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THERMAL DEGRADATION KINETICS OF THERMOTROPIC COPOLY (P-OXYBENZOATE-ETHYLENE TEREPHTHALATE-VANILLATE) BY A HIGH-RESOLUTION THERMOGRAVIMETRY

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Key Words: p-Hydroxybenzoic Acid Copolymer, Vanillic Acid-Containing Polymer, Liquid Crystal Polymer, Aromatic Polyester, High-Resolution Thermogravimetry, Thermal Degradation, Decomposition Kinetics, Isothermal Degradation

ABSTRACT

Thermotropic liquid crystalline terpolymers consisting of three units of p-oxybenzoate (B), ethylene terephthalate (E), and vanillate (V), were studied through a high-resolution thermogravimetry to ascertain their thermostability and kinetics parameters of thermal decomposition in nitrogen and air. Overall activation energy data of the major decomposition have been calculated through four calculating techniques. The thermal degradation occurs in three steps in nitrogen, but in four steps in air due to an additional thermo-oxidative step. The thermal degradation temperatures are higher than 436°C in nitrogen and 424°C in air and increase with increasing B-unit content at a fixed V-unit content

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of 5 mol%. The temperatures at the first maximum weight-loss rate are higher than 444°C in nitrogen and 431°C in air and increase slightly with an increase in B-unit content. The first, second, and third maximum weight-loss rates almost maintain at 10-11, 10-11, and 3.6-5.3%/min regardless of copolymer composition and testing atmosphere. The char yields at 500°C in both nitrogen and air are larger than 40 wt% and increases with increasing B-unit content. But the char yields at 800°C in nitrogen and air are quite different, i.e., 18-25 wt% in nitrogen and 0 wt% in air. The activation energy and Ln (pre-exponential factor) for the major decomposition are higher in nitrogen than in air and decrease slightly with an increase in B-unit content at a given V-unit content 5 mol%. There is no regular variation in the decomposition order with the variation of copolymer composition and testing atmosphere. It is found that the most V-unit-containing terpolymer exhibited the lowest degradation temperature, lowest activation energy, and lowest Ln (pre-exponential factor). The activation energy, decomposition order, and Ln (pre-exponential factor) of the thermal degradation for the terpolymers, are situated in the ranges of 121-248 kJ/mol, 1.5-2.8, 19-38 min⁻¹, respectively. These results indicate that the terpolymers exhibit high thermostability. The isothermal decomposition kinetics of the terpolymer at 450°C have also been discussed and compared with the results obtained based non-isothermal high-resolution thermogravimetry.

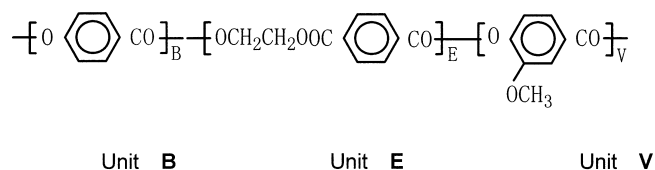
INTRODUCTION

There has been a continual increase in interest with respect to the utilization of liquid crystalline polymers as a means of preparing high strength, high modulus, and high heat resistant materials. It is well known that the thermotropic liquid crystalline polymers with largely aromatic repeat units show high thermostability [1-7]. However, relatively few studies have been reported on the thermostability and thermal degradation kinetics of the thermotropic polymers, especially BEV terpolymers in which B, E, and V denote p-oxyBenzoate, Ethylene terephthalate, and Vanillate units, respectively. It is considered that a more detailed study would be of value because the BEV terpolymers must encounter elevated temperatures at almost every step in the manufacturing, compounding and processing steps as well as in service and during repair. The synthesis, structure, and properties of the BEV terpolymers have been investigated and considered as a new kind of high performance polymer with good processing ability and high mechanical property [7-12].

In this article, we have attempted to investigate the thermostability and several important kinetic parameters of the **BEV** terpolymers by performing a detailed high-resolution thermogravimetric (TG) and derivative thermogravimetric (DTG) analyses at a variable heating rate and isothermal thermogravimetry in nitrogen and air. The variation of the thermostability and kinetic parameters of the **BEV** terpolymers is also discussed in detail. This topic may be important in revealing the intrinsic thermal degradation kinetics of the thermotropic liquid crystalline aromatic copolymers.

EXPERIMENTAL

The thermotropic liquid crystalline terpolymers studied in this paper are the terpolyesters synthesized from m-methoxy-p-acetoxybenzoic acid (i.e. acetoxyvanillic acid), p-acetoxybenzoic acid and poly(ethylene terephthalate) in different monomer ratios. The terpolymers were prepared according to the earlier procedures [7]. These terpolyesters are designated as BEV terpolymers for brevity in this study. These terpolymers have random statistical distribution of **B**, **E**, and **V** three units along the macromolecular chain according to 400 MHz ¹H-NMR spectral and wide-angle X-ray meridional diffraction studies [8, 9] and they have the general molecular structure:



TG analyses were performed under the nitrogen flow of 25 mL/min and air flow of 40 mL/min on a model high-resolution TGA 2950 thermal analyzer (Hi-ResTM TGA) induced by TA-Instruments Inc, New Castle, Delaware, using the high resolution mode interfaced to TA-Instruments 2000 controller with General V.4.1C microprocessor. High-resolution TG and DTG curves at a variable heating rate were obtained under the following conditions: sample size was 1.6-2.3 mg in nitrogen and 1.1-1.5 mg in air; the initial heating rate and resolution were fixed at 50°C/min and 3.0, respectively; the sensitivity was fixed at its default value of 1 in the temperature range of 25~800. Isothermal TG and DTG curves were obtained with the sample size 0.8 mg in nitrogen and 1.2 mg in air at a fixed temperature of 450°C. The thermal degradation temperatures and

kinetic parameters were determined using the techniques described previously [2-6].

Friedman method utilizes the following natural logarithmic equation [13]:

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

By plotting $\text{Ln } (d\alpha/dt) = \text{Ln } (1 - \alpha)$ against $1/T$, a straight line can be obtained with a slope of $-E'/R$ or $-E'/n \cdot R$.

Chang method uses the following equation [14]:

$$\text{Ln } [(d\alpha/dt) / (1 - \alpha)^n] = \text{Ln } Z - E'/R T \quad (2)$$

A plot of $\text{Ln } [(d\alpha/dt) / (1 - \alpha)^n]$ against $1/T$ will yield a straight line only if the decomposition reaction order n was correctly selected. The slope of the line will provide the E' and the intercept provides $\text{Ln } Z$.

Freeman-Carroll method uses the equation [15]:

$$[\Delta \text{Ln } (d\alpha/dt)] / \Delta \text{Ln } (1 - \alpha) = n - (E'/R) \cdot \Delta (1/T) / \Delta \text{Ln } (1 - \alpha) \quad (3)$$

From a plot of $[\Delta \text{Ln } (d\alpha/dt)] / \Delta \text{Ln } (1 - \alpha)$ against $\Delta (1/T) / \Delta \text{Ln } (1 - \alpha)$, $-E'/R$ and n may be determined from the slope and intercept of the plot when a regular $\Delta (1/T)$ value was taken.

Kissinger method can calculate the n value directly from the symmetrical index of derivative thermogravimetry (DTG) peak [16]:

$$n = 1.88 \cdot (d^2 \alpha/d t^2)_L / | (d^2 \alpha/d t^2)_R | \quad (4)$$

where indices L and R correspond the maximum and minimum $d^2 \alpha/d t^2$ values on the second derivative thermogravimetry (2DTG) curves.

Isothermal TG curves at a constant temperature could be predicted according to the equation [17]:

$$t = [1 - (1-\alpha)^{1-n}] \cdot \exp(E' / RT) / [Z(1-n)] \quad (n \neq 1) \quad (5)$$

The t is the lifetime of polymer to failure at the weight loss of α .

The degradation temperature, T_d , was obtained by an extrapolation of the initial degradation portion of the TG curve. T_{m1} , T_{m2} , T_{m3} , and T_{m4} correspond to the peak temperatures at the first, second, third, and fourth maxima on the DTG curves, respectively. $(d\alpha/dt)_{m1}$, $(d\alpha/dt)_{m2}$, $(d\alpha/dt)_{m3}$, and $(d\alpha/dt)_{m4}$ [or $(d\alpha/dT)_{m1}$, $(\alpha/dT)_{m2}$, $(d\alpha/dT)_{m3}$, and $(d\alpha/dT)_{m4}$] represent the maximal weight-loss rates at the first, second, third, and fourth maxima on the DTG curves, respectively. These data were compared with existing literature values obtained by a traditional TG at a constant heating rate published earlier by us [18].

The errors of determining the temperature and rate of the decomposition are less than 2% and the largest calculating errors in the kinetic parameters of thermal decomposition for the best three methods developed by Friedman, Chang, and Freeman-Carroll are ca. 5%.

RESULTS AND DISCUSSION

Figures 1 and 2 show the high-resolution thermogravimetry (TG), derivative thermogravimetry (DTG), the second derivative thermogravimetry (2DTG) and heating-rate curves for six BEV terpolymers with B/E/V molar ratios of 50/35/15, 60/39/1, 60/35/5, 65/30/5, 70/25/5, and 75/20/5 at an initial heating rate of 50°/min in nitrogen and air. The thermal decomposition results are given in Table 1. Comparing the thermal decomposition parameters in nitrogen with those obtained in air, all BEV terpolymers exhibit higher T_d , T_{m1} , T_{m2} , T_{m3} , char yield at 800°C listed in Table 1 in nitrogen. This results from the thermo-oxidative degradation or even combustion in air, because an obvious additional thermo-oxidative degradation peak appears at a higher temperature, designated here as T_{m4} . These suggest that the onset of the bond cleavage in the BEV terpolymers is basically thermal in nature and also influenced by the presence of oxygen.

As shown in Table 1, the T_d , T_{m1} , and char yield at 500°C increase with increasing B-unit content from 50 to 60 mol% at a fixed E-unit content 35 mol%, with increasing V-unit content from 1 to 5 mol% at a fixed B-unit content 60 mol%, or with increasing B-unit content from 60 to 75 mol% at a fixed V-unit content of 5 mol% in both testing atmospheres. But the T_{m4} decreases with an increase in B-unit content at a given V-unit content 5 mol%. It is concluded that

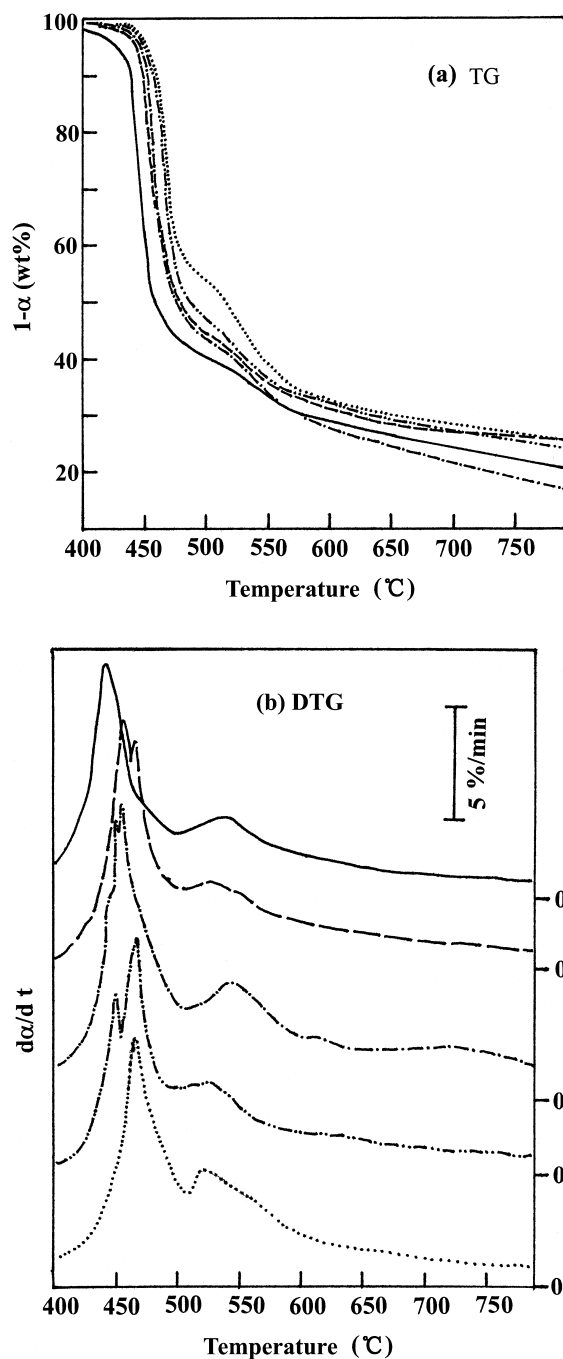


Figure 1. High-resolution TG (a), DTG (b), 2DTG (c) and heating rate (d) curves of copoly [p-oxybenzoate(B)-ethylene terephthalate(E)-vanillate(V)] with five B/E/V molar ratios in nitrogen at an initial heating rate of 50°C/min and resolution 3.0. (—) 50/35/15; (---) 60/39/1; (- · - ·) 60/35/5; (- · · ·) 65/30/5; (····) 70/25/5.

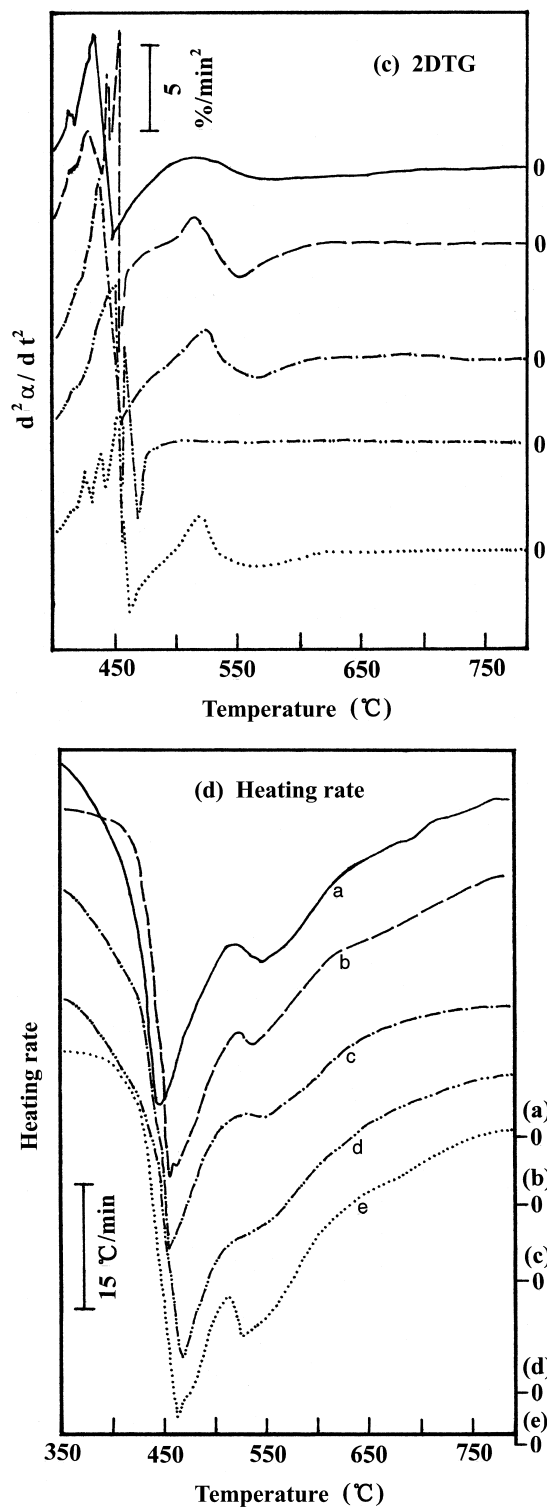


Figure 1. (continued).

TABLE 1. Thermostability Parameters of the B/E/V molar ratios: (\square) 50/35/15; (\circ) 60/39/1; (Δ) 60/35/5; (∇) 65/30/5; (\diamond) 70/25 Copolymers by High-Resolution Thermogravimetry

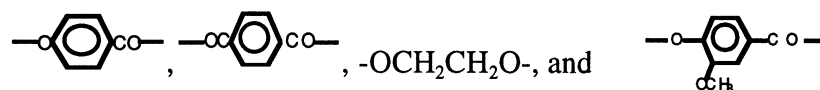
| B / E / V | $[\eta]^a$ | Atmos- | $T_d / T_{m1} / T_{m2} / T_{m3} / T_{m4}$ | $(d\alpha/dt)_{m1} / (d\alpha/dt)_{m2} / (d\alpha/dt)_{m3} / (d\alpha/dt)_{m4}$ | Char yield |
|-----------|------------|----------|---|---|---------------------------------|
| (mol) | (dL/g) | phere | ($^{\circ}\text{C}$) | (%/min) | at 500 / 800 $^{\circ}\text{C}$ |
| | | | | | (wt %) |
| 50/35/15 | -b | Nitrogen | 436 / 444 / - / 539 / - | 11 / - / 3.6 / - | 40 / 21 |
| 60/39/1 | 0.70 | Nitrogen | 446 / 452 / 459 / 522 / - | 11 / 10 / 3.8 / - | 45 / 25 |
| 60/35/5 | 0.76 | Nitrogen | 447 / 447 / 456 / 533 / - | 11 / 11 / 4.3 / - | 44 / 17 |
| 65/30/5 | 0.87 | Nitrogen | 448 / 450 / 465 / 527 / - | 8.1 / 10 / 4.1 / - | 47 / 25 |
| 70/25/5 | 1.02 | Nitrogen | 452 / 457 / 459 / 521 / - | 9.9 / 11 / 5.3 / - | 54 / 24 |
| 50/35/15 | -b | Air | 424 / 431 / - / 504 / 527 | 10 / - / 4.1 / 15 | 42 / 0 |
| 60/39/1 | 0.70 | Air | 436 / 439 / 446 / 516 / 578 | 9.6 / 12 / 3.6 / 11 | 42 / 0 |
| 60/35/5 | 0.76 | Air | 437 / 440 / 446 / 524 / 584 | 9.7 / 10 / 3.7 / 10 | 45 / 0 |
| 65/30/5 | 0.87 | Air | 439 / 442 / 447 / 518 / 580 | 10 / 9.8 / 4.0 / 13 | 47 / 0 |
| 70/25/5 | 1.02 | Air | 440 / 444 / 450 / 513 / 570 | 10 / 9.1 / 4.9 / 12 | 51 / 0 |
| 75/20/5 | 1.80 | Air | 445 / 452 / 456 / 518 / 563 | 10 / 9.8 / 5.3 / 14 | 54 / 0 |

a Measured in phenol / sym-tetrachloroethane (50/50 vol.) at 30 $^{\circ}\text{C}$

b Not measured

the thermostability of the BEV terpolymers will enhance with increasing B-unit content to some extent.

The final char residue was calculated on the basis of the BEV terpolymer structure [19]. The group contributions to char formation of,



are supposed to be 4, 1.25, 0, and 2.0, respectively. According to these data, the predicted char yield for the terpolymers with the B/E/V ratios of 50/35/15, 60/39/1, 60/35/5, 65/30/5, and 70/25/5 are 21.9, 23.5, 24.0, 25.8, and 27.6%, respectively. Apparently, the predicted char yield is rough in agreement with the char yield at 800°C in nitrogen. This indicates that the final char yield of the BEV terpolymers in inert atmosphere is an additive parameter.

If the DTG and 2DTG curves were obtained at a traditional constant heating rate, the respective $(d\alpha/dt)$ and $(d^2\alpha/dt^2)$ curves will be exactly the same as $(d\alpha/dT)$ and $(d^2\alpha/dT^2)$ curves. But the situation is different when the DTG and 2DTG curves were obtained at a variable heating rate of high-resolution mode. Compared Figures 2b and 2c with Figure 3, it demonstrates that the high-resolution $(d\alpha/dt)$ plots generally exhibit higher resolution than the high-resolution $(d\alpha/dT)$ plots. The $(d\alpha/dT)$ plots look smoother than the high-resolution $(d\alpha/dt)$ curves which exhibit a doublet. This doublet might result from the two different degradation processes of main chain. The respective weight losses after the first major DTG peak on the high-resolution $(d\alpha/dt)$ curves of six BEV terpolymers with the B/E/V molar ratios of 50/35/15, 60/39/1, 60/35/5, 65/30/5, 70/25/5, and 75/20/5 are 52.9, 52.0, 53.0, 50.3, 48.0 and no datum in nitrogen and 52.0, 51.8, 51.0, 50.2, 47.2, and 46.0% in air which are close to the weight losses of 51.9, 51.5, 50.9, 49.7, 48.3, and 47.0% after the complete loss of whole ester, ethylene, and methoxyl groups and hydrogen atom on the polymer chains. Therefore, it could be speculated that the first major thermal degradation of the BEV terpolymers might be attributed to the cleavage of the ester linkage and simultaneous removal of the ethylene and methoxyl groups and hydrogen atom. The subsequent degradation might result from the partial pyrolysis of aromatic carbon from benzene ring.

Figures 4-6 show the kinetic plots according to Friedman, Chang, and Freeman-Carroll methods. Based upon a visual examination of the plots in Figures 4 and 5, it is clear that applying a straight line analysis of the data in the whole temperature range appears incorrect. In many cases obvious curvature of

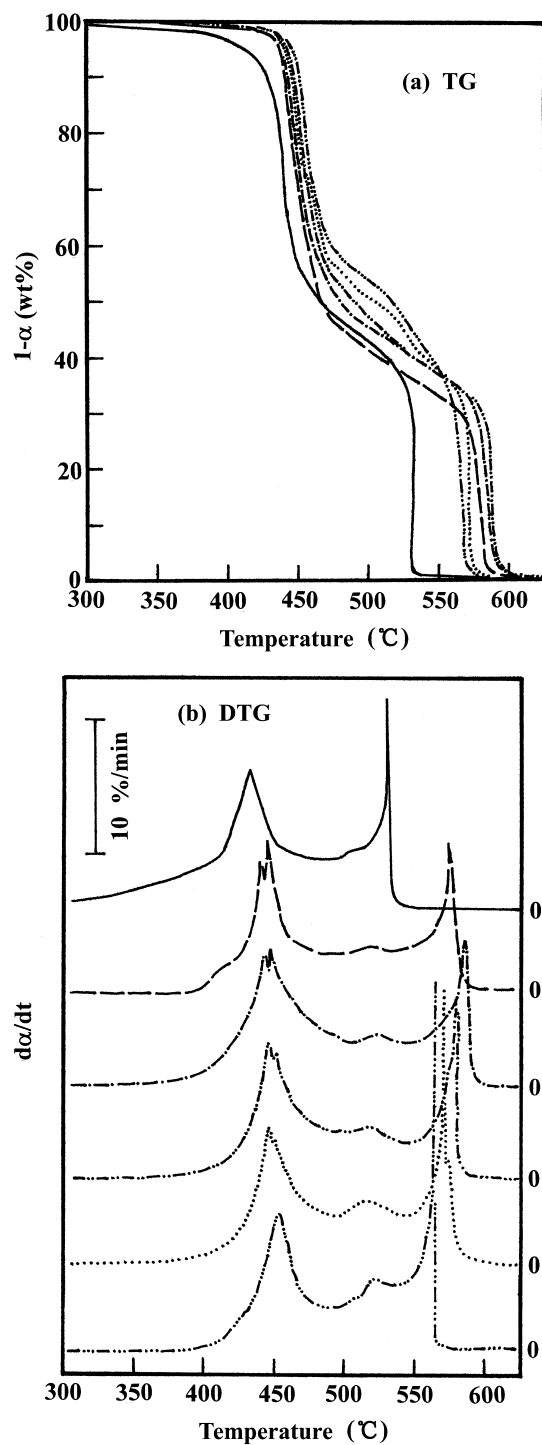


Figure 2. High-resolution TG (a), DTG (b), 2DTG (c) and heating rate (d) curves of copoly [p-oxybenzoate(B)-ethylene terephthalate(E)-vanillate(V)] with six B/E/V molar ratios in air at an initial heating rate of 50°C/min and resolution 3.0. (—) 50/35/15; (---) 60/39/1; (-·-·-·) 60/35/5; (-·-·-·) 65/30/5; (····) 70/25/5; (-·-·-·) 75/20/5.

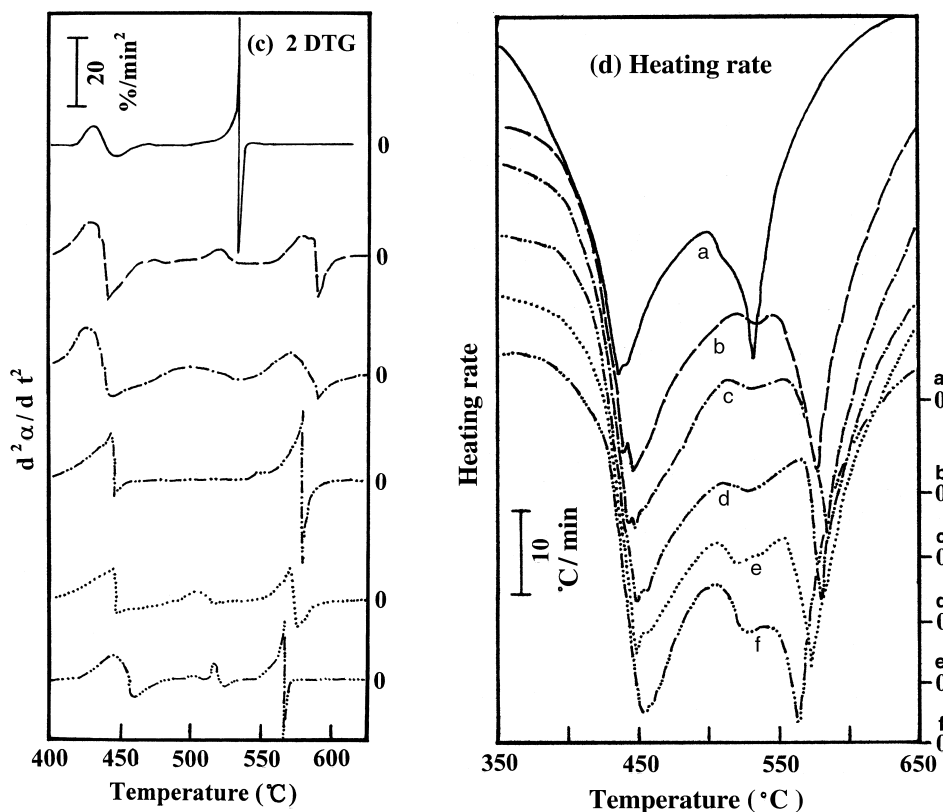


Figure 2. (continued).

the plots are evident. This is not to be unexpected based on the composition of the polyesters being studied. This is also borne out by the fact that n changes, not only with composition, but also with extent of degradation. However, a straight line analysis of the data in the reciprocal temperature range from 0.001365 to 0.001485 K^{-1} in nitrogen or 0.00139 to 0.001515 K^{-1} in air seems correct. The kinetic parameters of thermal degradation for BEV terpolymers obtained from Figures 4-6 in the above-mentioned temperature range by *Friedman*, *Chang*, *Freeman-Carroll*, and *Kissinger* methods are presented in Table 2. It can be seen from Table 2 that the variation of three kinetic parameters with the terpolymer composition is different from that of the degradation temperatures. The average E' and $\text{Ln } Z$ values increase with increasing B-unit content from 50 to 60 mol% at a fixed E-unit content 35 mol% in both testing atmospheres. However, the average E' and $\text{Ln } Z$ values decrease with increasing V-unit content from 1 to 5 mol% at a fixed B-unit content 60 mol% or with increasing B-unit content from

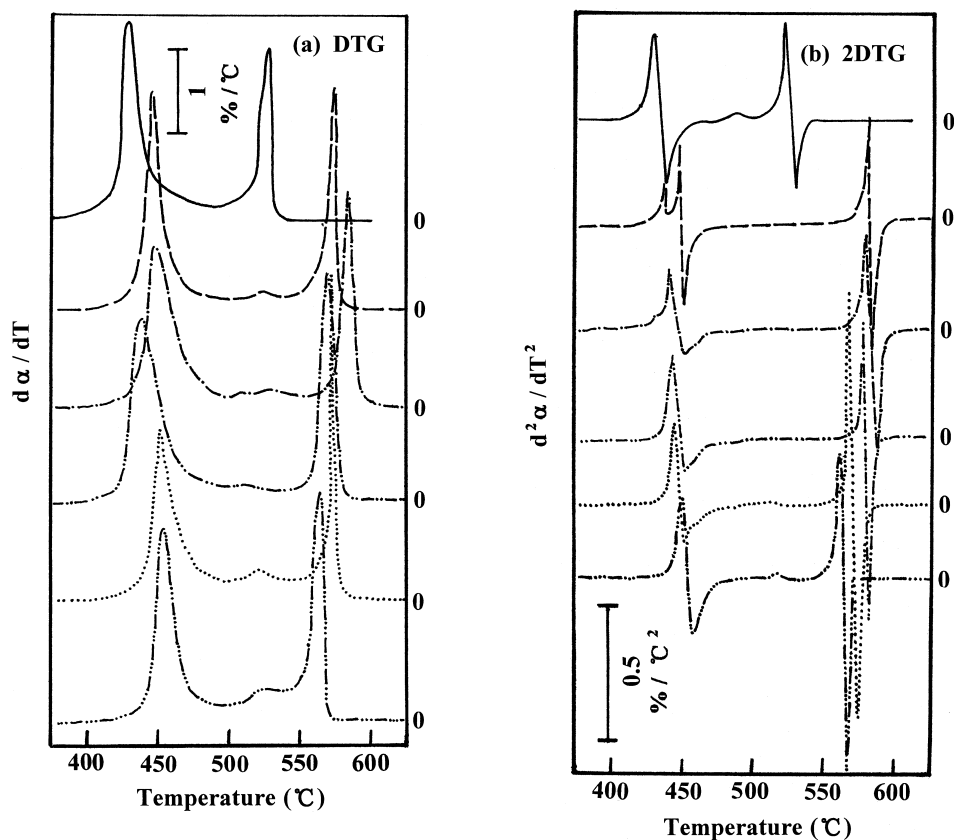


Figure 3. High-resolution ($d\alpha/dT$) curves (a) and ($d^2\alpha/dT^2$) curves (b) of copoly [p-oxybenzoate(B)-ethylene terephthalate(E)-vanillate(V)] with six B / E / V molar ratios in air at an initial heating rate of 50°C/min and resolution 3.0. (—) 50/35/15; (---) 60/39/1; (-·-·-) 60/35/5; (-·-·-·) 65/30/5; (····) 70/25/5; (-·-·-·-·) 75/20/5.

60 to 75 mol% at a fixed V-unit content of 5 mol%. A similar variation of the kinetic parameters for the BEV terpolymers has been observed by a traditional TG at a constant heating rate in nitrogen [18]. Especially, the B/E/V (60/39/1) terpolymer containing the smallest V-unit shows the largest activation energy and frequency factor among the six terpolymers. It is concluded that the thermal degradation rate of the BEV terpolymers in both nitrogen and air will lower with decreasing B-unit or V-unit content to some extent. This is different from the variation of the thermal degradation temperature with copolymer composition. Note that the decomposition reaction order n change irregularly with a variation of copolymer composition.

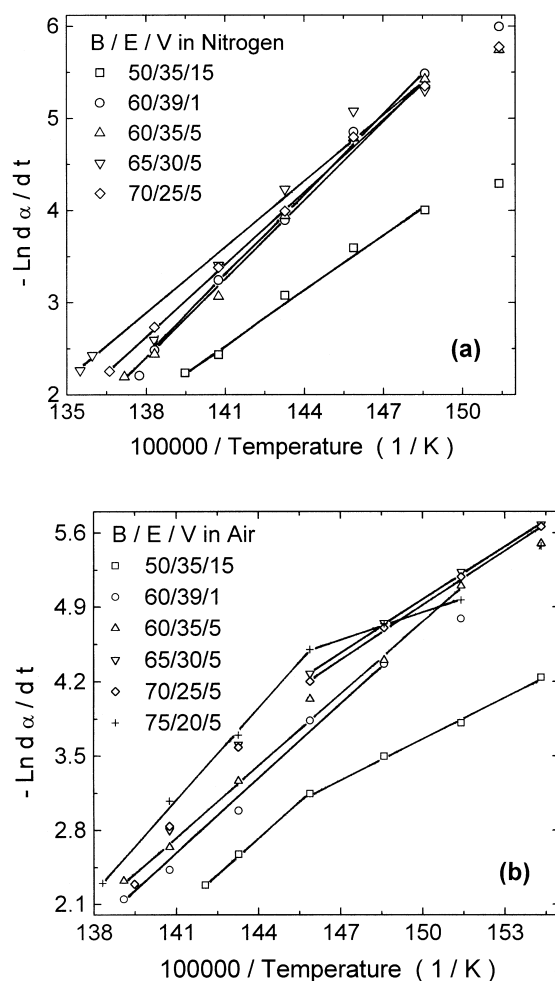


Figure 4. Application of Friedman method to the high-resolution TG data in nitrogen (a) and in air (b) of copoly [p-oxybenzoate(B)-ethylene terephthalate(E)-vanilate(V)] with six B/E/V molar ratios: (□) 50/35/15; (○) 60/39/1; (△) 60/35/5; (▽) 65/30/5; (◇) 70/25/5; (+) 75/20/5.

The correlation coefficient of two kinds of plots of calculating kinetic parameters ranges from 0.972 to 0.996. The three kinetic parameters obtained by Friedman, Freeman-Carroll, Chang methods are substantially the same. Only the n value obtained by Kissinger method is apparently larger. These indicate that the first three methods are all suitable for calculation of the kinetic parameters of the BEV terpolymers.

The T_d , T_{m1} , $(d\alpha/dt)_{m1}$, and char yield at elevated temperatures in nitrogen for the BEV terpolymers observed by high-resolution TG at a variable heat-

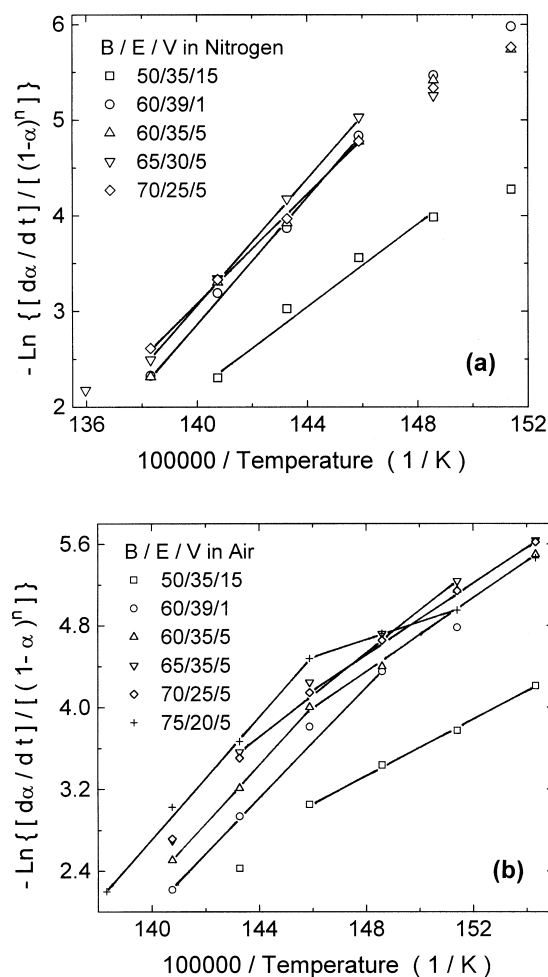


Figure 5. Application of Chang method to the high-resolution TG data in nitrogen (a) and in air (b) of copoly [p-oxybenzoate(B)-ethylene terephthalate(E)-vanillate(V)] with six B/E/V molar ratios: (\square) 50/35/15; (\circ) 60/39/1; (\triangle) 60/35/5; (∇) 65/30/5; (\diamond) 70/25/5; (+) 75/20/5.

ing rate at an initial heating rate of 50°C are higher than those by conventional TG at a constant heating rate of $5^\circ\text{C}/\text{min}$ [18] but three kinetic parameters (E' , n , and $\ln Z$) by the high-resolution TG are slightly lower.

The weight losses of the terpolymer with B/E/V molar ratio of 60/35/5 during isothermal heating under nitrogen and air were measured at 450°C , and are shown in Figure 7. The polymer exhibited rapid weight losses of 40% in nitrogen and 59% in air during isothermally heating of initial 25 minutes. The terpolymer rarely exhibits any significant weight loss in nitrogen during the heat-

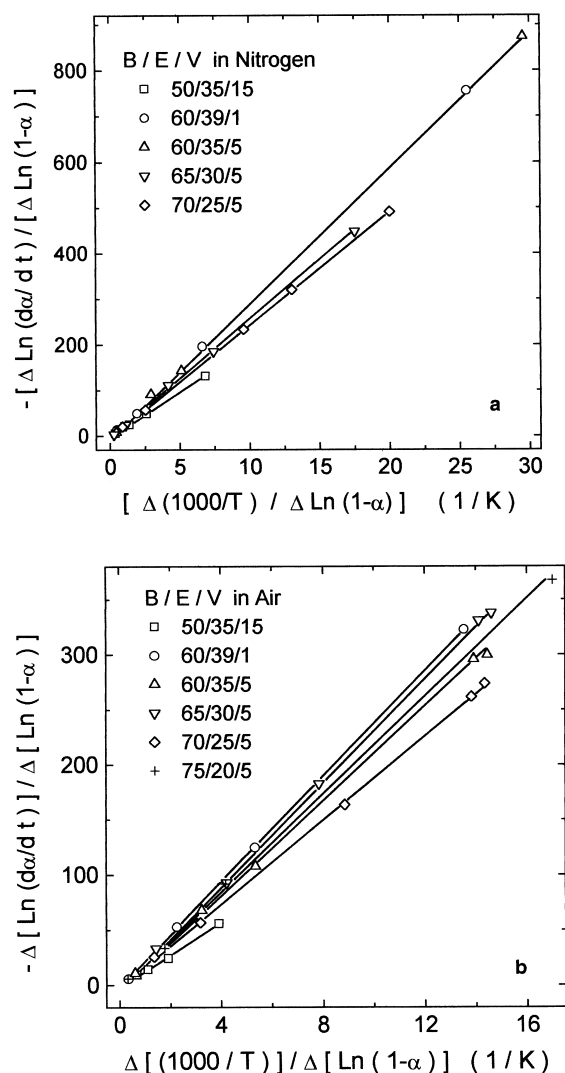


Figure 6. Application of Freeman-Carroll method to the high-resolution TG data in nitrogen (a) and in air (b) of copoly [p-oxybenzoate(B)-ethylene terephthalate(E)-vanillate(V)] with six B / E / V molar ratios: (□) 50/35/15; (○) 60/39/1; (△) 60/35/5; (▽) 65/30/5; (◇) 70/25/5; (+) 75/20/5.

ing time from 25 to 300 minutes until a char yield of 56%. But an additional slow weight loss in air has been observed during the heating time in the range from 25 to 160 minutes until a constant char yield of 13% in air at the isothermally heating time of 300 minutes. This behavior is similar to that found in the isothermal TG experiments of thermotropic poly(p-oxybenzoate-co-ethylene terephthalate) at 450°C [20], fully aromatic poly(p-oxybenzoate-co-2,6-naphthoate) at 500°C

TABLE 2. Kinetic Parameters of Major Thermal Degradation for B/E/V Copolymers by Four Calculating Techniques

| B/E/V (mol) | Friedman | | | | Chang | | | | Freeman-Carroll | | | Kissinger | Average | | |
|--------------------|-----------------|-----|-------------------|----------------|-----------------|-----|-------------------|----------------|-----------------|-----|-------------------|-----------------------|---------|-----|------|
| | E' ^a | n | Ln Z ^b | r ^c | E' ^a | n | Ln Z ^b | r ^c | E' ^a | n | Ln Z ^b | n | E' | n | Ln Z |
| In Nitrogen | | | | | | | | | | | | | | | |
| 50/35/15 | 158 | 1.1 | 24 | 0.990 | 164 | 1.1 | 25 | 0.983 | 162 | 0.9 | 25 | 3.2 | 161 | 1.6 | 24 |
| 60/39/1 | 251 | 2.1 | 38 | 0.996 | 247 | 2.1 | 39 | 0.994 | 247 | 1.7 | 38 | 2.5 | 248 | 2.1 | 38 |
| 60/35/5 | 248 | 1.9 | 38 | 0.992 | 246 | 1.7 | 38 | 0.988 | 247 | 1.4 | 38 | 5.7 | 247 | 2.7 | 38 |
| 65/30/5 | 226 | 1.5 | 35 | 0.987 | 223 | 1.3 | 34 | 0.987 | 225 | 1.3 | 34 | 1.9 | 225 | 1.5 | 34 |
| 70/25/5 | 205 | 2.5 | 31 | 0.996 | 207 | 2.4 | 32 | 0.996 | 206 | 1.8 | 31 | 3.7 | 206 | 2.6 | 31 |
| In Air | | | | | | | | | | | | | | | |
| 50/35/15 | 120 | 1.3 | 19 | 0.991 | 123 | 1.3 | 19 | 0.991 | 121 | 1.4 | 18 | 2.5(2.4) ^d | 121 | 1.6 | 19 |
| 60/39/1 | 202 | 1.9 | 32 | 0.994 | 201 | 2.0 | 32 | 0.989 | 200 | 2.0 | 31 | 1.8(2.0) ^d | 201 | 2.0 | 32 |
| 60/35/5 | 178 | 2.1 | 27 | 0.993 | 178 | 1.9 | 28 | 0.988 | 176 | 2.0 | 27 | 3.7(4.0) ^d | 177 | 2.4 | 27 |
| 65/30/5 | 185 | 2.3 | 28 | 0.982 | 194 | 2.2 | 30 | 0.986 | 195 | 2.0 | 30 | 4.7(4.5) ^d | 191 | 2.8 | 29 |
| 70/25/5 | 165 | 2.2 | 25 | 0.989 | 168 | 2.3 | 26 | 0.992 | 160 | 2.3 | 24 | 3.1(3.9) ^d | 164 | 2.6 | 25 |
| 75/20/5 | 183 | 1.6 | 26 | 0.974 | 181 | 1.6 | 28 | 0.972 | 181 | 1.4 | 27 | 2.0(2.6) ^d | 182 | 1.7 | 27 |

a The unit of E' is kJ/mol

b The unit of Ln Z is min⁻¹

c r means the correlation coefficient

d The values are obtained according to the equation $n = \left| \frac{(d^2\alpha/dT^2)_{Lmax}}{(d^2\alpha/dT^2)_{Rmax}} \right|$

[3] and poly(ether ether ketone ketone) in nitrogen [17, 21]. The BEV terpolymer is isothermally more stable than poly(p-oxybenzoate-co-ethylene terephthalate)[20] but less stable than wholly aromatic thermotropic liquid crystalline copolyesters such as poly(p-oxybenzoate-co-2,6-naphthoate) [3]. The dotted lines shown in Figure 7 was the isothermal TG curves at 450°C predicted by

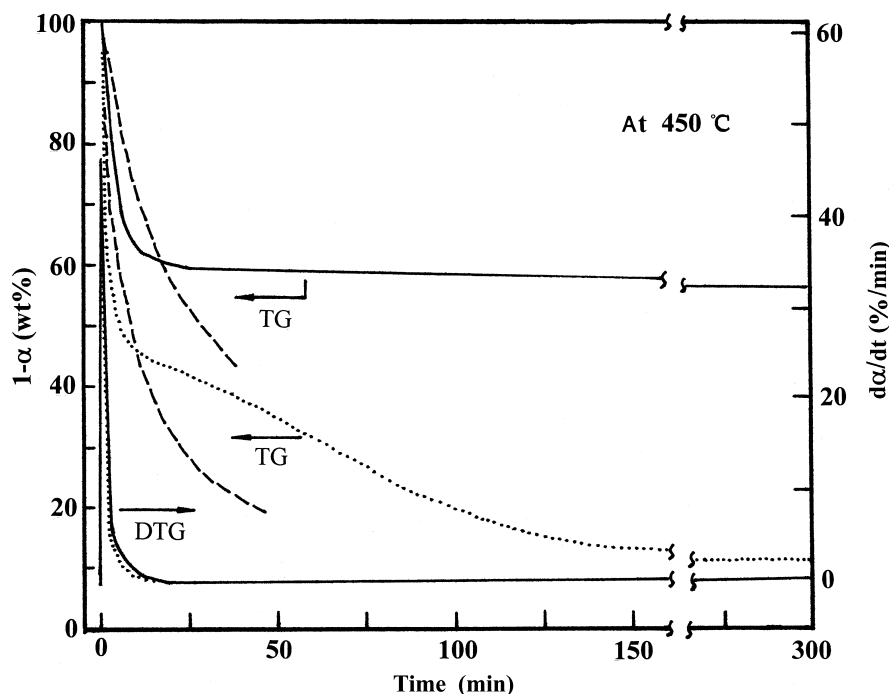


Figure 7. Isothermal TG and DTG curves for the copoly [p-oxybenzoate(B)-ethylene terephthalate(E)-vanillate (V)] with the B/E/V molar ratios: (□) 50/35/15; (O) 60/39/1; (Δ) 60/35/5; (∇) 65/30/5; (◇) 70/25 molar ratio of 60/35/5 at 450°C in nitrogen (—) and in air (····) and calculated isothermal TG curves (---) based on the average kinetic parameters listed in Table 3, the upper dotted line in nitrogen and lower dotted line in air.

Equation 5 on the basis of the average kinetic parameters listed in Table 2 for the non-isothermal degradation. An obvious difference between the experimental and predicted TG curves is found, indicative that the main degradation reaction of the B/E/V (60/35/5) terpolymer might follow different mechanism in isothermal and in non-isothermal degradation processes. Perhaps, the difference is due to the data analysis and evaluation, alternatively, due to diffusion control rather than chemical control of degradation process.

It is seen from Figure 7 that the maximum rate of weight loss at 450°C in nitrogen occurs at about 11% and the total overall weight loss is only 44%, and this corresponds exactly to 25% of the overall total weight loss. This implies that the isothermal pyrolysis of the B/E/V (60/35/5) polymer under nitrogen could be a random chain scission process since random decomposition should have a

maximum rate at the 25 wt% weight loss according to Flynn-Wall [21, 22]. The same random mechanism of isothermal decomposition for aromatic poly(p-oxybenzoate-co-2,6-naphthoate) and poly(p-oxybenzoate-co-ethylene terephthalate) has been speculated [3, 20].

It has been found that the temperatures, activation energy, and frequency factor of the thermal degradation for the BEV terpolymers are lower than those for the poly (p-oxybenzoate-co-ethylene terephthalate) [20]. Particularly, the BEV terpolymer with the highest content of V-unit of 15 mol% shows the lowest degradation temperatures, lowest activation energy, and lowest frequency factor among the six BEV terpolymers. This might indicate that an introduction of methoxyl group onto the benzene ring in the aromatic polyester chain will make the thermostability lower and the degradation rate accelerate [19]. In fact, the aliphatic methoxyl side group in the polyesters should exhibit lower thermostability than the polyester main chain consisting of aromatic p-phenylene, ethylene, and ester units.

CONCLUSION

High-resolution thermogravimetry at a variable heating rate and isothermal thermogravimetry at 450°C can provide more information of thermal and thermo-oxidative degradations of the thermotropic liquid crystalline copoly (p-oxybenzoate-ethylene terephthalate-vanillate) in a shorter time than the traditional thermogravimetry. The first major stage might be speculated to be ascribed to the removal of the ester, ethylene and methoxyl groups and hydrogen atom on the terpolymer chain and then an intermolecular condensations might occur to form carbonaceous char at a relatively high temperature. Further oxidation and combustion of the residual char were observed only in air. The high-resolution thermogravimetry and derivative thermogravimetry curves can be employed to calculate kinetic parameters of thermal degradation of copoly (p-oxybenzoate-ethylene terephthalate-vanillate) through conventional kinetic equations which were deduced for the conventional thermogravimetry at a constant heating rate. The activation energy (E'), decomposition order (n) and frequency factor (Z) of the thermal decomposition for the BEV terpolymers obtained by Friedman, Freeman-Carroll, and Chang techniques have only a small difference. Introducing methoxyl group onto the benzene ring in the aromatic polyester chain might lower the thermostability and accelerate the degradation rate in non-isothermal heating conditions.

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