A Study of the Thermal Degradation of Polystyrene by Thermal Volatilization Analysis

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Synopsis

A TVA study of several anionic polystyrene samples, having number average molecular weights in the range of 4.6×10^3 to 2×10^6, reveals a hitherto unobserved molecular weight dependence of the overall apparent Arrhenius preexponential factor as determined by the method of Roche.[2] The latter effect is discussed in terms of a model in which the zip length and chain-scission rate constants are both functions of molecular weight. It is suggested that the functional dependence of the kinetic parameters on molecular weight is a reflection of their hydrodynamic coupling to the viscosity of the molten polymer.

INTRODUCTION

Most previous attempts to rationalize the in vacuo thermal degradation reactions of macromolecules in kinetic and mechanistic terms have focused on their behavior under isothermal conditions at appropriate temperatures. In many technological applications, however, macromolecular materials are often exposed to nonisothermal conditions, and it is therefore highly relevant to explore their degradation behavior when the temperature is progressively changing. For many years, thermogravimetric analysis has been conducted in a linearly increasing temperature regime, and a general treatment of the thermogravimetry of polymers under these conditions has been presented by a number of authors.[1] The kinetic analysis of dynamic thermogravimetry inescapably leads to integral equations which require numerical solution. The numerous integral approximations have been reviewed.[1a] In a previous paper,[2] one of us showed, using a computer-simulation approach, that it is possible to circumvent the difficulties involved and to derive the Arrhenius parameters for a reaction if it is conducted under conditions where the temperature is linearly increasing at a number of different heating rates. It was also shown[2] that any level of mechanistic complexity can be incorporated into the computer-simulation program, and hence the behavior of complex systems under nonisothermal conditions can be predicted.

McNeill[3–7] has developed the use of the dynamic molecular still for the in vacuo study of polymer degradation reactions under a linearly increasing temperature regime. The latter use of the dynamic molecular still is called thermal volatilization analysis (TVA). Using this technique at a *fixed* heating rate, McNeill and co-workers have reported the results of a variety of polymer degradation studies (ref. 9 and references cited therein).

In the present paper we report the results of a TVA study of polystyrene. We have obtained the apparent Arrhenius parameters for the overall volatilization process using the $\ln \beta$-versus T_M^{-1}-method described previously.[2] In order to explore in detail the dependence of the observed kinetic behavior on the initial molecular weight of the polymer we have examined ten well-characterized samples of polystyrene ranging in number-average molecular weight from 4.6×10^3 to 2.7×10^6 g/mole. In order to account for our results quantitatively in terms of a molecular model for the reaction, it is necessary to include not only the mechanistic features delineated by earlier workers but also a molecular weight dependence for the chain-scission rate constant and the zip length of the depolymerization reaction. The latter molecular weight dependence is heuristically related to the melt viscosity of the degrading polymer mass. The molecular model proposed here can be incorporated in a straightforward way into the computer simulation of the TVA experiment described previously.[2] The parameters of the model have been adjusted to give the best fit to the experimental observations.

EXPERIMENTAL

Nine of the ten samples examined in the present study were obtained from the Pressure Chemical Co., Pittsburgh, Pa. These were all narrow molecular weight distribution polymers prepared anionically at room temperature using butyllithium in benzene. A tenth sample (S114) was prepared by the Dow Chemical Co. for the IUPAC round-robin program.[8] The characterizing data for these polymers are summarized in Table I (see Results).

The apparatus for thermal volatilization analysis has been described previously.[2] In the present study, the precision and accuracy of the temperature measurements were significantly improved by using a thermocouple (Fe/Constantan) sealed inside the degradation vessel and in contact with the surface of the reaction zone. The output voltage of the thermocouple was measured by a Hewlett-Packard Model 419A d.c. Voltmeter and recorded in one channel of a Linear Corporation Model 282 two-channel integrating recorder.

Samples of polymer for degradation were typically 1–2 mg in size and were spread as a fine powder on the bottom of the reaction vessel. For some experiments, a thin film of polymer was cast in situ in the reaction vessel from 1–2 ml of a solution of the polymer in toluene at a concentration determined by the range of film thickness required.

In a typical experiment, the apparatus was evacuated to 10^{-4} torr and continuously pumped for several hours before the linear increase in temperature was initiated. The improved accuracy in the measurement of temperature provided by the in situ thermocouple allowed the use of higher heating rates without the complications arising from temperature lag between the oven and the reaction zone discussed previously.[2,4] Nominal heating rates, β, of 5°, 8°, 10°, and 15°/min were used. The actual heating rate was measured in all experiments from the recorded temperature–time profile.

The apparent Arrhenius parameters for the overall process were evaluated from the measured values of β and T_M, the temperature of the maximum in the TVA thermogram, using the $\ln \beta$-versus-T_M^{-1} method described previously.[2] It is worth reemphasising here that this method requires only the

TABLE I
Maximum Temperature T_M of TVA Thermograms

Sample[a] no.	M_n	M_w/M_n	β, deg/min[b]			
			5	8	10	15
1	4.6×10^3	1.09	687.1 (689.3)[c]	695.7 (697.1)	699.1 (700.9)	705.7 (707.9)
2	9.7×10^3	1.06	682.1 (685.3)	690.1 (693.2)	694.3 (697.1)	699.9 (704.1)
3	1.9×10^4	1.04	681.6 (680.6)	690.3 (688.5)	693.9 (692.3)	699.9 (699.3)
4	4.9×10^4	1.04	677.1 (674.5)	684.5 (682.3)	688.1 (686.0)	696.1 (692.9)
5	9.62×10^4	1.02	671.9 (672.0)	679.5 (679.7)	685.1 (683.4)	690.9 (690.2)
6	1.64×10^5	1.05	670.8 (672.0)	677.7 (679.7)	681.3 (683.4)	688.6 (690.2)
7	3.92×10^5	1.05	669.5 (672.0)	677.6 (679.7)	681.1 (683.4)	687.1 (690.2)
8	7.73×10^5	1.12	673.1 (672.0)	680.5 (679.7)	685.1 (683.4)	691.3 (690.2)
9	1.99×10^6	1.03	673.3 (672.0)	680.1 (679.7)	683.3 (683.4)	690.3 (690.2)
10	2.7×10^6	1.5	673.5 (672.0)	682.5 (679.7)	684.3 (683.4)	690.9 (690.2)

[a] Samples 1–9 were obtained from the Pressure Chemical Co., Pittsburgh. Sample 10 is S114 from the Dow Chemical Co.

[b] These are the nominal values for the linear heating rate. Actual heating rates are $5(4.92 \pm 0.04)$; $8(7.78 \pm 0.11)$; $10(9.70 \pm 0.15)$; $15(14.33 \pm 0.33)$ deg/min.

[c] The values for T_M calculated from the model described by eq. (3) with $k_v = 3.65 \times 10^{16} \exp(-5.8 \times 10^4/RT)$; $k_{cs} = 1.67 \times 10^6 \exp(-4 \times 10^4/RT)$; $\gamma = 0.625$; and $\delta = 1.5$. (T_M in °K).

location of T_M for each value of β; it does not require the accurate measurement of the rate of volatilization.

RESULTS

A typical TVA thermogram is shown in Figure 1. The temperature at the maxima of the observed thermograms obtained at four different heating rates
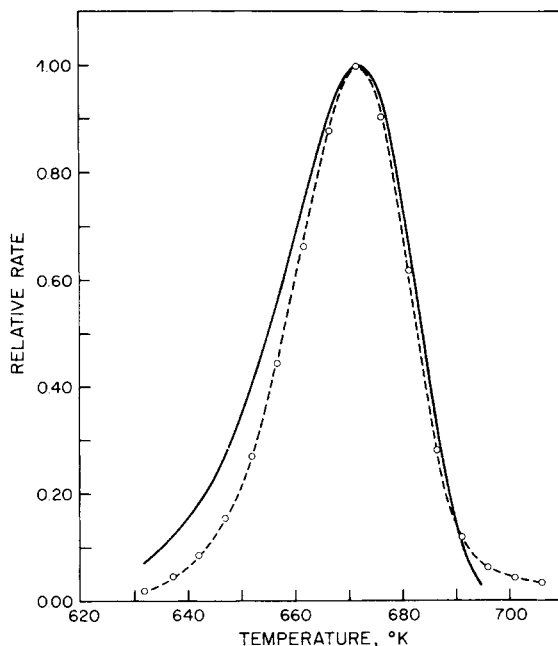

Fig. 1. (a) Observed (dashed curve) and (b) calculated (full curve) TVA thermogram for sample 5; $\beta = 5°/min$. Parameters of eq. (3) used in calculation of (b) are given in footnote b to Table I.
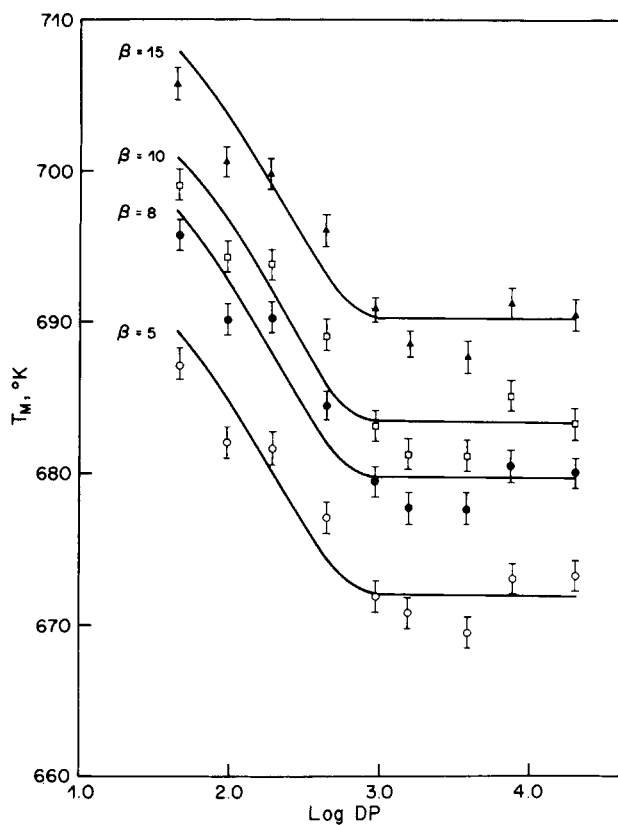
Fig. 2. (a) Observed (single points) and (b) calculated plots of T_M, °K, the temperature maxima of the TVA thermograms, vs. log (initial number-average degree of polymerization) for β = 5°, 8°, 10°, 15°/min (nominal; see Table I).
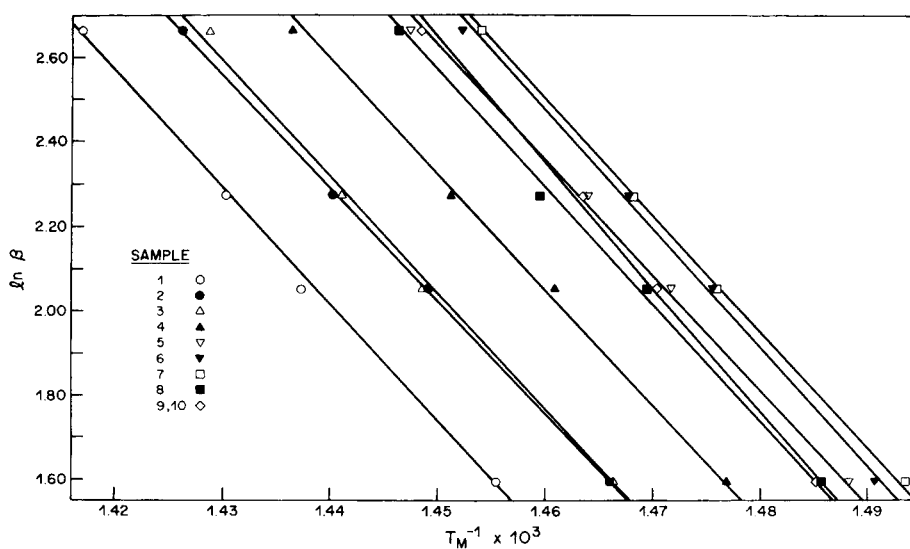

Fig. 3. Plots of ln β vs $T_M{}^{-1}$, °K.

TABLE II
The Overall Apparent Arrhenius Parameters for the
Thermal Degradation of Polystyrene

Sample no.	ΔE_0, kcal/mole		$\log A_0$, sec^{-1}	
1	52.9[a]	(54.96)[b]	14.5[a]	(14.6)[b]
2	52.2	(53.65)	14.5	(14.7)
3	52.9	(52.92)	14.6	(14.8)
4	52.6	(52.64)	14.7	(15.0)
5	51.3	(52.92)	14.8	(15.0)
6	51.5	(52.92)	14.9	(15.0)
7	52.5	(52.92)	14.9	(15.0)
8	52.4	(52.92)	14.8	(15.0)
9	54.6	(52.92)	14.9	(15.0)
10	53.3	(52.92)	14.9	(15.0)
	<52.7>	<53.2>		

[a] The values of the overall apparent Arrhenius parameters evaluated by the $\ln \beta - T_M^{-1}$ method[2].

[b] Calculated from the model described by eq. (3); see footnote c to Table I.

for each polymer are plotted versus the log of the number-average degree of polymerization in Figure 2 and are tabulated in Table I. The error bars ($\pm 1°$) shown in Figure 2 are based on the estimated errors in the measurement of the themocouple voltage. McNeill[9] has observed a similar trend in T_M with initial molecular weight for a series of polystyrene samples prepared
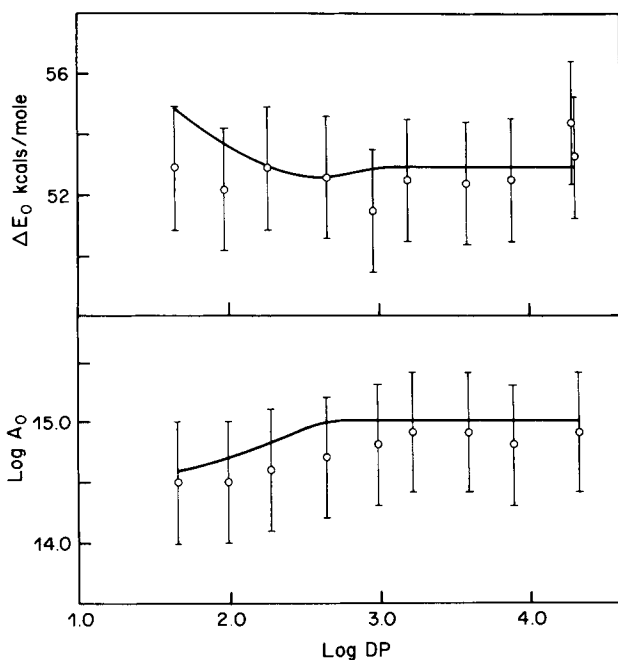

Fig. 4. (a) Observed (single points) and calculated (full curve) overall apparent activation energy ΔE_0, kcal/mole. (b) Observed (single points) and calculated (full curve) overall apparent preexponential factor, expressed as $\log A_0$, plotted vs. log initial number-average degree of polymerization.

by a variety of synthetic routes. He has also demonstrated[9] that the molecular weight effect disappears in the case of ultrathin films less than 1000 Å thick. We have confirmed McNeill's observations and have established that the results reported here, which are for powdered samples, correspond to the lower plateau in Figure 3 of McNeill's paper.[9]

When the data obtained at different heating rates are treated by the $\ln \beta$–T_M^{-1} method,[2] the plots shown in Figure 3 are obtained. The Arrhenius parameters derived from these plots are given in Table II and are plotted in Figure 4. The error bars on the values for the overall apparent activation energies, ΔE_0, and the log of the preexponential factors, $\log A_0$, are conservatively estimated at 2 kcal/mole and ±1 unit respectively. There is no obvious trend in the ΔE_0 values with molecular weight detectable within the limits of the experimental errors (Fig. 4a). The values of ΔE_0 lie in the range of 51.5–54.4 kcal/mole. These values are those obtained at the maximum in the TVA thermogram for each sample at which approximately 60% volatilization has occurred and agree well with the value of 54 kcal/mole obtained by Madorsky[10] at 50% degradation.

A trend in the apparent overall preexponential factor, A_0, with increasing initial molecular weight can be seen in Figure 3. Thus, the plots of $\ln \beta$ versus T_M^{-1} are spread along the T_M^{-1} axis. This displacement can only arise from differences in A_0 for the different molecular weights. The trend in $\log A_0$ with molecular weight is shown in Figure 4b. The values plotted in Figure 4b, and given in Table II, were obtained from a plot of $\log A$ versus T_M^{-1} constructed for $\Delta E = 52.7$ kcal/mole, which is the average value of ΔE_0 at $\beta = 5°$/min from the numerical data previously published.[2]

It is thus revealed by the $\ln \beta$–T_M^{-1} method that the trend in T_M shown in Figure 2 is largely due to the molecular weight dependence of A_0, the apparent overall Arrhenius preexponential factor for the degradation process. This effect can be discussed in terms of the model elaborated in the next section.

A MODEL FOR THE OVERALL DEGRADATION PROCESS

The essential point of departure from previous theoretical treatments of polymer degradation processes is the inclusion in our model of the effect of the instantaneous molecular weight of the degrading polymer mass on the chain-scission rate constant and the zip length of the depolymerization reaction. Heuristically, we relate the latter feature of our model to the viscosity of the molten polymer.

Simha and Wall[11] were the first to suggest that the melt viscosity of the polymer may influence its degradation kinetics. This suggestion was based on the notion that the Norrish-Smith[12] or gel effect, which causes an increase in the kinetic chain length in polymerization as a result of the increasing viscosity of the medium, may also play a similar role in depolymerization processes. Surprisingly, this suggestion has not been included explicitly in previous theoretical models for polymer degradation processes. The major difficulty in attempting to do so lies, perhaps, in trying to determine a priori whether the bulk viscosity or the internal viscosity of the chain is the important factor. We adopt a phenomenological approach here.

Since the relaxation times of the normal modes of the chain which determine both melt and internal viscosity are molecular weight dependent,[13,14] we can include the contribution of both in our model simply by making appropriate rate constants some function of molecular weight. In particular, we make the preexponential factor a function of molecular weight in order to be consistent with the phenomenology (Figs. 3 and 4b).

The essential features of the in vacuo thermal degradation of polystyrene have been known for many years and have been reviewed most recently by Cameron and MacCallum.[15] It now seems to be firmly established that the reaction mechanism involves a combination of random chain scission and chain end-initiated unzipping. Monomer accounts for approximately 42% by weight of the volatile products, the balance being dominated by molecules with an average molecular weight of 264. The latter observations suggest that both intra- and intermolecular transfers play a significant role in the overall mechanism and that the zip length of the chain depolymerization reaction is short. In their most recent theoretical model for polystyrene degradation under isothermal conditions, Simha, Wall, and co-workers[16] suggest that the zip length is of the order of 1% of the molecular chain length and a *decreasing* function of chain length.

In our model, we assume that the efficiency of chain scission increases with viscosity and hence is proportional to some function of molecular weight. This assumption is consistent with the experimental observation that the rate constant for chain scission increases with molecular weight.[17,18] It has been shown[15] that the random chain scission reaction does not lead to volatile production and is in that sense independent of the depolymerization reaction. Following the procedure described previously,[2] we simulate this reaction occurring under thermally dynamic conditions as a series of isothermal reactions occurring at intervals of 0.1° in temperature for $0.1\beta^{-1}$ minutes at each temperature, where β is the linearly programmed heating rate used in the TVA experiment. At each step in the simulation, the random scission is described by the following equation:

$$DP_t^{-1} = DP_{t-\Delta t}^{-1} + \alpha k_{cs}\Delta t \tag{1}$$

where $DP_{t-\Delta t}$ and DP_t are, respectively, the number-average degrees of polymerization at the beginning and end of the time interval $\Delta t = 0.1\beta^{-1}$ min, k_{cs} is the rate constant for random chain scission, and α is the assumed viscosity-dependent efficiency of chain scission.

Cameron has shown[19] that volatile production occurs exclusively at chain ends. We can thus write for the rate of weight loss

$$-\Delta W/\Delta t = Zk_vDP_t^{-1}W \tag{2}$$

where Z is the zip length, k_v is the overall rate constant for volatilization, DP_t is the number-average degree of polymerization at time t, and W is the weight of the sample at time t. We make no assumptions about the attainment of a steady-state concentration of depolymerizing chain radicals. Instead, we use the parameter Z, which can be defined as the ratio of the probability of depropagation to the probability of termination. We also assume that the zip length increases with viscosity and make it some function of molecular weight. The latter assumption is difficult to justify a priori. We can,

by analogy with the Norrish-Smith effect, argue that the segmental motion of the chain end into the transition state required for termination, which Cameron has demonstrated[19] is a first-order process, is in some way dependent on viscosity. As we shall demonstrate, the a posteriori justification for this assumption is quite compelling.

Introducing $Z = (DP)^\gamma$ and $\alpha = (DP)^\delta$ into eqs. (1) and (2) to express the assumptions discussed above and substituting eq. (1) in eq. (2) gives the following equation for our model:

$$-\Delta W/\Delta t = (DP_t)^\gamma k_v [DP^{-1}_{t-\Delta t} + (DP_{t-\Delta t})^\delta k_{cs} \Delta t] W. \qquad (3)$$

In order to fit the proposed model to the experimental data obtained in the TVA study (see Results), we introduce eq. (3) into the computer simulation
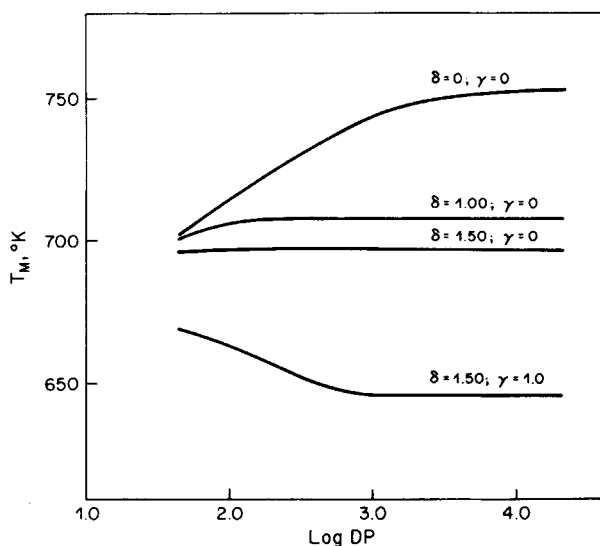

Fig. 5. Behavior of the theoretical model with variation in the values of γ and δ for $\beta = 5$ and $k_v = 3.65 \times 10^{16} \exp(-5.8 \times 10^4/RT)$; $k_{cs} = 1.67 \times 10^6 \exp(-4 \times 10^4/RT)$.

program described previously.[2] The parameters $k_v = A_v \exp(-\Delta E_v/RT)$, γ and δ were systematically varied in order to obtain the best fit to the data. The value of $k_{cs} = 1.67 \times 10^6 \exp(-4 \times 10^4/RT)$ mole/ml·sec obtained from the data presented in Boon and Challa's paper[17] was fixed in all the computer calculations. TVA thermograms were calculated for a variety of initial molecular weights including those values given for the samples studied here.

The full curves in Figures 1, 2, and 4 were considered to give the best fit to the data and were obtained with the following input values for the parameters of the model: $A_v = 3.65 \times 10^{16}$ sec^{-1}; $\Delta E_v = 58$ kcal/mole; $\gamma = 0.625$; and $\delta = 1.5$. The calculated T_M, ΔE_0, and log A_0 are given in Tables I and II. The agreement between calculated and observed values for the 40 T_M data points obtained with the ten samples at four different heating rates is quite satisfactory.

We approached the question of the uniqueness of the above solution by testing the behavior of the model for a variety of values of γ and δ. The

curves plotted in Figure 5 are illustrative of the results obtained. The significant feature of these results is that the observed trend in T_M (Fig. 2) cannot be reproduced if γ and/or δ is set equal to zero. Thus, if the effect of viscosity on either or both the zip length and efficiency of chain scission is not included in the model, it is impossible to quantitatively account for the data obtained in the present study. The model cannot be fitted to the data by variation of the activation energies ΔE_v and ΔE_{cs} alone.

Our model is oversimplified in one rather important respect. Because it deals only with the number-average degree of polymerization and does not take into account the initial molecular weight distribution and its evolution as the reaction proceeds, the model overestimates the rate of reaction in the initial stages (Fig. 1). This is not a serious limitation of the model because the TVA technique as applied here rests on the behaviour of T_M, the temperature at the maximum of the thermogram, and not on the absolute rates. We have not attempted to sophisticate the model at this stage because no molecular weight data are available for polystyrene degradation conducted in a dynamic temperature regime. For a discussion of the effect of molecular weight distribution on the kinetic behaviour of polymer degradation reactions, see Boyd and Lin.[20]

DISCUSSION

The results reported here serve to illustrate further the potential of TVA for the study of the degradation reactions of macromolecules. By taking into account the behavior of the reaction trajectory during its whole course through the linearly increasing temperature–time regime, it is possible to detect features that may have been overlooked or undetectable in an isothermal study based on initial rates. Any attempt to fit the observations to a molecular model is also faced with a stringent test if the TVA approach is adopted.

Perhaps the most controversial aspect of the degradation behavior of polystyrene in the last 20 years has been the vexed question of the origin of the initial very rapid drop in molecular weight. This initial phase is followed by a more gradual drop in molecular weight as the reaction proceeds. Grassie and Kerr[21] suggested that the initial phase of the reaction corresponds to the scission of a number of randomly distributed "weak links." The latter suggestion remains controversial not only because such structures remain elusive and have defied unequivocal chemical identification but also because theoretical treatments[16,20,22] provide a rationalization of the observed molecular weight behavior without the explicit inclusion of such structures. In the model presented here, the rapid deceleration of the random chain scission, which led Grassie and Kerr to their eminently plausible "weak link" hypothesis, finds a purely physical explanation in terms of the proposed viscosity dependence of the chain-scission rate constant. Conceivably, the "weak links" of Grassie and Kerr could be related to the chain entanglements which occur, in high molecular polymers, at intervals in the range 300–700 chain units apart.[23]

The values for the molecular weight exponents in our model, $\gamma = 0.625$ and $\delta = 1.5$, suggests that the zip length and chain-scission rate constants are not hydrodynamically coupled to the bulk viscosity. If the latter possibility were

the case, we would have expected an exponent of 3.4 for initial molecular weights exceeding the critical chain entanglement length.[23]   Alternatively, the coupling to the bulk viscosity may be weak.   More probably, the observed molecular weight dependence of A_0 (Fig. 4b) is due to a microviscosity effect on the chain segmental motion.   At the present time, it is not clear how the proposed hydrodynamic coupling can be deduced a priori from extant theories of chain segmental motion.   For the latter reason, our proposed model must remain a purely phenomenological one.

The latter comment notwithstanding, our model provides not only a plausible rationalization of the molecular weight dependence of our T_M data (Figs. 2 and 5), but also provides an explanation for McNeill's observation[9] that this dependence disappears in thin films of polystyrene and T_M is some 60° higher than for thick films.   McNeill[9] rationalized his observations in terms of the role played by intermolecular transfer in the mechanism of the overall degradation process and argued that transfer was minimized in ultrathin films. Since transfer leads to chain scission, it is included in our model via the empirical rate constant k_{cs} determined by Boon and Challa[17] and the parameter δ.   However, it is clear from Figure 5 that the molecular weight dependence of T_M disappears only when $\gamma = 0$.   Thus, the enhanced stability of thin films of polystyrene seems to be due to the shorter zip length implied by the requirement that $\gamma = 0$.   This implies that the termination reaction is more efficient in thin films.

Further evidence that thin-film geometry can affect the zip length of chain end-initiated depolymerization can be adduced from the observations of McNeill on the TVA behavior of poly(methyl methacrylate).[9]   This polymer degrades by two mechanisms which are well separated in activation energy and hence give two peaks in the TVA thermogram.   A low-temperature peak $(T_M = 300°C; \beta = 10°/min)$ corresponding to chain-end depolymerization and a high-temperature peak $(T_M = 402°C; \beta = 10°/min)$ corresponding to random scission-initiated depolymerization.   The area of the former peak is reduced, relative to that of the high-temperature peak, in thin films indicating that the monomer yield from chain-end depolymerization is reduced under these conditions.   In terms of our model, these observations can be accounted for by a decrease in the molecular weight exponent for zip length in thin films as discussed above.

The latter discussion also serves to emphasise the point, which is implicit in our model, that γ and δ have different values because they reflect different extents of hydrodynamic coupling for the two reactions.   Chain-end segments, because they have more free volume, are presumably more flexible and are less hydrodynamically coupled to the molten polymer mass than internal chain segments, and hence the value for γ is less than that for δ.

CONCLUSIONS

The present study of the in vacuo thermal degradation of polystyrene suggests that there may be a role played by the melt viscosity of the degrading polymer mass, analogous to the Norrish-Smith effect.

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