

GPO PRICE \$ _____

CFSTI PRICE(S) \$ _____

Hard copy (HC) _____

Microfiche (MF) _____

ff 653 July 65

THERMAL DEGRADATION ANALYSIS OF POLYMERIC MATERIALS BY
COMBINED MASS SPECTROMETRIC AND THERMOGRAVIMETRIC ANALYSIS

Donald E. Wilson and Frank M. Hamaker

Ames Research Center, NASA
Moffett Field, California 94035

INTRODUCTION

Studies of the thermal degradation of polymeric materials are important on two levels: the practical, and the scientific. On the practical level, these studies not only explain the behavior of polymers exposed to high temperature (1-3) but also aid in establishing criteria for the selection of materials for specific uses (4). More importantly, the kinetics of degradation - in particular, the effects of time, temperature, and pressure on the products of degradation - can be used in predicting the behavior of the polymer under various environmental conditions (5). On the scientific level, these studies provide insight into the molecular structure of the polymer (6), and aid in the determination of the strength of various bonds within the polymer (6). In addition, such studies can be used to suggest synthesis of new materials (7).

Existing techniques (1-4,7,8) for studying the thermal degradation of polymeric materials are either very time consuming or very qualitative, especially when the degradation reaction is complex. (Chatterjee (9) previously proposed a technique for the separation of complex reactions; however, quantitative calculations based on Chatterjee's method produced questionable results, as pointed out by Broido (10).) In this paper, a method that gives rapid, yet quantitative, results for the parameters of thermal degradation of polymeric material is presented. By this method, which combines mass spectrometry with thermogravimetric analysis, the degradation parameters can be determined, in many instances even when the degradation reaction is complex. The addition of the mass spectrometer to a suitable thermogravimetric

N 68-33303

(ACCESSION NUMBER)

(THRU)

30

(PAGES)

(CODE)

TMX-61159

(NASA CR OR TMX OR AD NUMBER)

(CATEGORY)



Aug. 1968

analysis apparatus permits following the course of any reaction that produces gaseous products by the dynamic identification and measurement of the rate of evolution of those products. The results obtained by the analytical scheme concurrently developed for determining the kinetic parameters of thermal degradation based on the data produced by the mass spectrometer is compared, for a number of polymers, to the results obtained for the same calculations based on the more usual thermogravimetric analysis techniques. The mass spectrometer, thermogravimetric analysis (MS-TGA) technique is then applied to a case that demonstrates its ability in the separation of complex reactions and in subsequent derivation of the kinetic parameters of degradation.

APPARATUS, MATERIALS, AND TEST PROCEDURE

Apparatus

Fig. 1 shows the balance, mass spectrometer head, sample heaters, and vacuum system used for the mass spectrometer-thermogravimetric analysis tests. The balance is an ultra-high vacuum, semimicro, analytical, automatic recording balance capable of measuring weight differences of 0.1 mg. The balance employs an automatic range switching system so that 390 mg of weight gained or lost can be automatically recorded in 10 mg increments. The mass spectrometer, a Varian quadrupole residual gas analyzer, has a mass range of 0-250 atomic mass units (a.m.u.). It produces an ion current signal for a given m/e species which is proportional to the number of molecules of that species in the vacuum system (11). The spectrometer is capable of measuring ion currents as low as 1×10^{-13} amperes.

The vacuum pumping system consists of a roughing pump (not shown in the figure) and a 1500 liter per second, 6-inch oil diffusion pump trapped with liquid nitrogen. The oil diffusion pump maintains chamber pressure below 5×10^{-5} torr for the sample sizes used. A system pressure below this value is essential to insure that the mass spectrometer signal for a given m/e species present in the system remains linearly proportional to the number of molecules of that species present. The high pumping speed also prevents the accumulation of degradation products in the chamber and insures that the number of molecules of a given m/e species is proportional to the instantaneous rate of evolution of that species from a degrading sample (11).

The sample heaters are quartz lamps with tungsten filaments. These lamps provide a low thermal mass, resulting in minimum time response to temperature changes. Temperature programming and control are provided by a closed-loop temperature controller. The system-control and sample-temperature thermocouples were located in the thermocouple crucible (Fig. 1) to prevent the thermocouples from directly "seeing" the heating elements. Thermocouples in this crucible had previously been calibrated with thermocouples temporarily placed in the upper or sample crucible and were found to represent the sample-temperature to within $\pm 2^\circ\text{C}$ for the test conditions of these experiments.

Materials

The materials selected for testing were poly(methyl methacrylate) (PMMA), polyoxymethylene (POM), polystyrene (PS), and poly(vinyl chloride) (PVC). The PMMA material, manufactured specifically for Ames Research Center, contained no additives beyond the azobisisobutyronitrile initiator. The POM, PS, and PVC materials were commercial sheet stock with the polymerization procedure and original manufacturer untraceable.

Test Procedure

Test samples were small shavings (~ 0.013 cm in thickness and cut from 0.08-cm-thick sheet stock) of the desired material. This sample provides a large surface area, thus minimizing the possibility of diffusion control of the evolution of gaseous degradation products and also minimizing thermal gradients within the sample. The pre-test weight of the test samples ranged from 5 to 25 mg. The upper limit of 25 mg was selected so that the vacuum pumping system could maintain a system pressure below 5×10^{-5} torr during sample degradation, and the lower limit of 5 mg was selected to maintain sample weighing errors within acceptable limits. The test sample of the desired material was weighed in its porcelain crucible to within ± 0.01 mg, then sample and crucible were placed in the vacuum system. The balance was then tared and the vacuum system pumped down to approximately 5×10^{-7} torr. The mass spectrometer was then activated and a determination of the background gas species was made. Fig. 2(a) shows a typical background spectrum with the major gas species present at a pressure of 2.1×10^{-7} torr, and a

temperature of 25°C. The sample chamber was then heated to about 60°C and allowed to equilibrate for 15 minutes. After thermal equilibration, the closed-loop temperature controller was switched to the program mode and the MS-TGA test was begun. A relatively slow rate of 1°C/minute was selected for these tests to minimize thermal gradients within the sample and to permit fine detail of the thermogram to be observed. The heating rate of 1°C/minute was maintained to within $\pm 0.02^\circ\text{C}/\text{minute}$. Programmed heating was continued for each test until either 100% weight loss of the sample had been achieved or until the sample temperature had reached approximately 435°C, the upper temperature limit of the system.

Throughout the course of the MS-TGA run, the spectrometer continuously and repetitively scanned the mass range from 5 to 120 a.m.u. at a rate of 2 sec/a.m.u. Thus, each mass peak in this range was sampled approximately once every 3.5 minutes, or, correspondingly, once every 3.5°C. Fig. 2(b) shows a typical mass spectrum recorded during the MS-TGA run on a sample of PMMA. The peaks at $m/e = 15, 39, 41, 69,$ and 100 are due to the thermal degradation products of the sample. The mass spectrometer signal values of these species, obtained from successive mass spectra scans, were recorded as a function of temperature and are assumed to be proportional to the rate of evolution of the species from the degrading sample. Thus, these plots represent, in effect, as a function of temperature, the rate of the reactions producing the gaseous species.

In the case of PMMA, it is well known that the major degradation product is methyl methacrylate monomer, $m/e = 100$ (12). When the mass spectrometer signal values of all the new m/e species are plotted as a function of temperature, all follow the same thermal behavior. Therefore, $m/e = 100$ is the main degradation product and the other peaks result from the usual ionization fragmentation of the methyl methacrylate in the ionization chamber of the mass spectrometer. Thus, any one of the peaks so produced can be used in following the course of the degradation reaction. For an unknown polymer sample, all m/e peaks should be examined by the above technique to ascertain whether they are ionization fragments of some parent peak or whether they are the result of separate degradation reactions. A set of peaks referring to one reaction's products and ionization fragments will not exhibit the same thermal behavior as a

set of peaks referring to a second reaction's products and ionization fragments.

Typical data for an MS-TGA test thus consist of a weight loss versus temperature record (thermogram) for the sample, and the mass spectrometer signal versus temperature curves for all peaks present in the test spectra (but not in the pre-test spectra).

Analysis

A simplified scheme for depicting the weight loss undergone by polymers during thermal degradation is:



where A_s = original solid reactant; B_s = solid residue which may or may not be present; and C_g = the gaseous product evolved.

Analytical methods based on the weight loss of A_s assume the rate of weight loss follows an equation of the type:

$$\frac{dw_t}{dt} = k(w_0 - w_t)^n \quad (2)$$

where dw_t/dt = instantaneous weight loss rate; k = temperature dependent rate constant; w_0 = initial weight of reacting material; w_t = weight of material reacted to time t ; and n = order of reaction.

The temperature dependence of k is then assumed to follow an Arrhenius equation:

$$k = A e^{-E/RT} \quad (3)$$

where A = temperature independent constant; E = activation energy of the reaction; R = ideal gas constant; and T = absolute temperature.

In isothermal weight loss studies, n is determined from equation (2) and k is then evaluated at several temperatures. The activation energy, E , is then determined by equation (3).

For thermogravimetric analysis tests, the temperature is usually programmed in a linear fashion according to:

$$T = \alpha + \beta t \quad (4)$$

where T = the temperature at time t ; α = the initial temperature; and β = the rate of temperature rise.

Several methods of analysis for obtaining n and E are then available by combining equations (2), (3), and (4).

One, for example, is what Flynn and Wall (13) have called the "simple differential" method.

$$\log \frac{dw_t/dT}{(w_0 - w_t)^n} = \log \frac{A}{B} - \frac{E}{RT} \quad (5)$$

where dw_t/dT = the change in weight with temperature at a given time (or temperature). Here, trial values of n are substituted in an Arrhenius type plot until a straight line is obtained from which E may be evaluated.

A second method, that of Freeman and Carroll (8), is obtained when equation (5) is rearranged and differentiated with respect to $\log(w_0 - w_t)$:

$$\frac{d \log(dw_t/dT)}{d \log(w_0 - w_t)} = \frac{-E}{R} \frac{d(1/T)}{d \log(w_0 - w_t)} + n \quad (6)$$

Here, $-E/R$ will be the slope and n the intercept when $d \log(dw_t/dT)/d \log(w_0 - w_t)$ is plotted versus $d(1/T)/d \log(w_0 - w_t)$.

The method discussed in this paper emerges when the reaction represented by equation (1) is reconsidered from the viewpoint of the evolved gas. The rate of evolution, as measured by the mass spectrometer, and the total weight of gas evolved can be used in the kinetic analysis of the reaction in the same fashion as can the weight loss rate and the total weight lost by the original sample. Fig. 3 shows a comparison, as a function of temperature, of the mass spectrometer ion current, s , of the $m/e = 41$ species (the predominant signal) evolved from degrading PMMA, and the dw_t/dT curve for the same material. The close similarity between the two curves suggests in this case that:

$$Ks = \frac{dw_t}{dT} \quad (7)$$

where K = a proportionality constant and s = the mass spectrometer ion current for an evolving species. Since

$$\int_{T=T_i}^{T=T_f} \frac{dw_t}{dT} dT = w_0 \quad (8)$$

where T_i = initial reaction temperature and T_f = final reaction temperature. Then

$$\int_{T=T_i}^{T=T_f} Ks \, dT = w_o = KS_o \quad (9)$$

where S_o = area under the mass spectrometer ion current curve as a function of temperature for an evolved species. (The single-hatched area in Fig. 3.) Similarly, then

$$\int_{T=T_i}^{T=T} \frac{dw_t}{dT} \, dT = w_t \quad (10)$$

and

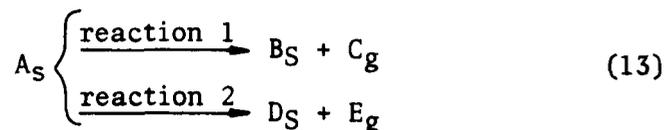
$$\int_{T=T_i}^{T=T} Ks \, dT = w_t = KS_t \quad (11)$$

where S_t = area under the mass spectrometer ion current versus temperature curve for an evolved species from T_i to T . (The double-hatched area in Fig. 3.) Therefore, one may propose, analogous to equation (5), the relationship:

$$\log \frac{Ks}{(KS_o - KS_t)^n} = \log \frac{KA}{B} - \frac{E}{RT} \quad (12)$$

Equation (12) may then be used to find the activation energy, E , by using trial values of n in an Arrhenius type plot. The trial values of n used were zero, 0.5, 1.0, 1.25, 1.5, 1.75, and 2. These values are consistent with the order of reaction usually reported for thermal degradation of polymers.

The advantage of the MS-TGA analytical technique in deriving values for n and E , as opposed to using TGA weight loss analytical techniques, can be seen if one now considers a complex reaction such as:



Here, two reactions are simultaneously competing for the original reacting material.

For a reaction such as that shown in equation (13) the weight loss and the dw_t/dT curves as a function of temperature represent a composite of reactions 1 and 2. However, the rate of evolution of the product C_g , as represented by a mass spectrometer signal for an m/e species corresponding to C_g , is a direct measurement of the rate of reaction 1. Similarly, a mass spectrometer signal

corresponding to E_g is a direct measurement of the rate of reaction 2. Thus, the values obtained for s , S_0 , and S_t , from plots of mass spectrometer signals as a function of temperature for $m/e = C_g$ and $m/e = D_g$, could then be used in equation (12) to determine the parameters n and E for reactions 1 and 2, respectively.

RESULTS AND DISCUSSION

Polymethylmethacrylate

Fig. 4 shows, as a function of temperature, the TGA thermogram, the change in weight with temperature at a given temperature (dw_t/dT), and the mass spectrometer ion current for the $m/e = 41$ ($C_2H_5^+$) species obtained when a sample of PMMA is degraded. As previously explained, the $m/e = 41$ species is an ionization fragment of the principal degradation product, methyl methacrylate. The $m/e = 41$ species produces the strongest ion current of all the species detected in the PMMA degradation spectrum, and on that basis has been selected here to represent the degradation process in PMMA.

Examination of Fig. 4 shows two temperature regions of weight loss, one from approximately 100° to $280^\circ C$, and a second from 280° to $420^\circ C$. The close comparison of the dw_t/dT and ion current curves as a function of temperature, together with an examination of the mass spectra taken throughout the course of the MS-TGA test indicates that the reaction product in both temperature regions is methyl methacrylate monomer. On inspection of the TGA thermogram alone, it is difficult to ascertain where the first reaction ends and the second begins. In the MS-TGA analytical technique, on the other hand, this determination is easily made by examining the ion current curve of the product for the occurrence of minimum values. The $m/e = 41$ curve in Fig. 4 obviously shows minima at about $100^\circ C$, $280^\circ C$, and $420^\circ C$. The area under the ion current curve from 100° to $280^\circ C$ is then used as the S_0 value for reaction 1 in Fig. 4, and kinetic parameter calculations can be made for this reaction according to equation (12). The area under the curve from 280° to $420^\circ C$ is then used as the S_0 value for reaction 2, and kinetic parameter calculations made for this reaction according to equation (12). Activation energy calculations are made from equation (12) by substituting trial values for the order of reaction, n , in the equation to determine the

Arrhenius plot which is most nearly linear. This best value of n is then considered to be the correct value for the order of reaction. Fig. 5 shows the Arrhenius plots obtained for the two reactions in PMMA when $n = 1$, the best value for both reactions for this polymer. The first, or lower temperature, reaction has an activation energy of 13.3 kcal/mole, and the second reaction, usually considered as the thermal degradation reaction of PMMA, has an activation energy of 44.9 kcal/mole. This latter value, as will be discussed later, falls well within the range of activation energy usually reported for the thermal degradation of PMMA (14).

Polyoxymethylene

The TGA thermogram, the change in weight as a function of temperature at a given temperature (dw_t/dT), and the ion current curve for $m/e = 29$ (CHO^+) as a function of temperature obtained when a sample of POM is degraded, are shown in Fig. 6. As was the case for PMMA, the close comparison of the dw_t/dT and ion current curves, together with the mass spectra recorded during the MS-TGA run, indicates that degradation occurs principally through the production of formaldehyde monomer. Inspection of the mass spectrometer curve for minimum values that would indicate more than one reaction occurring shows there are none. However, near 300°C , a plateau occurs in the ion current curve. This plateau indicates that a second reaction has probably begun which obscures the minimum value that would have been attained by the first reaction. An estimation for S_0 , the area under the ion current curve from 145° to 303°C , can be made and the kinetic parameters can be calculated for reaction 1 from equation (12). Additionally, an S_0 can be obtained from 303° to 412°C for the higher temperature reaction and its kinetic parameters can be calculated from equation (12). Fig. 7 shows the most linear Arrhenius plots obtained for POM for both reactions based on the ion current for $m/e = 29$. These plots result when the best value of one is used for the order of reaction in equation (12). The lower temperature reaction yields a calculated activation energy of 22 kcal/mole, and the higher temperature reaction yields 46 kcal/mole. This two-stage reaction for POM has also been observed by Igarashi et al. (15).

Polystyrene

Fig. 8 gives the TGA thermogram, the change in weight with temperature at a given temperature, dw_t/dT , and the ion current for $m/e = 104$ ($C_8H_8^+$ - the styrene monomer) obtained from degrading a sample of PS. Using the criteria established for PMMA and POM, the close comparison of the dw_t/dT and ion current curves for the styrene monomer indicates that a single reaction producing monomer is responsible for the thermal degradation of polystyrene. Fig. 9 shows the Arrhenius plots based on the ion current curve for $m/e = 104$, and a best value for the order of reaction equal to one. The calculated value for activation energy obtained from Fig. 9 is 60.9 kcal/mole, which is in agreement with the value of 60 ± 5 kcal/mole reported by others (16,17).

Under the test conditions employed here, where the major portion of weight loss occurred at high temperatures, the value of one found for the order of reaction is in agreement with results reported by other investigators. These investigators (16,17) using isothermal techniques have reported that the order of reaction for the thermal degradation of polystyrene can be either zero ($n = 0$) or one ($n = 1$), dependent upon the temperature range of investigation (17), with the latter value referring to high temperature degradation and the former value to low temperature degradation. In addition, these investigators have reported the volatile products of polystyrene degradation, while consisting mainly of monomer, also contain dimer and higher molecular weight fragments (16). In this investigation by the MS-TGA technique, the possible production of molecular weight fragments larger than monomer was not examined because of the limited mass range of the mass spectrometer used.

Poly(vinyl chloride)

The polymers discussed above have all been materials which degrade basically to their monomer units. Poly(vinyl chloride), the experimental results for which are shown in Fig. 10, is an example of a polymer which degrades by "side chain scission." The major gaseous thermal degradation product of PVC, as can be seen from Fig. 10, is $m/e = 36$, corresponding to hydrogen chloride (HCl^{35}). The hydrogen chloride is predominantly produced from PVC by combination of a hydrogen atom and a chlorine atom extracted from adjacent carbon atoms within the polymer chain. Reaction of

all the theoretical amount of chlorine present in PVC in this way would result in a residual weight of 38.5% of the original sample weight. The experimental values found for the residual weight of PVC in this investigation ranged from 33 to 38% of the original sample weight. This result, together with the close comparison of the dw_t/dT curve and the ion current curve for $m/e = 36$ from 210° to 410°C, indicates that only a single reaction resulting in the production of HCl is responsible for the degradation of PVC in this temperature range. The low temperature (80°-220°C) weight loss indicated by the dw/dT curve in Fig. 10 is the result of loss of plasticizer fragments from the PVC sample and not the result of the HCl producing thermal degradation reaction.

The Arrhenius plot for PVC, based on the ion current for $m/e = 36$ and equation (12), is shown in Fig. 11. When a best fit value for the order of reaction equal to 1.5 is used, an activation energy of 34.5 kcal/mole is calculated. Both the value for order of reaction and activation energy reported here for PVC agree with the values reported by other investigators (19).

Table 1 presents a summary of the analytical results obtained by applying the several different methods to the experimental results for the polymers investigated here. Where possible, these results are compared with isothermal results obtained by other investigators. The results given in Table 1 refer to the major reaction which occurs during degradation. The results reported for the MS-TGA technique are based on the m/e species which gave the strongest ion current signal during degradation. As can be seen from the table, the MS-TGA and simple differential analytical techniques give results for the activation energy of the investigated polymers which agree for a given polymer to within about 10% of each other. In addition, these values are generally in good agreement with those reported by other investigators for these materials.

In Table 1, there are two sets of values reported for the Freeman and Carroll technique. One set, that marked (a) in the table, is obtained when equation (6) is used for the simultaneous determination of order of reaction and activation energy. The variation in these results is similar to that found by Flynn and Wall (13) for the Freeman and Carroll method in a theoretical study of thermogravimetric analysis methods. A second set of results based on a suggestion made by Flynn and Wall in their study is also shown for this method. For these latter results, marked (b) in

Table 1, the activation energy was calculated early in the reaction, and the order of reaction was determined near the completion of the reaction. As can be seen from the table, this second set of results for the Freeman and Carroll method, while still not in good agreement with the results obtained by other methods, at least falls more closely to the values reported for those methods.

Polyvinyl Chloride-Polymethylmethacrylate Mixture

So far, it has been demonstrated that the MS-TGA method is capable of producing results for the kinetic parameters of degradation which are in reasonable agreement with those obtained by other analytical techniques. It will now be shown how the MS-TGA technique can be used in the separation of more complex degradation reactions, and in the subsequent calculation of the pertinent kinetic parameters.

Fig. 12 shows the experimental data obtained when a mixture of PVC and PMMA is thermally degraded. Shown in the figure as a function of temperature are the TGA thermogram, the ion current for $m/e = 36$ (PVC), and the ion current for $m/e = 41$ (PMMA). The ion currents for $m/e = 36$ and $m/e = 41$ in the figure show clearly the temperature regions where thermal degradation is a result of PVC degradation alone, PMMA degradation alone, or a combination of the two.

Using the area under the mass spectrometer signal curve of $m/e = 36$ from 220° to 430°C as S_0 in equation (12) permits calculation of the kinetic parameters referring to PVC only degradation. Using the area under the $m/e = 41$ curve from 100° to 280°C and the area under the curve from 280° to 430°C as S_0 's in equation (12) permits the calculation of the kinetic parameters of the two reactions which occur when PMMA degrades.

The resulting Arrhenius plots for these calculations are shown in Figs. 13 and 14, respectively. The values of activation energy obtained for PVC and PMMA from the mixture agree quite well with those obtained when the polymers are degraded separately.

Attempts to use the simple differential or the Freeman and Carroll analytical method in an instance such as the PVC-PMMA mixture are stymied by the uncertainty in assigning a w_0 value for any of the reactions. It can be seen from the thermogram (Fig. 12) that the dw_t/dT vs. T curve for the mixture contains a multiplicity of maxima and minima. In some cases, the dw_t/dT curve refers to PVC degradation

alone, PMMA degradation alone, or to a composite of the two degraded simultaneously. There is no a priori way to differentiate these cases on the basis of the dw_t/dT vs. T curve alone. Thus, both the simple differential and Freeman and Carroll techniques are unsuccessful in calculating the kinetic parameters.

CONCLUDING REMARKS

A new method, called the mass spectrometer-thermogravimetric analysis technique, has been developed for determining the kinetic parameters of thermal degradation of polymeric materials. The new method, based on measuring the rates of evolution of the gaseous products evolved during degradation by mass spectrometer, proves most valuable in those instances of degradation in which two or more reactions are competing for the original reactant. In these instances, the course of each reaction may be followed and the kinetic parameters may be derived for each reaction by determining the history of the appropriate gaseous degradation products.

The MS-TGA technique can be incorporated as an integral part of a program which characterizes new materials. The information provided by this technique can be applied to the evaluation of these materials on both the practical and scientific levels. The rapid determination of the kinetic parameters of thermal degradation by the MS-TGA technique and the identification of the products of degradation, coupled with the temperature range over which they occur, can be used both in predicting the thermal behavior of the material and in suggesting guidelines for the synthesis of new materials.

REFERENCES

1. L. Reich and D. W. Levi, *Makromol. Chem.* 66, 102 (1963).
2. D. W. Levi, L. Reich, and H. T. Lee, *Polymer Eng. Sci.* 5, 135 (1965).
3. H. L. Freidman, U. S. Dept. Comm. Office Tech. Serv. PB Rept. 145, 182 (1959).
4. C. D. Doyle, WADD Tech. Rept. 60-283, June 1960.
5. J. J. Lohr, D. E. Wilson, F. M. Hamaker, and W. J. Stewart, *J. Spacecraft Rockets* 5, 1, 68 (1968).
6. H. C. Anderson, *J. Appl. Polymer Sci.* 6, 484 (1962).
7. K. D. Jefferys, *Brit. Plastics* 36, 188 (1963).

8. E. S. Freeman and B. Carroll, *J. Phys. Chem.* 62, 394 (1958).
9. P. K. Chatterjee, *J. Polymer Sci. A* 3, 4253 (1965).
10. A. Broido, *J. Polymer Sci. B* 6, 5 (1968).
11. J. H. Beynon, *Mass Spectrometry and Its Application to Organic Chemistry* (American Elsevier Publishing Co., Inc., New York, 1960).
12. S. L. Madorsky, *Thermal Degradation of Organic Polymers* (Interscience Publishers, Inc., New York, 1964).
13. J. H. Flynn and L. A. Wall, *J. Research NBS* 70A, 6 (1966).
14. H. H. G. Jellinek, *Degradation of Vinyl Polymers* (Academic Press, Inc., New York, 1955).
15. S. Igarashi, I. Mita, and H. Kambe, *Bull. Chem. Soc. Japan* 37, 1160 (1964).
16. P. Bradt, V. H. Dibeler, and F. L. Mohler, *J. Research NBS* 50, 201 (1953).
17. D. A. Anderson and E. S. Freeman, *J. Polymer Sci.* 54, 253 (1961).
18. S. L. Madorsky, *J. Polymer Sci.* 9, 133 (1952).
19. R. R. Stromberg, S. Strauss, and B. G. Achhammer, *J. Polymer Sci.* 35, 355 (1959).

Table 1. Summary of Analytical Results

Sample	Method	n	E, kcal/mole	Temp. range, °C
Polymethylmethacrylate	Simple differential	1	50.3	318-381
	MS-TGA (m/e = 41)	1	44.9	318-381
	Freeman & Carroll (a)	3.8	24	280-420
	Freeman & Carroll (b)	1	59.3	280-420
Polyoxymethylene	Isothermal	1	30-55 (14)	160-320
	Simple differential	1	50.3	346-404
	MS-TGA (m/e = 29)	1	46	346-404
	Freeman & Carroll (a)	-0.15	13.2	303-415
Polystyrene	Freeman & Carroll (b)	1	39.2	303-415
	Simple differential	1	65.2	344-417
	MS-TGA (m/e = 104)	1	60.9	344-417
	Freeman & Carroll (a)	1.1	74.6	290-440
	Freeman & Carroll (b)	1	67.4	290-440
	Freeman & Carroll	0	46 (17)	325-370
Polyvinyl chloride	Freeman & Carroll	1	60 ± 5 (17)	370-430
	Isothermal	1	55 (18)	318-348
	Simple differential	1.5	36.8	240-370
	MS-TGA (m/e = 36)	1.5	34.5	240-370
	Freeman & Carroll (a)	2.9	41	210-410
	Freeman & Carroll (b)	1	35.3	210-410
	Isothermal	1.5	30.4 (19)	235-260

(a) Values determined by equation (6).

(b) Values modified according to Flynn & Wall.

FIGURE TITLES

Fig. 1 Mass spectrometer-thermogravimetric test apparatus.

Fig. 2 Comparison of background and test mass spectra for polymethylmethacrylate.

Fig. 3 Comparison of weight change at a given temperature and ion current signal with temperature for polymethylmethacrylate.

Fig. 4 Experimental results for thermal degradation of polymethylmethacrylate.

Fig. 5 Arrhenius plot for polymethylmethacrylate degradation as determined by the MS-TGA method.

Fig. 6 Experimental results for thermal degradation of polyoxymethylene.

Fig. 7 Arrhenius plot for polyoxymethylene degradation as determined by the MS-TGA method.

Fig. 8 Experimental results for thermal degradation of polystyrene.

Fig. 9 Arrhenius plot for polystyrene degradation as determined by the MS-TGA method.

Fig. 10 Experimental results for thermal degradation of polyvinyl chloride.

Fig. 11 Arrhenius plot for polyvinyl chloride degradation as determined by the MS-TGA method.

Fig. 12 Experimental results for thermal degradation of a polyvinyl chloride-polymethylmethacrylate mixture.

Fig. 13 Polyvinyl chloride degradation from a polyvinyl chloride-polymethylmethacrylate mixture as determined by the MS-TGA method.

Fig. 14 Polymethylmethacrylate degradation from a polyvinyl chloride-polymethylmethacrylate mixture as determined by the MS-TGA method.

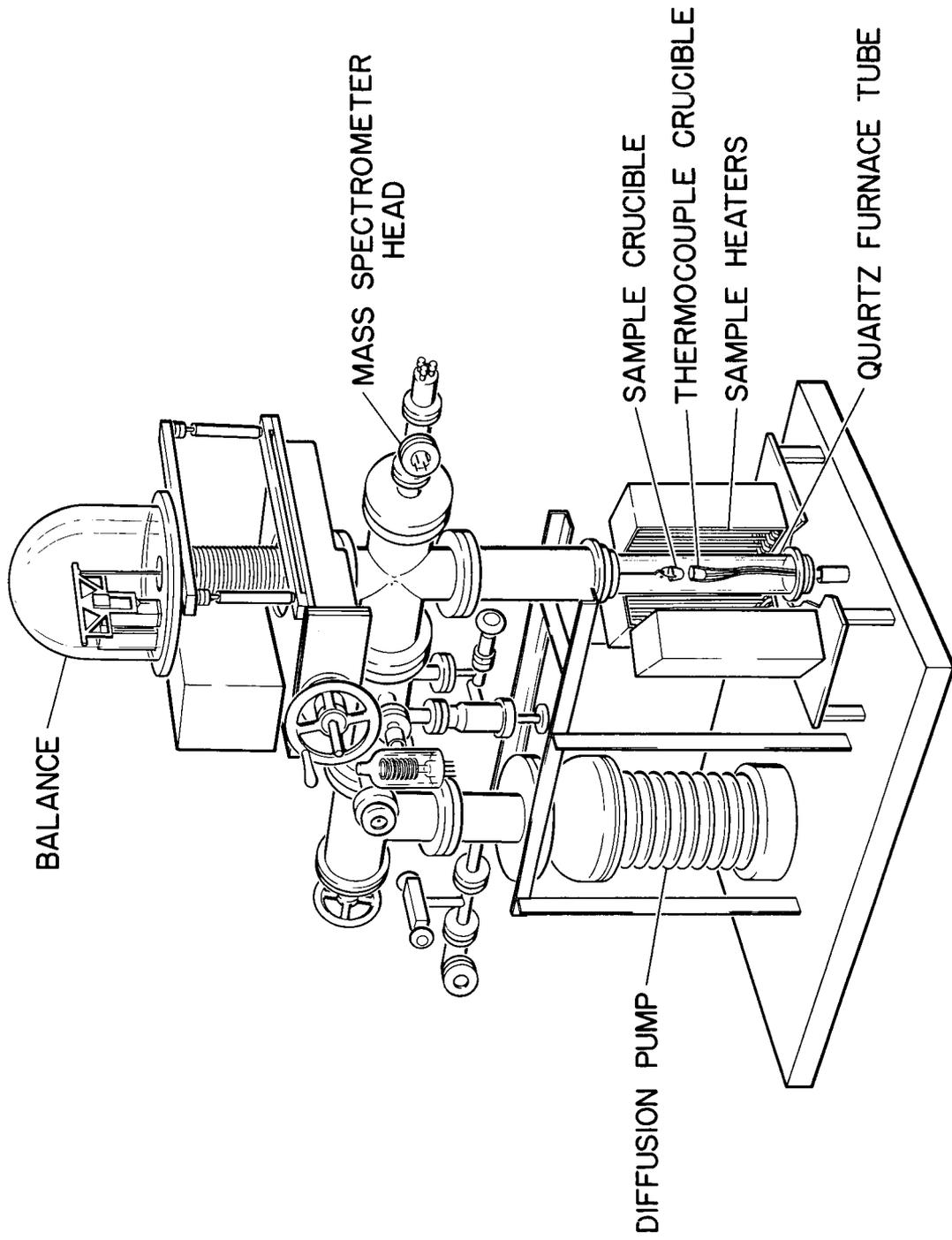


Figure 1.

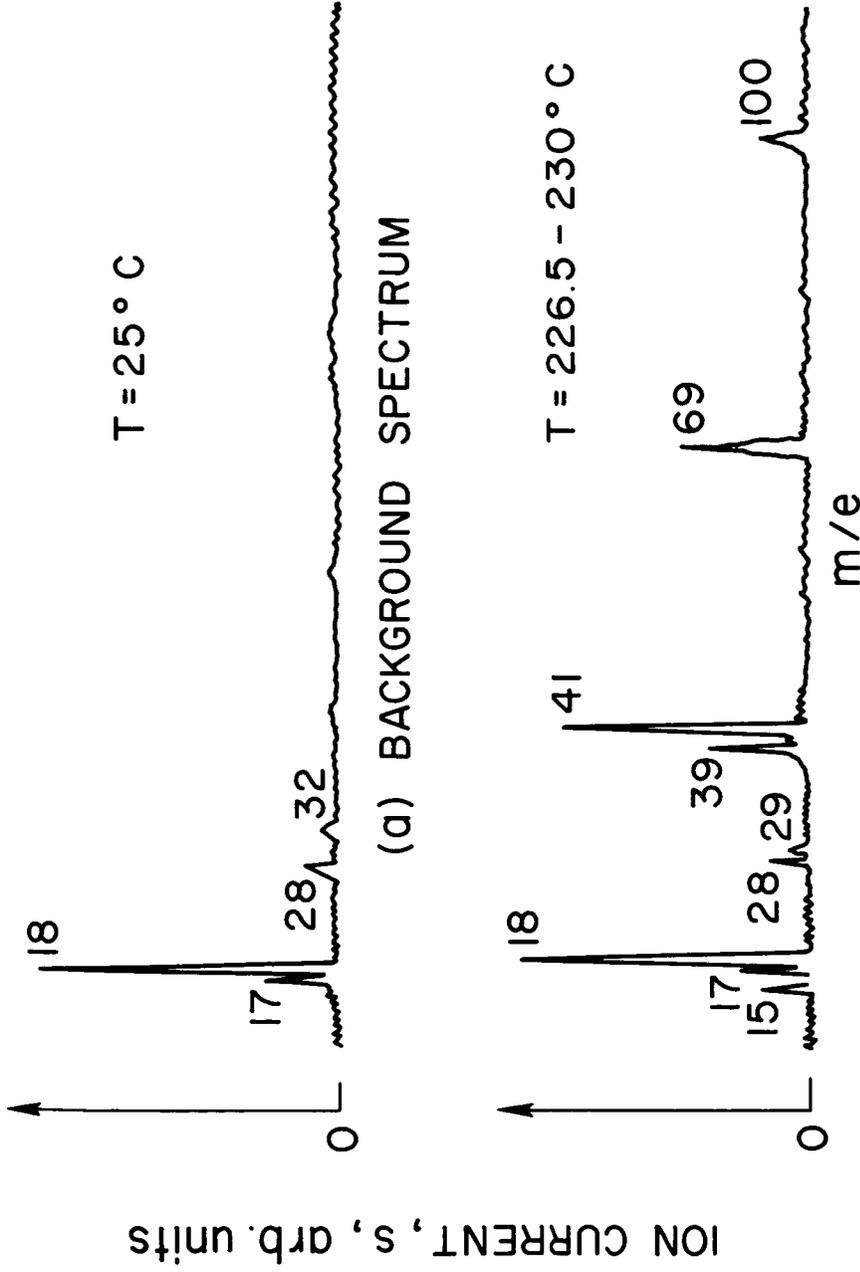


Figure 2.

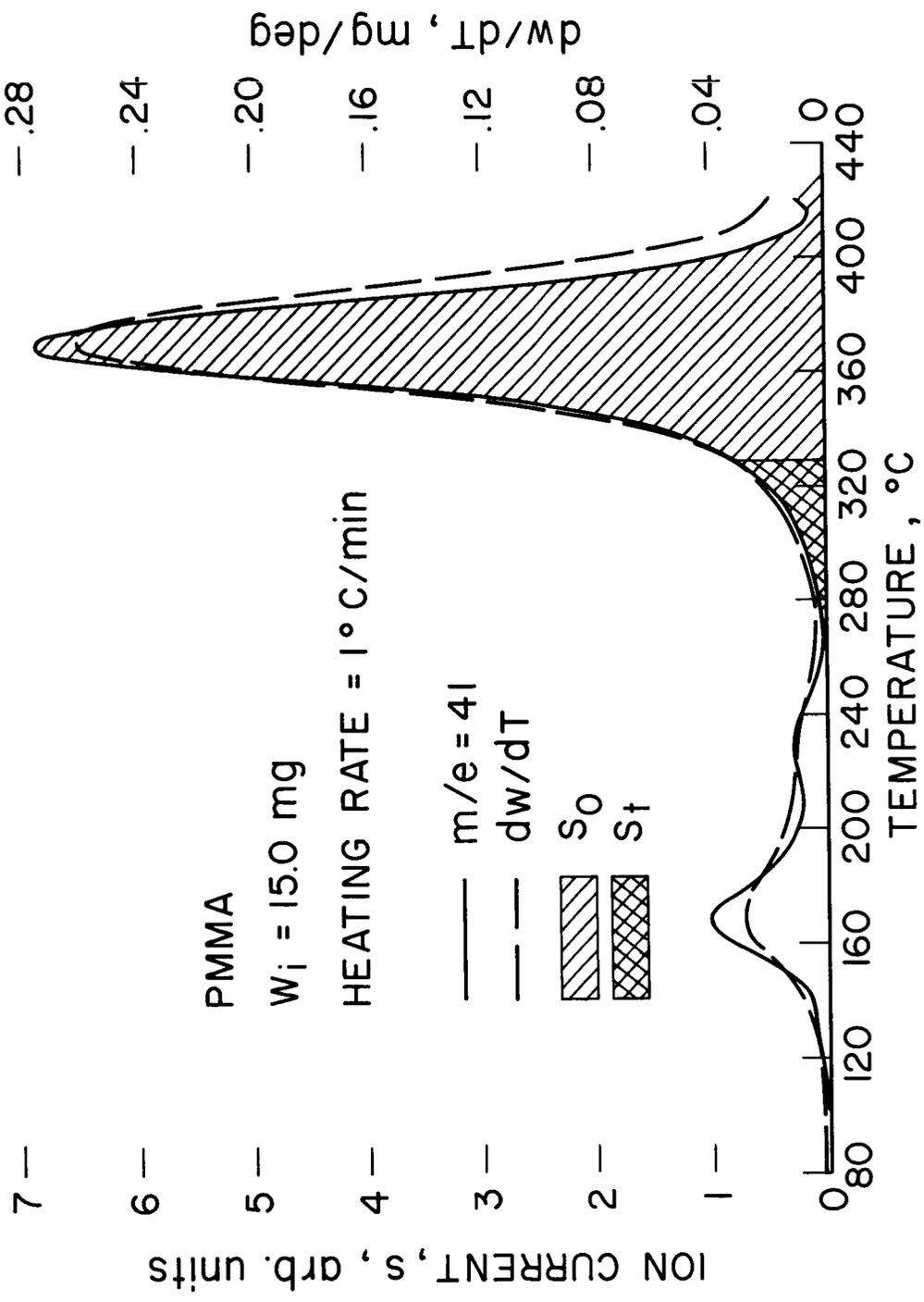


Figure 3.

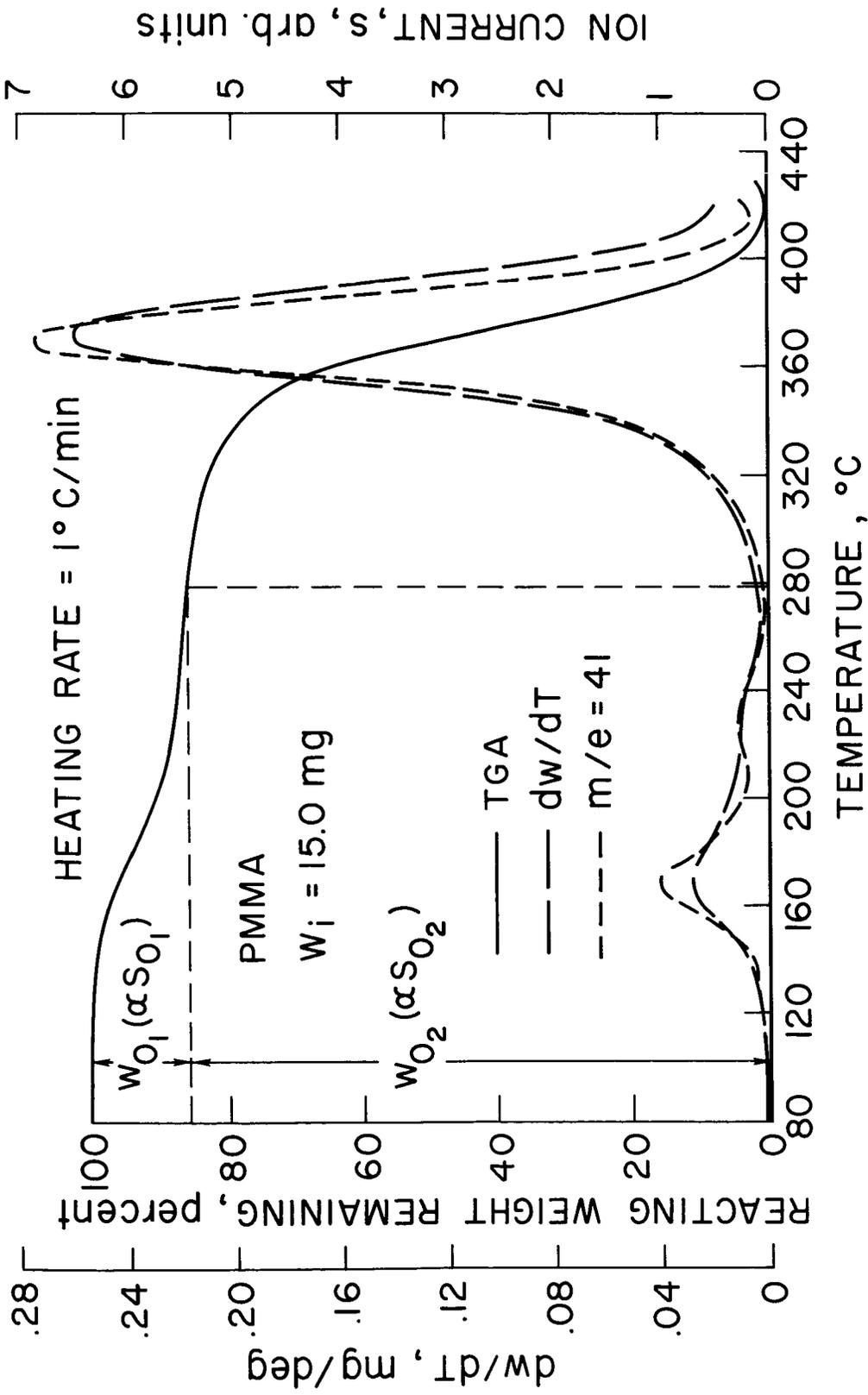


Figure 4.

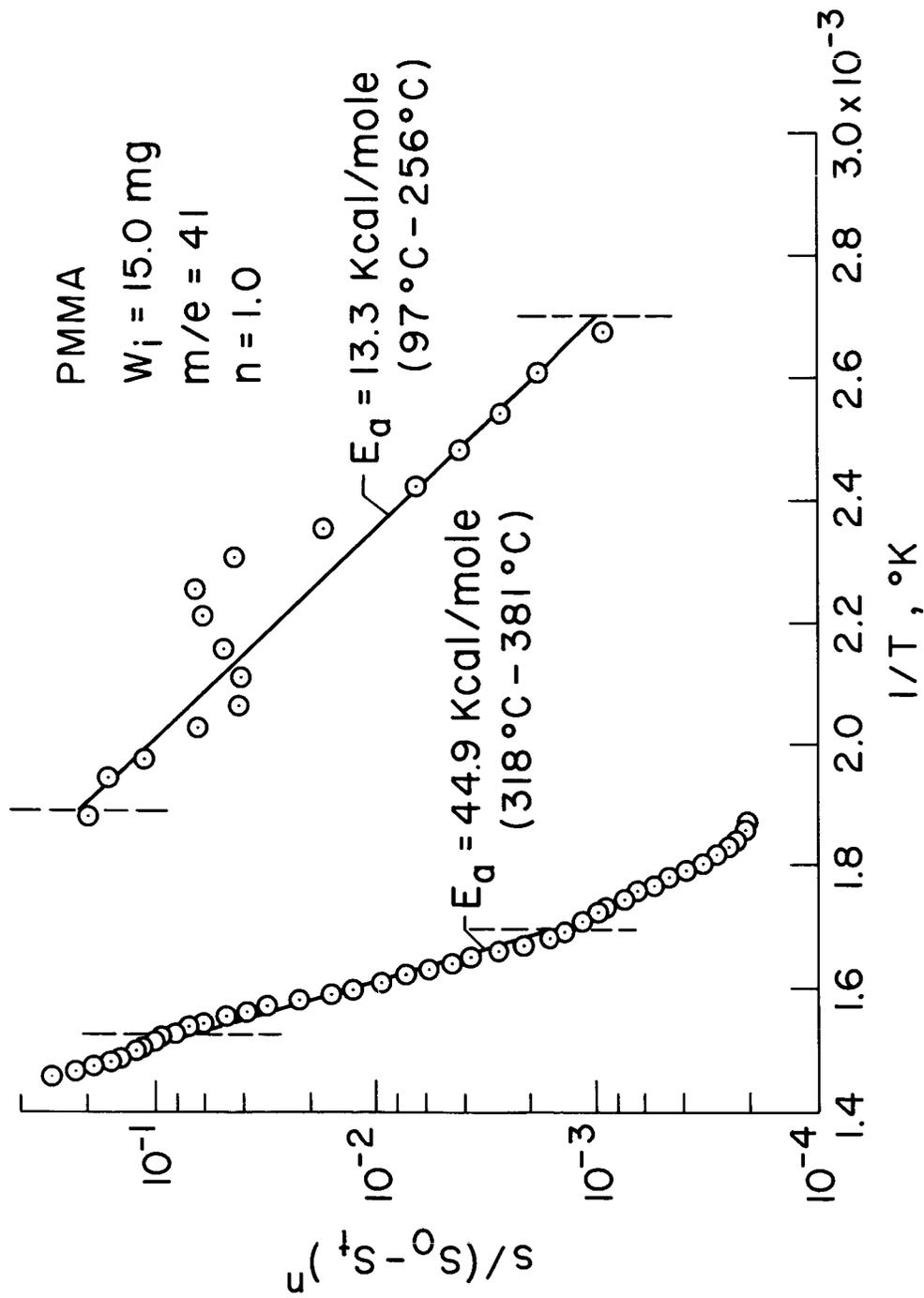


Figure 5.

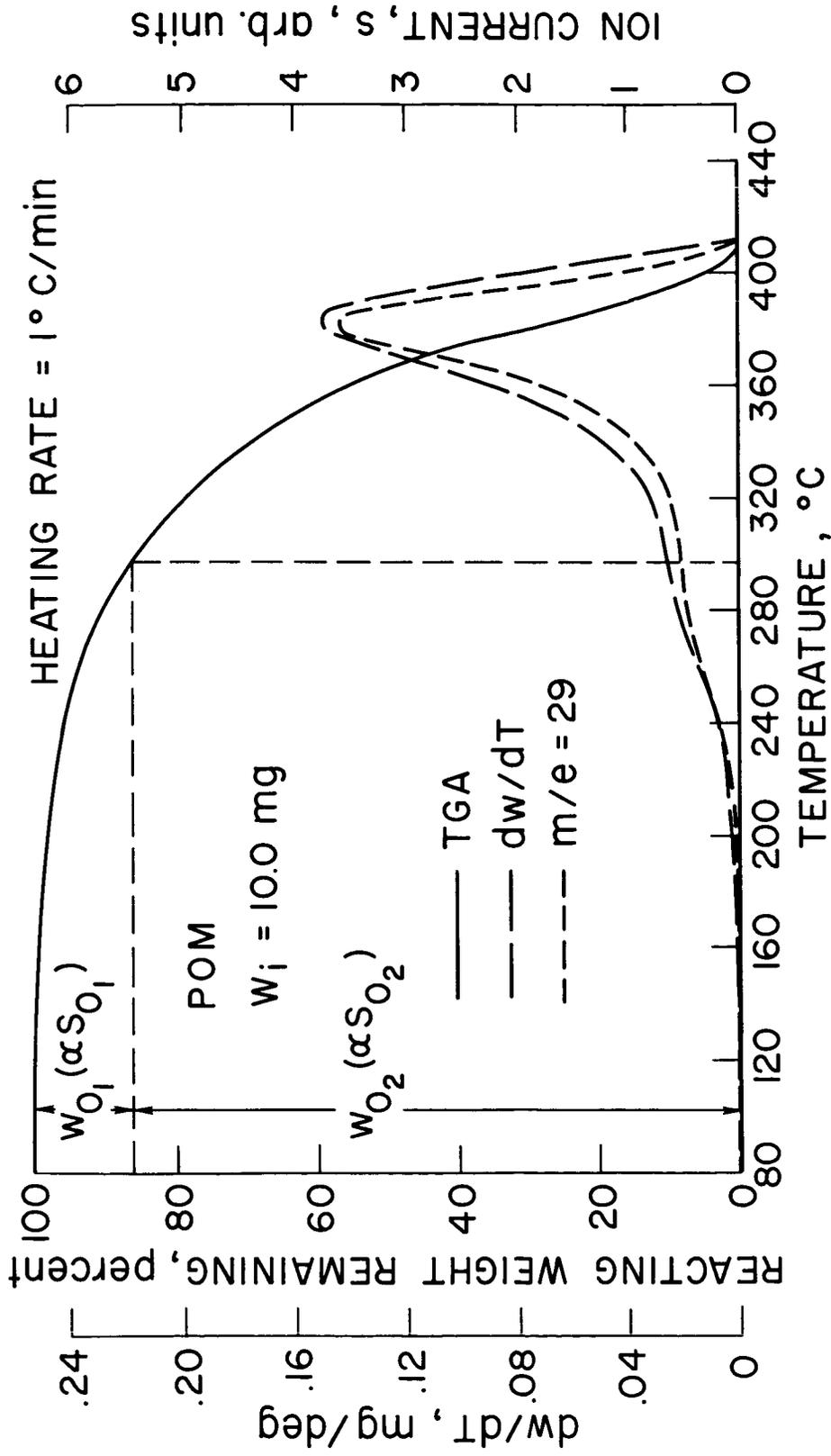


Figure 6.

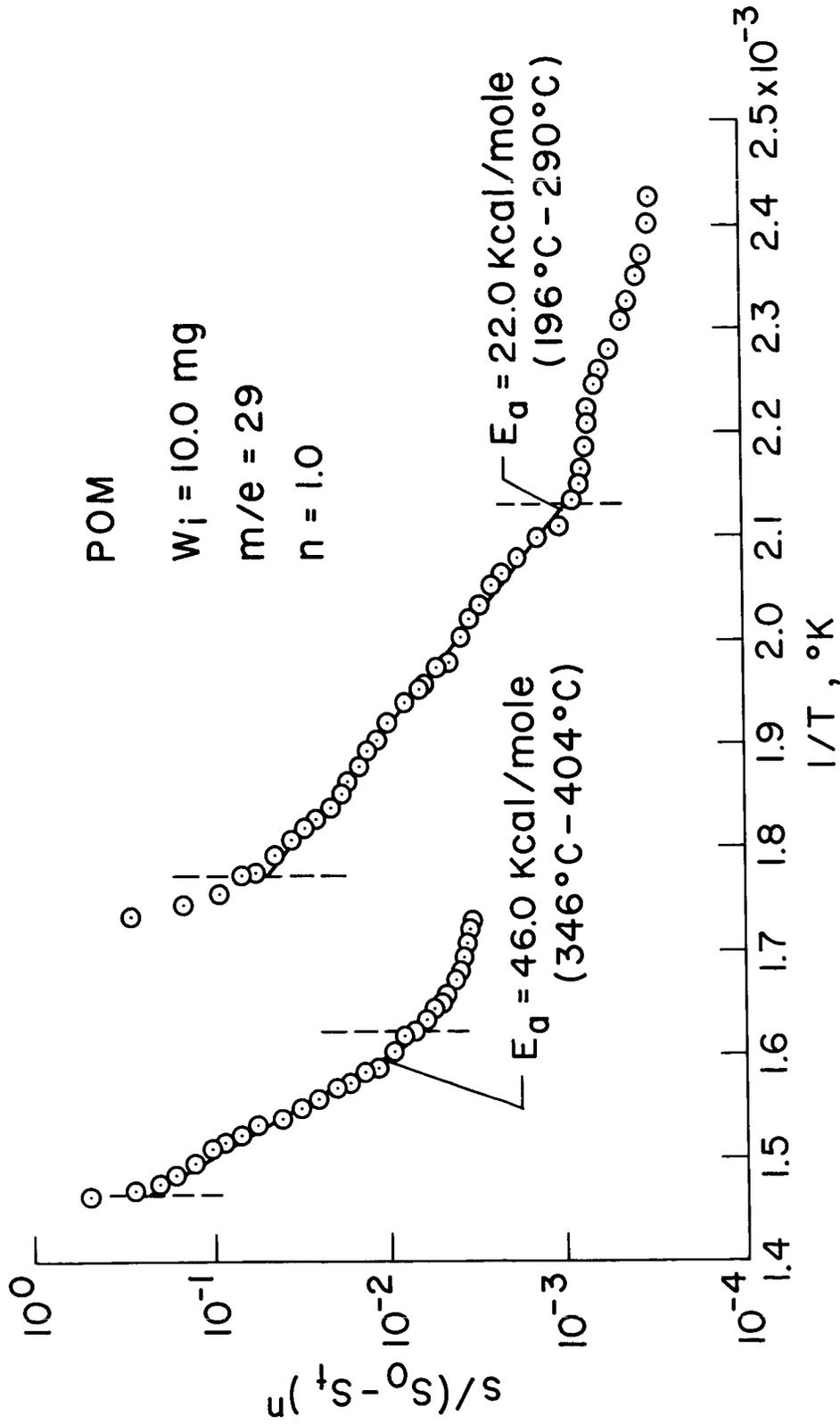


Figure 7.

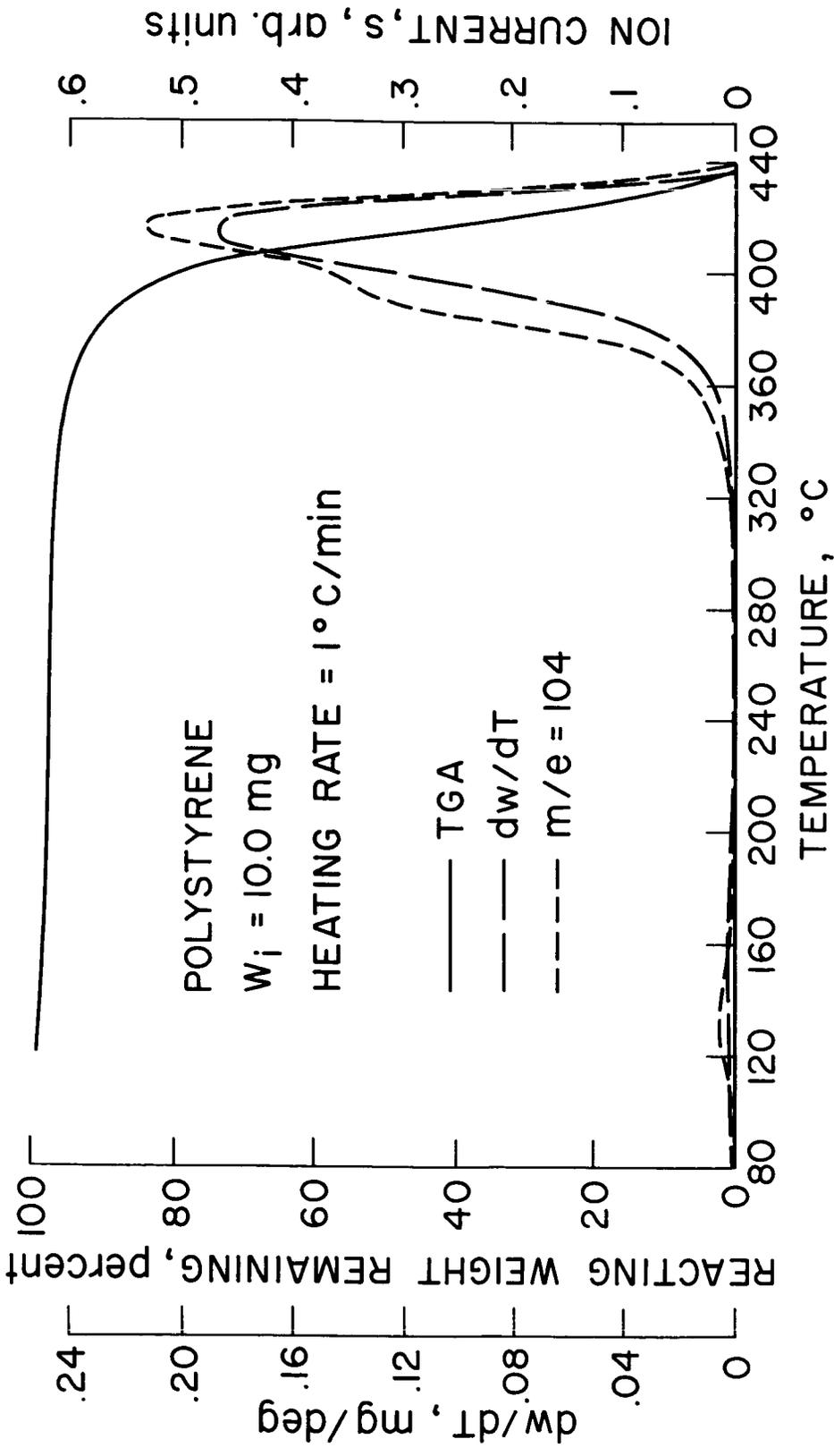


Figure 8.

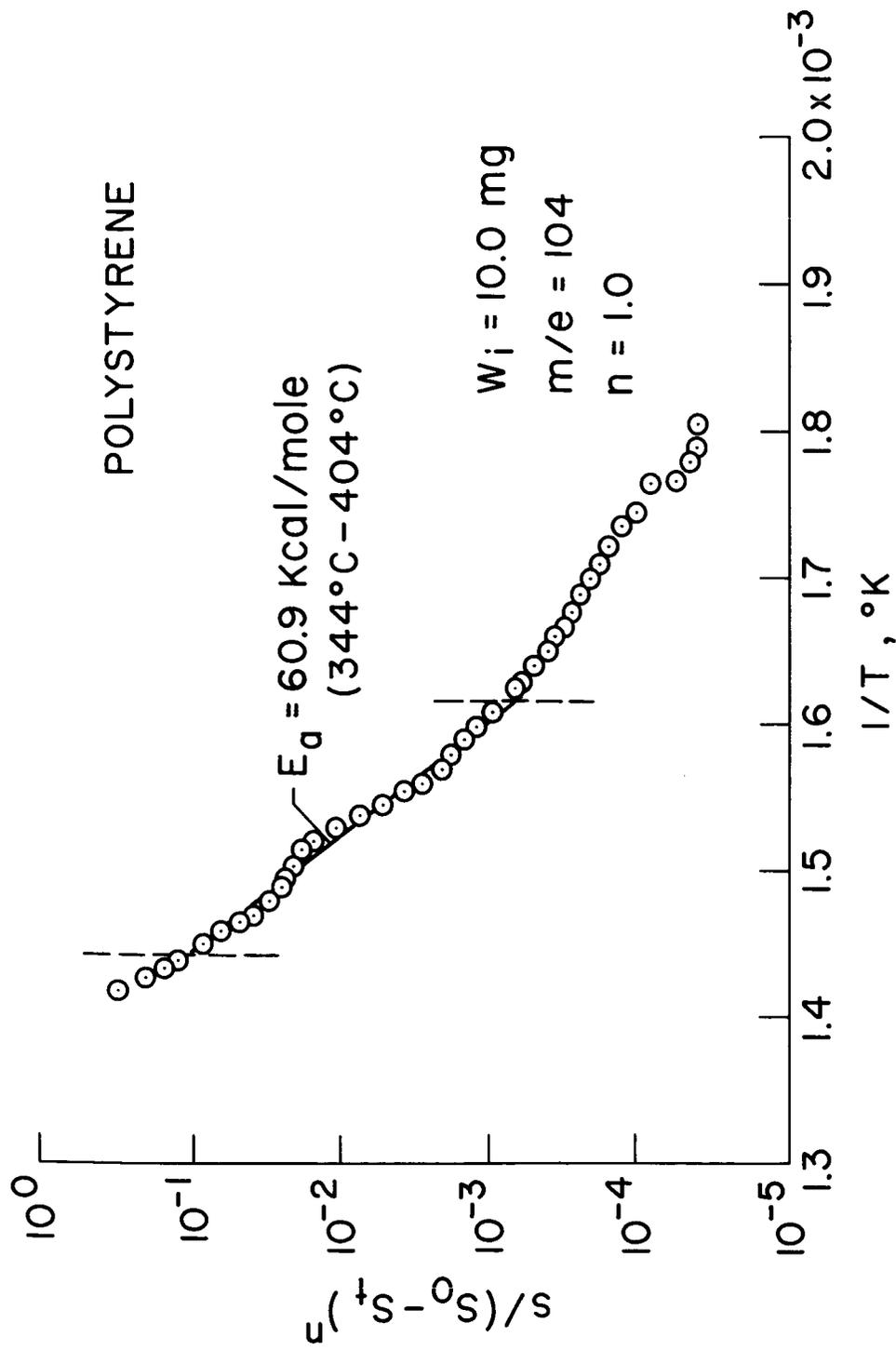


Figure 9.

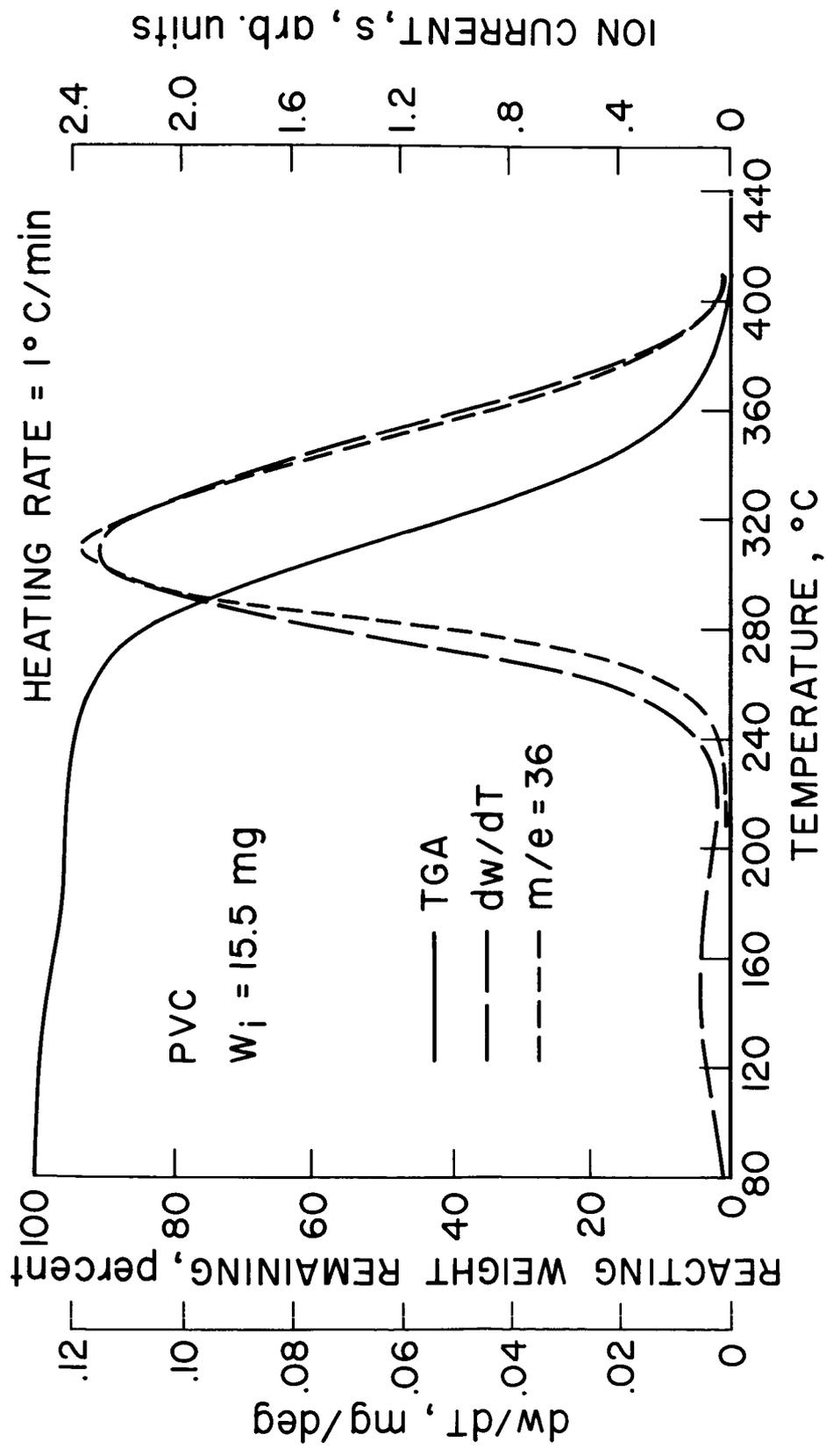


Figure 10.

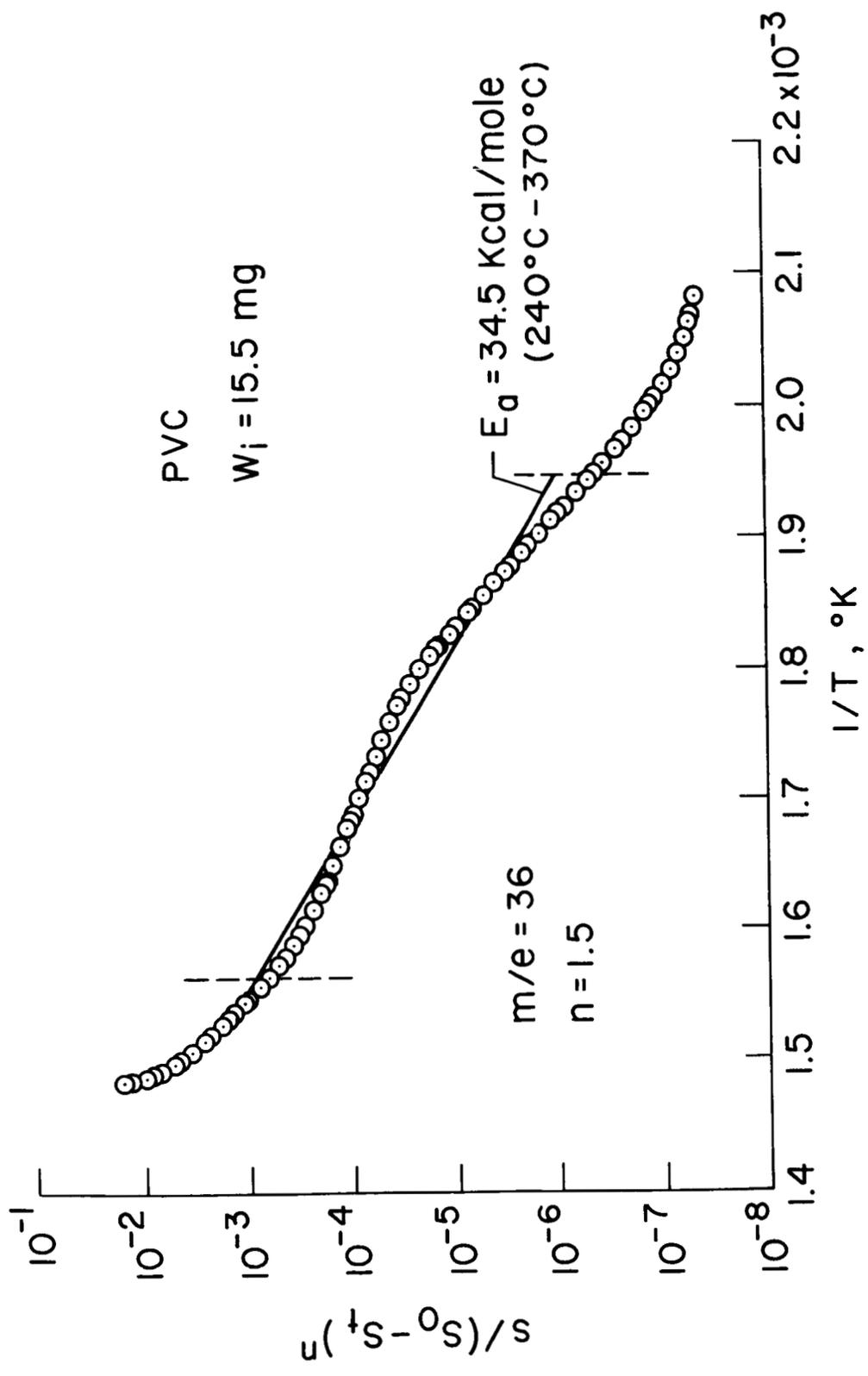


Figure 11.

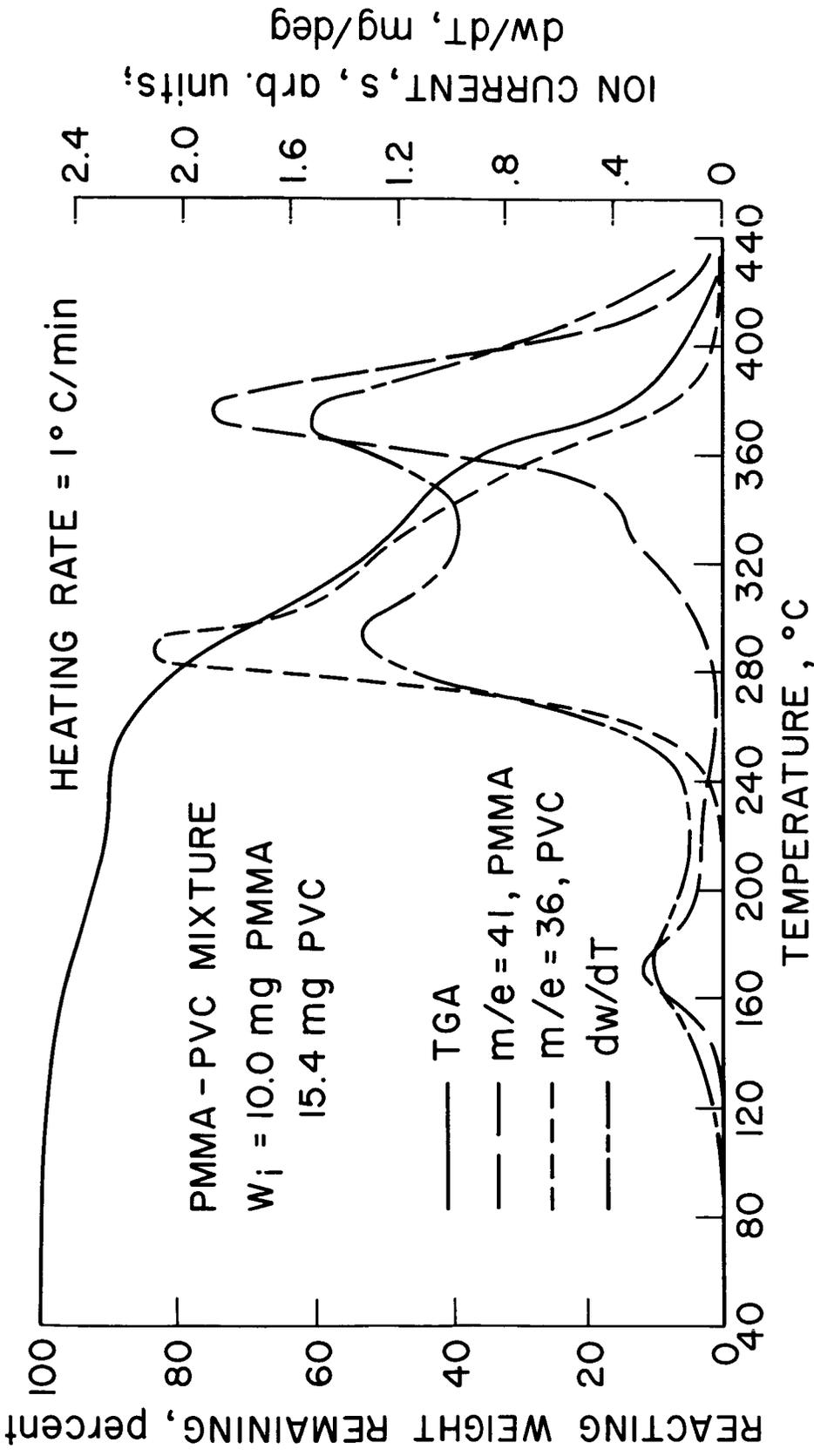


Figure 12.

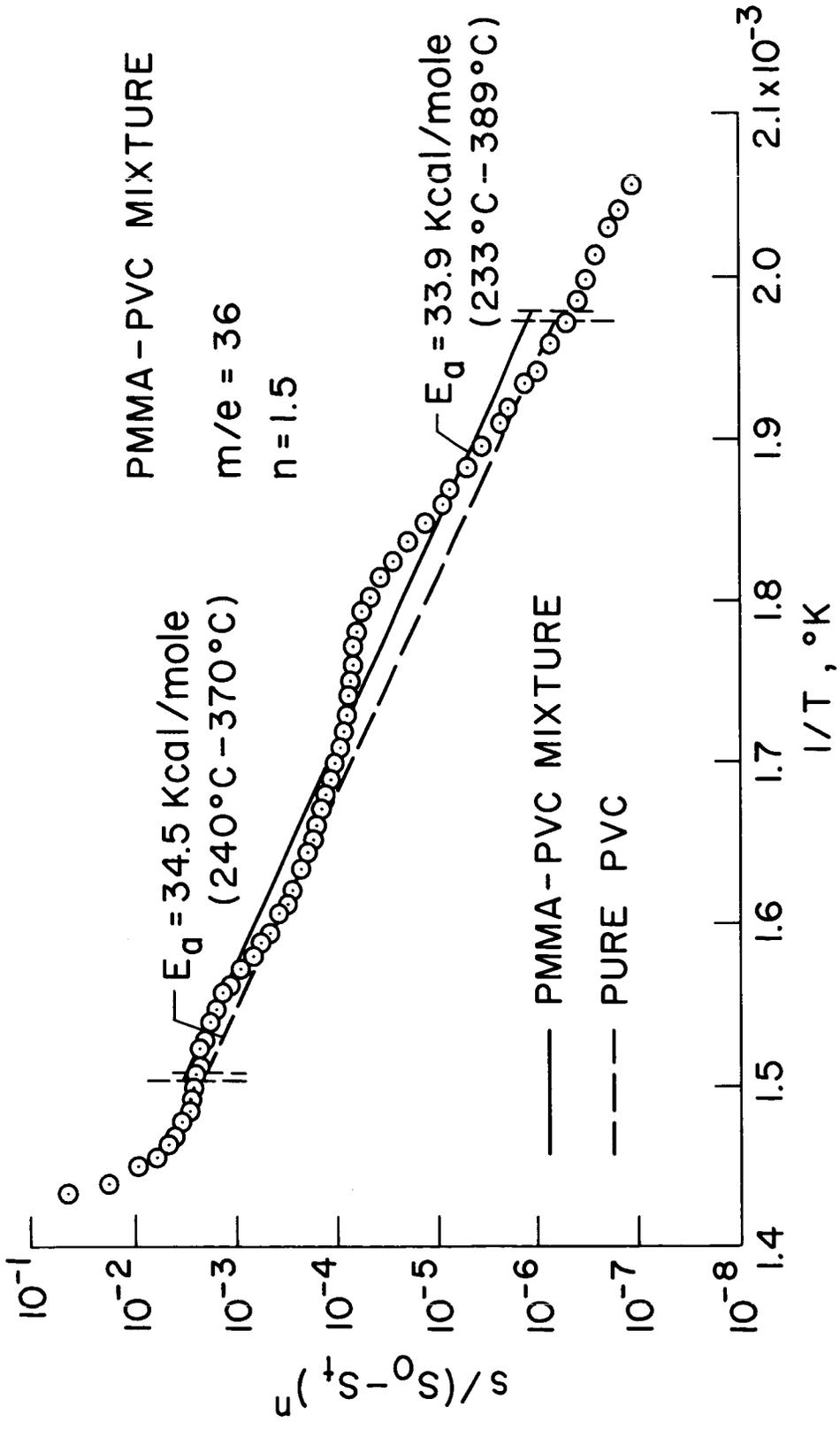


Figure 13.

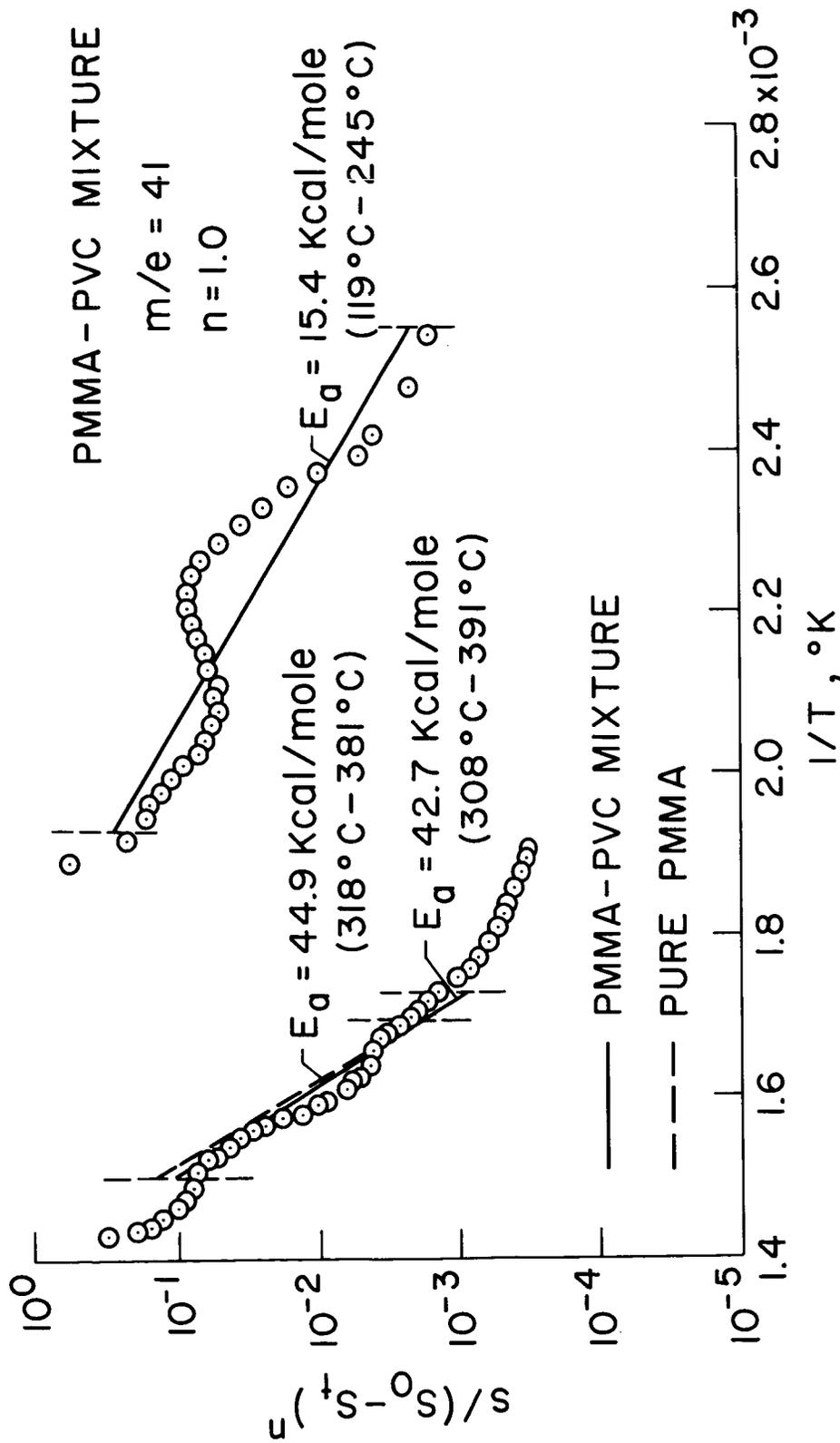


Figure 14.