Thermal Decomposition of Anionic and Emulsion Polymerized Polystyrenes

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Synopsis

The thermogravimetric behavior of anionic and emulsion polymerized polystyrenes was investigated in nitrogen at a heating rate of 18°C/min. Kinetic data were obtained by least squares analyses of experimental points obtained by differentiating primary thermograms. Degradation was generally zero order for about the first 25% of the reaction and first order thereafter. No molecular weight effects were observed for anionic polystyrenes with $M \geq 1 \times 10^5$. Anionic and emulsion polystyrenes differed significantly in thermal stability. Degradation of emulsion polymers proceeded more slowly and with higher activation energies in both the zero- and first-order regions. Activation energies for anionic polystyrenes were 28 and 44 kcal/mole in the zero- and first-order domains while the corresponding values for emulsion polymers were 36 and 60.5 kcal/mole, respectively. No tacticity differences were detected in 220 MHz NMR spectra. The differences in thermal stability are attributed to differences in end groups in the two polymer types.

INTRODUCTION

The thermal degradation of polystyrene has been extensively investigated although not all details of the reactions involved in this process are clear. It is generally agreed that volatile material is evolved as a result of free radical chain reactions which include varying amounts of intermolecular and intramolecular transfer. Although the rates of volatilization are consistent with end initiation, to our knowledge no systematic studies have been made of polystyrenes capped with different end groups. We report a comparison here of the thermogravimetric behavior of anionic and emulsion polymerized polystyrenes. The two polymer types do not differ detectably in tacticity, but their end groups are different. Some improved methods for handling thermogravimetric data are also reported in this paper.

EXPERIMENTAL

Thermogravimetric experiments were carried out with a duPont 950 balance attached to a model 900 differential thermal analysis unit. The heating rate, which was about 18°C/min, was monitored with a stopclock over the various regions of the thermogram. Samples were heated from ambient temperatures to 450°C under a 20 ml/min flow of dry nitrogen gas. The heating rate was observed to decrease about 5% between about 250 and 450°C. This decrease probably reflects deficiencies in the heat insulation of the system. Heating rate values quoted here are averaged over the range of decomposition temperatures.

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Sample weights were between 1.8 and 2.6 mg. Earlier experiments have established that thermogravimetric kinetic parameters are not affected by sample size in this range.[1] This conclusion is also consistent with the data of Kokta et al.,[2] who used a different thermogravimetric apparatus. The lack of sample size effects is probably due in part to the use of powdered polymer samples from which the release of gaseous products was not limited by the rate at which these species diffused to the polymer surface.

The sensitivity range of the unit was usually such that full scale on the recorder corresponded to a 2.4 mg weight.

Anionic polystyrenes were purchased from the Pressure Chemical Company. Broad distribution samples were made by emulsion polymerization.[3] After polymerization, excess monomer was removed by steam distillation and the emulsion was coagulated in acidified, saturated NaCl brine. The product was washed and dried and the polymer was purified by solution in benzene and precipitation with methanol. $\overline{M}_n$ of these polymers was measured by osmometry in toluene using deacetylated cellulose acetate membranes.

DATA TREATMENT

The method used is a variation of the technique of Freeman and Carroll,[4] as modified by Anderson and Freeman.[5,6] For decomposition reactions which proceed from a solid phase to solid plus gaseous products the general rate equation may be written

$$-\frac{dW}{dt} = kW^n \tag{1}$$

where W is the weight of active material remaining at time t for a particular reaction with order n, and k is the specific rate constant defined by this equation. It is assumed that the Arrhenius expression

$$k = Ae^{-E/RT} \tag{2}$$

applied, where the symbols have their usual meanings. Substituting in eq. (1) yields

$$\ln\left(-\frac{dW}{dt}\right) = \ln A - \frac{E}{RT} + n \ln W \tag{3}$$

If the preexponential factor A is independent of temperature and a constant heating rate is achieved in a dynamic thermogravimetric experiment then eq. (3) can be applied at two different temperatures to obtain

$$\Delta\ln\left(-\frac{dW}{dt}\right) = n \Delta\ln W - \frac{E}{R} \Delta\left(\frac{1}{T}\right) \tag{4}$$

Thus $\Delta\ln(-dW/dt)$ should be linear against $\Delta\ln W$, with slope n, when $\Delta(1/T)$ is held constant. The zero $\Delta\ln W$ intercept in such a plot will give the activation energy E.

We find that the best procedure for handling thermogravimetric data involves the use of eq. (3). The primary thermogram is differentiated with computer assistance with the results typically as shown in Figure 1. Some 10–15 data points are selected from the relevant portion of the thermogram and a computer-assisted least-squares fit to the functional form of eq. (3) yields the best
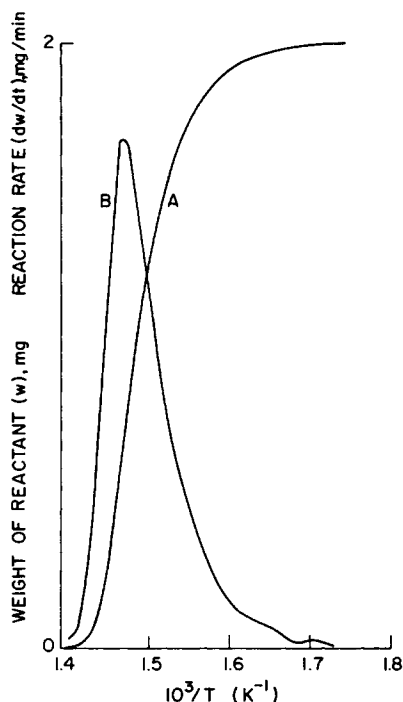
Fig. 1. Emulsion polystyrene (41°C polymerization). (A) Weight W vs $10^3/T$. (B) First time derivative dW/dt vs $1/T$.

values of A, E, and n, along with the 95% confidence limits or other statistical measures of the precision of these estimated values. This particular application of standard statistical procedures is new, so far as we know. It is most reliable, as shown below, when the value of n can be assigned *a priori* from other considerations.

Our results indicate that about the first 25% of the degradation follows zero-order kinetics. This conclusion follows from the linearity of the plot of $\ln(-dW/dt)$ against $1/T$ which has slope $-E/R$ and intercept of $\ln A$ when n in eq. (3) equals zero. The degradation limit at which the overall kinetics deviate from zero order can be located by that corresponding to the temperature at which this straight line relation fails. Figure 2 shows such a plot from the experimental data of Figure 1. The temperature at which the reaction order deviates from this initial zero value is reported in Table I as T_{0-1}.

Zero-order decomposition in the first stages of the reaction has been reported by previous investigators.[2,6]

The reaction order was generally close to unity in the 25%–100% degradation region. The calculated E and A values were highly correlated with the estimate of n, however. This resulted in the estimates of E and A being very sensitive to small variations in the calculated reaction order. Thus, if n were 1.1 the calculated E could differ by 5 kcal/mole from the figure estimated for $n = 1$. This effect has been experienced by other workers[2] who used the Anderson-Freeman method. The sharp swings in E are the consequence of the form of the mathematical model and experimental error rather than results of real variations in the degradation mechanism. In order to reduce these fluctuations we have
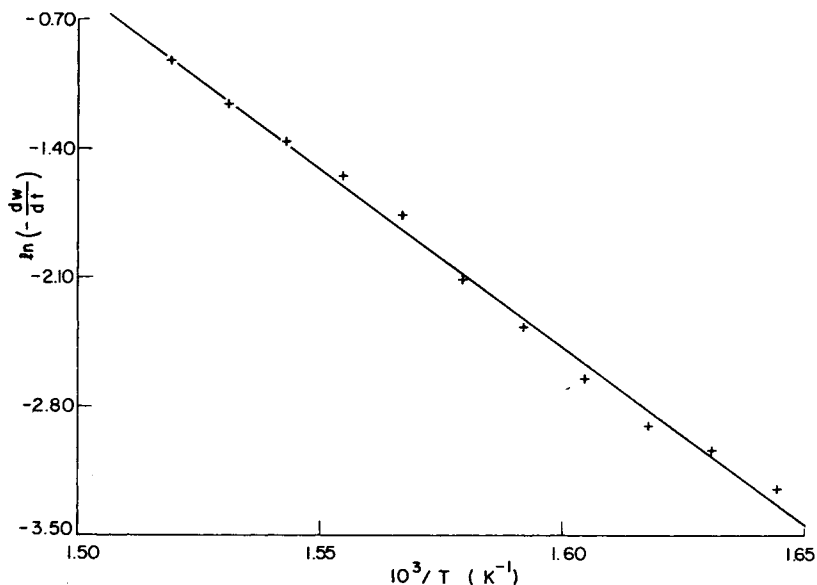
Fig. 2. Emulsion polystyrene (41°C polymerization). Plot of eq. (3) to establish limit of T^{-1} for zero-order kinetics.

followed the lead of Kokta and co-workers[2] and Wen and Dole[7] and set n identically equal to unity in the second degradation zone. The data points then yielded linear least-squares values of A and E from

$$\ln\left(-\frac{dW}{dt}\right) = \ln A - \frac{E}{RT} + \ln W \qquad (3a)$$

RESULTS

Table I summarizes the experimental polystyrene data. Thermograms were generally run in duplicate. Degradation of anionic polystyrenes started at 280–290°C and became quite rapid after 370°C. The temperature for loss of half the initial sample weight (T_w) is about 380°C while 80% of the polymer disappears by 400°C. Emulsion polystyrenes, on the other hand, are only 50 wt. % degraded at 400°C. This is most clearly shown in Figure 3 where thermograms of the three emulsion polystyrenes are compared to those of anionic polystyrenes with comparable molecular weights. The 60°C polymerized emulsion polystyrene appears to have degraded at lower temperatures than the 41 and 70°C samples. The reasons for this difference are not known.

The activation energies listed in Table I do not represent any particular reaction, but are characteristic of various kinetic chain steps in which the overall observed order was zero or unity with respect to polymer weight. The data are averages of two thermogravimetric experiments for each sample.

The activation energies measured here are effectively independent of polymer molecular weight in the range of samples studied. Kokta et al.[2] reported that activation energies for decomposition of anionic polystyrenes increased with molecular weights up to $M = 3.6 \times 10^5$, while we find no significant effects of molecular weights at $M \geq 1 \times 10^5$. The former authors reported E values for

TABLE I
Thermal Decomposition of Polystyrenes

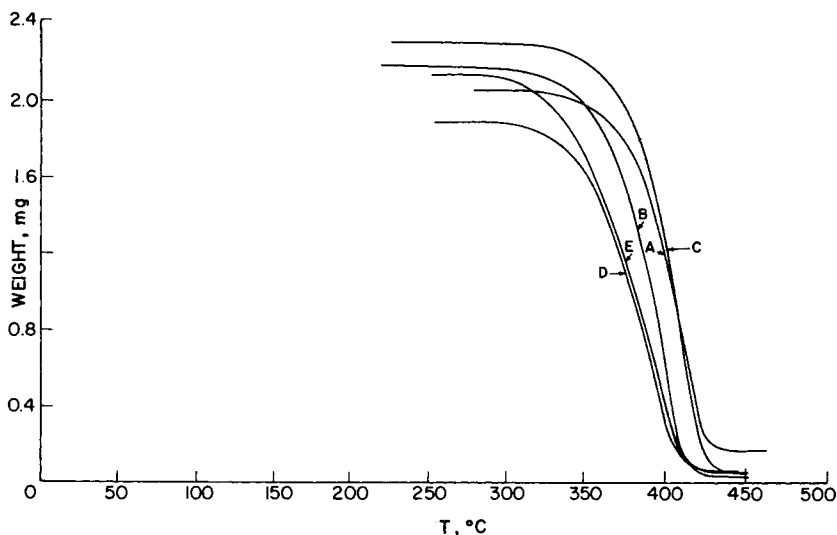| Polymer	Polymerization temperature, °C	$\bar{M}_n \times 10^{-5}$	Sample weight, mg	Heating rate, °C/min	Temperature for maximum decomposition rate T_M, °C	Temperature for half weight loss T_w, °C	Temperature for reaction order transition T_{0-1}, °C	Maximum decomposition rate V_m, %/min	Extent of reaction, % decomposition	Order of reaction, n	Activation energy, ΔE, kcal/mole	Frequency factor A, min^{-1}
Anionic		1.1	1.833	18.2	390	379	360	31.1	1.5–25	0	29.3 ± 0.9	5 × 10$^{9\pm1}$
									25–98	1.0	43.4 ± 3.3	2 × 10$^{14\pm2}$
		2.0	1.815	18.2	390	378	365	31.2	2.5–30	0	26.8 ± 1.4	6 × 10$^{8\pm1}$
									30–99.5	1.0	45.4 ± 2.9	9 × 10$^{14\pm2}$
		4.98	1.830	18.2	390	379	365	30.5	2.5–30	0	29.2 ± 1.5	4 × 10$^{9\pm1}$
									30–98	1.0	43.7 ± 2.1	3 × 10$^{14\pm1}$
		6.7	2.090	18.1	380	378	340	26.6	1–20	0	30.0 ± 1.9	1 × 10$^{10\pm1}$
									20–98	1.0	40.2 ± 3.6	2 × 10$^{13\pm2}$
		8.6	2.026	18.5	390	379	365	30.8	1–31	0	27.5 ± 0.9	1 × 10$^{9\pm1}$
									31–98	1.0	45.8 ± 3.0	1 × 10$^{15\pm2}$
		18.0	2.106	18.4	400	387	365	28.3	3–24	0	26.2 ± 1.4	3 × 10$^{8\pm1}$
									24–98	1.0	44.2 ± 4.2	2 × 10$^{14\pm2}$
Emulsion	40.7 ± 1	8.4	2.550	17.8	405	402	385	43.7	1–24	0	38.4 ± 2.1	2 × 10$^{12\pm1}$
									24–99.5	1.0	60.3 ± 2.4	3 × 10$^{19\pm1}$
	60 ± 1	6.85	2.155	18.3	400	391	370	39.2	2–24	0	34.4 ± 1.4	2 × 10$^{11\pm1}$
									24–97	1.0	56.9 ± 4.4	5 × 10$^{18\pm2}$
	69 ± 1	5.81	2.248	18.3	405	402	385	40.7	1.4–24	0	35.7 ± 1.4	3 × 10$^{11\pm1}$
									24–99	1.0	64.3 ± 4.5	5 × 10$^{20\pm2}$

Fig. 3. Thermograms of emulsion and anionic polystyrenes. (A) 41°C polymerized emulsion polymer $\overline{M}_n$ 8.4 × 10^{5}; (B) 60°C polymerized emulsion polymer $\overline{M}_n$ 6.9 × 10^{5}; (C) 70°C polymerized emulsion polymer $\overline{M}_n$ 5.8 × 10^{5}; (D) anionic polystyrene, $\overline{M}_n$ 6.7 × 10^{5}; (E) anionic polystyrene, $\overline{M}_n$ 5.0 × 10^{5};

the initial and final 50% of sample weight loss, however, whereas our activation energies are for the degradation intervals in which the kinetics were experimentally zero or first order. The different molecular weight effects which were found may reflect this difference in data treatment. Wegner and Patat[8] also found no molecular weight effects for $M > 100,000$.

DIFFERENCES BETWEEN ANIONIC AND EMULSION POLYSTYRENES

The anionic and emulsion polystyrene data in Table I appear to differ. The following analysis shows that this difference is statistically significant.

Our results were obtained by fitting eq. (3) to a straight line relation between the variables $\ln(-dW/dt)$ and $1/RT$. The activation energies are obtained from the slopes of these lines. The general linear equation is

$$y_i = m_i x_i + b_i \tag{5}$$

and the following statistical procedure was used to determine whether the slopes, m_1 and m_2 of data sets 1 and 2, respectively, were different. This indicates whether the corresponding activation energies are statistically different.

For the set of n_1 data points of set 1 (e.g., anionic polystyrenes) the linear least-squares fit to eq. (5) yielded values of m_1 and b_1 as usual and a value for the residual sum of squares SS_1. A similar procedure yielded SS_2 for the n_2 data points in set 2 (emulsion polystyrenes).

To check whether m_1 and m_2 are statistically different the x_1, y_1 and x_2, y_2 data points are combined to obtain a new set of $(n_1 + n_2)$ x, y values. A linear least-squares fit is now applied to

$$y = mx + b_1' \nu_1 + b_2' \nu_2 \tag{6}$$

where $\nu_1 = 1$, $\nu_2 = 0$ for the first data set and $\nu_1 = 0$, $\nu_2 = 1$ for the second data set. The resulting residual sum of squares SS_0 is obtained.

The F test is applied by calculating

$$F = \frac{(SS_0 - SS_1 - SS_2)(n_1 + n_2 - 4)}{(SS_1 + SS_2)x_2} \tag{7}$$

and comparing with an F distribution with $n_1 + n_2 - 4$ degrees of freedom. (The calculated F is likely to be positive since SS_0 is usually greater than $SS_1 + SS_2$.)

If the experimental F is greater than statistical F (with $n_1 + n_2 - 4$ degrees of freedom) the two activation energies are not equivalent. Table II compares the first-order decomposition activation energies of the emulsion and anionic polystyrenes.

Clearly, the emulsion polymer activation energies differ from those of the anionic polymers, even at the 97.5% confidence level. Table III applies the F test to the first-order activation energies of the anionic polystyrene set. There is no significant difference between the activation energy of the 498,000 molecular weight sample and any other polymer. This reinforces our conclusion that activation energies are independent of molecular weight in this range of molecular weights.

The three emulsion polymers are compared similarly in Table IV. There are no significant differences between the three samples.

A similar comparison of the zero order activation energies is summarized in Table V. Again, each emulsion polymer differs significantly from each anionic polystyrene.

DISCUSSION

Both the anionic and emulsion polystyrenes degrade thermally in an initial zero-order reaction which extends up to 25%–30% decomposition. This is followed by decomposition which is overall first order in sample weight up to about 98% decomposition. The activation energy for anionic polystyrenes in the initial zero-order region averaged about 28 kcal/mole while that for the emulsion polystyrene samples was 36 kcal/mole. The mean activation energies of the subsequent apparent first-order process also differ. The anionic samples averaged about 44 kcal/mole while the mean value for the emulsion polymers was 60.5 kcal/mole. The two polystyrene types differ significantly in their decomposition behavior, as demonstrated in the preceding section.

It has been suggested[9] that useful comparisons can be made through T_w, the temperature at which half the ultimate weight loss has occurred. The two polystyrenes differ also in this respect with T_w for anionic polystyrenes roughly at 380°C while that for the emulsion samples is about 400°C.

Anderson and Freeman[5] observed that the overall reaction order change for a commercial bulk polymerized polystyrene occurred at 370°C. These transitions, labeled T_{0-1} in Table I, occurred in our work at 340–365°C for anionic polymers and at 370–385°C for emulsion polymerized samples.

The preexponential factor is less in the first than the second stage of decomposition for both polymer types. The respective zero-order and first-order values for anionic polystyrenes are about 10^9 and 10^{14}, respectively, while those for the emulsion polymers are 10^{11} and 10^{19} min^{-1}.

Fuoss and co-workers[10] have computed the Arrhenius preexponential factor A from

TABLE II
Comparison of First-Order Decomposition Activation Energies of Emulsion and Anionic Polystyrenes

Emulsion polymerization temperature, °C	Set No. 1 (x_1, y_1) emulsion polystyrene	Set No. 2 (x_2, y_2) anionic polystyrene, $\overline{M}_n$	Activation energy, ΔE, kcal/mole	Preexponential factor, A, min^{-1}	No. of Points First set n_1	Second set n_2	Calculated	F values Statistical 95% confidence	Statistical 97.5% confidence
40.7 ± 1	$\overline{M}_n = 840{,}000$ $\Delta E = 60.3 \pm 2.4$ kcal/mole $A = 3 \times 10^{19 \pm 1}$ min^{-1}	110,000	43.4 ± 3.3	$2 \times 10^{14 \pm 2}$	9	11	33.560	4.494	6.115
		200,000	45.4 ± 2.9	$9 \times 10^{14 \pm 2}$	9	9	42.969	4.600	6.298
		498,000	43.7 ± 2.1	$3 \times 10^{14 \pm 1}$	9	10	72.892	4.543	6.200
		670,000	40.2 ± 3.6	$2 \times 10^{13 \pm 2}$	9	12	31.940	4.451	6.024
		860,000	45.8 ± 3	$1 \times 10^{15 \pm 2}$	9	10	34.406	4.543	6.200
		1,800,000	44.2 ± 4.2	$2 \times 10^{14 \pm 2}$	9	12	15.817	4.451	6.024
60 ± 1	$\overline{M}_n = 685{,}000$ $\Delta E = 56.9 \pm 4.4$ kcal/mole $A = 5 \times 10^{18 \pm 2}$ min^{-1}	110,000	43.4 ± 3.3	$2 \times 10^{14 \pm 2}$	9	11	16.219	4.494	6.115
		200,000	45.4 ± 2.9	$9 \times 10^{14 \pm 2}$	9	9	13.637	4.600	6.298
		498,000	43.7 ± 2.1	$3 \times 10^{14 \pm 1}$	9	10	23.267	4.543	6.200
		670,000	40.2 ± 3.6	$2 \times 10^{13 \pm 2}$	9	12	19.043	4.451	6.024
		860,000	45.8 ± 3	$1 \times 10^{15 \pm 2}$	9	10	12.691	4.543	6.200
		1,800,000	44.2 ± 4.2	$2 \times 10^{14 \pm 2}$	9	12	8.888	4.451	6.024
69 ± 1	$\overline{M}_n = 581{,}000$ $\Delta E = 64.3 \pm 4.5$ kcal/mole $A = 5.3 \times 10^{20 \pm 2}$ min^{-1}	110,000	43.4 ± 3.3	$2 \times 10^{14 \pm 2}$	9	11	32.127	4.494	6.115
		200,000	45.4 ± 2.9	$9 \times 10^{14 \pm 2}$	9	9	36.063	4.651	6.298
		498,000	43.7 ± 2.1	$3 \times 10^{14 \pm 1}$	9	10	55.344	4.543	6.200
		670,000	40.2 ± 3.6	$2 \times 10^{13 \pm 2}$	9	12	37.548	4.451	6.024
		860,000	45.8 ± 3	$1 \times 10^{15 \pm 2}$	9	10	34.227	4.543	6.200
		1,800,000	44.2 ± 4.2	$2 \times 10^{14 \pm 2}$	9	12	70.992	4.451	6.024

TABLE III
Comparison of First-Order Decomposition Activation Energies of Anionic Polystyrenes

Set No. 2 anionic polystyrene (x_2, y_2) $\bar{M}_n$	Activation energy, ΔE, kcal/ mole	Preexponential factor, A, min^{-1}	Number of Points		F Values		
			Set No. 1	Set No. 2	Calculated	Statistical 95% confidence	Statistical 97.5% confidence
110,000	43.4 ± 3.3	$2 \times 10^{14\pm2}$		11	0.017	4.451	6.042
200,000	45.4 ± 2.9	$9 \times 10^{14\pm2}$		9	0.630	4.543	6.200
670,000	40.2 ± 3.6	$2 \times 10^{13\pm2}$	10	12	1.330	4.414	5.978
860,000	45.8 ± 3.0	$1 \times 10^{15\pm2}$		10	0.924	4.494	6.115
1,800,000	44.2 ± 4.2	$2 \times 10^{14\pm2}$		12	0.019	4.414	5.978

Set No. 1 anionic polystyrene (x_1, y_1)

$\bar{M}_n = 498,000$

$\Delta E = 43.7 \pm 2.1$ kcal/mole

$A = 3 \times 10^{14\pm1}$ min^{-1}

TABLE IV
Comparison of First-Order Decomposition Activation Energies of Emulsion Polystyrenes

Set No. 1 (x₁, y₁) emulsion polystyrene	Set No. 2 (x₂, y₂) emulsion polystyrene		Activation energy, ΔE, kcal/mole	Preexponential factor, A, min⁻¹	Number of Points		Calculated	F values	
	Polymerization Temperature, °C	$\overline{M}_n \times 10^{-5}$			Set No. 1 n_1	Set No. 2 n_2		Statistical 95% confidence	Statistical 97.5% confidence
Polymerization temperature $= 69 \pm 1$°C $\overline{M}_n = 581{,}000$ $\Delta E = 64.3 \pm 4.5$ kcal/mole $A = 5.3 \times 10^{20 \pm 2}$ min⁻¹	40.7 ± 1	8.4	60.3 ± 2.4	$3 \times 10^{19 \pm 1}$	9	9	1.741	4.600	6.298
	60 ± 1	6.85	56.9 ± 4.4	$5 \times 10^{18 \pm 2}$		9	3.894	4.600	6.298
Polymerization temperature $= 40.7 \pm 1$°C $\overline{M}_n = 840{,}000$ $\Delta E = 60.3 \pm 2.4$ kcal/mole $A = 3 \times 10^{19 \pm 1}$ min⁻¹	60 ± 1	6.85	46.9 ± 4.4	$5 \times 10^{18 \pm 2}$	9	9	1.238	4.600	6.298

TABLE V

Comparison of Zero-Order Decomposition Activation Energies of Emulsion and Anionic Polystyrenes

Emulsion polymerization temperature, °C	Set No. 1 (x₁, y₁) emulsion polystyrene	Set No. 2 (x₂, y₂) anionic polystyrene, $\overline{M}_n$	Activation energy, ΔE, kcal/ mole	Preexponential factor, A, min⁻¹	No. of points		F values		
					First set n_1	Second set n_2	calculated	Statistical 95% confidence	Statistical 97.5% confidence
40.7 ± 1	$\overline{M}_n = 840{,}000$ $\Delta E = 38.4 \pm 2.1$ kcal/mole $A = 2 \times 10^{12 \pm 1}$ min⁻¹	110,000	29.3 ± 0.9	$5 \times 10^{9 \pm 1}$	11	12	45.812	4.381	5.922
		200,000	26.8 ± 1.4	$6 \times 10^{8 \pm 1}$		11	55.106	4.414	5.978
		498,000	29.2 ± 1.5	$4 \times 10^{9 \pm 1}$		10	29.922	4.451	6.042
		670,000	30.0 ± 1.9	$1 \times 10^{10 \pm 1}$		9	21.361	4.494	6.115
		860,000	27.5 ± 0.9	$1 \times 10^{9 \pm 1}$		15	66.734	4.301	5.786
		1,800,000	26.2 ± 1.4	$3 \times 10^{8 \pm 1}$		10	55.872	4.451	6.042
60 ± 1	$\overline{M}_n = 685{,}000$ $\Delta E = 34.4 \pm 1.4$ kcal/mole $A = 2 \times 10^{11 \pm 1}$ min⁻¹	110,000	29.3 ± 0.9	$5 \times 10^{9 \pm 1}$	14	12	18.991	4.301	5.786
		200,000	26.8 ± 1.4	$6 \times 10^{8 \pm 1}$		11	30.339	4.325	5.827
		498,000	29.2 ± 1.5	$4 \times 10^{9 \pm 1}$		10	11.432	4.351	5.872
		670,000	30.0 ± 1.9	$1 \times 10^{10 \pm 1}$		9	6.959	4.381	5.922
		860,000	27.5 ± 0.9	$1 \times 10^{9 \pm 1}$		15	43.834	4.242	5.686
		1,800,000	26.2 ± 1.4	$3 \times 10^{8 \pm 1}$		10	29.845	4.351	5.872
69 ± 1	$\overline{M}_n = 581{,}000$ $\Delta E = 35.7 \pm 1.4$ kcal/mole $A = 3 \times 10^{11 \pm 1}$ min⁻¹	110,000	29.3 ± 0.9	$5 \times 10^{9 \pm 1}$	12	12	38.019	4.351	5.872
		200,000	26.9 ± 1.4	$6 \times 10^{8 \pm 1}$		11	51.545	4.381	5.922
		498,000	29.2 ± 1.5	$4 \times 10^{9 \pm 1}$		10	23.742	4.414	5.978
		670,000	30.0 ± 1.9	$1 \times 10^{10 \pm 1}$		9	15.522	4.451	6.042
		860,000	27.5 ± 0.9	$1 \times 10^{9 \pm 1}$		15	59.414	4.279	5.750
		1,800,000	26.2 ± 1.4	$3 \times 10^{8 \pm 1}$		10	55.229	4.414	5.978

$$A = -\left(\frac{dW}{dt}\right)_M \left(\frac{\beta}{W_M}\right) \exp\left(\frac{E}{RT_M}\right) \tag{8}$$

where $(dW/dt)_M$ is the maximum rate of decomposition, which occurs at temperature T_M when the active mass of material is W_M and β is the linear rate of temperature increase. Equation (8), which is written for a first-order decomposition reaction, was used to check our different method of computation. Several comparisons are shown in Table VI, where it can be seen that the two procedures give closely comparable results.

Mehmet and Roche[11] examined the decomposition of a series of anionic polystyrenes using a thermal volatilization technique under vacuum. Their maximum decomposition temperatures are insensitive to polymer molecular weight in the range of molecular weights used in our study. We also find no influence of M on T_M in Table I. (Our T_M values are systematically lower by about 20°C. This discrepancy can be attributed[11] to the differences in sample configuration in the two sets of experiments.)

Published activation energies for polystyrene degradation are summarized in Table VII. These figures are quoted as reported by the cited authors and it is not clear how the plus-minus uncertainties attached to some of the activation energies were obtained. In any event, our data for emulsion polymers compare well with those obtained by other workers[5,12] with polymers which were also polymerized by free radical mechanisms. Our results with anionic polystyrenes seem to differ from those of Kokta and co-workers.[2] We have pointed out earlier that our conclusions with respect to molecular weight effects also differ and the probable reason is that the cited data[2] are for the first and last 50% of reaction

TABLE VI
Preexponential Factors

Sample	Preexponential factor	
	Method of this work	Method of Fuoss et al. (ref. 10)
Anionic, $M = 4.98 \times 10^5$	$10^{14\pm1}$	2.6×10^{14}
Anionic, $M = 1.8 \times 10^6$	$10^{14\pm2}$	2.05×10^{14}
Emulsion, 60° polymerization	$5 \times 10^{18\pm2}$	4.5×10^{18}
Emulsion, 69° polymerization	$5 \times 10^{20\pm2}$	5×10^{20}

TABLE VII
Summary of Published Activation Energies for Polystyrene Degradation

Method	Sample	Ref.	Activation energy ΔE, kcal mole^{-1}	
			Zero order	First order
Dynamic TGA	Bulk polymerized	5	46	60 ± 5
Dynamic TGA	Anionic	2	33 ± 5	50 ± 5
Isothermal TGA	Thermal initiation	12	—	55
Dynamic TGA	Not specified	13	35	58
Dynamic TGA	Anionic	This work	28	44
	Emulsion	This work	36	60.5

whereas our activation energies refer to the experimentally determined zero- and first-order decomposition ranges.

The foregoing summary shows that our data are consistent with those of other workers where such direct comparisons can be made. The observed differences between the decomposition behaviors of anionic and emulsion polymerized polystyrenes is thus very likely to be a real effect. There is no apparent reason to ascribe it to an artifact of our experimental procedures.

The ^{1}H NMR spectra of the polystyrenes were examined to determine whether there were any tacticity differences which might account for the variations in thermal stability. Spectra were recorded at 220 MHz and about 110°C in solutions of 5 g polymer per 100 ml tetrachlorethylene. The internal standard was hexamethyldisiloxane. There was no difference between any of the spectra of the 670,000 molecular weight anionic polystyrene, the 40 and 60°C emulsion polymers and a commercial bulk polystyrene with molecular weight about 300,000. The spectra of the 60°C emulsion polymer and the anionic sample are recorded in Figure 4. These spectra are very close to that reported for an "atactic" polystyrene by Inoue and co-workers[14] at 110 MHz with the same solvent and concentration. They are also very close to those given by Malhotra and co-workers[15] who found no difference between anionic and thermally initiated polystyrenes. The assignment of configurational sequences in such
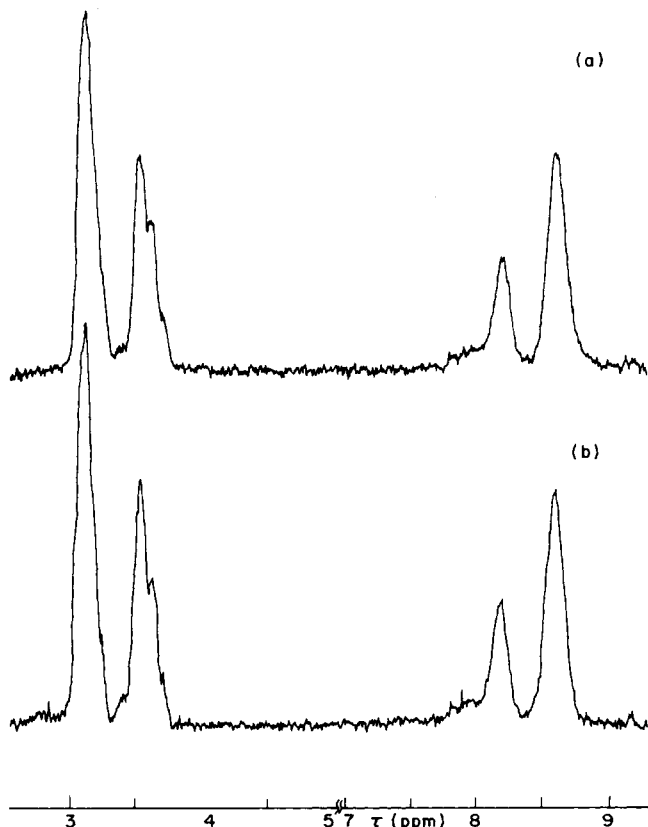

Fig. 4. ^{1}H spectra of polystyrenes observed at 220 MHz in 5% w/v solutions in tetrachlorethylene at 110°C: (a) emulsion polymer from 60°C reaction; (b) anionic polymer M = 670,000.

polystyrenes from ^{1}H NMR studies is not clearcut[16] but the important point in the present context is that the various polystyrenes exhibited no significant stereochemical differences. This is also in agreement with the conclusions of Randall[17] who found from ^{13}C NMR investigations that free radical and n-butyl lithium initiated polystyrenes had essentially equivalent atactic structures.

We conclude, then, that the differences in thermal stability which were observed do not result from tacticity differences. This leaves end groups as the likely cause of observations.

The anionic polystyrenes used are capped with a butyl group and styryl group. They differ from polystyrenes initiated by free radicals in their specific volumes[18] and partial specific volumes.[19] This reflects differences in end groups. The emulsion polystyrenes of this study are presumably capped by ^-O_3SO— and probably by some styryl and OH groups. Their thermal stabilities seem to be affected by these different end groups.

The essential features of the thermal degradation of polystyrene have been reviewed by Cameron and MacCallum.[20] It seems to be agreed that the mechanism involves a combination of random chain scission and unzipping which is initiated at chain ends. Intramolecular and intermolecular chain transfer steps are apparently significant and the zip length of chain depolymerization is short. The production of volatile material seems to occur almost exclusively at chain ends and it is perhaps not surprising that polystyrenes with different end groups would exhibit different thermal stabilities. It is not clear, however, why this difference in thermal stability should persist even after these end sites have decomposed. This can be rationalized, perhaps, by assuming that butyl and double-bonded groups are the most labile end structures. Unsaturated ends can be generated by transfer reactions once the decomposition of a molecule has been started.[20] The postulate that unsaturated groups initiate depropagation follows by analogy with poly(methyl methacrylate).[21,22]

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