of the data where $C_{trM} = 2.0 \times 10^{-5}$. There is a line based on

Table 1. Kinetic data obtained in the initial stage of polymerization

Initiator	$[C]_0$ (mmol l^{-1})	$[M]_0$ (mol l^{-1})	$10^6 R_{p0}$ (mol l^{-1} sec^{-1})	$\bar{p}_{n0}$
DIPDC	550	7.70	16.8	81
DIPDC	280	7.96	12.4	140
DIPDC	140	8.32	8.47	241
DIPDC	70	8.50	5.99	405
DIPDC	6.3	8.69	2.18	1910
DIPDC	0.70	8.69	0.73	6350
AIBN	275	8.32	3.63	1130
AIBN	138	8.52	2.64	1630
AIBN	68.8	8.62	1.97	2250
AIBN	34.4	8.65	1.43	3370
AIBN	17.2	8.69	1.01	4350

equation (3) in Fig. 2. The values obtained from the intercept and slope are $C_{trDIPDC} = 0.13 \pm 0.01$ and $f\,k_d = 1.3 \times 10^{-7}\,\text{sec}^{-1}$.
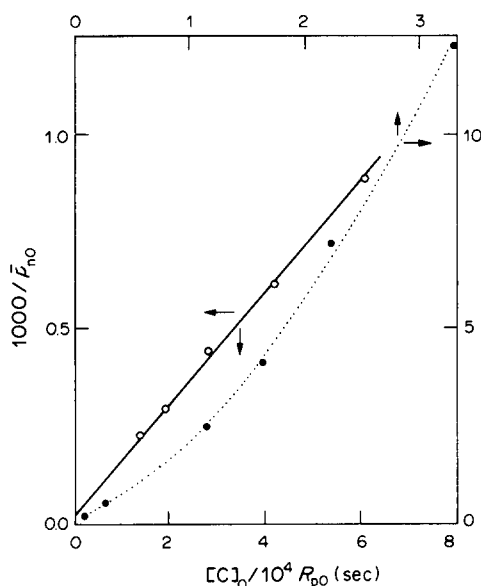

Fig. 1. Relationship between $1/\bar{p}_{n0}$ and $[C]_0/R_{p0}$ based on equation (2) in the polymerization initiated by AIBN (O) and DIPDC (●).
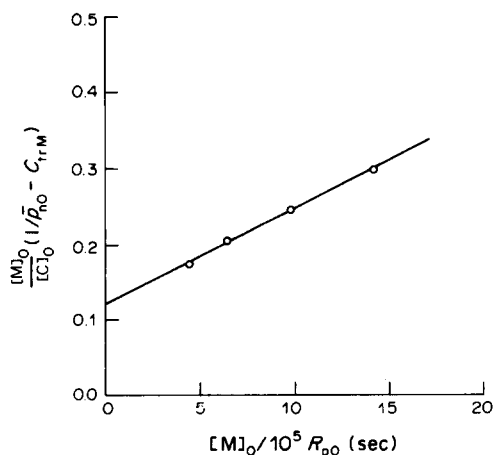

Fig. 2. Relationship between $([M]_0/[C]_0)(1/\bar{p}_{n0} - C_{trM})$ and $[M]_0/R_{p0}$ in the polymerization initiated by DIPDC.

When $[DIPDC]_0 = 0.55\,\text{mol l}^{-1}$, C_{trC} is so large that an approximation such as equation (4) may be used.

$$\bar{p}_n(\simeq \bar{p}_w/2) \simeq [M]/C_{trC}[C]. \qquad (4)$$

Using the further approximation [5]:

$$[M] \simeq (1 - x)[M]_0 \qquad (5)$$

we obtain [2]:

$$\bar{P}_n = x \bigg/ \int_0^x dx/\bar{p}_n \simeq -\bar{p}_{n0}x/\ln(1 - x) \qquad (6)$$

$$\bar{P}_w = \frac{1}{x}\int_0^x \bar{p}_w dx \simeq \bar{p}_{w0}(1 - x/2). \qquad (7)$$

In these calculations, $[C] \simeq [C]_0$ is also used because $[C] = 0.93[C]_0$ at $x \simeq 1$, where $k_d = 1.78 \times 10^{-7}\,\text{sec}^{-1}$ [1]. Equations (6) and (7) are applicable at almost all conversions, as shown in Fig. 3, where $\bar{p}_{n0}$ ($\simeq \bar{p}_{w0}/2) = 90 \pm 10$ is in a good agreement with $[M]_0/C_{trC}[C]_0 = 107 \pm 10$. Accordingly, when $[DIPDC] = 0.55\,\text{mol l}^{-1}$, it is estimated that transfer predominates. Such a predominance can be confirmed. The final conversion increases with increasing initiator concentration such as: $x = 0.99 \pm 0.03$ at $[C]_0 = 11.4\%$ (0.55 mol l^{-1}), 0.95 ± 0.03 at 5.8% (0.28) and 0.90 ± 0.02 at 1.4% (0.07). The same phenomenon was observed in the polymerization of methyl methacrylate (MMA) [1]. These resemble the increase in the final conversion with increasing solvent fraction [9]. Thus, in the preceeding paper [1], it was considered that the initiators as DIPDC and AIBN serve as solvents. When the weight fraction of initiator is less than 1%, that of polymer can be calculated regardless of it and is nearly equal to the conversion. However, when it is above 1%, to calculate that of the polymer, it cannot be neglected; in the present paper, the weight fraction of polymer is calculated by introducing it. That is, $x' = x/(1 + \lambda)$ where $x' \to x$ at $\lambda \to 0$. The $x'-t$ curves are shown in Fig. 4. The final weight fraction of polymer is found to be $x' = 0.90 \pm 0.03$ regardless of initiator concentration. Applying $x' = x/(1 + \lambda)$ to the previous data for the polymerization of MMA [1], the final weight fraction of polymer is also calculated to be $x' = 0.80 \pm 0.02$, which is insensitive to the kind of initiator and initiator concentration. In the previous
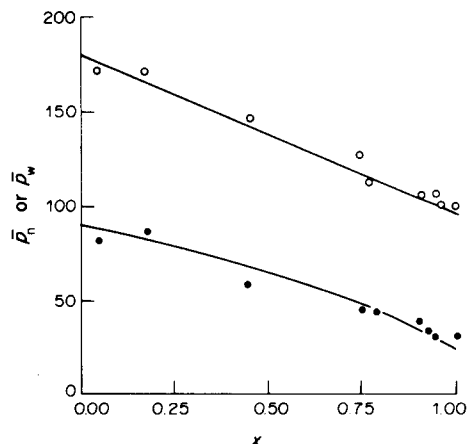

Fig. 3. Relationship between $\bar{p}_w$ (O) or $\bar{p}_n$ (●) and x in the polymerization when $[DIPDC]_0 = 0.55\,\text{mol l}^{-1}$.
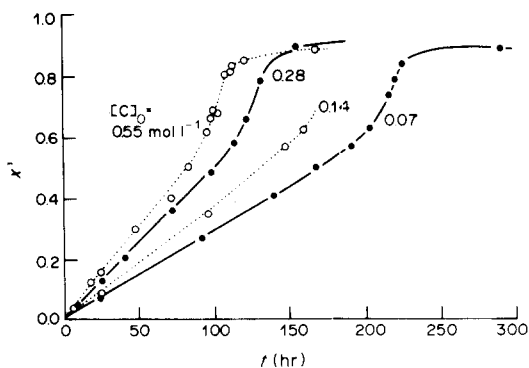
Fig. 4. Relationship between $x'[=x/(1+\lambda)]$ and t in the polymerization initiated by DIPDC.

papers [1, 3, 8, 10], it was shown that, when transfer predominates, the polymerization rate is proportional to $[C]^{1/2}$ even if termination rate depends on chain length. On this basis, the relationship between $R_p/[C]^{1/2}[M]$ and $[C]$ at given x' is shown in Fig. 5. The value of $R_p/[C]^{1/2}[M]$ is independent of $[C]$ when $x' \leq 0.6$ where $[C]_0 \geq 0.070$ mol 1^{-1}. Especially, when $[C]_0 = 0.55$ mol 1^{-1}, the independence is satisfied reasonably at almost all conversions. This result is consistent with the result obtained from the relationship between molecular weight and conversion. The value of $\bar{k}_{t0}/\bar{k}_t$ is calculated from (Table 2):

$$\frac{\bar{k}_{t0}}{\bar{k}_t} = \frac{R_p^2[C]_0[M]_0^2}{R_{p0}^2[C][M]^2}. \qquad (8)$$

The chain length at which polystyrene molecules entangle is above 300 in the undiluted polymer solution, and increases with decrease in polymer concentration, as $n_c = 300\,c^{-1 \sim -2}$ [11–14]. The chain lengths of polymers obtained here range from $\simeq 90$ at $x' \to 0$ to 50 at $x' \simeq 0.9$ ($x \to 1$). Such small molecules do not entangle. In this case, equation (1) is applicable and we obtain:

$$\ln(\bar{k}_{t0}/\bar{k}_t) = -\gamma v^*/v_{f0} + \gamma v^*/v_f \qquad (9)$$

where [1, 2, 15]:

$$v_f = \{[25 + 0.48(T - T_{gp})]c + [25 + 1.0(T - T_{gm})]$$
$$\times (1 - c)\}/1000 \qquad (10)$$

$$T_{gp} = 100 - 1.8 \times 10^5/(104\,\bar{P}_n). \qquad (11)$$

Equation (9) is applied to the data in Table 2 where $T_{gm} = -88.2$ [2]. A linear relationship between $\ln(\bar{k}_{t0}/\bar{k}_t)$ and v_f^{-1} is shown in Fig. 6. Its slope is $\gamma v^* = 0.39 \pm 0.04$ and its intercept is $\gamma v^*/v_{f0} = 3.5 \pm 0.4$, then $v_{f0} = 0.133$. In the free volume theory [16], the diffusion constant of a small molecule such as monomer is given by:

$$D_S = ga^*u\,\exp(-\gamma v^*/v_f). \qquad (12)$$

Here, in a solvent cage, monomer moves with the gas kinetic velocity and, then, u is written as [16]:

$$u = (3RT/m)^{1/2}[= 1.54 \times 10^4\,(T/m)^{1/2}\,\text{cm sec}^{-1}]. \qquad (13)$$

Introducing $g = 1/6$, $a^* = 6 \times 10^{-8}$ cm, $m = 104$ and $\gamma v^*/v_{f0} = 3.2$ into equations (12) and (13), D_S is calculated to be 1.6×10^{-5} cm^2 sec^{-1}, which is consistent with ordinary diffusion constant

Table 2. The values of $\bar{k}_{t0}/\bar{k}_t$ obtained when $[DIPDC]_0 = 0.55$ mol 1^{-1}

x	$10^6 R_p$ (mol 1^{-1} sec^{-1})	c	$\bar{k}_{t0}/\bar{k}_t{}^*$
0.2	16.8	0.158	1.5
0.3	16.8	0.241	2.0
0.4	16.8	0.326	2.6
0.5	17.0	0.413	4.5
0.6	30	0.502	18
0.7	48	0.595	76

In this calculation, $[C] = [C]_0 \exp(-1.78 \times 10^{-7} t)$ [1].

$(D_S \simeq 10^{-5}$ cm^2 sec$^{-1})$. Applying the above treatments to the previous data on the polymerization of MMA [1], D_S is also calculated to be 2.1×10^{-5} cm^2 sec^{-1}, where $\gamma v^* = 0.37$, $v_{f0} = 0.13$, $m = 100$, $a^* = 6 \times 10^{-8}$ cm and $g = 1/6$. In Ref. [17], assuming that $\bar{k}_t \propto n^{-1/2}$ when $n \leq n_c$, γv^* values were found to be about 1.0. However, it was shown that the equation $\bar{k}_t \propto n^{-1/2}$ did not fit the kinetic data obtained in the polymerization of MMA when transfer predominates [1]. Here, $\gamma v^* \simeq 1.0$ is examined in view of equations (12) and (13). The values calculated for the diffusion constant of MMA in the initial stage
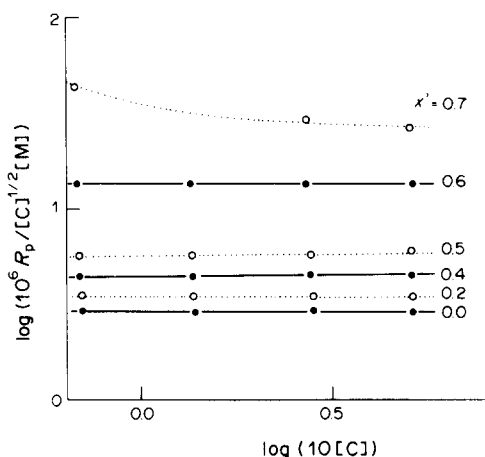

Fig. 5. Relationship between $R_p/[C]^{1/2}$ [M] and [C] where $[DIPDC]_0 \geq 0.070$ mol 1^{-1}.

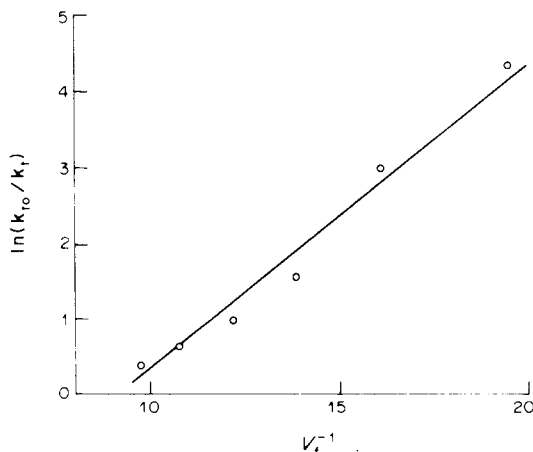Fig. 6. Relationship between $\bar{k}_{t0}/\bar{k}_t$ and v_f where $[DIPDC]_0 = 0.55$ mol 1^{-1}.

of polymerization are from 10^{-6} cm^2 sec^{-1} to 10^{-7} at 45–90°; these values are less than the ordinary diffusion constants by 10^{-1}–10^{-2}. Thus, $\gamma v^* \simeq 1.0$ is not valid. It is concluded that $\gamma v^* \simeq 0.4$ is better than $\gamma v^* \simeq 1.0$. On the above reasons, the equation $\bar{k}_t \propto n^{-1/2}$ when $n \leq n_c$ is not suitable to interpret more quantitatively termination rates at high conversion. Thus, equation (1) is better than $\bar{k}_t \propto n^{-1/2}$.

The author defined the onset of the gel effect as the point at which the termination rate changes abruptly at n_c [9]. However, as shown in Fig. 4, the polymerization rates increase abruptly at $x' \simeq 0.6$ ($x = 0.6$–0.7) in spite of the absence of entanglement. Such acceleration is probably caused by decrease of the free volume. Thus, the previous definition should be modified so that the onset of the gel effect is the point at which the termination rate changes abruptly because of decrease of the free volume when entanglement is absent, but at n_c when entanglement is present.

NOMENCLATURE

$\bar{k}_t$ = termination rate constant;
D = translational diffusion constant of polymer;
D_s = diffusion constant of small molecule;
R = reaction radius;
$g(n)$ = function of chain length n of polymer;
γ = overlap factor;
v^* = critical free volume sufficient to permit a segment to jump;
g = geometric factor;
a^* = the diameter of a small molecule such as monomer;
u = the kinetic velocity in a solvent cage;
R = gas constant;
m = molecular weight of small molecule;
$\bar{p}_n$ = instantaneous number-average degree of polymerization;
$\bar{p}_w$ = instantaneous weight-average degree of polymerization;
$\bar{P}_n$ = integrated number-average degree of polymerization;
$\bar{P}_w$ = integrated weight-average degree of polymerization;
$[C]$ = initiator concentration;

$[M]$ = monomer concentration;
C_{trA} = transfer constant to A (A = C or M);
f = initiator efficiency;
k_d = rate constant for initiator decomposition;
k_p = propagation rate constant;
t = time;
x = conversion;
x' = weight fraction of polymer;
λ = weight fraction of initiator to those of monomer and polymer;
T = absolute temperature;
T_{gm} = glass-transition temperature of the monomer;
T_{gp} = glass-transition temperature of the polymer;
suffix "0" = the initial stage (e.g. "0" in $\bar{k}_{t0}$).

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