Structure and high-resolution thermogravimetry of liquid-crystalline copoly(\(p\)-oxybenzoate-ethylene terephthalate-\(p\)-benzamide)

Xin-Gui Li,1,* Mei-Rong Huang1 and Yuliang Yang2

1Department of Polymer Materials Science & Engineering, College of Materials Science & Engineering, Tongji University, 1239 Siping Road, Shanghai 200092, People’s Republic of China
2Department of Macromolecular Science, Laboratory of Molecular Engineering of Polymers, Fudan University, Shanghai 200433, People’s Republic of China

Abstract: Thermotropic liquid-crystalline copoly(ester-amide)s consisting of three units of \(p\)-oxybenzoate (B), ethylene terephthalate (E) and \(p\)-benzamide (A) were studied by proton nuclear magnetic resonance at 200 and 400 MHz, wide-angle X-ray diffraction, and high-resolution thermogravimetry to ascertain their molecular and supermolecular structures, thermostability and kinetics parameters of thermal decomposition in both nitrogen and air. The assignments of all resonance peaks of \([1H]\)NMR spectra for the copoly(ester-amide)s are given and the characteristics of X-ray equatorial and meridional scans are discussed. Overall activation energy data of the first major decomposition have been evaluated through three calculating techniques. The thermal degradation occurs in three steps in nitrogen and air. The degradation temperatures are higher than 447°C in nitrogen and 440°C in air and increase with increasing B-unit content at a fixed A-unit content of 5 mol%. The temperatures at the first maximum weight-loss rate are higher than 455°C in nitrogen and 445°C in air and also increase with an increase in B-unit content. The first maximum weight-loss rates range between 11.1 and 14.5%/min\(^{-1}\) in nitrogen and between 11.9 and 13.5%/min\(^{-1}\) in air. The char yields at 500°C in both nitrogen and air range from 45.8 to 54.3 wt% and increase with increasing B-unit content. But the char yields at 800°C in nitrogen and air are quite irregular with the variation of copolymer composition and testing atmosphere. The activation energy and Ln (pre-exponential factor) for the first major decomposition are usually higher in nitrogen than in air and increase slightly with an increase in B-unit content at a given A-unit content of 5 mol%. The activation energy, decomposition order, and Ln (pre-exponential factor) of the thermal degradation for the copoly(ester-amide)s in two testing atmospheres, are situated in the ranges of 210±292 kJ mol\(^{-1}\), 2.0±2.8, 33±46 min\(^{-1}\), respectively. The three kinetic parameters of the thermal degradation for the aromatic copoly(ester-amide)s obtained by high-resolution thermogravimetry at a variable heating rate are almost the same as those by traditional thermogravimetry at constant heating rate, suggesting good applicability of kinetic methods developed for constant heating rate to the variable heating-rate method. These results indicate that the copoly(ester-amide)s exhibit high thermostability. The isothermal decomposition kinetics of the copoly(ester-amide)s at 450 and 420°C are also discussed and compared with the results obtained based on non-isothermal high-resolution thermogravimetry.

INTRODUCTION

There has been a continual increase in interest with respect to the utilization of liquid-crystalline polyesters and polyamide as a means of preparing high-strength, high-modulus and highly heat-resistant fibres. The synthesis and properties of the thermotropic liquid-crystalline copoly(ester-amide)s prepared from \(p\)-acetoxybenzoic acid (B), poly(ethylene terephthalate) (E) and \(p\)-acetaminobenzoic acid (A), have been investigated and the product considered as a new kind of high-performance polymer with good processing ability and high mechanical property.\(^1,2\) However, few studies have been reported on molecular and supermolecular structures, thermostability and ther-
mal degradation kinetics of the thermotropic copoly(ester-amide)s. It is believed that a more detailed study would be of value because the B/E/A copoly(ester-amide)s must encounter elevated temperatures at almost every step in the manufacturing compounding and processing steps as well as in service and during repair.

In this paper, we have attempted to investigate the molecular and supramolecular structures, thermostability and several important kinetic parameters of the B/E/A terpolymers by performing detailed 

\[^{1}\text{H}\]NMR spectra, X-ray meridional scans, and high-resolution thermogravimetric (TG), derivative thermogravimetric (DTG), and the second derivative thermogravimetric (2DTG) analyses at a variable heating rate and isothermal thermogravimetry in nitrogen and air. The variation of the thermostability and kinetic parameters of the B/E/A terpolymers is also discussed in detail. This topic may be important in revealing the structure, intrinsic thermal stability and degradation kinetics of thermotropic liquid-crystalline aromatic copoly(ester-amide)s.

**EXPERIMENTAL**

The thermotropic liquid-crystalline copoly(ester-amide)s studied in this paper are the terpolymers synthesized from p-acetoxybenzoic acid (B), poly(ethylene terephthalate) (E), and p-acetamidobenzoic acid (A) in three monomer ratios. The terpolymers were prepared according to an earlier procedure.\(^2\) The acid (A) in three monomer ratios. The terpolymers are designated as B/E/A terpolymers for brevity. They have the general molecular structure:

\[
\text{Unit B} \quad \text{Unit E} \quad \text{Unit A}
\]

The copolymers were dissolved in deuterated trifluoroacetic acid TFA at 5 wt% concentration. \[^{1}\text{H}\]NMR spectra were recorded on a Bruker AM-400 NMR spectrometer at 400 MHz for B/E/A(60/40/0) copolymer and on a Bruker AC-P 200 NMR spectrometer at 200 MHz for B/E/A (60/35/5), (65/30/5), and (70/25/5) terpolymers. The chemical shifts were read from tetramethylsilane added as an internal standard. The peak areas were determined by spectral integration.

The equatorial and meridional reflections of wide-angle X-ray diffractograms for as-drawn ribbons of the copolymers were obtained using a Rigaku X-ray diffractometer with nickel-filtered K\(_\alpha\) radiation.

The width at half height \(\beta\) (in degrees) or \(\beta^\prime\) (in radians) at the strongest meridional reflections at \(2\theta = 43.3 \pm 43.6^\circ\) can give the length \(L\) of coherent periodicity in the draw direction (i.e. the axial direction of polymer main-chain) by using one of the following two expressions:\(^3\)

\[
L = \lambda/[2(\sin \theta_1 - \sin \theta_2)]
\]

where \(\lambda = 0.154178 \text{nm}, \theta_1 = 21.75 + \beta/2, \theta_2 = 21.75 - \beta/2\) or

\[
L = \lambda/(\beta^\prime \cdot \cos \theta)
\]

where \(\beta^\prime = \beta \cdot \pi/180 = 0.0174532 \beta\)

TG analyses were performed under the nitrogen flow of 25 ml min\(^{-1}\) and air flow of 40 ml min\(^{-1}\) on a model high-resolution TGA 2950 thermal analyser (Hi-Res\(^\circledR\) TGA) induced by TA-Instruments Inc, New Castle, Delaware, using the high-resolution mode interfaced to a 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 1.1–1.8 mg in nitrogen and 1.0–2.1 mg in air; initial heating rate and resolution at 50°C min\(^{-1}\) and 3.0, respectively; sensitivity was fixed at its default value of 1 in the temperature range of 25–800°C. Traditional TG and derivative thermogravimetry curves at a constant heating rate of 10°C min\(^{-1}\) in 30 ml min\(^{-1}\) nitrogen was obtained by using an Netzsch–Geratebau GmbH TG 209 with sample size 1.94 mg. Isothermal TG and DTG curves were obtained by using the TGA 2950 thermal analyser with sample size 1.6 mg in nitrogen and 1.9 mg in air at 450°C and by using the Netzsch–Geratebau GmbH TG 209 with sample size 1.7 mg in 30 ml min\(^{-1}\) nitrogen and static air at 420°C. The thermal degradation temperatures and kinetic parameters were determined using the techniques described previously.\(^4\)–\(^9\)

**Friedman method**

This utilizes the following natural logarithmic equation:\(^10\)

\[
\ln \left(\frac{dx}{dt}\right) = \ln Z + n \cdot \ln (1 - x) - E'/RT
\]

By plotting \(\ln \left(\frac{dx}{dt}\right)\) or \(\ln (1 - x)\) against \(1/T\), a straight line can be obtained with a slope of \(-E'/R\) or \(-E/(n \cdot R)\).

**Chang method**

This uses the following equation:\(^11\)

\[
\ln [(dx/dt)/(1 - x)^n] = \ln Z - E'/RT
\]

A plot of \(\ln [(dx/dt)/(1 - x)^n]\) 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 \(Z\).

**Kissinger method**

This method can calculate the \(n\) value directly from the symmetrical index of derivative thermogravimetry (DTG) peak:\(^12\)

\[
n = 1.88 \cdot |(d^2x/dt^2)_L|/|(d^2x/dt^2)_R|
\]

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

Isothermal TG curves
These curves at constant temperature could be predicted according to the equation:

$$t = [1 - (1 - z)^{1-n}] \cdot \exp(E'/RT)/|Z(1-n)|$$

$$n \neq 1$$ (6)

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

The degradation temperature, $T_d$, was obtained by an 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. $(dx/dt)_{m1}$, $(dx/dt)_{m2}$, and $(dx/dt)_{m3}$ represent the maximal weight-loss rates at the first, second, and third maxima on the DTG curves, respectively.

RESULTS AND DISCUSSION
$[1^H]$NMR spectra and assignments of B/E/A terpolymers
According to an investigation on 400 MHz $[1^H]$NMR spectra for B/E bipolymers and B/E/3rd monomer unit terpolymers, the assignments of characteristic resonance peaks for B and E units in the copolymers have been determined. The 200 MHz and 400 MHz $[1^H]$NMR spectra for B/E/A terpolymers are shown in Fig 1. Obviously, the two doublets in the lowest field exhibit higher resolution for B/E/A(60/40/0) copolymer spectra obtained at 400 MHz than for three B/E/A terpolymer spectra at 200 MHz. Through combining a comparison of the peak areas with the effect of substituent groups on chemical shift of the protons on the benzene ring, the four types of peaks at 8.00, 7.75–7.84, 7.09, and 2.39–2.20 ppm for the A-unit in B/E/A(60/35/5) terpolymer shown in Fig 1 might be assigned to the a4 and b2 protons in $\text{OC} \quad \text{NH} \quad \text{OCCH}_3$ and $\text{OC} \quad \text{NH} \quad \text{OCCH}_3$ respectively. The a3 protons are supposed to exhibit the same chemical shift of 8.34 ppm as the a1 proton in $\text{OC} \quad \text{NH} \quad \text{OCCH}_3$, because a ratio of 8.14 ppm peak area to 8.34 ppm peak area, 1.08, is exactly the same as the molar ratio of a2 protons (see Table 1) to a3 protons, 35 × 2 ÷ (60 + 5) = 1.08. The assignments of all resonance peaks in the $[1^H]$NMR spectra for B/E/A terpolymers are listed in Table 1. It is seen that the chemical shift of every proton in the B/E/A terpolymers increases slightly with increasing B-unit content from 60 to 65 mol% at a given A-unit content of 5 mol%, possibly due to an increase in conjugated effect of B-unit as compared with E-unit. However, there is no further increase in chemical shift with increasing B-unit content from 65 to 70 mol%.

Estimation of degree of polymerization by end-group analysis
The proton peak in an acetoxy end group can be used to calculate roughly the number-average degree of polymerization ($DPn$) of the B/E/A terpolymers if the terpolymer composition is the same as the unit content of feed monomers and every terpolymer chain has only one acetoxy group and one carboxyl group. For the B/E/A (60/35/5) terpolymer, $DPn$ is calculated by the following equation:

$$DPn = [(b_1 + b_2 + b_3) \text{ peak area} \div d \text{ peak area} \times 2 \div 3] \div 0.65$$ (7)

The $DPn$ calculated for three terpolymers are listed in Table 1. Apparently, the $DPn$ appears lower than we...
speculate because the ribbons drawn from the three terpolymer melts are tough and exhibit high tensile properties and fibrillarity, but no brittleness at all. It seems that the molecular weight determined by end-group analysis based on \([1H]NMR\) spectra is lower than actual molecular weight. The fact that the terpolymers exhibit low DPn but good toughness may be indicative of polymer branching which occurred presumably due to the reaction of the hydrogen atoms on the amide groups.\(^1\)

**Table 1. Assignments of resonance peaks in 200 MHz \([1H]NMR\) spectra of p-oxybenzoate/ethylene terephthalate/p-benzamide (B/E/A) terpolymers**

<table>
<thead>
<tr>
<th>B/E/A (mol%)</th>
<th>a1</th>
<th>a2</th>
<th>a3</th>
<th>a4</th>
<th>b1</th>
<th>b2</th>
<th>b3</th>
<th>c</th>
<th>d</th>
<th>DPn</th>
</tr>
</thead>
<tbody>
<tr>
<td>60/35/5</td>
<td>8.34</td>
<td>8.14</td>
<td>8.34</td>
<td>8.00</td>
<td>7.40, 7.32</td>
<td>7.84—7.75</td>
<td>7.09</td>
<td>4.82</td>
<td>2.39, 2.20</td>
<td>43</td>
</tr>
<tr>
<td>65/30/5</td>
<td>8.38</td>
<td>8.21</td>
<td>8.38</td>
<td>8.05</td>
<td>7.45, 7.38</td>
<td>7.92—7.80</td>
<td>7.15</td>
<td>4.87</td>
<td>2.44, 2.27</td>
<td>20</td>
</tr>
<tr>
<td>70/25/5</td>
<td>8.38</td>
<td>8.19</td>
<td>8.38</td>
<td>8.03</td>
<td>7.43, 7.37</td>
<td>7.86—7.76</td>
<td>7.13</td>
<td>4.85</td>
<td>2.42, 2.23</td>
<td>27</td>
</tr>
</tbody>
</table>

\(a\) The main chain structure is:.

and the end groups are:

**Wide-angle X-ray diffraction of B/E/A terpolymers**

Figure 2 shows the equatorial and meridional intensity profiles for three B/E/A copolymers. The quantitative analytical results of the equatorial and meridional reflections are given in Table 2. Apparently, the B/E/A terpolymer exhibits a more diffuse broad peak on the equator than B/E bipolymers but a sharper peak than B/E/vanillate (V)\(^16\) and B/E/naphthylene terephthalate (N)\(^17\) terpolymers. Note that there is a weaker reflection on the equator in the 2\(^\circ\) range from 15 to 10\(^\circ\) for the terpolymers, which is not observed in the equatorial scans of B/E bipolymers and B/E/V terpolymers.\(^16\) This indicates that lateral molecular packing in the B/E/A terpolymer is poorer than in B/E bipolymers and B/E/V terpolymers.

As shown in Fig 2 and Table 2, three meridional reflections with d-spacings of 0.208—0.209 nm (strongest), 0.324 nm (medium), and 0.451—0.458 nm (weakest), were observed for B/E/A terpolymers. The d-spacings of the strongest and weakest reflections tend to increase with increasing B unit content from 60 to 70 mol% at a fixed A unit content of 5 mol% but the d-spacing of the medium reflections is invariant with terpolymer composition. It is reported that the strongest reflection at 0.208 nm might correspond to the third order of B unit.\(^16\) The peak width at half height of 0.208—0.209 nm and 0.324 nm seems to decrease from 1.86 to 1.68 and from 2.3 to 1.8 degrees respectively with an increase in B unit content from 60 to 70 mol% at a fixed A-unit content of 5 mol%. This corresponds to an increase in the correlation length from 5.12 to 5.66 nm, which implies an increase in the persistence length from 8 to 9 units (B unit length is 0.635 nm), indicative that the terpolymer chains become straighter. These results suggest that the macromolecular chains in the ribbons are oriented along the direction of draw, but lack crystalline order. The same behaviour has been found for B/E bipolymers and B/E/V and B/E/N terpolymers.\(^16,17\)

In addition, the variability of the d-spacing of the meridional maxima and the fact that they are not orders of one another indicate an aperiodic chain structure or a random sequence of monomer units. It is reported that most of the thermotropic liquid-
crystalline copolymers also give rise to aperiodic meridional data.\textsuperscript{16,17}

**Thermostability of B/E/A terpolymers**

Figures 3, 4 and 5 show the high-resolution thermogravimetry (TG), derivative thermogravimetry (DTG), and heating-rate curves for three terpolymers with B/E/A molar ratios of 60/35/5, 65/30/5, and 70/25/5 at an initial heating rate of 50°C min\(^{-1}\) in nitrogen and air. For comparison, Fig 5b shows the traditional TG, DTG and 2DTG curves for B/E/A terpolymer at 10°C min\(^{-1}\) in nitrogen. The thermal decomposition results are given in Tables 3 and 4. As listed in Table 3, comparing the thermal decomposition parameters in nitrogen with those obtained in air, all B/E/A terpolymers exhibit higher T\(_d\), T\(_m1\), T\(_m2\), and T\(_m3\), char yields at 500 and 800°C in nitrogen. This results from the thermo-oxidative degradation or even combustion in air, because an obvious thermo-oxidative degradation peak appears at a higher temperature. These suggest that the onset of the bond cleavage in the B/E/A terpolymers is basically thermal in nature and also influenced by the presence of oxygen.

As shown in Tables 3 and 4, the T\(_d\), T\(_m1\), T\(_m2\), T\(_m3\), and char yield at elevated temperature increase with increasing B-unit content from 60 to 70 mol% at a fixed A-unit content of 5 mol% in both testing atmospheres, possibly due to an increase in intrinsic viscosity [\(\eta\)] of the copoly(ester-amide)s. But there is no regular variation of T\(_m2\), (\(dx /dt\))\(_m\), (\(dx /dT\))\(_m\) with increasing B unit content. It is concluded that the thermolability of the B/E/A terpolymers will enhance with increasing B-unit content to some extent.

The final char residue was calculated on the basis of the B/E/A terpolymer structure.\textsuperscript{18} The group contributions to char formation of \(-\text{O}(-\text{CO}-), \text{OC}(-\text{CO})\_2, \text{OC}(-\text{CH}_2\text{CH}_2\text{O})\_2, \text{and} \text{-HN}(-\text{CO}-)\_2\) are assumed to be 4, 1.25, 0, and 2.2, respectively.\textsuperscript{19} According to these data, the predicted char yield for the terpolymers with B/E/A ratios of 60/35/5, 65/30/5, and 70/25/5 are 24.4, 26.2, and 28.0%, respectively. Apparently, the predicted char yields are larger than those observed experimentally at 800°C in nitrogen. This indicates that the final char yield of the B/E/A terpolymers in inert atmosphere might not be an additive parameter. The respective weight losses after the first major DTG peak on the high-resolution (\(dx /dt\)) curves of three terpolymers with B/E/A molar ratios of 60/35/5, 65/30/5, and 70/25/5 are shown in Table 4. It is coincidental that these weight losses are close to the weight losses predicted after the complete loss of whole ester, ethylene, and amide groups and hydrogen atom on the polymer chains (listed in Table 4).

Comparing Figs 3a and 4 with Fig 5, demonstrates that the high-resolution (\(dx /dt\)) and (\(d^2x /dt^2\)) plots generally exhibit higher resolution than the traditional (\(dx /dt\)) and (\(d^2x /dt^2\)) plots. The (\(dx /dt\)) and (\(d^2x /dt^2\)) plots look smoother and sharper than the high-resolution (\(dx /dt\)) and (\(d^2x /dt^2\)) curves. There is almost no second peak on the (\(dx /dt\)) plot obtained at 10°C min\(^{-1}\).  

**Kinetics of thermal degradation of B/E/A terpolymers**

The kinetic parameters of thermal degradation for B/E/A terpolymers obtained from Figs 6 and 7 by the Friedman, Chang, and Kissinger methods are presented in Table 5. It can be seen that the variation of activation energy and pre-exponential factor of the thermal degradation with the terpolymer composition is substantially the same as the variation of degradation temperatures. The average E' and Ln Z values increase with increasing B-unit content from 60 to 70 mol% at a fixed unit-A content of 5 mol%. A similar variation of the kinetic parameters for the B/E/m-oxybenzoate terpolymers has been observed.\textsuperscript{17,20} It is concluded that the thermal degradation rate of the B/E/m-oxybenzoate terpolymers in both nitrogen and air will decrease with increasing unit-B content to some extent. This is different from the variation of the activation energy of thermal degradation for B/E/V terpolymers with composition. Note that the decom-

---

**Table 2.** Peak position (2\(\theta\) and d-spacing) and peak width at half height of wide-angle X-ray diffraction for a drawn ribbon of copoly(p-oxybenzoate)-ethylene terephthalate-benzamide(A))

<table>
<thead>
<tr>
<th>B/E/A (mol%)</th>
<th>1(^{\text{st}}) peak</th>
<th>2(^{\text{nd}}) peak</th>
<th>3(^{\text{rd}}) peak</th>
<th>Persistance</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>2(\theta) (degree)</td>
<td>d (nm)</td>
<td>width (degree)</td>
<td>2(\theta) (degree)</td>
</tr>
<tr>
<td>Equatorial</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>65/30/5</td>
<td>20.1s</td>
<td>0.442</td>
<td>5.0</td>
<td></td>
</tr>
<tr>
<td>Meridional</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>60/35/5</td>
<td>19.7w</td>
<td>0.451</td>
<td>–</td>
<td>27.5m</td>
</tr>
<tr>
<td>65/30/5</td>
<td>19.6w</td>
<td>0.453</td>
<td>–</td>
<td>27.5m</td>
</tr>
<tr>
<td>70/25/5</td>
<td>19.4w</td>
<td>0.458</td>
<td>–</td>
<td>27.5m</td>
</tr>
</tbody>
</table>

\(^a\) Relative intensities are denoted as: s=strong, m=medium, w=weak.

---

position reaction order, \( n \), changes irregularly with a variation of terpolymer composition.

The correlation coefficient of two kinds of plot of calculating kinetic parameters ranges from 0.9873 to

---

**Figure 3.** (a) High-resolution TG and DTG, (b) 2DTG and heating rate curves of copoly [p-oxybenzoate (B) ethylene terephthalate (E)-p-benzamide (A)] with three B/E/A molar ratios in nitrogen at an initial heating rate of 50°C min \(^{-1}\) and resolution 3.0. (---) 60/35/5; (---) 65/30/5; (——) 70/25/5.

**Figure 4.** Representative (a) high-resolution TG and DTG, (b) 2DTG and heating rate curves of copoly [p-oxybenzoate (B) ethylene terephthalate (E)-p-benzamide (A)] with two B/E/A molar ratios in air at an initial heating rate of 50°C min \(^{-1}\) and resolution 3.0. (---) 65/30/5; (——) 70/25/5.
0.9997. The three kinetic parameters obtained by Friedman and Chang methods are substantially the same. Only the \( n \) value obtained by the Kissinger method is apparently larger. These indicate that the first two methods are both suitable for calculation of the degradation kinetic parameters of the B/E/A terpolymers.

It is seen from Table 5 that the three kinetic parameters of the thermal degradation for the aromatic copoly(ester-amide)s obtained by high-resolution thermogravimetry at a variable heating rate are nearly the same as those by traditional thermogravimetry at constant heating rate, indicating a good applicability of kinetic methods developed for constant heating-rate to the variable heating-rate method.

**Isothermal degradation of B/E/A terpolymer**

The weight losses of the terpolymer with B/E/A molar ratio of 65/30/5 during isothermal heating under nitrogen and air were measured at 450 and 420°C, and are shown in Figs 8 and 9. The terpolymer exhibited rapid weight losses of 50% in nitrogen and 56% in air during initial isothermal heating of 25 min at 450°C. The terpolymer will lose only 8% weight constant heating rate, indicating a good applicability of kinetic methods developed for constant heating-rate to the variable heating-rate method.

**Table 3.** Thermal degradation characteristics for copoly [p-oxybenzoate (B)-ethylene terephthalate (E)-p-benzamide (A)] by high-resolution thermogravimetry

<table>
<thead>
<tr>
<th>B/E/A (mol)</th>
<th>([\eta]) ((DL/g^{-1}))</th>
<th>(T_{\text{d}}/T_{\text{m}}/T_{\text{p}}) ((C))</th>
<th>((dx/dt)<em>{r1}/(dx/dt)</em>{r2}/(dx/dt)_{r3}) ((% min^{-1}))</th>
<th>((dx/dT)<em>{r1}/(dx/dT)</em>{r2}/(dx/dT)_{r3}) ((% ^{\circ}C^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>In Nitrogen</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>60/35/5</td>
<td>0.67</td>
<td>447/455, 463/526/614</td>
<td>11.5, 11.1/3.6/2.6</td>
<td>2.3, 3.1/0.18/0.1</td>
</tr>
<tr>
<td>65/30/5</td>
<td>0.83</td>
<td>451/456/665</td>
<td>11.4/3.5/2</td>
<td>3.5/0.25/0.38</td>
</tr>
<tr>
<td>65/30/5c</td>
<td>0.83</td>
<td>424/455/1.5</td>
<td>10.4/-/-</td>
<td>1.0/-/-</td>
</tr>
<tr>
<td>70/25/5</td>
<td>0.88d</td>
<td>463/456/517/668</td>
<td>14.5/5.3/1.8</td>
<td>5.9/0.39/0.06</td>
</tr>
<tr>
<td><strong>In Air</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>60/35/5</td>
<td>0.67</td>
<td>440/445/543</td>
<td>13.5/-/-</td>
<td>3.5/-/-</td>
</tr>
<tr>
<td>65/30/5</td>
<td>0.83</td>
<td>442/446/557</td>
<td>12.6/4.3/12.6</td>
<td>3.2/0.23/4.0</td>
</tr>
<tr>
<td>70/25/5</td>
<td>0.88d</td>
<td>449/453/557</td>
<td>11.9/4.7/12.5</td>
<td>3.1/0.29/2.6</td>
</tr>
</tbody>
</table>

\(a\) Measured in phenol/sym-tetrachloroethane (1/1 vol) at 30°C.
\(b\) A doublet.
\(c\) Its TG and DTG curves were observed at 10°C min\(^{-1}\).
\(d\) Partly soluble in the measuring solvent of phenol/sym-tetrachloroethane (1/1 vol.) at 30°C.
very slowly in nitrogen during the heating time from 25 to 300 min until a char yield of 42.2%, but an additional slow weight loss in air has been observed during the heating time in the range from 25 to 150 min until a constant char yield of 10% in air at the isothermal heating time of 300 min. It is found that the isothermal degradation of the terpolymer is slower at 420°C than at 450°C. The weight loss of 30% in both

Table 4. Weight loss after the first major degradation process and char yield at elevated temperature for copoly(p-oxybenzoate(B)-ethylene terephthalate(E)-p-benzamide (A))

<table>
<thead>
<tr>
<th>B/E/A (mol)</th>
<th>Experimental in nitrogen/air</th>
<th>Calculateda</th>
<th>At 500°C in nitrogen/air</th>
<th>At 800°C in nitrogen/air</th>
</tr>
</thead>
<tbody>
<tr>
<td>60/35/5</td>
<td>51.5/-</td>
<td>50.4</td>
<td>45.8/-</td>
<td>14.7/-</td>
</tr>
<tr>
<td>65/30/5</td>
<td>50.4(51.1)</td>
<td>49.1</td>
<td>47.6(40.1)</td>
<td>13.5(5.7)</td>
</tr>
<tr>
<td>70/25/5</td>
<td>45.7/46.6</td>
<td>47.8</td>
<td>54.3/48.7</td>
<td>26.4/0</td>
</tr>
</tbody>
</table>

a The calculated data corresponding to the exclusion of ethylene, ester, amide groups and all hydrogen atoms.

b The data in the parentheses are obtained from the TG curve at 10°C min⁻¹.

Figure 6. Application of Friedman method to the high-resolution TG and DTG data (a) in nitrogen and (b) in air of copoly(p-oxybenzoate (B)-ethylene terephthalate (E)-p-benzamide (A)) with three B/E/A molar ratios at an initial heating rate of 50°C min⁻¹ and resolution 3.0. (□) 60/35/5; (○) 65/30/5; (△) 70/25/5.

Figure 7. Application of Chang method to the high-resolution TG and DTG data (a) in nitrogen and (b) in air of copoly(p-oxybenzoate (B)-ethylene terephthalate (E)-p-benzamide (A)) with three B/E/A molar ratios at an initial heating rate of 50°C min⁻¹ and resolution 3.0. (□) 60/35/5; (○) 65/30/5; (△) 70/25/5.
nitrogen and air during isothermal heating of an initial 25 min at 420 °C was observed. The terpolymer will lose 49 wt% in nitrogen and 61.5 wt% in air during the heating time at 420 °C from 25 to 300 min until char yields of 21 wt% in nitrogen and 8.5 wt% in air at the heating time of 300 min. This behaviour is similar to that found in the isothermal TG experiments of thermotropic poly(p-oxybenzoate-ethylene terephthalate), copoly(p-oxybenzoate-ethylene terephthalate-vanillate) at 450 °C,17 wholly aromatic poly(p-oxybenzoate-co-2,6-naphthoate) at 500 °C6 and poly(ether ether ketone) in nitrogen.13,21 The B/E/A terpolymer is isothermally more stable than poly[p-oxybenzoate(B)-co-ethylene terephthalate(E)] (B/E=70/30)17 but less stable than wholly aromatic thermotropic liquid-crystalline copolyesters such as poly(p-oxybenzoate-co-2,6-naphthoate)6 and copoly(p-oxybenzoate(B)-ethylene terephthalate(E)-vanillate(V)) (B/E/V=60/35/5). The respective dotted lines shown in Fig 8 and short dash dotted lines in Fig 9 were the isothermal TG curves at 450 °C and 420 °C predicted by eqn (6) on the basis of the average kinetic parameters listed in Table 5 for the non-isothermal degradation. It is found that the predicted TG curves at 450 °C are very close to those observed experimentally during initial heating time of 10 min in nitrogen and air as well as the last heating time of longer than 125 min only in air. This indicates that the initial degradation reaction of the B/E/A (65/30/5) terpolymer might follow the same route as the reaction mechanism in non-isothermal degradation processes at 450 °C. However, an obvious difference between the experimental and predicted TG curves is found when the isothermal heating time ranges from 10 to 125 min, indicative that the middle isothermal degradation reaction is different from non-isothermal degradation. Apparently, two degradation steps in non-isothermal TG (eg Figs 3a and 4a) in both atmospheres and in isothermal TG (Fig 8) at 450 °C in air occur whereas only a single degradation process could be generally developed through kinetic equations.

The calculated TG curves at 420 °C are also close to those obtained experimentally during the heating time from 10 to 310 min in nitrogen and air. Note that bigger differences between calculated and experimental TG curves were observed within the initial heating time of 10 min because the real temperature of the copolymer during this period is much lower than 420 °C, as indicated by the temperature lines in Fig 9. It is seen from Fig 8 that the maximum rate of weight Table 5. Kinetic parameters of the first major thermal degradation for copoly[p-oxybenzoate(B)-ethylene terephthalate(E)-p-benzamide(A)] by three calculating techniques in the temperature range from 375 to 463 °C.

<table>
<thead>
<tr>
<th>B/E/A (mol)</th>
<th>Friedman</th>
<th>Chang</th>
<th>Kissinger</th>
<th>Average</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>E(^a)</td>
<td>n</td>
<td>Ln Z(^b)</td>
<td>p(^c)</td>
</tr>
<tr>
<td>In Nitrogen</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>60/35/5</td>
<td>212</td>
<td>2.7</td>
<td>33</td>
<td>0.9904</td>
</tr>
<tr>
<td>65/30/5</td>
<td>232</td>
<td>1.8</td>
<td>36</td>
<td>0.9874</td>
</tr>
<tr>
<td>65/30/5(^c)</td>
<td>226</td>
<td>1.7</td>
<td>36</td>
<td>0.9884</td>
</tr>
<tr>
<td>70/25/5</td>
<td>290</td>
<td>2.0</td>
<td>45</td>
<td>0.9982</td>
</tr>
<tr>
<td>In Air</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>60/35/5</td>
<td>212</td>
<td>2.3</td>
<td>33</td>
<td>0.9997</td>
</tr>
<tr>
<td>65/30/5</td>
<td>215</td>
<td>2.0</td>
<td>33</td>
<td>0.9905</td>
</tr>
<tr>
<td>70/25/5</td>
<td>243</td>
<td>1.7</td>
<td>38</td>
<td>0.9927</td>
</tr>
</tbody>
</table>

\(^a\) The units of E and Ln Z are kJ mol\(^{-1}\) and min\(^{-1}\), respectively.
\(^b\) r means the correlation coefficient.
\(^c\) Its TG and DTG were obtained at 10 °C min\(^{-1}\).
\(^d\) The values are obtained according to the equation n = |(d\(\Delta\alpha/d\(\Delta\theta\)) Lmax ||(d\(\Delta\alpha/d\(\Delta\theta\)) Rmax |.

Graph 8. Isothermal TG and DTG curves for the copoly[p-oxybenzoate(B)-ethylene terephthalate(E)-p-benzamide(A)] with the B/E/A molar ratio of 65/30/5 at 450 °C (—) in nitrogen and (—) in air and (—) calculated isothermal TG curves based on the average kinetic parameters listed in Table 5, the upper dotted line in nitrogen and lower dotted line in air.
loss at 450°C in nitrogen or air occurs at about 14 or 22wt% and the total overall weight loss is 57.8 or 90%. The maximum rate of weight loss at 420°C in nitrogen or air takes place at about 22.5 or 21.5wt% and the total overall weight loss is 79 or 91%. These weight losses correspond basically to 25% of the overall total weight loss. This implies that the isothermal pyrolysis of the B/E/A (65/30/5) terpolymer under nitrogen and air could be a random chain scission process since random depolymerization reactions should have a maximum rate at the weight loss of 25% based upon theoretical calculations by Flynn–Wall while for an unzipping mechanism it would occur at weight loss of 40%. The same random mechanism of isothermal degradation for aromatic poly(p-oxybenzoate-co-2,6-naphthoate), poly(p-oxybenzoate-co-ethylene terephthalate), and copoly(p-oxybenzoate(B)-ethylene terephthalate (E)-vanillate(V)) has been speculated.

It has been found that the temperatures, activation energy, and frequency factor of the thermal degradation for the B/E/A terpolymers are slightly higher than...
those for the poly(oxybenzoate-co-ethylene terephthalate), copoly(oxybenzoate-ethylene terephthalate-vanillate), and copoly(oxybenzoate-ethylene terephthalate-m-oxybenzoate). This might suggest that an introduction of only 5 mol% amide group into the aromatic polyester chain will increase thermostability and lower degradation rate.

Note that all of the \( T_{\text{ds}} \), \( T_{\text{m,dr}} \), maximum weight-loss rate, char yield, and kinetic parameters obtained by the traditional TG method at 10°C min\(^{-1}\) are lower than those by the high-resolution TG method at an initial heating rate of 50°C min\(^{-1}\).

**CONCLUSIONS**

\(^{1}H\)NMR spectra of thermotropic liquid-crystalline copoly(oxybenzoate-ethylene terephthalate-p-benzamide) obtained at 200 MHz have been resolved and their assignments have been determined. Equatorial and meridional scans of wide-angle X-ray diffraction of the copoly(ester-amide)s have been analysed. High-resolution thermogravimetry at a variable heating rate and isothermal thermogravimetry at 420–450°C can provide more information on thermal and thermo-oxidative degradations of the copoly(oxybenzoate-ethylene terephthalate-p-benzamide) in a short period. The first major stage might be ascribed to the removal of the ester, ethylene and amide groups and hydrogen atom on the terpolymer chain. Further oxidation and combustion of the residual char were also observed in nitrogen and 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-p-benzamide) through conventional kinetic equations which were deduced for the traditional thermogravimetry at a constant heating rate. The activation energy (\( E' \)), decomposition order (\( n \)) and frequency factor (\( Z \)) of the thermal decomposition for the B/E/A terpolymers obtained by Friedman and Chang techniques have only a small difference. The initial isothermal degradation mechanism of the terpolymer may be similar to its non-isothermal degradation mechanism. Introducing an amide group into the main chain of an aromatic polyester might enhance the thermostability and slow down the degradation rate in non-isothermal heating conditions. The thermostable and kinetic parameters obtained by the high-resolution method are slightly higher than those by the 10°C min\(^{-1}\) TG method.

**ACKNOWLEDGMENTS**

This project was supported by the Phosphor Plan of Science Technology for Young Scientists of Shanghai City of China (98QE14027), by the National Natural Science Foundation of China (29804008), and also by the Foundation of Laboratory of Molecular Engineering of Polymers of the Ministry of National Education of China.

**REFERENCES**