High-Resolution Thermogravimetry of Liquid Crystalline Copoly(*p*-oxybenzoate–ethylene terephthalate–*m*-oxybenzoate)

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ABSTRACT: Thermotropic liquid crystalline terpolymers consisting of three units of *p*-oxybenzoate (B), ethylene terephthalate (E), and *m*-oxybenzoate (M), were investigated through high-resolution thermogravimetry to evaluate their stability and kinetic parameters of thermal degradation in nitrogen and air. Overall activation energy data of the first major decomposition was calculated through three calculating methods. Thermal degradation occurs in three major steps in both nitrogen and air. Three kinds of degradation temperatures (T_d, T_{m1}, T_{m2}) are slightly higher and the first maximum weight-loss rates are slightly lower in nitrogen than in air, suggesting a higher thermostability in nitrogen. The thermal degradation temperatures range from 450 to 457°C in nitrogen and 441 to 447°C in air and increase with increasing B-unit content at a fixed M-unit content of 5 mol %. The temperatures at the first maximum weight loss rate range from 452 to 466°C in nitrogen and 444 to 449°C in air and increase slightly with an increase in B-unit content. The first and second maximum weight-loss rates are maintained at almost 9.2–10.8 and 4.0–6.1%/min in nitrogen (11.2–12.0 and 3.9–4.2%/min in air) and vary slightly with copolymer composition. The residues after the first major step of degradation are predicted on the basis of the complete exclusion of ester and ethylene groups and hydrogen atoms and compared with those observed experimentally. The char yields at 500°C in both nitrogen and air are larger than 42.6 wt % and increase with increasing B-unit content. However, the char yields at 800°C in nitrogen and air are different. The activation energy and ln(pre-exponential factor) for the first major decomposition are slightly higher in nitrogen than in air and increase with an increase in B-unit content at a given M-unit content of 5 mol %. There is no regular variation in the decomposition order with the variation of copolymer composition and testing atmosphere. The activation energy, decomposition order, and ln(pre-exponential factor) of the thermal degradation for the terpolymers are located in the ranges of 212–263 kJ mol^{-1}, 2.4–3.5, 33–41 min^{-1}, respectively. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 73: 2911–2919, 1999

Key words: hydroxybenzoic acid copolyester; *m*-hydroxybenzoic acid; aromatic polyester; thermotropic liquid crystalline polymer; high-resolution thermogravimetry; thermal degradation; decomposition kinetics

INTRODUCTION

Thermotropic liquid crystalline polymers have been utilized for manufacturing high-strength, high-modulus, highly heat-resistant, highly dimensional-stable, and fire-retardant materials. It is known that the terpolyester, consisting of three units of *p*-oxybenzoate (B), ethylene terephthalate (E), and *m*-oxybenzoate (M), is one of the important thermotropic copolymers with largely aromatic repeat units showing high thermostability.[1–6] The synthesis, structure, and properties of B/E/M or other third-monomer terpolyesters have been studied and considered as a new kind of high-performance polymer with good processing

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

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

Table I   Thermal Degradation Characteristics for Copoly[*p*-oxybenzoate (B)–ethylene terephthalate (E)–*m*-oxybenzoate (M)] by a High-Resolution Thermogravimetry

B/E/M (mol)	$[\eta]^a$ (dL/g)	$T_d/T_{m1}/T_{m2}/T_{m3}$ (°C)	$(d\alpha/dt)_{m1}/(d\alpha/dt)_{m2}/(d\alpha/dt)_{m3}$ (%/min)	$(d\alpha/dT)_{m1}/(d\alpha/dT)_{m2}/(d\alpha/dT)_{m3}$ (%/°C)
In Nitrogen				
60/35/5	0.50	450/456/513/612	10.8/4.0/2.4	2.3/0.21/0.08
65/30/5	0.72	450/452, 458, 461[b]/515/635	9.2/4.1/6.6	1.4/0.26/0.53
70/25/5	0.82	451/457/521/618	10.0/4.7/9.0	1.45/0.30/1.0
75/20/5	—[c]	457/466/527/659	9.3/6.1/5.8	1.18/0.43/0.42
In Air				
60/35/5	0.50	441/444, 447[d]/ 518/575	12.0/4.0/11.	3.1/0.22/3.7
65/30/5	0.72	442/447/518/578	11.6/4.2/13.0	2.3/0.23/4.2
70/25/5	0.82	443/447/512/546	11.5/3.9/14.0	2.9/0.28/5.5
75/20/5	—[c]	447/449/520/555	11.2/4.0/15.0	2.4/0.39/5.7

[a] Four terpolyesters are all partly soluble in phenol/*sym*-tetrachloroethane (1/1 v/v) at 30°C.
[b] A triplet.
[c] Most of the sample was insoluble in phenol/*sym*-tetrachloroethane (1/1 v/v) at 30°C, so its $[\eta]$ was not available with precision.
[d] A doublet.

ability and high mechanical properties.[7–12] However, no report has been found on the thermal stability and degradation kinetics of the thermotropic liquid crystalline terpolyesters, especially B/E/M terpolyesters. A more detailed study would be of value because the terpolyesters must encounter elevated temperatures at almost every step in the manufacturing, compounding, processing, and repairing steps, as well as in the application of terpolymers.

The thermostability and three important kinetic parameters of the B/E/M terpolyesters will be studied by performing a detailed high-resolution thermogravimetric (TG), derivative thermogravimetric (DTG), second derivative thermogravimetric (2DTG), and kinetics analyses at a variable heating rate in nitrogen and air. The

variation of the thermostability and kinetic parameters of the B/E/M terpolymers is discussed in detail. This topic may be of importance in revealing the intrinsic thermal stability and decomposition kinetics of the thermotropic liquid crystalline aromatic terpolyesters.

EXPERIMENTAL

The thermotropic liquid crystalline terpolyesters studied here are the copolymers synthesized from *p*-acetoxybenzoic acid (B), poly(ethylene terephthalate) (E), and *m*-acetoxybenzoic acid (M) in four monomer ratios. The terpolyesters were prepared according to an earlier procedure.[7] These terpolyesters are designated as B/E/M terpolymers for brev-

Table II   Weight Loss After the First Major Degradation and Char Yield at Elevated Temperatures for Copoly[*p*-oxybenzoate (B)–ethylene terephthalate (E)–*m*-oxybenzoate (M)]

B/E/M (mol)	Weight Loss (%) Corresponding to the First Major Degradation		Char Yield (wt %)	
	Experimental[a]	Calculated[b]	At 500°C[a]	At 800°C[a]
60/35/5	51.5/50.4	50.3	44.7/42.6	16.7/0
65/30/5	49.1/49.1	49.2	50.6/48.0	2.5/0
70/25/5	45.6/47.1	47.8	53.9/52.5	0/0
75/20/5	41.8/43.0	46.4	56.1/58.1	0/0

[a] In nitrogen/air.
[b] The calculated data correspond to the weight losses after exclusion of ethylene and ester groups and all hydrogen atoms.

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)–*m*-oxybenzoate (M)] with four B/E/M molar ratios in air at an initial heating rate of 50°C/min and resolution of 3.0: (——) 60/35/5; (——) 65/30/5; (– · – · – ·) 70/25/5; (· · ·) 75/20/5.

ity in this study. They have the general molecular structure

High-resolution TG analyses were performed under nitrogen flow of 25 mL/min and air flow of 40 mL/min on a high-resolution Model TGA 2950 thermal analyzer (Hi-Res™ TGA) induced by TA Instruments Inc., New Castle, DE, by using a 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 1.6–2.1

mg in nitrogen and 1.0–2.3 mg in air; the initial heating rate and resolution were fixed at 50°C/min and 3.0, respectively; and the sensitivity was fixed at its default value of 1 in a temperature range of ~ 25–800°C. The thermal degradation temperatures and kinetic parameters were determined using the following methods.[2–6]

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

$$\ln(d\alpha/dt) = \ln Z + n \ln(1 - \alpha) - E'/RT \quad (1)$$

By plotting $\ln(d\alpha/dt)$ or $\ln(1 - \alpha)$ against $1/T$, a straight line can be obtained with a slope of $-E'/R$ or $-E'/(nR)$.

The Chang method uses the following equation[14]:

Figure 4 Application of Friedman method to high-resolution TG data in nitrogen (a) and air (b) of co-poly[*p*-oxybenzoate (B)–ethylene terephthalate (E)–*m*-oxybenzoate (M)] with four B/E/M molar ratios: (□) 60/35/5; (○) 65/30/5; (△) 70/25/5; (▽) 75/20/5.

$$\ln[(d\alpha/dt)/(1 - \alpha)^n] = \ln Z - E'/RT \quad (2)$$

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

The Kissinger method can directly calculate the n value from the symmetrical index of DTG peak[15]

$$n = 1.88 \times |(d^2\alpha/dt^2)_L|/|(d^2\alpha/dt^2)_R| \quad (3)$$

where indices L and R correspond the maximum and minimum $d^2\alpha/dt^2$ values on the 2DTG curves.

Isothermal TG curves at a constant temperature could be predicted according to the equation[16]

$$t = [1 - (1 - \alpha)^{1-n}]\exp(E'/RT)/$$
$$[Z(1 - n)] \quad (n \neq 1) \quad (4)$$

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

The degradation temperature, T_d, was obtained by extrapolation of the initial degradation portion of the TG curve. T_{m1}, T_{m2}, and T_{m3} correspond to the peak temperatures at the first, second, and third maxima on the DTG curves, respectively. $(d\alpha/dt)_{m1}$, $(d\alpha/dt)_{m2}$, and $(d\alpha/dt)_{m3}$ [or $(d\alpha/dT)_{m1}$, $(d\alpha/dT)_{m2}$, and $(d\alpha/dT)_{m3}$] represent the maximal weight-loss rates at the first, second, and third maxima on the DTG curves, respectively. These data were compared with existing literature values of B/E/other third monomers obtained by high-resolution TG published earlier by us.[2,3,17]

RESULTS AND DISCUSSION

Figures 1 and 2 show the high-resolution TG, DTG, 2DTG, and the heating-rate curves for the terpolyesters with four B/E/M molar ratios of 60/35/5, 65/30/5, 70/25/5, and 75/20/5 at an initial heating rate of 50°C/min in nitrogen and air. The thermal decomposition results are given in Tables I and II. Comparing the thermal decomposition parameters in nitrogen with those obtained in air, nearly all B/E/M terpolyesters exhibit higher T_d, T_{m1}, T_{m2}, T_{m3}, and char yield, and lower $(d\alpha/dt)_{m1}$ and $(d\alpha/dt)_{m3}$ [or $(d\alpha/dT)_{m1}$ and $(d\alpha/dT)_{m3}$] in nitrogen. This results from the thermo-oxidative degradation or even combustion in air, because a strong thermo-oxidative degradation peak appears at a higher temperature, which suggests that the onset of the bond cleavage in the B/E/M terpolymers is basically thermal in nature and also influenced by the oxygen in air.

As seen in Tables I and II, the T_d, T_{m1}, T_{m2}, and char yield at 500°C increase with increasing B-unit content from 60 to 75 mol % at a fixed M-unit content of 5 mol % in both testing atmospheres. Similar results have been found for B/E bipolyesters and B/E/vanillate (V) terpolyesters. It can be concluded that the thermostability of the

B/E/M or other third monomer copolyesters will enhance with increasing B-unit content.

Although the final char residue of B/E and B/E/V copolyesters in nitrogen could be correctly predicted on the basis of the their molecular structure,[18] the final char yield of B/E/M terpolyesters predicted on the basis of their molecular structure are much higher than that observed experimentally in nitrogen (Table II) because there is an additional third degradation process at a much higher temperature as compared with the thermal degradation process of B/E and B/E/V copolyesters in nitrogen. The group contributions for char yield of $-o\langle\bigcirc\rangle co-$, $-oc\langle\bigcirc\rangle co-$, $-OCH_2CH_2O-$, and $-o\bigcirc co-$ are assumed to be 4, 1.25, 0, and 3.0, respectively.[18] According to this data, the predicted char yield for the terpolymers with four B/E/M ratios of 60/35/5, 65/30/5, 70/25/5, and 75/20/5 are 24.7, 26.5, 28.4, and 30.4%, respectively. Apparently, the final char yield of the B/E/M terpolyesters in inert atmosphere does not appear to be an additive parameter.

By comparing Figures 2(b,c) with Figure 3, high-resolution $(d\alpha/dt)$ and $(d^2\alpha/dt^2)$ plots always show higher resolution than the high-resolution $(d\alpha/dT)$ and $(d^2\alpha/dT^2)$ plots. The $(d\alpha/dT)$ and $(d^2\alpha/dT^2)$ plots look smoother than the high-resolution $(d\alpha/dt)$ and $(d^2\alpha/dt^2)$ curves that exhibit a doublet. This doublet might result from the two different degradation processes of terpolyester main chain. The respective weight losses after the first major DTG peak on the high-resolution $(d\alpha/dt)$ curves of the terpolyesters with the B/E/M molar ratios of 60/35/5, 65/30/5, 70/25/5, and 75/20/5 are listed in Table II. Apparently, these data are close to the weight losses predicted (also listed in Table II) on the basis of a complete loss of whole ester and ethylene groups and hydrogen atom on the polymer chains. This implies that the major thermal degradation of the B/E/M terpolyesters is attributed to the cleavage of the ester linkage and simultaneous removal of the carbon monoxide or dioxide, ethylene unit, and hydrogen atom. The subsequent degradation may result from the partial pyrolysis of aromatic carbon from benzene ring.

The kinetic parameters of thermal degradation for B/E/M terpolyesters obtained from Figures 4 and 5 by Friedman, Chang, and Kissinger methods are presented in Table III. The variation of three kinetic parameters with the B/E/M monomer ratios is the same as that of the degradation temperatures. The average E', n, and $\ln Z$ values increase slightly with increasing B-unit content

from 60 to 75 mol % at a fixed M-unit content of 5 mol %. It is concluded that the thermal degradation rate of the B/E/M terpolyesters in both nitrogen and air will lower with increasing B unit to some extent. Note that there is exception to the E' value in air and n value in nitrogen for B/E/M (75/20/5) terpolymer.

The correlation coefficient of two kinds of plots of calculating kinetic parameters ranges from 0.9851 to 0.9998. The three kinetic parameters obtained by Friedman and Chang methods are substantially the same. Only the n value calculated by Kissinger method is sometimes appar-

Figure 5 Application of Chang method to the high-resolution TG data in nitrogen (a) and air (b) of co-poly[p-oxybenzoate (B)–ethylene terephthalate (E)–m-oxybenzoate (M)] with four B/E/M molar ratios: ($\square$) 60/35/5; ($\bigcirc$) 65/30/5; ($\triangle$) 70/25/5; ($\triangledown$) 75/20/5.

Table III   Kinetic Parameters of the First Major Thermal Degradation for Copoly[*p*-oxybenzoate (B)–ethylene terephthalate (E)–*m*-oxybenzoate (M)] by Three Calculating Methods

B/E/M (mol)	Friedman				Chang				Kissinger	Average		
	E'^a	n	$\ln Z^a$	r^b	E'^a	n	$\ln Z^a$	r^b	n	E'	n	$\ln Z$
In Nitrogen												
60/35/5	222	2.1	34	0.9966	224	2.0	35	0.9945	3.3	223	2.4	35
65/30/5	237	2.7	36	0.9955	239	2.5	37	0.9973	2.4	238	2.5	37
70/25/5	242	2.6	38	0.9979	255	2.5	40	0.9957	5.4	249	3.5	39
75/20/5	252	2.5	39	0.9981	273	2.5	42	0.9997	4.0	263	3.0	41
In Air												
60/35/5	212	2.3	33	0.9912	211	2.2	33	0.9909	3.6 (2.7)^c	212	2.7	33
65/30/5	234	2.2	36	0.9998	240	2.0	38	0.9993	3.4 (3.1)^c	237	2.7	37
70/25/5	240	2.7	38	0.9993	240	2.5	38	0.9992	3.7 (2.4)^c	240	2.8	38
75/20/5	232	2.4	36	0.9888	246	2.2	39	0.9851	4.2 (2.6)^c	239	2.9	38

^{a} The units of E' and $\ln Z$ are kJ mol^{-1} and min^{-1}, respectively.
^{b} r is the correlation coefficient.
^{c} The values in parentheses are obtained according to the equation $n = |(d^2\alpha/dT^2)_{L\max}|/|(d^2\alpha/dT^2)_{R\max}|$.

ently larger, which indicates that the first two methods are both suitable for calculation of the kinetic parameters of the B/E/M terpolymers.

The T_d, T_{m1}, T_{m2}, T_{m3}, $(d\alpha/dt)_{m1}$, char yield at 500°C, and three kinetic parameters (E', n, and $\ln Z$) are basically higher but the char yield at 800°C is lower for the B/E/M terpolyesters than for B/E/V terpolyesters.[17] The B/E/M terpolyesters exhibit almost the same degradation temperature as the B/E bipolyesters with the same B-unit content from 60 to 75 mol %, but the B/E/M terpolyesters exhibit higher E', n, and $\ln Z$ values and lower $(d\alpha/dt)_{m1}$, with char yield at 800°C. In addition, the B/E/M terpolyesters exhibit lower degradation temperature but slightly higher activation energy and frequency factor than B/E/phenylene terephthalate (P) terpolymers. These all suggest following order of thermostability:

B/E/P terpolymer $\geq$ B/E/M terpolymer

$\geq$ B/E bipolymer $>$ B/E/V terpolymer

That is, an introduction of m-oxybenzoate unit into the B/E bipolyester chain will slightly enhance thermostability and lower the degradation rate.

On the basis of the three average kinetic parameters listed in Table III, the isothermal weight losses of the terpolymer with four B/E/M molar ratios at 440°C under nitrogen and air were predicted by eq. (4) and are shown in Figure 6.

The estimated isothermal TG curves for four terpolymers in nitrogen and air are found to be exponential with an increase in heating time from 0 to 90 min. The terpolymers exhibit a rapid weight loss of 50% during isothermal heating of initial $\sim$ 16–44 min in nitrogen and $\sim$ 15–26 min in air. This behavior is similar to that found in the isothermal TG experiments of thermotropic poly(*p*-oxybenzoate-*co*-ethylene terephthalate), copoly(*p*-oxybenzoate–ethylene terephthalate–vanillate) at 450°C,[13] fully aromatic poly(*p*-oxybenzoate-*co*-2,6-naphthoate) at 500°C[4] and poly(ether ether ketone ketone) in nitrogen.[11] It is found from Figure 6 that the estimated isothermal thermostability for the B/E/M terpolymers at 440°C may increase in the following order:

60/35/5 $<$ 65/30/5 $<$ 70/25/5

$<$ 75/25/5   (in nitrogen)

and

75/20/5 $<$ 70/25/5 $<$ 60/35/5

$<$ 65/30/5   (in air)

However, an obvious difference between the predicted isothermal TG curves for B/E/M terpolymers and experimental isothermal TG curves observed earlier for B/E/vanillate or B/E/*p*-benzamide terpolymers in air is found after the weight loss of >50 wt %

Figure 6 Predicted isothermal TG curves in nitrogen (a) and air (b) through eq. (4) for copoly[*p*-oxybenzoate (B)–ethylene terephthalate (E)–*m*-oxybenzoate (M)] with four B/E/M molar ratios: (□) 60/35/5; (○) 65/30/5; (△) 70/25/5; (▽) 75/20/5.

because an additional slow weight loss in air appears in the experimentally isothermal TG curves.[17]

CONCLUSIONS

High-resolution thermogravimetry at a variable heating rate has quickly provided more information of thermal and thermo-oxidative degradations of the thermotropic liquid crystalline copoly[*p*-oxybenzoate (B)–ethylene terephthalate (E)–*m*-oxybenzoate (M)]. The first major stage could be attributed to the removal of the ester, ethylene groups, and hy-

drogen atom on the terpolymer chain and then an intermolecular condensation could occur to form carbonaceous char at a relatively high temperature. Further oxidation and combustion of the residual char were observed in air. The high-resolution TG and DTG curves have be employed to calculate kinetic parameters of thermal degradation of co-poly(*p*-oxybenzoate–ethylene terephthalate–*m*-oxy-benzoate) through traditional kinetic equations that were deduced for the conventional TG at a constant heating rate. The activation energy (E'), decomposition order (n), and frequency factor (Z) of the thermal decomposition for the B/E/M terpolymers calculated by Friedman and Chang techniques exhibit only a small difference. Introducing the *m*-oxybenzoate unit into the B/E bipolyester chain could increase the thermostability and lower the degradation rate in nonisothermal heating conditions.

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