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CORRELATION BETWEEN POLYSTYRENE MOLECULAR WEIGHTS AND A CHARACTERISTIC TEMPERATURE DERIVED FROM THE THERMOGRAVIMETRIC WEIGHT LOSS CURVES

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ABSTRACT

A characteristic temperature was derived from the weight loss curves following the thermal decomposition of polystyrenes. The average molecular weights of the polystyrenes were found to be directly related to this temperature.

The thermal decomposition patterns of polystyrenes were fitted to a first-order kinetic model. The kinetic parameters obtained (energy of activation and frequency factor) were also found to be functionally dependent on the initial average molecular weight.

INTRODUCTION

The usual methods for the determination of molecular weights are gel permeation, viscosimetry, light scattering and colligative property measurements. All of these methods require the presence of a solvent [1,2]. A technique is discussed in this paper which determines the molecular weights of polystyrene samples from direct measurements of the thermal behaviour of the solids themselves. Our goal is to develop a method which will correlate the average molecular weight of a polymer to a characteristic decomposition temperature. Polystyrene was chosen as a prototype polymer.

EXPERIMENTAL

Samples were obtained from Scientific Polymer Products (anionic preparation and polydispersity below 1.06). The molecular weights M_w ranged between 517 and 19000 g mol^{-1}. The thermal decomposition of the polystyrene samples was conducted in a thermal analyser (Netzsch, Gerätebau

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Model STA 409). The operating conditions were as follows: air flow, 100 cm^3 min^{-1}; heating rate, 10 °C min^{-1}; sample weight, 25 mg. These conditions are similar to those used in an earlier study related to the characterization of different polymers derived from wood liquefaction [3].

RESULTS

A typical thermogram (TGA–DTG) of a polystyrene sample with a molecular weight $M_w = 7820$ g mol^{-1} is shown in Fig. 1. From the TGA–DTG data of the polystyrenes with various molecular weights we derived the following information.

(i) A temperature T_M (from the DTG curve) corresponding to the maximum rate of weight loss (i.e. $(df/dT)_M$) where f is the fractional conversion and T is the temperature. This temperature is observed between 382 and 404 °C.

(ii) The onset of pyrolysis (i.e. at about 5% weight loss). This starts at temperatures depending on the polystyrene molecular weights. These temperatures increase with the molecular weight as shown in Table 1.

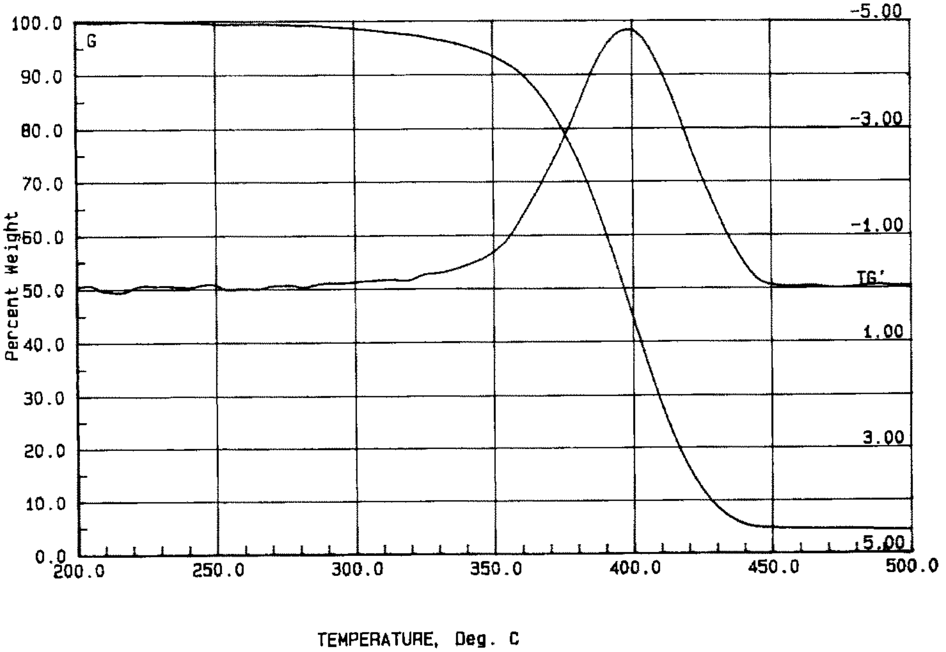

Fig. 1. Weight loss curve (G) and its derivative (TG′) for the thermal decomposition of polystyrene ($M_w = 7820$ g mol^{-1}). Conditions: Sample, 25 mg; heating rate, 10 °C min^{-1}; air atmosphere, 100 ml min^{-1}.

TABLE 1

Temperature of onset of pyrolysis of polystyrene as a function of initial average molecular weight

M_w (g mol^{-1})	T_{onset} (°C)
517	280
2000	305
2470	310
4000	330
7820	340

At $M_w > 7820$ g mol^{-1} the temperature of the onset of pyrolysis becomes constant at ≈ 340 °C.

(iii) The temperature of the end of pyrolysis. For the different polystyrenes pyrolysis ends at temperatures in the range 420–430 °C.

(iv) The characteristic temperature T_c which is obtained from the weight loss curve as the value of the intercept between the locus of $f = 0$ and the tangent line at $(df/dT)_M$. This characteristic temperature is shown in Fig. 2 as a logarithmic function of the molecular weights of the polystyrene samples. Above $M_w = 7820$ g mol^{-1}, the characteristic temperature stays approximately the same. Tanahashi et al. [4] have shown an analogous behaviour between the molecular weight M_w and the glass transition temperature T_g of polystyrenes.

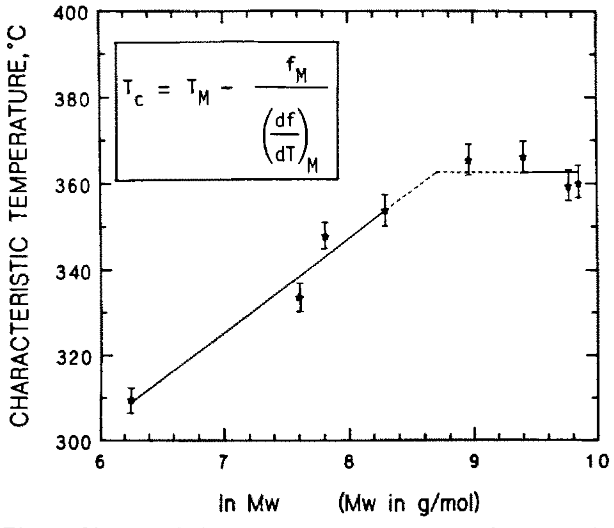

Fig. 2. Characteristic temperature T_c as a function of molecular weight of polystyrene. T_M is the temperature at the maximum decomposition rate $(df/dt)_M$ and f_M is the fractional conversion at T_M.

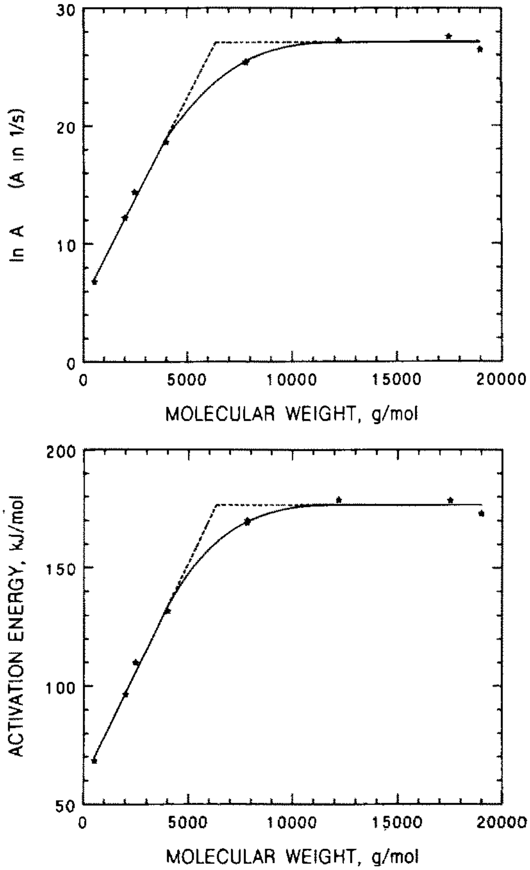

Fig. 3. Kinetic parameters, based on an Arrhenius first-order model, for the thermal decomposition of polystyrenes as a function of molecular weight.

A classical power law kinetic model ($\mathrm{d}f/\mathrm{d}t = k\ (1-f)^n$) was also used to fit the thermal decomposition patterns. It was assumed that the overall kinetic constant k follows Arrhenius kinetics (i.e. $k = A\ \exp(-E/RT)$).

Figure 3 shows the variation in E and A with molecular weight. It is apparent that both E and A increase with the initial molecular weight of polystyrene, reaching a plateau for molecular weights higher than ca. 10000 g mol^{-1}. The increase in E and A with M_w can be approximated by the simple expressions in the zone of low molecular weights ($M_w \leqslant 4000$ g mol^{-1}). Thus,

$$E = E_0(1 + aM_w)$$

with $E_0 = 60.1$ kJ mol^{-1}, $a = 3.06 \times 10^{-4}$ mol g^{-1} and $r = 0.994$, and

$$A = A_0\ \exp(bM_w)$$

with $A_0 = 211.6$ s^{-1}, $b = 3.40 \times 10^{-3}$ mol g^{-1} and $r = 0.996$. The profiles of

TABLE 2

Activation energy of thermal decomposition of polystyrenes obtained from the literature

Reference	E (kJ mol^{-1})
Dickens [5]	188
Bouster et al. [6]	280
Anderson and Freeman [7]	190–250
Kokta et al. [8]	140–210
Mehmet and Roche [9]	220
This work	170–180

E vs. M_w and ln A vs. M_w show the same trends as the plot of T_c vs. ln M_w.

The literature values of the activation energy of the thermal decomposition of polystyrenes range between 140 and 250 kJ mol^{-1}. This is not surprising when the large variation in experimental conditions used by the various workers is considered. A summary of these values is presented in Table 2.

Our limiting values ($E = 170$–180 kJ mol^{-1} for $M_w \geqslant 7820$ g mol^{-1}) fall within the established range. When the amount of sample used is decreased (down to about 5 mg) and the heating rate is decreased (to about 1°C min^{-1}), an asymptotic limiting value of 130 kJ mol^{-1} is obtained for the energy of activation of long polymers ($M_w \geqslant 7820$ g mol^{-1}). This fact gives support to the importance of matrix and diffusion effects during thermal decomposition.

CONCLUSIONS

A simple log–linear correlation was found between the molecular weight of polystyrene and a characteristic temperature derived from the thermogram. This correlation was valid for medium size polymers (DP = 5 to DP = 90) and was obtained for a given set of experimental conditions (25 mg samples and heating rates of 10°C min^{-1} in air). The thermal decomposition patterns can be modelled by simple first-order kinetics. This leads to linear correlations of both the energy of activation and the logarithmic function of the pre-exponential factor with the molecular weight of polystyrene.

Thus the TGA technique can be used, within a limited range of molecular weights, to determine a characteristic temperature from which an average molecular weight of polystyrene can be derived, assuming that the polymer is essentially monodispersed. This finding should encourage further research in this area since an extension of this result to other polymers (under specific analytical conditions for each polymer) would provide a dry method to determine average molecular weights of organic polymers within useful ranges of molecular weights.

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REFERENCES

1 P.R. Gupta and D.A.I. Goring, Can. J. Chem., 38 (1960) 270.
2 W.J. Connors, S. Sarkanen and J.L. McCarthy, Holzforschung, 34 (1980) 80.
3 J. Bouchard, S. Léger, R.P. Overend and E. Chornet, Biomass, 9 (1986) 161.
4 M. Tanahashi, T. Aoki and T. Higuchi, Holzforschung, 36 (1982) 117.
5 B. Dickens, Polym. Degrad. Stabil., 2 (1980) 249.
6 C. Bouster, C. Comel, P. Vermande and J. Veron, J. Therm. Anal., 20 (1981) 115.
7 D.A. Anderson and E.S. Freeman, J. Polym. Sci., 54 (1961) 253.
8 B.V. Kokta, J.L. Valade and W.N. Martini, J. Appl. Polym. Sci., 17 (1973) 1.
9 Y. Mehmet and R.S. Roche, J. Appl. Polym. Sci., 20 (1976) 1955.