Free radical polymerization of *p*-methyl styrene

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An experimental investigation is reported of the free-radical synthesis kinetics of poly(*p*-methyl styrene) in cyclohexane at low monomer conversion in the temperature range 50°–70°C using AIBN initiator. The *p*-methyl styrene monomer contained greater than 97% *para*isomer. Isothermal conversion/time curves were obtained using glass ampoule reactors and gravimetry and molecular weight distribution and weight-average molecular weights were measured by s.e.c. and low angle laser light scattering photometry (*LALLSP*). Transfer to small molecules (monomer, cyclohexane, ---) was found to be small or negligible with virtually all of the polymer chains formed by termination by combination. Predicted and measured weight-average molecular weights are in good agreement for polymer synthesized at low conversions.

(Keywords: kinetics; free-radical polymerization; solution; low temperature; chemical initiation)

THEORETICAL DEVELOPMENT

The reactions which are considered in the solution polymerization of *p*-methyl styrene at low temperatures and conversion with a chemical initiator follow.

(1) *Initiation:*

$$I \xrightarrow{k_d} 2R_c^{\bullet}$$

$$R_c^{\bullet} + M \xrightarrow{k_{pc}} R_1^{\bullet}$$

(2) *Propagation:*

$$R_r^{\bullet} + M \xrightarrow{k_p} R_{r+1}^{\bullet}$$

(3) *Termination by combination disproportionation:*

$$R_r^{\bullet} + R_s^{\bullet} \xrightarrow{k_{tc}} P_{r+s}$$

$$R_r^{\bullet} + R_s^{\bullet} \xrightarrow{k_{td}} P_r + P_s$$

(4) *Chain transfer (to small molecules):*

$$R_r^{\bullet} + Y \xrightarrow{k_{fY}} P_r + \dot{Y}$$

where Y could be monomer, solvent or initiator. There is the possibility of transfer to polymer (methyl hydrogen) at higher conversions, however, in this study, solution polymerization at low conversions, it is neglected.

In the batch isothermal solution polymerization of *p*-methyl styrene, one can neglect the change in reaction volume with monomer conversion and write the following rate expressions:

$$\frac{d[I]}{dt} = -k_d[I] \qquad (1)$$

$$[I] = [I]_0 \exp(-k_d t) \qquad (1a)$$

$$\frac{d[M]}{dt} = -k_p[M][R^{\bullet}] \qquad (2)$$

$$[M] = [M]_0 \exp(-k_p[R^{\bullet}]t) \qquad (2a)$$

Equation (2) invokes the long chain approximation (LCA) which neglects the consumption of monomer by all reactions other than propagation. For equation (2a), it is assumed that for low conversion, the radical initiation rate and the total polymer radical concentration ($R^{\bullet}$]) are constant. The radical initiation rate (R_I) is given by:

$$R_I = 2fk_d[I] \qquad (3)$$

and the total polymer radical concentration by (invoking the stationary-state hypothesis (SSH)):

$$[R^{\bullet}] = (R_I/k_t)^{1/2} \qquad (4)$$

The termination constant k_t is in general equal to the sum of k_{tc} and k_{td} for termination by combination and disproportionation. It will be later shown that k_{td} is negligible for the polymerization of *p*-methyl styrene.

Introduction of monomer conversion into equations (2)

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and (2a), one obtains:

$$\left(\frac{1}{1-X}\right)\frac{\mathrm{d}X}{\mathrm{d}t}=\left(\frac{k_\mathrm{p}}{k_\mathrm{t}^{1/2}}\right)(2fk_\mathrm{d}[\mathrm{I}])^{1/2} \tag{2b}$$

$$X=1-\exp\left\{-\left(\frac{k_\mathrm{p}}{k_\mathrm{t}^{1/2}}\right)(2fk_\mathrm{d}[\mathrm{I}])^{1/2}t\right\} \tag{2c}$$

For low conversions the accumulated and instantaneous molecular weight distributions are effectively one and the same and are given by:

$$W(r)=(\tau+\beta)(\tau+\beta/2(\tau+\beta)r)r\exp(-[\tau+\beta]r) \tag{5}$$

where $W(r)$ is the weight fraction of polymer of chain length r (having r-monomer units in the chain) and:

$$\tau=k_\mathrm{fY}[\mathrm{Y}]/(k_\mathrm{p}[\mathrm{M}])+(k_\mathrm{td}\mathrm{R}_\mathrm{I})^{1/2}/(k_\mathrm{p}[\mathrm{M}]) \tag{5a}$$

$$\beta=(k_\mathrm{tc}\mathrm{R}_\mathrm{I})^{1/2}/(k_\mathrm{p}[\mathrm{M}]) \tag{5b}$$

where Y is some small molecule which takes part in a chain transfer reaction. For polymer synthesized at low conversions, the accumulated and instantaneous molecular weight averages are effectively the same and are given by:

$$M_\mathrm{N}=M_\mathrm{m}/(\tau+\beta/2) \tag{6a}$$

$$M_\mathrm{W}=M_\mathrm{m}(2\tau+3\beta)/(\tau+\beta)^2 \tag{6b}$$

EXPERIMENTAL

Isothermal solution polymerizations of *p*-methyl styrene in cyclohexane with AIBN initiator were done in sealed glass ampoules. The inhibitor (*t*-butyl catechol) was removed from the monomer by vacuum distillation and oxygen was removed from the ampoules by the standard freeze–thaw technique using liquid nitrogen and vacuum. The polymer was recovered with precipitation in methanol, washing with methanol and then drying to constant weight under vacuum.

Weight-average molecular weights were measured with a low angle laser light scattering photometer (KMX6 with a helium-neon laser $\lambda=632.8$ nm). The d*n*/d*c* for poly(*p*-methyl styrene) in toluene at 20°C was measured with a Brice–Phoenix differential refractometer and found to be 0.093 ml g^{-1}. The second virial coefficient varied from about $4\text{–}8\times10^{-4}$ over the weight-average molecular weight range, $1\text{–}2.5\times10^{4}$.

Molecular weight distributions were measured by s.e.c. using THF at 20°C and μ-Styragel packing. The molecular weight calibration curve for poly(*p*-methyl styrene) was found using the universal molecular weight calibration curve based on polystyrene and two broad *MWD* poly(*p*-methyl styrene) standards with known weight-average molecular weights (these were synthesized and M_W values measured by *LALLSP* in this investigation).

RESULTS AND DISCUSSION

Typical conversion/time curves are shown in *Figures 1, 2* and *3* for temperatures of 50°, 60° and 70°C. The conversions reached are generally less than 25% and one might therefore expect that diffusion-controlled termination would not play a major role in the synthesis kinetics. *Table 1* and *Figures 4, 5* and *6* show data for initial polymerization rates and confirm that the initial rate ($V_0=-(d[M]/dt)_0$) is first-order with respect to monomer and half-order with respect to initiator concentration. Also shown in *Table 1* are data for the group of

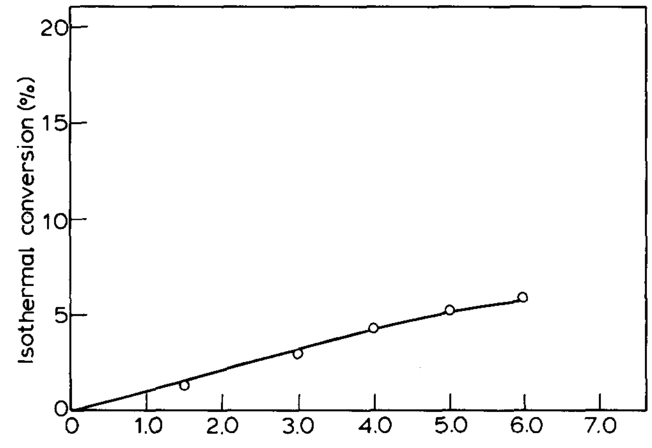

Figure 1 Isothermal conversion/time curve ($T=50$°C, $[\mathrm{M}]=5\,\mathrm{m}/l$, $[\mathrm{I}]=0.005\,\mathrm{m}/l$)

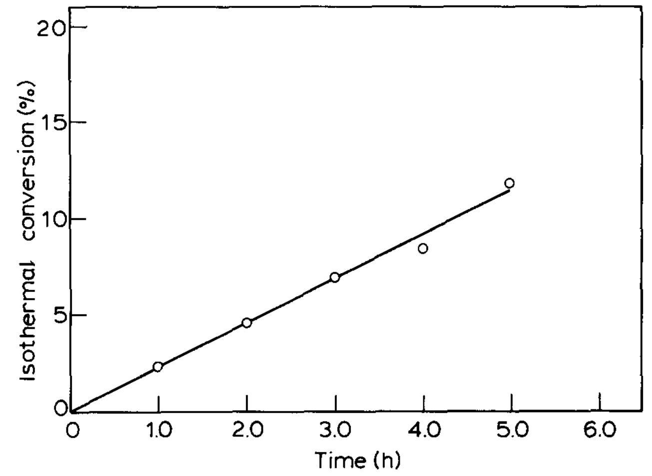

Figure 2 Isothermal conversion/time curve ($T=60$°C, $[\mathrm{M}]=5\,\mathrm{m}/l$, $[\mathrm{I}]=0.005\,\mathrm{m}/l$)

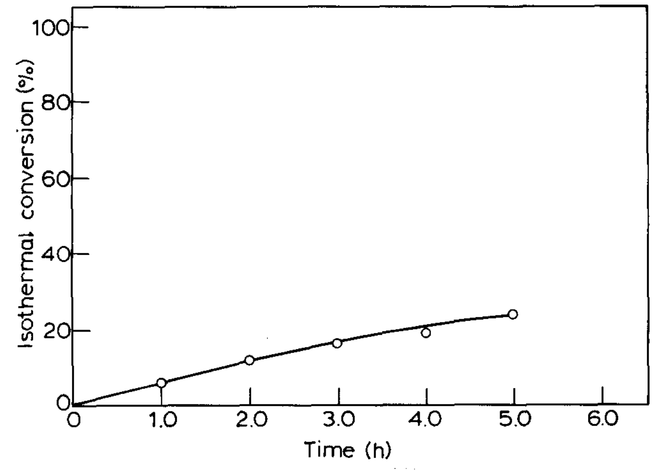

Figure 3 Isothermal conversion/time curve ($T=70$°C, $[\mathrm{M}]=5\,\mathrm{m}/l$, $[\mathrm{I}]=0.005\,\mathrm{m}/l$)

Table 1 Solution polymerization of *p*-methyl styrene in cyclohexane. Initial rate data

T (°C)	[M] (m/l)	[I] (m/l)	V_0 (m/(l)(s))	*k* ($l^{1/2}/(m^{1/2})(s)$)
50	1	0.005	1.76×10^{-6}	2.50×10^{-5}
50	2	0.005	3.99×10^{-6}	2.82×10^{-5}
50	5	0.005	1.35×10^{-5}	3.84×10^{-5}
60	1	0.005	4.48×10^{-6}	6.33×10^{-5}
60	5	0.005	3.05×10^{-5}	8.64×10^{-5}
70	1	0.010	1.53×10^{-5}	1.53×10^{-4}
70	2	0.005	2.23×10^{-5}	1.58×10^{-4}
70	2	0.010	3.14×10^{-5}	2.22×10^{-4}
70	2	0.053	5.61×10^{-5}	1.22×10^{-4}
70	4	0.010	8.25×10^{-5}	2.00×10^{-4}
70	7.54	0.010	2.82×10^{-4}	3.74×10^{-4}

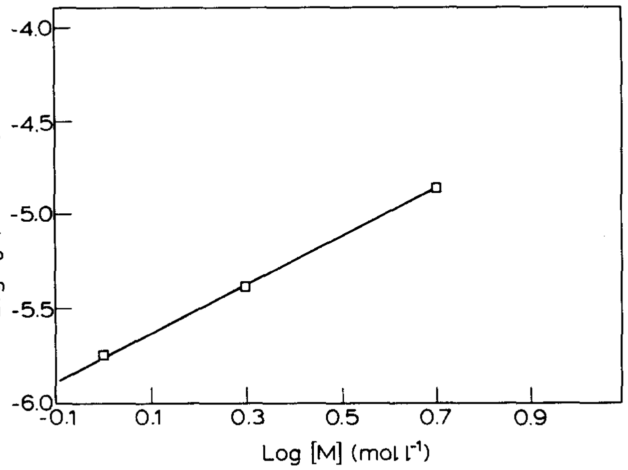

Figure 4 Initial rate *versus* monomer concentration ($T = 50°C$, $[I] = 0.005$ m/*l*)

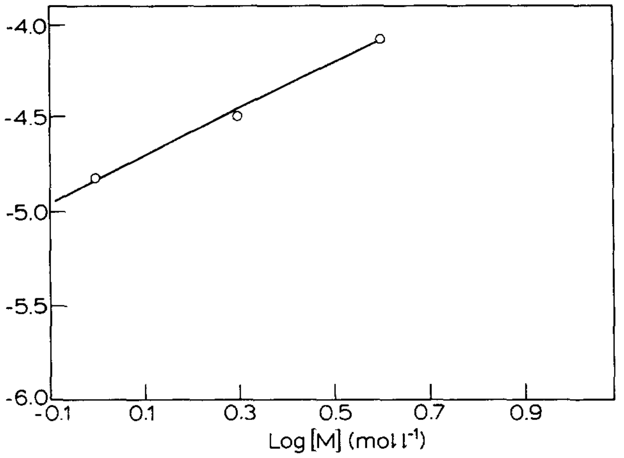

Figure 5 Initial rate *versus* monomer concentration ($T = 70°C$, $[I] = 0.005$ m/*l*)

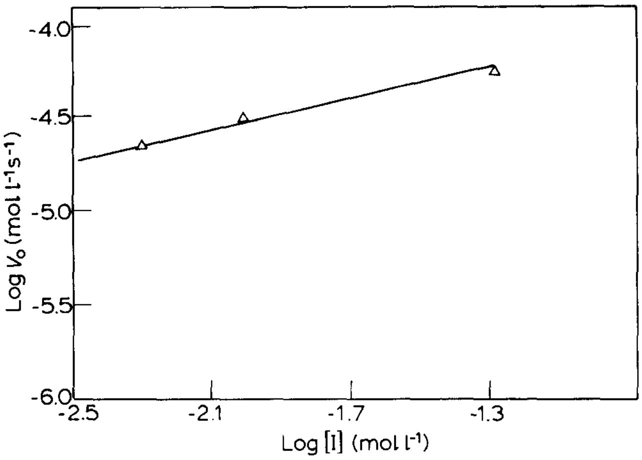

Figure 6 Initial rate *versus* initiator concentration ($T = 70°C$, $[M] = 2$ m/*l*)

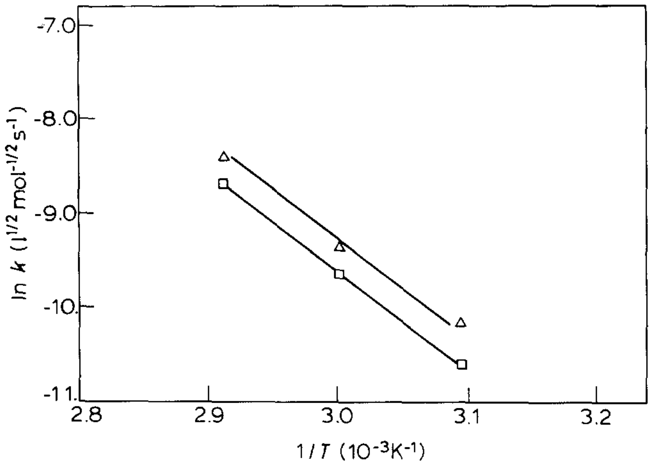

Figure 7 Arrhenius plot for initial rates at two monomer concentration levels ($[M] = 1$ and 5 m/*l*, $[I] = 0.005$ m/*l*)

rate constants *k*, where *k* equals $(k_p/k_{tc}^{1/2})(2fk_d)^{1/2}$. *Figure 7* shows an Arrhenius plot for *k* which indicates two straight lines almost parallel for two monomer concentration levels. The intercepts are significantly different and this is interpreted to be due to a solvent effect on the propagation constant suggested by Henrici Olive[1]. Duerksen *et al.*[2] have successfully applied a solvent correction factor after Henrici Olive and Olive[1] in the free radical polymerization of styrene in benzene. This correction factor takes the form:

$$\Phi_p = [M]_{bulk}/([S](\tau_s/\tau_m) + [M]) \qquad (7)$$

with

$$k_p = \Phi_p k_{p_{bulk}} \qquad (8)$$

Application of a solvent correction factor of $\tau_s/\tau_m = 1.7$

appears to give a single straight line for $\ln \bar{k}$ *versus* $1/T$ where $\bar{k}$ is given by $(k_{p_{bulk}}/k_{tc}^{1/2})$. The data for 3-monomer levels and 1-initiator level corrected for the solvent effect are shown plotted in *Figure 8*. The equation of the line in *Figure 8* is given by:

$$\ln \bar{k} = 3.196 - 1926/T \qquad (9)$$

The Arrhenius equation for the decomposition constant of AIBN used to find $\bar{k}$ from k is given by[3,4]:

$$k_d = 1.056 \times 10^{15} \exp(-30\,720/RT)\,s^{-1} \qquad (10)$$

To evaluate the reliability of the measurements of average molecular weights by *LALLSP* and s.e.c., M_w values found using these measurement techniques were compared. These values along with synthesis conditions are given in *Table 2*. The agreement between M_w values measured by *LALLSP* and s.e.c. is within experimental error. This suggests that the synthesized polymer is essentially linear with negligible long chain branching. With significant long chain branching, one would have observed larger values for M_w by *LALLSP* than by s.e.c. as this latter measurement technique underestimates M_w for polymers with long chain branching. It is also of interest to note that M_w increases significantly with conversion. In the absence of long chain branching, this is a sure sign that the termination reaction is diffusion-controlled and that chain transfer to small molecule is likely not significant. Polydispersities less than two indicate that termination by combination is important. Values of polydispersity greater than 1.5 may be due to some termination by disproportionation and chain transfer to small molecules such as monomer. The importance of these reactions will be considered shortly. It should be mentioned that on a theoretical basis, a polydispersity of 1.5 is expected when all of the polymer chains are produced by termination by combination in a small conversion interval near zero conversion. The conversion intervals for the accumulated polymer in *Table 2* range from 0–0.21 to 0–0.88. These large conversion intervals are likely responsible for polydispersities greater than 1.5 particularly when termination is diffusion-controlled.

To assess the importance of termination by disproportionation and transfer to small molecules, one can initially assume that these reactions are negligible. This permits one to estimate β in equation (5b) from initial rate data and an appropriate decomposition constant k_d for AIBN such as equation (10) and an initiator efficiency f. The initiator efficiency was taken to be 0.5[3] and values of β calculated. These β values were then substituted into equation (6b) to calculate M_w. A value of τ was then assumed and M_w values recalculated using equation (6b). These data are shown in *Table 3*. It is clear that with a value of $\tau = 10^{-4}$ all of the predicted M_w values are smaller than those measured by *LALLSP*. One can

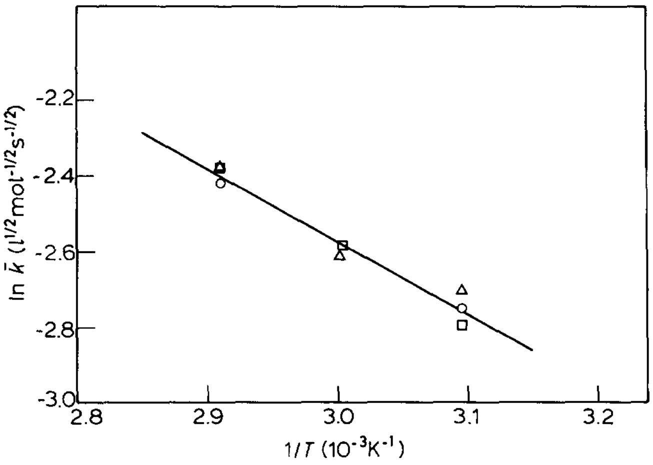

Figure 8 Arrhenius plot for $k(k_p/k_{tc}^{1/2})$ corrected for solvent effect at three monomer levels ([M] = 1, 2 and 5 m/*l*). (k_p should apply to bulk polymerization)

Table 2 Solution polymerization of *p*-methyl styrene in cyclohexane. Molecular weight measurements by *LALLSP* and s.e.c.

T (°C)	[M] (m/*l*)	[I] (m/*l*)	X	M_w (*LALLSP*)	M_w (g.p.c.)	M_w/M_n (g.p.c.)
90	1.89	0.012	0.50	36400	34600	2.52
70	2	0.050	0.46	14800	14900	1.55
70	2	0.010	0.28	37600	40000	1.72
70	2	0.005	0.21	51800	60000	1.74
70	5	0.005	0.23	175000	174000	2.01
70	5	0.005	0.50	188000	180000	1.98
70	5	0.005	0.88	200000	193000	1.95
70	7.54	0.010	0.40	218000	193000	2.89
70	7.54	0.010	0.71	252000	271000	3.00

Table 3 Solution polymerization of *p*-methyl styrene in cyclohexane. Comparison of M_w by *LALLSP* with predicted values (synthesis $T = 70$°C)

[M] (m/*l*)	[I] (m/*l*)	X	M_w (*LALLSP*)	M_w predicted ($\tau = 0$)	($\tau = 10^{-4}$)
2	0.050	0.46	14800	13200	13100
2	0.010	0.28	37600	36300	35600
2	0.005	0.21	51800	53000	51100
5	0.005	0.23	175000	181000	169400
5	0.005	0.50	188000	181000	169400
5	0.005	0.88	200000	181000	169400

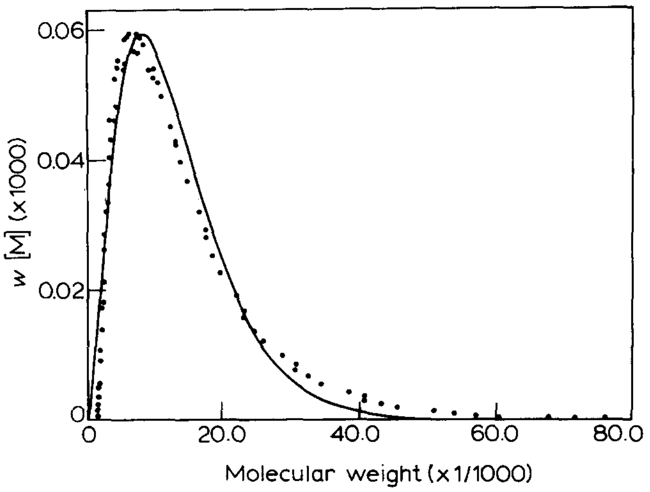

Figure 9 Molecular weight distributions, measured by s.e.c. and predicted by equation (5) with $\tau = 0$ and β evaluated from initial rates ($T = 70°C$, $[M] = 2\,m/l$, $[I] = 0.05\,m/l$, $X = 0.46$

therefore conclude that $\tau < 10^{-4}$ and with values of β of the order 2×10^{-3} to 3×10^{-2}, we can safely assume that termination by disproportionation and chain transfer to small molecules are negligible at 70°C for the chemically initiated polymerization of *p*-methyl styrene in cyclohexane.

Figure 9 shows a molecular weight distribution measured by s.e.c. compared with a predicted distribution (equation (5) with chain length r replaced by molecular weight M and τ set equal to zero). The agreement is excellent. In general, the agreement is less satisfactory for samples at higher conversions since equation (5) is an instantaneous distribution which should apply near $X = 0$ and s.e.c. gives the accumulated distribution, one which has greater breadth.

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REFERENCES

1 Olive, G. Henrici and Olive, S. *Makromol. Chemie*. 1962, **58**, 188
2 Duerksen, J. H., Hamielec, A. E. and Hodgins, J. W. *AIChE J*. 1967, **13**, 1081
3 Marten, F. L. and Hamielec, A. E. *J. Appl. Polym. Sci.* 1982, **27**, 489
4 van Hook, J. P. and Tobolsky, A. V. *J. Polym. Sci.* 1958, **23**, 429
5 Mutschler, H. 'On the Kinetics of the Free Radical Polymerization of *p*-Methyl Styrene in Cyclohexane', Diplomarbeit der Ruprecht-Karls-Universitat Heidelberg, 1983