Investigation of Thermal Degradation of Polystyrene by Differential Scanning Calorimetry

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Synopsis

Thermal degradation of polystyrene was performed in a differential scanning calorimeter under nitrogen atmosphere, and the glass transition temperature was measured continuously. From random chain scission kinetics and T_g–molecular weight relationships, the rate constant for random scission was obtained. The rate constant was found to undergo a drastic change at a critical molecular weight ($\simeq 45,000$), which corresponds to a similar observation in relaxation studies. A viscosity-dependent mechanism for radical chain end termination is thus suggested.

INTRODUCTION

Thermal degradation of polystyrene is a widely studied subject, and the techniques employed have included solution viscometry,[1,2] osmometry,[3] melt viscosity,[4] thermogravimetric analysis,[5] thermal volatilization analysis,[6,7] differential scanning calorimetry,[8] and mass spectrometry.[8,9] A novel approach is used in the present study where the glass transition temperature (T_g) is used to compute the number-average molecular weight ($\overline{M}_n$) of standard polystyrene samples of different starting molecular weights which have been subjected to varying degrees of thermal decomposition. Since both T_g and thermal measurements of the polymer can be performed in the differential scanning calorimeter, this method presents a clean, fast, and direct way of studying the thermal degradation of polystyrene, which has not been hitherto exploited.

THEORY

The T_g–molecular weight relationship for polystyrene has long ago been reported by Fox and Flory,[10] but recently a new phenomenon has been observed which relates to the existence of a critical molecular weight for the molecular weight dependance of T_g[11,12]:
for

$$\overline{M}_n > M_c, \qquad T_g = T_{g1}^\infty - K_1/\overline{M}_n \qquad (1)$$

$$\overline{M}_n < M_c, \qquad T_g = T_{g2}^\infty - K_2/\overline{M}_n \qquad (2)$$

when $M_c \simeq 35,000$.

For a random degradation of polymer molecules, a pseudo zero-order reaction can be assumed as long as the total number of chain bonds is large compared to the number broken,[13,14] and the following expression can be applied:

$$\frac{1}{\overline{DP}_t} - \frac{1}{\overline{DP}_0} = kt \qquad (3)$$

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where k is the rate constant for chain scission and $\overline{DP}_0$ and $\overline{DP}_t$ are the number average degrees of polymerization at zero and time t, respectively.

Thus, if both $\overline{DP}_0$ and $\overline{DP}_t$ are greater than DP_c, from eqs. (1) and (3) it follows that

$$T_g = T_g^0 - K_1 kt/104 \tag{4}$$

since $DP = \overline{M}_n/104$ (where 104 is the molecular weight of the repeating styrene unit), where $T_g^0 = T_g$ at time zero.

Similarly if both $\overline{DP}_0$ and $\overline{DP}_t$ are less than DP_c

$$T_g = T_g^0 - K_2 kt/104 \tag{5}$$

If $\overline{DP}_0 > DP_c$ and $\overline{DP}_t < DP_c$, then

$$T_g = \frac{K_2}{K_1} T_g^0 + T_{g2}^\infty - \frac{K_2}{K_1} T_{g1}^\infty - \frac{K_2 kt}{104} \tag{6}$$

It can be readily seen from eqs. (4)–(6) that a plot of T_g against time of degradation under isothermal heating will show one or two linear regions, the slope of which will yield the rate constant k provided the constants K_1 and K_2 are predetermined. Alternatively, $(1/\overline{DP}_t - 1/\overline{DP}_o)$ can be obtained from the T_g − $1/\overline{M}_n$ relationship and used directly to obtain the rate constant k by plotting it against the time of degradation, t. It is thus possible to follow the thermal degradation of polystyrene in a differential scanning calorimeter *in situ* by alternately heating the polystyrene sample to the desired degradation temperature for the required period of time, followed by cooling and scanning for the T_g.

EXPERIMENTAL

Materials

All polystyrene samples used were standard samples purchased from Polysciences Inc., Warrington, Pa. with $\overline{M}_w/\overline{M}_n < 1.1$.

Instrumentation

The Perkin-Elmer DSC-1 was calibrated at the scan rate of 40°/min using a Standard Indium sample and the manufacturer's specified procedure. Under isothermal conditions the calibrated temperature was about 7° higher than the nominal average temperature reading.

Sample Preparation

About 10 mg of polystyrene was placed in an aluminum DSC sample pan which was then transferred to the DSC cell assembly. The sample was heated from 290°K to 473°K at a rate of 2.5°/min under nitrogen atmosphere. It was held at 473°K for 15 min and then cooled to 290°K at 40°/min. This procedure ensured the formation of a thin polymer film which had good thermal contact with the sample pan and which was free of cracks or entrapped air bubbles. The recorded thermogram is shown in Figure 1.

The interception of the two linear extrapolations indicates the T_u transition,[15]
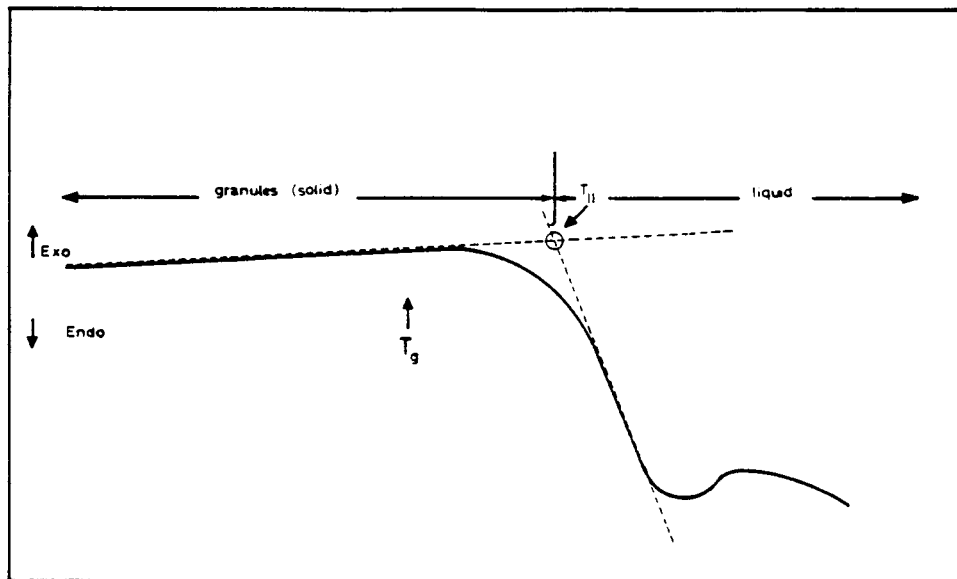
Fig. 1. "Melting" thermogram of polystyrene.

which corresponds to flow. T_g is not shown at this low scan rate and low sensitivity scale (Range 8). Since T_u increases to over 473°K for molecular weight exceeding 10^5,[11] it may not be possible to form a good film for high molecular weight polystyrene without thermal degradation.

Thermal Degradation

The polymer film prepared above was heated at 80°/min (under N_2) to the set temperature reading of 583°K (actual temperature was 590°K) and maintained for the required period of time isothermally. It was then cooled at 40°/min to 293°K. T_g measurements were taken of the sample before it was heated to 590°K again for further thermal treatment.

T_g Measurement

The polymer sample was heated at a scanning rate of 40°/min from 293°K to 400°K at the most sensitive range (Range 2) of the Perkin Elmer DSC-1. From the thermogram shown in Figure 2, T_g is determined by the intersection point of the two linear extrapolations. The sample was cooled to 293°K, and the procedure was repeated. The average of two or three readings was taken as the T_g.

RESULTS

T_g–($1/\overline{M}_n$) Relationship

The T_g vs $1/\overline{M}_n$ plot for the standard polystyrenes is shown in Figure 3. It is seen that the intersection of the two linear regions occurs at $1/\overline{M}_n = 2.2 \times 10^{-5}$, i.e., $M_c \simeq 45{,}000$. The following expressions represent the relationships thus observed:
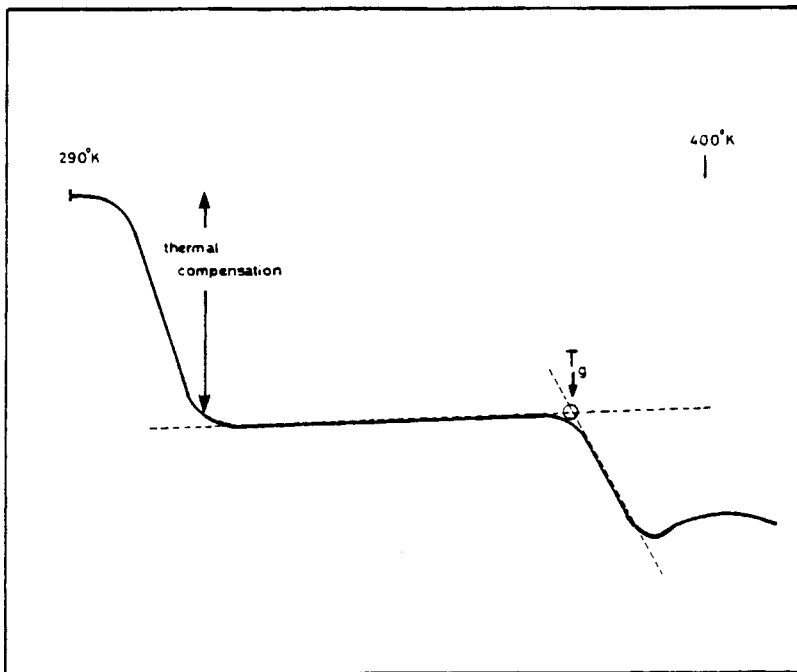
Fig. 2. DSC thermogram of polystyrene showing glass transition.

$$\text{for } \overline{M}_n > M_c, \qquad T_g = 376.15 - 24 \times 10^4 \, \overline{M}_n^{-1} \qquad (°\text{K})$$

$$\text{for } \overline{M}_n < M_c, \qquad T_g = 371.4 - 6 \times 10^4 \, \overline{M}_n^{-1} \qquad (°\text{K})$$

The above values agree quite well with those reported by Stadnicki et al.[11]

T_g vs. Time of Heating at 590°K

Polystyrene samples of starting $\overline{M}_n$'s 80,000, 63,000, 37,000, and 17,500 were subjected to different periods of heating at 590°K and T_g measurements were taken after each stage of degradation. The results are shown in Figure 4.

$1/\overline{\text{DP}}_t - 1/\overline{\text{DP}}_0$, vs. Time of Heating

Figure 5 shows the translated value of $(1/\overline{\text{DP}}_t - 1/\overline{\text{DP}}_0)$ from the corresponding T_g values plotted against time of degradation, t. Two linear regions are clearly observed for sample with $(\overline{M}_n)_0 = 80,000$. The point of intersection corresponds to an $\overline{M}_n$ value of 45,000. For sample with $(\overline{M}_n)_0 = 17,500$ a single linear plot is observed. For the intermediate samples, $(\overline{M}_n)_0 = 37,000$ and 63,000, respectively, a wider scatter is observed initially, but, subsequently, the points fall on a straight line the slope of which is equal to that of sample $(\overline{M}_n)_0 = 17,500$ and of the second stage of sample $(\overline{M}_n)_0 = 80,000$. The rate constants for the two portions are 0.03×10^{-6} s^{-1} and 0.45×10^{-6} s^{-1}, respectively.
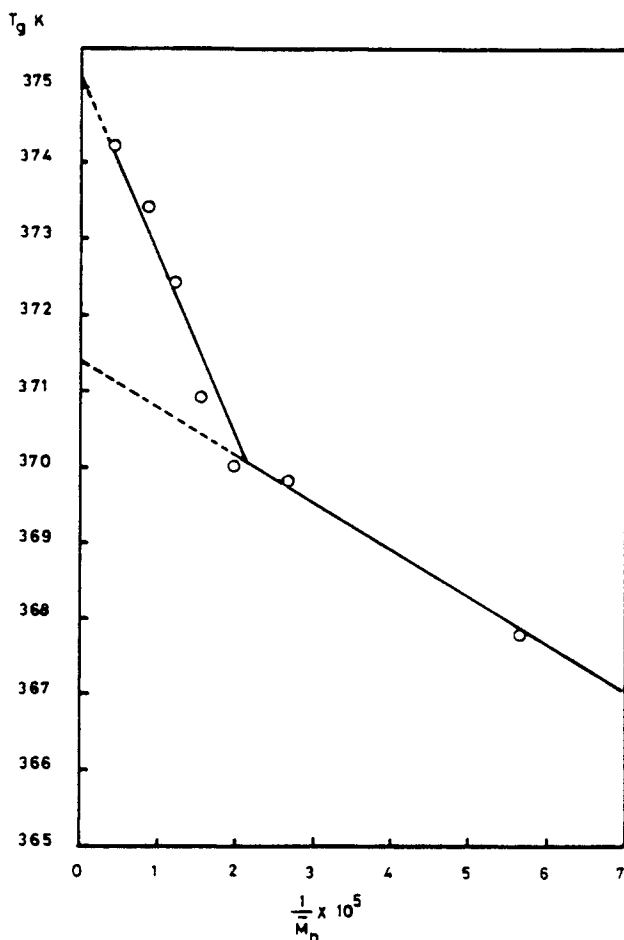
Fig. 3. Relationship of T_g with $1/\overline{M}_n$ for polystyrene.

DISCUSSION

It can be seen from Figures 3–5 (for sample with $\overline{M}_0 = 80,000$) that a critical point exists which corresponds to $(\overline{M}_n)_c \simeq 45,000$. Figure 5 shows that the rate constant is increased by a factor of 15 after the polymer is degraded below $(\overline{M}_n)_c$. The fact that the change in rate of degradation occurs at a point which corresponds to the "break" in the T_g vs. $1/\overline{M}_n$ plot is both significant and interesting.

Assuming that thermal degradation of polystyrene is mainly due to random scission of the backbone molecules of the polymer at temperatures below 320°C and that volatilization due to end-initiated unzipping depolymerization is negligible,[16] the observed phenomenon is more likely to be associated with the hydrodynamic properties of the polymer melt rather than with the actual mechanism of degradation. From the zero-shear melt viscosity vs. $\overline{M}_n$ data as presented by Standnicki et al.,[11] which is reproduced in Figure 6, it can be seen that a "break" occurs at a molecular weight of about 35,000, which is sufficiently close in magnitude to our observed $(\overline{M}_n)_c$. It is thus reasonable to postulate that the viscosity of the polymer melt exerts an influence on the ability of the radical chain ends, caused by random scission, to terminate by disproportionation or transfer.
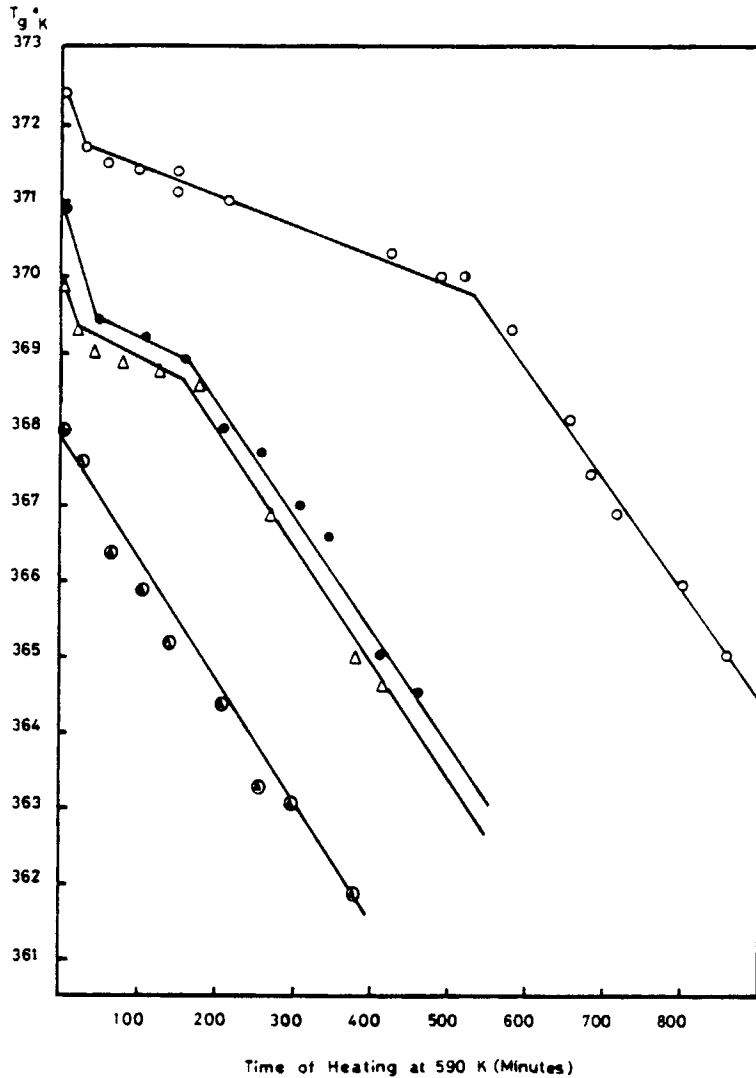
Fig. 4. $\overline{M}_n$: (O) 80,000; (●) 63,000; (△) 37,000; (⊚) 17,500.

Since the segmental motion of the chain end into the transition state required for the termination is dependent on viscosity,[7] it is possible that when $\overline{M}_n <$ $(\overline{M}_n)_c$, the radical pair formed by random chain scission can diffuse and affect other chain scissions through intramolecular transfer. When $\overline{M}_n > (\overline{M}_n)_c$, the newly formed pairs of radicals diffuse apart less easily and tend to recombine or disproportionate in a "cage."

Several other authors[4,7,17] have reported molecular weight influence on the thermal degradation of polystyrene. Mehmet and Roche,[7] using thermal volatization analysis, observed a critical change in their T_m (temperature of maximum rate of volatization) at a molecular weight of around 45,000. They assumed a model where chain scission and chain-end-initiated depolymerization take place simultaneously, but argued that there was a positive dependence of the chain scission rate constant on viscosity in order to fit the experimental observation. Boon and Challa[4] using melt viscosity data observed some molecular weight ef-
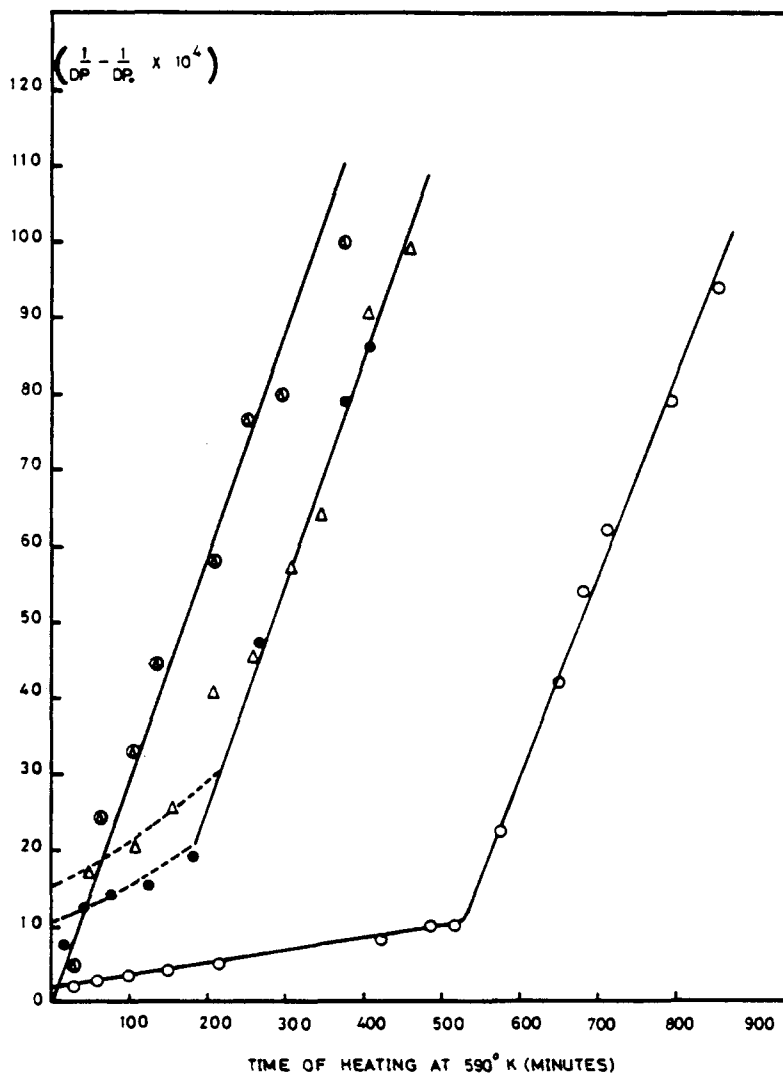
Fig. 5. $(\bar{M}_n)_0$: (O) 80,000; (●) 63,000; (△) 37,000; (◬) 17,500.

fects but these were not definitive, and the assumption of $\log \eta = A + 3.4 \log \bar{M}_n$ for all molecular weights is incorrect.[18] Cameron and Kerr[17] observed some positive dependence of the rate constant on the molecular weight over the range 200,000–600,000 for anionic polystyrenes. On the other hand, Rudin et al.[5] found no molecular weight effects for $M > 1 \times 10^5$ for anionic polystyrenes in their activation energy studies by thermogravimetric analysis.

CONCLUSIONS

Present study suggests that a critical molecular weight exists in the thermal degradation of polystyrene where the random chain scission rate constant undergoes a drastic increase after the molecular weight is decreased beyond this crtitical value. That this value ($\simeq$ 45,000) corresponds to the M_c observed in other relaxation phenomena of polystyrene[11,12,15] further suggests that the change
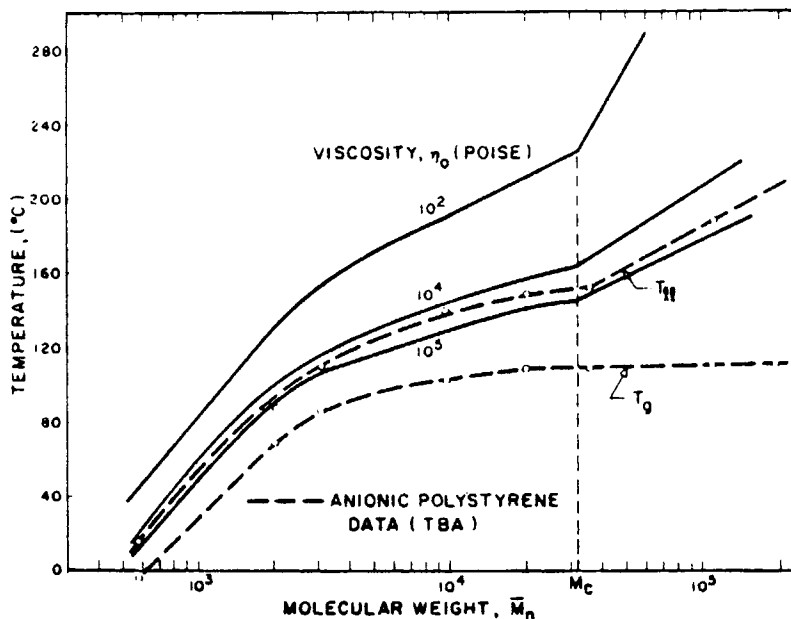
Fig. 6. Zero-shear melt viscosity data. Temperature (°C) vs. log $\overline{M}$ for different isoviscous levels.

in the rate of random chain scission is due to the change in the hydrodynamic behavior of the polymer melt, which may have retarded the termination of the radical chain ends at molecular weights $>(M_n)_c$.

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