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Pyrolysis of Monodisperse Poly-α-Methylstyrene*

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Pyrolysis of monodisperse poly-α-methylstyrene of wide molecular weight range (M:25,000–5,000,000) was studied isothermally under vacuum in the temperature range 240–280 °C. Thermogravimetric analysis was used for measuring the rate of degradation, and gel permeation chromatography for analyzing the molecular weight and molecular weight distribution as a function of conversion.

The initial rate of monodisperse poly-α-methylstyrenes, and the deuterated samples (poly-α-trideuteromethyl-β, β-dideuterostyrene) increases with increasing molecular weight. At molecular weight higher than 1×10^6, the initial rate continues to increase almost linearly instead of being constant as concluded from earlier work. The molecular weight distribution ratio, M_w/M_n, increases as a function of conversion and approaches the most probable distribution. The results conform to a degradation mechanism with random initiation.

The curves of initial rate as a function of molecular weight lead to higher zip lengths than previous estimates. Attempts at simultaneous estimation of zip length and transfer constant from the rate and molecular weight data led to inconsistent results. If the variation of termination rate with molecular weight plays a role, this variation must be less than that derived naively from melt viscosity. Bimodal molecular weight distributions were not found.

Key Words: Degradation; deuterated poly-α-methylstyrene; molecular weight; poly-α-methylstyrene; pyrolysis; termination; transfer; zip length.

1. Introduction

Poly(alpha-methylstyrene) occupies a position of special simplicity in the free radical chain theory of polymer pyrolysis. It yields monomer almost exclusively, and in the low molecular weight range the rate is nearly proportional to molecular weight.

It is generally agreed that initiation is at random along the chain and that the zip length (ratio of propagation to termination plus transfer) is large, but numerical estimates of the zip length and other kinetic parameters have scattered considerably (table 1) [1–6].[1] The availability of monodisperse poly-(alpha-methylstyrene) of higher molecular weight up to five million, as well as deuterated analogs, led us to reinvestigate the kinetic relations in the hope of resolving disagreements. In addition, following the pioneer work of Cowie and Bywater [3] we examined molecular weight distributions as a function of conversion. The most pertinent experimental data are the rate of volatilization and the molecular weight of residue as a function of conversion to volatiles, and the initial rate of volatilization as a function of initial molecular weight. Primary comparisons have been made with the rate eq (1) due to Simha, Wall and Bram [7]

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** Deceased.

[1] Figures in brackets indicate literature references at the end of this paper.

TABLE 1. *Activation energy and kinetic parameters of thermal degradation of poly-α-methylstyrene.*

Description of Polymer Sample	Technique used	E_a (kJ/mole)	Z(0)	σ(0)	Ref.
M_v: 70,000	T.G.A.	188	–	–	6
M: 350,000	T.G.A.	243	–	–	5
M: 79,000–1,120,000 (fractionated)	T.V.A.	272 ± 21	1,340	–	1
M: 410,000 (anionic polym.)	G.P.C.		50 250	100 (226 °C) 11 (236 °C)	3
M: 158,000 428,000 660,000 Monodisperse in solutions of decalin/diphenylether	V.P.C.	259 ± 8	5 × P_n (0)	–	2
M_v: 7,400–1,210,000 (monodisperse) in mixtures with polystyrene	V.P.C.	272	–	–	4

and with the "intermediate" eq (2) of Simha [8, 9] which connects rates of molecular weight change and of conversion to volatiles.

$$\lim_{\tau\to 0} dC/d\tau = (1+\sigma)N - 4S/N$$

$$\begin{aligned} S = {} & (1+\sigma)[(N^2 - L^2)/4] \\ & - (2+\sigma)(1 - 3\epsilon/4)[(1-\epsilon)/\epsilon^2] \\ & \times \{(N\epsilon/2)(1-\epsilon)^{-1} - 1 - [(L/2 - 1) \\ & \cdot \epsilon(1-\epsilon)^{-1} - 1](1-\epsilon)^{(N-L)/2}\}. \end{aligned} \tag{1}$$

$$\begin{aligned} & \frac{dC}{dt}\left\{1 + \frac{2}{P_n}\left(\frac{1}{\epsilon} - 2\right)\right\} \\ & + 2\left(\frac{1}{\epsilon} - 2\right)[(1-C)/P_n{}^2]\frac{dP_n}{dt} = 2k_1\left\{\frac{1}{\epsilon} + \sigma \right. \\ & \left. - \left(\frac{3}{\epsilon} - 1\right)\Big/P_n + \left(\frac{\sigma}{2}\right)\left(\frac{3}{\epsilon} - 7\right)\Big/P_n\right\}(1-C) \end{aligned} \tag{2}$$

These equations, developed in the references cited, presuppose a radical chain process of four steps:

Initiation

$$P_n \xrightarrow{k_1} R_{n-i} + \mathrm{R}_i$$

Propagation

$$R_i \xrightarrow{k_2} R_{i-1} + M$$

Transfer (Intermolecular)

$$R_i + P_n \xrightarrow{k_3} P_i + R_j + P_{n-j}$$

Termination (Disproportionation)

$$R_i + R_j \xrightarrow{k_4} P_i + P_j$$

where R_i = free radical species of chain length i
P_i = polymer molecules of chain length i, in reaction equations only.

Symbols have the following meanings:

W = sample weight
C = conversion = $1 - (W/W_0)$
τ = k_1t, reduced time
P = degree of polymerization, except in reaction equations
$P_n(\tau)$ = number average degree of polymerization at reduced time τ
N = number of chain carbon atoms = $2P$
L = number of chain carbon atoms in smallest molecule that cannot evaporate
σ = $\dfrac{\text{probability of transfer}}{\text{probability of initiation}} = (k_3R/k_1)$
Z = number average ziplength $1/\epsilon - 1$
$= \dfrac{\text{probability of propagation}}{\text{probability of transfer + probability of termination}}$.
ϵ = implicitly defined via Z

For random initiation [7]

$$Z = \frac{k_2}{k_4R(1+\sigma/2)} \tag{3}$$

Related equations due to Boyd [10–14] are also considered.

2. Experimental

2.1 Materials

The monodisperse polymers are listed in table 2. They include poly-α-methylstyrene (M = 25,000 − 5 × 10^6) and poly-α-trideuteromethyl-β,β-dideuterostyrene (M = 10^5 − 5 × 10^6).

The deuterated monomer was prepared by Grignard reaction using perdeutero-acetone bromobenzene and magnesium. The polymer samples were prepared by initiation by n-butyllithium in benzene and termination by methanol or tetrachloroethylene at a temperature of −78 °C [15–16]. The monofunctional initiators (such as isomers of butyllithium) have an important advantage over the electron transfer initiators (such as Na-biphenyl and Na-naphthalene), because the former give products with unimodal distribution while the latter results in a polymer with bimodal distribution due to accidental killing of one of the two carbanions of the growing chains.

The initially precipitated and dried polymers contained monomer and the lithium salt as the only expected impurities. Purifications were carried out by precipitating the polymer solution in benzene with methanol, twice. The precipitations were done by slowly dripping the polymer solution from a separatory funnel into a beaker containing excess methanol with continuous stirring by a mechanical stirrer. The precipitates were then filtered, rinsed with methanol, dissolved in benzene and freeze-dried. After freeze drying the fluffy material was dried in a high vacuum line having a diffusion pump. This drying process lasted at least a week, in which the freeze-dried sample (kept in a round bottom flask) was heated daily for eight hours at 90 °C. The drying process was checked by thermogravimetric analysis, yielding less than 0.5 percent volatiles for most material. For the degradation studies, the presence of traces of benzene was not critical.

2.2 Molecular Weight Measurement

The viscosity average molecular weight of poly-α-methylstyrene as listed in table 2 was determined from the intrinsic viscosity measurement in benzene as solvent and was calculated using the Mark-Houwink equation: $[\eta] = 1.08 \times 10^{-4} M_v^{0.71}$. It was assumed that the relation is valid for the high molecular weight range both for the nondeuterated and the deuterated samples of poly-α-methylstyrene. Gel permeation chromatography was used as described elsewhere. [17].

TABLE 2. *List of polymer samples used in the experiments.*

A. *Monodisperse Poly-α-methylstyrene.*

Sample No.	$[\eta]$ 30 °C	M_v (Viscometry)	M_n (G.P.C.)	M_w (G.P.C.)	M_w/M_n
1				25,000	
2	0.282	65,000			
3	0.411	110,000	105,000	110,000	1.05
4	1.018	400,000	360,000	400,000	1.11
5	1.045	412,000			
6	1.762	853,000			
7	1.995	1,151,000	1,046,000	1,151,000	1.10
8	2.376	1,321,000			
9	2.968	1.784,000			
10	5.335	4,570,000			
11	6.328	5,165,000			

Note: The G.P.C. curves are symmetrical and narrow for all the above polymers which indicate the monodispersity of the samples

B. *Monodisperse Poly-α-trideuteromethyl-β,β-dideuterostyrene*

Sample No.	$[\eta]$ 30 °C	M_v
1	0.4080	109.000
2	1.7216	830,000
3	2.5826	1,470,000
4	7.4530	6,540,000

2.3 Thermal Decomposition

Rate of volatilization experiments were done using 10 mg samples in a high vacuum and a recording electrobalance. Temperatures were in the range 240 to 280 °C. For molecular weight and distribution studies, 400 mg samples were pyrolyzed in vacuum at 240 °C. At this low temperature of degradation the rate of degradation was slow enough so that the degradation taking place during the sample heating from room temperature to temperature of the experiment can be neglected. The time scale of the experiment, depending upon initial molecular weight of the sample and the extent of conversion expected, ran from 2 to 100 h.

2.4 Rates of Volatilization

The rate of degradation is presented as the rate of volatilization, dC/dt, versus conversion C, where

$$C = \frac{W_o - W}{W_o}$$

with W_o = initial weight of the sample, W = weight of the degraded sample at time t. The dC/dt were obtained by taking the slopes manually from the T.G.A. curves at different conversions.

Since the rate of conversion versus C is first order for poly-α-methylstyrene within the range up to 50 percent conversion, an extrapolation procedure was done on the linear portion to get the initial rate, $(dC/dt)_{C\to 0}$ with an uncertainty within 3 percent.

Figures 1 to 4 show the rate of degradation of poly-α-methylstyrene at different temperatures for four samples of different molecular weight, i.e. M = 5,165,000; 853,000; 400,000, and 25,000.

At the lower temperatures shown, the initial portion is atypical and may be horizontal or even exhibit a broad maximum.

The initial rates for each polymer sample at several degradation temperatures are given in table 3 from which the Arrhenius plot of log $(dC/dt)_{c\to 0}$ versus $1/T$ as shown in figure 5 and the plot of initial rate versus initial molecular weight as shown in figure 6 were obtained. The preexponential factor and the activation energy are included in table 3. The activation energy of the degradation of monodisperse poly-α-methylstyrene as obtained from this investigation has a value of 267 ± 10 kJ per mole of chemical repeating unit, which is independent of the initial molecular weight of the

Table 3. *Initial rates of degradation.*
A. *Monodisperse Poly-α-methylstyrene*

M	T (K)	$(dC/dt)_{C\to 0}\cdot 10^2$ (min^{-1})	E_a (kJ)	$I = \log(dC/dt)_{C\to 0}$ at $1/T = 0$
25,000	533.0	0.024	270.7 ± 4.2	22.93 ± 0.05
	553.0	0.230		
	563.0	0.620		
65,000	529.0	0.035	269.0 ± 5.9	23.15 ± 0.60
	533.6	0.066		
	543.0	0.165		
	553.2	0.530		
	566.0	1.960		
110,000	523.0	0.033	274.5 ± 3.8	23.93 ± 0.36
	533.0	0.105		
	543.0	0.350		
	553.0	1.020		
400,000	523.0	0.060	274.9 ± 18.4	24.26 ± 0.87
	533.0	0.200		
	543.0	0.630		
853,000	513.0	0.024	282.0 ± 10.9	25.18 ± 1.10
	523.0	0.120		
	533.0	0.330		
	545.5	1.530		
	553.5	3.200		
1,151,000	513.0	0.040	260.2 ± 7.5	23.13 ± 0.28
	523.0	0.130		
	533.0	0.370		
	543.0	1.200		
1,321,000	513.0	0.058	245.6 ± 8.4	21.76 ± 0.83
	533.0	0.500		
	538.0	0.750		
	543.0	1.490		
1,784,000	513.0	0.055	248.9 ± 5.4	22.10 ± 0.54
	523.0	0.180		
	533.0	0.480		
	543.0	1.450		
4,570,000	513.0	0.070	272.4 ± 10.5	24.60 ± 1.05
	523.0	0.244		
	533.0	0.900		
	543.0	2.300		
5,165,000	517.0	0.155	271.5 ± 7.1	24.65 ± 0.72
	523.0	0.350		
	533.0	1.000		
	543.0	3.400		

Note: The average of the above activation energies is $E_a = 266.9 \pm 10.5$ kJ.

Table 3. *Initial rates of degradation.*
B. *Monodisperse poly-α-trideuteromethyl-β,β-dideueterostyrene*

M	T (K)	$(dC/dt)_{C\to 0}\cdot 10^2$ (min^{-1})	E_a (kJ)	$I = \log(dC/dt)_{C\to 0}$ at $1/T = 0$
109,000	523.0	0.024	264.8 ± 7.1	22.81 ± 0.68
	533.0	0.065		
	553.0	0.580		
	563.5	1.900		
830,000	513.0	0.021	303.3 ± 18.0	27.20 ± 1.80
	523.4	0.066		
	533.0	0.320		
	543.0	0.980		
1,470,000	515.0	0.045	255.6 ± 18.0	22.60 ± 0.90
	533.5	0.343		
	543.0	1.000		
6,540,000	513.0	0.130	254.4 ± 16.3	23.02 ± 1.62
	523.0	0.350		
	528.1	0.670		
	533.1	1.250		

sample. The same values had been reported by Brown and Wall [1] and Richards and Salter [4], while other values of 188 and 243 kJ/repeating unit had been reported by Jellinek [6] and by Madorsky [5].

The effect of initial molecular weight on the initial rate of degradation at 260 °C as shown in figure 6 up to $M = 10^6$ shows the same type of curves as was previously reported [1]. In the low molecular weight range, where radicals unzip to the end of the chain, the initial rate is proportional to the initial molecular weight, while in the high molecular weight range the zip length parameter governs and the initial rate should be independent of the molecular weight. Since previously the highest molecular weight of poly-α-methylstyrene ever degraded was of the order of one million, it was expected that the curvature occurring around $M = 10^6$ would continue leveling off at higher molecular weight. Instead, we find in the higher molecular weight range up to 5–6 × 10^6 a continuous (almost linear) increase of the initial rate with increasing molecular weight.

The degradation rate curves of the deuterated poly-α-methylstyrene show the same behavior as those of the nondeuterated sample, except the curves of the sample with $M_v = 830{,}000$ which indicate a sharp initial decrease in the rate before it degrades linearly. We think this is accidental, due to the presence of low molecular weight substances which would evaporate at the temperature used for the degradation.

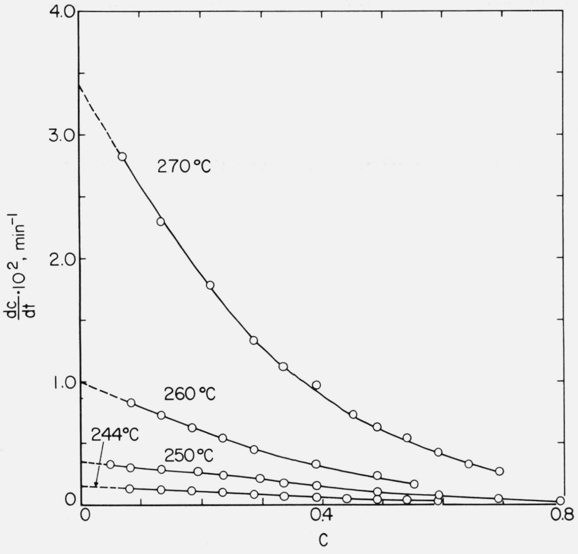

Figure 1. *Rate of volatilization of poly-α-methylstyrene with M = 5,165,000.*

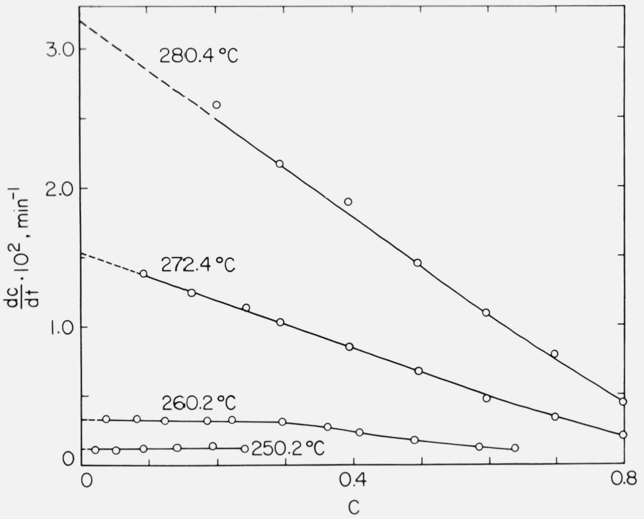

FIGURE 2. *Rate of volatilization of poly-α-methylstyrene with M = 853,000.*

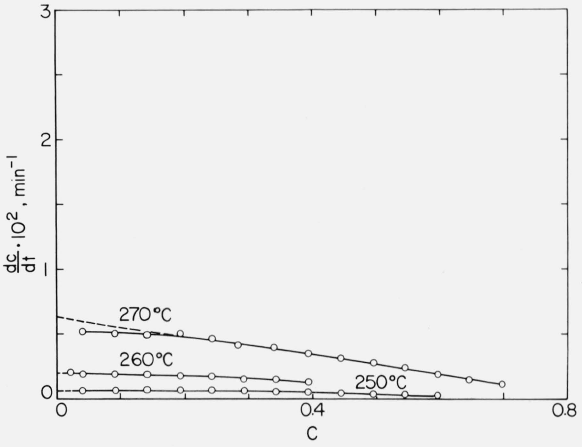

FIGURE 3. *Rate of volatilization of poly-α-methylstyrene with M = 400,000.*

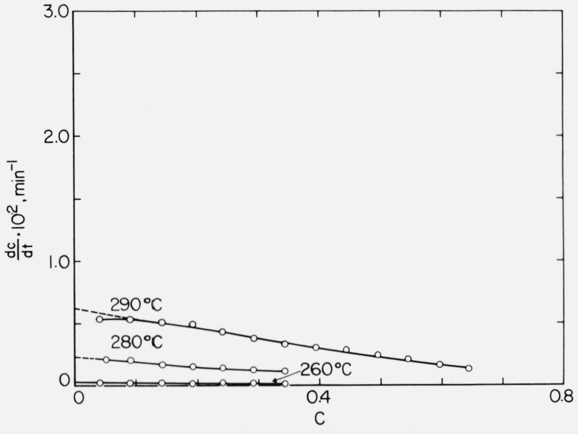

FIGURE 4. *Rate of volatilization of poly-α-methylstyrene with M = 25,000.*

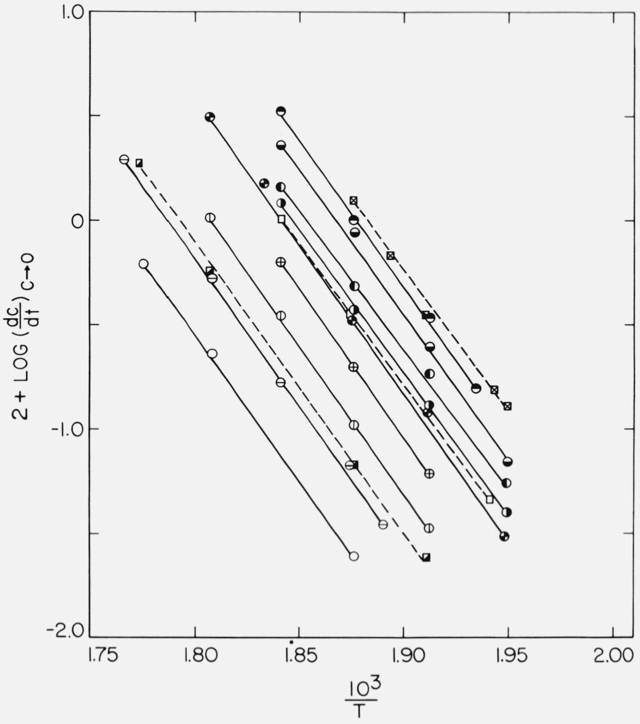

FIGURE 5. *Arrhenius plot of initial rates of volatilization of poly-α-methylstyrene. Molecular weights and symbols:*

Deuterated: ◪: 109,000; □: 1,470,000; ⊠: 6,540,000.

Nondeuterated: ○: 25,000; ⊖: 65,000; ⦶: 110,000; ⊕: 400,000; ◕: 853,000; ◑: 1,151,000; ◐: 1,321,000; ◒: 4,570,000; ◓: 5,165,000.

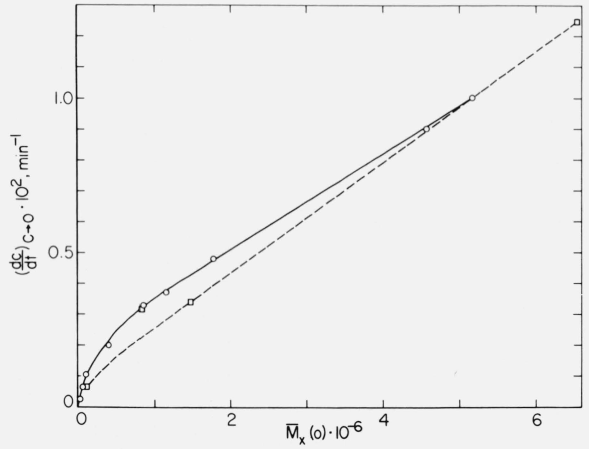

FIGURE 6. *The initial rate of degradation at 260 °C as a function of molecular weight.*

○: monodisperse poly-α-methylstyrene

□: monodisperse poly-α-trideuteromethyl-β,β-dideuterostyrene

These deuterated samples give the same activation energy as the non-deuterated samples, i.e. 270 kJ per mole of monomer unit, which was determined from the Arrhenius plot. Comparison of the initial rate curves versus molecular weight of the deuterated and the nondeuterated samples as shown in figure 6 indicates that the deuterated samples do not degrade at a significantly lower rate than the nondeuterated.

2.5 Molecular Weights and Distribution

Table 4 shows the variation of molecular weight as a function of conversion at 240 °C for several initial molecular weights. These results are roughly consistent with ref. [1]. Some peculiarities of mixtures are analyzed elsewhere [17]. The approach to $M_w/M_n = 2.0$ is evident. The much more rapid broadening of the high molecular weight component is notable. The pure monodisperse samples failed to give any indication of the bimodal distribution of Cowie and Bywater [3].

TABLE 4. *The molecular weight and molecular weight distribution of monodisperse poly-α-methylstyrene as function of conversion.*

Conversion %	$M_n \cdot 10^{-3}$		$M_w \cdot 10^{-3}$ GPC	M_w/M_n GPC
	OSM	GPC		
0	—	1030	1081	1.05
2.9	—	890	1011	1.24
8.9	—	730	920	1.26
16.5	—	603	829	1.37
42.5	270	270	515	1.91
73.4	120	114	231	2.03
81	75	74	163	2.20
0	410	410	430	1.05
6.5	370	357	400	1.12
10	349	346	393	1.14
39.5	158	149	255	1.71
49.5	135	139	238	1.71
58	93	88	175	1.98
0	107	104	107	1.03
4.0	98	97	105	1.08
8.1	97	94	104	1.11
18.9	90	85	97	1.14
27.3	85	80	94	1.18
32.	68	75	90	1.20
40.	61	69	87	1.26

3. Discussion

The present results all indicate that the zip length is large, in agreement with all previous work. However, there is wide disagreement between our estimates of zip length from rates of weight loss of small samples at higher temperatures and our estimates involving molecular weight changes of larger samples at 240 °C. The types of data will be considered separately, therefore.

3.1 Overall Arrhenius Parameters

There is no demonstrable variation in the activation energies of table 3. The values and standard deviations given are from least square lines for the Arrhenius equation, using the rate and temperature data listed. Although the TGA balance is probably accurate to 1 to 2 percent in instantaneous weights, the graphical methods used for estimating instantaneous rate and for extrapolating rates to zero conversion make a relative error of less than 3 percent in initial rates unlikely. The average E is $= 267 \pm 10$ kJ. The individual fluctuations in log of the pre-exponential A with E hide the systematic variation with molecular weight, which is better seen in rates at one temperature. The mechanism predicts a variation of E with molecular weight; as in the earlier literature [1] its absence must be attributed to a compensation in the activation energies for propagation and termination, E_2 and E_4.

TABLE 5. *Kinetic parameters deduced from figure 7 shift factors*

T K	$4k_1Z$ min^{-1}	Zm_0 g mol^{-1}	Z	k_1 min^{-1}
553	1.0×10^{-1}	6.9×10^5	5800	4.31×10^{-6}
543	3.1×10^{-2}	6.4×10^5	5400	1.45×10^{-6}
533	1.0×10^{-2}	6.9×10^5	5800	4.31×10^{-7}
523	3.1×10^{-3}	6.4×10^5	5400	1.45×10^{-7}

3.2 Correlation of Initial Rate and Molecular Weight

The relation of initial rate and molecular weight at constant temperature satisfies eq. (1) indicating the large but not closely determined zip lengths of table 5. This is best shown by first transforming eq. (1).

$$\lim_{\tau \to o} \frac{dC}{d\tau} = (1 + \sigma)N - \frac{4S}{N} \tag{1}$$

where

$$S = (1 + \sigma)\left(\frac{N^2 - L^2}{4}\right) - (2 + \sigma)\left(1 - \frac{3\epsilon}{4}\right)\left(\frac{1 - \epsilon}{\epsilon^2}\right)$$

$$\times \left\{ \frac{N\epsilon}{2(1 - \epsilon)} \right.$$

$$\left. - 1 - \left[\left(\frac{L}{2} - 1\right)\epsilon(1 - \epsilon)^{-1} - 1\right](1 - \epsilon)\,\frac{N - L}{2} \right\}$$

Take $N \gg L$, $L = 4$, consistent with exclusive monomer production and also $\frac{1}{\epsilon} \gg 1$

$$S \doteq (1 + \sigma)\,\frac{N^2}{4} - (2 + \sigma)\left(\frac{1}{\epsilon^2}\right)$$

$$\cdot\left\{\frac{N\epsilon}{2}-1-[1\cdot\epsilon\cdot 1-1](1-\epsilon)^{\frac{N}{2}}\right\}$$

$$\lim\frac{dC}{d\tau}\doteq(1+\sigma)N-(1+\sigma)N$$

$$+\frac{4(2+\sigma)}{N\epsilon^2}\left\{\frac{N\epsilon}{2}-1+(1-\epsilon)^{\frac{N}{2}}\right\}$$

$$\doteq\frac{8(1+\sigma/2)}{N\epsilon^2}\left\{\frac{N\epsilon}{2}-1+(1-\epsilon)^{\frac{N}{2}}\right\}$$

Substituting $N = 2P$

$$\lim_{\tau\to o}\frac{dC}{d\tau}\doteq\frac{4(1+\sigma/2)}{P\epsilon^2}\{P\epsilon-1+(1-\epsilon)^P\}$$

$$\lim_{\tau\to o}\frac{\epsilon}{4\left(1+\frac{\sigma}{2}\right)}\frac{dC}{dt}\doteq 1-\frac{1}{P\epsilon}+\frac{1-\epsilon)^P}{P\epsilon}$$

Now

$$(1-\epsilon)^P=\left[(1-\epsilon)^{\frac{1}{\epsilon}}\right]^{\epsilon P}.$$

For large $1/\epsilon$ the quantity in brackets has the limit e^{-1} and numerically approaches it within a few percent for $1/\epsilon > 10$ [18]. Thus, for sufficiently large $1/\epsilon$ and any P, and noting that $\tau = k_1 t$

$$\lim_{t\to o}\frac{\epsilon}{4k_1(1+\sigma/2)}\frac{dC}{dt}\doteq 1-\frac{1}{P\epsilon}(1-e^{-P\epsilon})$$

The right hand side is a function of $P\epsilon$ only. At small and large $P\epsilon$ the limits are $\frac{P\epsilon}{2}$ and 1, respectively, in agreement with previous work [7]. For small ϵ we can substitute $Z = \frac{1}{\epsilon} - 1$ for $\frac{1}{\epsilon}$ and use the alternative form

$$\lim_{t\to o}\frac{1}{4k_1Z(1+\sigma/2)}\frac{dC}{dt}\doteq 1-\frac{Z}{P}\left(1-e^{-\frac{P}{Z}}\right)\qquad(4)$$

A plot of $\log\frac{dC}{dt}$ against $\log P$ or $\log M$ is therefore described by the universal function of $\frac{P}{Z}$ above, with shift factors, as shown in figure 7 and its legend. Applying the numerical values there, we obtain the zip lengths and $k_1\left(1+\frac{\sigma}{2}\right)$ values of table 5. The possibility of large diagonal shifts implies an uncertainty of 50 percent. Arrhenius treatment of these values yields an activation energy of 251 kJ for k_1, in agreement with table 3 but poorly defined. According to these rate data, the higher molecular weight polymers offer no feature not contained in eq (1) and its limiting form eq (4) but the zip length is revised upward.

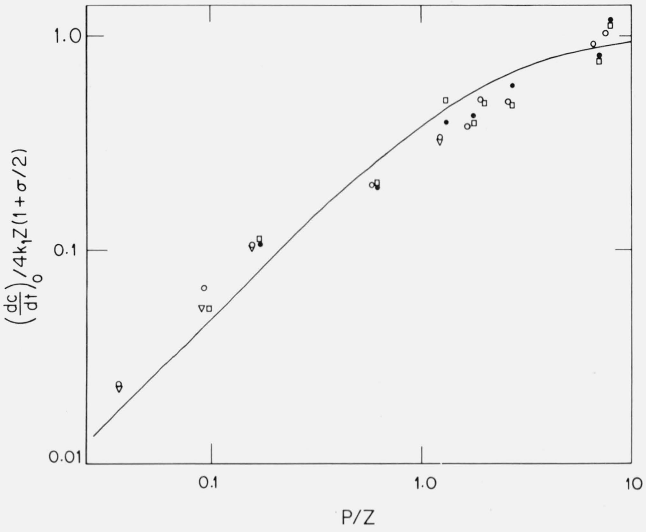

FIGURE 7. *Initial rate as a function of molecular weight. Curve and coordinates, equation 4. Point symbols and corresponding temperatures, rates coinciding with $(dC/dt)_0/4k_1Z = 1$, and molecular weights coinciding with $P/Z = 1$:*

▽, 553 K, 10×10^{-2} min^{-1}, 6.9×10^5; □, 543 K, 3.12×10^{-2} min^{-1}, 6.4×10^5; ○, 533 K, 1×10^{-2} min^{-1}, 6.9×10^5; ●, 523 K, 3.12×10^{-3} min^{-1}, 6.4×10^5.

The deuterated polymers should have a lower k_3 and σ, since deuteration of a sensitive position commonly lowers its susceptibility to chain transfer. They may also have lower values of the depropagation rate constant k_2, according to speculation relying on equilibrium data [16]. The absence of any marked effect on depolymerization rate indicates that k_2 is not greatly lowered by deuterium substitution. The result of a concurrent lowering of k_2 and σ in the expression for the zip-length, eq (3), might appear ambiguous, but the $\sigma/2$ term in the denominator is always too small to make much difference. Perhaps very precise molecular weight measurements, or a more sophisticated analysis of rate as a function of conversion, will be able to demonstrate effects of deuteration on a very small σ.

The changes of rate with conversion or of conversion with time are in general agreement with ref. [1] but furnish no new information. Boyd [10] has stated a number of relations easily convertible to linear plots, which would be very informative if samples having the "most probable" distribution were available. Unfortunately, his computations for narrow distribution with no transfer [13] show that these relations do not always apply to narrow distributions.

3.3 Molecular Weight Changes

Molecular weights were studied under different conditions from those used for volatilization rates, and this may impede comparison with rate data.

1. The temperature was low, 240 °C. Few TGA rate data are available for correlation and the few runs made showed an atypical course.

2. Thicker layers were used which may have retarded monomer escape [19].

3. Plots of conversion against time exhibited scattering of data, which suggests possible temperature excursions. Plots of molecular weight against conversion were relatively smoother, figure 8. They make a rough match with Boyd's theoretical results [13] for *Z* in the neighborhood of 1000, with no transfer. This is also in accord with the earlier data and calculation of ref. [1]. The molecular weight distribution data also agree roughly with Boyd's results on this basis, figure 9. Attempts were made also to apply the "intermediate equation", of Simha (eq 2) but to do this it was necessary either to extrapolate the TGA rates downward or alternatively to suppose that the relation of molecular weight to conversion was insensitive to temperature. The latter is assumed in figure 10. Equation 2 with large zip takes the approximate form

$$\frac{1}{P}\frac{dC}{dt}\left\{(1-C)^{-1}+\frac{d\ln P}{dC}\right\}=\frac{1}{2Z}\cdot 2k_1$$

$$\left(Z+\sigma-\frac{3Z}{P}-\frac{3}{2}\frac{Z}{P}\sigma\right) \qquad -\frac{1}{2Z}\frac{dC}{dt}(1-C)^{-1} \quad (5)$$

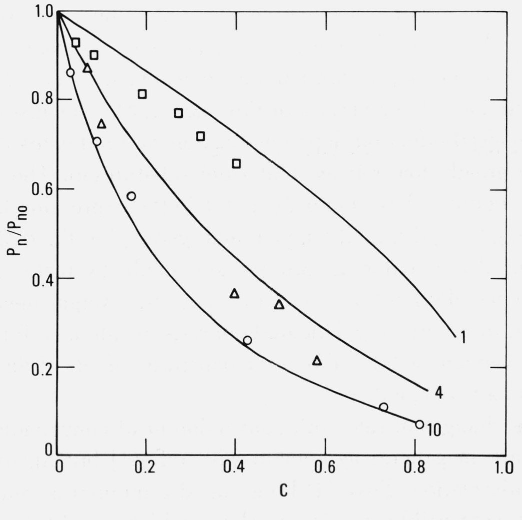

FIGURE 8. *Number average DP as a function of conversion for monodisperse poly-α-methylstyrene at 240 °C.*

Initial DP: ○, 8730; △, 3480; □, 881. Curves, computed by Boyd [12] for initial M_w/M_n = 1.11. Numbers on curves, Boyd P_{no}/Z values.

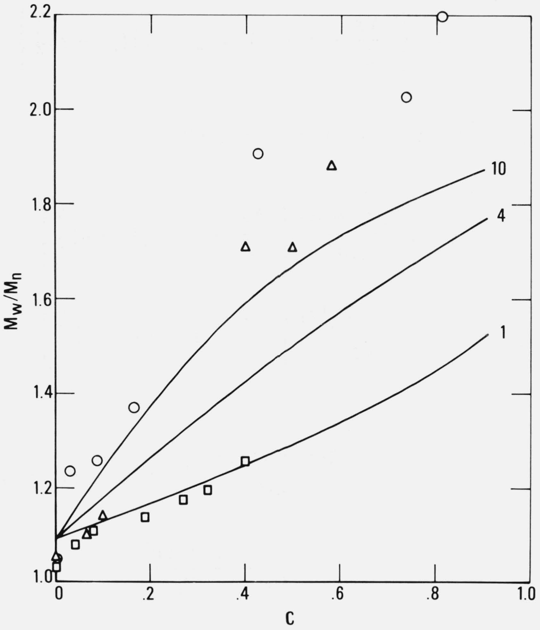

FIGURE 9. *Change of molecular weight distribution with conversion.*

Experimental: ⊙ M_{vo} = 1,151,000, △ 400,000 □ 110,000. Curves from computations of Boyd [12] for initial M_w/M_n = 1.1. Numbers on curves P_n (0)/Z.

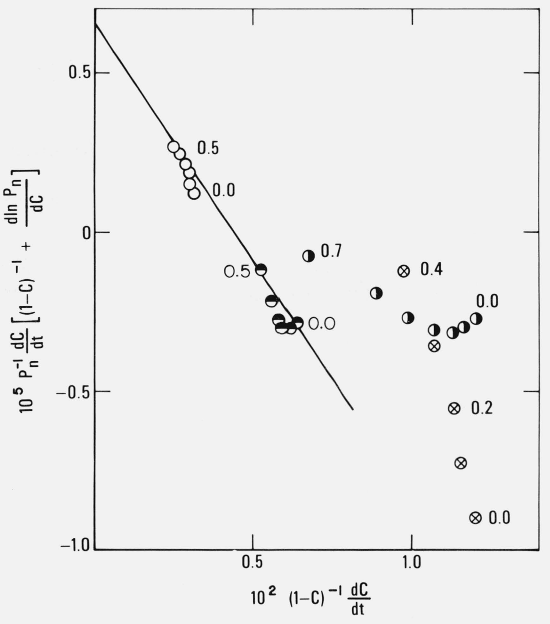

FIGURE 10. *Intermediate equation plot based on $P_n(C)$ data at 240 °C and dC/dt(C) data at 270 °C.*

Initial molecular weights: ○ 110,000; ◒ 400,000; ◑ 1,151,000 old GPC values; ⊗ 1,151,000 GPC values of Table. 4. Numbers near points indicate conversion.

For $Z \gg \sigma$ and $Z \gg \frac{Z}{P}$, a plot of the left side versus $\frac{dC}{dt}(1 - C)^{-1}$ has an intercept of k_1 and a slope $-\frac{1}{2Z}$. From figure 10 we derive $Z = 324$ and an associated $k_1 = 0.64 \times 10^{-5}$ min^{-1} at 270 °C for the two lower molecular weights there. The data for the 1,151,000 molecular weight sample deviate, especially at low conversion, and would indicate a higher zip. Thus these data show an internal inconsistency between high and low molecular weights and indicate a considerably lower zip than our rate data. Simpler forms of eq (5) valid at zero conversions exhibited the same mutual inconsistencies. Equation 5 formally offers a relation involving σ independent of the rate eq (1); however σ here is additively combined with a large Z and thus a small σ cannot be determined without unattainably precise experimental data. The generally smaller Z indicated by the low-temperature molecular weight experiments agrees with some earlier reports on temperature effects [2, 3] and might be explained by a change of mechanism. In these geometrically thicker and less fluid samples monomer escape could be retarded [19]. Transfer to monomer, even to a small extent, would then appreciably reduce the zip length [20].

3.4 Possible Variation of Zip Length with Diffusion Controlled Termination

Although the rate data seem consistent with eqs (1) and (4), the inconsistencies of figure 10 suggest that Z might vary with molecular weight of polymer. In the simple case of no transfer (ref. [10], eq (7), (10b))

$$Z = \frac{1}{2}\left(\frac{m}{\rho}\right)^{\frac{1}{2}} \frac{k_2}{k_1^{\frac{1}{2}} k_4^{\frac{1}{2}}}.$$

Both k_1 and k_4 may be diffusion controlled [20]; if so, Z is essentially variable. Although theory is in an incomplete state [21–25] the weight of opinion is that the influence of molecular size of itself on k_4 is rather small in the range of large molecular sizes, but that k_4 should vary as the reciprocal of the medium viscosity. Since melt viscosity usually goes as M for low molecular weights and as $M^{3.4}$ for higher M, a large indirect effect of molecular weight on k_4 could be expected.

Viscosity effects on k_1 via cage recombination of fragments are difficult to compute directly. One approach has been to assume exact compensation of effects on k_1 and k_4 as a consequence of detail balancing [20] and therefore no net viscosity effect on radical concentration and rate of monomer production. Another extreme possibility is that the initiating chain scission is followed rapidly by loss of a monomer unit rendering the cage ineffective, so that k_1 is not appreciably subject to cage effects. If k_4 alone varies one would predict $k_4 \; \alpha \; M^{-3.4}$, $Z \; \alpha \; M^{1.7}$. A reexamination of figure 7 shows a log slope of about 0.5 over a large part of the middle range. If this behavior is reinterpreted as due exclusively to variation of Z, where $P/Z \gg 1$, it indicates $Z \; \alpha \; M^{0.5}$ in place of the expected exponent 1.7. Thus the variation, if it exists, is much smaller than predicted from viscosity.

4. Summary

In pyrolyzing samples of monodisperse poly(α-methylstyrene), the initial rate of monomer production as a function of molecular weight increases steadily in the range up to $M = 5{,}000{,}000$. The approach to the asymptotic upper limit is slow. This behavior is entirely in accord with the rate equation of Simha, Wall and Brown, as demonstrated by conversion to an analytic function of the ratio of the degree of polymerization to zip length, valid at high zip length. Completely deuterated samples behave much like the ordinary ones, contradicting an earlier supposition that the reverse propagation rate constant would be appreciably less in the deuterated polymer. The rate data considered alone are compatible with a constant zip length of about 5000, which is larger than previous estimates. The concurrent rates and molecular weight changes of larger samples at 240 °C lead to a considerably lower zip length in the neighborhood of 324, inconsistent with the above, which varies with molecular weight in some treatments of data. The possibility of a molecular weight dependent termination rate constant and zip length was briefly considered as an explanation, but these lower and varying apparent zip lengths are more readily explained by Jellinek's suggestion of chain transfer to monomer in samples having retarded monomer escape.

5. References

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