

Thermal Decomposition Kinetics of Thermotropic Poly(oxybenzoate-co-trimethylene terephthalate)

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ABSTRACT: A new kind of thermotropic liquid crystalline, poly(oxybenzoate-co-trimethylene terephthalate), was prepared from *p*-hydroxybenzoic acid (B) and poly(trimethylene terephthalate) (PTT or T) by melting polycondensation. The monomer ratio of B to T is 60:40. The dynamic thermogravimetric kinetics of the copolymer B/T (60:40) and PTT in nitrogen were analyzed by four single heating rate techniques and two multiple heating rate techniques. The effects of the heating rate and the calculating technique on the thermostable and degradation kinetic parameters of the B/T copolymer and PTT are systematically discussed. The four single heating rate techniques used in this work include Friedman, Freeman-Carroll, Chang, and the second Kissinger techniques, whereas the two multiple heating rate techniques are the first Kissinger and Flynn-Wall techniques. Additionally, the isothermal thermogravimetric kinetics of B/T (60:40) in nitrogen were investigated by the Flynn technique. The activation energy, the order, and the frequency factor of the degradation reaction for B/T (60:40) copolymer are determined to be 185 kJ/mol, 1.8, and $7.14 \times 10^{13} \text{ min}^{-1}$, respectively. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 78: 2025–2036, 2000

Key words: poly(oxybenzoate-co-trimethylene terephthalate); poly(trimethylene terephthalate); copolyester; thermogravimetry; thermostability; degradation kinetics

INTRODUCTION

Poly(oxybenzoate-co-ethylene terephthalate), B/E copolymer, is a well-known and commercially available liquid crystalline polymer, which has been studied extensively.^{1–5} Poly(trimethylene terephthalate) (PTT) is a semicrystalline, polymeric material currently developed by Shell Chemical Company for fiber and engineering thermoplastic applications.^{6,7} Because PTT has

outstanding resiliency and a lower melt point, poly(oxybenzoate-co-trimethylene terephthalate), B/T copolymer, might have smaller fibrillar or woody trends and more application than B/E copolymer. Hitherto, no attention has been given to B/T copolymer.

Thermal stability of a polymeric material is one of the most important properties for both processing and application. Thermogravimetry (TG) is the most widely used technique to characterize thermal decomposition of polymer materials. In this report, the thermal degradation temperature and the kinetics of B/T copolymer with the monomer mol ratio, B/T (60:40), and PTT were studied by several calculating methods through either nonisothermal or isothermal TG

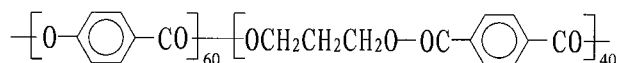
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thermograms. The dependencies of the degradation temperature and kinetic parameters on the heating rate and calculating method are discussed in detail.

EXPERIMENTAL

PTT was synthesized following the transesterification route.⁸ Its intrinsic viscosity ($[\eta]$) was measured at the concentration of 0.5 g/dL in 1,1,2,2-tetrachloroethane/phenol (1:1, w/w) at 25°C. B/T (60:40) was prepared in a similar manner as B/E polymer,¹ except that the reaction temperature of B with T was lower by about 40 K than that of B with E. B/T (60:40) shows multicolor stripes under cross polarized light from ambient to 350°C, and two melt points (213 and 310°C) were observed under nitrogen by differential scanning calorimeter. We cannot measure the intrinsic viscosity ($[\eta]$) of B/T (60:40) because the material obtained only partially dissolves in trifluoroacetic acid, dimethyl sulfoxide, *N,N*-dimethyl acetamide, tetrahydrofuran, and *N*-methyl-2-pyrrolidone. The B/T (60:40) copolymer possesses the following nominal molecular structure:



TG and derivative thermogravimetry (DTG) curves were gained by using a Perkin-Elmer 7 series analyzer under a dynamic nitrogen atmosphere flowing at 40 mL/min, varying heating rate from 2 to 40 K/min, while the sample weights were kept at 1.0 ± 0.1 mg.

Isothermally programmed TG analyses were performed at 312, 318, 333, 338, 350, and 358°C in nitrogen at a flow rate of 40 mL/min with a sample size of 1 mg. The furnace was heated to the selected temperature at a heating rate higher than 150 K/min. As soon as the system reached the selected temperature, the variation of sample weight with time was registered immediately.

Friedman Technique⁵

$$\ln(Z) = \ln(d\alpha/dt) - n \cdot \ln(1 - \alpha) + E_a/(R \cdot T) \quad (1)$$

where α is the weight loss of the polymer undergoing degradation at time t ; R is the gas constant ($8.3136 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$) and T is the absolute

temperature (K); Z , n , and E_a are the frequency factor, the order, and the activation energy of the thermal decomposition reaction, respectively. The plot of $\ln(d\alpha/dt)$ versus $1/T$ should be linear with $-E_a/R$ as the slope. Additionally, the $E_a/(n \cdot R)$ value could be determined from the slope of the linear plot of $\ln(1 - \alpha)$ versus $1/T$.

Freeman-Carroll Technique⁵

$$\Delta \ln(d\alpha/dt) / \Delta \ln(1 - \alpha) = n - (E_a/R) \times \Delta(1/T) / \Delta \ln(1 - \alpha) \quad (2)$$

$\Delta \ln(d\alpha/dt)$ and $\Delta \ln(1 - \alpha)$ values are taken at regular intervals of $1/T$, in this case $\Delta(1/T) = 0.00002 \text{ K}^{-1}$. By plotting $\Delta \ln(d\alpha/dt) / \Delta \ln(1 - \alpha)$ against $\Delta(1/T) / \Delta \ln(1 - \alpha)$, a straight line was obtained, and the slope and intercept are equal to $-E_a/R$ and n , respectively. In addition, the Z value can be evaluated using eq. (1).

Chang Technique⁵

Equation (1) can be rewritten in the following form:

$$\ln[(d\alpha/dt)/(1 - \alpha)^n] = \ln(Z) - E_a/(R \cdot T) \quad (3)$$

A plot of $\ln[(d\alpha/dt)/(1 - \alpha)^n]$ against $1/T$ will yield a straight line if the decomposition order n is selected correctly. The slope and intercept of this line will provide the $-E_a/R$ and $\ln(Z)$ values, respectively.

The First Kissinger Technique⁹

$$\ln(q/T_{dm}^2) = \ln[n \cdot (1 - \alpha_m)^{n-1} \cdot Z \cdot R/E_a] - E_a/(R \cdot T_{dm}) \quad (4)$$

where q is the heating rate; T_{dm} and α_m are the absolute temperature and weight loss at the maximum weight-loss rate $(d\alpha/dt)_m$. The slope of $\ln(q/T_{dm}^2)$ versus $1/T_{dm}$ is equal to $-E_a/R$, whereas its intercept (I) is equal to $\ln[n \cdot (1 - \alpha_m)^{n-1} \cdot Z \cdot R/E_a]$. The n value can be estimated from the following equation:

$$n = (1 - \alpha_m) \cdot E_a \cdot [\exp(I)] \times \{\exp[-E_a/(R \cdot T_{dm})]\} / [R \cdot (d\alpha/dt)_m] \quad (5)$$

Then the Z value can be calculated by substituting n into the intercept equation:

$$I = \text{Ln}[n \cdot (1 - \alpha_m)^{n-1} \cdot Z \cdot R/E_a] \quad (6)$$

The Second Kissinger Technique⁹

The n value can be obtained directly from the symmetrical index of a single DTG peak:

$$n = 1.88 \cdot |(d^2\alpha/dt^2)_L|/|(d^2\alpha/dt^2)_R| \quad (7)$$

where indices L and R denote the left and right peak values of the second DTG curves. Then E_a and $\text{Ln}(Z)$ can be calculated from the equation:

$$n \cdot (1 - \alpha_m)^{n-1} = 1 + (n - 1) \times 2 \cdot R \cdot T_m/E_a \quad (n \neq 1) \quad (8)$$

Flynn-Wall Technique⁹

$$\text{Ln}(q) = \text{Ln}(Z \cdot E_a/R) - \text{Ln}[F(\alpha)] - E_a/(R \cdot T) \quad (9)$$

where q is the heating rate, E_a value can be calculated from the plot of $\text{Ln}(q)$ against $1/T$ for a fixed weight loss, since the slope of such a line is equal to $-E_a/R$.

Flynn Technique⁹

The kinetic method of isothermal TG is based on the following Flynn equation:

$$\text{Ln}(t) = \text{Ln}[(1 - 2 \cdot \alpha)/Z] + E_a/(R \cdot T) \quad (10)$$

The natural logarithm of the time t corresponding to a certain weight loss α is linearly depending on the reciprocal of the temperature T . Provided that the order of the decomposition reaction n keeps constant within the temperature and weight-loss intervals under consideration, E_a and $\text{Ln}(Z)$ can be respectively calculated in terms of the slope and intercept of the linear relationship of $\text{Ln}(t)$ versus $1/T$ for various α values.

RESULTS AND DISCUSSION

The TG and DTG curves of B/T (60:40) and PTT in nitrogen at heating rates of 2, 5, 10, 20, 30, and 40 K/min are shown respectively in Figures 1 and 2.

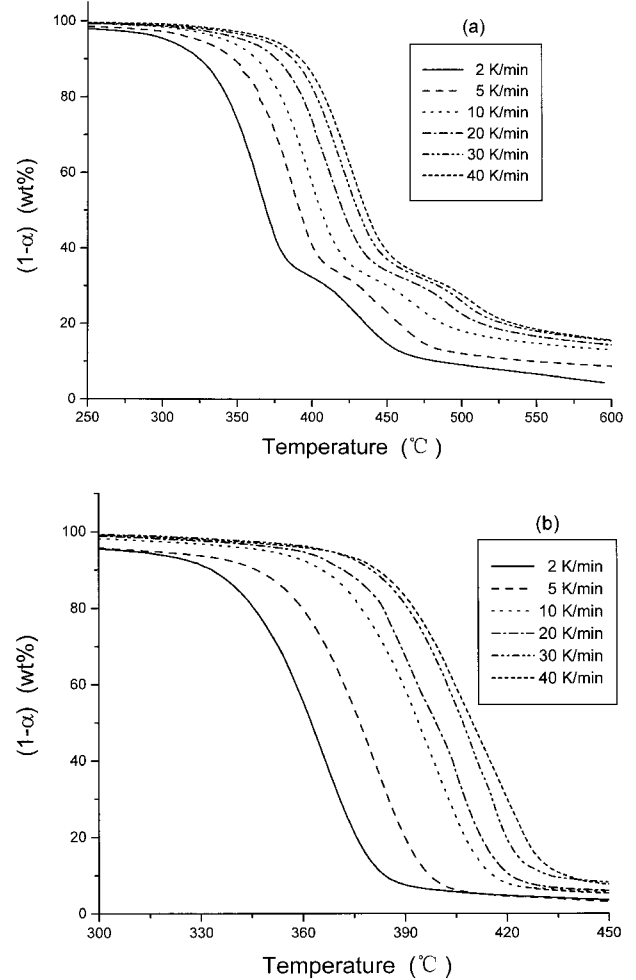


Figure 1 Dynamic TG curves at six heating rates ranging from 2 to 40 K/min in nitrogen: (a) B/T (60:40); (b) PTT.

The DTG curves of B/T (60:40) indicate that two weight-loss stages occur during degradation, whereas the DTG curves of PTT indicate that only one weight-loss stage occurs during degradation. Poly(oxybenzoate-co-ethylene terephthalate) with monomer mol ratio 60:40 shows two weight-loss stages in nitrogen at low heating rates (1 and 2 K/min).⁵ Generally, in the case of random copolymer, stepwise degradation of individual B and T homopolymer segments may merge into a single step decomposition. The maximum decomposition temperature of the random copolymer mediates between the maximum degradation temperatures of the two corresponding homopolymers.⁵ For stepwise degradation of individual B and T segments in block copolymer, however, the maximum degradation temperatures get close with each other. Moreover, the temperature at the

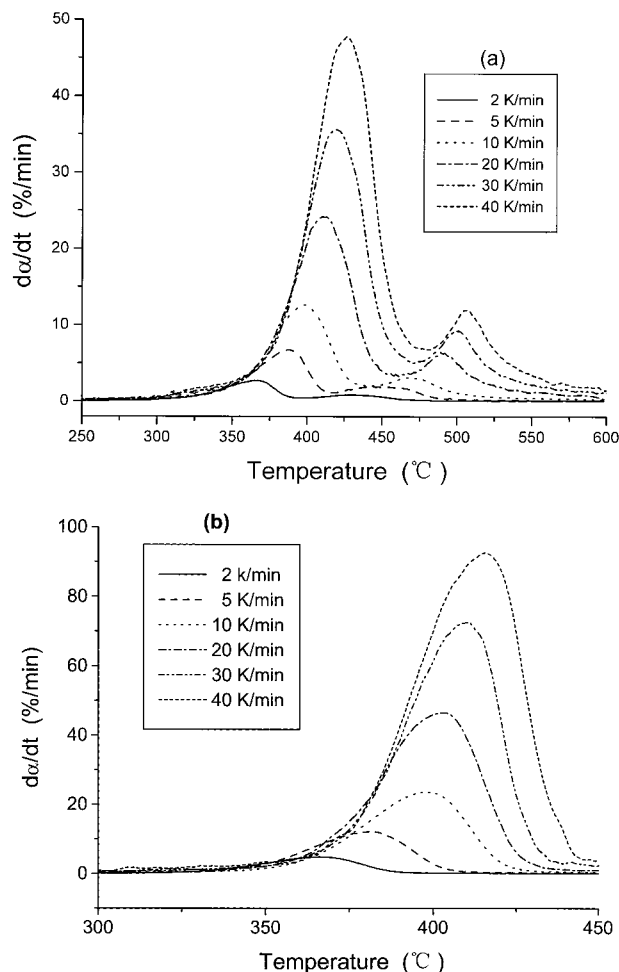


Figure 2 Dynamic DTG curves at six heating rates ranging from 2 to 40 K/min in nitrogen: (a) B/T (60:40); (b) PTT.

maximum weight loss rate of the second degradation stage (T_{dm2}) for B/T (60:40) in nitrogen at 10 K/min (467°C) is much lower than 515 or 530°C which is reported by Garozzo and co-workers¹⁰ for low and high molecular weight polyoxybenzoate (B) in nitrogen at 10 K/min. Therefore it suggests that B/T (60:40) may contain two phases; one comprises more than 40% T unit in mol, whereas the other comprises more than 60% B unit. Phase separation has also been validated by differential scanning calorimeter as aforementioned (two melting peaks). Therefore, the first stage of thermal degradation in nitrogen which appears in the thermograms of the B/T (60:40) might be ascribed to the degradation of both T and B units, whereas the second stage might be mainly attributed to the degradation of the B unit.

Kinetics of Nonisothermal Decomposition Analyzed by Single Heating Rate Techniques

All of the techniques, Friedman, Freeman-Carroll, Chang, and the second Kissinger, can determine the kinetic parameters for the thermal degradation of B/T (60:40) and PTT by using only one heating rate. Figure 3 shows the relationship given by eq. (1) of the Friedman technique. Because the lines of either $\text{Ln}(d\alpha/dt)$ versus $1/T$ or $\text{Ln}(1 - \alpha)$ versus $1/T$ overlapped each other, the Waterfall Graph (in Microcal Origin version 5.0, Microcal Software, Inc., Northampton, MA) was used to obtain a distinct view. Each dataset is displayed as a line data plot, which is offset by a specified amount in both the X and Y direction. For the Friedman technique, the absolute X and Y

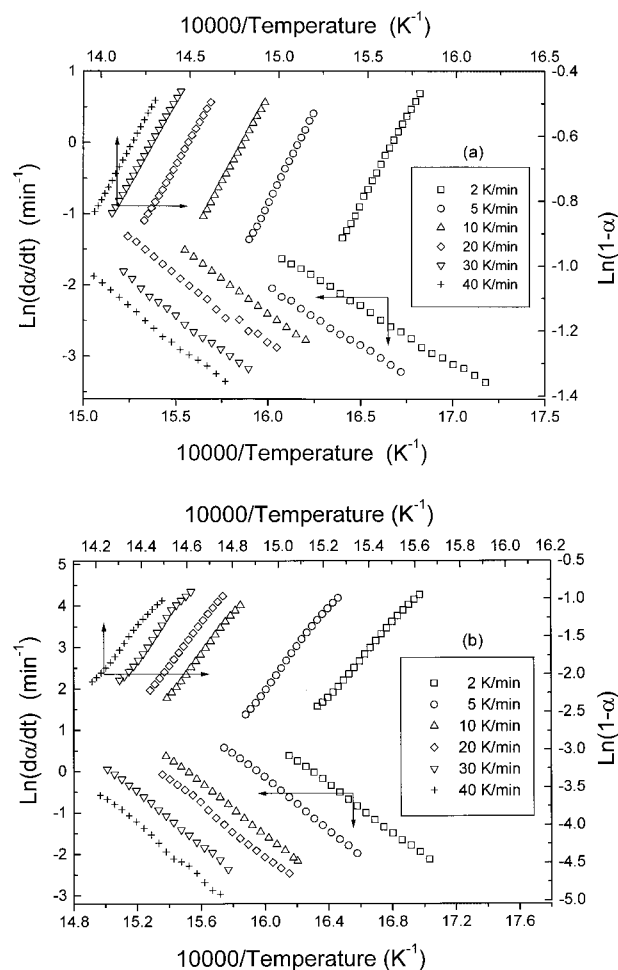


Figure 3 Friedman plots of $\text{Ln}(d\alpha/dt)$ or $\text{Ln}(1 - \alpha)$ vs $1/T$ for the direct calculation of E_a or n value of thermal degradation in nitrogen at six heating rates: (a) B/T(60:40); (b) PTT. [Total X offset is 0 for both (a) and (b); Total Y offset is 50% for both (a) and (b).]

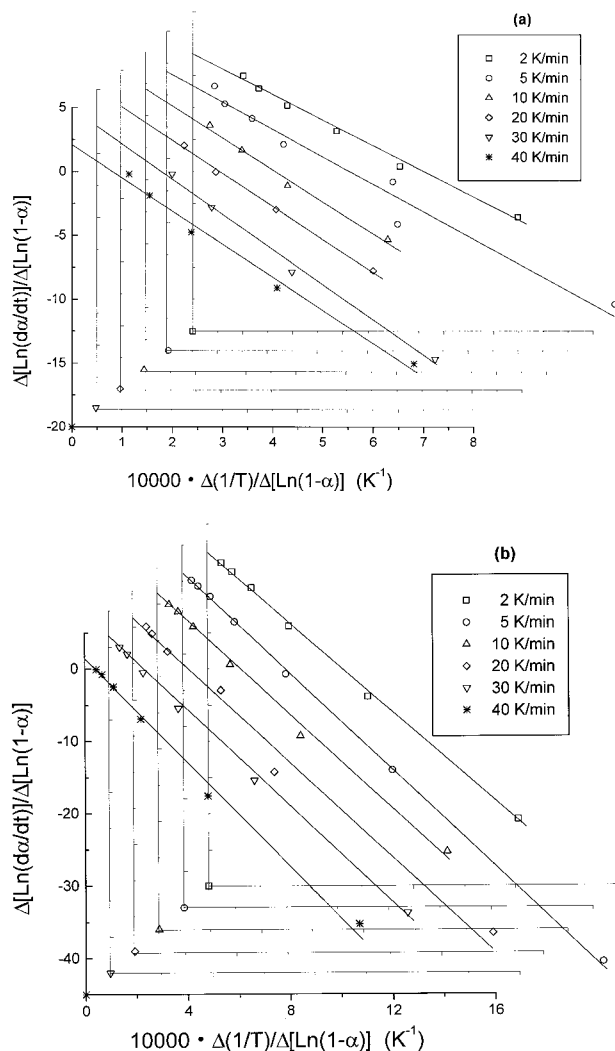


Figure 4 Freeman-Carroll plots of $\Delta[\text{Ln}(d\alpha/dt)]/\Delta[\text{Ln}(1-\alpha)]$ versus $\Delta(1/T)/\Delta[\text{Ln}(1-\alpha)]$ for the degradation in nitrogen at different heating rates: (a) B/T (60:40); (b) PTT.

values do not affect the calculation of thermal degradation kinetic parameters, so the offset X - and Y -axes are omitted here. Figure 4 shows the relationship of $\Delta[\text{Ln}(d\alpha/dt)]/\Delta[\text{Ln}(1-\alpha)]$ versus $\Delta(1/T)/\Delta[\text{Ln}(1-\alpha)]$, whereas the value of $\Delta(1/T)$ equals 0.00002 K^{-1} . Because the Freeman-Carroll lines also overlapped each other, we plot these lines on a set of parallel coordinate planes. Figure 5 shows the relationship proposed by Chang where the decomposition orders are assumed to be $1.2 \sim 1.25$ for PTT and $1.5 \sim 1.9$ for B/T (60:40). The Waterfall Graph was also used for the Chang plots. For the Chang technique, the absolute X and Y values also do not affect the calculation of thermal degradation kinetic param-

eters, so the offset X - and Y -axes are also omitted here. Figure 6 shows the relationship between the maximum weight loss rate $(d\alpha/dt)_m$ and heating rate for the first and second decomposition stages of B/T (60:40) as well as the decomposition of PTT and B/E (60:40).

The kinetic parameters of the first thermal degradation stage calculated by the four single heating rate techniques for the B/T (60:40) are summarized in Table I. The data for PTT, except the E_a and $\text{Ln}(Z)$ values from the second Kissinger technique, are listed in Table II. Because the reaction order n of PTT is calculated to be 1, we cannot obtain the E_a and $\text{Ln}(Z)$ values from the second Kissinger technique. The average kinetic parameters of thermal degradation calculated from the Friedman, Freeman-Carroll, and Chang techniques for B/E (60:40)⁵, B/T (60:40) (the first degradation stage), and PTT are listed in Table III. The onset degradation temperature (T_d), the temperature at the maximum weight loss rate (T_{dm}) or the temperature at the first maximum weight-loss rate (T_{dm1}), and the temperature at the second maximum weight-loss rate (T_{dm2}) of B/E (60:40), B/T (60:40), and PTT at different heating rates are also listed in Table III.

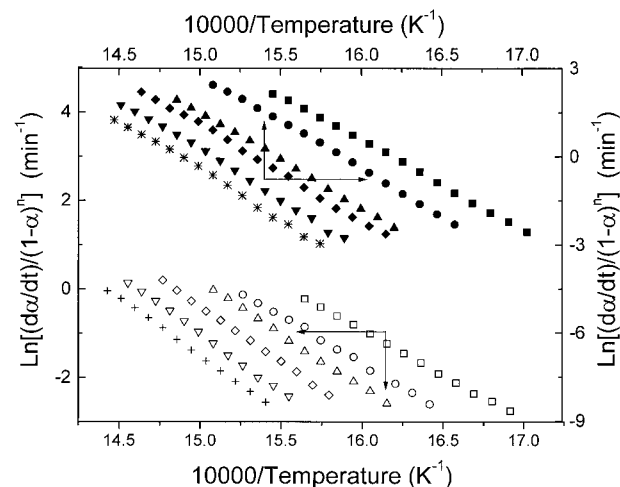


Figure 5 Chang plots of $\text{Ln}[(d\alpha/dt)/(1-\alpha)^n]$ versus $1/T$ for the thermal degradation of B/T (60:40) and PTT in nitrogen at different heating rates. For B/T (60:40): (\square), 2 K/min, $n = 1.6$; (\circ), 5 K/min, $n = 1.5$; (\triangle), 10 K/min, $n = 1.9$; (\diamond), 20 K/min, $n = 1.9$; (∇), 30 K/min, $n = 1.9$; ($+$), 40 K/min, $n = 1.9$. For PTT: (\blacksquare), 2 K/min, $n = 1.2$; (\bullet), 5 K/min, $n = 1.2$; (\blacktriangle), 10 K/min, $n = 1.2$; (\blacklozenge), 20 K/min, $n = 1.2$; (\blacktriangledown), 30 K/min, $n = 1.2$; ($*$), 40 K/min, $n = 1.25$. Total X offset is 0; total Y offset is 30%.

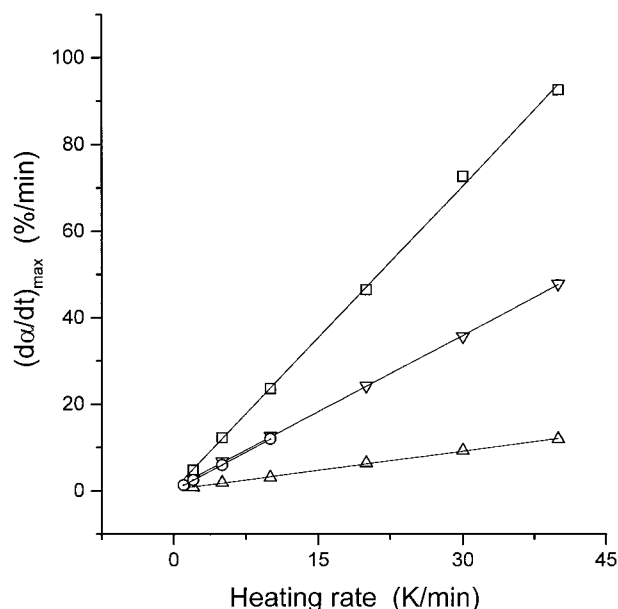


Figure 6 Effects of heating rate on the maximum decomposition rate. (▽), B/T (60:40), the first degradation stage; (△), B/T (60:40), the second degradation stage; (○), B/E (60:40), the first degradation stage⁵; (□), PTT.

The Effect of Heating Rate

From Tables I and III it can be concluded that the kinetic parameters of B/T (60:40) change with the heating rate, and most of E_a , $\text{Ln}(Z)$, T_d , T_{dm1} , and T_{dm2} values increase significantly with heating rate, whereas the n values keep roughly the same as the heating rate changes from 10 to 40 K/min. That is to say, when the heating rate is high enough, the effect of the concentration of decomposition products from B/T (60:40) on thermal

degradation reaction will remain roughly unchanged.

From Tables II and III, it can be seen that the reaction order n for PTT varies little with the heating rates adopted in this article. But the variation of the E_a , $\text{Ln}(Z)$, T_d , and T_{dm} with heating rates is similar to that of B/T (60:40). This indicates that heating rate has somewhat different effects on B/T (60:40) and PTT.

As seen in Table III, the T_d , T_{dm1} , and T_{dm2} for B/E (60:40) increase with increasing heating rate. The E_a and $\text{Ln}(Z)$ values calculated by the Friedman technique⁵ also increase with heating rate.

Additionally, Figure 6 shows good linear dependency between $(d\alpha/dt)_m$ and heating rate for all degradation processes studied in this article, including the first and the second decomposition stages of B/T (60:40), the first decomposition stage of B/E (60:40), and the decomposition of PTT, and the $(d\alpha/dt)_m$ values increase linearly with heating rate.

Generally, the variation of these kinetic parameters reveals the change of thermal degradation mechanism, i.e., transformation from the diffusion-controlled kinetics into the decomposition-controlled kinetics, or vice versa.⁹ The effect of heating rate on E_a , n , and $\text{Ln}Z$ can be explained as expressed below. At lower heating rates, the diffusion of degradation products apparently does not affect the kinetics of the decomposition process. So kinetic parameter values were relatively low. Alternatively, at higher heating rate, the degradation of polymer is probably faster than the diffusion of degradation products through the polymer melt, therefore the kinetics of the degradation process is controlled by the diffusion of

Table I Kinetic Parameters of Thermal Degradation of B/T (60 : 40) under Nitrogen Calculated by Four Single Heating Rate Techniques, Respectively

Heating Rate (K/min)	Friedman			Freeman-Carroll			Chang			The Second Kissinger		
	E_a (kJ/mol)	n	$\text{Ln}(Z)$ (min^{-1})	E_a (kJ/mol)	n	$\text{Ln}(Z)$ (min^{-1})	E_a (kJ/mol)	n	$\text{Ln}(Z)$ (min^{-1})	E_a (kJ/mol)	n	$\text{Ln}(Z)$ (min^{-1})
2	133	1.6	21.7	166	1.6	28.6	168	1.6	29.1	25	0.9	1.6
5	136	1.5	23.0	173	1.6	29.8	179	1.5	30.9	25	0.9	2.4
10	162	1.9	28.0	208	2.1	36.2	200	1.9	34.9	35	1.4	4.9
20	164	2.0	28.3	213	2.1	37.1	209	1.9	36.3	29	1.3	4.4
30	166	2.0	28.7	229	2.1	39.7	219	1.9	38.0	27	1.3	4.2
40	172	2.0	29.9	214	2.0	37.1	218	1.9	37.8	30	1.3	5.0
Average	156	1.8	26.6	201	1.9	34.7	199	1.8	34.5	28	1.2	3.8

Table II Kinetic Parameters of Thermal Degradation of Poly(trimethylene terephthalate) ($[\eta] = 1.12$ dL/g) Under Nitrogen Calculated by Four Single Heating Rate Techniques, Respectively

Heating Rate (K/min)	Friedman			Freeman-Carroll			Chang			The Second Kissinger
	E_a (kJ/mol)	n	$\text{Ln}(Z)$ (min^{-1})	E_a (kJ/mol)	n	$\text{Ln}(Z)$ (min^{-1})	E_a (kJ/mol)	n	$\text{Ln}(Z)$ (min^{-1})	n
2	241	0.8	43.0	256	1.1	46.2	252	1.2	45.4	1.1
5	259	0.8	46.2	274	1.1	49.2	267	1.2	48.1	1.1
10	260	0.8	45.9	266	0.9	47.0	271	1.2	48.3	1.0
20	262	0.8	46.5	263	0.6	46.5	272	1.2	48.8	1.0
30	265	0.8	47.0	273	0.9	48.5	281	1.2	50.2	1.2
40	274	0.9	48.6	289	1.0	51.4	283	1.25	50.6	0.9
Average	260	0.8	46.2	270	0.9	48.1	271	1.2	48.6	1.1

degradation products. Consequently, higher kinetic parameters were observed with increasing heating rate.⁵

The Effect of Calculating Technique

Table II demonstrates that kinetic parameters depend not only on the experimental conditions (such as heating rate, sample weight, and atmosphere), but also on the mathematical treatment of the data. The results obtained by the second Kissinger technique are much different than those calculated by

the other three, especially for the E_a and $\text{Ln}(Z)$ values. However the results derived from the other three techniques have no significant distinction, except that the E_a and $\text{Ln}(Z)$ values given by Friedman are somewhat lower. A similar situation can be found for B/E copolymer.⁵ If one calculates the value of n from eq. (7) and substitutes it into eq. (8) to estimate E_a , this procedure may result in considerable errors.⁹

From Table III, it is obvious that the results derived from the Friedman, Freeman-Carroll, and Chang techniques are in agreement with one

Table III Characteristic Temperature and Average Kinetic Parameters Calculated by Friedman, Freeman-Carroll, and Chang Techniques for Thermal Degradation of B/E (60 : 40), B/T (60 : 40), and PTT Under Nitrogen

Heating Rate (K/min)	B/T (60 : 40) ^a				PTT ^b				B/E (60 : 40) ^c			
	$T_d/T_{dm1}/T_{dm2}$ (°C)	E_a (kJ/mol)	n	$\text{Ln}(Z)$ (min^{-1})	T_d/T_{dm} (°C)	E_a (kJ/mol)	n	$\text{Ln}(Z)$ (min^{-1})	$T_d/T_{dm1}/T_{dm2}$ (°C)	E_a (kJ/mol)	n	$\text{Ln}(Z)$ (min^{-1})
1									387/408/462	253	3.0	42
2	335/367/428	156	1.6	26.4	345/366	250	1.0	44.9	398/414/475	262	3.3	43
5	356/388/441	163	1.5	27.9	357/382	266	1.0	47.8	403/437/—	250	2.3	41
10	368/399/467	190	2.0	33.0	374/398	266	1.0	47.1	425/453/—	239	2.2	39
20	381/411/489	195	2.0	33.9	379/403	266	0.9	47.2				
30	388/419/499	205	2.0	35.5	388/411	273	1.0	48.6				
40	394/427/507	201	2.0	34.9	390/416	282	1.1	50.2				
Average ^d	353/385/445	170	1.7	29.1	359/382	261	1.0	46.6	409/435/—	251	2.6	41
Average ^e	370/402/472	185	1.8	31.9	372/396	267	1.0	47.6				

^a Sample weight, 1 mg.

^b The first degradation stage, $[\eta] = 1.12$ dL/g; sample weight, 1 mg.

^c The first degradation stage, $[\eta] = 0.60$ dL/g; sample weight, 22 mg.⁵

^d Calculated with the heating rate ranging from 2 to 10 K/min.

^e Calculated with the heating rate ranging from 2 to 40 K/min.

another except that the E_a and $\text{Ln}(Z)$ values gained the Friedman technique are a little lower than those obtained by the other two techniques.

The Friedman, Freeman-Carroll, and Chang techniques did not give the same results because different calculating techniques respectively appropriate for the thermal degradation behaviors in different temperature ranges. In fact, kinetic parameters change more or less with temperature, even though we assume that they do not vary with temperature in every mathematical technique.

In the case of the Friedman technique (see Fig. 3 and Table III), the E_a value was derived from the slope of $\text{Ln}(d\alpha/dt)$ versus $1/T$. However, the linear relation between $\text{Ln}(d\alpha/dt)$ and $1/T$ for B/T (60:40) or PTT stands only in the temperature range from $(T_d - 30 \text{ K})$ to T_d . Then from the slope of $\text{Ln}(1 - \alpha)$ versus $1/T$ and the derived E_a value, the n value can be calculated, and the relationship between $\text{Ln}(1 - \alpha)$ and $1/T$ for B/T (60:40) or PTT keeps linear in the temperature range from $(T_{dm} - 10 \text{ K})$ to $(T_{dm} + 10 \text{ K})$. Finally, $\text{Ln}(Z)$ can be given by substituting the derived E_a and n value into eq. (1), in which both $n \cdot \text{Ln}(1 - \alpha)$ and $\text{Ln}(d\alpha/dt)$ are so small compared with $E_a/(R \cdot T)$ that $\text{Ln}(Z)$ is mainly determined by the E_a value. Therefore, E_a and $\text{Ln}(Z)$ values given by the Friedman technique mainly indicate the thermal decomposition behavior in the temperature range from $(T_d - 30 \text{ K})$ to T_d .

On the contrary, in the case of the Freeman-Carroll technique (see Fig. 4 and Table III), the linear relation can be gained in the temperature interval from $(T_{dm} - 42 \text{ K})$ to T_{dm} for PTT and $(T_{dm} - 34 \text{ K})$ to T_{dm} for B/T (60:40). Meanwhile, in the case of the Chang technique (see Fig. 5 and Table III), the linear relation can be obtained in the temperature interval from $(T_{dm} - 59 \text{ K})$ to T_{dm} for PTT and $(T_{dm} - 45 \text{ K})$ to T_{dm} for B/T (60:40). Moreover, according to eq. (1) and Freeman-Carroll plots the E_a , n , and $\text{Ln}(Z)$ can be derived, whereas according to Chang plots, the E_a and $\text{Ln}(Z)$ can be calculated directly. So it can be concluded that E_a and $\text{Ln}(Z)$ values derived from the Freeman-Carroll technique describe behaviors of thermal degradation in the temperature range from $(T_{dm} - 42 \text{ K})$ to T_{dm} for PTT and $(T_{dm} - 34 \text{ K})$ to T_{dm} for B/T (60:40); meanwhile those values derived from the Chang technique describe the behavior of thermal degradation in the temperature ranging from $(T_{dm} - 59 \text{ K})$ to T_{dm} for PTT and $(T_{dm} - 45 \text{ K})$ to T_{dm} for B/T (60:40).

From the outcomes given above, it can be concluded that the Freeman-Carroll and Chang techniques cover similar temperature ranges, whereas the Friedman technique covers a lower temperature range. Moreover, the Chang technique covers the widest temperature range, whereas the Freeman-Carroll technique takes the second place. Generally, for a thermal degradation process, lower temperature may lead to smaller kinetic parameters, and a wider calculating temperature range will result in better reliability with smaller errors. Consequently, the Freeman-Carroll and Chang techniques provide very similar values of kinetic parameters, whereas those gained by the Friedman technique are somewhat lower. Although the Chang technique gives linear relation in the widest temperature range, one can not use this technique alone because the n value must be assumed before calculation. Moreover, the Chang technique has low sensitivity to n values, which means that a good linear relation can be obtained in a wide range of n values. Therefore, Freeman-Carroll is the most reliable technique, whereas the Chang technique can be used to check the results gained by other techniques. It should be noted that even for the Friedman technique, the temperature range is also wide enough to obtain credible results. Additionally, it can also indicate that PTT has a wider calculating temperature range than B/T (60:40), whereas the interval between T_{dm} and T_d for PTT (24 K) is smaller than that for B/T (60:40). This means that there are smaller differences among the temperature ranges used for PTT in the three single heating rate techniques, so the results obtained were in better agreement with one another.

Kinetics of Nonisothermal Decomposition Analyzed by Multiple Heating Rate Techniques

The first Kissinger and Flynn-Wall techniques are different than the four techniques mentioned above, which require multiple TG curves at various heating rates to calculate the thermal degradation parameters. The Flynn-Wall technique can only give the activation energy (E_a) values, whereas the first Kissinger technique can supply all three kinetic parameters.

The first Kissinger plots for the first, second decomposition stages of B/T (60:40), and the decomposition of PTT in nitrogen are shown in Figure 7. Three reasonable straight lines were obtained. E_a , n , and $\text{Ln}(Z)$ values calculated from

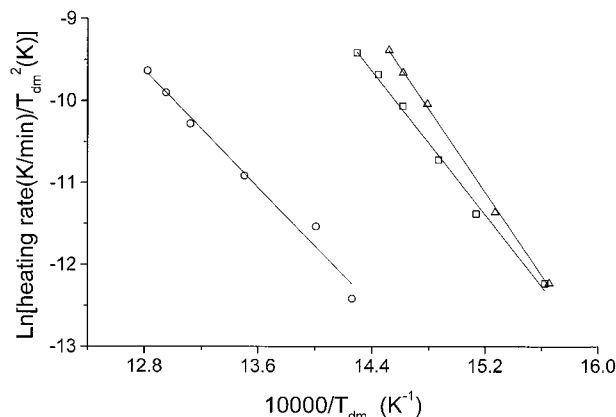


Figure 7 The first Kissinger profiles of $\text{Ln}(\text{heating rate}/T_{dm}^2)$ versus $1/T_{dm}$ for the thermal degradation. (\square), B/T (60:40), the first degradation stage; (\circ), B/T (60:40), the second degradation stage; (\triangle), PTT.

the slope and intercept of these straight lines are listed in Table IV.

Comparing Table IV with Table III, it is obvious that the results given by the first Kissinger technique for B/T (60:40) are in good agreement with the average data obtained by single heating rate techniques. The results for PTT also do not deviate much from the average data obtained by single heating rate techniques. The reason for these outcomes is as follows. The first Kissinger technique describes the thermal degradation of polymers at T_{dm} , which is just located in the temperature range used by most of the single heating rate techniques. Additionally, as listed in Table IV and shown in Figure 6, the second stage of thermal degradation for B/T (60:40) in nitrogen

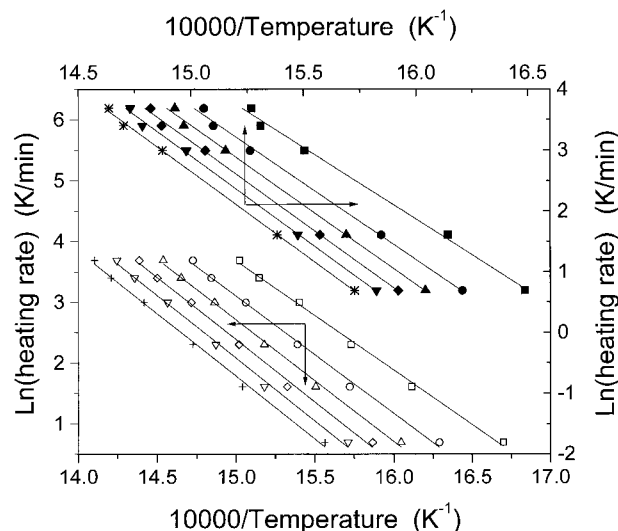


Figure 8 Flynn-Wall profiles of B/T (60:40) and PTT degraded in nitrogen. For B/T (60:40): (\square), $\alpha = 10\%$; (\circ), $\alpha = 18\%$; (\triangle), $\alpha = 26\%$; (\diamond), $\alpha = 34\%$; (∇), $\alpha = 42\%$; (+), $\alpha = 50\%$. For PTT: (\blacksquare), $\alpha = 10\%$; (\bullet), $\alpha = 18\%$; (\blacktriangle), $\alpha = 26\%$; (\blacklozenge), $\alpha = 34\%$; (\blacktriangledown), $\alpha = 42\%$; (*), $\alpha = 50\%$.

has lower E_a , $\text{Ln}(Z)$, and $(d\alpha/dt)_m$ values than those of the first stage, which indicates that a different kinetic process occurs with the second stage. The same situation can be found for B/E (75:25).⁵

According to eq. (9) of the Flynn-Wall technique, twelve straight lines over the fractional weight-loss range 10–50 wt % are shown in Figure 8, of which six lines are given for B/T (60:40) and six lines are given for PTT. The activation energies E_a gained from the Flynn-Wall technique are shown in Table IV. Obviously, as the

Table IV Kinetic Parameters of Thermal Degradation of B/T (60 : 40) and PTT in Nitrogen Calculated by Two Multiple Heating Rate Techniques, Respectively

Calculating Technique	First Step Degradation			Second Step Degradation			Average		
	E_a (kJ/mol)	n	$\text{Ln}(Z)$ (min^{-1})	E_a (kJ/mol)	n	$\text{Ln}(Z)$ (min^{-1})			
The first Kissinger	B/T (60 : 40)	182	2.2	31.7	149	2.3	24.1		
	PTT	209	1.0	37.1					
Flynn-Wall		Weight Loss (wt %)	10	18	26	34	42	50	
	B/T (60 : 40)	E_a (kJ/mol)	149	160	166	170	172	171	165
PTT	E_a (kJ/mol)	196	210	218	222	225	225	225	216

Table V Kinetic Parameters of Isothermal Degradation of B/T (60 : 40) in Nitrogen Calculated by the Flynn Technique

Weight Loss (wt %)	5	10	15	20	30	45	Average
E_a (kJ/mol)	157	167	171	173	179	183	172
$\text{Ln}(Z)$ (min^{-1})	29.6	30.8	31.0	30.9	31.1	30.0	30.6

fraction of weight loss increases from 10 to 50 wt %, the activation energy (E_a) increases steadily, which indicates the variation in the thermal degradation kinetics. Additionally, the average E_a value obtained by the Flynn-Wall technique is lower than the average value obtained by single heating rate techniques.

Thermal Stability

Except for the first and second Kissinger techniques, no matter which technique was used above, the fundamental equation is the same:

$$d\alpha/dt = Z \cdot (1 - \alpha)^n \cdot \exp[-E_a/(R \cdot T)] \quad (11)$$

Because the value of $(1 - \alpha)$ is always less or equal to 1, da/dt decreases with increasing n , and the zero order ($n = 0$) characterizes the most rapid decomposition reaction.⁵ From eq. (11), it can be concluded that higher n and E_a values or a lower Z value result in a lower da/dt value, which means higher thermal stability.

As shown in Figure 6, the data of the first decomposition of B/T (60:40) and B/E (60:40)⁵ are almost superposed, indicating the same maximum weight-loss rate for B/T (60:40) and B/E (60:40). This may be attributed to the resemblance between B/T (60:40) and B/E (60:40) in molecular structures. The average T_d , T_{dm1} , E_a , n , and $\text{Ln}(Z)$ values listed in Table III for B/T (60:40) calculated from the heating rates of 2, 5, and 10 K/min are lower than those for B/E (60:40). The heat stability of T units is poor as compared with E units because the T unit has more hydrogen atoms than the E unit and the degradation of a polymer containing more hydrogen atoms might lead to the formation of more volatile products resulting in a decrease of carbonaceous mass and faster degradation.⁵ Additionally, the average sample weight of B/E (60:40) (22 mg) is much larger than that of B/T (60:40) (1 mg), and a large amount of sample will retard the diffusion of degradation products inclining to diffusion-controlled kinetics, which may lead to higher kinetic parameters.

As shown in Table III, the average T_d for B/T (60:40) calculated from the heating rate range of 2 to 40 K/min (370°C) is almost equal to that for PTT (372°C). This may be attributed to the existence of T units in both B/T (60:40) and PTT. T units are less heat-stable than B units as mentioned, and thermal decomposition starts at the weakest linkages, so B/T (60:40) and PTT may have the same onset degradation temperature T_d . Both the average n calculated from the heating rate range of 2 to 40 K/min by single heating rate techniques and the n value obtained from the first Kissinger technique for B/T (60:40) are about two times larger than those for PTT, whereas $(da/dt)_m$ values at different heating rates shown in Figure 6 for B/T (60:40) are about half of those for PTT, and the average $\text{Ln}(Z)$ and T_{dm1} values for B/T (60:40) are also higher than that for PTT. This may be attributed to the difference between B/T (60:40) and PTT in molecular structures. It has been mentioned that the higher the n value, the slower the decomposition. More aromatic carbon atoms (or less hydrogen atoms) will decrease the thermal degradation rate and increase thermal stability. B/T (60:40) possesses a higher n value and lower degradation rate than PTT because of the existence of B units. On the contrary, the average E_a value calculated from the heating rate range of 2 to 40 K/min by single heating rate techniques as well as the E_a values derived from the first Kissinger and Flynn-Wall techniques are lower than that for PTT. This could be attributed to the effect of molecular weight. In the melt polycondensation process, PTT degrades first and then copolymerizes with *p*-acetoxybenzoic acid. Because of the poor copolymerization ability, long blocks of B units formed, which may increase the melt viscosity greatly and may make the further polycondensation become impossible in the melt state. So B/T (60:40) studied in this report, which was obtained through melt polycondensation, has lower molecular weight than PTT. It is evident that the lower the molecular weight, the more the end groups. End groups can initiate thermal decomposition.⁵ As a result, lower molecular weight leads to a lower E_a

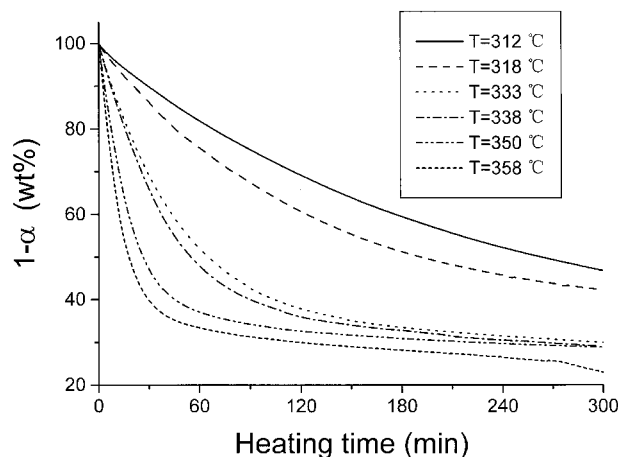


Figure 9 Isothermal TG traces of B/T (60:40) in nitrogen at six temperatures ranging from 312 to 358°C.

value. Therefore, a higher E_a value would be obtained if the molecular weight of B/T (60:40) could be increased through solid-state polymerization.

Kinetics of Isothermal Decomposition

The weight losses of B/T (60:40) during isothermal heating in nitrogen were measured at six temperatures of 312, 318, 333, 338, 350, and 358°C. The TG curves are shown in Figure 9. The B/T (60:40) exhibited a slow and steady decomposition at 313 and 318°C, and lost about 53 and 58% of the initial weight after 300 min at these temperatures. Above 330°C, the decomposition became much more rapid within a short period from the beginning (30 min for the experiment at 358 and 350°C and 60 min for the experiment at 333 and 338°C), whereas after this initial period, subsequent decomposition got much slower, and the weight loss nearly kept constant after 100 min at these temperatures. In the case of 358 and 350°C, within the initial 30 min the sample lost 78 and 75% of the weight that it lost at 300 min. Meanwhile, in the case of the experiment at 338 and 333°C, within the initial 60 min, the sample lost 77 and 69% of the weight that was lost at 300 min.

According to eq. (10) of the Flynn technique, seven straight lines corresponding to the fractional weight loss ranging from 5 to 45 wt % are shown in Figure 10. Respective E_a and $\ln(Z)$ values obtained from the slopes and intercepts of these straight lines are listed in Table V. It can be concluded that only E_a increases with increasing weight loss, whereas $\ln(Z)$ roughly keeps con-

stant. This indicates that the degradation mechanism varies with the weight loss. The average E_a (172 kJ/mol) and $\ln(Z)$ (30.6 min^{-1}) values of B/T (60:40) obtained under isothermal conditions conform with those obtained from nonisothermal condition. Submitting kinetic parameters listed in Table V into eq. (1) and assuming $\alpha = 30 \text{ wt } \%$, we can derive n values, which are 1.6 at 312°C and 1.5 at 338°C, respectively. This suggests that the isothermal decomposition and the dynamic heating decomposition of B/T (60:40) follow a similar mechanism.

CONCLUSIONS

B/T (60:40) shows two weight-loss stages during degradation in nitrogen. Higher $(d\alpha/dt)_m$, E_a , and $\ln(Z)$ values were obtained for the first stage, whereas higher T_{dm} and n values were gained for the second stage. Thus, the first one might be ascribed to the degradation of both T and B units, whereas the second one might be mainly attributed to the degradation of B units. Compared with PTT, B/T (60:40) has a similar T_d and higher T_{dm} and n , but lower $(d\alpha/dt)_m$, E_a , and $\ln(Z)$. All these parameters except for E_a indicate that B/T (60:40) is more heat stable than PTT.

In accordance with the dynamic TG, the T_d , T_{dm} , and $(d\alpha/dt)_m$ values, as well as E_a , and $\ln(Z)$ values derived from single heating rate techniques increase significantly with heating rates, and the E_a value derived from the Flynn-Wall

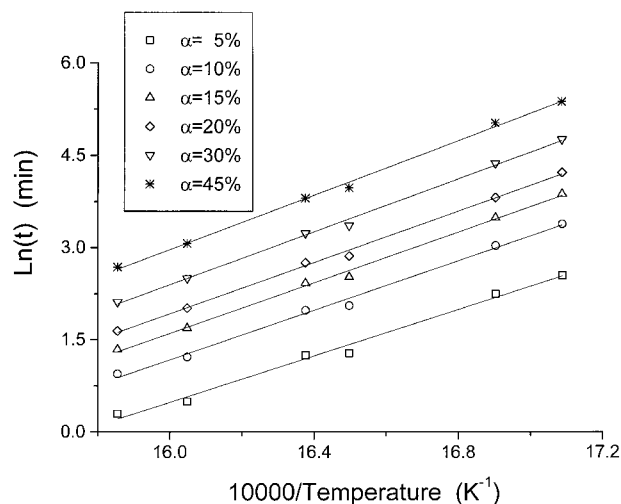


Figure 10 Flynn diagrams of $\ln(t)$ versus $1/T$ for the isothermal degradation of B/T (60:40) at different fractional weight losses α .

technique increases steadily with the weight-loss fraction. Meanwhile, in the isothermal TG, the weight-loss rate increases significantly as the temperature increases, and the E_a value calculated from the Flynn technique also increases steadily with weight-loss fraction.

In the case of single heating rate techniques, Freeman-Carroll can provide the most reliable E_a , n , and $\ln(Z)$ values, the Friedman technique may offer a little lower values, and the Chang technique can only be used to validate the outcomes from other techniques; nevertheless, the second Kissinger technique cannot give the correct E_a and $\ln(Z)$ values.

Additionally, the results given by the first Kissinger and Flynn-Wall techniques are in good agreement with each other, and these results do not deviate much from those given by single heating rate techniques.

Finally, the average results of isothermal TG given by the Flynn technique are conformed to those of dynamic TG.

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