

Comparative Study of Various Methods for Thermal Degradation of Poly[3-Dimethyl(methacryloyloxyethyl) Ammonium Propanesulfonate]

WEN-FU LEE, *Department of Chemical Engineering and
Technology, Tatung Institute of Technology, Taipei, Taiwan, 10451,
Republic of China*

Synopsis

The comparative study of thermal degradation for poly[3-dimethyl(methacryloyloxyethyl)ammonium propanesulfonate] [poly(DMAPS)] was studied by various methods under different conditions. The reaction order, the activation energy, and the preexponential factor were evaluated from thermal gravimetric curves. The activation energy and the preexponential factor increase with increasing heating rate in a nitrogen atmosphere and decrease with increasing heating rate in air. The activation energy is higher in an air atmosphere at lower heating rates (5, 10, 20°C/min), for any of the methods used.

INTRODUCTION

Thermogravimetric analysis (TGA) is widely used as a method to investigate the thermal degradation of polymers and to determine the kinetic parameters such as activation energy, preexponential factor, and reaction order. TGA methods are classified into two groups: integral and differential methods. The detailed description of those methods are not given here since it has been covered in detail by others.¹⁻⁷

In a previous article,⁸ we investigated the effect of polymer sample weight on the degradation rate, temperature interval, and weight loss. The aim of the present article is to study the thermal degradation of a polysulfobetaine made by various methods at different conditions such as different heating rates and environments.

METHODS FOR DETERMINATION OF KINETIC PARAMETERS

The rate of weight loss, dC/dt , in the process of the thermal degradation is generally expressed by

$$dC/dt = kf(C) \quad (1)$$

The weight loss C is defined by

$$C = 1 - W/W_0 \quad (2)$$

where W_0 and W represent initial weight and weight at a particular time, respectively. The rate constant k is expressed by the Arrhenius equation

$$k = A \exp(-E/RT) \quad (3)$$

where A , E , R , and T represent the preexponential factor, the activation energy, the ideal gas constant, and the absolute temperature, respectively. $f(C)$ is a function of weight loss, is independent of temperature, and is expressed in homogeneous kinetics as

$$f(C) = (1 - C)^n \quad (4)$$

where n is the apparent order of reaction.

Substitution of eqs. (3) and (4) into eq. (1) gives

$$dC/dt = A \exp(-E/RT)(1 - C)^n \quad (5)$$

In the thermogravimetric analysis, the heating rate, $\beta = dT/dt$, is kept constant. Thus,

$$dC/dt \cdot \beta = A \exp(-E/RT)(1 - C)^n dT/dt \quad (6)$$

Cancelling dt and rearrangement of eq. (6) give

$$dC/(1 - C)^n = (A/\beta) \exp(-E/RT) dT \quad (7)$$

or

$$dC/dT = (A/\beta) \exp(-E/RT)(1 - C)^n \quad (8)$$

Introducing the initial condition given by $C = 0$ at $T = T_0$ (room temperature) and integrating, eq. (7) becomes

$$\int_0^C dC/(1 - C)^n = A/\beta \int_{T_0}^T \exp(-E/RT) dT \quad (9)$$

Integral Methods

The relationship between C and T can be obtained from the TG curve. The integral methods use this relation to integrate eq. (9) for determining the values of A , E , and n . There have been various methods to approximate the integration of the exponential integral. Representative methods are summarized in Table I.

Differential Methods

The differential methods are used to determine the values of A , E , and n satisfying eq. (8). This is done by using the relationship between dC/dT and T , which is given by the differentiation of the TG curves. Friedman's method⁷

TABLE I
 Representative Integral Methods

Authors	Equations
van Krevelen et al. ¹	$\ln \ln(1 - C) = \ln \left[\frac{A}{\beta} \left(\frac{0.368}{T_m} \right)^{E/RT_m} \frac{1}{E/RT_m + 1} \right] + \left(\frac{E}{RT_m} + 1 \right) \ln T$ (n ≠ 1) (10)
	where T_m is the temperature at maximum weight loss rate, dC/dt
Coats and Redfern ²	$\log \frac{C}{T^2} = \log \frac{AR}{\beta E} \left(1 - \frac{2RT}{E} \right) - \frac{E}{2.3RT}$ (n = 0) (11)
Reich and Levi ³	$\ln \ln(1 - C) = -\frac{E}{RT} + \ln \left(\frac{T}{\beta} \right)$ (n = 1) (12)
	where T is the temperature intervals for reading of C
Reich ⁴	$E = \frac{4.6 \log(\beta_2/\beta_1)(T_1/T_2)^2}{(1/T_1 - 1/T_2)}$ (13)
Horowitz and Metzger ⁵	$\ln \ln(1 - C) = \ln \frac{AE}{\beta R} - 5.33 - \frac{1.052}{T_s} + \frac{1.052E\theta}{RT_s^2}$ (n ≠ 1) (14)
	where T_s is the temperature at maximum weight loss rate and $\theta = T - T_s$
	$\ln \ln(1 - C) = \frac{E\theta}{RT_s^2}$ (n = 1) (15)
	where T_s is the temperature at $1 - C = 1/e$, and $\theta = T - T_s$
Ozawa ⁶	$-\log \beta_1 - 0.4567 \frac{E}{RT_1} = -\log \beta_2 - 0.4567 \frac{E}{RT_2}$ (16)

is selected to approximate the following equation:

$$\ln[\beta(dC/dT)] = \ln[Af(C)] - E/RT \quad (17)$$

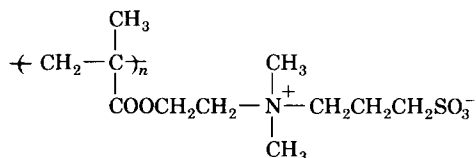
where $f(C) = (1 - C)^n$.

EXPERIMENTAL

Preparation of DMAPS and poly(DMAPS)

The monomer, 3-dimethyl(methacryloyloxyethyl)ammonium propane sulfonate (DMAPS), and polymer [poly(DMAPS)] were prepared as described previously.^{8,9} The monomer was characterized by elemental analysis techniques, IR and NMR, as described before and was quite hygroscopic [mp 280°C (decomposition)].⁸ The polymer was brittle and white, and its intrinsic

viscosity was 3.46 dL/g in a 0.25M NaClO₄ solution.⁹ Its structure is



Thermal Analysis

Thermal analysis was measured by a Perkin-Elmer thermal mechanical analyzer, Model TGS-II, associated with derivative equipment. Finely powdered 5-mg samples were heated at heating rates 5, 10, 20, and 40°C/min in nitrogen and air atmospheres. The chart speed, which was kept at 5 mm/min, recorded the change in both the temperature and the weight loss of sample weight.

RESULTS AND DISCUSSION

In our previous article,⁸ we investigated the kinetic parameters for the thermal degradation of poly(DMAPS), and found that $E = 103.3$ kJ/mol, $\log A = 8.88$ min⁻¹, and $E = 154.8$ kJ/mol, $\log A = 12.38$ min⁻¹ in nitrogen and in air atmospheres, respectively. We present various methods with which one can determine the kinetic parameters for the thermal degradation of polymers by using only one heating rate.

The TG curves of poly(DMAPS) showed two stages and three stages of thermal degradation in nitrogen and in air, respectively, but in the present article we compare first stage kinetic parameters determined by various methods for the poly(DMAPS) with different heating rates and environments.

Various methods summarized in Table I were applied individually to the experimental results. A representative result is shown in Figure 1 where the TG curves for the thermal degradation of the 5-mg poly(DMAPS) sample are shown with several heating rates.

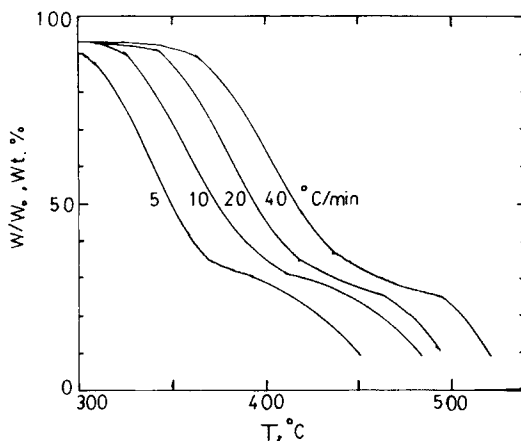


Fig. 1. TG curves of poly(DMAPS) for various heating rates in a nitrogen atmosphere.

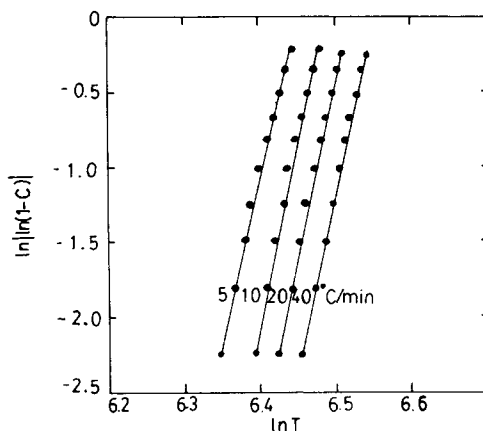


Fig. 2. Application of van Krevelen's method¹ to experimental data in a nitrogen atmosphere.

Figures 2 and 3 show the relationship given by eq. (11) of van Krevelen et al.¹ Assuming the reaction order to be unity, linear relations were obtained, and the activation energies were calculated from the slope with different heating rates in nitrogen and in air atmospheres, respectively. The results are listed in Table II.

Figures 4 and 5 show the relationship proposed by Coats and Redfern.² In this method we assume that all reactions are zero-order reactions at low conversion in each heating rate and different environments. From the two figures, we obtain a good linear relationship for each heating rate and the kinetic parameters obtained are shown in Table III.

Figures 6 and 7 show the relationship suggested by Reich and Levi,³ where the weight loss was taken at a fixed temperature interval ($\Delta T = 5^\circ\text{C}$), the reaction orders are assumed to be unity, and the results are shown in Table IV.

Table V shows the results determined by the Reich's⁴ method with heating rates at 10 and $40^\circ\text{C}/\text{min}$, in nitrogen and in air atmospheres, respectively.

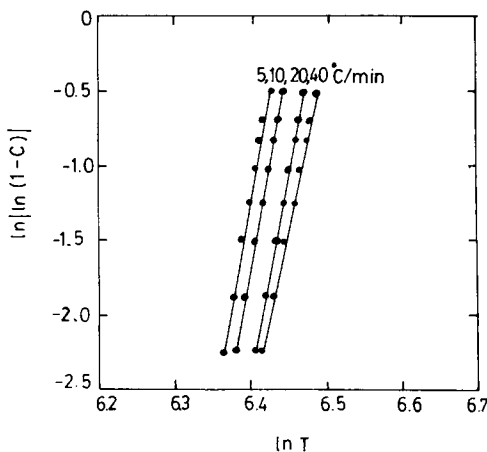


Fig. 3. Application of van Krevelen's method¹ to experimental data in an air atmosphere.

TABLE II
Comparison of Kinetic Parameters Obtained by van Krevelen's Method¹
under Different Conditions ($W_0 = 5$ mg)

Heating rate (°C/min)	N ₂		Air	
	E (kJ/mol)	$\log A$	E (kJ/mol)	$\log A$
5	112.2	8.5	146.4	11.56
10	122.4	9.32	141.8	11.16
20	121.3	9.35	137.5	10.84
40	127.4	9.64	121.0	9.53

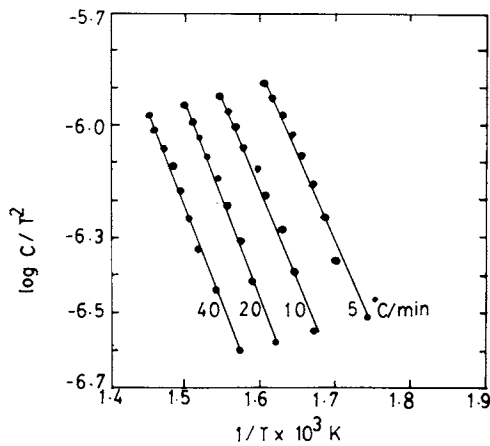


Fig. 4. Application of the Coats and Redfern method² to experimental data in a nitrogen atmosphere.

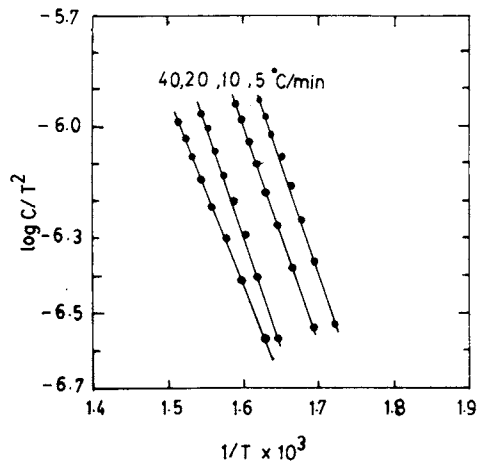


Fig. 5. Application of the Coats and Redfern method² to experimental data in an air atmosphere.

TABLE III
Comparison of Kinetic Parameters Obtained by the Coats and Redfern Method²
under Different Conditions

Heating rate (°C/min)	N ₂		Air	
	E (kJ/mol)	log A	E (kJ/mol)	log A
5	89.3	6.42	114.7	8.69
10	97.1	7.08	112.1	8.56
20	99.3	7.34	110.0	8.38
40	104.4	7.76	96.6	7.39

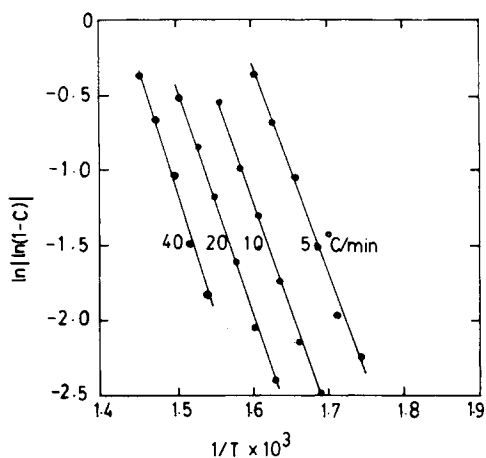


Fig. 6. Application of the Reich and Levi method³ to experimental data in a nitrogen atmosphere.

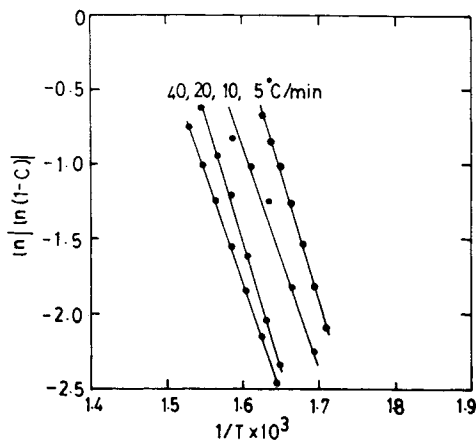


Fig. 7. Application of the Reich and Levi method³ to experimental data in an air atmosphere.

TABLE IV
Comparison of Kinetic Parameters Obtained by Reich and Levi's Method³
under Different Conditions

Heating rate (°C/min)	N ₂		Air	
	E (kJ/mol)	log A	E (kJ/mol)	log A
5	116.8	9.35	143.0	11.59
10	123.0	9.78	135.7	10.99
20	131.3	10.44	105.3	8.40
40	137.5	10.9	123.1	10.13

TABLE V
Activation Energy Obtained from Reich's method⁴
at the Different Conditions

Heating rate (°C/min)	E (kJ/mol)	
	N ₂	Air
10 and 40	106.2	121.9

With this method, preexponential factors cannot be calculated. Figure 8 shows the relationship for the case of $n = 1$ between the weight loss and the heating rate at a fixed temperature in the air atmosphere. Good linear relationships were obtained; it was shown that the reaction is first order in experimental conditions.

Horowitz and Metzger,⁵ represented by eqs. (14) and (15), obtained both the reaction order and the activation energy from experimental data. Assuming the reaction order to be unity, the relationship shown in Figure 9 is linear, and the results using different heating rates and different environments are shown in Table VI. The method developed by Ozawa⁶ permits the determination of activation energy through the TG curves by changing the heating rate. The results obtained by Ozawa's method were shown in the previous article.⁸

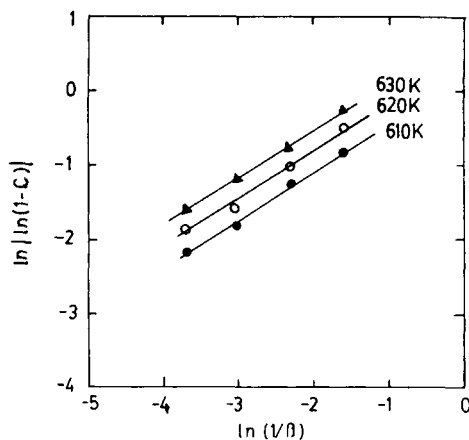


Fig. 8. $\ln|\ln(1 - C)|$ vs. $\ln(1/\beta)$ for Reich's method.⁴

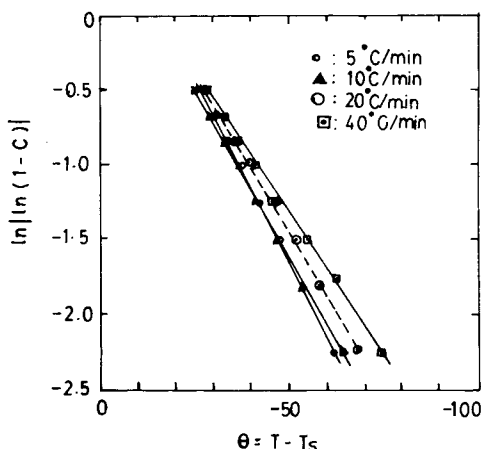


Fig. 9. Application of the Horowitz and Metzger method⁵ to experimental data ($^{\circ}\text{C}/\text{min}$) in an air atmosphere: (●) 5; (▲) 10; (○) 20; (□) 40.

Friedman⁷ used eq. (17) to calculate the activation energies and the intercepts from the relation both $\ln(\beta dC/dT)$ and $1/T$. Further, the reaction order and the preexponential factor ($\ln A$) can be obtained from the relation both intercept and $\ln(1 - C)$. The horizontal lines shown by Figure 10 suggests a zero-order reaction and the intercepts give the activation energies.

Figure 11 shows the relationship between weight loss and temperature given by a computer approximation method directly from eq. (8). In this method, we first assess the reaction order, the activation energy, and the preexponential factor; then we assign a weight loss at a given temperature. From this result, we fit the experimental data until the average error approaches a minimum value. Finally we find that the activation energy is 108.87 (kJ/mol), $\log A$ is 8.176, and n is 0.999, approaching 1, with a heating rate of $10^{\circ}\text{C}/\text{min}$ in nitrogen atmosphere.

From Tables II–IV and VI, we can conclude that the activation energy of thermal degradation for poly(DMAPS) is increased with increasing heating rate in nitrogen atmosphere and decreases with increasing heating rate in air atmosphere. However, the activation energy is larger in air atmosphere than in nitrogen atmosphere with heating rates of 5, 10, and $20^{\circ}\text{C}/\text{min}$, but the opposite result is obtained at a heating rate of $40^{\circ}\text{C}/\text{min}$. The preexponential

TABLE VI
Comparison of Kinetic Parameters Obtained Horowitz and Metzger's Method⁵
under Different Conditions

Heating rate ($^{\circ}\text{C}/\text{min}$)	N_2		Air	
	E (kJ/mol)	$\log A$	E (kJ/mol)	$\log A$
5	135.3	10.33	167.8	13.03
10	149.1	11.33	166.0	12.68
20	150.2	11.29	159.8	12.45
40	150.7	11.08	144.1	11.22

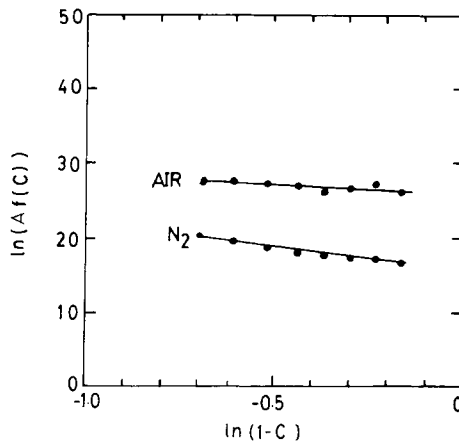


Fig. 10. Relationship obtained by Friedman's method⁷ for estimating n and A .

factor has the same result as the activation energy for the different heating rates and in the different environments.

The above results are summarized in Tables VII–X for the heating rates 5, 10, 20, and 40°C/min, respectively. From Table VII, the activation energies and preexponential factors obtained from various methods are lower in the nitrogen atmosphere than in the air atmosphere. From Table VII, the activation energy obtained by Horowitz's method is slightly higher in the two environments. This is because the residual weight, 0.368 mg, under the selected value of T_s is located on the inflection range of TG curve, and this value is out of the experimental range. Thus, it resulted in a 13% error. In the method developed by Coats and Redfern² the order is assumed to be zero at low conversions. Application of experimental data to this method gives the

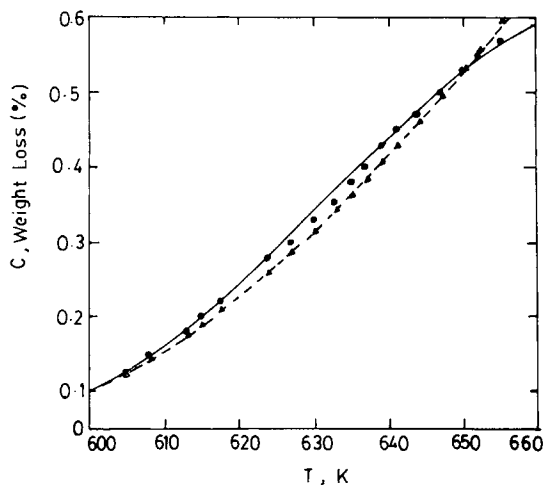


Fig. 11. The comparison of the experimental curve (—) and the computer-fitting method curve (---) for the degradation of the poly(DMAPS) in a nitrogen atmosphere.

TABLE VII
Comparison of Kinetic Parameters Obtained by Various Methods
at a Heating Rate of 5°C/min

Methods	N ₂			Air		
	<i>n</i>	<i>E</i> (kJ/mol)	log <i>A</i>	<i>n</i>	<i>E</i> (kJ/mol)	log <i>A</i>
van Krevelen ¹	1.0	112.2	8.5	1.0	146.4	11.56
Coats and Redfern ²	0 (assumed)	89.3	6.42	0 (assumed)	114.7	8.69
Horowitz and Metzger ⁵	1.0	135.3	10.33	1.0	167.8	13.03
Reich and Levi ³	1.0	116.8	9.35	1.0	143.0	11.59
Ozawa ⁶	1.0	103.3	8.91	1.0	154.8	12.49

activation energies of 89.3 and 114.7 kJ/mol in nitrogen and in air atmospheres, respectively. Excluding these extraordinarily low or high values, the activation energy with the reaction order being determined to be unity was found to lie in the range of 110.8 ± 6.8 and 148.1 ± 6.1 kJ/mol in nitrogen and in the air atmosphere, respectively.

From Table VIII, the results obtained by using a computer approximation from eq. (8) agree fairly well with those values which obtained by other methods for the degradation of poly(DMAPS) at a heating rate of 10°C/min in the nitrogen atmosphere. As for the activation energy, the value obtained by the method of Horowitz and Metzger⁵ is extremely high. Therefore, the activation energy, except for this high value, with the reaction order being to be unity, was found to lie in the range of 112.8 ± 9.3 kJ/mol in the nitrogen atmosphere at 10°C/min.

TABLE VIII
Comparison of Kinetic Parameters Obtained by Various Methods
at a Heating Rate of 10°C/min

Methods	N ₂			Air		
	<i>n</i>	<i>E</i> (kJ/mol)	log <i>A</i>	<i>n</i>	<i>E</i> (kJ/mol)	log <i>A</i>
van Krevelen ¹	1.0	122.4	9.32	1.0	141.8	11.16
Coats and Redfern ²	0 (assumed)	97.1	7.08	0 (assumed)	112.1	8.56
Horowitz and Metzger ⁵	1.0	149.1	11.33	1.0	166.0	12.68
Reich and Levi ³	1.0	123.0	9.78	1.0	135.7	10.99
Reich ⁴	—	106.2	—	—	121.9	—
Ozawa ⁶	1.0	103.3	8.88	1.0	154.8	12.38
Friedman ⁷	0	107.2	7.89	0	153.3	11.72
Computer approximation	1.0	108.9	8.18	—	—	—

TABLE IX
Comparison of Kinetic Parameters Obtained by Various methods
at a Heating Rate of 20°C/min

Methods	N ₂			Air		
	<i>n</i>	<i>E</i> (kJ/mol)	log <i>A</i>	<i>n</i>	<i>E</i> (kJ/mol)	log <i>A</i>
van Krevelen ¹	1.0	121.3	9.35	1.0	137.5	10.84
Coats and Redfern ²	0 (assumed)	99.3	7.34	0 (assumed)	110.0	8.38
Horowitz and Metzger ⁵	1.0	150.2	11.29	1.0	159.8	12.45
Reich and Levi ³	1.0	131.3	10.44	1.0	105.3	8.40
Ozawa ⁷	1.0	103.3	8.91	1.0	154.8	12.49

TABLE X
Comparison of Kinetic Parameters Obtained by Various Methods
at a Heating Rate of 40°C/min

Methods	N ₂			Air		
	<i>n</i>	<i>E</i> (kJ/mol)	log <i>A</i>	<i>n</i>	<i>E</i> (kJ/mol)	log <i>A</i>
van Krevelen ¹	1.0	127.4	9.64	1.0	121.0	9.53
Coats and Redfern ²	0 (assumed)	104.4	7.76	0 (assumed)	96.6	7.39
Horowitz and Metzger ⁵	1.0	150.7	11.08	1.0	144.1	11.22
Reich and Levi ³	1.0	137.5	10.9	1.0	123.1	10.13
Reich ⁴	—	106.2	—	—	121.9	—
Ozawa ⁶	1.0	103.3	8.91	1.0	154.8	12.49

It is apparent that the activation energies of the first stage thermal degradation for the poly(DMAPS) obtained by various methods have some difference at the same heating rate and at the same environment, but, obviously, whatever method is used, the activation energies of the first-stage degradation for the same sample weights are larger in air atmosphere with different heating rates, except for 40°C/min. As shown in the previous article,⁸ it is known that the higher sample weight decreases the rate of degradation of this polymer. This result was also observed by others.^{2, 10, 11} Kokta et al.¹¹ has also shown that the effect of the heating rate on the activation energy is not apparently regular for polystyrene, but the present result has shown that the higher heating rate increases the activation energy in nitrogen atmosphere and decreases the activation energy in air atmosphere for the same sample weight of poly(DMAPS). The activation energy is larger in air at the lower heating rate, but is larger in nitrogen than in air at the higher heating rate (40°C/min).

References

1. D. W. van Krevelen, C. van Heerden, and F. J. Huntjens, *Fuel*, **30**, 253 (1951).
2. A. W. Coats and J. P. Redfern, *J. Polym. Sci., Polym. Lett. Ed.*, **3**, 917 (1965).
3. L. Reich and D. W. Levi, *Makromol. Chem.*, **66**, 106 (1963).
4. L. Reich, *J. Polym. Sci., Polym. Lett. Ed.*, **3**, 231 (1965).
5. H. H. Horowitz and G. Metzger, *Anal. Chem.*, **35**, 1464 (1963).
6. T. Ozawa, *Bull. Chem. Soc. Jpn.*, **38**, 1881 (1965).
7. H. L. Friedman, *J. Polym. Sci., Part C*, **6**, 183 (1963).
8. D. J. Liaw and W. F. Lee, *J. Appl. Polym. Sci.*, **30**, 4697 (1985).
9. D. J. Liaw and W. F. Lee, *J. Appl. Polym. Sci.*, **34**, 999 (1987).
10. A. E. I. Newkirk, *Anal. Chem.*, **32**, 1568 (1960).
11. B. V. Kokta, J. L. Valade, and W. N. Martin, *J. Appl. Polym. Sci.*, **17**, 1 (1973).

Received February 22, 1988

Accepted August 10, 1988