

THERMAL DEGRADATION OF THERMOTROPIC LIQUID CRYSTALLINE TERPOLYESTERS BASED ON VANILLIC ACID, *p*-HYDROXYBENZOIC ACID AND POLY(ETHYLENE TEREPHTHALATE)*

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ABSTRACT

Nine thermotropic liquid crystalline terpolyesters based on vanillic acid(V), *p*-hydroxybenzoic acid(H) and poly(ethylene terephthalate)(E) were investigated by thermogravimetry to ascertain their thermostability and the kinetic parameters for thermal degradation. Overall activation energy data of the degradation had been calculated over the range 5 ~ 70% weight loss. The temperatures and the activation energy of the degradation lie in the ranges of 384 ~ 394 °C at a heating rate of 1 °C/min and 176 ~ 205 KJ/mol at the weight loss of 5%, respectively, which suggests that the terpolyesters have good thermostability.

INTRODUCTION

In the last decade, there has been a continual increase in interest with respect to the utilization of liquid crystalline polymers as a means of obtaining high strength, high modulus and high heat resistant materials. The synthesis and characterization of thermotropic liquid crystalline HE copolyesters, where H and E represent *p*-hydroxybenzoic acid unit and ethylene terephthalate unit respectively, were first reported in 1976^[1]. It is known that the HE copolyesters with largely aromatic repeat units have good thermostability^[2]. However, very few papers have been published on the thermostability and the kinetics on the thermal degradation of these kinds copolyesters, especially VHE terpolyesters in which V denotes vanillic acid unit. It was considered that a more detailed study would be of value, because the copolyesters must encounter elevated temperatures at almost every step in the manufacturing, compounding and processing stages as well as in service and during repair. Thus, we have attempted to investigate the thermostability and the kinetic parameters of the VHE terpolyesters by performing a detailed thermogravimetric(TG) analysis.

EXPERIMENTAL

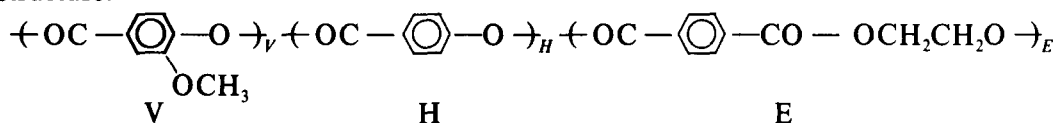
The thermotropic liquid crystalline terpolyesters used in this study are the

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terpolyesters prepared from m-methoxy-p-acetoxybenzoic acid, p-acetoxybenzoic acid and poly (ethylene terephthalate) in different ratios. They have the general structure:



and are designated here as VHE terpolyesters for brevity. The terpolyesters were prepared according to the earlier procedures^[3]. Weight loss experiments were performed by using a Du Pont Instrument 9900 Computer/Thermal Analyzer. All the TG and the derivative thermogravimetric (DTG) curves were obtained under the following conditions: the nitrogen flow was kept constant at 50ml/min, the sample weight was being about 25mg, the heating rates were 1,2,5, and 10 °C/min.

The data obtained in this study have been analyzed by means of the method proposed by Flynn and Wall^[4]. Flynn-Wall method uses the following approximate equation derived from the general equation for the rate of weight loss at a constant weight loss in a thermal degradation process:

$$E' = -4.35 \times d(\log \beta) / d(1/T)$$

where, E' is the activation energy, β is the heating rate, and T is the absolute temperature. From this equation it is clear that E' can be calculated from the slope of a plot of $\log \beta$ versus $1/T$ at a given weight loss.

RESULTS AND DISCUSSION

Representative results are shown in Fig.1 and Fig.2 where the TG and DTG curves for the thermal degradations of (a) 5V/60H/35E and (b) 5V/75H/20E terpolyester samples are shown with four heating rates. The initial degradation temperature T_d was taken at the point in which the TG curve deviated from the horizontal line. From the DTG curves, $T_{\max}$ values were determined as those temperatures at which the rate of degradation reached its maximum value. In Table 1, we can see that T_d and $T_{\max}$ increase as the unit H content, intrinsic viscosity $[\eta]$,

Table 1 The initial degradation temperature T_d and the temperature $T_{\max}$ of maximum degradation rate of the VHE terpolyesters in nitrogen

V/H/E (mol)	$[\eta]^a$ (ml/g)	$T_d/T_{\max}$ (°C)			
		1 °C /min	2 °C /min	5 °C /min	10 °C /min
0/60/40	60	386/412	396/423	411/437	437/455
0/75/25	87	390/419	401/433	417/447	444/477
0/100/0 ^b	Insoluble		450/504		501/530
0.05/60/39.95	64	385/413	396/426	413/446	
1.5/60/38.5	73	384/409	397/426	413/446	
2.5/60/37.5	71	384/411	397/426	412/446	
5/60/35	75	389/415	398/427	413/449	442/461
5/65/30	87	384/416	397/428	417/445	
5/70/25	102	390/419	396/429	416/449	
5/75/20	140	394/422	399/431	421/450	445/471

^a Measured at 0.5% concentration in phenol/sym-tetrachloroethane 50/50 (by volume) at 30 °C.

^b Data from ref. [6].

or heating rate increases. A possible explanation for this deviation may be the fact that the samples with high unit H content and high $[\eta]$ have high chain rigidity or the heat flow to the samples at high heating rates can become rate determining. However, the effect of unit V content on T_d and T_{max} is complicated, because both benzene ring and methoxyl group contents increase with unit V content: the former results in the increase of T_d and T_{max} , the latter the decrease of T_d and T_{max} . In addition, the range (0 ~ 5%) of unit V content is too narrow for exactly determining the dependence of T_d and T_{max} on unit V content. As it can be seen from Table 1 that the maximum difference between T_d and T_{max} values for the terpolyesters is 36 °C and the minimum difference 18 °C.

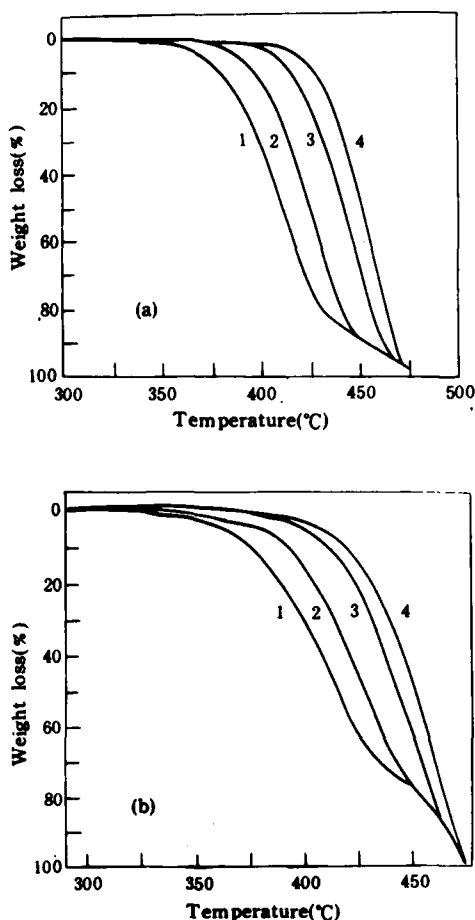


Fig.1 Part TG curves of the terpolyesters with different monomer ratios of (a) V/H/E = 5/60/35 and (b) V/H/E = 5/75/20 in nitrogen at four heating rates: 1) 1 °C/min; 2) 2 °C/min; 3) 5 °C/min and 4) 10 °C/min.

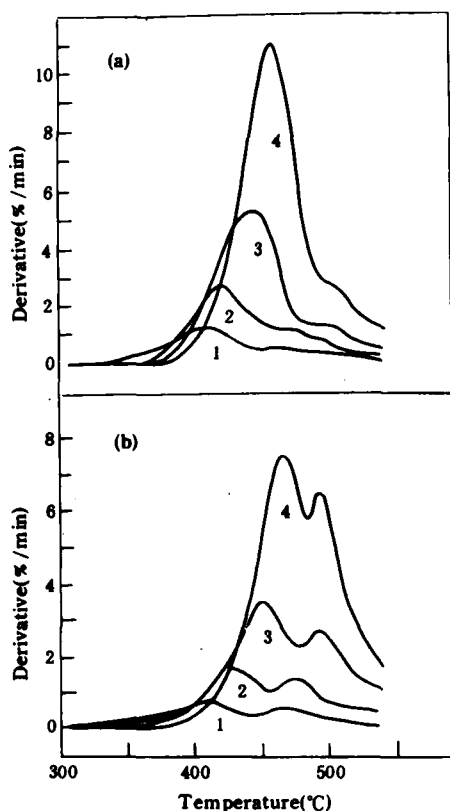


Fig.2 DTG curves of the terpolyesters with different monomer ratios of (a) V/H/E = 5/60/35 and (b) V/H/E = 5/75/20 in nitrogen at four heating rates: 1) 1 °C/min; 2) 2 °C/min; 3) 5 °C/min and 4) 10 °C/min.

The DTG curves of the VHE terpolyesters showed two stages of thermal deradation in nitrogen. The weight loss (about 45%) in the first stage may be

associated with the ester linkages, the ethylene glycol unit and methoxyl group degradation which produce volatile products (CO , CO_2 , $\text{CH}_2=\text{CH}_2$, CH_3CHO , CH_4 , etc) and subsequent chain scission^[5]. The residue after the first stage is naturally the aromatic substance consisting of benzene ring mainly, thus the second stage of degradation in the terpolyesters is related to the thermal pyrolytic reactions of the aromatic substance, which leads to greater weight loss.

In the present article we investigate the first stage kinetic parameters for the VHE terpolyesters with different heating rates. Typical plots of the logarithms of the heating rates against the reciprocal of the absolute temperature obtained for (a) 5V/60H/35E and (b) 5V/75H/20E terpolyesters degraded for the first reaction stage in nitrogen are shown in Fig.3. Nine reasonable straight lines were

1 for the experiments performed, and the activation energy E' values

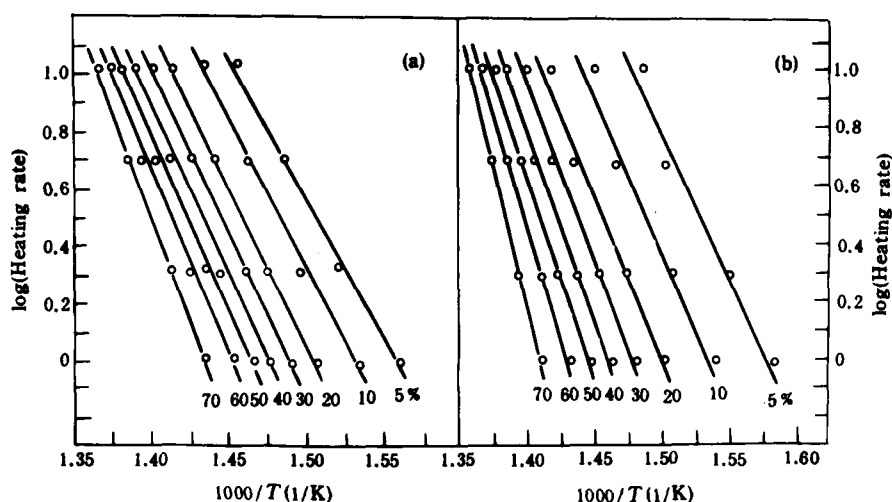


Fig.3 Plots of $\log(\text{heating rate})$ vs. $1/T$ at various weight losses for the terpolyesters with different monomer ratios of (a) V/H/E = 5/60/35 and (b) V/H/E = 5/75/20.

were calculated from the slope, confirming the apparent simple kinetic in nitrogen. Table 2 summarizes the values of E' of the VHE terpolyesters obtained at weight losses of 5, 10, 20, 30, 40, 50, 60, and 70%. As it can be seen, the greater the weight loss, or the more the rigid unit H content, the greater is E' . When the weight loss

Table 2 Activation energy E' (KJ/mol) of the VHE terpolyesters at different weight losses in N_2

V/H/E	Weight loss (%)	5	10	20	30	40	50	60	70
0/60/40		176	187	199	202	207	212	217	230
0/75/25		189	196	219	228	245	262	296	407
0/100/0 ^a		186	191	250	275	270	246	174	
0.05/60/39.95		180	191	203	204	206	209	215	225
2.5/60/37.5		191	196	205	203	207	212	219	232
5/60/35		192	203	216	222	231	239	251	268
5/65/30		201	197	203	211	223	239	262	308
5/70/25		186	217	220	217	231	250	282	374
5/75/20		205	217	234	251	266	285	319	381

^a Data from ref. [6].

is less than 30%, the more the unit V content, the greater is E' . E' increases with the unit H or V content due to the strengthening of the rigidity of the terpolyester chain, which is the feature common to all liquid crystalline copolyesters containing flexible unit E. Of all eight copolyesters, 5V/75H/20E terpolyester, as a matter of fact, which is more stable than the poly(p-hydroxybenzoate) and Xydar copolyester^[6], has the highest thermostability. The VHE terpolyesters show typical high temperature stability of aromatic copolyesters.

Table 3 Thermal degradation temperature $T_d/T_{\max}$ and activation energy E' versus the sequence distributions of the VHE terpolyesters

V/H/E	0/60/40	5/60/35	5/65/30	5/75/20
$\bar{L}_{nH}/\bar{L}_{nE}$	2.17/1.45	2.00/1.30	2.24/1.08	3.23/1.06
F_{HHH}/F_{EEE}	17.2/4.10	14.3/2.01	20.1/0.17	34.8/0.08
$T_d/T_{\max}$ (°C) ^a	396/423	398/427	397/428	399/431
$T_d/T_{\max}$ (°C) ^b	411/437	413/449	417/445	421/450
E'^c/E'^d (KJ/mol)	176/217	192/251	201/262	205/319

^a Determined at a heating rate of 2 °C/min.

^b Determined at a heating rate of 5 °C/min.

^c Values at weight loss of 5%.

^d Values at weight loss of 60%.

Table 3 gives the values of the sequence distribution parameters^[7], the thermal degradation temperatures at the heating rates of 2 and 5 °C/min, and the activation energy at the weight losses of 5% and 60% of the VHE terpolyesters. It is found that there is no apparent relationship between T_d , $T_{\max}$ or E' and number-average sequence length $\bar{L}_{nH}$ or trial concentration F_{HHH} of rigid unit H of the terpolyesters. It should be noted, however, that the T_d , $T_{\max}$ and E' decrease as the number-average sequence length $\bar{L}_{nE}$ or trial concentration F_{EEE} of the flexible unit E of the terpolyesters increases. This suggests that longer blocks of flexible unit E may accelerate the decomposition of the VHE terpolyesters.

CONCLUSIONS

Thermogravimetry is capable of providing some very useful information on the thermostability of the VHE terpolyesters provided that care is taken in the interpretation. The degradation temperatures and the kinetic data for the terpolyesters heated in nitrogen indicate that the terpolyesters have good thermostability. The content of the unit H plays an important role in increasing the thermal stability of the terpolyesters. The degradation appears to be a random chain scission process with two stage characteristics.

Keywords:

Thermotropic liquid crystal; Vanillic acid; Terpolyester; Thermogravimetry; Thermal degradation; Thermostability; Kinetic analysis.

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