# Thermal Decomposition Behavior of Main-Chain Thermotropic Liquid Crystalline Polymers, Vectra A-950, B-950, and Xydar SRT-900

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**ABSTRACT:** We investigated the thermal decomposition behavior of three commercially available liquid crystalline polymers (LCPs), Vectra A950, Vectra B950, and Xydar SRT-900. The apparent activation energies  $(E_{\alpha})$  associated with the thermal degradation processes were determined by the Ozawa and Kissinger methods, using data from dynamic thermogravimetric analysis (TGA) experiments. The magnitudes of the  $E_{\alpha}$  for these LCPs follow the order: Xydar > Vectra A > Vectra B in both air and N<sub>2</sub> environments. The stability of the samples at the beginning of the degradation processes follows the same order. This order may result from the kink naphthoyl units in Vectra A and a relatively weak bond dissociation energy of C-N in Vectra B. However, at 560°C the weight loss values of these three LCPs in  $N_2$  become close (around 37%). After 600°C, the stability order surprisingly changes to Vectra B950 > Vectra A950 > Xydar SRT-900. This suggests that the more stable the sample is at the beginning, the less stable the corresponding residue is. Fourier Transform Infra-red (FTIR) spectra imply that random chain scission and hydrogen abstraction are the degradation mechanisms in N<sub>2</sub> atmosphere and the bands of C=O stretching for all 3 LCPs decrease after 560°C, indicating the finish of the ester bond rupture process. Further increasing temperature mainly results in carbonization. For all three LCPs, CO<sub>2</sub> is the dominant degradation product during the entire testing periods in both  $N_2$  and air environments and the change of  $CO_2$  amount is consistent with the degradation rate. Residues after TGA experiments in  $N_2$  were analyzed and found to have a relatively high percentage of oxygen element, indicating the formations of ether and ketone structures during the thermal degradation of these three LCPs. Forty-seven percent of the nitrogen element remaining in the case of Vectra B950 indicates the formation of the structures containing nitrogen. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 73: 2195-2207, 1999

**Key words:** liquid crystalline polymers; Vectra; Xydar; thermal degradation; TGA–FTIR

# INTRODUCTION

Main-chain liquid crystal polymer (LCP) is one of the most advanced materials used in electronic devices and fiber composites because it offers unique rheological behavior and outstanding mechanical properties. Currently, most modern, high-precision, thin-walled electronic connectors and couplings are made from LCPs, whereas most military helmets and bulletproof vests are made from LCP fibers. In general, a polymer that ex-

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hibits liquid crystal (LC) behavior is synthesized from stiff and rod-like molecules so that the longrange molecular orientational order persists in the absence of various types of short range translational order. This class of ordering is a direct result of specific types of intermolecular interactions and manifests itself by unique macroscopic physical properties. Certain LCPs can be highly oriented to produce materials with exceptional tensile properties and in some cases unique optical properties. As a result, LCPs have attracted interest from both academia and industry. Several review articles and books have described the scientific progress on this subject.<sup>1–8</sup>

Two approaches have been developed to exhibit a polymer in a LC state. One is to form LC behavior in a solution (lyotropic LCP), and the other is in a melt (thermotropic LCP). Du Pont's Kevlar is a lyotropic aramid, while Hoechst Celanese's (Summit, NJ) Vectra is a thermotropic copolyester (including copolyester-amide). Kevlar maintains its performance and is extremely stable at elevated temperatures but with two major drawbacks: it is wet-spun from a corrosive  $H_2SO_4$  solution and is not melt-processable. Some thermotropic LCPs are able to overcome these two deficiencies. Not only can they be melt-spun to yield high-modulus and high-strength fibers, but they can also be injection-molded into complicated 3-dimensional parts without losing the uniqueness of LCP characteristics. Thus, most of thermotropic LCPs applications are for injection molding, whereas Kelvar is for high performance composites.

To expand the use of thermotropic LCPs into microelectronics, defense, composites, and aerospace applications where thermal oxidation property becomes critical, a fundamental understanding of thermotropic LCPs at elevated temperatures is needed urgently. Crossland et al.<sup>9</sup> used thermogravimetric analysis (TGA) and pyrolysisgas chromatograph/mass spectrometry (Py-GC/ MS) to research the thermal stability and thermal degradation mechanisms of the homopolymer of p-hydroxybenzoic acid (p-HBA) and its copolymer with terephthalic acid (TA), and biphenol (BP). They also calculated the overall activation energy for degradation by regression analysis of the isothermal TGA data. It was found that the homopolymer was less stable than the copolymers. They suggested that the products of degradation can be explained on the basis of chain scission and hydrogen abstraction reactions, and the scission of the ester groups is the major breakdown route in flash pyrolysis. Dufour et al.<sup>10</sup> analyzed the

thermal decomposition products of Vectra A950 and Xydar SRT-500 by TGA-MS. Hummel et al.<sup>11</sup> used MS and FTIR spectrometer to analyze the decomposition products from linear-temperature programmed pyrolysis and they discussed the degradation mechanisms including Fries-analogue rearrangements. Sueoka et al.<sup>12</sup> studied the thermal degradation mechanisms of the LCP from p-HBA, BP, and TA with a 2:1:1 molar ratio of PHB/BP/TA, which is the composition of Xydar SRT-900. The origin of the main pyrolysis products from the corresponding comonomer units were estimated after experiments on the LCPs containing deuterated TA units and those having different comonomer ratios. They suggested that benzene is formed mainly from the TA unit, whereas phenyl benzoate and biphenyl are produced mostly by the recombination reaction of PHB and TA units, and as the C—C bond between aromatic rings is not easily cleaved, products larger than phenyl benzoate are formed from the BP unit. Sato et al.<sup>13</sup> studied the flame-resistant and self-extinguishing mechanisms of Vectra A950, Xydar SRT-500, and X7G by directly coupled thermal analysis MS. They concluded that flame resistance mechanisms of LCPs can be attributed mainly to the endothermic reaction at the ester linkage rupture process, char formation, and diluting  $O_2$  by evolution of  $CO_2$ . Besides these reports on the commercial LCPs of Vectra, Xydar, and LCPs with similar structures, Foti et al.,14 Schild et al.,<sup>15</sup> Skovby et al.,<sup>16</sup> and Lorente et al.<sup>17</sup> have studied the thermal degradation processes of some LCPs synthesized by themselves.

However, to our knowledge, no one has reported the TGA-FTIR data for the three commercial LCPs used in our study. Pyrolysis-MS was used in most of the studies on the Vectra and Xydar LCPs. Because the heating process in normal pyrolysis is so fast that all the degradation reactions occur almost simultaneously, the sample analyzed is actually a multi-component mixture of the degradation products at different degradation stages. The information about the loss of sample weight is unavailable in the pyrolysis experiment. Different matter can have the same mass units in MS spectra, so identifying the evolved products by FTIR also has its own advantages. Most pyrolysis-MS work on LCPs either were conducted in vacuum atmosphere or an inert gas was used as the purge gas, though Sato et al.<sup>13</sup> have discussed the thermal degradation of LCPs with thermal analysis-MS under quasi-air atmosphere. Therefore, although previous articles have provided some descriptions of the thermal decomposition process of LCPs, it is still interesting and worthwhile to revisit this subject by TGA-FTIR. In addition, to our knowledge, no report has been made on the activation energy,  $E_a$ , of the thermal degradation for these three LCPs from dynamic TGA data. We intend to determine the  $E_a$  values using Ozawa's and Kissinger's methods.<sup>18,20</sup> The C/H/N elemental analysis is made on the residues after TGA in N<sub>2</sub> and the raw samples.

# **EXPERIMENTAL**

#### Materials

Three commercial thermotropic LCP resins were studied, namely Vectra A950, Vectra B950 (Ticona Corp, Summit, NJ) and Xydar SRT900 (Amoco, Alpharetta, GA). All the samples were in pellet state. Vectra A950 is composed of HBA and 2,6-hydroxynaphthoic acid (HNA) monomer units with an HBA/HNA molar ratio of 73/27. Vectra B950 is made of HNA, p-hydroxyl acetaniline (HAA), and terephthalic acid (TA) units with an HNA/HAA/TA molar ratio of 60/20/20. Xydar SRT-900 is synthesized from HBA, BP, and TA units with an HBA/BP/TA molar ratio of 2/1/1.

All the samples were dried overnight in vacuum at 120°C before the experiments.

#### Conditions

## TGA

The TGA system used comprises a Perkin-Elmer (Norwalk, CT, USA) TGA 7 Thermogravimetric Analyzer with a TAC 7 Instrument Controller. Nickel and iron are used for the temperature calibration. The purge gas for balance is  $N_2$ . The flow rates of the balance purge and sample purge are 40 and 20 ml/min, respectively. Dynamic experiments were conducted at 5, 10, 20, and 40°C/min both in air and  $N_2$ . The sample weight is 5–7 mg.

# TGA-FTIR

The conditions for TGA part are the same as described above, except that the heating rate is fixed at 10°C/min both in air and N<sub>2</sub>. The exhausted products from TGA are flushed through a transfer line, to a gas cell of a Perkin-Elmer Spectrum 2000 FT-IR spectrometer. N<sub>2</sub> is used in the transfer line with the flow rate of 35 ml/min. The gas cell, where IR spectra are obtained, is fitted with KBr windows, which are spring-loaded to

maintain a gas seal at all operating temperatures. The temperatures of the transfer line and the gas cell during experiments are both kept at 200°C. The IR scan is performed continuously with four scans per slice. The IR resolution is 8 cm<sup>-1</sup>.

#### **Elemental Analysis**

The elemental analysis was done on a Perkin-Elmer 2400 CHN elemental analyzer. This instrument uses the classical combustion method to convert the sample elements to simple gases of  $CO_2$ ,  $H_2O$ , and  $N_2$ . The resulting gases are then controlled to exact conditions of pressure, temperature, and volume. Finally, they are separated and measured as a function of thermal conductivity. All the content other than C, H, N is regarded as oxygen element. The sample weight is  $\approx 1$  mg.

#### **RESULTS AND DISCUSSION**

# TGA

# Background of Ozawa's<sup>18</sup> and Kissinger's<sup>20</sup> Methods

The degree of conversion in a thermal degradation process is defined as:

$$\alpha = \frac{W_0 - W}{W_0 - W_f}$$

where W,  $W_0$ , and  $W_f$  are the actual, initial, and final weights of the samples, respectively. The rate of degradation can be expressed as:

$$\frac{d\alpha}{dt} = k \cdot f(\alpha) \tag{1}$$

$$k = A \, \exp\!\left(-\frac{E_a}{RT}\right) \tag{1a}$$

where t is the reaction time, and  $f(\alpha)$  is a function of  $\alpha$  and is usually expressed as  $(1 - \alpha)^n$ , A is the pre-exponential factor,  $E_a$  is the apparent activation energy of the degradation reaction, R is the universal gas constant. Since the heating rate r is equal to d T/d t, eq. (1) can be rewritten as follows:

$$\frac{rd\alpha}{dT} = A \, \exp\left(-\frac{E_a}{RT}\right) f(\alpha) \tag{2}$$

Equation 2 can be rearranged as

$$g(\alpha) = \int_{0}^{\alpha} \frac{d\alpha}{f(\alpha)} = \frac{A}{r} \int_{0}^{T} \exp\left(-\frac{E_{\alpha}}{RT}\right) dT = \frac{AE_{\alpha}}{rR} h(x)$$
(3)

where,

$$x = \frac{E_a}{RT}, \ h(x) = -\int_{\infty}^x \frac{\exp(-x)}{x^2} \, dx$$

Ozawa<sup>18</sup> used Doyle's approximation<sup>19</sup> by assuming the integral h(x) can be expressed as  $\log h(x) \approx -2.315 - 0.457 x$  or  $\ln h(x) \approx -5.330 - 1.052 x$  if 20 < x < 60, thus from equation 3, we can get

$$\ln g(\alpha) = \ln \frac{AE_a}{rR} - 5.330 - 1.052 \frac{E_a}{RT} \quad (4)$$

In equation 4, *A*, *R* are constant, and at a specific  $\alpha$  or weight loss percentage,  $g(\alpha)$  is also constant. Equation 4 can then be written as:

$$\ln r = C - 1.052 \, \frac{E_a}{RT} \tag{5}$$

where C is a constant and is equal to  $\ln [(AE_a)/[g(\alpha)R]] - 5.330$ . Using this equation, the  $E_a$  value at any specific weight loss can be calculated from the linear dependence of  $\ln r$  vs. 1/T at different heating rates.

Kissinger<sup>20</sup> derived the following equation by taking a derivative of eq. (2) and assuming  $f(\alpha) = (1 - \alpha)^n$ :

$$rac{d^2lpha}{dT^2} = rac{dlpha}{dT}\left[rac{E_a}{RT^2} - rac{An}{r}\exp\!\left(-rac{E_a}{RT}
ight)(1-lpha)^{n-1}
ight]$$

If  $T_m$  is chosen as the temperature at the maximum of the first derivative of the weight loss curves for different heating rates, then  $d^2\alpha/dT^2$  is equal to zero at  $T_m$ . This relationship yields:

$$rac{E_a}{RT_m^2} - rac{An}{r} \expigg(-rac{E_a}{RT_m}igg)(1-lpha_m)^{n-1} = 0$$

or

$$\ln \frac{r}{T_m^2} = \ln \frac{nRA(1 - \alpha_m)^{n-1}}{E_a} - \frac{E_a}{RT_m}$$
(6)



**Figure 1** (a): TGA in  $N_2$  of Vectra B950 (heating rates: 5, 10, 20, 40°C/min); (b): TGA in air of Vectra B950 (heating rates: 5, 10, 20, 40°C/min).

The  $E_a$  value may be calculated from the linear dependence of  $\ln(r/T_m^2)$  on  $1/T_m$  at different heating rates by assuming that  $\alpha_m$  or weight loss percentage at  $T_m$  is constant.

# TGA Result and Data Analysis

Figure 1 shows the TGA curves for the experiments with Vectra B950 in  $N_2$  and air. The curves plotting the first derivative of the 10°C/min TGA curves are also given. The curves for Vectra A950 and Xydar SRT-900 are similar to those of Vectra B950 and not given here. There is only one primary weight loss step during the thermal decomposition processes in  $N_2$ , whereas there are two steps in air. No residue is left after TGA experiments in air atmosphere, however 41, 49, and 38% weight remains after experiments in  $N_2$  for Vectra A950, Vectra B950, and Xydar SRT-900, respectively. The temperatures at 5 and 10% weight loss percentages are listed in Table I, from which it can be seen that the order of thermal

Heating rate (°C/min)		Vectra A950				Vectra B950			Xydar SRT-900			
	5	10	20	40	5	10	20	40	5	10	20	40
Weight loss												
In air (%)												
5	493	513	524	546	480	493	516	530	508	525	536	549
10	505	525	535	554	493	504	531	544	519	541	551	563
In N <sub>2</sub> (%)												
5	487	503	522	540	481	502	520	534	488	505	525	539
10	498	513	531	547	491	510	531	547	506	519	537	553

Table I Temperatures at 5%, 10% TG Weight Loss

TG, thermogravimetric.

stability is Xydar SRT-900 > Vectra A950 > Vectra B950 both in air and N<sub>2</sub>, whereas the weight remain after TG in N<sub>2</sub> follows the contrary order.

According to the Ozawa method,<sup>18</sup> at any specific  $\alpha$  or weight loss percentage, the  $E_a$  values can be calculated from the linear dependence of  $\ln r$ on 1/T at different heating rates, from eq. (4) it can be seen that  $E = -R \cdot Slope/1.052$ . Figure 2 shows the plots of  $\ln r$  vs. 1/T at different weight loss percentages for the experiments of Vectra B950 in air and N<sub>2</sub>. The plots for Vectra A950 and Xydar SRT-900 are similar and therefore not given here.

Figure 3 shows that the appearances of  $E_a$  curves for TGA in N<sub>2</sub> are different with different samples.  $E_a$  for TGA in air has a maximum point at a weight loss of 40, 35, and 45% for Vectra A, Vectra B, and Xydar SRT-900, respectively. These values of weight loss are very close to those at the deflection points between the two maximums of the first derivative TG curves, which are 45, 35, 48%, respectively for 10°C/min TGA experiments. This suggests that  $E_a$  reaches a maximum after the first degradation stage, and then decreases continuously to the end.

The Kissinger method<sup>20</sup> was used to determine the  $E_a$  associated with the first degradation stage. If  $\alpha_m$  or weight loss percentage at  $T_m$  is assumed to be constant then the  $E_a$  value could be calculated from the linear dependence of  $\ln(r/T_m^2)$  on  $1/T_m$  at different heating rates. To check the validity of this assumption, we found that in the case of Vectra B950, at the heating rates of 5, 10, 20, and 40°C/min, the weight loss percentages at  $T_m$  in air atmosphere were 16, 15, 16, and 18.5%, respectively. They were 19, 20.5, 20.5, and 19.5%, respectively at the first  $T_m$  in N<sub>2</sub>. The weight loss percentages at  $T_m$  are also very close at different heating rates for Vectra A950 and Xydar SRT-900. Thus, it may be reasonable to take  $\alpha_m$  at  $T_m$  as a constant. From eq. (6) we can get that  $E_a = -\text{R}\cdot\text{Slope}$ . Because  $T_m$  for the second degradation stage in air is unclear, no corresponding data processing was done. The values of  $T_m$  for differ-



**Figure 2** (a):  $\ln r \text{ vs. } 1/T \text{ of TGA for Vectra B950 in nitrogen (heating rates: 5, 10, 20, 40°C/min); (b): <math>\ln r \text{ vs. } 1/T \text{ of TGA for Vectra B950 in air (heating rates: 5, 10, 20, 40°C/min).}$ 



**Figure 3** (a): Apparent activation energy of the decomposition reaction for Vectra A950; (b): apparent activation energy of the decomposition reaction for Vectra B950; (c): apparent activation energy of the decomposition reaction for Xydar SRT-900.

ent experiments in air and N<sub>2</sub>, the slopes of ln  $(r/T_m^2)$  vs.  $1/T_m$ , the,  $R^2$  (correlation coefficient), and the  $E_a$  results are listed in Table II.

It can be seen that the  $E_a$  values obtained by the Ozawa method (Fig. 3) are close to those by the Kissinger method both in air and N<sub>2</sub>. In both cases, the magnitudes of the  $E_a$  follow the same order: Xydar SRT-900 > Vectra A950 > Vectra B950 in all conditions. This is in accord with the result of stability. The value of  $E_a$  in N<sub>2</sub> is higher than that in air. Dufour et al.<sup>10</sup> have hypothesized that the naphthoyl units in Vectra A950 disturb its linearity and thus make its backbone less rigid and the initial decomposition temperature lower than that of Xydar SRT-500. Perhaps, for the same reason,  $E_a$  and stability of Vectra A950 is lower than Xydar SRT-900. In the case of Vectra B950 vs Vectra A950, this is due to the fact that the average bond dissociation energy of C—N (about 73 kcal/mol) is smaller than that of C—O (about 85 kcal/mol), thus the introduction of amide bonds as well as the naphthoyl structure certainly makes Vectra B950 even less thermally stable than Vectra A950.

#### **TGA-FTIR**

The TGA curves for TGA-FTIR experiments shown in Figure 4 are almost the same as those for 10°C/min TGA experiments except that the decomposition processes in TGA-FTIR experiments are somewhat faster. The reason is that in TGA experiments there are only balance purge and sample purge gases in furnace; in TGA-FTIR experiments there is additionally an exhaust purge gas. So the decomposition products can be taken away more easily, and the degradation processes are promoted. For Vectra A and Xydar, as predicted, the rate of degradation in air is faster than in  $N_2$  at the beginning of the degradation. However, it is noteworthy that in the case of Vectra B, the rate of degradation in N<sub>2</sub> is faster than in air at the beginning of the degradation even though  $E_a$  in N<sub>2</sub> is higher than in air. This phenomenon has been reproduced several times in both cases with and without FTIR connection if the TGA heating rate is 10°C/min. One of the possible reasons is that the pre-exponential A for the decomposition reaction in N<sub>2</sub> may be apparently higher than that in air for Vectra B 950. Calculation of A is not done here because of the absence of a reliable method.

The general characteristics of the evolution of the degradation products can be observed from Figures 5 and 6, which show the stacked FT-IR spectra for the exhausted products from TG in N<sub>2</sub> and air, respectively. By observing the bands around 2350 cm<sup>-1</sup> and 670 cm<sup>-1</sup>, we can see that  $CO_2$  is the dominant product in all the experiments, which exists all through the degradation process, and the amount of  $CO_2$  is consistent with the thermal decomposition rate. To see more details, several spectra are selected and superimposed as shown in Figures 7–10.

	Vect	ra A950	Vect	ra B950	Xydar SRT-900		
	$N_2$	Air	$N_2$	Air	$N_2$	Air	
$T_m^{a}$ (°C)							
5°C/min	515	505	507	498	548	519	
10°C/min	538	515	524	514	564	535	
20°C/min	550	535	545	541	574	551	
40°C/min	560	550	559	560	590	566	
Slope $(\times 10^3)$	-27.91	-26.65	-23.66	-19.13	-34.15	-27.69	
Correlation coefficient, $R^2$	0.9471	0.9855	0.9924	0.9904	0.9912	0.9989	
$E_a$ (kJ/mol)	232.04	221.57	196.71	159.05	283.92	230.21	

#### Table II Data of Kissinger Method

<sup>a</sup> In the case of TG in air,  $T_m$  is the  $T_m$  at the first  $(\partial W/\partial t)_m$ .

#### TGA-FTIR in N<sub>2</sub> Atmosphere

Figures 7-9 show the FT-IR spectra for Vectra A950, Vectra B950, and Xydar SRT-900, respectively. According to Sueoka's analysis<sup>12</sup> in wholly aromatic polyesters with the structure  $\phi_1$ —CO—  $O-\phi_2$ , the C-O bonds between CO-O are preferentially cleaved over the C-O bonds between  $O-\phi_2$ , and the C-C bonds between  $\phi_1$ -CO are preferentially cleaved over the other types of C-C bonds. Thus, before the O-C bonds between  $O_{-\phi_2}$  breaks, the other two bonds may break first. Therefore the aryl ester structure  $\phi_1$ —CO—O— $\phi_2$  cannot produce CO<sub>2</sub> directly, which must be produced from the terminal  $\phi$ —COO•. The CO<sub>2</sub> appearing at the beginning of the decomposition could be from the original terminal carboxyl group. However, the molecular weights of these three LCPs are more than 10 kg/mol, so the original amount of terminal  $\phi$ —COO• units should be very small and new terminal carboxyl groups must be formed during the thermal decomposition in N<sub>2</sub>. CO can be observed by its characteristic double bands at the right wing of the  $CO_2$  2350 cm<sup>-1</sup> band. CO is produced at  $\approx 510$  °C for Vectra A950 and Xydar SRT-900, and  $\approx 460^{\circ}$ C for Vectra B950 after the formation of  $\phi$ —CO• by chain scission. Its amount decreases gradually after the maximum weight loss  $(\partial W/\partial t)_m$  and it still exists at the end of the decomposition process, which suggests that  $\phi$ —CO• should be formed in the residue. The weak bands around 1300-1700 cm<sup>-1</sup> and 3500-3800 cm<sup>-1</sup> appearing from 460°C to the end show the formation of a small amount of water.

*Vectra A950.* In Figure 7, the 1604  $\text{cm}^{-1}$  and 1498  $\text{cm}^{-1}$  bands represent the vibration of the aromatic rings. The 1604  $\text{cm}^{-1}$  band becomes no-

ticeable at 460°C, and the 1498  $cm^{-1}$  band appears at around 500°C, 40°C before the temperature of  $(\partial W/\partial t)_m$ . The reason why the 1604 cm<sup>-1</sup> becomes noticeable before the 1498  $cm^{-1}$  band will be discussed later. These two bands last to the end. The 1263 and 1189  $\text{cm}^{-1}$  bands existing from 500 to 800°C are associated with C-O stretching; they suggest the presence of aromatic ethers. From 510°C onward, bands appear at 3652, 3056, 1762, 1720, 1323, and 747  $cm^{-1}$  almost simultaneously. The 3652 cm<sup>-1</sup> band represents the O-H stretching vibration. The 3056 cm<sup>-1</sup> band is ascribed to the C—H stretch of the aromatic ring. The 1762 cm<sup>-1</sup> band results from stretching of the ester carbonyl. A band of ester C—O stretching is formed between 1263 and 1189  $cm^{-1}$ , at the shoulder of the 1189  $cm^{-1}$  band. The 1720 cm<sup>-1</sup> band results from the stretching of ketone carbonyls. The 1323  $\text{cm}^{-1}$  band is caused by the in-plane deformation of the phenol O-H. The 747  $\text{cm}^{-1}$  band is assigned to the out of plane bending of C-H on the aromatic ring. These bands indicate the presence of phenols and aryl esters and ketones. The 3056 and 747 cm<sup>-1</sup> bands disappear at about 600°C, 60°C above the  $(\partial W/$  $\partial t$ )<sub>m</sub> temperature, but 1604 and 1498 cm<sup>-1</sup> bands continue to exist. This suggests the formation of the aromatic rings, some H atoms on which have been substituted. The 3652, 1323  $\text{cm}^{-1}$  phenol bands and  $1762 \text{ cm}^{-1}$  ester bond also disappear after 600°C. The 1062 cm<sup>-1</sup> band appears after 525°C, and a shoulder at 1158 cm<sup>-1</sup> also develops gradually from 525°C onward. The 1158 and 1062  $cm^{-1}$  bands appear later than the 3056 and 747 cm<sup>-1</sup> bands; they represent the in-plane deformation of C—H on the substituted rings, and they indicate hydrogen substitution reactions on the aromatic rings.



**Figure 4** (a): TGA data of TGA-IR for Vectra A950 (heating rate: 10°C/min); (b): TGA data of TGA-IR for Vectra B950 (heating rate: 10°C/min); (c): TGA data of TGA-IR for Xydar SRT-900 (heating rate: 10°C/min)

Normally, when a charge disturbance occurs within the aromatic ring through electronic interaction between the ring and the substituents, the intensity of bands of the aromatic rings, particularly those near 1600 cm<sup>-1</sup>, will increase. The 1604 cm<sup>-1</sup> band becomes noticeable before the appearance of the 1498 cm<sup>-1</sup> band and continues to be noticeable at 800°C. So the strong intensity of the 1604 cm<sup>-1</sup> band supports the existence of substitution on the aromatic rings with groups such as carbonyl or oxygen. Moreover, this result agrees with the fact that the 1720 cm<sup>-1</sup> ketone band still exists even at 800°C.

According to the above analysis, we can see that as a consequence of the random chain scission mainly on the carboxyl bond between the carbonyl carbon and the phenolic oxygen, before 500°C some aryl ethers are produced from the recombination reactions. Around 510°C some ar-



Figure 5 (a): Stacked IR spectra of the products from TGA for Vectra A950 in  $N_2$  (heating rate: 10°C/min); (b): stacked IR spectra of the products from TGA for Vectra B950 in  $N_2$  (heating rate: 10°C/min); (c): stacked IR spectra of the products from TGA for Xydar SRT-900 in  $N_2$  (heating rate: 10°C/min).





**Figure 6** (a): Stacked IR spectra of the products from TGA for Vectra A950 in air (heating rate: 10°C/min); (b): stacked IR spectra of the products from TGA for Vectra B950 in air (heating rate: 10°C/min); (c): stacked IR spectra of the products from TGA for Xydar SRT-900 in air (heating rate: 10°C/min).

omatic esters, ketones, and phenols are formed, and then the production of CO becomes noticeable. Phenol and ester bands disappear at  $\approx$  600°C.

*Vectra B950.* The rough baseline of the spectra in Figure 8 suggests that more decomposition products are formed than that of Vectra A. This is due to the fact that amide bonds exist in Vectra B950, correspondingly more bands appear in the 3500-3800 cm<sup>-1</sup> range, which relates to stretching of



Figure 7 Selected IR spectra of the products from TGA for Vectra A950 in  $N_2$  (heating rate: 10°C/min).

the N—H bond. The 1628 cm<sup>-1</sup> band represents deformation vibration of the primary amine N—H, the deformation vibration of the second amine N—H is usually very weak, and the bands around 1341 cm<sup>-1</sup> are assigned to the aromatic amine C—N stretching vibrations. These bands imply the existence of aromatic amine. The 1765 cm<sup>-1</sup> band represents the stretching vibration of ester carbonyl, and the bands around 1715 cm<sup>-1</sup> represent the stretching of ketone and amide carbonyl groups. The 1490 cm<sup>-1</sup> band and the bands around 1600 cm<sup>-1</sup>, which overlap with the 1628 cm<sup>-1</sup> one, represent the aromatic ring vibrations. The 1265 and 1183 cm<sup>-1</sup> bands of ethers continue to exist long after  $(\partial W/\partial t)_m$ .

The decomposition products that exist at  $(\partial W/\partial t)_m$  appear almost simultaneously around 480°C. After 560°C, 50°C above  $T_m$ , most degradation products continue to exist and they decrease only gradually until the end of the decomposition. This suggests that the random chain scission happens on the ester and amid bonds almost at the same



Figure 8 Selected IR spectra of the products from TGA for Vectra B950 in  $N_2$  (heating rate: 10°C/min).



Figure 9 Selected IR spectra of the products from TGA for Xydar SRT-900 in  $N_2$  (heating rate: 10°C/min).

time and the various degradation processes develop at similar rates.

Xydar SRT-900. The IR spectra of products from TGA of Xydar SRT-900 are more similar to that of Vectra A950 than that of Vectra B950. In Figure 9, the three bands in the range of 3500-3800 cm<sup>-1</sup> suggest the existence of three different OH groups because the existence of BP unit increases the variety of aromatic rings. The 3061 cm<sup>-1</sup> band is caused by the aromatic ring C—H stretching, whereas the 829 and 746 cm<sup>-1</sup> bands correspond to the out-of-plane bending of the aromatic ring C—H. These aromatic C—H bands apparently decrease after 560°C range and become unnotice-able after 600°C. This suggests the hydrogen abstraction and substitution reactions on the aromatic rings.

The 1762 and 1709 cm<sup>-1</sup> bands are ascribed to the stretching of ester and ketone carbonyl groups, respectively. The presence of the 1261 cm<sup>-1</sup> and 1185 cm<sup>-1</sup> ether bands, and the 1069 cm<sup>-1</sup> band for the deformation of C—H on the substituted aromatic rings is also similar to the results of Vectra A950.

From Figures 7–9, it can be seen that the  $T_m$  of Vectra B950 is much lower than those of Vectra A950 and Xydar SRT-900. The weight loss of Vectra B950 is much higher than those of Vectra A950 and Xydar SRT-900 until  $\approx 560^{\circ}$ C. However, at 560°C, the weight loss values of the three LCPs become close ( $\approx 37\%$ ). After 600°C, the weight loss of the three LCPs are of this order: Xydar SRT-900 > Vectra A950 > Vectra B950. Correspondingly, in the IR spectra of all the three LCPs, the bands of C=O stretching decrease apparently after 560°C, which suggests the finish of the ester bond rupture process. In the process of the following carbonization, the more stable the

sample is at the beginning, the less stable the corresponding residue is.

#### TGA-FTIR in Air Atmosphere

Figure 10 shows the IR spectra of the products from the degradation process in air environment.



**Figure 10** (a): Selected IR spectra of the products from TGA for Vectra A950 in air (heating rate: 10°C/ min); (b): Selected IR spectra of the products from TGA for Vectra B950 in air (heating rate: 10°C/min); (c): Selected IR spectra of the products from TGA for Xydar SRT-900 in air (heating rate: 10°C/min).

	Eleme	nt Perce Samp	entage o les (%)	f Fresh	Element Percentage of the Residue After TGA-IR in $N_2$ (%)				Weight Remain (%)	Elem	Element Loss Percentage (%)			
LCP	С	Н	Ν	0	С	Н	Ν	0	_	С	Н	Ν	0	
Vectra A950	73.34	3.44	0.06	23.16	85.94	1.22	0.07	12.77	42.5	50.20	84.93	_	76.57	
Vectra B950	76.17	3.73	1.85	18.25	84.64	1.00	1.86	12.50	47	47.77	87.40	52.75	67.81	
Xydar SRT900	73.79	3.26	0.02	22.93	85.02	1.34	0.03	13.61	38	56.22	84.38	_	77.45	

Table III Elemental Analysis Results

LCP, liquid crystalline polymer; TGA, thermogravimetric analysis.

In contrast to the thermal decomposition in  $N_2$ atmosphere, less amount of degradation products other than CO<sub>2</sub> and CO are formed in air atmosphere. From the common character of flat baselines and the absence of complicated bands, we can say that the degradation mechanisms are similar for the three LCPs in air atmosphere, and there are only a few degradation products other than  $CO_2$  and CO. For all the three LCPs, COdoes not appear until the first  $(\partial W/\partial t)_m$  stage. Its amount becomes nearly inconceivable in the period between the two maximum degradation stages and then increases again around the second stage. This suggests that the formation of CO follows two different mechanisms in the two degradation stages. Probably during the first stage, CO is mainly from the terminal  $\Phi$ —CO•, whereas in the second stage, CO is mainly from the oxidation of the chars. Four apparent bands appear in the range of 3500–3800 cm<sup>-1</sup> from the first ( $\partial W$ /  $\partial t$ <sub>m</sub> until the end. These bands are caused by stretching of the free O-H, but they do not represent the existence of H<sub>2</sub>O without the corresponding  $H_2O$  bands around 1630 cm<sup>-1</sup>.

In the case of Vectra A950 [Fig. 10(a)], the characteristic bands of  $H_2O$  at around 3500 cm<sup>-1</sup> and 1630 cm<sup>-1</sup> appear at the first  $(\partial W/\partial t)_m$ ; they decrease to become unnoticeable between the two  $(\partial W/\partial t)_m$  temperatures, and a very small amount of H<sub>2</sub>O is formed at the second  $(\partial W/\partial t)_m$ . There are also broad bands appearing at 1263  $cm^{-1}$  and 1184 cm<sup>-1</sup>, which correspond to the C—O stretching vibrations, indicating the formation of products with ester or ether structures. They may also indicate the existence of phenols, since there are C—O bands in phenols also. For Xydar SRT-900 [Fig. 10(c)], small amount of  $H_2O$  appears at the first  $(\partial W/\partial t)_m$  through to the second  $(\partial W/\partial t)_m$ , and there are also weak bands at  $1265 \text{ cm}^{-1}$  and 1177 $\mathrm{cm}^{-1}$  at the first  $(\partial W/\partial t)_m$ . There is no apparent  $H_2O$  band in the case of Vectra B950 [Fig. 10(b)]. The existence of H<sub>2</sub>O at the end of the decomposition in the case of Vectra A950 and Xydar SRT-900 strongly indicates that the oxidation of char is not the only reaction during the end of the decomposition of these two polymers.

The difference among the weight loss processes of the three LCPs in air atmosphere is very small before the first  $T_m$  ( $\approx$ 518°C). After the first  $T_m$ , the weight loss percentages gradually develops to the order of Xydar SRT-900 > Vectra A950 > Vectra B950. It is noteworthy that this order is the same as the previous order in N<sub>2</sub> test if the temperature of TGA is greater than 600°C. Similarly, the more stable the sample is at the beginning, the less stable the corresponding residue is after the first  $T_m$ . The reasons are discussed later in this article.

#### **Elemental Analysis**

Table III lists the results of elemental analysis on the residue after TGA-IR in N<sub>2</sub> with 10°C/min heating rate. The element loss percentage in Table III is calculated with the formula  $[(100 \times P_1) - (W \times P_2)]/(100 \times P_1)$  where  $P_1$  is the measured weight percentage of the element in the fresh sample,  $P_2$  is the measured weight percentage of the element in the residue, and W is the weight remaining of the sample.

The theoretical C/H/N/O ratios of Vectra A950, Vectra B950, and Xydar SRT-900 are 72.62/3.43/ 0/23.95, 75.29/3.64/1.87/19.20, and 73.37/3.63/0/ 23.0, respectively according to their chemical structures. After comparing the theoretical and measured values, we can say that the experiment data are reliable. The loss percentages of C, O elements follow the same order as that of the stability at the beginning of decomposition which are measured by TGA, i.e., Xydar SRT-900 > Vectra A950 > Vectra B950.

There are H atoms on the amide bonds as well as aromatic rings in the structure of Vectra B950, and these H atoms may be taken away during the



**Figure 11** The degradation mechanism of poly(4-oxybenzoyl) suggested by Hummel et al.<sup>11</sup>

rupture of amide bonds. So the values of H loss percentage are almost the same for Vectra A and Xydar, and apparently higher for Vectra B. The H loss percentages are  $\approx 85\%$  for all three LCPs, which suggests the hydrogen abstraction reactions on the aromatic C—H during the thermal decomposition. Approximately 20–30% of oxygen left in the sample supports the existence of ketone and ether structures in the residues of the three LCPs. The result that 47% of nitrogen left in the residue of Vectra B950 suggests the existence of the nitrile end group, R—N=N—R or other structures with nitrogen.

We have also conducted FTIR experiments on KBr pellets of the char after dynamic TGA tests in  $N_2$  which end at 900°C, but it is difficult to get the spectra with apparent characteristic bands other than those of  $H_2O$  and  $CO_2$ .

Hummel et al.<sup>11</sup> suggested that thermal decomposition of poly(4-oxybenzoyl) in vacuum follows the mechanism as shown in Figure 11. The thermal degradation of the present three LCPs in  $N_2$  before  $T_m$  probably follows similar mechanisms as Hummel's proposal and the char forma-

tion is the main mechanism after  $T_m$ . The oxygen gas in air can react with the eliminated H atoms to form water and thus promote the hydrogen abstraction reaction.  $O_2$  can also directly replace the aromatic ring H atoms adjacent to the phenolic oxygen or benzoate carbonyl and links up the two aromatic rings to form either aryl ethers or any ketones. Therefore,  $O_2$  can lower the  $E_a$  of the degradation reaction. During the second degradation stage, O2 breaks down the crosslinking formed in the first degradation stage and the char begins to degrade by oxidation reactions. With the decrease in the extent of crosslinking and the amount of the char left,  $E_a$  decreases gradually. This second degradation stage does not exist in N<sub>2</sub> with the absence of  $O_2$ .

The more stable the sample is at the beginning of the thermal degradation, the more difficulty the ester bonds are to break, thus the less extent the crosslinking is. This is probably the reason why the weight remaining of the residues after  $\approx 560$ °C in N<sub>2</sub> or after the first  $T_m$  in air follows the contrary order of the stability of the three LCPs at the beginning of the thermal decomposition process. This supposition is not supported completely by the result of  $E_a$  curves obtained by the Ozawa method,<sup>18</sup> probably because the reaction at the higher weight loss stage is complicated and cannot be represented with only one equation of degradation rate.

# CONCLUSION

With the influence of naphthoyl units and amide bonds, the  $E_a$  and stability of the three LCPs at the beginning of the decomposition process follow the order: Xydar SRT-900 > Vectra A950 > Vectra B950. However, the percentages of weight remaining after 560°C in N<sub>2</sub> or after the first  $T_m$  in air follow the contrary order.

 $CO_2$  is the dominant product in all the degradation processes. It exists during the entire degradation process, and its amount is consistent with the degradation rate. CO does not appear until the formation of  $\phi$ —CO• by chain scission. The  $\phi$ —CO• and new  $\phi$ —COO• terminal groups are formed during degradation in N<sub>2</sub> to produce CO and CO<sub>2</sub> continuously.

The degradation mechanisms at the beginning stage in  $N_2$  atmosphere are the random chain scission and the crosslinking accompanying the hydrogen abstraction reactions. Under air atmosphere the degradation mechanisms in the first stage are similar to those in  $N_2$ , but  $O_2$  also takes part in the degradation reaction and lower the  $E_a$  values. In the second stage,  $O_2$  breaks down the crosslinking formed in the first degradation stage and the oxidation reactions causes char to decompose.

The flat baselines and the simple bands in the FT-IR spectra of the degradation products from TG in air compared with the rough baselines and the complicated bands in  $N_2$  suggest that degradation is more complete and the products are simpler in air environment.

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