Dynamic Thermogravimetric Analysis of Polystyrene: Effect of Molecular Weight on Thermal Decomposition

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Synopsis

A dynamic TGA method was used to study the effect of the molecular weight of well-defined polystyrene samples as well as the effect of heating rate and sample weight on the kinetic parameters of the thermal decomposition. It is shown that the maximum rate, the average specific rate, and the activation energy of the decomposition increase up to molecular weights of about 360,000 and then level off. The activation energy for the first part of the decomposition was 33 ± 5 kcal/mole and 50 ± 5 kcal/mole for the second part. An activation energy of 42 ± 5 kcal/mole was determined for the overall decomposition of polystyrene.

INTRODUCTION

In the last two decades, several authors[1-7] investigated the kinetics of the thermal degradation of polystyrene (PS). Some of the published results are contradictory, and the contradiction is ascribed to the influence of the molecular weight on the degradation rate and on the activation energy.

For example, Jellinek[6] found a decrease in reaction rate with an increase in the chain length of the PS fractions, while Madorsky[4] found the opposite. Madorsky[4] reported a higher degradation rate with a PS fraction of a $\bar{M}_n$ of 584,000 than with a fraction of a $\bar{M}_n$ of 106,000. In a later publication, Madorsky et al.[8] reported a higher degradation rate for a $\bar{M}_n$ of 51,000 than for a $\bar{M}_n$ of 24,000, but the same rate for a $\bar{M}_n$ of 2,000,000 and 5,000,000. Activation energies ΔE for the thermal degradation of PS are reported to be in the range of 39 kcal/mole to 58 kcal/mole,[2,4] with the reaction order n varying from zero to unity.[3,9]

Anderson and Freeman[5] suggested that the differences in activation energy and in reaction order could be due to two different reaction mechanisms. One would be dominant at a lower temperature range and the other, at a higher one. The same authors[5] found that the initial part of the degradation, up to 370°C, followed zero-order kinetics, with a ΔE of 46 kcal/mole. These values compare to $n = 0$ and $\Delta E = 44.7$ kcal/mole reported by Jellinek[3] to $n = 0$ and $\Delta E = 50$ kcal/mole reported by Atherton[7] and $n = 0$ to 1 and $\Delta E = 58$ kcal/mole reported by Madorsky.[4] Atherton[7] also found

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n to be unity and ΔE of 60 ± 5 kcal/mole at temperatures above $370°C$. At a temperature range of $200°$ to $300°C$, Wegner and Patat[9] determined the reaction to be of first order, with a ΔE of 48 kcal/mole.

Most of the discussed investigations[3,4,9,7] were carried out by isothermal thermogravimetric analysis (TGA). Anderson and Freeman,[5] however, employed dynamic TGA, which is less time consuming than the isothermal method but is more difficult to analyze and interpret. Unfortunately, this investigation did not show how their experimental conditions such as a sample weight of 100 mg, a heating rate of 5°C/min, and a $\bar{M}_n$ of 360,000 could influence ΔE and n. Furthermore,, the possible effect of molecular weight on ΔE and degradation rate, which could explain the contradictory results of Jellinek[3] and Madorsky,[4] has not been studied at all.

Thus, this study was undertaken to provide information on the effect of the molecular weight, heating rate, and sample weight on the kinetic parameters of the thermal degradation of well-defined PS samples. Dynamic TGA was employed throughout this investigation.

EXPERIMENTAL

Apparatus. A Perkin-Elmer TGS-1 thermobalance was used with a heating rate of 40°C/min and a sample weight of 0.1 to 3.0 mg. For most runs, the sensitivity range was at 1 mg for full-scale recorder with a chart speed of 40 mm/min. Dried nitrogen gas was used as inert carrier at a flow rate of 20 ml/min.

Polymers. The PS was obtained from Pressure Chemical Co. The molecular weights of these samples are summarized in Table I.

TABLE I
Molecular Weight Specifications for Polystyrene Samples

$\bar{M}_n$	$\bar{M}_w$	$\bar{M}_w/\bar{M}_n$	Note
1.05×10^3		1.10	
2.05×13^3		1.10	$\bar{M}_n$ averaged from V.P.O., cryoscopy,
3.60×10^3		1.10	and viscosity
9.60×10^3	1.00×10^4	1.06	
2.02×10^4	2.08×10^4	1.06	
5.01×10^4	5.05×10^4	1.06	
1.54×10^5	1.60×10^5	1.06	
3.92×10^5	3.94×10^5	1.06	$\bar{M}_n$ by membrane osmometer, $\bar{M}_w$ by
4.04×10^5	5.07×10^5	1.20	light scattering
6.40×10^5	6.70×10^5	1.10	
1.61×10^6	1.70×10^6	1.20	

RESULTS AND DISCUSSION

Data Treatment

The definitions of variables and constants used in evaluating the thermograms are listed in Table II. An example of a thermogram is shown in

TABLE II
Definition of Variables and Constants

$$\Delta w = \frac{w}{w_o} \times 100$$

$$\Delta T = T_E - T_S$$

$$\bar{v} = \Delta w \times \Delta T^{-1}$$

$$v_m = \left(\frac{d\Delta w}{dt}\right)_{T_m} \equiv \left(\frac{d\Delta w}{dT}\right)_{T_m}$$

$$v = \frac{d\Delta w}{dt}$$

$\bar{v}$	average specific rate of decomposition, in.%/°C
w	weight loss between T_E and T_S, in mg
w_o	initial weight, in mg or %
Δw	weight change between T_E and T_S, in %, as defined in Fig. 1
T_m	temperature at the maximum rate of the decomposition, in °C
T_S	extrapolated temperature at start of decomposition, in °C
T_E	extrapolated temperature at end of decomposition, in °C
t	time, in min
v_m	maximum rate of decomposition, in%/°C
SS	scanning speed, in °C/min
ΔE_{50-100}	activation energy between 50% and 100% of decomposition, in kcal/mole
ΔE_{1-50}	activation energy between 1–50% of decomposition in kcal/mole
v	rate of the decomposition, in %/°C

Index 0.5	weight = 0.5 mg;	SS = 40°C/min
Index 0	weight = 0 mg;	SS = 40°C/min
Index 0.0	weight = 0 mg;	SS = 0°C/min
Index 0, —	weight = 0 mg	
Index 0.5, —	weight = 0.5 mg	

Figure 1. The thermogravimetric curve contains all the information necessary to calculate the rate of weight loss v (tangent of the weight loss curve), the average specific rate of weight loss $\bar{v}$, the temperature interval of the decomposition reaction ΔT, and the weight loss Δw.

The activation energy ΔE of the decomposition process was calculated with the modified Freeman and Carrol procedure given by Anderson and Freeman.[5] The method is based on the following expression:

$$\Delta \log (dw/dt) = n \, \Delta \log w_r - (\Delta E/2.3R)\Delta(1/T) \tag{1}$$

where dw/dt is the reaction rate, n is the reaction order, ΔE is the activation energy, R is the gas constant, and T is the absolute temperature; w_r is obtained from $(w_o - w_c)$, where w_c is the weight loss at the point where dw/dt is taken and w_o is the total weight loss associated with the reaction. In order to determine dw/dt and w_r at constant $\Delta(1/T)$, the first derivation of the primary TGA curve and the corresponding w_r are plotted as a function of the reciprocal absolute temperature. To evaluate the constant in eq. (1), $\Delta \log dw/dt$ was plotted against $\Delta \log w_r$, while the $\Delta(1/T)$ values
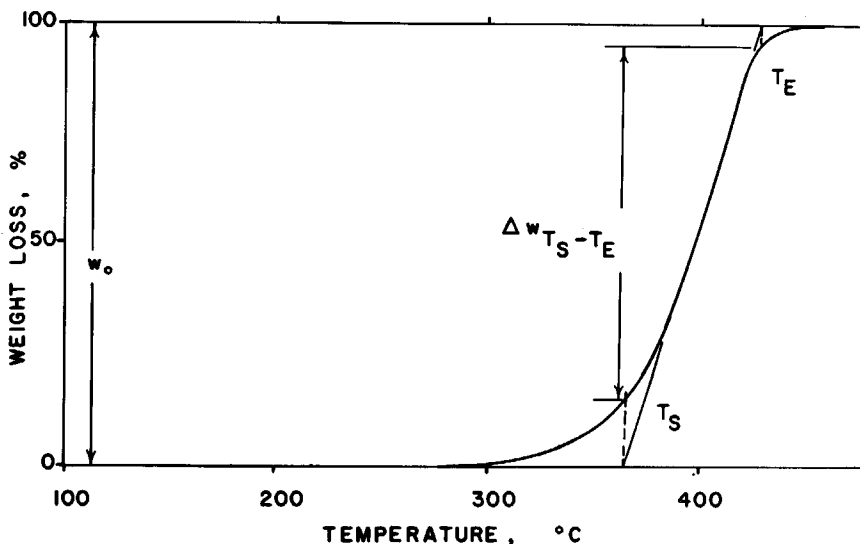
Fig. 1. Example of TGA thermogram of polystyrene with definition of temperature of the start (T_S) and the end (T_E) of decomposition, weight loss (Δw), and total weight loss (w_o).

were kept constant. The order of reaction, n, was determined from the slope and the energy of activation from the intercept at log $w_r = 0$. Using eq. (1) with our experimental data resulted in a ΔE which was quite sensitive to very small variations in reaction order. The reaction order was generally close to unity in the range of 50% to 95% degradation.

In order to eliminate fluctuations of ΔE, the values were recalculated for each interval ($\Delta(1/T) = 1 \times 10^{-5}\,°\mathrm{K}^{-1}$) of Δlog (dw/dt) and Δlog w_r in the 50% to 95% degradation range. The reaction order n was taken to be unity. All calculated values of ΔE were averaged to yield a single value defined as ΔE_{50-95}.

The activation energy of the first half of the degradation showed zero-rather than first-order kinetics, and this is in agreement with Anderson and Freeman.[5] The values were obtained from the slopes of plotted log dw/dt against $1/T$. All values were then averaged to give a single value defined as ΔE_{1-50}.

The activation energies based on these interpretations do not represent an particular reaction but rather encompass several reaction mechanisms for initiation, propagation, etc.

Effects of Sample Weight and Heating Rate

A PS with a $\bar{M}_n$ of 3600 was used to investigate the influence of sample weight, at a constant heating rate of 40°C/min, on v_m, Δw, ΔT, v, and ΔE. The results are summarized in Table III and plotted in Figures 2, 3, and 4. In addition, part (a) of Table III contains data on the effect of the heating
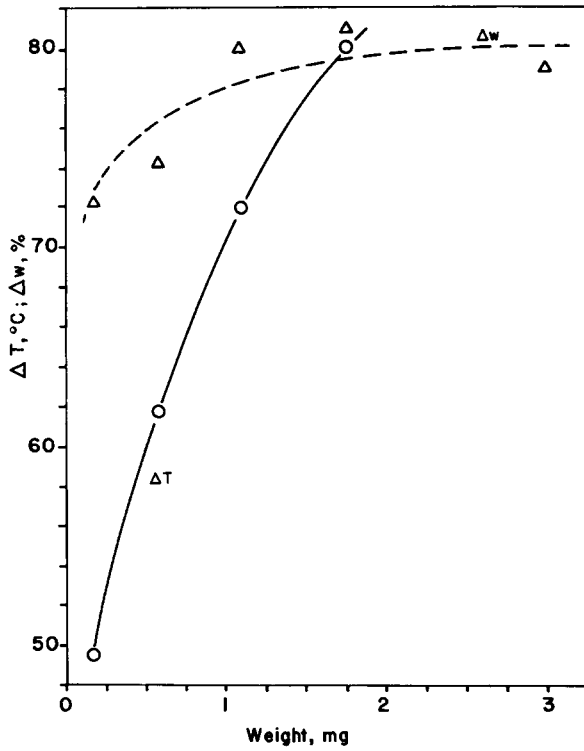
Fig. 2. Effect of sample weight on temperature interval ΔT and weight loss Δw; $\bar{M}_n$ = 3,600; scanning speed = 40°C/min.
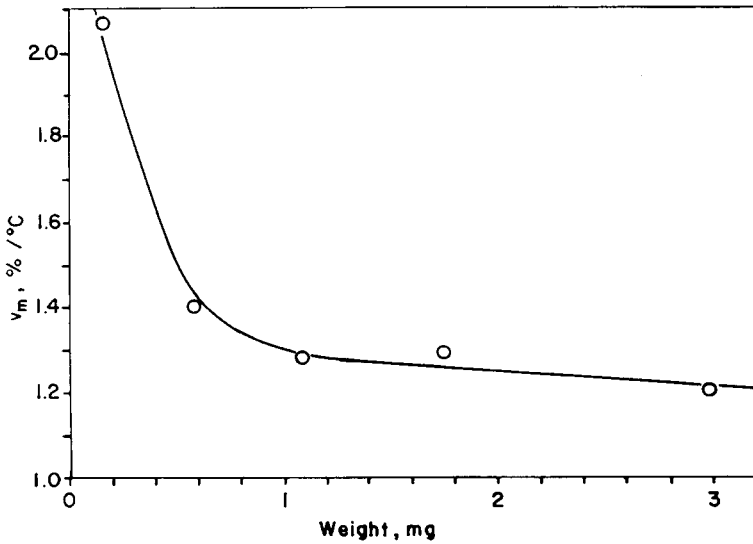

Fig. 3. Effect of sample weight on maximum rate of decomposition v_m; $\bar{M}_n$ = 3,600; scanning speed = 40°C/min.

TABLE III

Effect of $\bar{M}_n$, w_0, and SS on v_m, $\bar{v}$, Δw, ΔT, and ΔE

$M_n \times 10^{-3}$	w_0, mg	T_m, °C	v_m, %/min	$\dot{v}_m$, %/°C	$\bar{v}$, %/°C	Δw, %	ΔT, °C	T_S, °C	T_E, °C	$\phi\Delta E_{50-96}$, kcal/mole	$\phi\Delta E_{1-50}$, kcal/mole	SS, °C/min
						Part (a)						
3.60	0.582	380	58.2	1.40	1.20	74.3	61.8	346	408	32.3	23.0	40
3.60	0.157	355	81.6	2.07	1.46	72.6	49.7	330	380	29.7	25.0	40
3.60	1.746	410	51.8	1.29	1.00	80.9	80.6	364	444	33.0	22.0	40
3.60	1.083	390	51.4	1.28	1.08	80.0	74.0	352	426	31.8	21.5	40
3.60	2.983	442	48.2	1.20	0.97	79.2	81.6	384	465	42.0	19.0	40
3.60	0.479	410	115.5	1.44	0.97	80.6	82.8	353	436	25.0	19.5	80
3.60	0.590	420	128.0	1.60	1.02	80.7	79.1	362	442	29.6	23.0	80
3.60	0.525	445	193.2	1.21	0.91	79.6	88.8	382	471	47.9	19.6	160
3.60	0.585	440	217.0	1.35	0.85	78.4	85.9	384	470	31.8	20.3	160
3.60	0.460	345	16.9	1.69	1.38	76.0	55.3	314	369	29.6	21.7	10
3.60	0.556	360	35.3	1.76	1.30	76.6	59.1	323	383	29.6	24.2	20
3.60	0.488	360	28.7	1.43	1.22	74.5	63.7	326	389	31.2	23.2	20

Part (b)

20.20	0.917	385	15.6	1.56	1.29	79.4	61.6	349	411	38.7	20.9	10
20.20	0.625	400	28.2	1.41	1.12	80.6	71.9	356	427	39.2	21.2	20
20.20	0.882	440	59.5	1.48	1.20	78.6	65.6	392	457	—	22.0	40
20.20	0.496	430	107.3	1.34	1.07	76.6	71.7	390	462	39.1	25.0	80
20.20	0.421	470	108.0	1.35	1.08	77.6	71.7	423	495	43.6	23.6	80
20.20	0.657	460	253.0	1.58	1.06	77.0	72.6	411	483	39.9	20.0	160
154.	0.413	370	18.0	1.81	1.47	77.5	52.6	341	394	34.3	27.0	10
154.	0.261	390	37.6	1.88	1.48	77.0	51.9	361	413	65.3	28.5	20
154.	0.332	415	63.6	1.59	1.29	80.7	62.8	377	440	49.2	26.9	40
154.	0.295	440	123.0	1.54	1.26	80.7	64.3	394	458	48.5	28.9	80
154.	0.476	465	317.0	1.98	1.33	75.2	56.4	424	480	31.4	27.2	160

Part (c)

392.	0.921	395	15.4	1.54	1.20	75.6	62.7	359	422	47.0	20.2	10
392.	0.294	395	21.4	2.14	1.70	75.9	44.5	370	415	66.1	26.6	10
392.	0.845	425	46.1	2.30	1.77	77.2	43.7	398	442	—	45.4	20
392.	0.770	430	75.4	1.88	1.46	75.0	51.5	402	453	55.6	31.5	40
392.	0.490	435	151.0	1.89	1.48	76.3	51.5	413	465	58.6	40.8	80
392.	0.327	420	273.0	1.70	1.30	79.5	61.1	388	449	43.2	27.7	160
392.	0.450	450	246.0	1.53	1.10	76.7	70.0	408	478	46.0	29.0	160

rate using a sample weight of approximately 0.5 mg PS.   These results are
corrected to 0.5 mg and to zero weight and plotted in Figures 5 through 9.

The response of higher molecular weight PS to different heating rates is
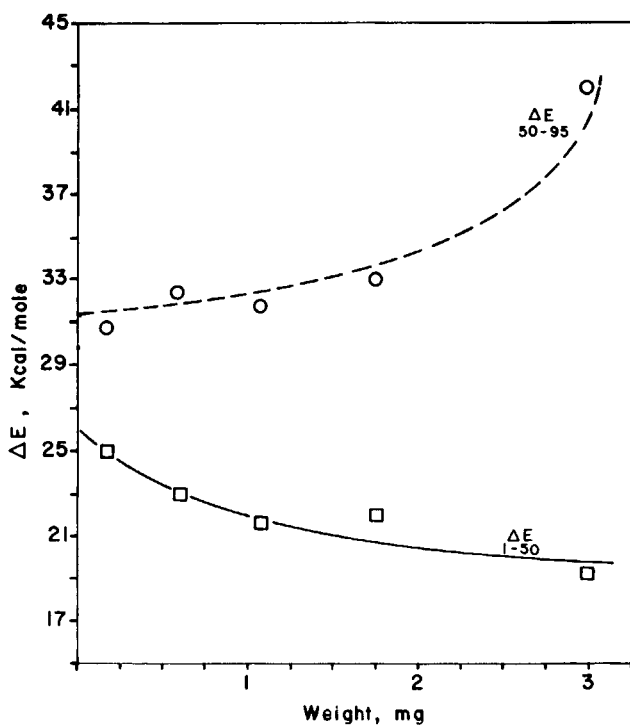shown in parts (b) and (c) of Table III.   Samples with molecular weight

Fig. 4. Effect of sample weight on activation energy ΔE_{50-95} and ΔE_{1-50} of decomposition;
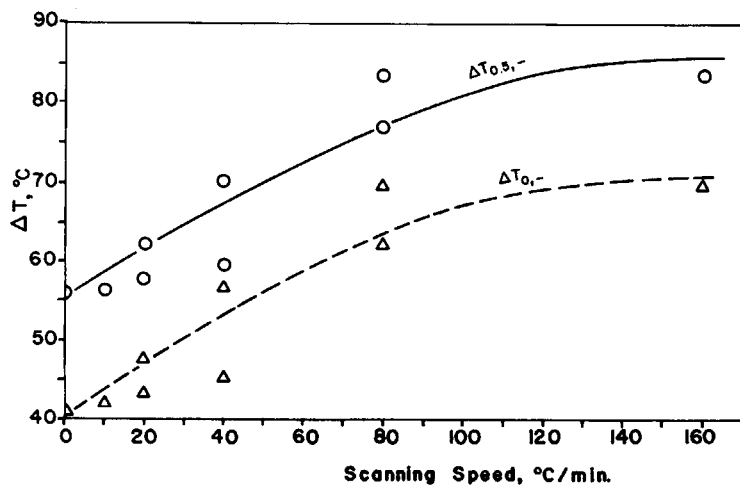$\bar{M}_n = 3,600$; scanning speed $= 40°C/min$.

Fig. 5. Effect of scanning speed on temperature interval $\Delta T_{0.5,-}$ and $\Delta T_{0,-}$; $M_n = 3600$.
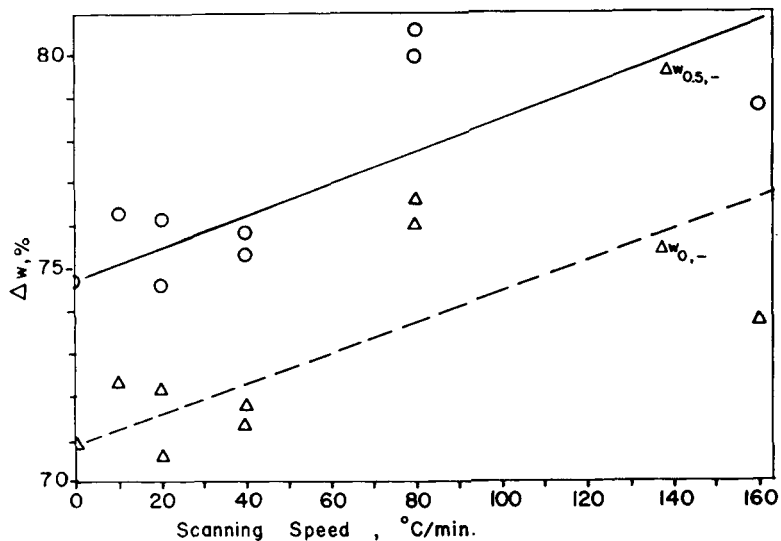
Fig. 6. Effect of scanning speed on weight loss $\Delta w_{0.5, -}$ and $\Delta w_{0, -}$; $\bar{M}_n = 3600$.
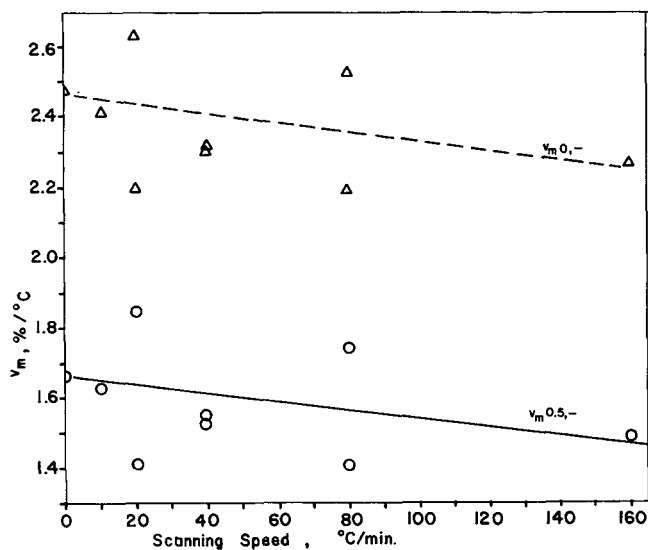

Fig. 7. Effect of scanning speed on maximum rate $v_{m0.5, -}$ and $v_{m0, -}$ of decomposition; $\bar{M}_n = 3600$.

of 20,200, 154,000, and 392,000 showed comparable effects to different heating rates, as is given by a $\bar{M}_n$ of 3600 (part (a) of Table III). Figures 10 to 12 show the effect of the heating rate on the weight loss, maximum decomposition rate, and temperature interval of a PS with a $\bar{M}_n$ of 392,000. The slopes of the curves are similar to the ones obtained with the lower molecular weight PS shown in Figures 5 through 9. The ΔE values, how-
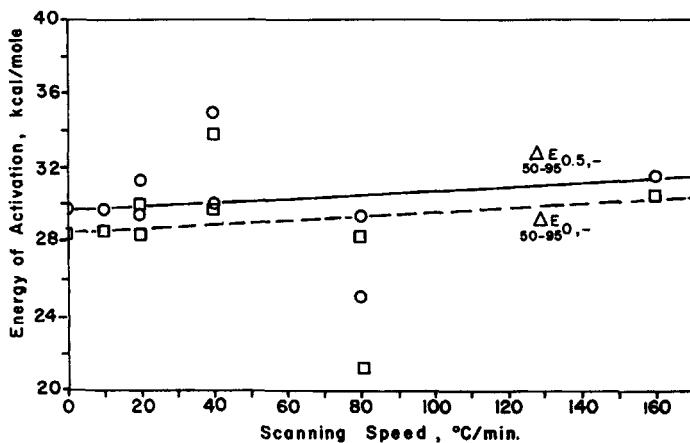
Fig. 8. Effect of scanning speed on activation energy $\Delta E_{0.5, -(50-95)}$ and $\Delta E_{0, -(50-95)}$; $\bar{M}_n = 3600$.
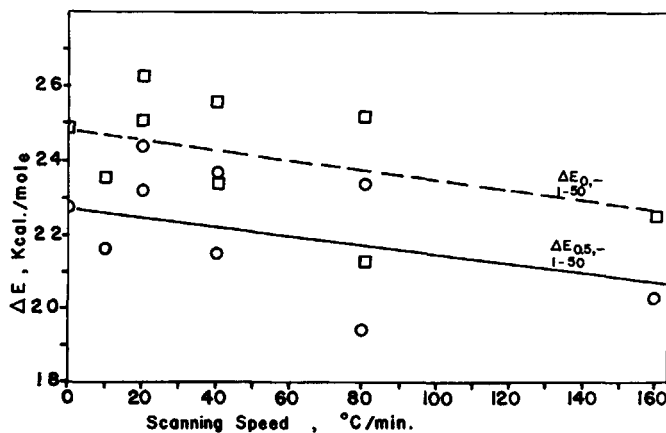

Fig. 9. Effect of scanning speed on activation energy $\Delta E_{0.5, -(1-50)}$ and $\Delta E_{0, -(1-50)}$; $\bar{M}_n = 3600$.

ever, are too scattered (part (c) of Table III) to allow drawing of conclusions.

Since the effect of heating rates and sample weights are comparable for the different molecular weight PS, the values could be used for extrapolation to zero scanning speed and zero sample weight. Figures 2, 3, 5, and 7 show that higher heating rates and larger sample weights produced a larger ΔT and a slower v_m and $\bar{v}$. This agrees with the results obtained by Newkirk[11] and Coats et al.[12] The effect of the heating rate on ΔE is not so pronounced as the effect of the sample weight (Fig. 2).

The influence of the molecular weight on the thermal parameters is summarized in Table IV. These values are recalculated (Tables V and VI) to zero and 0.5 mg sample weight with a scanning speed of 40°C/min, and to
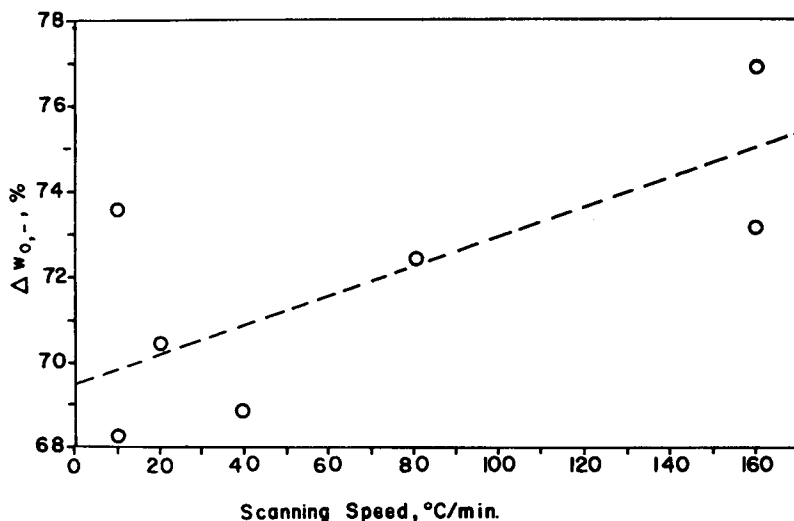
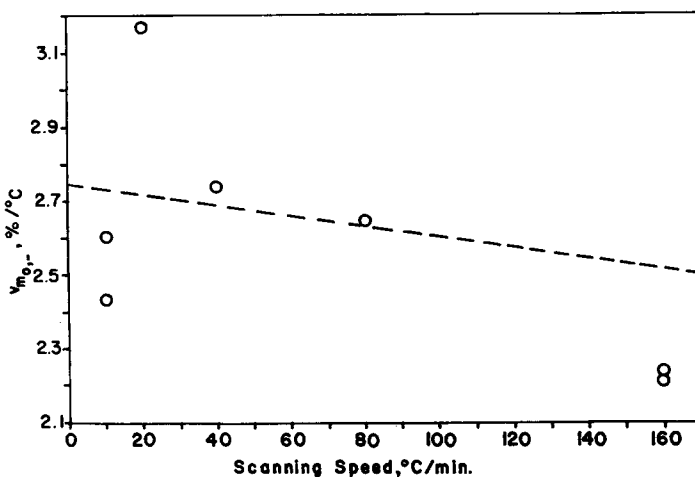Fig. 10. Effect of scanning speed on weight loss $\Delta w_{0,-}$; $\bar{M}_n = 392,000$.

Fig. 11. Effect of scanning speed on maximum rate $v_{m0,-}$ of decomposition; $\bar{M}_n = 392,000$.

zero weight with zero scanning speed.   The effect of the recalculated values on molecular weight, ΔT, and Δw is shown in Figures 13 and 14.   It can be seen that ΔT increased with increasing molecular weight and then leveled off.   The values of ΔT, however, were proportional to sample weight and heating rate.   The portion of Δw lost between T_E and T_S also increased with increasing molecular weight until a plateau was reached at a $\bar{M}_n$ of 65,000.   The plateau for ΔT was reached at about $\bar{M}_n$ of 360,000.

When the corrected maximum rate v_m and the specific average rate $\bar{v}$ are plotted versus log $\bar{M}_n$ (Fig. 15), a definite dependence on the molecular

TABLE IV

Effect of $\bar{M}_n$ and w_o on v_m, $\bar{v}$, Δw, ΔT, and ΔE^a

$\bar{M}_n \times 10^{-3}$	w_o, mg	T_m, °C	v_m, %/min	v_m, %/°C	$\bar{v}$, %/°C	Δw, %	ΔT, °C	T_S, °C	T_E, °C	$\phi\Delta E_{50-95}$, kcal/mole	$\phi\Delta E_{1-50}$, kcal/mole
1.05	0.731	430	45.2	1.13	0.926	72.7	78.5	397	476	33.4	20.9
2.05	0.971	440	50.8	1.23	0.972	75.8	78.0	398	476	39.4	19.2
3.60	0.552	420	57.8	1.44	1.051	76.2	72.5	374	446	35.1	21.3
9.60	0.568	425	62.6	1.56	1.211	76.9	63.5	391	454	39.5	29.7
20.2	0.397	425	62.5	1.56	1.302	76.8	59.0	386	445	41.3	20.7
50.1	0.496	426	64.3	1.61	1.251	78.2	62.5	392	454	34.0	27.0
154.	0.202	425	57.0	1.42	1.18	77.7	66.0	375	441	39.8	32.0
392.	0.293	425	70.6	1.76	1.434	77.5	54.0	387	441	50.3	25.3
404.	0.932	430	81.7	2.04	1.480	76.2	51.5	399	450	52.8	32.5
640.	0.346	429	76.3	1.90	1.800	75.7	42.0	403	445	54.5	31.5
1610.	0.438	415	79.3	1.98	1.430	77.4	54.0	387	441	48.3	30.5

^{a} $SS = 40$°C/min.

TABLE V

Effect of $\bar{M}_n$ on $v_{m0.5}$, $v_{m0.0}$, $v_{0.5}$, v_0, and $\bar{v}_{0.0}$

$\bar{M}_n \times 10^{-3}$	w_o, mg	v_m, %/°C	$v_{m0.5}$, %/°C	v_{m0}, %/°C	$v_{m0.0}$, %/°C	$\bar{v}$, %/°C	$\bar{v}_{0.5}$, %/°C	$\bar{v}_0$, %/°C	$\bar{v}_{0.0}$, %/°C
1.05	0.731	1.13	1.202	2.109	2.165	0.926	0.985	1.146	1.392
2.05	0.971	1.23	1.346	2.130	2.186	0.972	1.200	1.328	1.670
3.60	0.552	1.44	1.522	2.306	2.262	1.051	1.065	1.263	1.543
9.60	0.568	1.56	1.660	2.440	2.496	1.211	1.240	1.530	1.971
20.2	0.397	1.56	1.398	2.182	2.238	1.302	1.293	1.542	1.982
50.1	0.496	1.61	1.52	2.311	2.367	1.251	1.247	1.532	1.959
154.	0.202	1.42	0.953	1.737	1.793	1.180	1.082	1.262	1.492
392.	0.293	1.76	1.435	2.219	2.275	1.434	1.32	1.64	2.128
404.	0.932	2.04	2.146	2.93	2.986	1.480	1.832	2.66	2.580
640.	0.346	1.90	1.660	2.440	2.496	1.800	1.652	2.262	2.350
1610.	0.438	1.98	1.884	2.668	2.724	1.430	1.392	1.777	2.410

TABLE VI

Effect of $\bar{M}_n$ on $\Delta E_{0.5}$, ΔE_0, and $\Delta E_{0.0}$

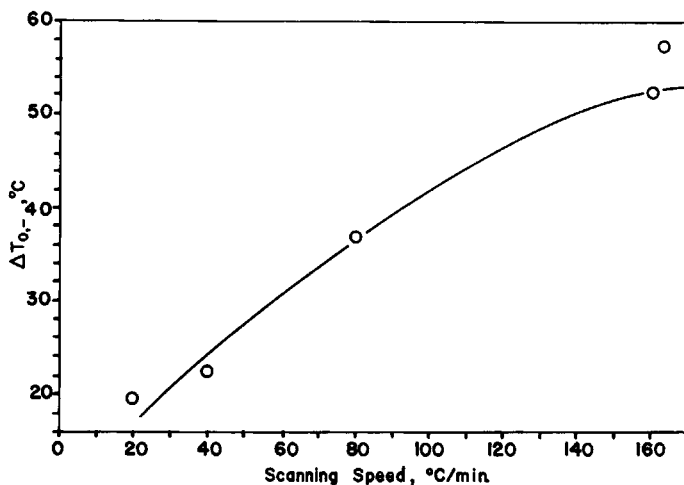| $\bar{M}_n \times 10^{-3}$	w_o, mg	$\phi \Delta E_{50-100}$, kcal/mole	$\Delta E_{0.5(50-100)}$, kcal/mole	$\Delta E_{0(50-100)}$, kcal/mole	$\Delta E_{0.0(50-100)}$, kcal/mole	$\phi \Delta E_{1-5}$, kcal/mole	$\Delta E_{0.5(1-50)}$, kcal/mole	$\Delta E_{0(1-50)}$, kcal/mole	$\Delta E_{0.0(1-50)}$, kcal/mole
1.05	0.731	33.4	32.9	31.7	31.3	20.9	21.8	23.7	24.2
2.05	0.971	39.4	38.3	37.2	36.8	19.2	21.0	22.9	23.4
3.60	0.552	35.1	35.0	33.9	33.4	21.3	21.5	23.4	23.9
9.60	0.568	39.5	39.4	38.2	37.8	29.7	30.0	31.9	32.4
20.2	0.397	41.3	41.5	40.4	40.0	20.7	20.3	22.2	22.7
50.1	0.496	34.0	34.0	32.9	32.5	27.0	27.0	28.9	29.4
154.	0.202	39.8	40.5	39.3	38.9	32.0	30.9	32.8	33.3
392.	0.293	50.3	50.6	49.6	49.2	25.3	24.5	26.4	26.9
404.	0.932	52.8	51.8	50.7	50.2	32.5	34.1	36.0	36.6
640.	0.346	54.5	54.8	53.7	53.3	31.5	30.9	32.8	33.3
1610	0.438	48.3	44.4	47.3	46.9	30.5	30.3	32.2	32.7

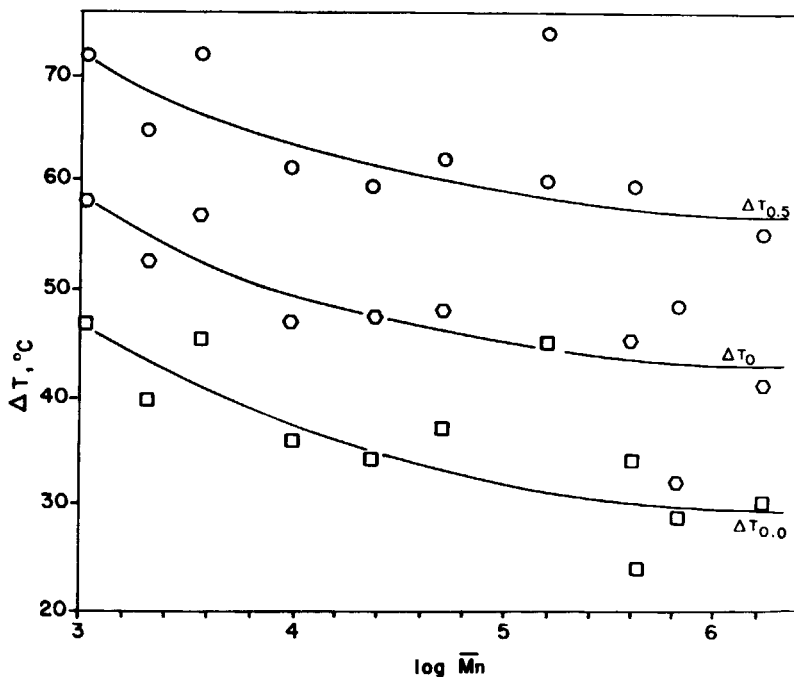Fig. 12. Effect of scanning speed on temperature interval $\Delta T_{0,-}$; $\bar{M}_n = 392,000$.

Fig. 13. Effect of number-average molecular weight on temperature interval $\Delta T_{0.5}$, and $\Delta T_{0.0}$.

weights shows up. The maximum rate and specific average rate increase to log $\bar{M}_n = 5.6$, which corresponds to a $\bar{M}_n$ of 360,000, before they level off. The $\bar{v}$ values, though lower than v_m show a slightly steeper dependence on log $\bar{M}_n$. The highest v_m and $\bar{v}$ are encountered with zero sample weight and zero heating rate, which corroborates the findings of Newkirk.[11]
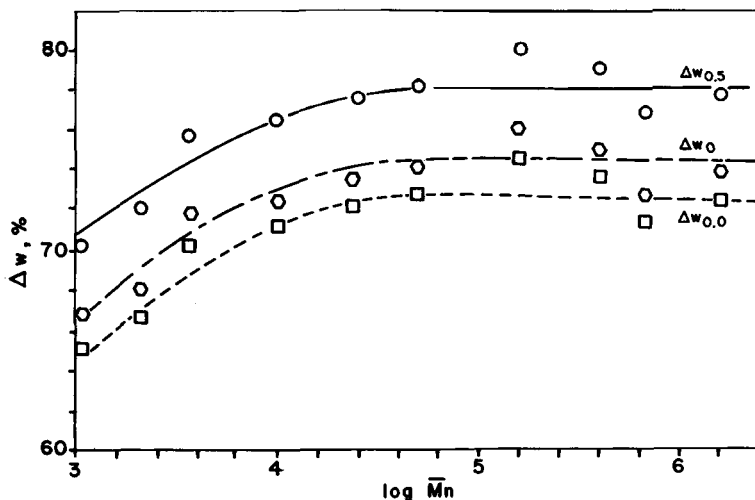
Fig. 14. Effect of number-average molecular weight on weight loss $\Delta w_{0.5}$, Δw_0, and $\Delta w_{0.0}$.
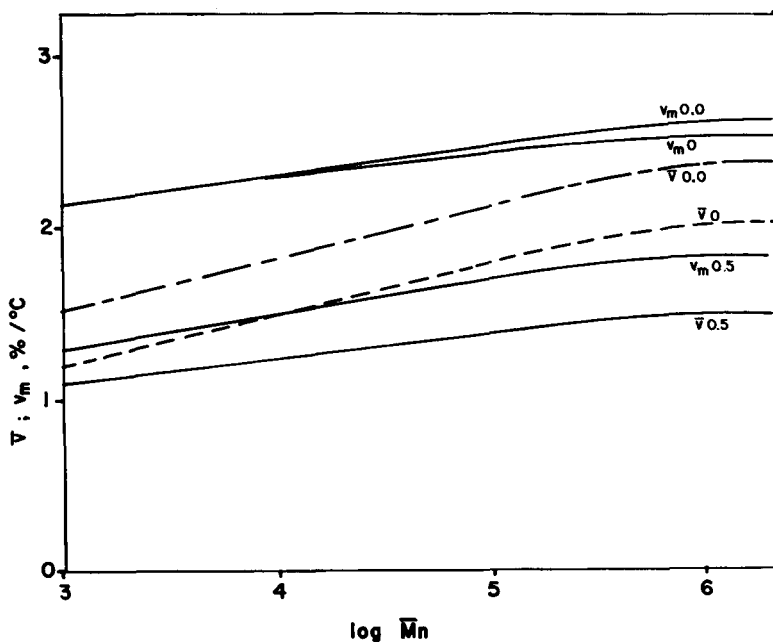

Fig. 15. Effect of number-average molecular weight on specific average rates $\bar{v}_{0.5}$, $\bar{v}_0$, and $\bar{v}_{0.0}$ and maximum rate of decomposition $v_{m0.5}$, v_{m0}, and $v_{m0.0}$.

The effect of the molecular weight on the activation energy is summarized in Table VI and plotted in Figure 16. A fairly linear increase in ΔE is shown by both the 1-to-50% and the 50-to-95% thermal degradation of PS. The second part, 50-to-95% degradation, is steeper and results in a ΔE of 50 ± 5 kcal/mole, while the first part, 1 to 50% degradation, gives a ΔE of
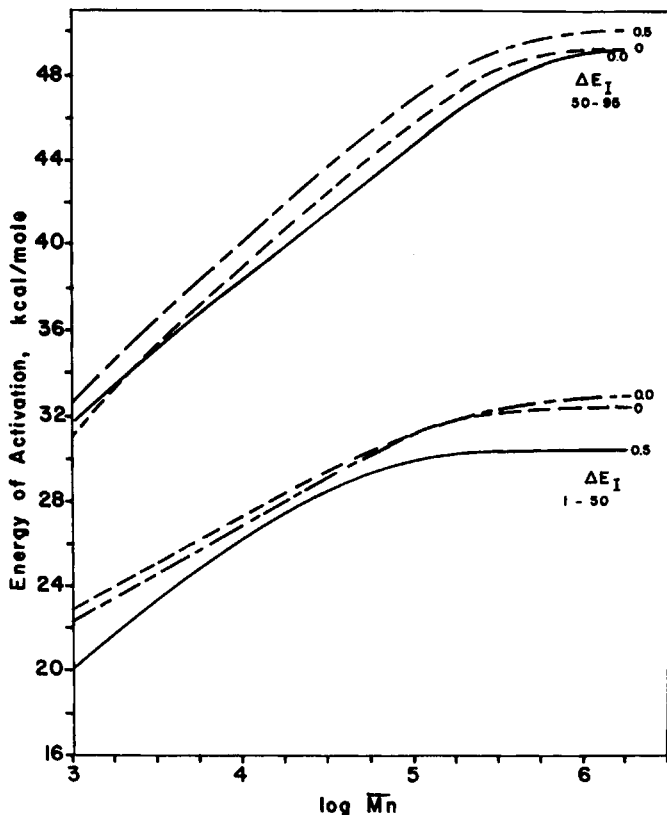
Fig. 16. Effect of number-average molecular weight on activation energies of the first ($\Delta E_{0.5(1-50)}$, $\Delta E_{0(1-50)}$, $\Delta E_{0.0(1-50)}$) and second half ($\Delta E_{0.5(50-95)}$, $\Delta E_{0(50-95)}$, $\Delta E_{0.0(60-95)}$) of decomposition.

33 ± 5 kcal/mole; 42 ± 5 kcal/mole is the average value for the entire degradation process.   Only after a $\bar{M}_n$ of 360,000 is reached becomes ΔE independent of the molecular weight.

The activation energy of the PS degradation obtained by various authors using different methods are compared to our values in Table VII.   The activation energies are listed and defined as ΔE_1 for the first stage (1% to 50%), ΔE_2 for the second stage (50% to 95%), and ΔE_{12} for the full range. The reported ΔE from mechanical and thermal degradation[13] are in excellent agreement with our values obtained by dynamic TGA.   It is suggested that the presence of "weak" bonds in PS as reported by Jellinek,[3] Atherton,[7] Amelin et al.,[13] and Korshak and Vinogradova[15] could affect the kinetics of the first degradation stage.   These "weak" bonds will have an important effect on the overall mechanical properties.

Contrary to Anderson and Freeman[5] who assume two different reaction mechanism responsible for the degradation, we believe that the differences are being caused by the presence of "weak" bonds in the PS.   The first

TABLE VII
Activation Energies for Polystyrene Decomposition

Method	Author	Energy of activation first decomp. ΔE_1, kcal/mole	Energy of activation second decomp. ΔE_2, kcal/mole	Overall activation energy ΔE_{12}, kcal/mole
Gas chromatography (formation of the styrene recorded)	Kysel[1]		52	
Mass spectrometry (formation of the volatile products)	Amelin et al.[13]	35	55	45
Mechanical destruction	Amelin et al.[13]	33		
TGA, isothermal	Madorsky[14]		55	
TGA, isothermal	Jellinek[3]			44.7
Melt viscosities	Boon et al.[2]			39
Thermal extraction	Wegner et al.[9]			48
TGA, dynamic	Anderson et al.[5]	(46)	(60 ± 5)	(53)
TGA, dynamic	Present work	33 ± 5	50 ± 5	44

degradation stage of ΔE_1 of 33 kcal/mole, is so low because of the presence of weak bonds. In the second stage, after all weak bonds have been eliminated, the activation energy ΔE_2 increases to 52 kcal/mole, the activation energy for the overall degradation process being 44 kcal/mole.

Jellinek[3] in his investigation assumed that the cumulative rates of monomer formation were the same throughout a considerable part of the degradation range. Since he used the slopes of the degradation curves to obtain average values of the rates, the resulting value can be regarded as being the one for the overall activation energy ΔE_{12}. Madorsky,[14] on the other hand, extrapolated the second part of the degradation curve to zero degradation. Thus, his value would exclude the initial activation energy ΔE_1 and represents ΔE_2.

Amelin et al.[13] specified his values as either for first- or second-stage degradation. The values of Boon et al.[2] and Wegner and Patat[9] were reported to represent the overall degradation process. The result of Wegner and Patat[9] indicates that they succeeded in eliminating "weak" bonds by using extremely "clean" conditions in the preparation of the PS. Furthermore, they were able to work with extremely low O_2, H_2O, and CO_2 levels during the thermal degradation. These conditions resulted in an almost complete elimination of the first-stage degradation, characterized by a low activation energy of 33 kcal/mole, and give a single activation energy value of ΔE_2.

Thus, most values listed in Table VII show remarkably good agreement of the activation energies if they are classified as suggested. Thus, the activa-

tion energy for the first stage, ΔE_1, equals 33 ± 3 kcal/mole; the activation energy for the second stage, ΔE_2, equals 52 ± 3 kcal/mole; and the activation energy for the overall process, ΔE_{12}, equals 44 ± 4 kcal/mole. The activation energies reported by Anderson and Freeman,[5] however, are rather high, and it is suggested that experimental conditions, especially the large sample weight of 100 mg, are responsible for this increase.

The increase in ΔE with increasing molecular weight of PS is not described in the literature. Jellinek,[3] however, found that the ΔE of polyethylene varied from 46.0 to 66.1 kcal/mole with molecular weights from 11,000 to 23,000. In our case, we believe that the change in ΔE was observed because of the use of fairly linear PS fractions. The contradictory results of activation energies reported by both Jellinek[3] and Madorsky[4] (no change with molecular weights) may have been caused by the use of molecular weight close to or behind the plateau shown in Figure 16. As for the decomposition rate, our results coincide with those of Madorsky[4] but are different from those of Jellinek.[3] In our opinion, Jellinek's[3] results could have been influenced by the use of polymer samples of different structure, different molecular weight distribution, or different history of formation. These differences in samples may also explain the inconsistent differences in reaction rates of PS fractions reported by Jellinek[3] and Madorsky.[4] It is recognized, however, that further work is needed to elucidate the effect of each single parameter on the thermal decomposition of PS before all conflicting values can be satisfactorily explained.

The specific average rate, as defined in this work, is dependent on the molecular weight, and it is suggested that it can be useful in the characterization of polymers as was shown in recent work by Kokta, Valade, and Lepoutre.[16,17]

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