Thermogravimetric Kinetics of Thermotropic Copolyesters Containing *p*-Oxybenzoate Unit by Multiple Heating-Rate Methods

XIN-GUI LI

Department of Polymer Materials Science & Engineering, College of Materials Science & Engineering, Tongji University, 1239 Siping Road, Shanghai 200092, People's Republic of China

ABSTRACT: Two series of thermotropic liquid crystalline copolyesters containing mainly the *p*-oxybenzoate unit were studied by thermogravimetry to ascertain the kinetic parameters of their thermal degradation by six multiple heating-rate techniques for the first time. The two copolyesters are (1) poly(*p*-oxybenzoate-*co*-ethylene terephthalate-*co*-vanillate) and (2) poly(*p*-oxybenzoate-*co*-2,6-oxynaphthoate). The effect of copolymer composition, degradation stage, and test atmosphere on the three kinetic parameters of the thermal degradation in the weight loss range from 5 to 70% is discussed. Comparison of the multiple heating-rate techniques with single heating-rate techniques for calculating the kinetic parameters of thermal degradation was made. The respective activation energy, order, and natural logarithm of the frequency factor of the thermal degradation in nitrogen for the poly(*p*-oxybenzoate-*co*-ethylene terephthalate-*co*-vanillate)s are between 180 and 230 kJ/mol, between 2.0 and 5.0, and between 28 and 38 min^{-1} for the first degradation step and between 250 and 390 kJ/mol, between 6.4 and 7.6, and between 38 and 64 min^{-1} for the second degradation step of the poly(*p*-oxybenzoate-*co*-ethylene terephthalate-*co*-vanillate)s with the unit-B content in the range of 70–75 mol %. The respective activation energy, order, and natural logarithm of frequency factor of the first degradation stage for the poly(*p*-oxybenzoate-*co*-2,6-oxynaphthoate) (Vectra) are between 380 and 570 kJ/mol, between 2.0 and 3.1, and between 55 and 68 min^{-1} in nitrogen and between 160 and 210 kJ/mol, between 0.8 and 1.8, and between 25 and 32 min^{-1} in air. The best methods of calculating the kinetic parameters of the thermal degradation for the copolymers are suggested. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 74: 2016–2028, 1999

Key words: thermotropic liquid crystalline polymer; aromatic copolyester; thermal degradation; thermogravimetry; degradation kinetics; multiple heating-rate method

INTRODUCTION

Thermotropic liquid crystalline aromatic polymers represent one of the new class of high-per-

formance engineering thermoplastics. These polymers have become the subject of numerous investigations due to their unique liquid crystalline melt processing, mechanical and heat-resistant properties, high glass transition temperature, and highly oriented structure.[1–5] There are many reports on the morphology, rheology, mechanical and dynamic mechanical properties, and DSC thermal analysis of the liquid crystalline aromatic polymers, but there is relatively little reported on the thermal degradation behavior of the
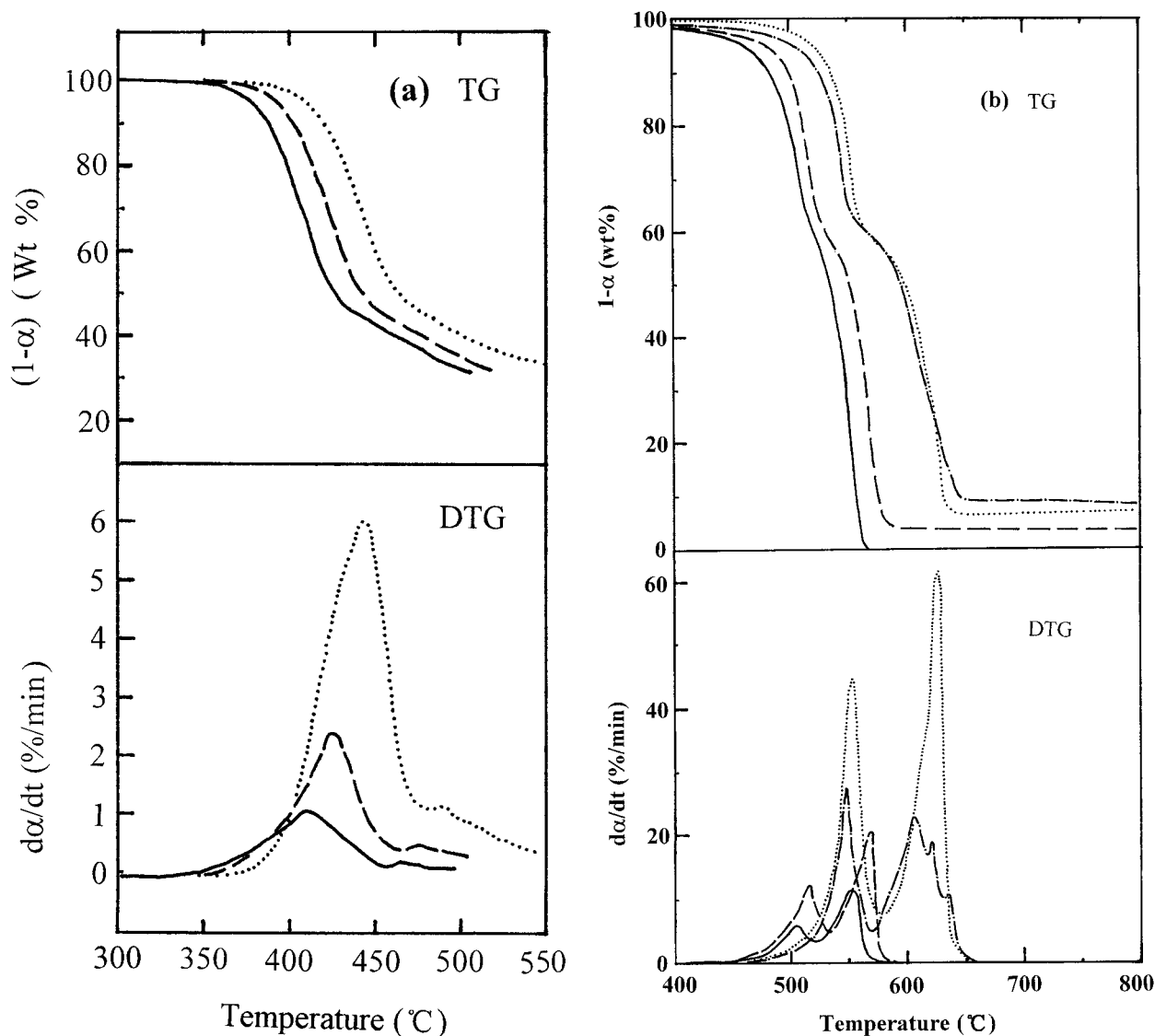
Figure 1 Typical TG and DTG thermograms of thermotropic liquid crystalline co-polyesters of (a) B/E/V (60/37.5/2.5) in nitrogen at three heating rates: (—) 1°C/min; (- - -) 2°C/min; (· · ·) 5°C/min, and (b) B/N Vectra copolymer in air at four heating rates: (—) 5°C/min; (- - -) 10°C/min; (-·--) 20°C/min; (· · ·) 30°C/min.

liquid crystalline aromatic polymers, especially the kinetics aspect. It has been widely accepted that thermogravimetry (TG) and derivative thermogravimetry (DTG) are quite useful measurements for the thermal degradation of the polymers. The kinetics of the thermal degradation of the thermotropic polymers have been studied on the basis of the equations which need only one TG and DTG obtained at a single heating rate.[6] Especially, the analyses of the thermal degradation process of the polymers by single heating-rate methods give important information about the kinetics of the thermal degradation. However, very little on the kinetic analyses of thermal degradation by multiple heating-rate techniques has been available until now. It appears that the analytic techniques based on several curves obtained at different heating rates present a lower risk of creating errors than do techniques based on a single thermogram.[7] The present article aimed to analyze the kinetics of thermal degradation by six types of multiple heating-rate methods and the results obtained are compared with those obtained by single heating-rate methods.
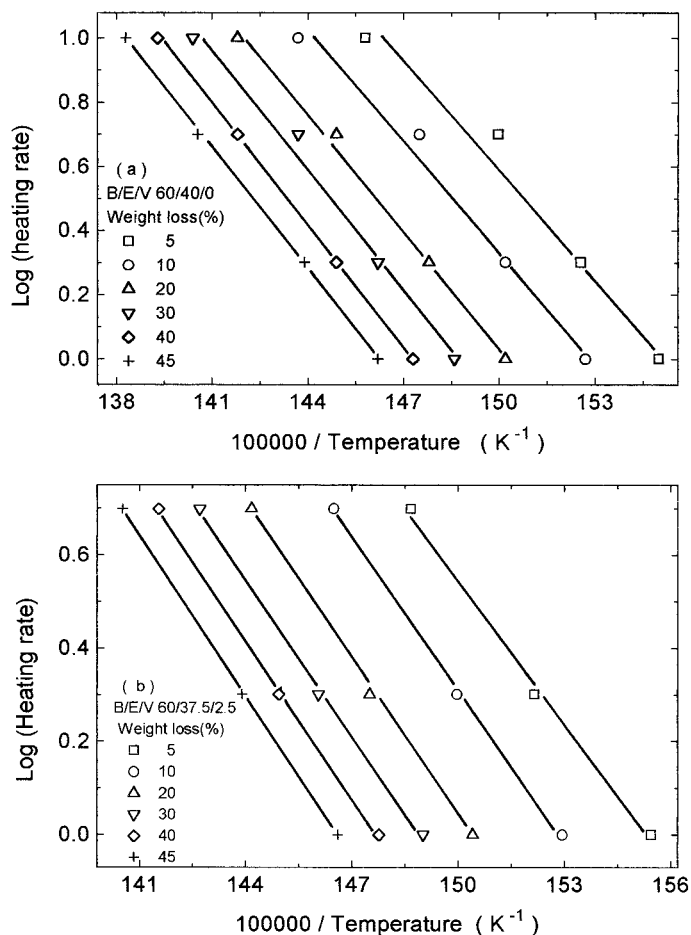
Figure 2 Flynn–Wall method applied to calculate activation energy of thermal degradation for thermotropic liquid crystalline copolyesters of (a) B/E/V (60/40/0) and (b) (60/37.5/2.5) in nitrogen.

EXPERIMENTAL

The random B/E/V copolymers with the structural formula shown in Scheme 1 were synthesized by following the procedure described elsewhere[6]: The intrinsic viscosity of the copolymers was measured at a 0.5% concentration in phenol/*sym*-tetrachloroethane 50/50 (vol) at 30°C. The Vectra random copolyester resin chip used in this study was kindly supplied by the Celanese Co. The Vectra copolyester is composed of 4-hydroxybenzoic acid and 2,6-hydroxynaphthoic acid with the mol ratio of 58 and 42%, as shown in Scheme
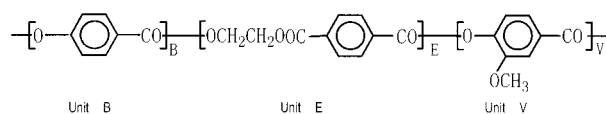
2. The B/E/V copolymers have the following molecular structure:
The B/N Vectra copolymer has the following molecular structure:
TG and DTG thermograms for the B/E/V copolymers were obtained using a DuPont Instrument 9900 computer/thermal analyzer under a dynamic nitrogen atmosphere flowing at 50 mL/min. Degradation experiments under nitrogen were conducted at the heating rates of 1, 2, 5, and 10°C/min using 22–35-mg samples. TG and DTG
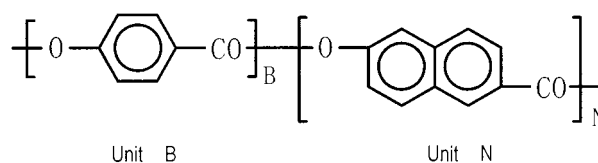
Scheme 1

Scheme 2

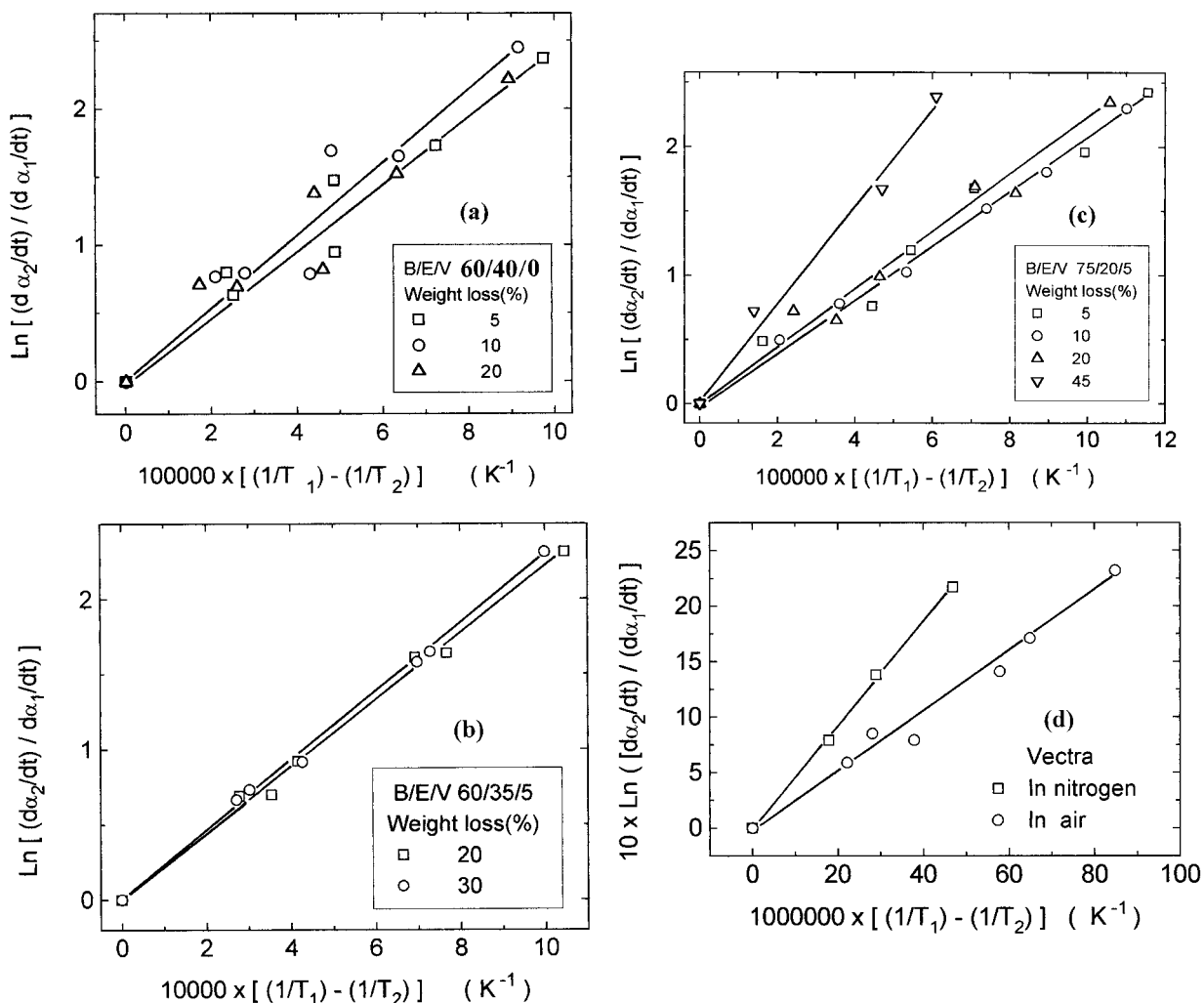**Figure 3** Hernandez-Sanchez method applied to calculate activation energy of thermal degradation for the polymers with the following B/E/V ratios (in nitrogen): (a) 60/40/0, (b) 60/35/5, (c) 75/20/5, and (d) for B/N Vectra copolymer in nitrogen and air at a weight loss of 20%.

curves for the B/N copolymer were obtained with a TA 2950 high-resolution thermogravimetric analyzer. The heating rates for the TG measurements of the B/N copolymer were 1, 4, 5, 10, 20, and 30°C/min in both nitrogen and air at a flowing rate of 30 mL/min with the sample size of 1.2–2.5 mg to provide a control set of values for thermal decomposition parameters. The TG and DTG curves were then printed.

Several methods for the calculation of kinetic parameters of the thermal degradation by TG measurements have been developed. They can be classified into three groups: integral, differential, and direct-solution methods, based on the way of solution of eq. (1):

$$d\alpha/dt = Z(1 - \alpha)^n \exp(-E'/RT) \qquad (1)$$

where $d\alpha/dt$ is the weight-loss rate; Z, the frequency factor; α, the weight loss; E', the activation energy of thermal degradation, R, the gas constant (8.3136 J mol^{-1} K^{-1}); and T, the absolute temperature.

The methods of calculating the kinetic parameters can also be divided into two groups: single heating-rate method and multiple heating-rate method. The single heating-rate method, such as the Friedman, Freeman–Carroll, Chang, and Coats–Redfern methods, can calculate the kinetic parameters from one TG curve and one DTG curve obtained at a single heating rate, as re-
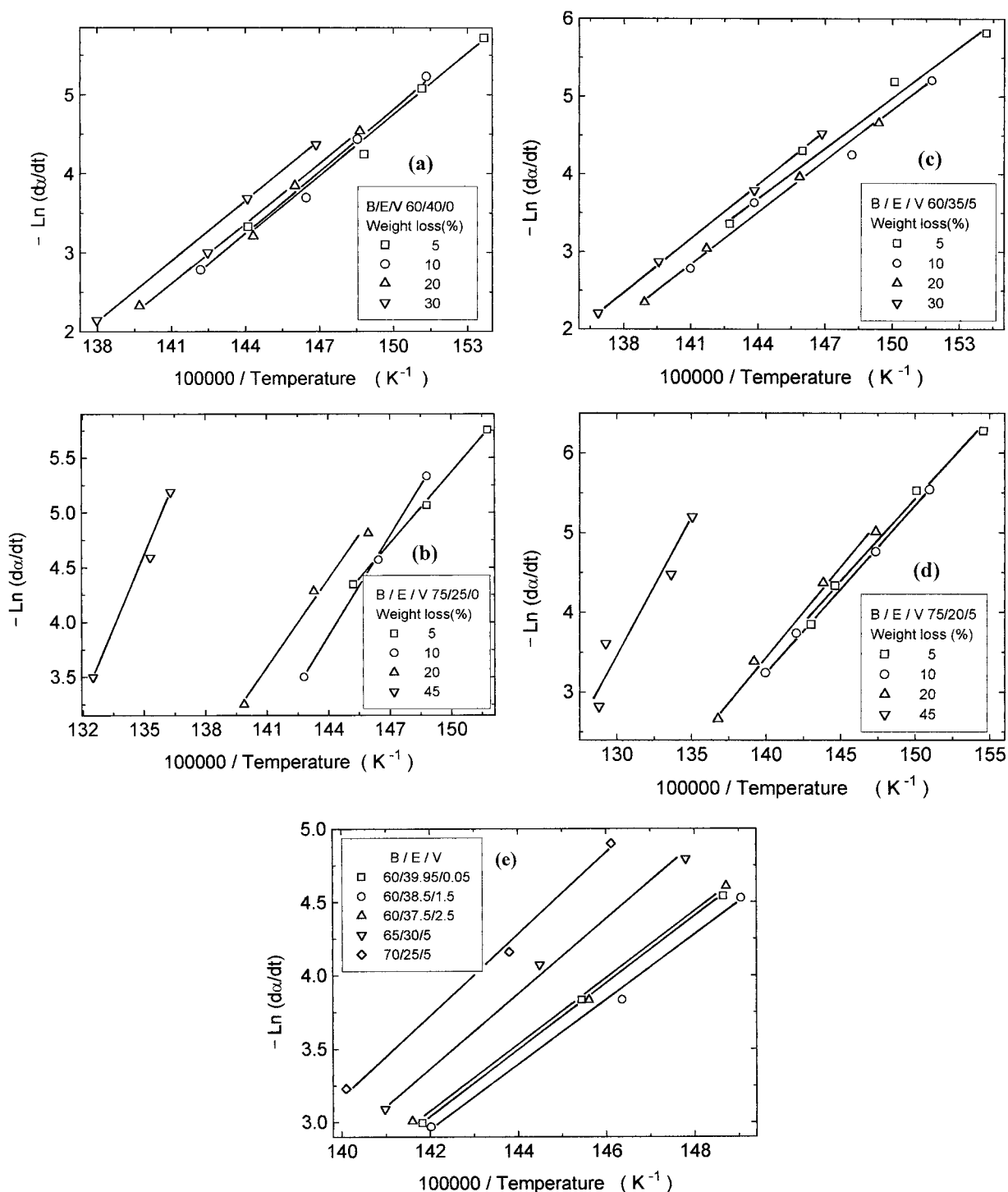
Figure 4   Friedman method [Ln($d\alpha/dt$) versus reciprocal temperature plot] applied to calculate activation energy of thermal degradation for B/E/V polymers with the following monomer ratios: (a) 60/40/0; (b) 75/25/0; (c) 60/35/5; (d) 75/20/5 at the weight loss range from 5 to 45%; (e) five other different B/E/V molar ratios at a given weight loss of 20%.

ported previously.[6–8] The multiple heating-rate method, like the Flynn–Wall,[9] Reich,[10] Friedman,[11] Kim–Park,[12] Kissinger,[13] and Hernandez-

Sanchez[14] methods, allows calculation of the kinetic parameters from at least two thermograms obtained at various heating rates. Since the single
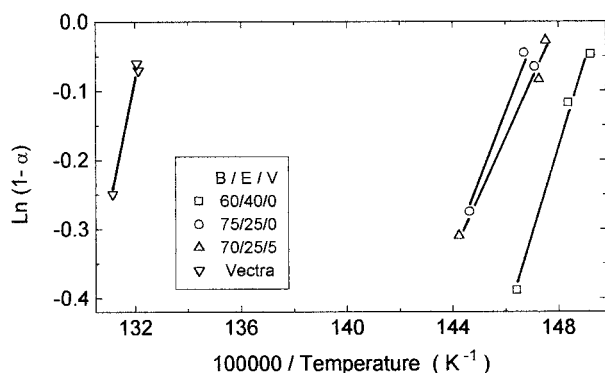
Figure 5 Friedman method [Ln(1 − α) versus 1/T plot] applied to calculate reaction order n of thermal degradation for B/E/V polymers with three monomer ratios and B/N Vectra polymer.

heating-rate method of the TG kinetic analysis in the case of the degradation of thermotropic liquid crystalline copolyesters was reported,[6,8] the data obtained in this study was analyzed using six multiple heating-rate methods which need at least three TG and DTG curves obtained using at least three heating rates. It seems that the multiple heating-rate technique is a little bit more reliable but requires more data than the single heating-rate technique:

1. The first multiple heating-rate method proposed by Flynn–Wall uses the following approximate equation at a constant weight loss in a thermal degradation process[9]:

$$\text{Log } q = \text{Ln}(E'Z/R) - \text{Ln } F(\alpha)$$
$$- 0.457(E'/RT) \quad (2)$$

where q is the heating rate in the TG

measurement. From this equation, E' can easily be calculated based on the slope of a plot of Log q versus 1/T at a fixed weight loss.

2. The second method proposed by Reich uses the equation[10]

$$E' = R \text{ Ln}[(q_2/q_1)(T_1/T_2)^2]/[(1/T_1) - (1/T_2)] \quad (3)$$

where the subscripts 1 and 2 mean the two different parameters at two heating rates, that is, T_1 and T_2 are the two temperatures of the polymer at the same weight loss observed at two different heating rates of q_1 and q_2, respectively.

3. The third method is the Friedman method, which is both a single heating-rate method and a multiple heating-rate method.[11] The multiple heating-rate Friedman method is based on a comparison of weight-loss rates $(d\alpha/dt)$ for a fractional weight loss, determined at different heating rates. This method utilizes the following natural logarithmic equation:

$$\text{Ln}(d\alpha/dt) = \text{Ln } Z + n \text{ Ln}(1 - \alpha) - E'/RT \quad (4)$$

By plotting $\text{Ln}(d\alpha/dt)$ against $1/T$ for a constant α, E' can be obtained from the slope. The decomposition order n can also be calculated from the slope $(= E'/R)$ of the plot of $\text{Ln}(1 - \alpha)$ versus $1/T$ at a constant $d\alpha/dt$. Then, the Ln Z can easily be obtained from the derived E' and n values according to eq. (4).

4. The fourth method proposed by Kim–Park uses the equations[12]

Table I   Relationship Between Weight Loss and Activation Energy (kJ/mol) of Thermal Degradation in Nitrogen for the Copolymers of B/E/V Molar Ratios of 60/40/0 ([η] = 0.6 dL/g, Sample Size = 22–27 mg); 75/25/0 ([η] = 0.87 dL/g, Sample Size = 30–32 mg); 60/35/5 ([η] = 0.75 dL/g, Sample Size = 25–35 mg); and 75/20/5 ([η] = 1.4 dL/g, sample size = 25–27 mg)

Weight Loss (%)	Flynn–Wall				Hernandez-Sanchez				Reich	
	60/40/0	75/25/0	60/35/5	75/20/5	60/40/0	75/25/0	60/35/5	75/20/5	60/40/0	75/25/0
5	176	189	192	205	195	177	172	169	162	209
10	187	196	203	217	214	251	175	169	193	203
20	199	219	216	234	192	217	183	179	169	232
30	202	228	222	251	192	a	189	a	174	235
45	209	254	235	276	a	330	a	306	184	260

a The data were unacceptable.

Table II Relationship Between Weight Loss and Activation Energy E' (kJ/mol) of Thermal Degradation for Vectra Bipolymer in Nitrogen (Sample Size = 1.5–2.5 mg) and Air (Sample Size = 1.2–1.6 mg)

Weight Loss (%)	Flynn–Wall		Hernandez-Sanchez		Friedman	
	In Nitrogen E'	In Air E'	In Nitrogen E'	In Air E'	In Nitrogen E'/n/Ln Z[a]/r[b]	In Air E'/n/Ln Z[a]/r[b]
5	499	126	377	182	413/2.5/62/0.9806	180/0.8/25/0.9918
10	443	156	384	204	372/2.3/55/0.9898	209/0.9/29/0.9922
20	416	168	388	220	387/2.4/58/0.9998	217/1.0/31/0.9948
30	411	191	451	201	453/2.8/68/0.9951	207/0.9/30/0.9970
40	475	202	c	c	570/—/—/0.9999	163/—/—/0.9996
45	559	160	c	156	568/—/—/0.9999	81/—/9/1.0

[a] The unit of Ln Z is min^{-1}.
[b] r in Tables II and III and V–VII is the linear correlation coefficient.
[c] These data were unacceptable.

$$\text{Ln } q = \text{Ln } Z + \text{Ln}(E'/R)$$
$$+ \text{Ln}[1 - n + (n/0.944)]$$
$$- 5.3305 - 1.0516 \, E'/RT_{\text{dm}} \quad (5)$$
$$n = E'(1 - \alpha_m)/[RT_{\text{dm}}^2(d\alpha/dT)_m] \quad (6)$$

where T_{dm} is the absolute temperature at the maximum rate of thermal decomposition; α_m, the weight loss at the maximum rate of decomposition; and $(d\alpha/dt)_m$, the maximum decomposition rate. E' can be obtained from the slope of Ln q versus $1/T_{\text{dm}}$, and n can be calculated according eq. (6) and the derived E' value. Then, Ln Z is calculated from the intercept value of the line of eq. (5) and derived E' and n values.

5. The fifth method is the Kissinger method

using the following equations[13]:

$$\text{Ln}(q/T_{\text{dm}}^2) = \text{Ln}[n(1 - \alpha_m)^{n-1} ZR/E']$$
$$- E'/RT_{\text{dm}} = \mathbf{I} - E'/RT_{\text{dm}} \quad (7)$$
$$n = (1 - \alpha_m)E' \exp(\mathbf{I})$$
$$\times [\exp(-E'/RT_{\text{dm}})]/R(d\alpha/dt)_m \quad (8)$$

The E' value can be calculated from the slope of the plotting of $\text{Ln}(q/T_{\text{dm}}^2)$ as a function of $1/T_{\text{dm}}$ at the maximum weight-loss rate. The n value can be obtained from eq. (8) using E' and the intercept determined from eq. (7). Finally, the Ln Z value can be calculated from eq. (7) after the n value is known.

6. The sixth method proposed by Hernandez-

Table III Relationship Between Weight Loss and Kinetic Parameters of Thermal Degradation in Nitrogen for B/E/V Copolymers by Friedman Multiple Heating-Rate Method

Weight Loss (%)	60/40/0 E'[a]/n/Ln Z[b]/r	75/25/0 E'[a]/n/Ln Z[b]/r	60/35/5 E'[a]/n/Ln Z[b]/r	75/20/5 E'[a]/n/Ln Z[b]/r
5	204/2.0/32/0.9904	178/2.2/27/0.9992	175/1.4/27/0.9886	173/2.8/26/0.9960
10	226/2.2/36/0.9830	253/3.2/40/0.9997	177/1.5/27/0.9899	171/2.7/26/0.9994
20	208/2.1/33/0.9844	215/2.7/33/0.9934	184/1.5/29/0.9989	182/2.9/28/0.9958
30	212/2.1/34/0.9772	c	190/1.6/30/0.9997	c
45	c	360/—/54/0.9949	c	264/—/40/0.9605

[a] The unit of E' is kJ/mol.
[b] The unit of Ln Z is min^{-1}.
[c] These data were unacceptable.

**Table IV   Effect of B/E/V Ratio on Kinetic Parameters of Thermal Degradation at Weight Loss of 20%
in Nitrogen for B/E/V Copolymers by Friedman Multiple Heating-Rate Method**

B/E/V (mol)	E' (kJ/mol)	n	Ln Z (min^{-1})	Correlation Coefficient
60/40/0	208	2.1	33	0.9844
60/39.95/0.05	188	1.2	29	0.9999
60/38.5/1.5	182	1.4	29	0.9976
60/37.5/2.5	186	1.7	29	0.9986
60/35/5	184	1.5	29	0.9989
65/30/5	207	1.8	33	0.9974
70/25/5	229	3.1	36	0.9978
75/20/5	182	2.9	28	0.9958

Sanchez and Vera-Graziano uses the following two equations[14]:

$$\text{Ln}[(d\alpha_2/dt)/(d\alpha_1/dt)] = (E/R)[(1/T_1) - (1/T_2)] \quad (9)$$

where $d\alpha_1/dt$ and $d\alpha_2/dt$ (or T_1 and T_2) are the two different weight-loss rates (or different temperatures) of the polymer at the same weight loss observed at two different heating rates, respectively. It is clear that E' can be evaluated from the slope of plot of $\text{Ln}[(d\alpha_2/dt)/(d\alpha_1/dt)]$ versus $[(1/T_1) - (1/T_2)]$ at a given weight loss:

$$\text{Ln}[(d\alpha_2/dt)/(d\alpha_1/dt)] = n \, \text{Ln}[(1 - \alpha_2)/(1 - \alpha_1)] \quad (10)$$

where the slope is the decomposition order n at a given temperature.

RESULTS AND DISCUSSION

Relationship Between Weight Loss and the Kinetic Parameters

Figure 1 illustrates the representative TG and DTG curves for the B/E/V (60/37.5/2.5) copolymers in (a) nitrogen and (b) the B/N Vectra polymer in air. The TG and DTG curves for other B/E/V polymers and the Vectra polymer in nitrogen were shown in our earlier articles.[6,15–18] Figure 2 shows the representative plots of the Log(heating rate) against the reciprocal temperature of the Flynn–Wall method for (a) B/E/V (60/40/0) and (b) (60/37.5/2.5). Figure 3 shows representative plots of $\text{Ln}[(d\alpha_2/dt)/(d\alpha_1/dt)]$ versus $[(1/T_1) - (1/T_2)]$ of the Hernandez-Sanchez

method applied to calculate the activation energy E' of the thermal degradation for the polymers with the following B/E/V ratios: (a) 60/40/0, (b) 60/35/5, and (c) 75/20/5 and (d) for the Vectra copolymer in nitrogen and air. Figure 4 shows the typical function of $\text{Ln}(d\alpha/dt)$ against the recipro-
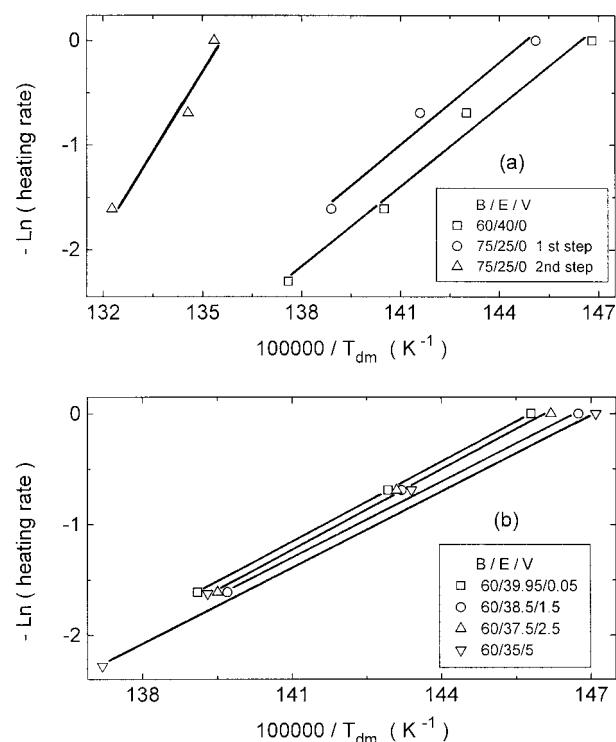

Figure 6   Kim–Park method [Ln(heating rate) versus $1/T_{\text{dm}}$ plot] applied to calculate activation energy of thermal degradation for the polymers with the following B/E/V ratios: (a) (□) 60/40/0, (○) 75/25/0 at the first degradation step, and (△) 75/25/0 at the second degradation step; (b) (□) 60/39.95/0.05, (○) 60/38.5/1.5, (△) 60/37.5/2.5, and (▽) 60/35/5.
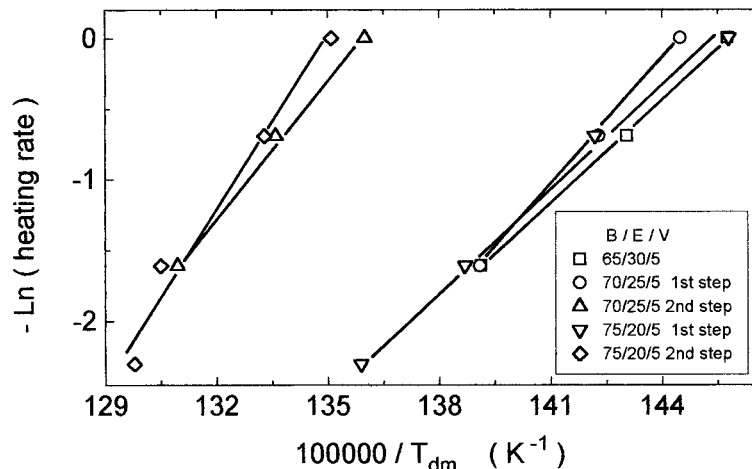
Figure 7 Kim–Park method applied to calculate activation energy of thermal degradation for the polymers with the following B/E/V ratios: (□) 65/30/5; (○) 70/25/5 at the first degradation step; (△) 70/25/5 at the second degradation step; (▽) 75/20/5 at the first degradation step; (◇) 75/20/5 at the second degradation step.

cal temperature applied to calculate the activation energy of the thermal degradation for B/E/V polymers with the following monomer ratios: (a) 60/40/0, (b) 75/25/0, (c) 60/35/5, and (d) 75/20/5 in a weight-loss range from 5 to 45% and (e) five other different B/E/V molar ratios at a given weight loss of 20% of the Friedman method. Figure 5 shows the typical function of $Ln(1 - \alpha)$ versus the reciprocal of the absolute temperature in order to calculate the reaction order n of the thermal degradation for B/E/V polymers with different monomer ratios and the B/N Vectra polymer.

The activation energies E' of the thermal degradation for the B/E/V and B/N Vectra polymers calculated by the Flynn–Wall, Hernandez-Sanchez, and Reich methods are listed in Tables I–III. It can be seen from Tables I–III that the E' values for the four B/E/V polymers obtained by the Flynn–Wall method and for the B/E/V (60/35/5) and (75/20/5) polymers by the Friedman method increase steadily with an increase in weight loss from 5 to 45%. The E' values of the Vectra polymer in air by the Flynn–Wall method and in nitrogen by the Hernandez-Sanchez method also increase continuously with increasing weight loss from 5 to 40%, as listed in Table II. The other E' values generally exhibit an increasing tendency but sometimes decrease with enhancing weight loss. The decomposition order n values obtained by the Friedman method vary in a small range with a variation of weight loss. In detail, the n values are between 0.8 and 1.0 for

the Vectra polymer in air, between 2.0 and 2.2 for the B/E/V (60/40/0) polymer, between 1.4 and 1.6 for the B/E/V (60/35/5) polymer, and between 2.7 and 2.9 for the B/E/V (75/20/5) polymer.

Effect of Polymer Composition on Kinetic Parameters

According to the information in Table IV from Figure 4, the kinetic parameters for the B/E/V polymer family calculated at a fixed weight loss of 20% by the Friedman method exhibit a small variation with a changing unit-V content from 0
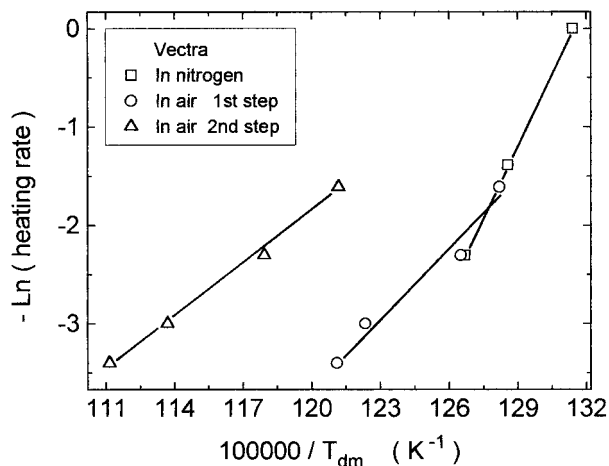

Figure 8 Kim–Park method applied to calculate activation energy of thermal degradation for B/N Vectra copolymer in nitrogen and air.
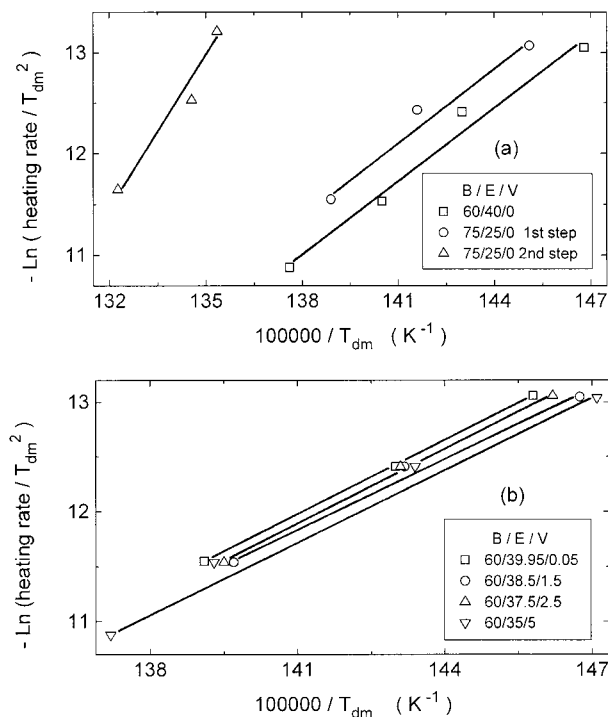
Figure 9 Kissinger method [Ln(heating rate/T_{dm}^2) versus $1/T_{dm}$ plot] applied to calculate activation energy of thermal degradation for the polymers with the following B/E/V ratios: (a) ($\square$) 60/40/0, ($\bigcirc$) 75/25/0 at the first degradation step, and ($\triangle$) 75/25/0 at the second degradation step; (b): ($\square$) 60/39.95/0.05, ($\bigcirc$) 60/38.5/1.5, ($\triangle$) 60/37.5/2.5, and ($\triangledown$) 60/35/5.

to 5 mol % or unit-B content from 60 to 75 mol %. The B/E/V (70/25/5) polymer shows the largest E' value of 229 kJ/mol, while both the B/E/V (60/38.5/1.5) and (75/20/5) polymers show the smallest E' of 182 kJ/mol.

Figures 6–8 show the plots of the Ln(heating rate) versus $1/T_{dm}$ of the Kim–Park method to calculate activation energy E' of the thermal degradation for the B/E/V and B/N Vectra polymers. Figures 9 and 10 show plots of the Ln(heating rate/T_{dm}^2) versus $1/T_{dm}$ according the Kissinger method applied to calculate the activation energy E' of the thermal degradation for the B/E/V polymers. Figure 11 shows typical plots of the Ln[($d\alpha_2/dt$)/($d\alpha_1/dt$)] against Ln[$(1 - \alpha_2)/(1 - \alpha_1)$] of the Hernandez–Sanchez method to calculate the decomposition reaction order n of the thermal degradation for the B/E/V (75/25/0) and B/N Vectra polymers, respectively.

As seen in Tables V and VI, the variation of the kinetic parameters of the B/E/V polymers calculated by the Kim–Park, Kissinger, and Hernandez-Sanchez techniques with the B/E/V monomer molar ratio is also small. The variation range of the E' for the first stage of thermal degradation is from 176 to 235 kJ/mol. The kinetic parameters of the second stage of thermal degradation are higher than those of the first-stage degradation.
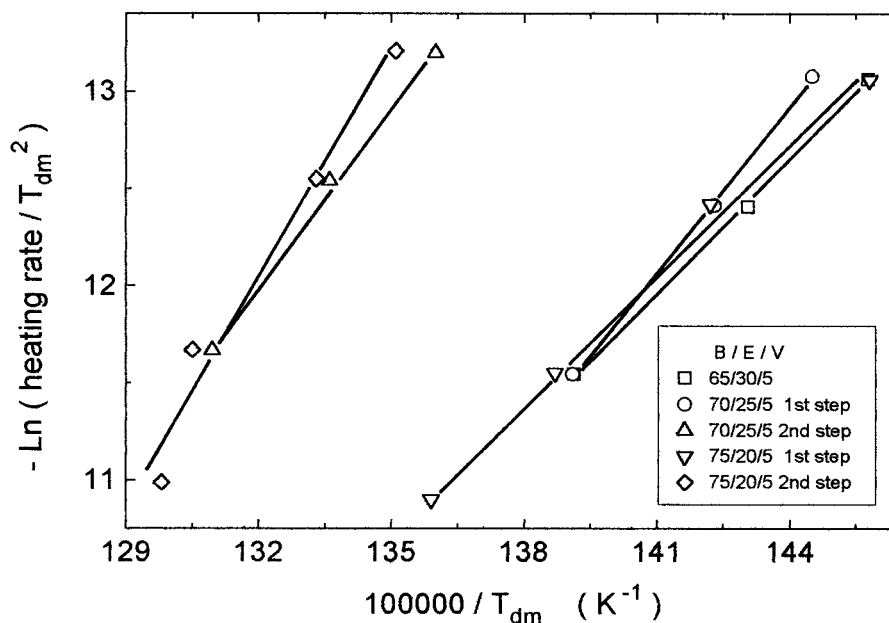

Figure 10 Kissinger method applied to calculate E' values of thermal degradation for the polymers with the following B/E/V ratios: ($\square$) 65/30/5; ($\bigcirc$) 70/25/5 at the first degradation step; ($\triangle$) 70/25/5 at the second degradation step; ($\triangledown$) 75/20/5 at the first degradation step; ($\diamond$) 75/20/5 at the second degradation step.
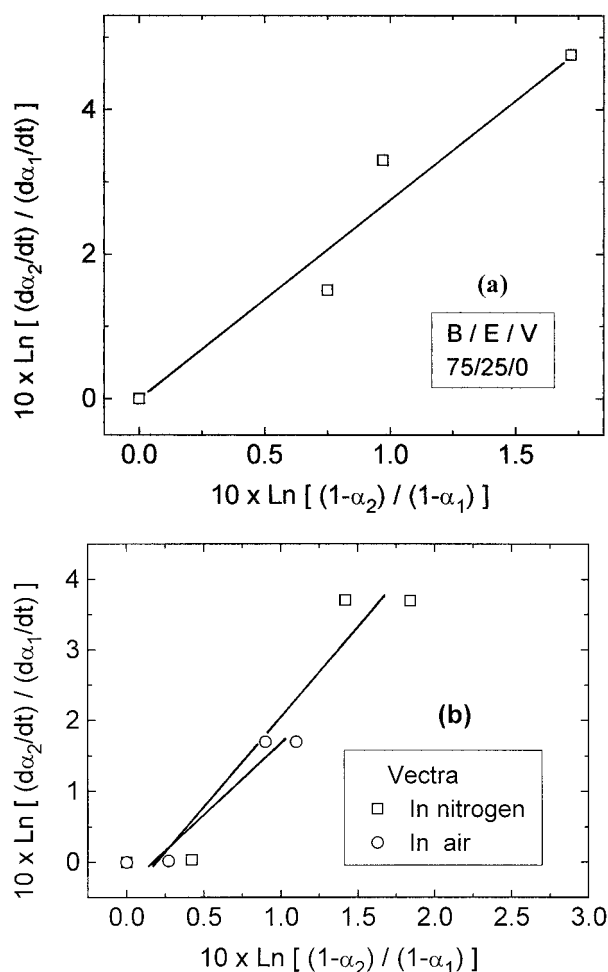
Figure 11 Hernandez-Sanchez method applied to calculate reaction order n of thermal degradation for (a) B/E/V (75/25/0) polymer and (b) B/N Vectra polymer in nitrogen and air.

The largest E', n, and Ln Z at the second degradation stage were found to be 397 kJ/mol, 7.1, and 64 min^{-1} for the B/E/V (75/25/0) polymer. It appears that the some heat-resistant polymers such as aromatic liquid crystalline polyesters and aromatic polyimide exhibit much larger E' and n values, suggesting a much slower decomposition kinetics. On the contrary, according to Table VII, the kinetic parameters of the thermal degradation of the Vectra polymer in air are higher at the first stage than at the second stage, whereas the kinetic parameters of the degradation for the Vectra polymer at the first stage are higher in nitrogen than in air, indicative a higher thermostability in nitrogen.

Effect of Calculating Method on the Kinetic Parameters

According to Tables I–III and V–VII and our previous articles,[6,15–18] the kinetic parameters of the thermal degradation for the B/E/V and B/N Vectra polymers change slightly with the variation of the calculating methods. Only a wider variation in the calculated E' value by the Flynn–Wall, Hernandez-Sanchez, and Friedman techniques was sometimes observed in the case of the B/N Vectra copolyester listed in Table II. This suggests that all the six methods used in this article appear suitable to calculate the kinetic parameters of the thermal degradation of the thermotropic liquid crystalline polymers and the kinetic parameters obtained could be correct. Note that the Hernandez-Sanchez method is the most complicated and the most difficult to use, and appears to show the smallest linearly correlation coefficients for calculation of the activation energy. Es-

Table V   Kinetic Parameters of the First Stage of Thermal Degradation in Nitrogen for the B/E/V Copolymers Calculated by Multiple Heating-Rate Methods

B/E/V (mol)	Sample Size (mg)	Kim–Park E' [a]/n/Ln Z[a]/r	Kissinger E' [a]/n/Ln Z[a]/r	Hernandez-Sanchez E' [a]/n/Ln Z[a]/r
60/40/0	22–27	203/2.4/33/0.9914	202/2.2/32/0.9904	192/2.4/30/0.9552
75/25/0	30–32	203/4.2/32/0.9881	201/4.1/32/0.9864	217/2.9/34/0.9900
75/25/0[b]	30–32	390/7.0/61/0.9810	397/7.1/64/0.9799	330/[c]/[c]/0.9249
60/39.95/0.05	26–29	189/2.2/30/0.9995	187/2.1/29/0.9995	188/[c]/[c]/0.9997
60/38.5/1.5	25–27	178/2.1/28/0.9927	176/1.9/28/0.9918	183/[c]/[c]/0.9931
60/37.5/2.5	24	190/2.3/30/0.9993	189/2.3/30/0.9992	185/[c]/[c]/0.9957
60/35/5	25–35	182/2.4/29/0.9920	179/2.7/28/0.9908	183/1.7/28/0.9963

[a] The units of E' and Ln Z are kJ/mol and min^{-1}, respectively.
[b] The kinetic parameters of the second stage of thermal degradation.
[c] These data were unacceptable.

Table VI   Kinetic Parameters of the Thermal Degradation in Nitrogen for the B/E/V Terpolymers with Different B-unit Content Calculated by Multiple Heating-Rate Methods[a]

B/E/V (mol)	Sample Size (mg)	Degradation Stage	Kim–Park[a] E'/n/Ln Z/r	Kissinger[a] E'/n/Ln Z/r	Hernandez-Sanchez[a] E'/n/Ln Z/r
60/35/5	25–35	First stage	182/2.4/29/0.9920	179/2.7/28/0.9908	183/1.7/28/0.9963
65/30/5	23–25	First stage	191/2.8/30/0.9998	189/2.9/30/0.9996	208/2.2/33/0.9938
70/25/5	27–29	First stage	235/5.4/38/0.9997	235/5.7/37/0.9996	218/4.6/35/0.9819
70/25/5	27–29	Second stage	252/6.4/38/0.9987	253/6.7/40/0.9987	220/[b]/[b]/0.9992
75/20/5	25–27	First stage	186/4.8/29/0.9978	184/4.5/28/0.9975	179/2.3/27/0.9854
75/20/5	25–27	Second stage	320/6.6/49/0.9860	324/7.6/52/0.9851	306/[b]/[b]/0.9930

[a] The units of the E' and Ln Z are kJ/mol and min^{-1}, respectively.
[b] These data were unacceptable.

pecially, the determination of the decomposition order by the Hernandez-Sanchez method seems to be uncertain. Sometimes, the decomposition activation energy and order cannot be evaluated by the Hernandez-Sanchez method, as shown in Tables I and V–VII. Through the Flynn–Wall and Reich methods, only the activation energy can be obtained. Both the Kim–Park and Kissinger methods can be employed to calculate the three kinetic parameters of the thermal degradation only at the maximum weight losses, although the Kim–Park method is more easily used than is the Kissinger method. Obviously, only the Friedman method exhibits the largest linearly correlation coefficients and can be the most easily used to calculate three kinetic parameters at different weight losses at the same time.

Generally speaking, the multiple heating-rate methods including the Kim–Park, Kissinger, and Hernandez-Sanchez methods employed in this study are more complex and difficult than are the single heating-rate methods discussed in our earlier articles.[6,8,16,17] The kinetic parameters calculated through both types of methods are hardly ever the same. The kinetic parameters of the first degradation stage for the B/E/V polymers in nitrogen and the B/N Vectra polymer in air calcu-

lated by multiple heating-rate methods are smaller than those calculated by single heating-rate methods,[6,17] but the kinetic parameters of the second degradation stage for the B/E/V (75/25/0), (70/25/5), and (75/20/5) polymers calculated by multiple heating-rate methods are larger. Only the activation energies of the Vectra polymer calculated by multiple heating-rate methods are larger than those by single heating-rate methods. As shown in Table II, the two smallest activation energy values were found to be 81 kJ/mol determined by the Friedman method and 126 kJ/mol by the Flynn–Wall method for the B/N Vectra polymer at the weight losses of 45 and 5%, respectively, but the largest activation energy value was 570 kJ/mol for the thermal degradation at the weight loss of 40–45% of the B/N Vectra copolymer in nitrogen determined by the Friedman method.

CONCLUSIONS

The thermogravimetric kinetics of the two series of thermotropic liquid crystalline copolymers, that is, (1) poly(*p*-oxybenzoate-*co*-ethylene terephthalate-*co*-vanillate) and (2) poly(*p*-oxybenzoate-*co*-2,6-

Table VII   Kinetic Parameters of the Thermal Degradation in Nitrogen and Air for B/N Vectra Bipolymer Calculated by Three Multiple Heating-Rate Methods[a]

Testing Atmosphere	Sample Size (mg)	Degradation Stage	Kim–Park E'/n/Ln Z/r	Kissinger E'/n/Ln Z	Hernandez-Sanchez E'/n/Ln Z/r
Nitrogen	1.5–2.5	First stage	387/3.1/59/0.9999	370/2.0/56	388/2.4/58/0.9995
Air	1.2–1.6	First stage	187/1.7/27/0.9912	208/1.9/30	220/1.8/32/0.9897
Air	1.2–1.6	Second stage	141/0.3/19/0.9977	152/0.3/20	156/—/—/0.9642

[a] The units of the E' and Ln Z are kJ/mol and min^{-1}, respectively.

oxynaphthoate), can be analyzed successively by six multiple heating-rate techniques. It appears that there is a significant influence of the copolymer composition, weight loss, degradation stage, test atmosphere, and calculating technique on the kinetic parameters of the thermal degradation. The Friedman and Kim–Park techniques could be the best techniques of the six techniques for evaluation of the thermogravimetric kinetic parameter.

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