Designation: E 1641 – 99

Standard Test Method for
Decomposition Kinetics by Thermogravimetry[1]

This standard is issued under the fixed designation E 1641; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ϵ) indicates an editorial change since the last revision or reapproval.

1. Scope

1.1 This test method covers determination of the kinetic parameters, Arrhenius activation energy, and preexponential factor by thermogravimetry, based on the assumption that the decomposition obeys first-order kinetics.

1.2 This test method is generally applicable to materials with well-defined decomposition profiles, namely, a smooth, continuous mass change with a single maximum rate.

1.3 This test method is normally applicable to decomposition occurring in the range from 400 to 1300K (100 to 1000°C). The temperature range may be extended depending on the instrumentation used.

1.4 Computer or electronic-based instruments, techniques, or data treatment equivalent to this test method may also be used.

NOTE 1—Users of this test method are expressly advised that all such instruments or techniques may not be equivalent. It is the responsibility of the user of this test method to determine the necessary equivalency prior to use. Only the manual procedures described in this test method are to be considered valid in the case of dispute.

1.5 The values stated in SI units are to be regarded as the standard.

1.6 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.*

2. Referenced Documents

2.1 *ASTM Standards:*
E 473 Terminology Relating to Thermal Analysis[2]
E 1142 Terminology Relating to Thermophysical Properties[2]
E 1582 Practice for Calibration of Temperature Scale for Thermogravimetry[2]
E 1877 Practice for Calculating Thermal Endurance of Materials From Thermogravimetric Decomposition Data

3. Terminology

3.1 Technical terms used in this test method are defined in Terminologies E 473 and E 1142.

4. Summary of Test Method

4.1 This test method consists of heating a series of four or more test specimens, taken from the original sample, each at a different heating rate between 1 and 10K/min, through their decomposition region. The specimen mass is recorded continuously as a function of temperature. The temperatures for constant conversion are determined from the resultant mass loss curves. The Arrhenius activation energy is then determined from a plot of the logarithm of heating rate versus the reciprocal of the absolute temperature at constant conversion level. This activation energy may then be used to calculate thermal endurance and an estimate of the lifetime of the material at a certain temperature.

5. Significance and Use

5.1 Thermogravimetry provides a rapid method for determining the temperature-decomposition profile of a material.

5.2 This test method can be used for estimating lifetimes of materials, using Test Method E 1877 provided that a relationship has been established between the thermal endurance test results and actual lifetime tests.

6. Apparatus

6.1 The essential equipment required to provide the minimum thermogravimetric analytical capability of this test method includes:

6.1.1 *A thermobalance,* composed of (*a*) a *furnace* to provide uniform controlled heating of a specimen at a constant rate within the temperature range from ambient to 900 K; (*b*) a *temperature* sensor to provide an indication of the specimen/furnace temperature to ± 0.1 K; (*c*) an *electrobalance* to continuously measure the specimen mass with a minimum capacity of 20 mg and a sensitivity of ± 50 μg; and (*d*) a means of sustaining the specimen/container under *atmospheric control* of an inert or reactive purge gas of 99.99 % purity at a rate of 20 to 50 $\pm$ 5 mL/min.

6.1.2 *A temperature controller,* capable of executing a specific temperature program by operating the furnace between selected temperature limits at a rate of temperature change between 1 and 10 K/min to within ± 0.1 K/min.

6.1.3 *A recording device,* either analog or digital, capable of recording and displaying the change in mass with of ± 50 μg and temperature with a resolution of 0.1 K.

6.1.4 *Containers (pans, crucibles, and so forth)* which are inert to the specimen and which will remain dimensionally stable over the temperature range from ambient to 900 K.

6.2 *High-Purity (99.99 %) Nitrogen Supply,* for purge gas.

NOTE 2—Other atmospheres may be used but shall be specified.

7. Precautions

7.1 It is essential that the samples be representative since milligram quantities of specimen are to be used.

7.2 The value of the calculated activation energy is independent of reaction order in the early stages of decomposition. This assumption does not hold for the later stages and shall be used with caution. An upper limit of 10 % decomposition is suggested, although 20 % is justified in certain cases. It is strongly suggested that calculations be made at several different levels of decomposition, for example, 5, 10, 15, and 20 %. Variations in the results among these determinations could indicate the inapplicability of one of them. For instance, volatile, low-level impurities would affect the results of the lowest conversion determination more than those at higher conversions. Consistent results for all conversions validate the method for the range of conversions examined.

7.3 Toxic or corrosive effluents, or both, may be released during the heating process and may be harmful to the personnel or apparatus.

8. Sampling

8.1 Powdered or granular specimens, which have a high surface-to-volume ratio, are preferred, although films, fibers, and fabrics may be used providing that care is taken to make all of the specimens uniform in size and shape. Under circumstances in which material parts are available, the specimens should be prepared by filing or rasping the part. All specimens should be mixed thoroughly prior to sampling if possible, and they should be sampled by removing portions from various parts of the container. These portions should in turn be combined and mixed well to ensure a representative sample for the determination.

NOTE 3—Care should be exercised during sample preparation to avoid contamination.

NOTE 4—The specimen size and surface-to-volume ratio are known to affect the results of this test. A narrow range of specimen sizes should be used, as noted in 9.5. Uniformity in particle size can be achieved, without the loss of volatiles, by using a liquid nitrogen mill to grind the sample to a fine powder. To prevent the condensation of moisture, the mill should be opened only after returning fully to ambient temperature, or the operation should be performed in a glove box filled with dry gas.

8.2 In the absence of other information, the samples are assumed to be analyzed as received except for the mechanical treatment noted in 8.1. If some heat treatment, such as drying, is applied to the sample prior to analysis, this treatment and any resulting mass loss must be noted in the report.

8.3 Certain materials require more sophisticated conditioning, such as maintaining the sample at a specified room temperature and relative humidity for an extended period of time. Such conditioning may be conducted, but procedural

details shall be included in the report.

9. Procedure

9.1 Calibrate the instrument mass balance in accordance with the procedure recommended for the instrument in use.

9.2 Place the temperature sensor within 2 mm of the outside of the specimen holder. Care must be taken to ensure that the specimen holder is not touched in any way by the sensor and that it is not moved after temperature calibration.

9.3 Maintain a constant flow rate of purge gas in the range from 20 to 50 mL/min throughout the experiment.

NOTE 5—In the case of samples that may be sensitive to oxidative degradation, it will be necessary to maintain inert gas purging for a time sufficient to ensure that all residual oxygen is removed from the system prior to the start of the temperature program. It may be necessary to evacuate the system prior to initiating inert gas purging for some instruments.

9.4 Calibrate the instrument furnace temperature in accordance with the calibration procedure in Practice E 1582 using the same heating rate, purge gas, and flow rate to be used for the specimens. The temperature calibration shall be performed both prior to every change in heating rate and at that heating rate.

9.5 Place 3 ± 1 mg of the specimen under test into a clean, tared instrument specimen holder. Other specimen sizes may be used but shall be indicated in the report.

NOTE 6—The specimen holder should be tared in the fully assembled system, with the purge gas flowing.

NOTE 7—Powdered or granular specimens should be distributed evenly over the specimen holder so as to maximize the exposed surface. A one-grain thick layer would be optimal.

9.6 Equilibrate the specimen at a temperature, in kelvins (K), of ten times the heating rate in kelvins per minute below the known decomposition temperature. If the percentage mass loss is to be recorded, establish zero percent loss at this time.

NOTE 8—If zero percent mass loss is established at the time at which the specimen is placed into the instrument, the specimen mass at the equilibration temperature can be greater than 100 % due to buoyancy effects. A blank should be run for accurate determination of the buoyancy effect throughout the temperature range of the experiment. The blank can be a piece of platinum of approximately the same volume as the specimen. The balance drift at any temperature can be determined in this manner.

9.7 Heat the specimen at a constant rate through the decomposition profile until a constant mass is obtained or the temperature is well beyond the useful temperature range of the material tested. Record the accompanying thermal curve, with mass or percentage mass loss displayed on the ordinate and specimen temperature on the abscissa.

9.8 Once the decomposition of the test specimen is complete, cool the instrument to room temperature, remove, clean, and replace the specimen holder, and retare the instrument in preparation for additional experiments. Use the same specimen holder for the entire series of runs to eliminate buoyancy problems.

9.9 Repeat the procedures described in 9.4-9.8 at three additional heating rates covering the range from 1 to 10 K/min. Other heating rates, and more than four, may be used but shall be noted in the report.

NOTE 9—The use of heating rates greater than 10 K/min affects both the
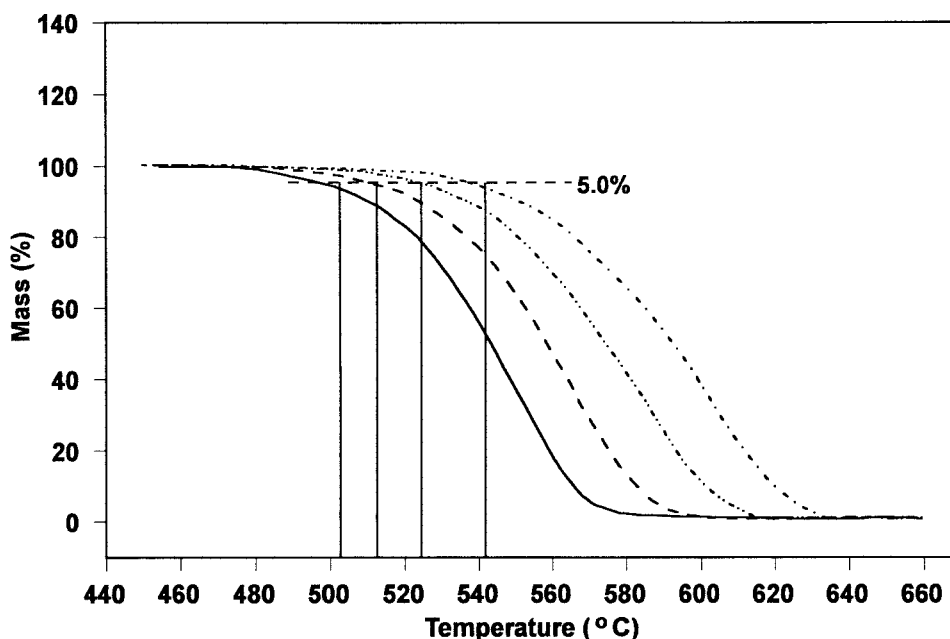
FIG. 1 Examples of Mass Loss Curves at the Following Heating Rates: 1°C/min, 2°C/min, 5°C/min, 10°C/min
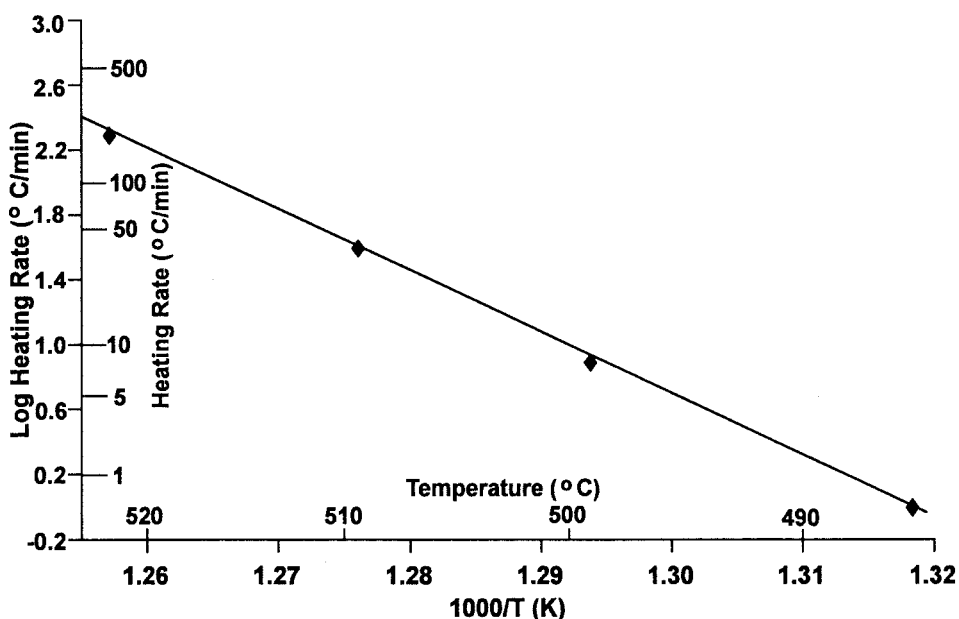

FIG. 2 Arrhenius Plot of Heating Rate, Temperature of Constant Conversion Data

precision of the temperature measurement and the kinetics of the decomposition. Diffusion of volatiles from the sample may become the rate-controlling process at high heating rates.

10. Calculation

10.1 From each of the thermal curves obtained in 9.5-9.9, determine the absolute temperature at constant conversion, α, for each of the constant conversion values to be used in the calculations as noted in 7.2. For example, see Fig. 1. The temperature corresponding to other conversion levels (not greater than 20 %) may be used in the determination, but it must be noted in the report.

NOTE 10—These calculations are simplified if the percent mass loss rather than actual mass is recorded on the ordinate.

NOTE 11—The value is determined from the difference of the initial and final sample mass, with the initial mass taken as the mass at the equilibration temperature and the final mass taken once the plateau has been reached at the end of weight loss. For example, if the initial mass is 100.3 % and the final mass is 80 %, then = 0.05 corresponds to 0.05 (100.3 to 80.0) or 1.02 % mass loss. Thus, 5 % decomposition occurs on the ordinate at 99.3 % (100.3 % − 1.02 % = 99.28 %).

10.2 Plot the logarithm of the heating rate expressed as kelvins per minute against the reciprocal of the absolute temperature at which the conversion level, selected in 10.1, was reached. A straight line, similar to that in Fig. 2, should result. This test procedure is not applicable if the curve is nonlinear.

3

NOTE 12—An apparent nonlinearity may result from erroneous determinations. It is recommended that any nonlinear points be repeated for verification.

10.3 Using the least-squares method fit a straight line to these data without weighing factors, and determine the slope

$$\Delta(\log\beta)/\Delta(1/T)$$

NOTE 13—If the values obtained from this test method are to be used in Test Method E 1877, an estimation of the uncertainty for activation energy (E) and preexponential factor (A) is required. These uncertainties may be derived from the uncertainty in the slope value of $m = \Delta (\log \beta)/\Delta (1/T)$. If the calculation tool used to obtain the slope of the straight line provides an estimation of uncertainty in the determined slope (δm), record it. Otherwise, the uncertainty in the slope may be obtained using the procedure in Appendix X1.

10.4 The following definitions apply to 10.2-10.9:

E	=	refined Arrhenius activation energy, J/mol,
A	=	pre-exponential factor, min^{-1},
R	=	gas constant, 8.314 J/(mol·K),
$\Delta(\log\beta)/\Delta(1/T)$	=	slope of the line obtained in 10.2,
β	=	heating rate, K/min,
β'	=	heating rate nearest the midpoint of the experimental heating rates, K/min,
T	=	temperature (K) at constant conversion,
b	=	approximation derivative from Table 1 (use $b = 0.457$/K on first iteration),
a	=	approximation integral taken from Table 1,
α	=	conversion value of decomposition, and
T_c	=	temperature for point of constant conversion for β', K.

10.5 Calculate an estimation of the activation energy using Eq 1(**1, 2**),[3] making use of the value of $\Delta(\log\beta)/\Delta(1/T)$ determined in 9.2 and a value of 0.457/K for b in this first iteration:

$$E = -(R/b)*\Delta(\log\beta)/\Delta(1/T) \tag{1}$$

10.6 Calculate the value for E/RT_c, where T_c = the temperature at constant conversion for the heating rate closest to the midpoint of the experimental heating rates.

10.7 Using the value for E_e/RT_c obtained in 10.6, obtain a new estimation of b from Table 1. Resubmit this value of b to Eq 1.

10.8 Repeat 10.4 and 10.5 until the value for the activation energy changes by less than 1 %. This refined value, E_r, is reported as the Arrhenius activation energy.

10.9 Select the mass loss curve for the heating rate nearest the midpoint of the experimental heating rates, and calculate the pre-exponential factor, A, using Eq 2 (**1, 2, 3, 4**) and the value of the exponent, a, obtained from Table 1 for the refined value of E_e/RT_c determined in 10.7.

$$A = -(\beta'/E_r)*R*ln\,(1-\alpha)*10^a \tag{2}$$

NOTE 14—This mathematical treatment to solve for E_r and A has been tailored specifically to make it possible to perform by hand. Commercial

---

[3] The boldface numbers in parentheses refer to the list of references at the end of this standard.

TABLE 1 Numerical Integration Constants

E/RT	a	b(1/K)
8	5.3699	0.5398
9	5.8980	0.5281
10	6.4167	0.5187
11	6.928	0.511
12	7.433	0.505
13	7.933	0.500
14	8.427	0.494
15	8.918	0.491
16	9.406	0.488
17	9.890	0.484
18	10.372	0.482
19	10.851	0.479
20	11.3277	0.4770
21	11.803	0.475
22	12.276	0.473
23	12.747	0.471
24	13.217	0.470
25	13.686	0.469
26	14.153	0.467
27	14.619	0.466
28	15.084	0.465
29	15.547	0.463
30	16.0104	0.4629
31	16.472	0.462
32	16.933	0.461
33	17.394	0.461
34	17.853	0.459
35	18.312	0.459
36	18.770	0.458
37	19.228	0.458
38	19.684	0.456
39	20.141	0.456
40	20.5967	0.4558
41	21.052	0.455
42	21.507	0.455
43	21.961	0.454
44	22.415	0.454
45	22.868	0.453
46	23.321	0.453
47	23.774	0.453
48	24.226	0.452
49	24.678	0.452
50	25.1295	0.4515
51	25.5806	0.4511
52	26.0314	0.4508
53	26.4820	0.4506
54	26.9323	0.4503
55	27.3823	0.4500
56	27.8319	0.4498
57	28.2814	0.4495
58	28.7305	0.4491
59	29.1794	0.4489
60	29.6281	0.4487

kinetics software may use other numerical methods of integrating the general differential form of the rate equation (the Flynn and Wall equations) and solving for the parameters. The interim values E_a, a, and b, which are part of the numerical iteration, are thus not reported.

10.10 *Example calculation for E (from Fig. 2)*:

$$T_c=510°C$$
$$=783 \text{ K, and } \Delta (\log \beta)/\Delta(1/T)$$
$$=[1.000-0.000]/[0.001258-0.001319]$$
$$=-16\,394$$

10.10.1 As the first estimation:

$$b'=0.457/\text{K} \text{ (10.5)}$$

10.10.2 Using Eq 1:

$$E' = [-8.314 \text{ J/(mol}\times\text{K)}(-16\,394)/\{0.457/k\}] = 298\,249 \text{ J/mol}$$

10.10.3 Calculating the value of E'/RT_c:

$E'/RT_c = [298\ 249\ \text{J/mol}]/[8.314\ J/(mol \times K) \times 783\ K] = 45.81$

10.10.4 From Table 1 for $E/RT = 45.81$:

$$b' = 0.453/K$$

10.10.5 *Reiterating Yields*:

E = 300 882 J/mol
E/RT_c = 46.22
b' = 0.453/K
E' = 300 882 kJ/mol

10.11 Example calculation for pre-exponential factor (A):

β = 5 K/min
α = 0.05

10.11.1 From 10.10 and Table 1:

E = 300 882 J/mol
a = 23.321

10.11.2 Using Eq 2:

$$A = \frac{-5\ \text{K/min} \times 8.314\ \text{J/(mol} \times \text{K)}}{300\ 882\ \text{J/mol}}$$

$$\times [1n\ (1-0.05)] \times [10^{23.321}]$$

$$A = [-10^{-3,860}][-10^{-1.290}][10^{23.321}]/\text{min}$$

$$A = 10^{18.171}$$

$$\log A = 18.17 \Rightarrow 1n\ A = 41.84$$

NOTE 15—When recording direct measurements, all digits known, plus one digit, which may be uncertain due to estimation, shall be recorded. When data is obtained from a digital display or printout from an instrument, all available digits shall be recorded. When calculating results, retain all available significant figures rounding only at the final results. Final results shall be rounded to the least significant figure whose significance is not greater that 0.5 times nor less than 0.05 times the standard deviation

11. Report

11.1 Report the following information:

11.1.1 Designation of the material under test, including the name of the manufacturer, lot number, and supposed chemical composition when known.

11.1.2 Description of the thermogravimetric analyzer used.

11.1.3 Purge gas, flow rate, and composition.

11.1.4 Specimen masses, temperature range, and heating rates used.

11.1.5 Determined Arrhenius activation energy, E_r, and pre-exponential factor.

12. Precision and Bias

12.1 The precision and bias of this test method were determined in an interlaboratory test (ILT) on powdered poly(tetrafluoroethylene) conducted in 1988–89. Nine laboratories using thermogravimetric analyzers from two manufacturers, participated in the ILT. Each laboratory reported two sets of data with each set containing data from four heating rates between 1 and 10 K/min. Temperature calibration was made using nickel and perkalloy magnetic reference materials that bracketed the decomposition region of PTFE. The kinetic constants were determined for 5 % decomposition. The results were statistically treated by Test Method E 691.

12.2 *Precision*:

12.2.1 Within laboratory variability may be described using the repeatability value (r) obtained by multiplying the standard deviation by 2.8. The repeatability value estimates the 95 % confidence limit.

12.2.1.1 Repeatability values of 26 kJ/mol and 4.2 were obtained for the activation energy and natural logarithm of the pre-exponential factor (1/min), respectively.

12.2.2 The between laboratory variability may be described using the reproducibility value (R) obtained by multiplying the standard deviation by 2.8. The reproducibility value estimates the 95 % confidence limit.

12.2.2.1 Reproducibility values of 45 kJ/mol and 8.2 were obtained for the activation energy and natural logarithm of the pre-exponential factor (1/min), respectively.

12.3 *Bias*:

12.3.1 An estimation of the bias is obtained by comparing the mean values obtained in this study with values obtained from the literature.

12.3.2 The mean activation energy obtained in this study was 327 kJ/mol. The mean natural logarithm of the pre-exponential factor (1/min) obtained was 45.7.

12.3.3 Mean values and standard deviation for activation energy and natural logarithm of the pre-exponential factor taken from the literature (5, 6, 7, 8, 9, 10) were E = 320 ± 24 kJ/mol and ln A (1/min) = 45.6 ± 4.1, which are non-weighted average values from six independent references.

12.3.4 The values for activation energy and natural logarithm of pre-exponential factor obtained in this study are not statistically different from those obtained from the literature. This indicates an absence of significant bias.

12.3.5 Information supporting the precision and bias information below is available on loan from ASTM Headquarters. Request RR: E37-1021.

13. Keywords

13.1 Arrhenius activation energy; Arrhenius pre-exponential factor; kinetic parameters; thermal decomposition; thermogravimetric analysis

APPENDIX

(Nonmandatory Information)

X1. ESTIMATING THE UNCERTAINTY IN THE ACTIVATION ENERGY AND PRE-EXPONENTIAL FACTOR

X1.1 The imprecision in activation energy (δE) is related to the imprecision in the determination of the slope value m = Δ log β/Δ (1/T) obtained in 10.3. This relationship is given by:

$$\delta m/m = \delta E/E$$

X1.2 The uncertainty in the slope of a straight line **(12)**.

$$\delta m = \left[\frac{n\Sigma(\delta y_i)^2}{(n-2)[n\Sigma x_i^2 - (\Sigma x_i)^2]}\right]^{1/2}$$

where:
y = Δ log β,
x = 1/T,
δm = uncertainty in the value of m,

m = nΔ (log β)/Δ (1/T),
n = number of individual sets of x and y data,
x_i = an individual x data point,
y_i = an individual y data point,
Σ = mathematical function equivalent to "sum of all,"
δy_i = the uncertainty in an individual y value and is given by, and $\delta y_i = y_i - (m \times x_i - b)$

X1.3 The uncertainties in the pre-exponential factor (δA) or its natural logarithm ($\delta \ln A$) are related to the uncertainty in the activation energy by:

$$\delta \ln A \equiv \delta A/A = \left[\frac{1}{E} + \frac{1}{RT}\right]\delta E$$

REFERENCES

(**1**) Flynn, J. H., Wall, L. A., *Polym. Lett.,* Vol 4, 1966, p. 323.
(**2**) Flynn, J. H., *J. Therm. Anal.,* Vol 27, 1983, p. 95.
(**3**) Toop, D. J., *IEE Trans. Elec. Insul.,* Vol EI-6, 1971, p. 2.
(**4**) Doyle, C. D., *J. Appl. Polm. Sci.,* Vol 5, 1961, p. 285.
(**5**) Krizanovsky, L., Mentlik, V., *J. Therm. Anal.,* Vol 13, 1978, p. 571.
(**6**) Fuoss, R. M., Sayler, I. O., Wilson, H. S., *J. Polm. Sci.,* Vol A2, 1964, p. 3137.
(**7**) Madorsky, S. L., Hart, V. E., Straus, S., Sedlak, V. A., *J. Res. Nat. Bur. Stand.,* Vol 51, No. 6, 1953, p. 327.
(**8**) Cox, J. M., Wright, B. A., Wright, W. W., *J. App. Polm. Sci.,* Vol 8, 1964, p. 2935.
(**9**) Siegle, J. C., Mures, L. T., Lin, Tung-Po, Larson, H. A., *J. Polym. Sci.,* Vol A2, 1964, p. 391.
(**10**) Jellenek, H. H. G., Kachi, H., *Makromol. Chem.,* Vol 85, 1965, p. 1.
(**11**) Jellenek, H. H. G., Kachi, H., *Polm. Eng. Sci.,* Vol 5, 1965, p. 200.
(**12**) Baird, D. C., *Experimentation: An Introduction to Measurement Theory and Experimental Design,* Prentice Hall, Englewood Cliffs, NJ, 1962, pp. 133–140.