Thermal polymerization of *p*-methyl styrene at high conversions and temperatures

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An experimental investigation of the kinetics of the thermally initiated free radical polymerization of *p*-methyl styrene in bulk at temperatures of 120°, 140° and 160° in the conversion range, 0–96% is reported. Conversions were measured gravimetrically and by gas chromatography and molecular weight distributions and weight-average molecular weights by size exclusion chromatography (SEC) and low angle laser light scattering photometry (LALLSP). A kinetic model which accounts for diffusion-controlled termination and predicts conversion/time and molecular weight and long chain branching development for nonisothermal polymerizations has been developed. This model should find use in the design, simulation and optimization of poly(*p*-methyl styrene) reactors.

(Keywords: *p*-methyl styrene; thermal polymerization; kinetics; high temperatures; conversions)

INTRODUCTION

The Mobil Chemical Co. has recently begun the commerical production of *p*-methyl styrene having greater than 97% *para* isomer, a monomer which may soon be competitive (in cost) with styrene. A particularly attractive feature of poly(*p*-methyl styrene) is its high glass transition point (110°C–113°C for 97+% *para* isomer based polymer)[1]. The commercial production of poly(*p*-methyl styrene) and copolymers based on *p*-methyl styrene appears imminent.

The free radical polymerization kinetics of styrene and *p*-methyl styrene are similar[1] and it is therefore likely that the thermal initiation mechanism includes a Diels–Alder adduct intermediate[2]. The mechanism of thermal initiation for *p*-methyl styrene should be similar to that for styrene outlined in *Figures 1* and *2*[2]. During the thermal polymerization of styrene small quantities of dimeric and trimeric styrenes as well as monoradicals are formed. The reaction scheme is based on the Mayo mechanism in which a Diels–Alder reaction between two styrene molecules occurs. An unstable Diels–Alder adduct (Z) is formed and secondary reactions of this intermediate results in phenyltetralin, cyclic trimers and monoradicals which initiate the polymerization. *Cis*- and *trans*-1,2 diphenylcyclobutanes are formed in a separate reaction involving two styrene molecules. The dimeric and trimeric styrenes, although present in small quantities, usually less than 1% based on polystyrene, are objectionable and attempts are made to remove them during the devolatilization of the monomer. Investigations by Olaj led to the development of a reaction mechanism in which two intermediates of different reactivities are present (see *Figure 2* and Kirchner and Riederle[2]). Intermediate ZA rapidly reaches its stationary level and radical formation proceeds exclusively through ZA. Trimers as well as monoradicals are formed from ZA. The intermediate ZA also undergoes chain transfer reactions. Kirchner and Riederle[2] have shown that the reactions involved in thermal initiation of styrene do not become diffusion-controlled at high monomer conversions ($\leqslant 97\%$) in bulk polymerizations. The same conclusions are likely true for

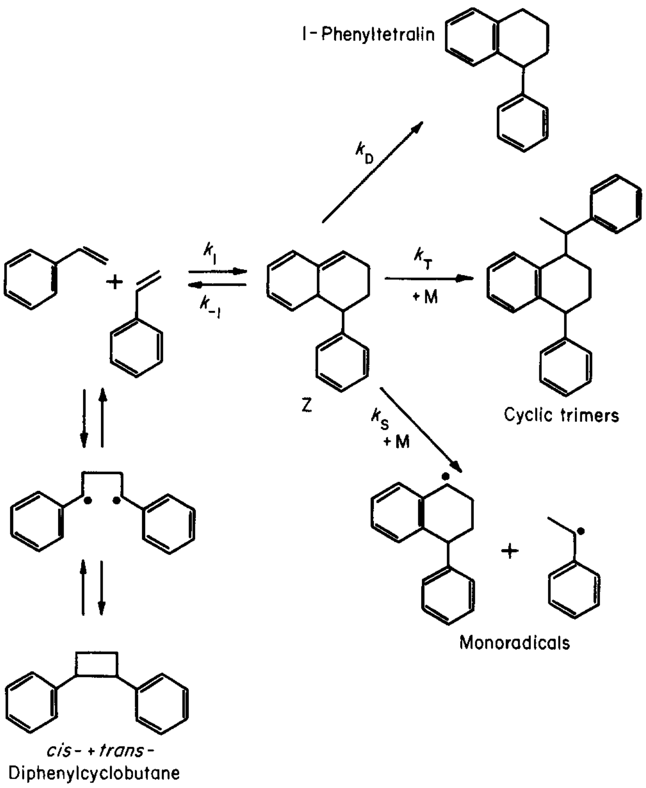

Figure 1 Mechanism of thermal initiation of styrene after Mayo[2]

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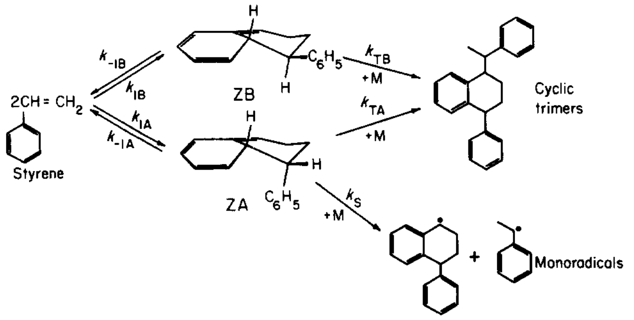


Figure 2 Mechanism of thermal initiation of styrene after Mayo and modified by Olaj[2]

the thermal bulk polymerization of *p*-methyl styrene. A detailed investigation of the reactions involved in the thermal initiation of *p*-methyl styrene has not been carried out in the present investigation.

MODEL DEVELOPMENT

The reactions which are considered in the model include:

Initiation

The rate of polymer radical initiation by the thermal initiation mechanism shown in *Figures 1* and *2* may be given by $R_1 = 2k_i[M]^3$. Following the original work on thermal bulk polymerization of styrene[3,4] we assume that the radical initiation rate is third order in monomer. It is likely that an initiation rate second order in monomer would have fit the rate data equally well as was found with styrene[3]. There is however no simple test to unambiguously find the correct order with respect to monomer for thermal initiation. The use of a solvent might affect the propagation rate constant and possibly the initiation reactions.

Propagation

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

Termination by combination

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

Chain transfer (small molecules)

$$R_r^{\bullet} + M \xrightarrow{k_{fm}} P_r + R_1^{\bullet}$$

$$R_r^{\bullet} + X \xrightarrow{k_{fX}} P_r + R_1^{\bullet}$$

where X is a small molecule with a labile hydrogen.

Chain transfer to polymer (trifunctional branching)

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

The rate of monomer consumption is given by

$$-\frac{1}{V}\frac{dN_M}{dt} = k_p[M][R^{\bullet}] = R_p \qquad (1)$$

where V is the volume of the polymerizing solution in a batch reactor
N_M is the number of moles of monomer
$[M]$ is the monomer concentration
$[R^{\bullet}]$ is the total polymer radical concentration

Application of the stationary-state hypothesis for polymer radicals gives

$$[R^{\bullet}] \approx (2k_i[M]^3/k_{tc})^{1/2} \qquad (2)$$

Replacing $[R^{\bullet}]$ in equation (1) and introducing conversion $x = (N_{M_0} - N_M)/N_{M_0}$ gives

$$\frac{dx}{dt} = [\sqrt{2}k_i^{1/2}k_p/k_{tc}^{1/2}][M]_0^{3/2}(1-x)^{5/2}/(1+\varepsilon x)^{3/2} \qquad (3)$$

Letting $\qquad \phi(x) = [\sqrt{2}k_i^{1/2}k_p/k_{tc}^{1/2}][M]_0^{3/2}$

one can say that for isothermal polymerization at high temperatures (temperatures above the glass-transition temperature of the polymer being synthesized)

$$\phi(x)/\phi(0) = (k_{tc_0}/k_{tc})^{1/2} \qquad (4)$$

Or in other words, we assume that the propagation reaction and reactions involved in thermal initiation do not become diffusion-controlled. $\phi(x)$ is therefore a measure of diffusion-controlled termination. It is assumed that the volume varies linearly with conversion with ε, a constant contraction factor.

At monomer conversions below which transfer to polymer reactions are negligible, the polymer chains are linear and the instantaneous and accumulated molecular weight distributions $(w(r), \bar{w}(r))$ molecular weight averages (M_n, M_w and $\bar{M}_n$, $\bar{M}_w$) are given by

$$w(r) = (\tau+\beta)(\tau + B/2(\tau+\beta)r)r\exp(-(\tau+\beta)r) \qquad (5)$$

$$\bar{w}(r) = \int_0^x w(r)dx/x \qquad (6)$$

$$M_n = M_m/(\tau+\beta/2) \qquad (7)$$

$$M_w = M_m(2\tau+3\beta)/(\tau+\beta)^2 \qquad (8)$$

$$\bar{M}_n = x/\int_0^x (1/M_n)dx \qquad (9)$$

$$\bar{M}_w = \int_0^x M_w dx/x \qquad (10)$$

where

$$\tau = k_{fm}/k_p + (k_{f_{ZA}}/k_p)([ZA]/[M]) + (k_{f_D}/k_p)([D]/[M]) + (k_{fT}/k_p)([T]/[M]) \qquad (11)$$

$$\beta = (k_{tc}^{1/2}/k_p)(2k_i)^{1/2}([M])^{1/2} \qquad (12)$$

In this study the quantitative measurements of [ZA], [D] and [T] (Diels–Alder adduct, dimers and trimers: see *Figures 1* and *2*) were not carried out and to account for the possible transfer to these species we employed the following empirical equation

$$\tau = C_m + B_1 X \qquad (13)$$

where B_1X accounts for chain transfer to the accumulating species ZA, D and T. A similar procedure has been successfully applied in the thermal bulk polymerization of styrene[3,4].

At higher monomer conversions and when transfer to polymer is significant, polymer chains with trifunctional long chain branches form. The use of the instantaneous molecular weight distribution (equation (5)) is no longer valid and one must resort to the use of the method of moments to calculate molecular weight development and account for long chain branching. Equations for the leading moments of the molecular weight distribution and branching frequency follow.

$$\frac{dY_1}{dt} = R_p V(\tau + \beta/2) \qquad (14)$$

$$\frac{dY_2}{dt} = R_p V \qquad (15)$$

$$\frac{dY_3}{dt} = R_p V\left[\left(1 + \frac{C_p Y_3}{[M]V}\right)\left(2\tau + 3\beta + \frac{2C_p Y_2}{[M]V} + \beta\frac{C_p Y_3}{[M]V}\right)\Big/ \left(\tau + \beta + \frac{C_p Y_2}{[M]V}\right)^2\right] \qquad (16)$$

$$\frac{dY_4}{dt} = R_p V\left(\frac{C_p Y_2}{[M]V}\right) \qquad (17)$$

where $Y_1 = Q_0 V$
$Y_2 = Q_1 V$
$Y_3 = Q_2 V$
$Y_4 = Q_0 \bar{B}_n V$
$C_p = (k_{fp}/k_p)$
and $\bar{M}_n = M_m Q_1/Q_0 \qquad (18)$

$$\bar{M}_w = M_m Q_2/Q_1 \qquad (19)$$

$$\bar{\lambda}_n = 1000\, M_m \bar{B}_n/\bar{M}_n \qquad (20)$$

where $\bar{B}_n$ is the number of long branches per polymer molecule and $\bar{\lambda}_n$ is the number of long branches per 1000 methyl carbons on the polymer chains. V is the volume of the reacting mixture and

$$Q_i = \sum_2^{\infty} r^i [P_r) \text{ and } i = 0, 1, 2, 3, \ldots$$

EXPERIMENTAL

Thermal polymerizations of *p*-methyl styrene in bulk were carried out isothermally at 120°C, 140°C and 160°C in sealed glass ampoules (5 and 8 mm o.d.). The monomer, *p*-methyl styrene (>97% *para* isomer) was provided by Mobil Chemical Co., Edison, N.J. The inhibitor t-butyl catechol was removed using several washings with sodium hydroxide. Oxygen was removed by vacuum degassing using the freeze–thaw technique. Conversions were measured by gas chromatography and gravimetry. Weight-average molecular weights were measured by low angle laser light scattering photometry (Chromatix KMX6). The refractive index increment (d*n*/d*c*) was measured with a laser differential refractometer (Chromatrix KMX16). All measurements were carried out at room temperature with toluene as solvent. Molecular weight distributions and number and weight-average molecular weights were measured by SEC (Waters 150C) using toluene as the mobile phase at 40°C and u-Styragel packing. The molecular weight calibration curve for poly(*p*-methyl styrene) was found using the universal calibration curve based on polystyrene and broad *MWD* poly(*p*-methyl styrene) standards with known $\bar{M}_w$ found by using LALLSP offline[6].

RESULTS AND DISCUSSION

Parameters found for poly(p-*methyl styrene*) *characterization*

Refractive index increment

d*n*/d*c* = 0.0913 at 25°C in toluene (c in g/cm^3) with $\lambda = 632.8$ nm.

Kinetic model parameters

Kinetic parameters (equations (21)–(28)) were found by fitting the measured rate and molecular weight data following published procedures[3].

Third-order thermal initiation ($R_1 = 2k_i[M]^3$)

$$k_i = 1.13 \times 10^4 \exp(-24\,560/RT) l^2/(m^2)(s) \qquad (21)$$

$$k_p/k_{tc_0}^{1/2} = 217.0 \exp(-6080/RT) l^{1/2}/(m^{1/2})(s^{1/2}) \qquad (22)$$

$$C_m = 0.150 \exp(-5630/RT) \qquad (23)$$

$$B_1 = -[1.1 \times 10^{-3} + 2.56 \times 10^{-6} (T - 393.12)] \log_{10}\left(\frac{473.12 - T}{202.5}\right) \qquad (24)$$

$$k_{tc}/k_{tc_0} = \exp(-2[A_1 x + A_2 x^2 + A_3 x^3]) \qquad (25)$$

$$A_1 = 0.405 - 5.05 \times 10^{-3} T \qquad (26)$$

$$A_2 = 16.65 - 1.76 \times 10^{-2} T \qquad (27)$$

$$A_3 = 8.98 + 7.85 \times 10^{-3} T \qquad (28)$$

An estimate of C_p for the temperature range, 120°C–160°C was found to be about 1.1×10^{-4}. Branching frequencies were too low to permit the temperature dependence of C_p to be found.

Comparison of predicted and measured data

Conversion/time curves

Figure 3 shows measured conversion/time curves at three temperatures 120°C, 140°C and 160°C for the thermal polymerization of *p*-methyl styrene. Also shown are the predicted conversion/time curves using the kinetic model with the kinetic parameters shown above. The agreement is clearly excellent with good fits up to high conversions with third-order initiation. The good fits are not unexpected as the variation of the termination constant (equation (25)) ensures a good fit. A second-order thermal initiation model would have given an equally good fit[3].

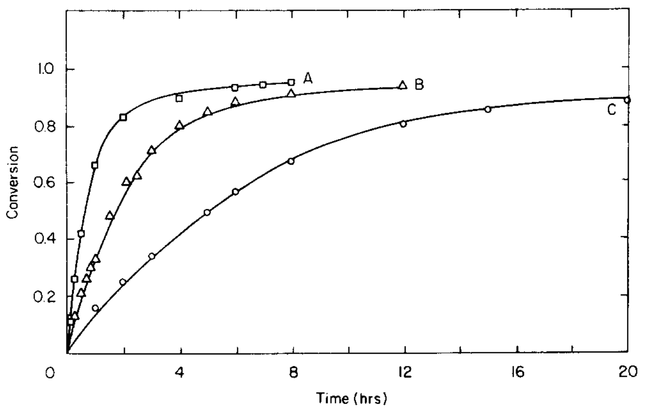


Figure 3 Measured and predicted conversion/time curves for the thermal polymerization of p-methyl styrene. Curve A: 160°C; curve B: 140°C; curve C: 120°C

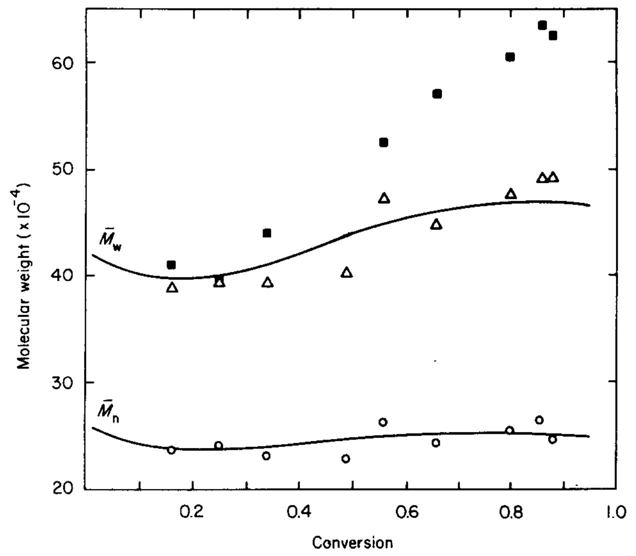


Figure 4 Measured ((○), (△): SEC and (■): LALLSP) and predicted ($C_p = 0$) molecular weight average *versus* conversion at 120°C

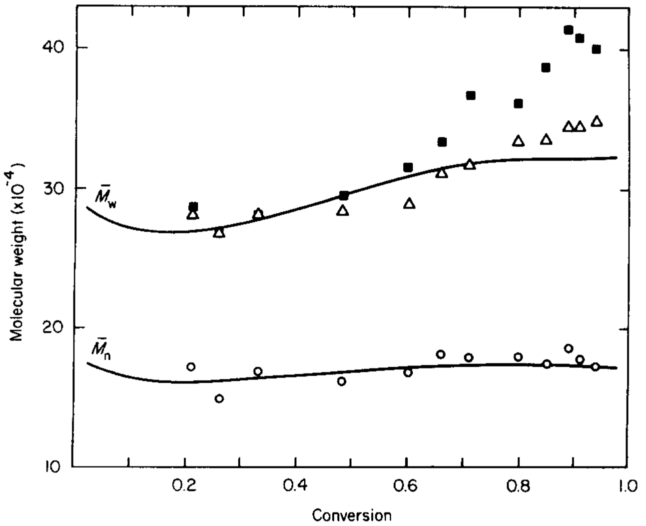


Figure 5 Measured ((○), (△): SEC and (■): LALLSP) and predicted ($C_p = 0$) molecular weight averages *versus* conversion at 140°C

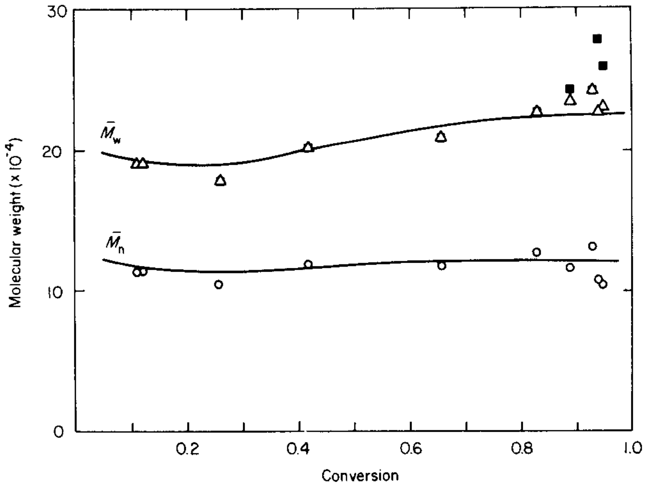


Figure 6 Measured ((○), (△): SEC and (■): LALLSP) and predicted ($C_p = 0$) molecular weight averages *versus* conversion at 160°C

Molecular weight/conversion curves

Figures 4, 5 and *6* show measured $\bar{M}_n$ and $\bar{M}_w$ by SEC and LALLSP plotted *versus* conversion for three polymerization temperatures 120°C, 140°C and 160°C. Also shown are $\bar{M}_n$ and $\bar{M}_w$ predicted by the kinetic model. It should be pointed out that the kinetic model does not include long chain branching reactions such as transfer to polymer and hence at high conversions if branching occurs the model should predict $\bar{M}_w$ values which are lower than those measured by SEC and LALLSP. It should also be pointed out that LALLSP gives the correct $\bar{M}_w$ and that for polymers with long chain branching SEC underestimates $\bar{M}_w$. And finally it should be mentioned that transfer to polymer reactions do not affect $\bar{M}_n$ but only $\bar{M}_w$ and higher molecular weight averages. The model fits on $\bar{M}_n$ are good, but model predictions of $\bar{M}_w$ are always too low at high conversions. Transfer to polymer reactions are clearly significant in the thermal polymerization of p-methyl styrene at high conversions. The large differences in $\bar{M}_w$ values at high conversions measured by SEC and LALLSP for 120°C polymerization are at first consideration unusually large as compared to those at 140°C and 160°C. One should, however, not forget that the polymerization times at 120°C are very much larger than those at 140°C and 160°C and also that the gel effect (diffusion-controlled termination) is stronger at the lower temperatures, giving relatively high radical concentrations at high conversion. In fact, at $x = 0.9$ the radical concentrations are almost the same for the three temperature levels. Plots of total polymer radical concentrations *versus* conversion for the three temperatures are shown in *Figure 7*. It is interesting to note the rapid drop in radical concentration for all three temperatures at high levels of conversion. This is typical for polymerizations where radicals are generated by thermal initiation and radical initiation rates are proportional to monomer concentration raised to some high power. It thus appears that high long chain branching frequencies would be difficult to obtain using thermal initiation. A chemical initiator with sufficiently long half-life would maintain high radical concentrations at high polymer concentrations (at high conversions) and give appreciably higher long chain branching frequencies than those obtained with thermal initiation. The almost constant radical concentration observed over intermediate

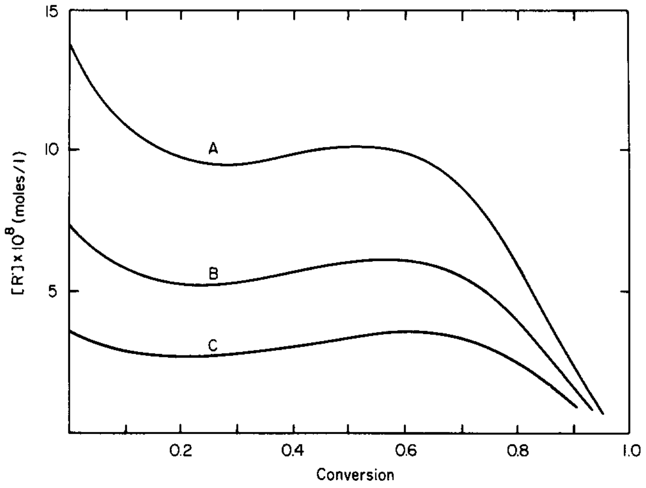


Figure 7 Predicted radical concentration *versus* conversion at 3 temperature levels. Curve A: 160°C; curve B: 140°C; curve C: 120°C

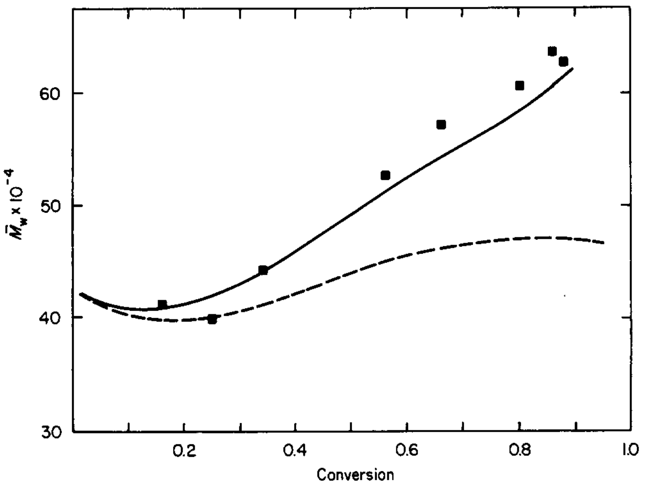


Figure 8 Measured ((■) LALLSP and predicted weight-average molecular weights (C_p=0: (-----) and C_p=1.1×10^{-4}: (——)) at 120°C

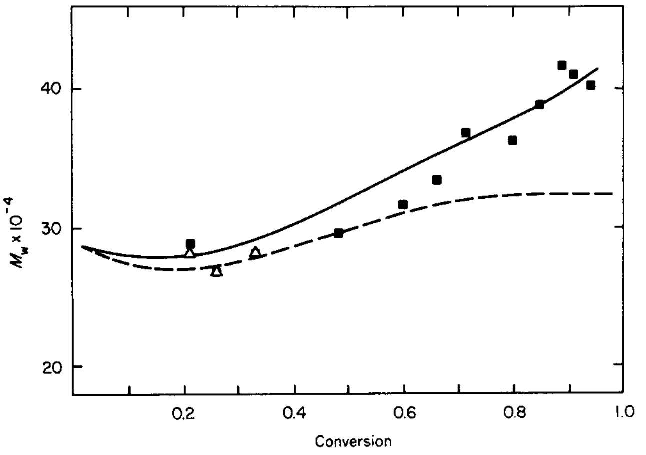


Figure 8 Measured ((■) LALLSP) and predicted weight-average molecular weights (C_p=0: (-----) and C_p=1.1×10^{-4}: (——)) at 140°C

conversions is due to diffusion-controlled termination. Comparing branching frequencies for the three temperatures at the same high conversion, it is now clear why the higher branching frequencies occur at 120°C.

Figures 8 and *9* show the model predictions of $\bar{M}_w$ at 120°C and 140°C, with C_p set equal to zero and 1.1 × 10^{-4}.

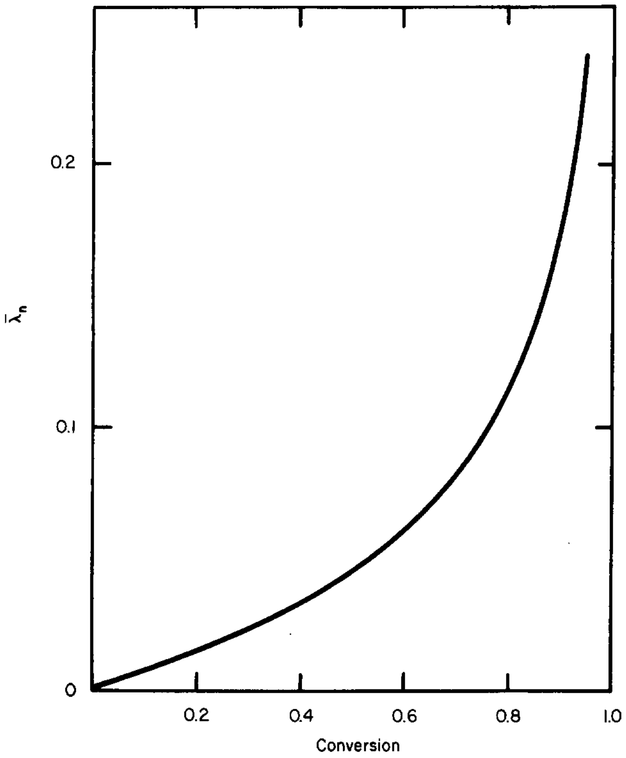


Figure 10 Predicted long chain branching frequency *versus* conversion at 120°C (C_p=1.1×10^{-4})

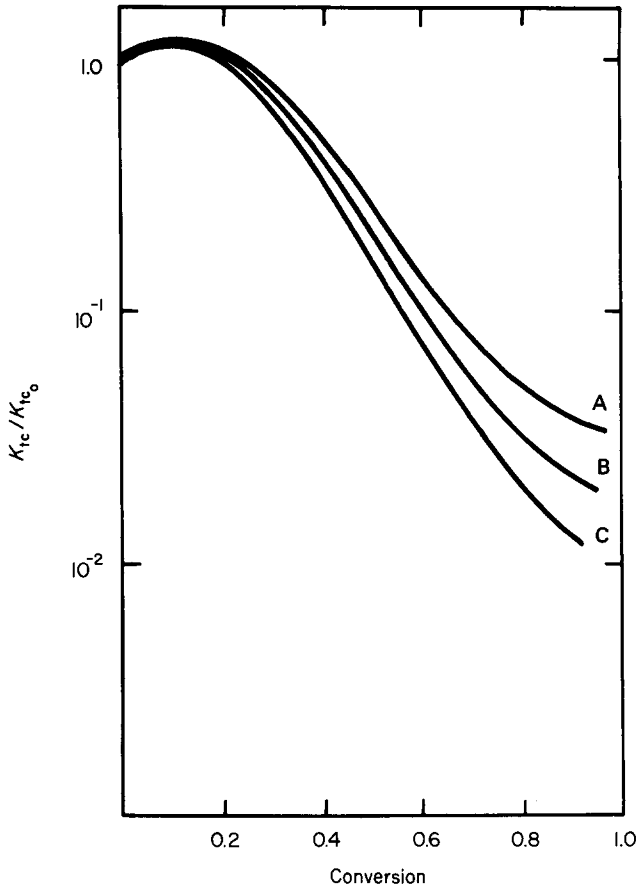


Figure 11 Diffusion-controlled termination: measured decrease in k_{tc} with conversion at 3-temperature levels (curve A: 160°C; curve B: 140°C; curve C: 120°C) for *p*-methyl styrene polymerization

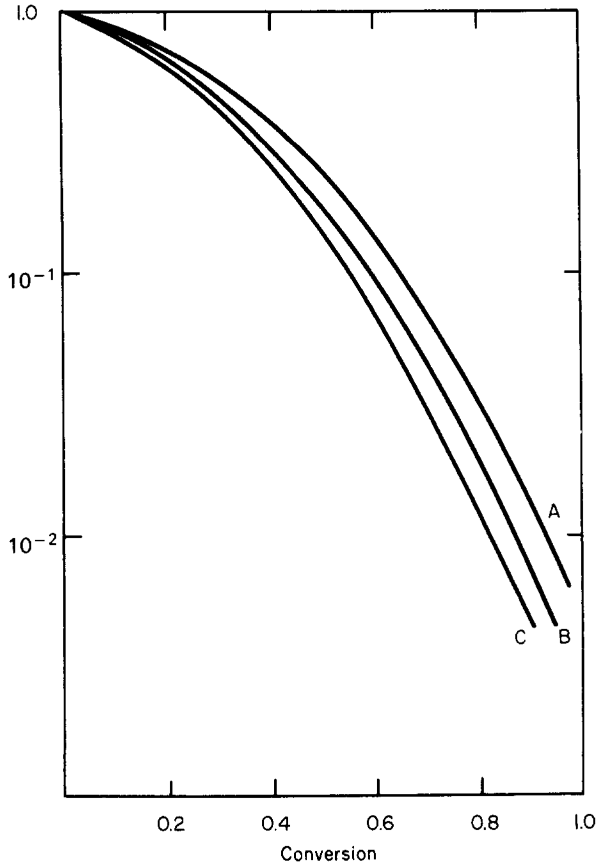
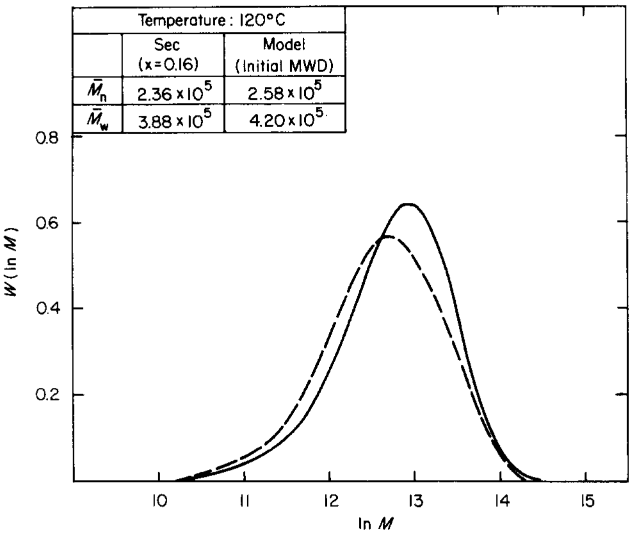


Figure 12 Diffusion-controlled termination: measured decrease in k_{tc} with conversion at 3-temperature levels (curve A: 160°C; curve B: 140°C; curve C: 120°C) for styrene polymerization



Temperature : 120°C		
	Sec (x=0.16)	Model (Initial MWD)
$\bar{M}_n$	2.36×10^5	2.58×10^5
$\bar{M}_w$	3.88×10^5	4.20×10^5

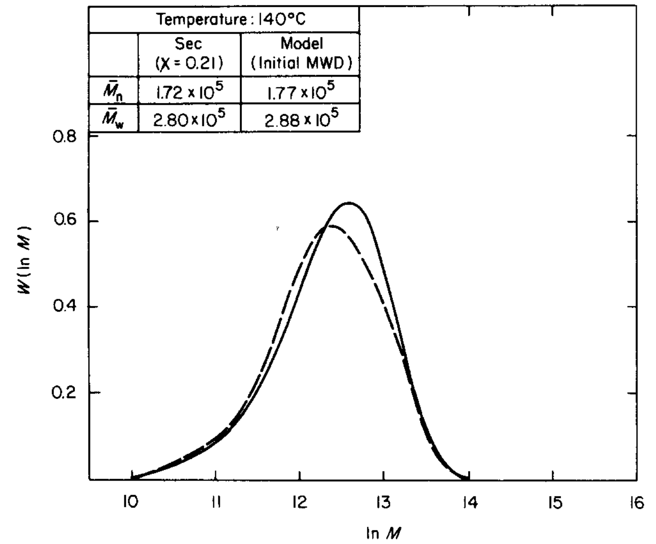
Figure 13 Measured (SEC) and predicted molecular weight distributions at low conversions and 120°C (X=0.16)

Also shown are $\bar{M}_w$ values measured by LALLSP. The value of $C_p = 1.1 \times 10^{-4}$ seems to underestimate $\bar{M}_w$ at 120°C but is about right for 140°C. Considering the low branching frequencies observed and measurement errors, it is not possible to find the temperature dependence of C_p. The site for transfer to polymer is most certainly a hydrogen on the methyl group. This has been confirmed in an independent study on the kinetics of the copolymerization of styrene/*p*-methyl styrene[5], where it was observed that long chain branching frequencies approached zero as the composition of the copolymer approached 100% styrene.

Figure 10 shows model predictions of $\bar{\lambda}_n$ for 120°C and the typical rapid increase at high conversions. The branching frequencies are clearly very low for the thermal polymerization of *p*-methyl styrene. As mentioned previously, branching frequencies could be substantially increased with the use of a chemical initiator, particularly one which generates hot radicals.

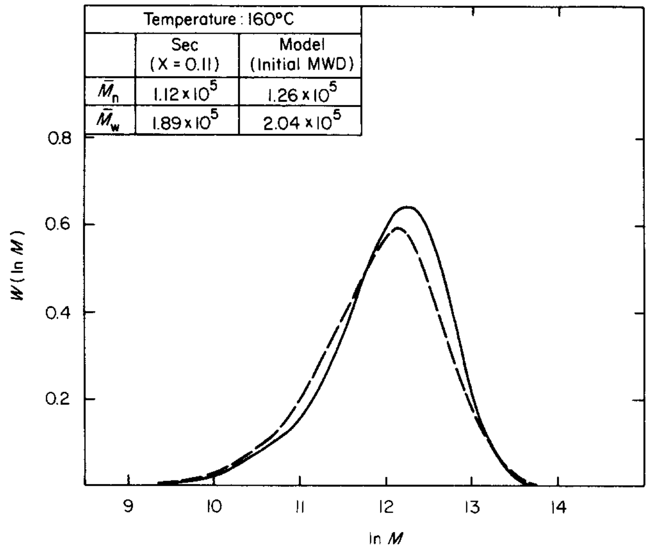
Figures 11 and *12* show the decrease of the diffusion-controlled termination constant with conversion for the thermal polymerization of styrene and *p*-methyl styrene. It is interesting to note that the decrease in k_{tc} is much greater for styrene. One could attribute this to the methyl group on the benzene ring as being responsible for the generation of free volume by its rotation and thus increasing the self-diffusion of the poly(*p*-methyl styrene) radicals at high conversions. *Figure 11* indicates a small increase in k_{tc} before a rapid decrease. This may be due to a greater dependence of polymer coil size on concentration for poly(*p*-methyl styrene).

Figures 13, *14* and *15* show measured and predicted



Temperature : 140°C		
	Sec (X=0.21)	Model (Initial MWD)
$\bar{M}_n$	1.72×10^5	1.77×10^5
$\bar{M}_w$	2.80×10^5	2.88×10^5

Figure 14 Measured (SEC) and predicted molecular weight distributions at low conversions and 140°C (X=0.21)



Temperature : 160°C		
	Sec (X=0.11)	Model (Initial MWD)
$\bar{M}_n$	1.12×10^5	1.26×10^5
$\bar{M}_w$	1.89×10^5	2.04×10^5

Figure 15 Measured (SEC) and predicted molecular weight distributions at low conversions and 160°C (X=0.11)

molecular weight distributions for poly(*p*-methyl styrene) synthesized at low conversions where long chain branching is not significant. The theoretical curves are instantaneous at zero conversion. The agreement between measured and predicted distributions is likely within experimental error.

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