

The Thermal Stability of Poly(aryl-Ether-Ether-Ketone) as Assessed by Thermogravimetry*

M. DAY, J. D. COONEY, and D. M. WILES, *Division of Chemistry, National Research Council of Canada, Ottawa, Ontario, Canada, K1A 0R9*

Synopsis

The high temperature engineering thermoplastic poly(aryl-ether-ether-ketone) (PEEK) has been subjected to dynamic and isothermal thermogravimetry in both nitrogen and air. The dynamic data have been analyzed using both the Kissinger peak maximum technique and an isoconversional procedure developed by Flynn. These techniques gave apparent global activation energies of 223.5 and 235.7 kJ/mol, respectively, for the degradation of PEEK in nitrogen, in good agreement with the value of 219.7 determined from the isothermal experiments. The thermal stability of PEEK in air is substantially less than in nitrogen, and the decomposition mechanism is more complex. The global apparent activation energies for the weight loss in air were found to be 116.9 and 159.5 kJ/mol from dynamic slow heat rate data and isothermal data, respectively. The data obtained from fast heating rate experiments in air were found to be misleading, suggesting caution in the use of "commercial" software packages for lifetime estimates under these conditions, especially where oxidative processes may be occurring.

INTRODUCTION

The last few years have seen an increasing use of high temperature thermoplastics, either alone or as matrices for advanced composites. Associated with these high temperature applications is the need for test procedures to assess and predict performance under service conditions. The measurement of weight loss as a function of temperature or time, i.e., thermogravimetry (TG), represents one technique which has been used to predict thermal stability. However, it should be noted that physical properties, such as the mechanical strength, need to be related to the weight-loss data before predictions regarding thermal stability and "lifetime" in service predictions are made.¹⁻³ TG experiments, meanwhile, are capable of providing information on the kinetics of the thermal decomposition of polymers, and an insight into the complex degradation mechanisms.¹⁻⁵

The aromatic polymer, poly(aryl-ether-ether-ketone) (PEEK), represents one of the new class of high-performance engineering thermoplastics. The aromatic structure of PEEK is responsible for its relatively high melting point (335°C).⁶ Consequently, the material must encounter elevated temperatures at almost every step in the manufacturing, compounding, and processing stages, as well as in service and during repair. Fundamental kinetic information is therefore needed regarding the thermal behavior of this material before its widespread acceptance in demanding applications such as aerospace and

*Issued as NRCC No. 29850.

aviation. The literature contains at least two references to the thermal stability of PEEK as measured by TG data. A dynamic TG kinetic study in nitrogen and air indicated that PEEK's decomposition kinetics were nearly identical in the two environments with almost identical "lifetime" estimates, and no indication of thermal degradation below 500°C.⁷ Another study, meanwhile, showed that the thermal stability of PEEK is diminished in air relative to an inert atmosphere with evidence of degradation at 400°C in air.⁸

In this study we have attempted to clarify the thermal stability of PEEK by performing a detailed TG kinetic study of the thermal degradation. To assess the relative importance of the pyrolytic and thermooxidative processes, the weight-loss curves were measured in both nitrogen and air atmospheres.

EXPERIMENTAL

The PEEK polymer used in this study was a 0.217-mm-diameter monofilament prepared from ICI resin by Albany International. This material had an intrinsic viscosity of 0.81 dL/g, measured at 30°C in 96% H₂SO₄. The density measured by the floatation technique in calcium nitrate solution was 1.2945 g/cm³. This corresponds to a crystallinity of 27% assuming densities of 1.264 g/cm³ for amorphous and 1.378 g/cm³ for crystalline PEEK.⁹

Isothermal and dynamic programmed TG analyses were carried out with a DuPont 951 module coupled to a 1090 thermal analyzer. Because of the known dependence of kinetic parameters on sample mass,¹⁰ the sample sizes were standardized at 12.1 ± 0.2 mg. The experiments were conducted in either nitrogen or air at a flow rate of 50 mL/min. The dynamic TG experiments were performed at nine heating rates from 0.01 to 20°C/min. For the isothermal heating experiments, the furnace was initially heated to the selected temperature for a period of 45 min before the previously weighed sample was inserted in the furnace and data collection commenced.

RESULTS AND DISCUSSION

Dynamic Experiments

Typical results for TG and derivative thermogravimetry (DTG) on PEEK degraded in nitrogen and air at a heating rate of 1°C/min are shown in Figure 1. The DTG curve for the sample degraded in nitrogen indicates that the weight loss appears to occur in one stage. Below 500°C the sample appears to be stable, and only shows noticeable weight loss above 500°C, where the rate of weight loss gradually increases to a maximum rate at 532°C. The rate of weight loss then gradually falls off with a 60% residue at a temperature of about 575°C. Further increase in the temperature up to about 1000°C caused only slight additional reduction in the residual weight.

The TG and DTG curves for the PEEK heated in air indicate that two main weight-loss stages occur during degradation in this environment. The first reaction appears to commence around 480°C and ends around 540°C with a maximum rate at 527°C. This initial reaction stage corresponds closely to that observed in nitrogen, although in air the temperatures of initial and maximum rate of weight loss are reduced. In air there is also a second reaction stage which appears between 540 and 575°C with a maximum rate of weight

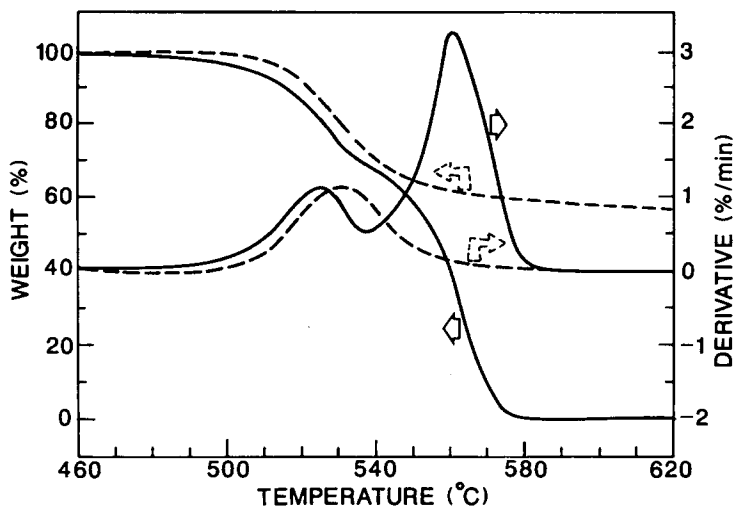


Fig. 1. Thermogravimetric curves for PEEK heated in air (—) and nitrogen (---) at 1°C/min.

loss at 561°C. This second stage, which goes to 0% residue at 580°C, appears to be oxidative in nature since it is not observed in nitrogen, and has a noticeable exotherm associated with it.

TG measurements were carried out at nine heating rates to determine the kinetic parameters for the reaction stages noted above. Representative DTG curves for PEEK degraded in nitrogen and air are shown in Figures 2 and 3, respectively. In these figures we have plotted the rate with respect to temperature ($d\alpha/dT$) instead of the usual manner with respect to time ($d\alpha/dt$) because the heating rate (β) acts as a normalization factor and allows all curves to be plotted on the same scale, and allows comparisons to be made with the theoretical curves developed by Flynn.¹¹ The data obtained in nitrogen are shown in Figure 2. The value of the peak maximum increased, the peak shape narrowed and moved to lower temperatures as the heating rate decreased from 10 to 0.01°C/min. These curves closely correspond to the theoretical curves calculated for a first-order weight-loss mechanism.¹¹ The DTG curves in air, however (Fig. 3), are far from simple and show a variety of changes with heating rate. These changes imply that, in the case of PEEK degrading in air, several reaction mechanisms are involved.

There are many methods for the kinetic evaluation of the TG thermal degradation data, and these have been described and discussed in several publications.^{1,3-5,12} Because the DTG curves shown in Figures 2 and 3 indicated discrete weight-loss stages, the relatively simple Kissinger method¹³ was initially used to determine the apparent activation energy E for each of the stages. This method allows the calculation of E from one point (the maximum temperature T_m on the DTG curve) at several heating rates. This method involves the following expression derived by Kissinger:

$$\ln(\beta/T_m^2) = \ln[A_n(1 - \alpha)_m^{n-1}] - E/RT_m$$

where β is the heating rate, R the universal gas constant, α the fractional weight loss, A the preexponential factor, and n the reaction order. A plot of

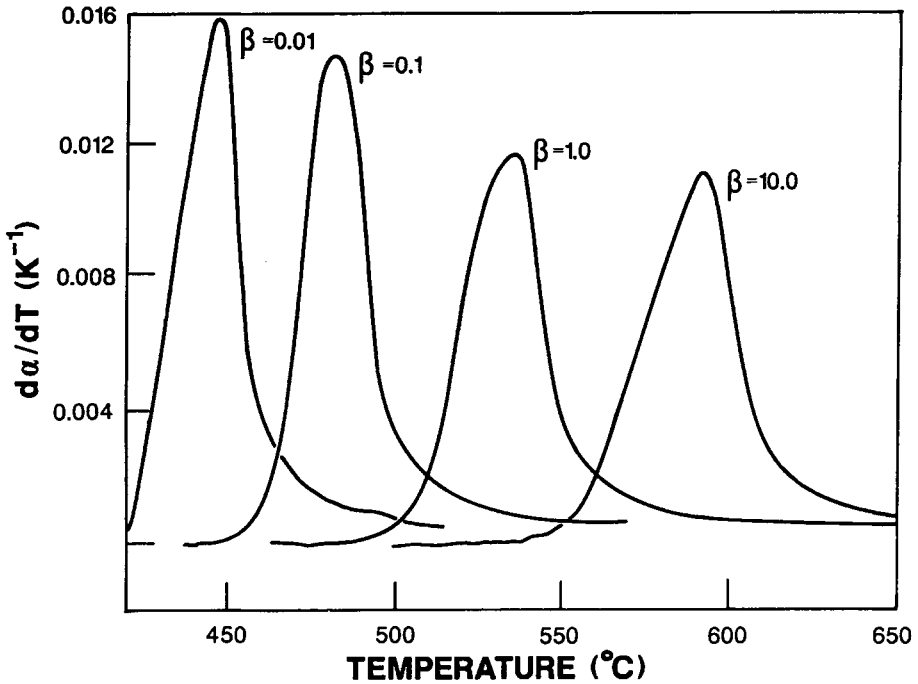


Fig. 2. $d\alpha/dT$ vs temperature plots for PEEK degraded in nitrogen at heating rates (β) of 0.01, 0.1, 1, and 10°C/min.

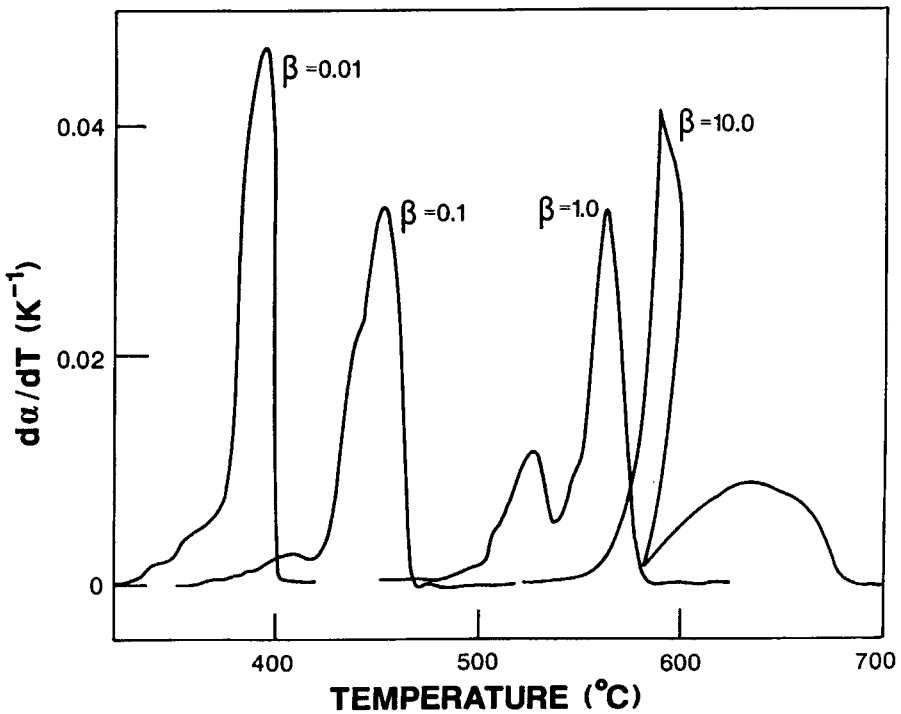


Fig. 3. $d\alpha/dT$ vs temperature plots of PEEK degraded in air at heating rates (β) of 0.01, 0.1, 1, and 10°C/min.

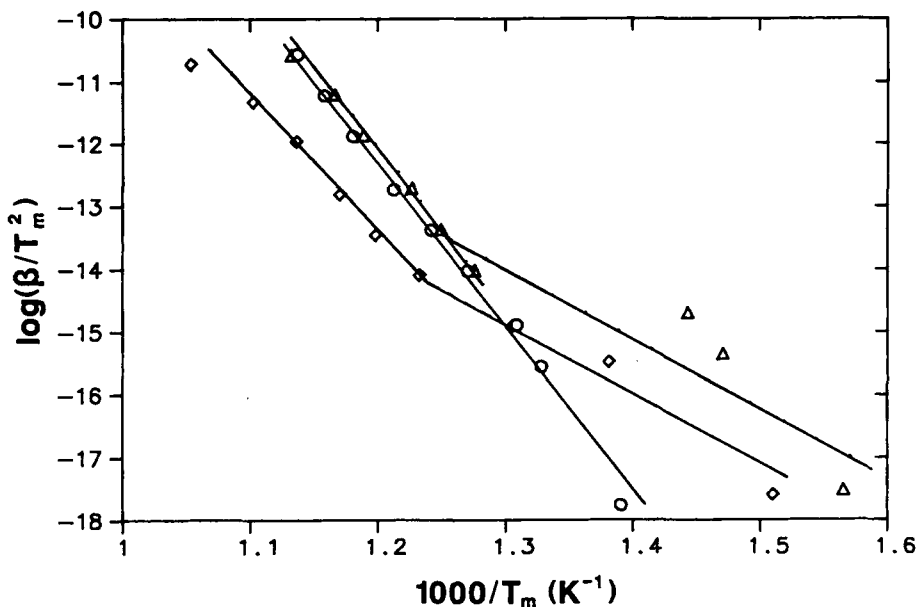


Fig. 4. Kissinger plots of PEEK degraded in nitrogen (○) and air [first stage data (◇) and second stage data (△)].

$\ln(\beta/T_m^2)$ as a function of $(1/T_m)$ then gives E from the slope of the line. The plot obtained for PEEK degraded in nitrogen and the plots for the first and second reaction stages in air are shown in Figure 4. A single reasonable straight line was obtained for the experiments performed in nitrogen, and an E value of 223.5 kJ/mol was calculated from the slope, confirming the apparent simple kinetics in nitrogen. The plots for the first and second stages in air, however, can each be separated into two straight line portions having quite different slopes. At faster heating rates (high values of T_m), the slopes of both the first and second reaction stages are greater than those at the slower heating rates (low values of T_m). Consequently, the calculated E values at the fast heating rates ($\geq 1^\circ/\text{min}$) of 159.3 and 202.7 kJ/mol for the first and second reaction stages, respectively, are higher than those measured at the slow heating rates ($\leq 1^\circ\text{C}/\text{min}$) of 104.0 and 93.3 kJ/mol. This variation in E with heating rate clearly indicates the complex nature of the degradation mechanism in air.

While the Kissinger method is apparently relatively simple in concept, it does rely upon the peak temperature to be known with a great deal of accuracy. Unfortunately, the data in the vicinity of the maximum rate usually have the least sensitivity due to the endotherms or exotherms associated with the weight-loss process.¹⁴ In our studies of the TG kinetics of poly(ethylene terephthalate), both treated¹² and untreated with flame retardants,¹⁵ we have found the isoconversional method described by Flynn¹⁶ to be the most reliable. This technique proposed independently by Ozawa¹⁷ and Flynn and Wall,¹⁸ is based upon the following expression, which is an approximate solution¹⁹ of the integrated rate equation:

$$\log F(\alpha) = \log(EA/R) - \log(\beta) - 2.315 - 0.4567E/RT$$

The apparent activation energy E can then be obtained from a plot of $\log \beta$ against $1/T$ for a fixed degree of conversion since the slope of such a line is given by $-0.4567E/R$. In addition, the derived E values can be used to calculate $\log A$ from the intercept value. Figure 5 shows some of the isoconversional plots for the pyrolysis of PEEK in nitrogen for the range of heating rates employed in this study. The nearly parallel straight lines over the fractional weight-loss range 0.05–0.3 indicate that a single reaction mechanism is in operation with a constant activation energy. This consistency of activation energy with fractional weight loss is illustrated in Figure 6, from which a weighted mean E value of 235.7 ± 2.3 kJ/mol ($\log A = 15.4 \pm 0.1$ min⁻¹) has been calculated. This E value is very close to the reported value⁷ of 231.8 kJ/mol obtained using a similar technique and kinetic analysis.

The experimental DTG curves for the experiments conducted in air (Fig. 3) indicate that multiple reactions are occurring. Some of the isoconversional plots for these experiments are shown in Figure 7. Clearly these plots are neither linear nor parallel, implying that in air the weight-loss process is more complex, involving several reaction mechanisms. Interestingly, the data presented in Figure 7 can be separated into two parts: (i) the fast heating rate region $\geq 1^\circ\text{C}/\text{min}$ and (ii) the slow heating rate region $\leq 1^\circ\text{C}/\text{min}$ and isoconversional values of E can be determined for each region. The calculated E values are graphically represented in Figure 8 for both these heating rate regions. In the case of the slow heating rate data, it appears that the first reaction stage ($\alpha = 0-0.4$) has a weighted mean apparent activation energy of 121.9 ± 3.2 kJ/mol ($\log A = 8.5 \pm 0.2$ min⁻¹), while the overall global value is not much different with a value of $E = 116.9 \pm 2.3$ kJ/mol ($\log A = 8.5 \pm$

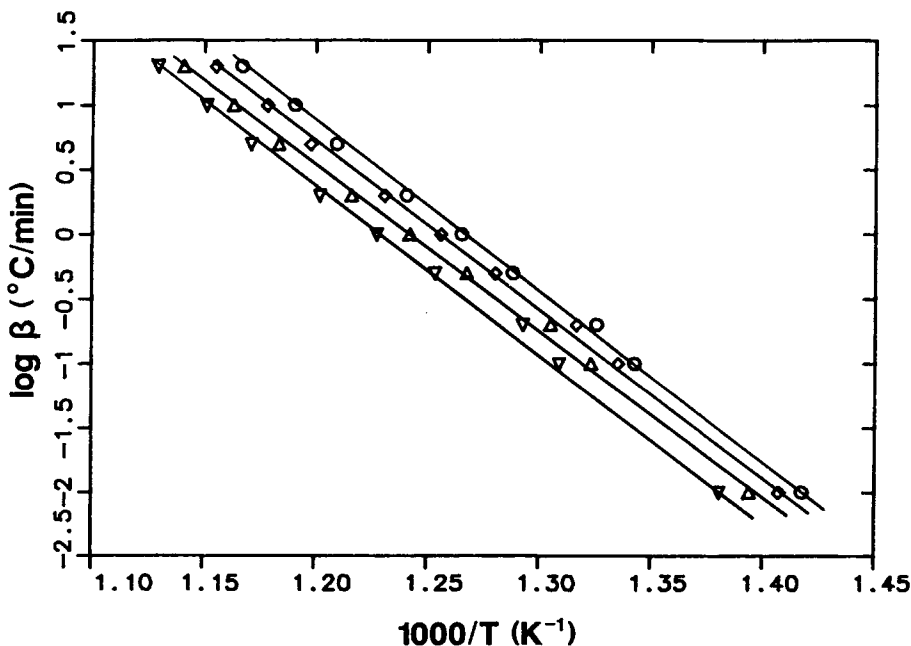


Fig. 5. Isoconversional plots of PEEK degraded in nitrogen for α values of: (○) 0.05; (◇) 0.1; (△) 0.2; (▽) 0.3.

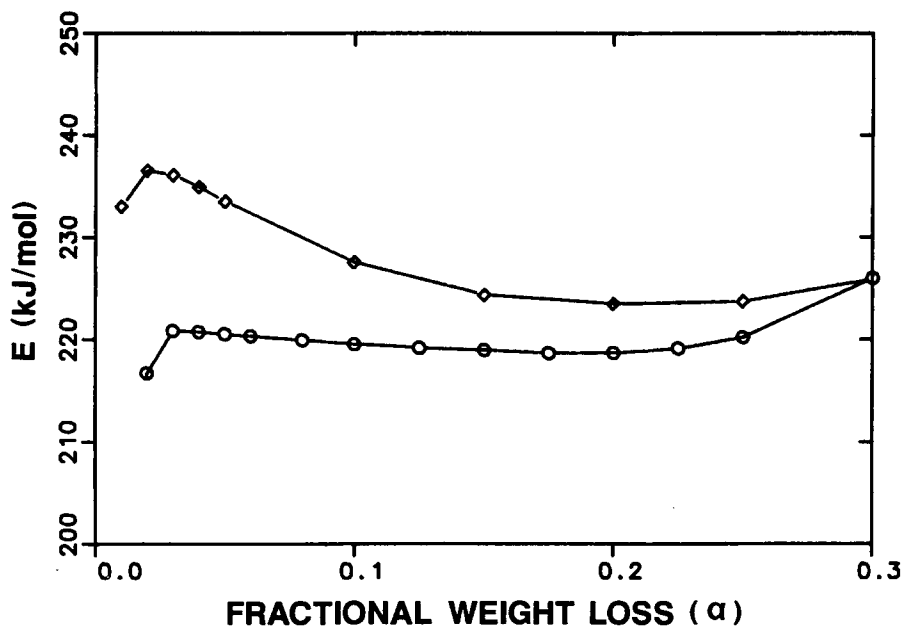


Fig. 6. Calculated activation energies (E) as a function of fractional weight loss (α) for PEEK degraded in nitrogen. Values calculated from nonisothermal data (\diamond) and isothermal data (\circ).

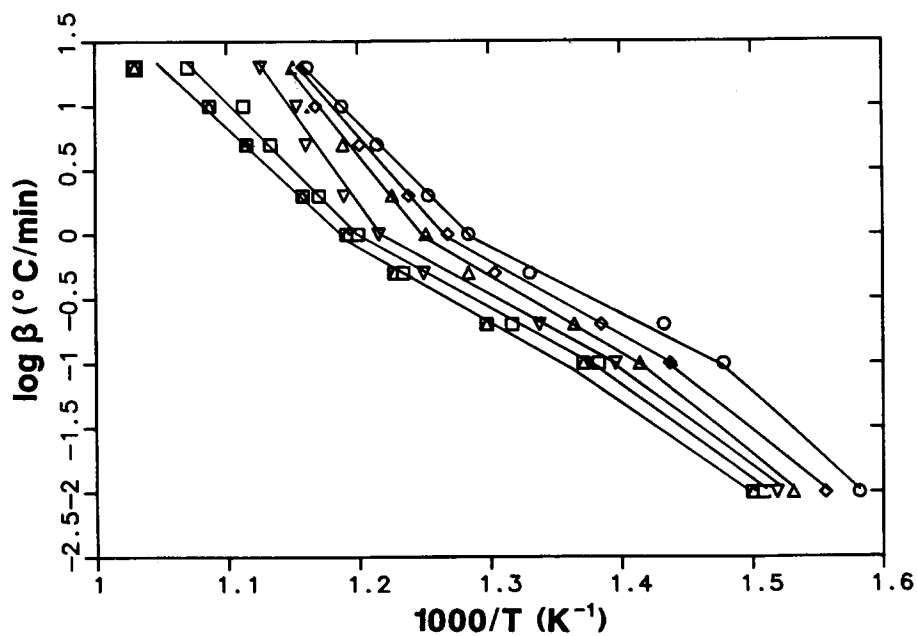


Fig. 7. Isoconversional plots of PEEK degraded in air for α values of (\circ) 0.05; (\diamond) 0.1; (Δ) 0.2; (∇) 0.4; (\square) 0.6; (\boxtimes) 0.8.

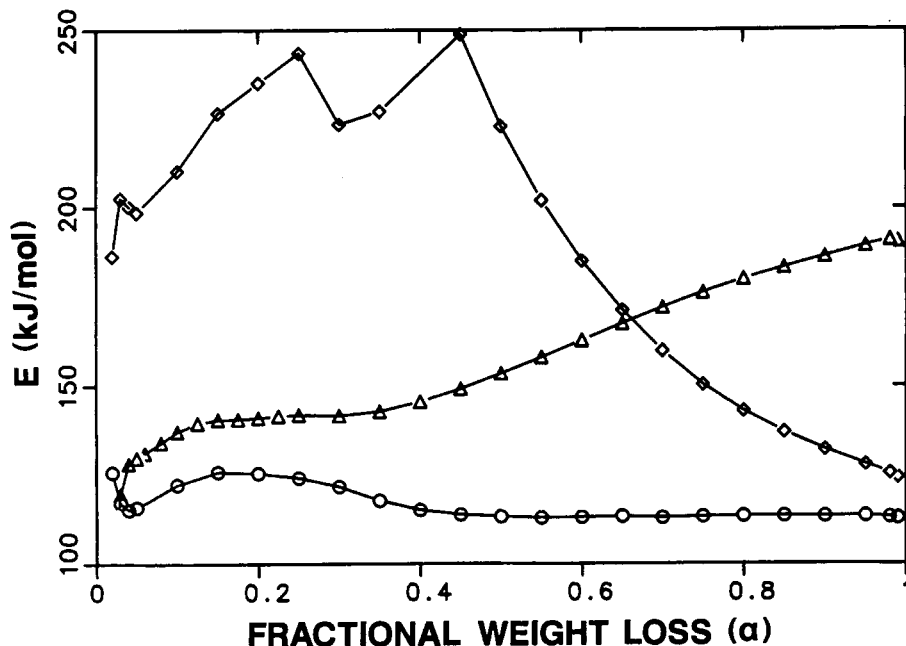


Fig. 8. Calculated activation energies (E) as a function of fractional weight loss (α) for PEEK degraded in air. Nonisothermal heating rate obtained at fast (\diamond) and slow heating rates (\circ); (Δ) isothermal data.

0.1 min^{-1}). The data obtained using the fast heating rates do not show this consistency. Instead, E changes with the extent of reaction, increasing from a value of $198.0 \pm 5.0 \text{ kJ/mol}$ ($\alpha = 0.02\text{--}0.1$) to a maximum value of $234.2 \pm 11.9 \text{ kJ/mol}$ ($\alpha = 0.15\text{--}0.5$) before gradually falling to a value of 124.2 kJ/mol at $\alpha = 0.99$. The fact that the activation energy is changing with α under the fast heating rate conditions suggests that changes in the kinetics are taking place. Typical changes in the degradation of polymeric systems responsible for these variations are shifts from diffusion-controlled kinetics to chemical-controlled kinetics or vice versa. Comparing the data from the fast and slow heating rate experiment performed in both nitrogen and air suggests that in air the controlling mechanism is the transport of oxygen through the melt which is then responsible for the thermal oxidative degradation. Under the fast heating rate conditions in air, this oxygen diffusion is probably too slow in comparison to the heating rate and temperature rise. Consequently, the degradation observed at the fast heating rates combine both pyrolytic kinetics (similar to nitrogen) and some from oxidative degradation kinetic process.

However, the interpretation of the experimental data in air is also further complicated by the presence of a detectable exotherm which causes a perturbation in the measured temperature. This heat release in the presence of air therefore causes shifts in the measured value of β from the selected value. These shifts are then capable of influencing the kinetic value of E calculated from the plots of $\log \beta$ against $1/T$. These perturbations are much larger at the higher heating rates than at the slower heating rates, where there is usually a longer time period for the heating system to respond to the heat

output of the exothermic oxidative reactions. Modderman et al.⁷ have reported an E of 236.8 kJ/mol for the degradation of PEEK in air from heating rate data of 2–20°C/min at an isoconversional value of $\alpha = 0.05$. However, the values of E as demonstrated above very much depend on heating rate and conversion and as such reflect a complex reaction mechanism. The slow heating rate values, meanwhile, which do not have the same restraints, give values that agree with those reported by Prime and Seferis⁸ of ~ 100 kJ/mol obtained from isothermal TG experiments in air.

Isothermal Experiments

In view of the complex nature of the isoconversional plots noted above in which both heating rate and conversion-dependent E values are observed, it was decided to correlate the above data with those derived from isothermal heating experiments.

The weight loss from PEEK during isothermal heating in nitrogen was measured for a range of different temperatures between 397 and 528°C, and some of these data are shown in Figure 9, while Figure 10 shows a few of the rates of weight loss as a function of fractional weight loss (α). The rate of weight loss curves (Fig. 10) are characterized by similarly shaped curves which pass through a maximum value between $\alpha = 0.06$ and $\alpha = 0.10$ before decreasing. For the purpose of determining activation energies, the maximum reaction rate has been used in a variety of studies.^{20–23} This method represents a simple approach to the determination of E from the slope of the plot of $\ln(d\alpha/dt)$ maximum against the reciprocal of the isothermal temperature. Applying this technique to our isothermal data obtained in nitrogen gave a

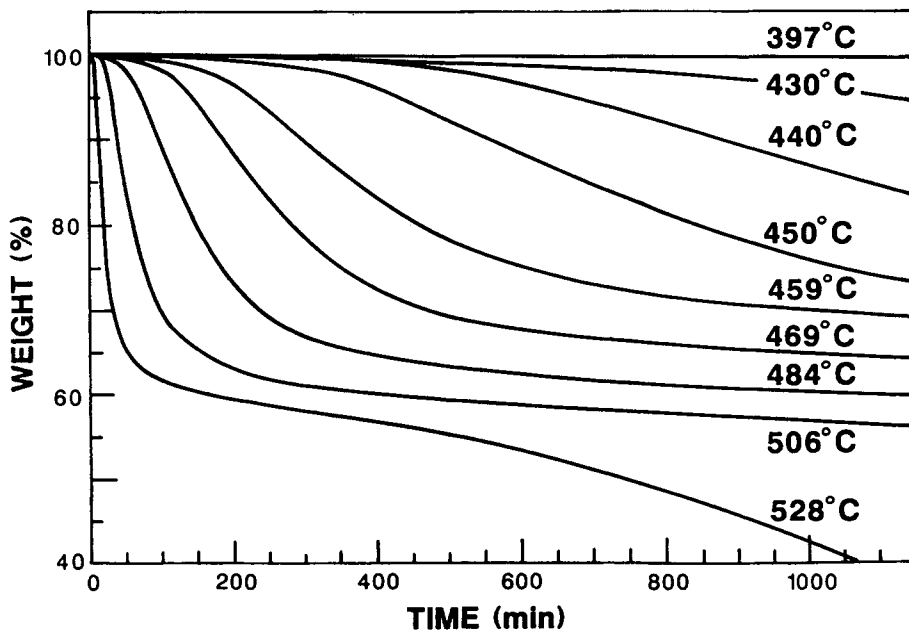


Fig. 9. Weight loss curves of PEEK degraded in nitrogen by isothermal heating at various temperatures.

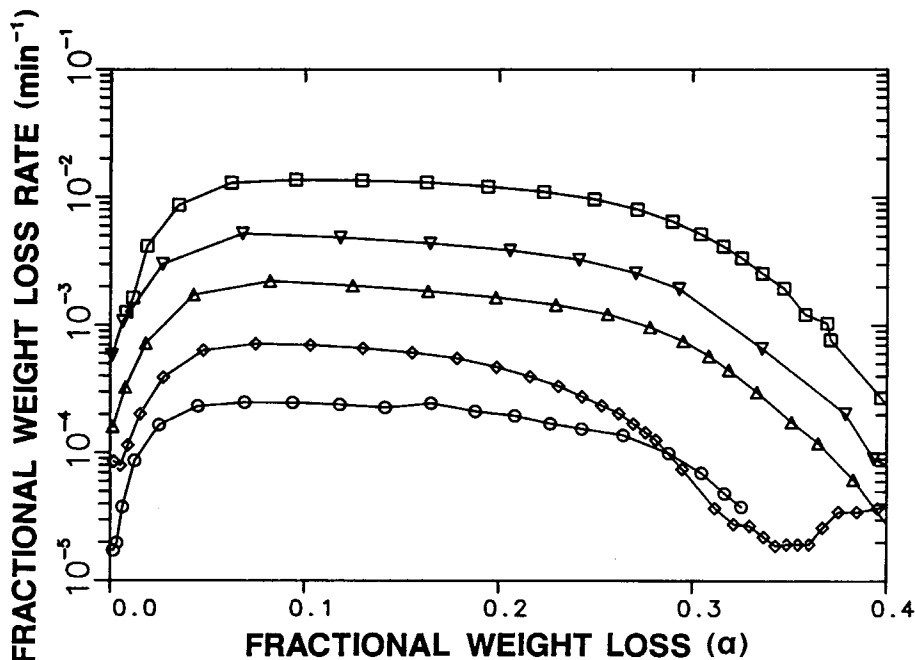


Fig. 10. Plots of rate of weight loss as a fraction of weight loss for PEEK degraded isothermally in nitrogen at temperatures ($^{\circ}\text{C}$) of: (\circ) 440; (\diamond) 459; (Δ) 484; (∇) 506; (\square) 528.

value of 198.4 kJ/mol for the activation energy and a log A value of 11.1. The use of this approach, however, has been criticized for performing kinetic analysis of reactions where phase-boundary or diffusion-controlled reactions are involved.²⁴ Based upon theoretical calculations by Flynn and Wall,²⁵ random depolymerization reactions should have a maximum rate at $\alpha = 0.25$ while for an unzipping mechanism it would occur at about $\alpha = 0.40$. Because the maximum rate of weight loss in nitrogen occurs at about $\alpha = 0.08$ and the total overall weight loss is only about 40%, this corresponds very closely to 25% of the overall total weight loss. This finding would suggest that the pyrolysis of PEEK in nitrogen is a random chain scission process.

Some of the weight-loss curves from PEEK heated isothermally in air are shown in Figure 11. In all, at least 15 different temperatures were used ranging from 375 to 509 $^{\circ}\text{C}$. In Figure 12, the calculated rates of weight loss are plotted against the fractional weight loss (α). The complex degradation mechanism in air is immediately clear from the complex shapes of these curves. The apparent activation energies were calculated from the rate of maximum weight loss and values of 158.6 and 250.1 kJ/mol were obtained for the first and second maximum rate regions, respectively. However, as we have already pointed out, the significance of these values must be questioned especially in the air environment, where it appears that diffusion-controlled reactions could be playing a significant role.

In view of the apparent complex nature of the thermal degradation of PEEK, especially in an oxidative environment, the determination of kinetic parameters at specific α values should only be used with extreme caution. For that reason we felt that the determination of these values over a range of α

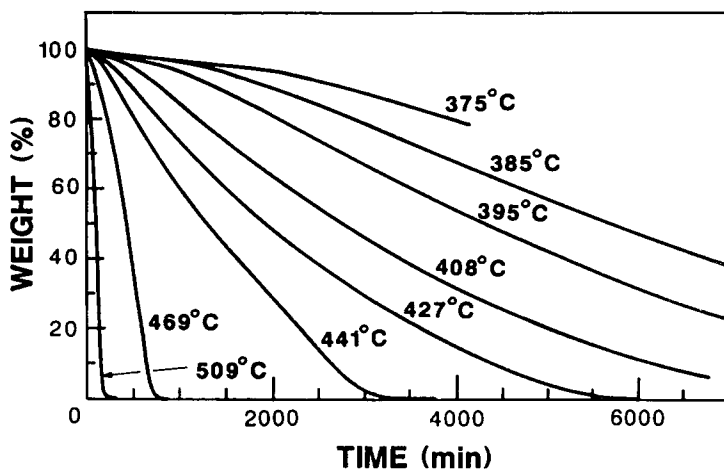


Fig. 11. Weight loss curves of PEEK degraded in air by isothermal heating at various temperatures.

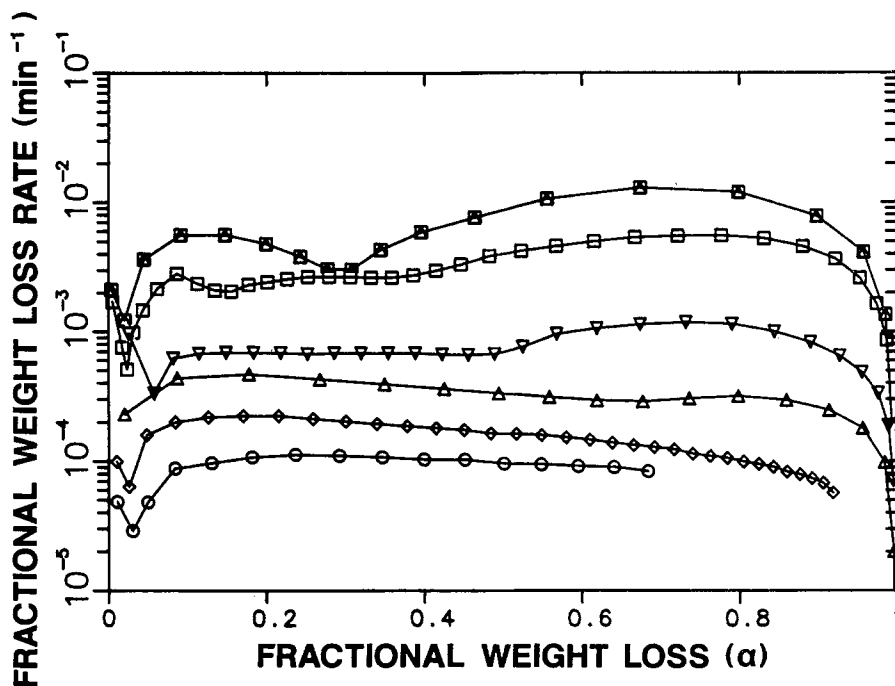


Fig. 12. Rate of weight loss as a function of weight loss for PEEK degraded isothermally in air at temperatures °C of: (○) 385; (◇) 408; (△) 441; (▽) 460; (□) 490; (⊞) 509.

values (as was used in the analysis of the dynamic data) would be more appropriate. To this end, we used the method initially proposed by Flynn,²⁶ which has been successfully used by others.²⁷⁻²⁹ This method involves the integral form of the general kinetic equation for the thermal decomposition of solids under isothermal conditions,³⁰

$$g(\alpha) = kt,$$

and the well-known Arrhenius expression,

$$k = A \exp(-E/RT)$$

By combining these two functional equations, taking logarithms and transposing, the following expression is obtained:

$$\ln t = \ln g(\alpha) - \ln A + E/RT$$

Provided that the preexponential factor A and the order of the reaction n do not change in the temperature and α intervals studied, the activation energies can be obtained for the whole range of α values. The calculated values of E from the isothermal experiments have been plotted in Figures 6 and 8 for the nitrogen and air experiments respectively, enabling comparisons to be made with the nonisothermal data.

In the case of the isothermal experiments conducted in nitrogen (Fig. 6), the agreement in the activation energies between the dynamic and isothermal data is very good. The weighted mean value of 219.7 ± 0.6 kJ/mol shows good agreement with the literature value⁷ of 231.8 kJ/mol and the dynamic value of 235.7 kJ/mol reported here. While the value of the preexponential factor A cannot be determined directly by this method, estimates of $\log A$ can be calculated from the intercept on the $\ln t$ axis by assuming values for $g(\alpha)$ and using the calculated E value in the above equation. These values were found to behave in a similar fashion to the E values and ranged from 11.5 to 12.8 (min^{-1}) with a weighted mean value of 12.2 ± 0.1 (min^{-1}).

Similar analysis of the data from the isothermal experiments in air, meanwhile, gave the E values shown in Figure 8. In this figure direct comparison is possible of the E values derived from the isothermal data with those obtained from the multiple heating rate technique. The E values obtained under isothermal experimental conditions are in good agreement with those values obtained by the dynamic method at slow heating rates and in the α range 0.01-0.4, but not with the values obtained from the fast heating rate experiments. This close agreement is reflected in the similarity of the kinetic parameters as summarized in Table I.

Lifetime Predictions

One of the major applications of TG kinetic parameters relates to their use in predicting the useable temperature regimes and estimated lifetimes of samples fabricated from a material. However, when this approach is taken, it should not be forgotten that weight loss alone is no criterion of stability. Many systems can undergo irreversible loss in physical properties while

TABLE I
Summary of the Kinetic Parameters and Lifetime Estimates

Experimental conditions	Environment	E (kJ/mol)	$\log A$ (min^{-1})	Lifetime at 400°C (h)	10-year lifetime max temp (°C)
Dynamic					
Kissinger peak max	N ₂	223.5	—	—	—
Isoconversional					
Mean, ^a $\alpha = 0.02-0.3$	N ₂	235.7	15.4	—	—
$\alpha = 0.05$	N ₂	236.6	15.7	183	314
Isothermal					
Maximum rate	N ₂	198.4	11.1	—	—
Mean, ^a $\alpha = 0.02-0.3$	N ₂	219.7	12.2	—	—
$\alpha = 0.05$	N ₂	220.5	12.1	98	301
Dynamic					
Fast rate					
Kissinger peak max, 1st stage	Air	202.7	—	—	—
2nd stage	Air	159.3	—	—	—
Mean, ^a $\alpha = 0.1-0.99$	Air	176.0	12.0	—	—
$\alpha = 0.05$	Air	198.6	13.3	84	290
Slow rate					
Kissinger peak max, 1st stage	Air	93.3	—	—	—
2nd stage	Air	104.0	—	—	—
Mean, ^a $\alpha = 0.01-0.99$	Air	116.9	8.5	—	—
$\alpha = 0.05$	Air	115.9	7.8	5.4	185
Isothermal					
Maximum rate, 1st stage	Air	158.6	8.3	—	—
2nd stage	Air	250.1	14.9	—	—
Mean, ^a $\alpha = 0.01-0.99$	Air	259.5	8.2	—	—
$\alpha = 0.05$	Air	132.6	6.13	12.5	217

^a Weighted mean value.

minimal weight loss occurs. Thus, before the weight-loss kinetic technique is used for lifetime predictions, correlation of test results with actual lifetime information is required to establish the viability of the method and the nature of any correlations should they exist.

Once the viability of the weight-loss kinetic approach has been established, it offers a simple and convenient approach for quality control laboratories to use as an accelerated aging procedure to predict product lifetime. Essentially the procedure takes the weight-loss kinetics at elevated temperatures and extrapolates back to the service conditions for which the lifetime prediction is required. This procedure is so commonly employed that several thermal analytical instruments and several computer software packages have been developed solely for this purpose. Using the kinetic data derived in this study, we have constructed "lifetime" estimates for PEEK generated from the $\alpha = 0.05$ data, and the results are presented in Figure 13. These results allow 1-, 2-, 5-, or even 10-year lifetime temperature maximums to be predicted, and these values have been used to demonstrate the excellent thermal stability of PEEK resins.⁷ Using this approach on our kinetic data yields 10-year lifetime temperature maxima of 314 and 301°C for PEEK heating in an inert nitrogen

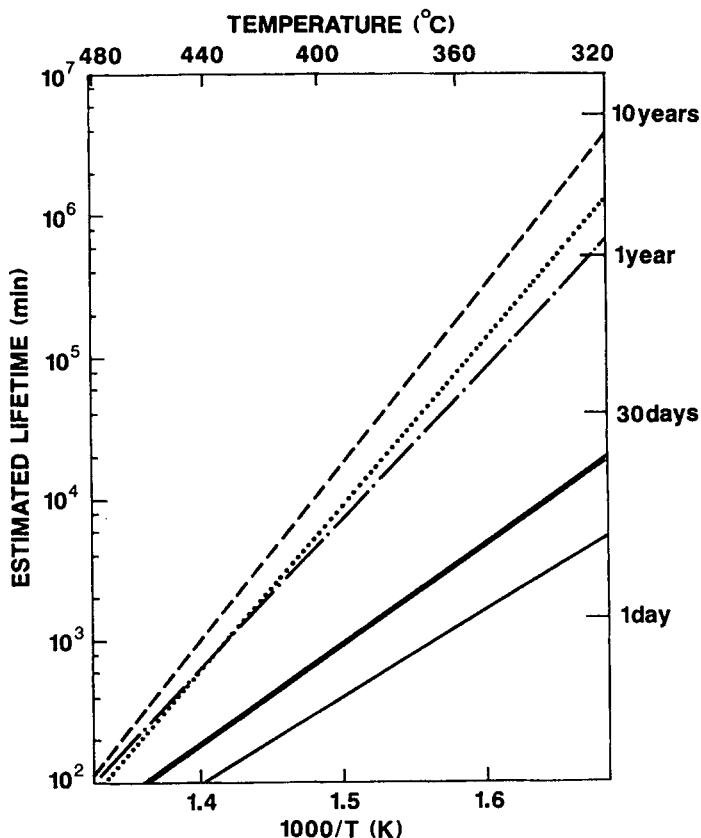


Fig. 13. Estimated lifetime prediction curves based on $\alpha = 0.05$ values: (---) nonisothermal data in nitrogen; (- · - ·) nonisothermal data in air at fast heating rates; (—) nonisothermal data in air at slow heating rates; (· · ·) isothermal data in nitrogen; (—) isothermal data in air.

atmosphere from the dynamic and isothermal data, respectively. These values agree very well with those reported⁷ and indeed confirm the excellent thermal stability of PEEK in a nitrogen environment. When PEEK is heated in air, however, the situation is different. Our data indicate the 10-year lifetime temperature maximum of PEEK in air to be either 185 or 217°C, depending upon whether the dynamic data at slow heating rates is employed or the isothermal data. The thermal stability of PEEK in air is certainly much less than in nitrogen and nowhere near that reported previously,⁷ which estimated a 10-year lifetime temperature maximum of 315°C in air. Clearly the problem lies with the use of the high heating rate data in the dynamic experiments since our data also suggested a high 10-year temperature of 290°C from fast heating rate experiments.

CONCLUSIONS

Thermogravimetry is capable of providing some very useful information on the thermal stability of PEEK provided that care is taken in the interpretation. The TG kinetic data for PEEK heated in nitrogen indicate that the material has excellent thermal stability. The degradation appears to be a

random chain scission process with rates comparable to those previously reported. The thermal stability of the material is, however, greatly reduced in an oxidative environment. The decomposition mechanism is also more complex in air due to the role of oxygen in the degradation process. The experiments in air also identified the need for caution in the use of computers and dedicated software routines for the analysis of data and estimation of lifetimes in thermal stability studies.

References

1. J. H. Flynn, in *Aspects of Degradation and Stabilization of Polymers*, H. H. G. Jellinek, Ed., Elsevier, Amsterdam, 1978, Chap. 12, p. 573.
2. J. H. Flynn, *Polym. Eng. Sci.*, **20**(10), 675 (1980).
3. H. A. Schneider, in *Degradation and Stabilization of Polymers*, H. H. G. Jellinek, Ed., Elsevier, Amsterdam, 1983, Chap. 10, p. 506.
4. J. R. MacCallum and J. Tanner, *Eur. Polym. J.*, **6**, 907 (1970).
5. B. Dickens and J. H. Flynn, *ACS Advances in Chemistry Series*, C. D. Craver, Ed., Am. Chem. Soc., Washington, DC, 1983, Vol. 203, p. 209.
6. D. J. Blundell and B. N. Osborn, *Polymer*, **24**, 953 (1983).
7. W. E. Modderman, W. C. Bowling, E. E. Tibbitts, and R. B. Whitaker, *Polym. Eng. Sci.*, **26**(21), 1469 (1986).
8. R. B. Prime and J. C. Seferis, *J. Polym. Sci. Polym. Lett. Ed.*, **24**, 641 (1986).
9. J. N. Hay, D. J. Kemmish, J. I. Langford, and A. I. Rae, *Polym. Commun.*, **25**, 175 (1984).
10. K. Krishnan and K. N. Ninan, *Thermochim. Acta*, **90**, 229 (1985).
11. J. H. Flynn, *Thermochim. Acta*, **37**, 225 (1980).
12. J. D. Cooney, M. Day, and D. M. Wiles, *J. Appl. Polym. Sci.*, **28**, 2887 (1983).
13. H. E. Kissinger, *Anal. Chem.*, **21**, 1702 (1957).
14. G. Varhegyi, *Thermochim. Acta*, **110**, 95 (1987).
15. J. D. Cooney, M. Day, and D. M. Wiles, *J. Appl. Polym. Sci.*, **29**, 911 (1984).
16. J. H. Flynn, *J. Therm. Anal.*, **27**, 95 (1983).
17. T. Ozawa, *Bull. Chem. Soc. Jpn.*, **38**, 1881 (1965).
18. J. H. Flynn and L. A. Wall, *Polym. Lett.*, **4**, 323 (1966).
19. C. D. Doyle, *J. Appl. Polym. Sci.*, **5**, 285 (1961).
20. S. Straus and L. A. Wall, *J. Res. Natl. Bur. Stds.*, **60**, 39 (1958).
21. L. A. Wall and R. E. Florin, *J. Res. Natl. Bur. Stds.*, **60**, 451 (1958).
22. S. R. Dharwadkar, A. B. Phadnis, M. S. Chandrasekharaiah, and M. D. Karkhanavala, *J. Therm. Anal.*, **18**, 185 (1980).
23. S. L. Madorsky, *Thermal Degradation of Organic Polymers*, Wiley-Interscience, New York, 1964.
24. J. M. Criado, *J. Therm. Anal.*, **21**, 155 (1981).
25. J. H. Flynn and L. A. Wall, *J. Res. Natl. Bur. Stds.*, **70A**(6), 487 (1966).
26. J. H. Flynn, in *Laboratory for Macromolecular Chemistry*, E. McCuffrey, Ed., McGraw-Hill, New York, 1970, p. 255.
27. K. Krishnan, K. N. Ninan, and P. M. Madhusudanan, *Thermochim. Acta*, **79**, 279 (1984).
28. K. Krishnan, K. N. Ninan, and P. M. Madhusudanan, *Thermochim. Acta*, **90**, 229 (1985).
29. S. Basan and O. Guven, *Thermochim. Acta*, **106**, 169 (1986).
30. J. Sestak, *Thermochim. Acta*, **3**, 1 (1971).

Received February 16, 1988

Accepted March 17, 1988