High-Conversion Diffusion-Controlled Polymerization of Styrene. I

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Synopsis

A kinetic model based on the free volume theory has been proposed for the polymerization of styrene. The model, which is capable of describing the course of polymerization in both bulk and solution, accounts for diffusion-controlled termination and propagation and gives a limiting conversion.

INTRODUCTION

The gel effect has, since it was first reported by Tromsdorff,[1] been the subject of several investigations. A general mathematical concept capable of describing the observed rate phenomena, independently of the type of monomer, has however never been presented. Recently, it was shown that the polymerization of MMA over a wide range of experimental conditions could be described by means of a semiempirical model.[2] The kinetic model proposed was based on the free volume theory. The aim of this report is to test the applicability of this model in the case of styrene polymerization.

This first article in a series of two deals explicitly with the polymerization when performed at temperatures below 80°C. The second article[3] will consider the more interesting, seen from an industrial point of view, temperature range of 100–200°C. This division is made because the thermal initiation can be considered negligible compared to the chemical one at the low temperatures. This means that the second report,[3] besides using the same kinetic concepts as the first, must differentiate between the proposed thermal initiation mechanisms.

THEORY

Kinetic Model

The main purpose of the derivation shown below is to obtain k_t and k_P as a function of temperature, conversion, and molecular weight. It is assumed, as in Ref. 1, that the termination reaction becomes diffusion controlled when the diffusion coefficient for a polymer radical D_P becomes less than or equal to a critical diffusion coefficient $D_{P_{cr}}$. The termination rate constant after the start of the diffusion control is assumed proportional to the diffusion coefficient. This can be written as

$$k_t = k_1 D_{P_{cr}} \tag{1}$$

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According to Beuche,[4] the diffusion coefficient can be related to the free volume and the molecular weight by means of the following equation:

$$D_P = \frac{\phi_0 \delta^2}{k_2 M} \exp\left(\frac{-A}{V_F}\right) \qquad (2)$$

where M is molecular weight of polymer (monodisperse), ϕ_0 is jump frequency, δ is jump distance, k_2 is constant, A is constant, and V_F is free volume fraction. V_F is in the general form given as

$$V_F = [0.025 + \alpha_P (T - T_{gP})] \frac{V_P}{V_T}$$
$$+ [0.025 + \alpha_M (T - T_{gM})] \frac{V_M}{V_T} + [0.025 + \alpha_S (T - T_{gS})] \frac{V_S}{V_T} \qquad (3)$$

where M, P, and S denote monomer, polymer and solvent, respectively; T is polymerization temperature; V is volume; V_T is total volume; T_g is glass transition point; $\alpha = \alpha_l - \alpha_g$; α_l is expansion coefficient for the liquid state; and α_g is expansion coefficient for the glassy state.

The glass transition temperature of the polymer is related to the molecular weight of polymer by means of the following equation:

$$T_{gP} = T_{g\infty} - \frac{Q}{\overline{M}_N} \qquad (4)$$

where: $T_{g\infty}$ is glass temperature at infinite molecular weight, Q is constant, and $\overline{M}_N$ is number-average molecular weight.

It was shown in Ref. 1 that the best correlation with the experimental data was achieved when the cumulative weight-average molecular weight to the $1/2$ power was used instead of M in eq. (2).

Combination of eqs. (1) and (2) gives k_t as a function of conversion, molecular weight, and temperature. For unentangled polymer solutions,

$$k_t = k_1 \left(\frac{\phi_0 \delta^2}{k_2 \overline{M}_w^{1/2}}\right) \exp\left(\frac{-A}{V_F}\right) \qquad (5)$$

and for entangled polymer solutions,

$$k_t = \overline{k}_1 \left(\frac{\phi_0 \delta^2}{\overline{k}_2 \overline{M}_w^{1.75}}\right) \exp\left(\frac{-A}{V_F}\right) \qquad (6)$$

If it is assumed that the termination reaction becomes diffusion controlled before the occurrence of entanglements, then one has at the onset of the gel effect:

$$K_3 = \frac{k_1 \cdot \phi_0 \delta^2}{k_{t_0} k_2} = \overline{M}_w^{0.5} \exp\left(\frac{A}{V_F}\right) \qquad (7)$$

It is seen that for each weight-average molecular weight, at constant temperature, there will be one and only one conversion for which eq. (7) is satisfied. This conversion denotes the one at which the gel effect starts. The fact that $\overline{M}_w$ changes with initiator and solvent and chain transfer agent concentration means that the conversion at which the gel effect starts also is dependent on initiator and solvent concentration.

If it is assumed that chain entanglements occur soon after k_t becomes diffusion controlled, then one has a good approximation

$$\frac{k_t}{k_{t_0}} = \left(\frac{\overline{M}_{w_{cr1}}}{\overline{M}_w}\right)^{1.75} \exp\left[-A\left(\frac{1}{V_F} - \frac{1}{V_{F_{cr1}}}\right)\right] \tag{8}$$

where $M_{w_{cr1}}$ and $V_{F_{cr1}}$ are the weight-average molecular weight and free volume fraction which satisfied eq. (7).

The fact that the propagation reaction becomes diffusion controlled at high conversion means that a critical conversion is reached where

$$k_{P_0} = \psi_1 D_{M_{cr}} = k_p \tag{9}$$

where k_{P_0} is the propagation rate constant below the critical conversion, $D_{M_{cr}}$ is the diffusion coefficient of the monomer at the critical conversion, and ψ_1 is a proportionality factor.

The diffusion coefficient of a small molecule in a polymer solution can be expressed as follows[4]:

$$D_M = \left(\frac{\phi_2 \delta_2^2}{6}\right) \exp\left(\frac{-B}{V_F}\right) \tag{10}$$

k_P is therefore given by the following expression beyond the critical conversion:

$$k_P = k_{P_0} \exp\left[-B\left(\frac{1}{V_F} - \frac{1}{V_{F_{cr2}}}\right)\right] \tag{11}$$

According to Beuche,[4] $B = 1.0$.

If k_t and k_P given by eqs. (8) and (11) respectively are inserted in the classic rate expression for polymerization, one obtains

$$\frac{dx}{dt} = \left(\frac{k_{P_0}^2}{k_{t_0}}\right)^{1/2} \left(\frac{\overline{M}_w}{\overline{M}_{w_{cr1}}}\right)^\alpha \exp\left[-B\left(\frac{1}{V_F} - \frac{1}{V_{F_{cr2}}}\right)\right] \exp\left[\frac{A}{2}\left(\frac{1}{V_F} - \frac{1}{V_{F_{cr1}}}\right)\right]$$

$$\times \left[\frac{fk_d [I]_0}{(1 - \epsilon x)}\right]^{1/2} (1 - x) \exp\left(-k_d \frac{t}{2}\right) \tag{12}$$

where

Interval 1: $\alpha = 0$ $B = 0$ $A = 0$

Interval 2: $\alpha = 0.875$ $B = 0$ $A = 0.348$

Interval 3: $\alpha = 0.875$ $B = 1$ $A = 0.348$

f is initiator efficiency; k_d is decomposition rate constant; $[I]_0$ is initial initiator concentration; $\epsilon = (d_P - d_M)/d_P$, volume concentration factor; d_P is density of polymer; d_M is density of monomer; x is degree of conversion; and t is time. The expression contains the parameters A and $V_{F_{cr1}}$ the values of which have to be estimated by means of the experimental results.

Molecular Weight Equations

Due to the fact that k_t is a function of not only conversion and temperature but also molecular weight, one has to solve simultaneously for the molecular weights and the conversion. The equation which gives the average molecular weights when termination is assumed to take place solely by combination are

$$\frac{1}{\overline{x}_n} = \tau + \frac{\beta}{2} \qquad \overline{x}_w = \frac{2[\tau + 3(\beta/2)]}{(\tau + \beta)^2}$$

where

$$\tau = C_M + C_S \frac{[S]}{[M]} + C_I \frac{[I]}{[M]}$$

$$\beta = \frac{2 \, (f \, k_d [I])^{1/2}}{(k_p^2/k_t)^{1/2} \, [M]}$$

where $\bar{x}_n$ is instantaneous number average degree of polymerization, $\bar{x}_w$ is instantaneous weight average degree of polymerization, C_M is chain transfer constant to monomer, C_S is chain transfer constant to solvent, C_I is chain transfer constant to initiator, [S] is concentration of solvent, and [M] is concentration of monomer. The assumption that termination takes place by means of combination is in good agreement with previous work.[5-9]

The cumulative molecular weights are given by

$$\text{cum } \bar{M}_n = \frac{M_0 x}{\int_0^x [\tau + (\beta/2)] \, dx}$$

$$\text{cum } \bar{M}_w = \frac{2}{x} M_0 \int_0^x \frac{[\tau + 3 \, (\beta/2)]}{(\tau + \beta)^2} \, dx$$

where M_0 is molecular weight of monomer, $\bar{M}_n$ is number-average molecular weight, and $\bar{M}_w$ is weight-average molecular weight.

EXPERIMENTAL

Commercial ST and AIBN were placed in test tubes which were sealed with rubber plugs and placed in a constant-temperature batch. These runs were done to obtain limiting conversions at 30, 40, and 60°C. The O_2 level is thus unimportant. The test tubes were broken at different time intervals and the polymer was extracted over a 12-hr period with methylene chloride, using a Soxhlet extractor. A small amount of hydroquinone was added to the solvent to prevent further polymerization. The mixture of methylene chloride was then poured into a large excess of methanol and the polymer was filtered off, dried, and weighed.

RESULTS

Time, h	Temp., °C	Initiator concentration, mol/L	Degree of conversion
295	30	0.0100	0.435
436	30	0.0100	0.821
511	30	0.0100	0.824
138.8	40	0.0992	0.847
161	40	0.0992	0.845
210	40	0.0992	0.846
30	60	0.0972	0.915
30	60	0.0972	0.915
55	60	0.0972	0.916
102	60	0.0972	0.919

DISCUSSION

Parameter Estimation

In order to calculate V_F as a function of conversion, it is necessary to know T_g of the monomer and the polymer. The data shown under results and data obtained from the literature[10–13] were used to estimate T_g and T_{gM}. It is to be noticed in Figure 1 that the agreement between data found in this work and those in the literature is quite satisfactory. If eq. (3) is rewritten to give the limiting conversion x as a function of T_{gP} and T_{gM}, one has

$$x = \frac{\alpha_M (T - T_{gM})}{\alpha_M (T - T_{gM}) - \alpha_p (T - T_{gp}) \left(\dfrac{d_M}{d_p} \right)}$$

The theoretical expression shown was fitted to the experimental data by adjusting T_{gP} and T_{gM} by means of a simplex optimization routine. The best values obtained for T_{gP} and T_{gM} were 93.5 and $-88.2°C$, respectively. The value obtained for T_{gP} is in good agreement with Refs. 10, 15–18. The value for T_{gM} seems not to have been reported previously.

The values of A and V_{Fcr2} were estimated by means of all the conversion vs. time data reported at 60°C. The theoretical expression shown in eq. (12) was fitted to the experimental data using a fourth-order fixed-step Runge Kutta integration procedure and a simplex optimization procedure. The values of A and V_{Fcr2} determined at 60°C were used at all other temperatures.

The temperature dependence of K_3 and (k_p^2/k_t) were determined using all of the reported data. The optimization technique used was the same as the one mentioned above.

The parameters used for the simulations of the conversion versus time curves are shown below.
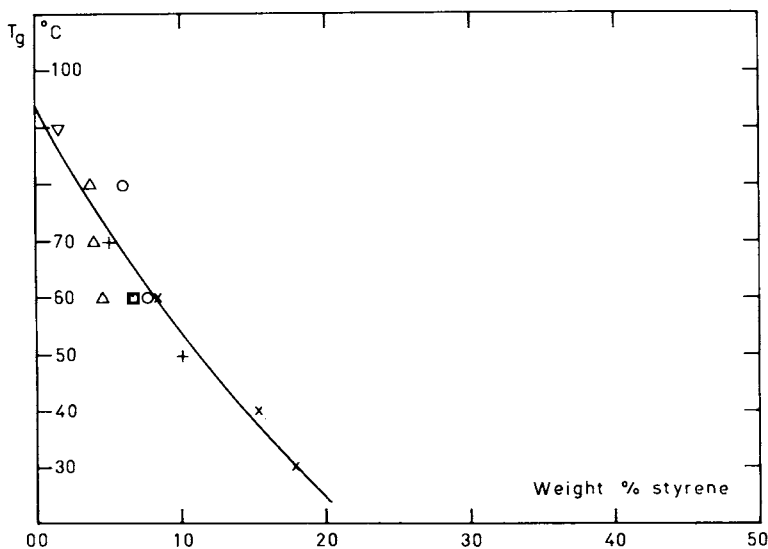

Fig. 1. T_g of PS vs. content of St: (×) from this work; (+) data of Sundberg and James[10]; (□) data of Nishimura[11]; (○) data of Arai and Saito[12]; (△) data of Tobolsky et al.[13]; (▽) data of Eremina et al.[14]; (——) model prediction.
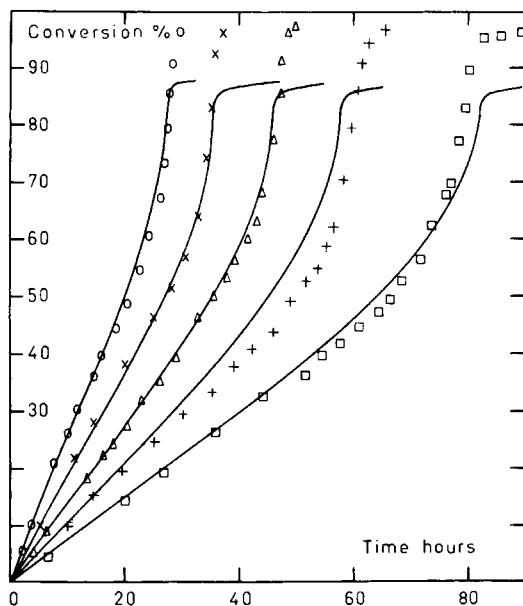
Fig. 2. Bulk polymerization of St at 45°C: (O) $[I]_0 = 0.2$ mol AIBN/L; (×) $[I]_0 = 0.1$ mol AIBN/L; (△) $[I]_0 = 0.05$ mol AIBN/L; (+) $[I]_0 = 0.025$ mol AIBN/L; (□) $[I]_0 = 0.0125$ mol AIBN/L. Data of Ito[23]; (——) model prediction.

Parameters estimated by means of the optimizations:

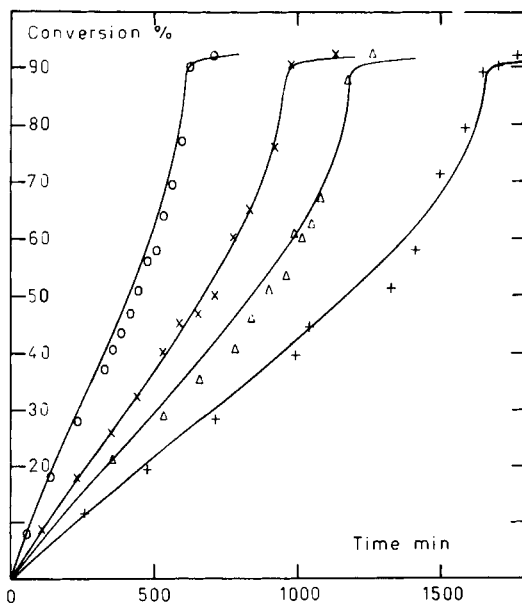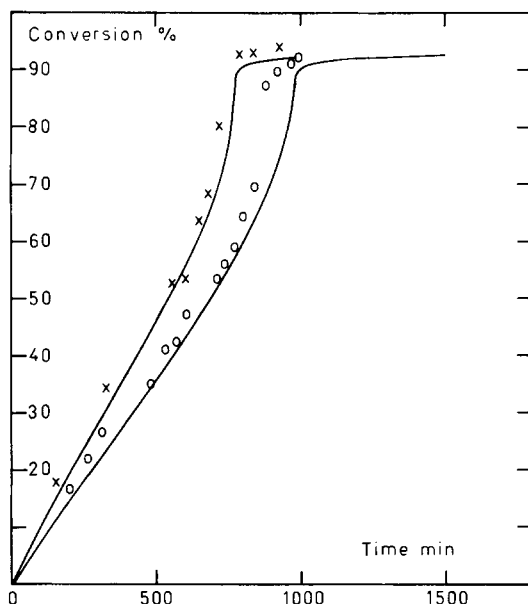$$\left(\frac{k_P^2}{k_t}\right)_0 = 7.47 \times 10^9 \exp\left(\frac{-7030}{T}\right) \text{L/mol min}$$

Fig. 3. Bulk polymerization of St at 60°C: (O) $[I]_0 = 0.0992$ mol AIBN/L; (×) $[I]_0 = 0.0268$ mol AIBN/L; (△) $[I]_0 = 0.0164$ mol AIBN/L; (+) $[I]_0 = 0.00858$ mol AIBN/L. Data of Arai and Saito[12]; (——) model prediction.

Fig. 4. Bulk polymerization of St at 60°C: (×) $[I]_0$ = 0.05 mol AIBN/L; data of Nishimura[11]; (○) $[I]_0$ = 0.024 mol AIBN/L, data of Braks[24]; (——) model prediction.

This Arrhenius equation was determined by means of data found in this work and in Ref. 3, with K_3 = 9.44 exp (1929/T) (g/mol)$^{1/2}$, $V_{F_{cr2}}$ = 0.033, A = 0.348, T_{g_M} = −88.2°C, and T_g = 93.5°C.

Parameters from Literature:	Reference
$C_M = 1.00 \exp\left(\dfrac{-3212}{T}\right)$	19
$C_S = 0.0188 \exp\left(\dfrac{-2196}{T}\right)$	19

The subscript S stands for toluene.

C_M and C_S as a function of temperature were determined by means of all data shown in the *Polymer Handbook.*[19]

AIBN: Reference

$$k_d = 3.8 \times 10^8 \exp\left(\frac{-15,460}{T}\right) h^{-1} \qquad 20$$

f = 0.7   21
Q = 17 × 10^5 (g/mol) degree   18
α_P = 0.48 × 10^{-3} (°C)$^{-1}$ 4
α_M = 1.0 × 10^{-3} (°C)$^{-1}$ 4
α_S = 1.0 × 10^{-3} (°C)$^{-1}$ 4
d_M = (0.924 − (0.000918 K^{-1} × (T − 273.15 K))) g/cm^3 16
d_p = (1.084 − (0.000605 K^{-1} × (T − 273.15 K))) g/cm^3 16
B = 1.0   4
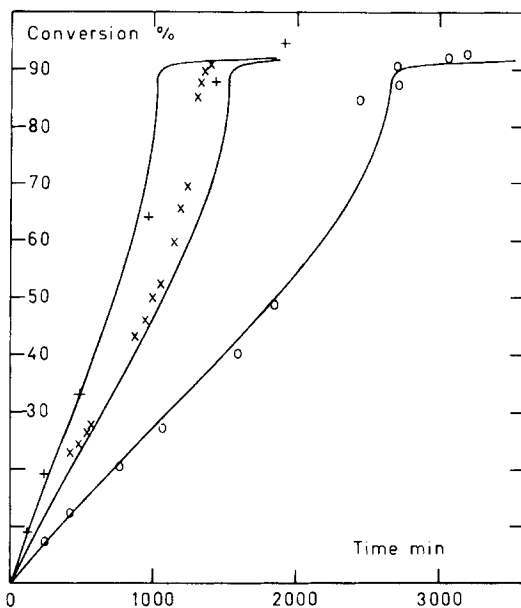T_{g_S} (toluene) = 113 K   22

Fig. 5. Bulk polymerization of St at 60°C: (+) $[I]_0$ = 0.0216 mol AIBN/L, data of Tobolsky et al.[13]: (×) $[I]_0$ = 0.010 mol AIBN/L, data of Braks[24]; (O) $[I]_0$ = 0.0036 mol AIBN/L, data of Nishimura[11]; (——) model prediction.

Comparison between Model Prediction and Experimental Data

Bulk Polymerization

Figure 2 shows the bulk rate data after Ito[23] obtained at 45°C. The agreement between predicted and experimental data is good at conversions below 85% over
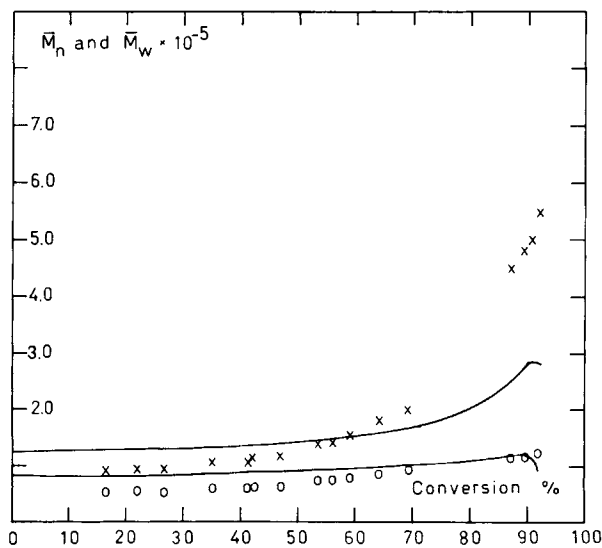

Fig. 6. Bulk polymerization of St at 60°C. Effect of conversion on molecular weight averages: (O) $\overline{M}_n$; (×) $\overline{M}_w$; $[I]_0$ = 0.024 mol AIBN/L. Data of Braks[24]; (——) model prediction.
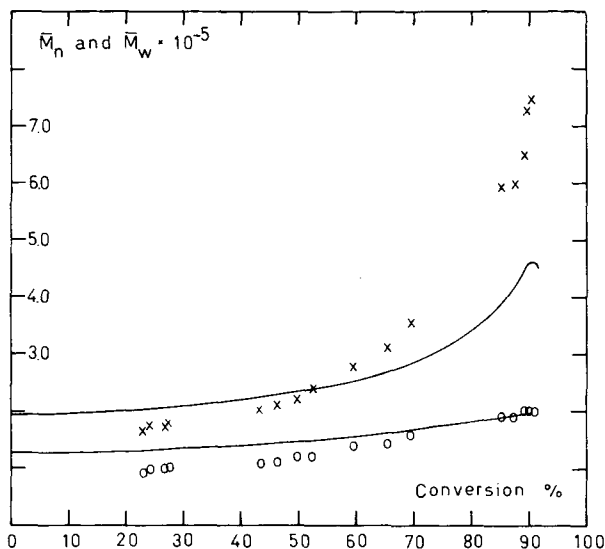
Fig. 7. Bulk polymerization of St at 60°C. Effect of conversion on molecular weight averages: (○) $\overline{M}_n$; (×) $\overline{M}_w$; $[I]_0 = 0.010$ mol AIBN/L. Data of Braks[24]; (——) model prediction.

the entire range of initiator concentrations used (0.2–0.0125 mol AIBN/L). However, at higher conversions, the agreement is poor due to the fact that the limiting conversions predicted are considerably lower than those measured by Ito. The limiting conversions reached in the reported experimental data do, however, not agree with the extensive data shown in Figure 1. This suggests that isothermal conditions in Ito's experiments were not achieved at higher conversions where the highest reaction rate is found.
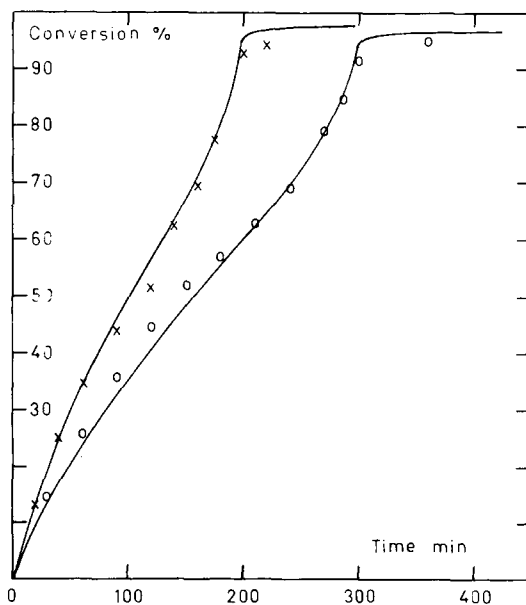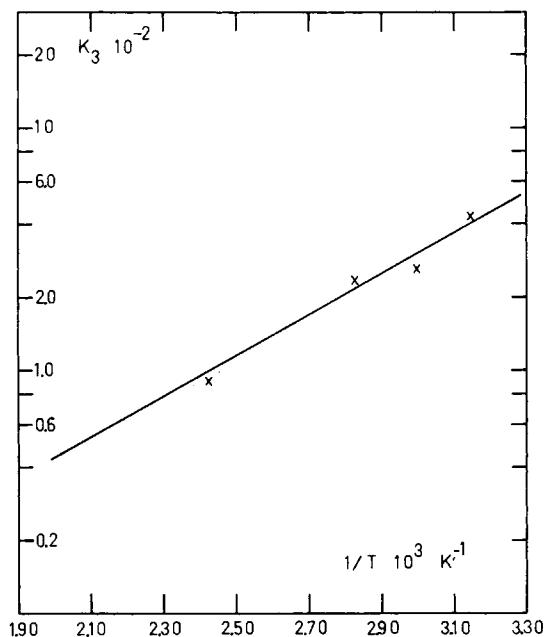

Fig. 8. Bulk polymerization of St at 80°C: (×) $[I]_0 = 0.05$ mol AIBN/L, data of Nishimura[11]; (○) $[I]_0 = 0.0212$ mol AIBN/L, data of Tobolsky et al.[13]; (——) model prediction.

Fig. 9. Arrhenius plot of K_3.

Figures 3, 4, and 5 show the comparison between model prediction and experimental data after Arai et al.,[12] Nishimura,[11] Tobolsky et al.,[13] and Braks et al.[24] obtained at 60°C. The agreement between experimental and predicted data is excellent in all cases except for the data of Braks et al.[24] The range in initiator concentrations covered is 0.0992–0.0036 mol/L. The comparison with the molecular weight data after Braks et al.[24] and the theoretical predicted is shown in Figures 6 and 7. The agreement between the $\overline{M}_n$ values is excellent, but with $\overline{M}_w$ it is only fair at intermediate and low conversions. The deviation from the theoretical predicted at higher conversion found both in rate and molecular weight data presented by Braks et al.[24] seems to indicate the presence of a stronger gel effect in their case. Fewer impurities to which there are chain transfer would give exactly this effect. Unfortunately, the molecular weight data presented by Braks et al. are the only ones available in the literature for bulk polymerization at low temperatures.

Figure 8 shows rate data after Nishimura[11] and Tobolsky et al.[13] obtained at 80°C. The agreement between experimental and theoretical is excellent, even at very high conversion.

Figure 9 shows K_3 as a function of temperature.

Figure 10 shows the k_p^2/k_t values derived in this work compared with the ones available in the literature.[25] The agreement at low temperatures is good.

Solution Polymerization

The capability of the model to describe the solution polymerization of styrene was also tested. Data from Hui et al.[5,21] for the solution polymerization of styrene in toluene were used for this purpose. Figures 11, 12, 13, and 14 show the
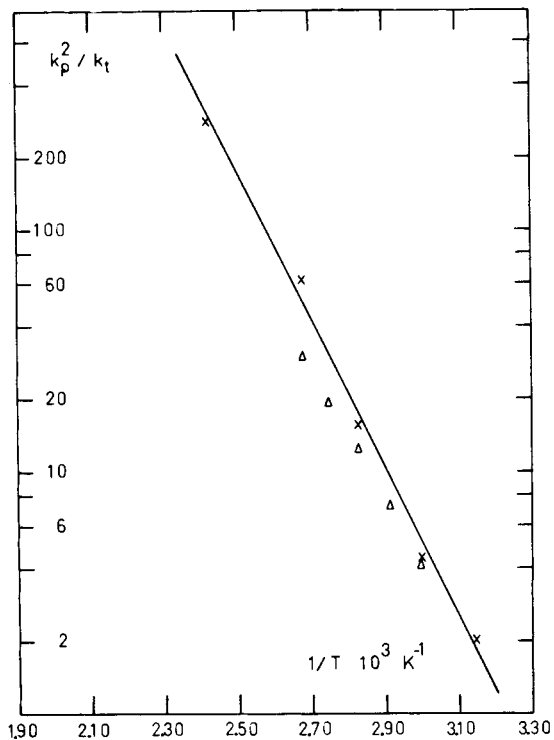
Fig. 10. k_p^2/k_t as function of $1/T$: (×) data estimated in this work; (△) data of Offenbach and Tobolsky.[25]
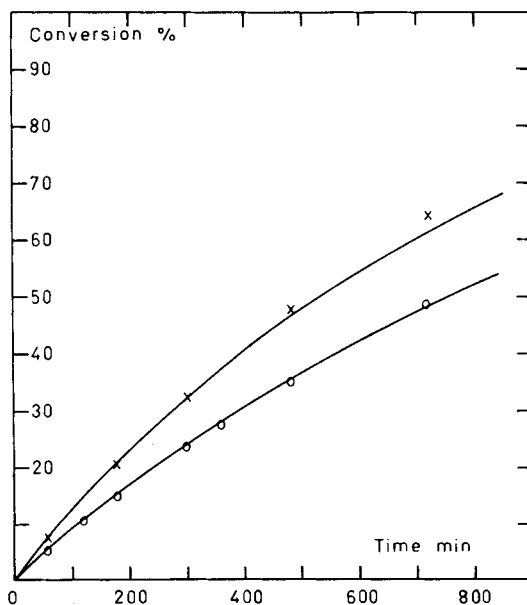

Fig. 11. Solution polymerization of St with toluene as solvent; temperature 60°C: (×) $[I]_0 = 0.08$ mol AIBN/L; (○) $[I]_0 = 0.04$ mol AIBN/L. Solvent concentration 1.80 mol/L. Data of Hue and Hamielec[21]; (——) model prediction.
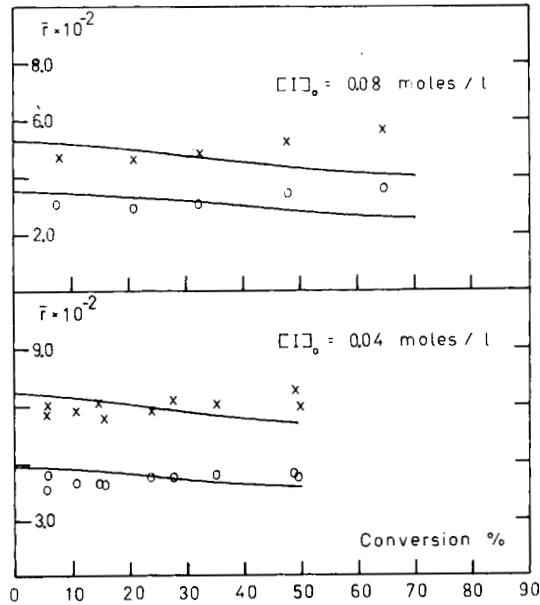
Fig. 12. Solution polymerization of St with toluene as solvent, temperature 60°C. Average degree of polymerization vs. conversion, solvent concentration 1.80 mol/L: (×) weight-average degree of polymerization $\bar{r}_w$; (O) number-average degree of polymerization $\bar{r}_n$. Data of Hui and Hamielec[21]; (——) model prediction.

comparison between model prediction and experimental data at 60°C. The agreement is quite satisfactory at all solvent and initiator levels.

The agreement between experimental and theoretical at 80°C at the lower solvent level is quite good with respect to the conversion vs. time predictions,
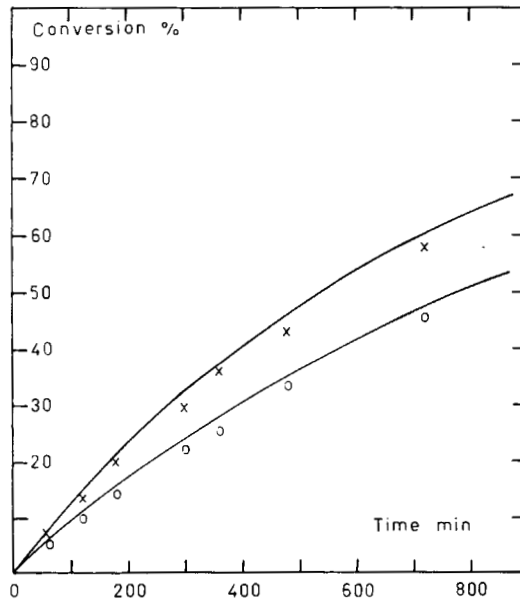

Fig. 13. Solution polymerization of St with toluene as solvent, temperature 60°C: (×) $[I]_0 = 0.08$ mol AIBN/L; (O) $[I]_0 = 0.04$ mol AIBN/L; solvent concentration 3.60 mol/L. Data of Hui and Hamielec[21]; (——) model prediction.
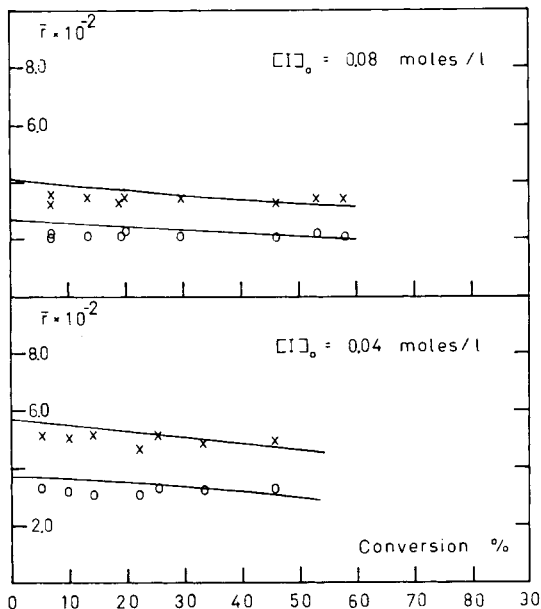
Fig. 14. Solution polymerization of St with toluene as solvent; temperature 60°C. Average degree of polymerization vs. conversion, solvent concentration 3.60 mol/L: (✕) weight-average degree of polymerization $\bar{r}_w$; (O) number-average polymerization $\bar{r}_n$. Data of Hui and Hamielec[21]; (——) model prediction.

as can be seen in Figure 15. The deviation between predicted and reported molecular weight data in Figure 16 is at higher conversions rather poor, at least in the case of $\bar{r}_w$.

The model shows some deficiency in describing the data obtained at very high solvent levels (Fig. 17). It must be mentioned that the lines representing model
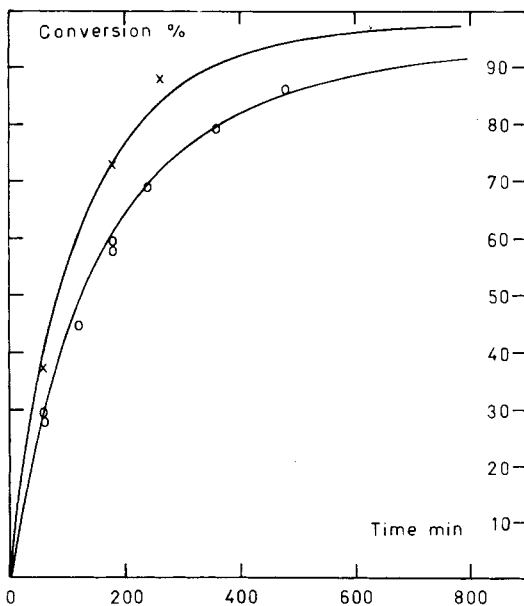

Fig. 15. Solution polymerization of St with toluene as solvent; temperature 80°C: (✕) $[I]_0 = 0.08$ mol AIBN/L; (O) $[I]_0 = 0.04$ mol AIBN/L; solvent concentration 1.80 mol/L. Data of Hui and Hamielec[21]; (——) model prediction.
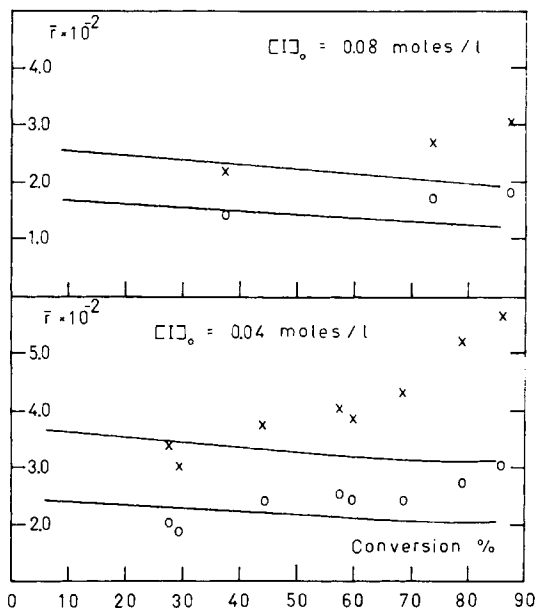
Fig. 16. Solution polymerization of St with toluene as solvent; temperature 80°C. Average degree of polymerization vs. conversion, solvent concentration 1.80 mol/L: (×) weight-average degree of polymerization $\bar{r}_w$; (O) number-average degree of polymerization $\bar{r}_n$. Data of Hui and Hamielec[21]; (——) model prediction.

prediction has been constructed without the presence of any gel effect. It is therefore reasonable to assume that some sort of solvent effect occurs at this high level of solvent. Such an effect will lead to a decrease in the k_P, which means
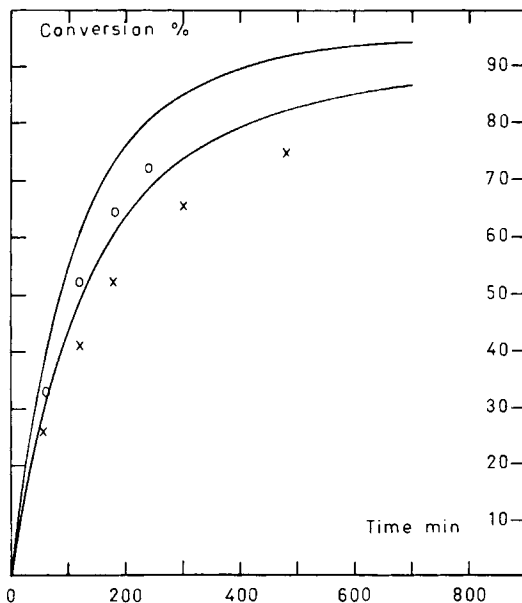

Fig. 17. Solution polymerization of St with toluene as solvent, temperature 80°C: (×) $[I]_0 = 0.08$ mol AIBN/L; (O) $[I]_0 = 0.04$ mol AIBN/L; solvent concentration 3.60 mol/L. Data of Hui and Hamielec[21]; (——) model prediction.
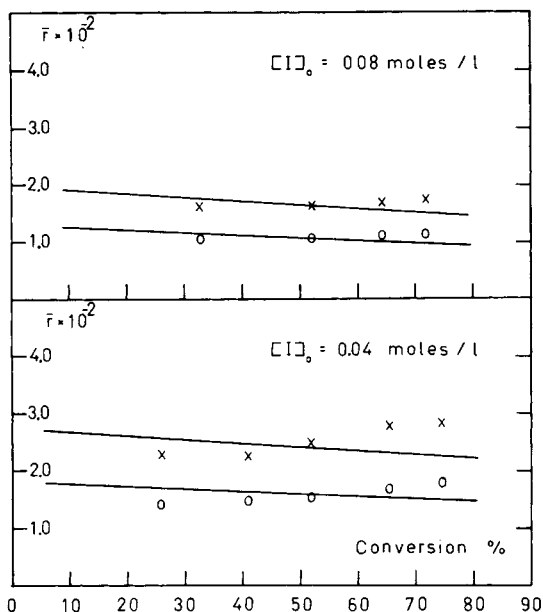
Fig. 18. Solution polymerization of St with toluene as solvent, temperature 80°C. Average degree of polymerization vs. conversion, solvent concentration 3.60 mol/L: (✕) weight-average degree of polymerization $\bar{r}_w$; (O) number-average degree of polymerization $\bar{r}_n$. Data of Hui and Hamielec[21]; (—) model prediction.

that the experimental conversion data should indicate a lower conversion than the one predicted by conventional kinetics. This is exactly what can be seen in Figure 17. The solvent effect, in the case of styrene, has been discussed and described by several authors.[26–34] The agreement between predicted and measured molecular weight data is however very satisfactory, as can be seen in Figure 18.

CONCLUSIONS

A rate model for free radical polymerization identical to the one proposed for MMA[1] has been developed. The model, which is based on free volume theory concepts, accounts for diffusion-controlled termination and propagation and gives a limiting conversion. The model shows an excellent agreement with measured rate data for bulk and solution polymerization over wide ranges of temperature and initiator concentrations.

Nomenclature

A	constant
B	constant
C_I	chain transfer constant to initiator
C_M	chain transfer constant to monomer
C_S	chain transfer constant to solvent
D_M	diffusion coefficient of the monomer

$D_{M_{cr}}$ diffusion coefficient of the monomer at the conversion where the propagation becomes diffusion controlled

D_P diffusion coefficient of a polymer radical

$D_{P_{cr}}$ diffusion coefficient of a polymer radical at the conversion where the termination becomes diffusion controlled

d_M density of monomer

d_P density of polymer

f initiator efficiency

$[I]_0$ initial initiator concentration

K_3 temperature-dependent constant

k_d decomposition rate constant

k_{P_0} propagation rate constant at zero conversion

k_P propagation rate constant

k_{t_0} termination rate constant in the absence of gel effect

k_t termination rate constant

$k_{t_{cr}}$ termination rate constant at the conversion where the termination becomes diffusion controlled

k_1 temperature-dependent constant

$\tilde{k}_1$ temperature-dependent constant

k_2 constant

$\tilde{k}_2$ constant

M molecular weight of monodispersed polymer

$[M]$ monomer concentration

$\overline{M}_n$ number-average molecular weight

M_0 molecular weight of monomer

$\overline{M}_w$ weight-average molecular weight

$\overline{M}_{w_{cr1}}$ weight-average molecular weight at the conversion where the gel effect starts

Q constant

r degree of polymerization

$[S]$ concentration of solvent

T polymerization temperature

T_{g_M} glass transition temperature of monomer

T_{g_P} glass transition temperature of polymer

T_{g_S} glass transition temperature of solvent

T_{g_∞} glass transition temperature of polymer with infinite molecular weight

t time

V_F free volume fraction

$V_{F_{cr1}}$ free volume fraction at the conversion at which the gel effect starts

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