

Thermal Decomposition Kinetics of Thermotropic Copolyesters Made from *trans-p*-Hydroxycinnamic Acid and *p*-Hydroxybenzoic Acid

Wei Tang,¹ Xin-Gui Li,² Deyue Yan¹

¹College of Chemistry and Chemical Technology, Shanghai Jiao Tong University, 800 Dongchuan Road, Shanghai 200240, China

²Department of Polymer Materials Science and Engineering, State Key Laboratory of Concrete Materials Research, College of Materials Science and Engineering, Tongji University, 1239 Siping Road, Shanghai 200092, China

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ABSTRACT: A series of thermotropic copolyesters were synthesized by direct thermal melt polycondensation of *p*-acetoxybenzoic acid (PHB) with *trans-p*-acetoxybenzoic acid (PHC). The dynamic thermogravimetric kinetics of the copolyesters in nitrogen were analyzed by four single heating-rate techniques and three multiple heating-rate techniques. The effects of the heating rate, copolyester composition, degradation stage, and the calculating techniques on the thermostability and degradation kinetic parameters of the copolyesters are systematically discussed. The four single heating-rate techniques used in this work include Friedman, Freeman–Carroll, Chang, and the second Kissinger techniques, whereas the three multiple heating-rate techniques are the first Kissinger, Kim–Park, and Flynn–Wall

techniques. The decomposition temperature of the copolyesters increases monotonically with increasing PHB content from 40 to 60 mol %, whereas their activation energy exhibits a maximal value at the PHB content of 50 mol %. The decomposition temperature, activation energy, the order, and the frequency factor of the degradation reaction for the thermotropic copolyester with PHB/PHC feed ratio of 50/50 mol % were determined to be 374°C, 408 kJ/mol, 7.2, and $1.25 \times 10^{29} \text{ min}^{-1}$, respectively. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 91: 445–454, 2004

Key words: *p*-hydroxybenzoic acid; *trans-p*-hydroxycinnamic acid; copolyesters; thermogravimetry; thermostability

INTRODUCTION

Liquid crystalline polymers have been used to prepare high-strength, high-modulus, and highly heat resistant fibers and plastics.¹ The synthesis and properties of thermotropic liquid crystalline aromatic copolyesters from *p*-acetoxybenzoic acid (PHB) and *trans-p*-acetoxybenzoic acid (PHC) containing a double bond, have been investigated and considered as a promising kind of high-performance polymer with good processing ability, high mechanical property, low cost, and further potential reactivity and application.^{2–4} Compared with other typical copolyesters such as Vectra and X7G, which have the similar structures, the aromaticity of PHB/PHC copolyesters chain is between that of Vectra and X7G, leading to moderate processibility and mechanical property. Moreover, the potential reactivity and modification could be expected because of the presence of the double bond on each PHC unit. However, relatively few studies were

reported on the thermostability and thermal degradation kinetics of the thermotropic copolyesters. It is considered that a more detailed study on thermal decomposition would be of value because the PHB/PHC copolyesters will encounter elevated temperatures at almost every step in the manufacturing, compounding, processing, and repairing steps.

In this study, we have attempted to investigate the thermostability and three important kinetic parameters of the PHB/PHC copolyesters by performing a detailed high-resolution thermogravimetric (TG) and derivative thermogravimetric (DTG) analyses at multiple heating rates in nitrogen for the first time. The variation of the thermostability and kinetic parameters of the PHB/PHC copolyesters with the comonomer ratio, testing parameters, and calculating methods, is also discussed in detail. This topic may be of importance in revealing the intrinsic thermal degradation kinetics of the thermotropic liquid crystalline aromatic copolyesters.

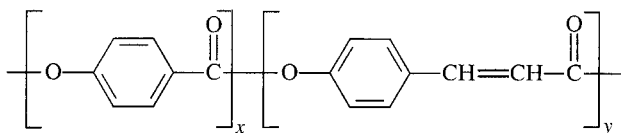
Correspondence to: D. Yan (dyyan@mail.sjtu.edu.cn).

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EXPERIMENTAL

The thermotropic liquid crystalline copolyesters are synthesized from *p*-acetoxybenzoic acid (PHB) and *trans-p*-acetoxybenzoic acid (PHC) with a series of

five PHB/PHC monomer ratios of 40/60, 45/55, 50/50, 55/45, and 60/40, according to an earlier procedure.^{3,4} All the copolyesters show multicolor stripes under cross-polarized light from ambient to 350°C. The intrinsic viscosity ($[\eta]$) of the copolyesters could not be obtained because the material obtained only partially dissolves in typical solvents including trifluoroacetic acid, dimethyl sulfoxide, *N,N*-dimethyl acetamide, tetrahydrofuran, and *N*-methyl-2-pyrrolidone. The copolyesters possess the following nominal molecular structure:



TG and derivative thermogravimetry (DTG) curves of PHB/PHC copolyesters were gained by using a Perkin-Elmer 7 series analyzer (Perkin Elmer Cetus Instruments, Norwalk, CT) under a dynamic nitrogen atmosphere flowing at 40 mL/min (the heating rate was varied from 5 to 40 K/min), and those of PHB/PHC molar feed ratio from 40/60 to 60/40 at a heating rate of 20 K/min were also obtained, whereas the sample weights were kept at 2.0 ± 0.1 mg.

There are several techniques for the kinetics evaluation of the TG thermal degradation data, and they were previously discussed in several publications.⁵⁻⁷ The thermal decomposition kinetics was examined by seven evaluation techniques.

Friedman technique^{8,9}

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

where α is the weight loss of the polymer undergoing degradation at time t ; R is the gas constant ($8.3136 \text{ J mol}^{-1} \text{ K}^{-1}$), and T is the absolute temperature (K); Z , n , and E_a are the frequency factor, the order, and the activation energy of the thermal decomposition reaction, respectively. The plot of $\ln(d\alpha/dt)$ versus $1/T$ should be linear with E_a/R as the slope. Additionally, the $-E_a/(nR)$ value could be determined from the slope of the linear plot of $\ln(1 - \alpha)$ versus $1/T$.

Freeman-Carroll technique^{8,10}

$$\frac{\Delta \ln(d\alpha/dt)}{\Delta \ln(1 - \alpha)} = n - (E_a/R) \frac{\Delta(1/T)}{\Delta \ln(1 - \alpha)} \quad (2)$$

The $\Delta \ln(d\alpha/dt)$ and $\Delta \ln(1 - \alpha)$ values are taken at regular intervals of $1/T$, in this case $\Delta(1/T) = 2 \times 10^{-6} \text{ K}^{-1}$. By plotting $\Delta \ln(d\alpha/dt)/\Delta \ln(1 - \alpha)$ against $\Delta(1/T)/\Delta \ln(1 - \alpha)$, a straight line was obtained, and the slope and intercept are equal to $-E_a/R$ and n , respec-

tively. In addition, the Z value can be evaluated using eq. (1).

Chang technique^{8,11}

Equation (1) can be rewritten in the following form:

$$\frac{\ln(d\alpha/dt)}{(1 - \alpha)^n} = \ln(Z) - E_a/(RT) \quad (3)$$

A plot of $\ln[(d\alpha/dt)/(1 - \alpha)^n]$ against $1/T$ will yield a straight line if the decomposition order n is selected correctly. The slope and intercept of this line will provide the $-E_a/R$ and $\ln(Z)$ values, respectively.

The first Kissinger technique^{12,13}

$$\ln(q/T_{dm}^2) = \ln[n(1 - \alpha_m)^{n-1}ZR/E_a] - E_a/(RT_{dm}) \quad (4)$$

where q is the heating rate; T_{dm} and α_m are the absolute temperature and weight loss, respectively, at the maximum weight-loss rate $(d\alpha/dt)_m$. The slope of $\ln(q/T_{dm}^2)$ versus T_{dm} is equal to $-E_a/R$, whereas its intercept (I) is equal to $\ln[n(1 - \alpha_m)^{n-1}ZR/E_a]$. The n value can be estimated from the following equation:

$$n = (1 - \alpha_m)E_a[\exp(I)] \times \{[\exp - E_a/(RT_{dm})]\}/[R(d\alpha/dt)_m] \quad (5)$$

Then the Z value can be calculated by substituting n into the intercept equation:

$$I = \ln[n(1 - \alpha_m)^{n-1}ZR/E_a] \quad (6)$$

The second Kissinger technique^{12,14}

The n value can be obtained directly from the symmetrical index of a single DTG peak.

$$n = 1.88[(d^2\alpha/dt^2)_L]/[(d^2\alpha/dt^2)_R] \quad (7)$$

where indices L and R denote the left and right peak values of the second DTG curves. Then E_a and $\ln(Z)$ can be calculated from the following equation:

$$n(1 - \alpha)^{n-1} = 1 + (n - 1) \times 2RT_m/E_a \quad (n \neq 1) \quad (8)$$

Kim-Park¹⁵

$$\ln q = \ln Z + \ln(E'/R) + \ln[1 - n + (n/0.944)] - 5.3305 - 1.0516E'/RT_{dm} \quad (9)$$

$$n = E'(1 - \alpha_m)/[RT_{dm}^2(d\alpha/dT)_m] \quad (10)$$

TABLE I
Polymerization Yields and Properties of PHB/PHC Copolyesters with Different Molar Feed Ratios

PHB/PHC molar ratio (%)		Polymerization yield (%)	Polymer color	Temperature at weight loss ^b (°C)			Decomposition temperature at maximum weight loss rate ^b (°C)	
Feed	Calculated ^a			2 wt %	5 wt %	10 wt %	T_{dm1}	T_{dm2}
40/60	38/62	93.8	White	310.1	365.2	414.4	436.04	595.23
45/55	42/58	94.5	Yellowish	313.1	377.4	421.9	436.43	604.11
50/50	45/55	95.3	White	320.7	391.3	422.4	440.24	604.33
55/45	51/49	96.2	White	335.3	392.3	426.4	443.22	633.21
60/40	55/45	94.7	Yellowish	350.3	399.5	426.9	443.25	637.10

^a PHB/PHC molar ratio was calculated based on the elemental analyses.

^b From TGA measurements at a heating rate of 20°C/min in nitrogen.

where T_{dm} is the absolute temperature at the maximum rate of thermal decomposition; α_m is the weight loss at the maximum rate of decomposition; and $(d\alpha/dt)_m$ is the maximum decomposition rate. E' can be obtained from the slope of $\ln(q)$ versus $1/T_{dm}$ and n can be calculated according to eq. (10) and the derived E' value. Then, $\ln(Z)$ is calculated from the intercept value of the line of eq. (9) and derived E' and n values.

Flynn-Wall technique^{16,12}

$$\ln(q) = \ln(ZE_a/R) - \ln[F(\alpha)] - E_a/(RT) \quad (11)$$

where q is the heating rate. The E_a value can be calculated from the plot of $\ln(q)$ against $1/T$ for a fixed weight loss, given that the slope of such a line is equal to $-E_a/R$.

The errors of determining the temperature and rate of the decomposition are less than 2% and the largest calculating errors in the kinetic parameters of thermal decomposition for the best two methods developed by Friedman and Chang are about 7%.

RESULTS AND DISCUSSION

Thermostability

Polymerization yields and properties of aromatic PHB/PHC copolyesters with different molar feed ratios are listed in Table I. The TG and DTG curves of PHB/PHC copolyesters with different molar feed ratios from 40/60 to 60/40 and those of PHB/PHC (50/50) copolyester in nitrogen at five heating rates of 5, 10, 20, 30, and 40 K/min and are shown in Figures 1 and 2, respectively. It is noted that all the copolyesters exhibit a similar pattern of decomposition without significant weight loss below 400°C under nitrogen. The decomposition of the copolyesters proceeds with two thermal degradation periods and the thermostability of the copolymers increases slightly from 310 to 350°C with the increase of the PHB content from 40 to

60 mol %, as shown in Table I. The same is true with the temperature at the maximum weight-loss rate. This enhancement of the thermostability is probably attributable to the enhancement of macromolecular chain rigidity as a result of increase of the PHB content, which is consistent with the increase of the phase-transition temperature in the DSC curves as discussed in our previous study.¹⁸ It is noted that these copolyesters are somewhat less thermostable than PHB homopolymer^{9,20} because of the presence of the double bonds.

Generally, the group that contains more oxygen and hydrogen atoms is of poorer thermal stability because its degradation products are easier to volatilize. Ac-

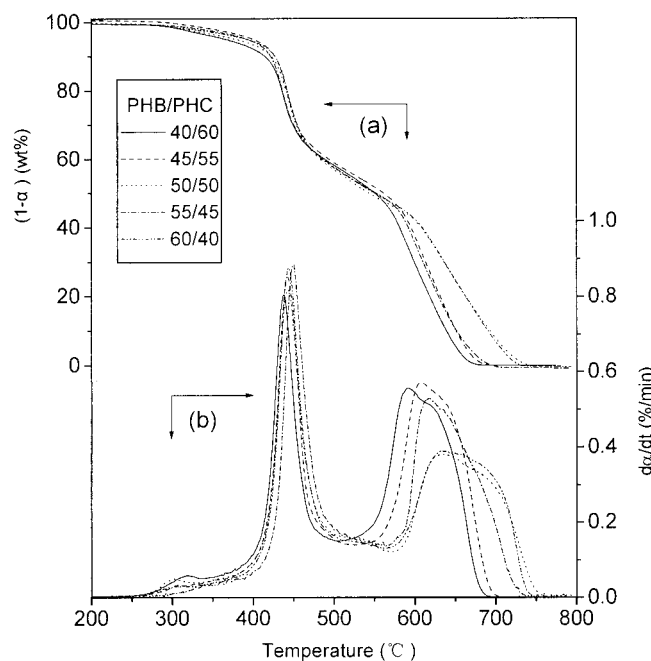


Figure 1 (a) Dynamic TG curves and (b) dynamic DTG curves for the degradation of PHB/PHC copolyesters with different molar feed ratios in nitrogen at a heating rate of 20 K/min.

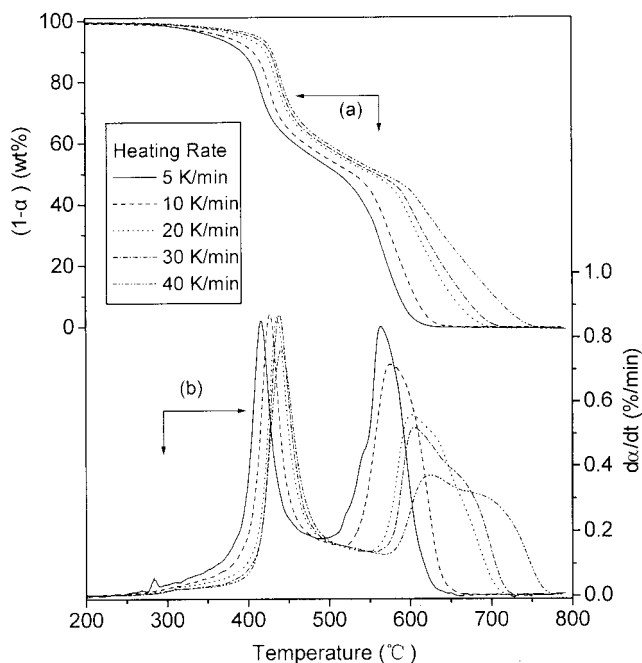


Figure 2 (a) Dynamic TG curves and (b) dynamic DTG curves for the degradation of PHB/PHC (50/50) copolyester at five different heating rates ranging from 5 to 40 K/min in nitrogen.

cordingly, the ester groups and the cinnamyl groups in copolyester chain are much easier to degrade thermally than the aromatic ones. The transition point

between two degradation periods is near the weight loss of 54%, which is equal to the summation of the weight percentages of ester groups, cinnamyl groups, and aromatic hydrogen atoms in copolyester chains. Therefore, the relatively faster degradation of copolyester in the initial heating period could be attributed to the removal of the ester groups, cinnamyl groups, and aromatic hydrogen atoms. During this initial period, an intermolecular condensation (probably resulting from the recombination of aromatic radicals formed) occurs to form carbonaceous char. The subsequent decomposition of copolyester in nitrogen should be ascribed to the further pyrolysis of the carbonaceous char.¹

Additionally, a significant influence of heating rate on the thermostability of the copolymers was found, as shown in Table III. The decomposition temperature (T_d), as well as the first and second decomposition temperature at the maximum weight-loss rate (T_{dm1} and T_{dm2}) all steadily increase with heating rate increasing from 5 to 40 K/min. This could be explained by equilibrium theory. When the heating rate is low enough, equilibrium could be readily obtained at any point of increasing temperature, whereas with increasing heating rate, the heating rate is too fast for the equilibrium to reach because of heat diffusion, making T_d , T_{dm1} , and T_{dm2} increase steadily. As a result, higher decomposition temperatures would be observed if faster heating rates were applied.

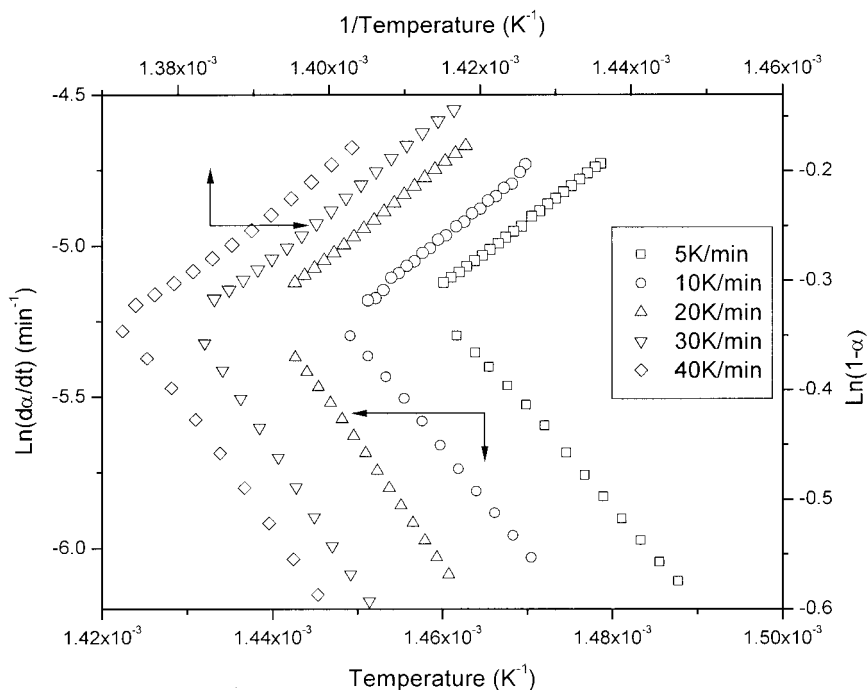


Figure 3 Friedman plots of $\ln(d\alpha/dt)$ or $\ln(1-\alpha)$ versus $1/T$ for the direct calculation of E_a or n value of thermal degradation of PHB/PHC (50/50) copolyester in nitrogen at five different heating rates. (Total x offset is 0; total y offset is 50%.)

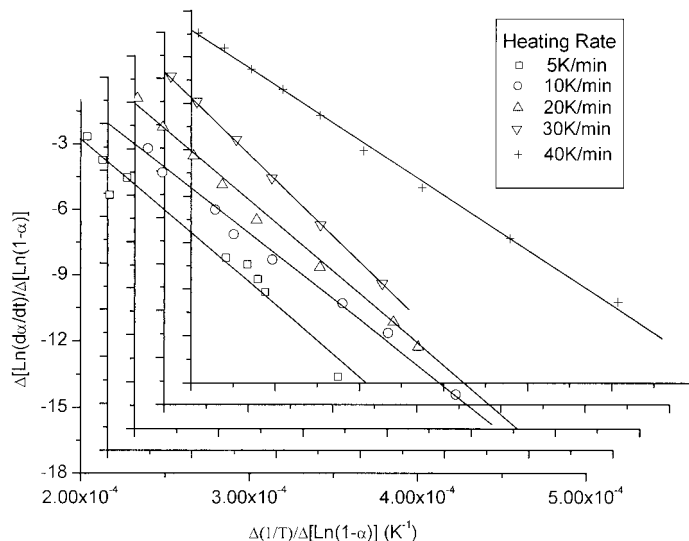


Figure 4 Freeman–Carroll plots of $\Delta \ln(d\alpha/dt)/\Delta \ln(1 - \alpha)$ versus $\Delta(1/T)/\Delta \ln(1 - \alpha)$ for the degradation of PHB/PHC (50/50) copolyester in nitrogen at five different heating rates.

Kinetics of decomposition analyzed by single heating-rate techniques

All of the techniques, Friedman, Freeman–Carroll, Chang, and the second Kissinger, can determine the kinetic parameters for the thermal degradation of PHB/PHC (50/50) copolyester by using only one heating rate. Figure 3 shows the relationship given by eq. (1) of the Friedman technique. Because the lines of either $\ln(d\alpha/dt)$ versus $1/T$ or $\ln(1 - \alpha)$ versus $1/T$ overlapped each other, the Waterfall Graph (in Origin Pro7.0, OriginLab Co., Northampton, MA) was used to obtain a distinct view. Each data set is displayed as a line data plot, which is offset by a specified amount in both the x and y directions. For the Friedman technique, the absolute x and y values do not affect the calculation of thermal degradation kinetic parameters, so the offset x - and y -axes are omitted here. Figure 4 shows the relationship of $\Delta[\ln(d\alpha/dt)]/\Delta[\ln(1 - \alpha)]$ versus $\Delta(1/T)/\Delta[\ln(1 - \alpha)]$, whereas the value of $\Delta(1/T)$ equals $2 \times 10^{-6} \text{ K}^{-1}$. Because the Freeman–Carroll lines also overlapped each other, we plot these lines on a set of parallel coordinate planes.²¹ Figure 5 shows the relationship proposed by Chang where the decomposition orders are assumed to be 6.4–7.7 for the PHB/PHC (50/50) copolyester.

The kinetic parameters of the first thermal degradation stage calculated by the four single heating-rate techniques for the PHB/PHC (50/50) copolyester at five heating rates are summarized in Table II. The average kinetic parameters of thermal degradation calculated from the Friedman, Freeman–Carroll, and Chang techniques of PHB/PHC (50/50) copolyester at different heating rates are also listed in Table III.¹⁹

Effect of heating rate

From Table II it may be concluded that the kinetic parameters of PHB/PHC copolyesters change with the heating rate, and most of E_a and $\ln(Z)$ values increase significantly with heating rate, whereas the n values keep roughly the same as the heating rate changes from 10 to 40 K/min. That is to say, when the heating rate is high enough, the effect of the concentration of decomposition products from PHB/PHC copolyesters on thermal degradation reaction will remain roughly unchanged. The E_a and $\ln(Z)$ values calculated by the Friedman technique also increase with heating rate. Generally, the variation of these

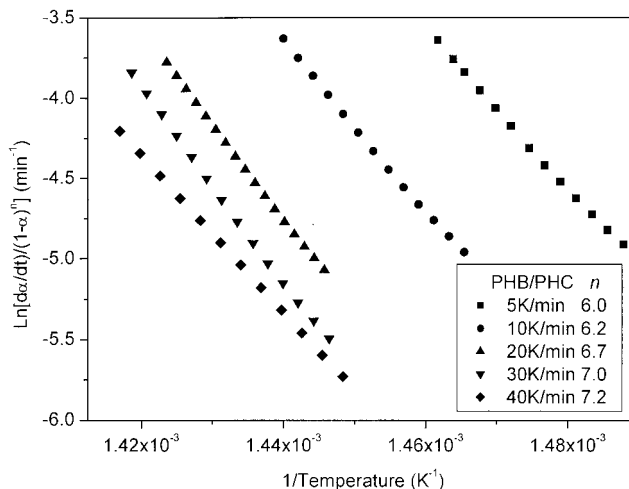


Figure 5 Chang plots of $\ln[(d\alpha/dt)/(1 - \alpha)^n]$ versus $1/T$ for the thermal degradation of PHB/PHC (50/50) copolyester in nitrogen at five different heating rates.

TABLE II
Kinetics Parameters of the First Thermal Degradation Stage of PHB/PHC (50/50) Copolyester under Nitrogen
Calculated by Four Single Heating Rate Techniques, Respectively

Heating rate (K/min)	Friedman			Freeman–Carroll			Chang			The Second Kissinger		
	E_a^a	n	$\ln(Z)^b$	E_a^a	n	$\ln(Z)^b$	E_a^a	n	$\ln(Z)^b$	E_a^a	n	$\ln(Z)^b$
5	264	6.0	48	426	6.8	71	409	6.4	68	21	2.1	-0.57
10	290	6.2	47	470	7.4	78	437	6.8	72	21	2.1	-0.54
20	334	7.2	54	510	8.2	84	490	7.7	80	22	2.4	-0.47
30	364	7.8	59	516	8.3	84	502	8.1	81	22	2.6	-0.38
40	312	7.4	50	401	6.9	64	403	7.2	64	21	2.5	-0.76
Average	213	6.9	52	465	7.5	76	446	7.2	73	214	2.3	-0.54

^a E_a (kJ/mol).

^b $\ln(Z)$ (min^{-1}).

kinetic parameters reveals the change of thermal degradation mechanism (i.e., transformation from the diffusion-controlled kinetics into the decomposition-controlled kinetics, or vice versa).¹² The effect of heating rate on E_a , n , and $\ln(Z)$ can be explained as expressed below. At lower heating rates, the diffusion of degradation products apparently does not affect the kinetics of the decomposition process; thus kinetic parameter values were relatively low. Alternatively, at higher heating rates, the degradation of polymer is probably faster than the diffusion of degradation products through the polymer melt; therefore the kinetics of the degradation process is controlled by the diffusion of degradation products. Consequently, higher kinetic parameters were observed with increasing heating rate.⁸

Effect of calculating techniques

Tables II and III demonstrate that kinetic parameters depend not only on the experimental conditions (such as heating rate, sample weight, and atmosphere), but also on the mathematical treatment of the data. The results obtained by the second Kissinger technique are quite different from those calculated by the other three, especially for the E_a and $\ln(Z)$ values. However, the results derived from the other three techniques have no significant distinction, except that the E_a and

$\ln(Z)$ values given by Friedman are somewhat lower. If one calculates the value of n from eq. (7) and substitutes it into eq. (8) to estimate E_a , this procedure may result in considerable errors.¹² From Table II, it is obvious that the results derived from the Friedman, Freeman–Carroll, and Chang techniques are in agreement with one another except that the E_a and $\ln(Z)$ values gained from the Friedman technique are somewhat lower than those obtained by the other two techniques. The Friedman, Freeman–Carroll, and Chang techniques did not give the same results because different calculating techniques are appropriate for the respective thermal degradation behaviors in different temperature ranges. In fact, kinetic parameters change more or less with temperature, even though we assume that they do not vary with temperature in every mathematical technique.⁸

In the case of the Friedman technique (see Fig. 3, Table II), the E_a value was derived from the slope of $\ln(d\alpha/dt)$ versus $1/T$. However, the linear relationship between $\ln(d\alpha/dt)$ and $1/T$ for PHB/PHC (50/50) copolyester stands only in the temperature range from ($T_{dm} - 25$ K) to T_{dm} . Then from the slope of $\ln(1 - \alpha)$ versus $1/T$ and the derived E_a value, the n value can be calculated, and the relationship between $\ln(1 - \alpha)$ and $1/T$ for the PHB/PHC (50/50) copolyester keeps linear in the temperature range from ($T_{dm} - 10$ K) to ($T_{dm} + 10$ K). Finally, $\ln(Z)$ can be given by substituting

TABLE III
Characteristic Temperature and Average Kinetic Parameters Calculated by Friedman, Freeman–Carroll, and Chang
Techniques for the First Thermal Degradation Stage of PHB/PHC (50/50)

Heating rate (K/min)	T_d (°C)	T_{dm1} (°C)	T_{dm2} (°C)	$(d\alpha/dt)_{m1}$ (%/min)	$(d\alpha/dt)_{m2}$ (%/min)	E_a (kJ/mol)	n	$\ln(Z)$ (min^{-1})
5	345	416	564	85.2	83.3	363	6.4	62
10	356	427	575	87.2	71.6	399	6.8	66
20	378	436	602	86.3	55.8	445	7.7	73
30	390	439	604	87.1	51.8	461	8.1	75
40	400	441	625	76.3	37.0	372	7.2	60
Average	374	432	594	84.4	59.9	408	7.2	67

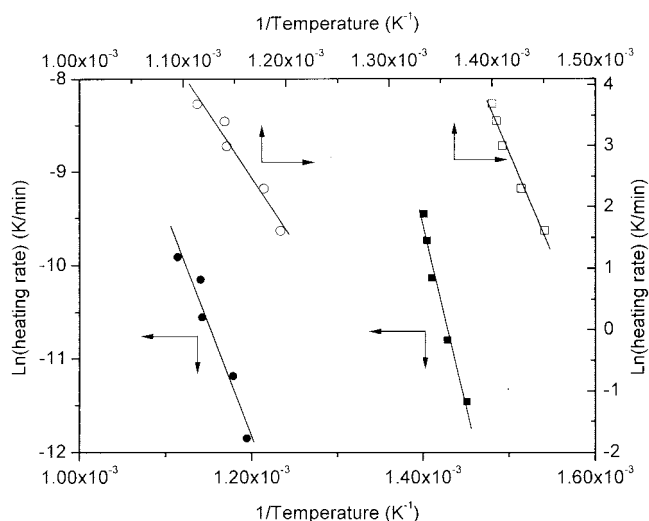


Figure 6 The first Kissinger profiles (■, ●) of $\ln(\text{heating rate}/T_{dm}^2)$ versus $1/T_{dm}$ and Kim-Park profiles (□, ○) of $\ln(\text{heating rate})$ versus $1/T_{dm}$ for the thermal degradation of PHB/PHC (50/50) copolyester.

the derived E_a and n values into eq. (1), in which both $n \cdot \ln(1 - \alpha)$ and $\ln(d\alpha/dt)$ are so small compared with $E_a/(RT)$ that $\ln(Z)$ is mainly determined by the E_a value. Therefore, E_a and $\ln(Z)$ values given by the Friedman technique mainly indicate the thermal decomposition behavior in the temperature range from $(T_{dm} - 25 \text{ K})$ to T_{dm} .

On the contrary, in the case of the Freeman-Carroll technique (see Fig. 4, Table II), the linear relation can be observed in the temperature interval from $(T_{dm} - 31 \text{ K})$ to T_{dm} for the PHB/PHC (50/50) copolyester. Meanwhile, in the case of the Chang technique (see Fig. 5, Table II), the linear relation can be obtained in the temperature interval $(T_{dm} - 40 \text{ K})$ to T_{dm} for the PHB/PHC (50/50) copolyester. Moreover, according to eq. (1) and Freeman-Carroll plots the E_a , n , and $\ln(Z)$ can be derived, whereas according to Chang plots, the E_a and $\ln(Z)$ can be calculated directly. So it can be concluded that E_a and $\ln(Z)$ values derived from the Freeman-Carroll technique describe behaviors of thermal degradation in the temperature range from $(T_{dm} - 31 \text{ K})$ to T_{dm} for the PHB/PHC (50/50) copolyester; meanwhile those values derived from the

Chang technique describe the behavior of thermal degradation in the temperature ranging from $(T_{dm} - 40 \text{ K})$ to T_{dm} for the PHB/PHC (50/50) copolyester. Similar results were obtained for PHB/PHC copolyesters with different molar feed ratios from 40/60 to 60/40%.

From the outcomes given above, it can be concluded that the Freeman-Carroll and Chang techniques cover similar temperature ranges, whereas the Friedman technique covers a lower temperature range. Moreover, the Chang technique covers the widest temperature range, whereas the Freeman-Carroll technique takes the second place. Generally, for a thermal degradation process, lower temperature may lead to smaller kinetic parameters, and a wider calculating temperature range will result in better reliability with smaller errors. Consequently, the Freeman-Carroll and Chang techniques provide very similar values of kinetic parameters, whereas those calculated by the Friedman technique are somewhat lower. Although the Chang technique gives linear relation in the widest temperature range, one cannot use this technique alone because the n value must be assumed before calculation. Moreover, the Chang technique has low sensitivity to n values, which means that a good linear relation can be obtained in a wide range of n values. Therefore, Freeman-Carroll is the most reliable technique, whereas the Chang technique can be used to check the results gained by other techniques. It should be noted that even for the Friedman technique, the temperature range is also wide enough to obtain credible results.

Kinetics of decomposition analyzed by multiple heating-rate techniques

The first Kissinger, Kim-Park, and Flynn-Wall techniques are apparently different from the four techniques mentioned above, which require multiple TG curves at various heating rates to calculate the thermal degradation parameters. The Flynn-Wall technique can give only the activation energy (E_a) values, whereas the first Kissinger and Kim-Park techniques can supply all three kinetic parameters. The first Kissinger and Kim-Park plots for the first and second decomposition stages of PHB/PHC (50/50) copolyes-

TABLE IV
Kinetic Parameters of Thermal Degradation of PHB/PHC (50 : 50) in Nitrogen
Calculated by Two Multiple Heating-Rate Techniques, Respectively

Calculating technique	First-step degradation			Second-step degradation		
	E_a (kJ/mol)	n	$\ln(Z)$ (min^{-1})	E_a (kJ/mol)	n	$\ln(Z)$ (min^{-1})
The First Kissinger	319	1.9	55	198	3.8	27
Kim-Park	314	1.8	61	202	3.8	34

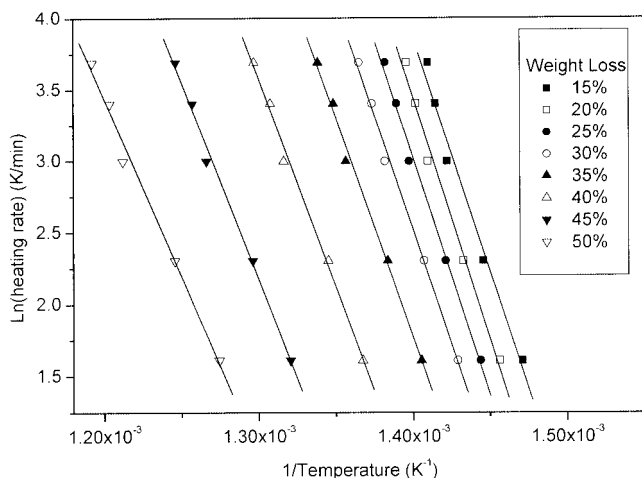


Figure 7 Flynn–Wall profiles of the thermal degradation of PHB/PHC (50/50) copolyester in nitrogen.

ter in nitrogen are shown in Figure 6. Four reasonable straight lines were obtained. E_a , n , and $\ln(Z)$ values calculated from the slope and intercept of these straight lines are listed in Table IV. Comparing Table II with Table IV, it is obvious that the results given by the first Kissinger and Kim–Park techniques for PHB/PHC (50/50) copolyester are fairly different from the average data obtained by single heating-rate techniques. Generally speaking, the multiple heating-rate methods including the first Kissinger, Kim–Park, and Flynn–Wall techniques employed in this study are more complex and difficult than the single heating-rate ones. The kinetic parameters calculated through both types of techniques are hardly ever the same.¹²

Additionally, as listed in Table IV, the second stage of thermal degradation for PHB/PHC (50/50) copolyester in nitrogen has lower E_a , $\ln(Z)$, and $(d\alpha/dt)_m$ values and larger n than those of the first stage, which indicates that a different kinetic process occurs during the second stage. According to eq. (11) of the Flynn–Wall technique, eight straight lines over the fractional weight-loss range 15–50 wt % are shown in Figure 7. The activation energies E_a gained from the Flynn–Wall technique are also shown in Table V. Obviously, as the fraction of weight loss increases from 15 to 20 wt %, the E_a value increases, but as the fraction of weight loss increases consecutively from 25 to 50 wt %, the E_a value decreases steadily, which indicates the variation in the thermal degradation kinetics. Additionally, the average E_a value obtained by the Flynn–Wall tech-

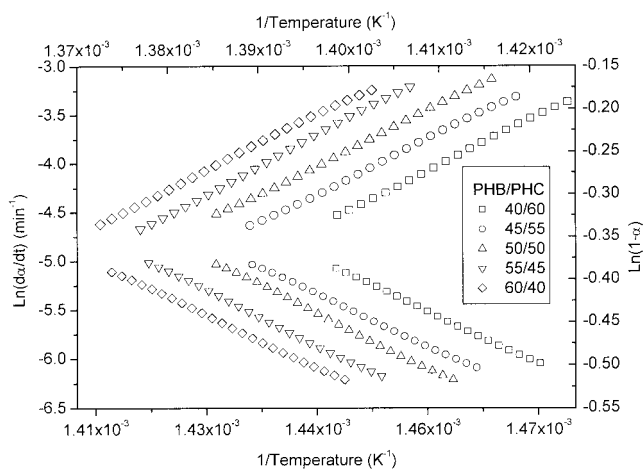


Figure 8 Friedman plots of $\ln(d\alpha/dt)$ or $\ln(1 - \alpha)$ versus $1/T$ for the direct calculation of E_a or n value of thermal degradation of PHB/PHC copolyesters with different molar feed ratios in nitrogen at a heating rate of 20 K/min.

nique is also much lower than the average value obtained by single heating-rate techniques. According to Table IV, It appears that the first Kissinger and Kim–Park techniques could achieve similar results and could be ascribed as the reliable techniques.

Effect of copolyester composition on kinetic parameters

Except for the first and second Kissinger techniques, no matter which technique was used above, the fundamental equation is the same:

$$d\alpha/dt = Z(1 - \alpha)^n \exp[-E_a/(RT)] \quad (12)$$

Because the value of $(1 - \alpha)$ is always less than or equal to 1, $d\alpha/dt$ decreases with increasing n , and the zero order ($n = 0$) characterizes the most rapid decomposition reaction.⁸ From eq. (12), it can be concluded that higher n and E_a values or a lower Z value result in a lower $d\alpha/dt$ value, which means higher thermal stability.

Three single heating-rate techniques—Friedman, Freeman–Carroll, and Chang—were used to determine the effect of copolyester composition on kinetic parameters. Figures 8, 9, and 10 show the plots of $\ln(d\alpha/dt)$ versus $1/T$ or $\ln(1 - \alpha)$ versus $1/T$, $\Delta[\ln(d\alpha/dt)]/\Delta[\ln(1 - \alpha)]$ versus $\Delta(1/T)/\Delta[\ln(1 - \alpha)]$, and that put forward by the Chang technique, and the kinetic

TABLE V
Kinetic Parameter of Thermal Degradation of PHB/PHC (50 : 50) in Nitrogen Calculated by Flynn–Wall Technique

Weight loss (wt %)	15	20	25	30	35	40	45	50	Average
E_a (kJ/mol)	272	280	274	265	254	242	229	207	253

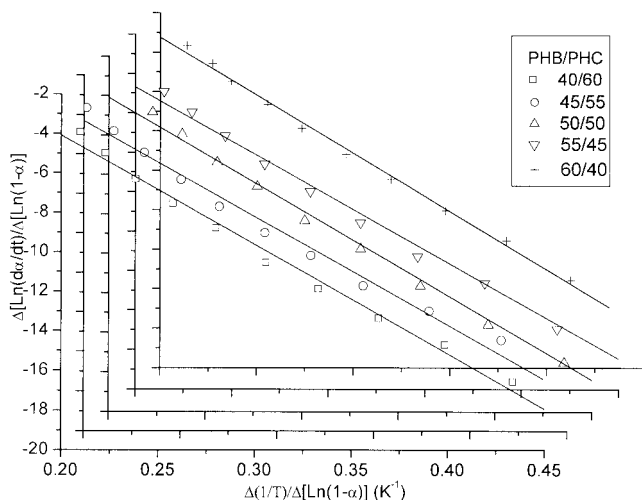


Figure 9 Freeman-Carroll plots of $\Delta \ln(d\alpha/dt)/\Delta \ln(1 - \alpha)$ versus $\Delta(1/T)/\Delta \ln(1 - \alpha)$ for the degradation of PHB/PHC copolyesters with different molar feed ratios in nitrogen at a heating rate of 20 K/min.

parameters as well as the average kinetic parameters of the first thermal degradation stage calculated by the three single heating-rate techniques for the PHB/PHC copolyesters with different molar feed ratios from 40/60 to 60/40 are summarized in Table VI.

The results derived from the three techniques have no significant distinction, except that the E_a and $\ln(Z)$ values given by Friedman are lower to some extent, which is similar to the results calculated by single heating-rate techniques discussed above. According to the information in Table VI, the kinetic parameters for the PHB/PHC copolyesters at a fixed heating rate of 20 K/min exhibit a small variation with a changing PHB content from 40 to 60 mol % for all three single heating-rate techniques, Friedman, Freeman-Carroll, and Chang techniques. It appears that some heat-resistant polymers such as aromatic liquid crystalline polyesters and aromatic polyimide exhibit much larger E_a and n values.⁸ The PHB/PHC (50/50) copolyester shows the largest E_a and n values for all

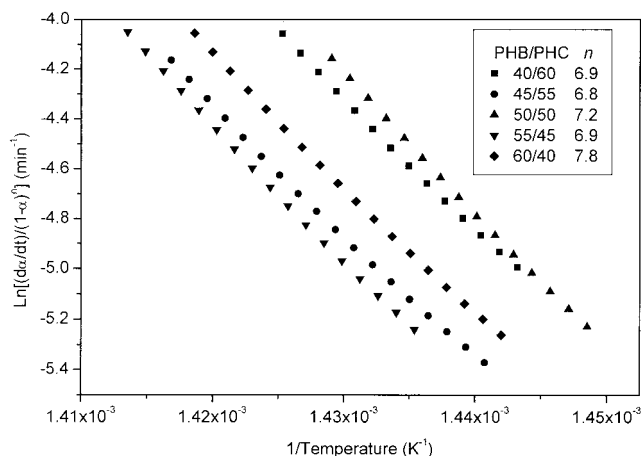


Figure 10 Chang plots of $\ln[d\alpha/dt]/(1 - \alpha)^n$ versus $1/T$ for the thermal degradation of PHB/PHC copolyesters with different molar feed ratios in nitrogen at a heating rate of 20 K/min.

three techniques, indicating that the copolyester with this composition has the highest thermostability. One of the reasons may be that, because the double bonds could crack the mesophase moieties, the higher content of the PHC content, the lower the liquid crystallinity of the copolyesters. On the other hand, the PHB content could not be too high for the formation of liquid crystalline phase in the copolyester chain, which means relatively lower PHB content would favor better liquid crystallinity. As a result, the copolyester with the molar feed ratio of PHB/PHC (50/50) copolyester may produce the highest liquid crystallinity, leading to the largest E_a and n values. The highest thermostability could also be ascribed to the high molecular weight and high chain rigidity of the PHB/PHC (50/50) copolyester. Because higher PHB content could lead to earlier solidification in the process of copolymerization, whereas higher PHC content could lead to lower thermal inertia, the copolyester with PHB/PHC (50/50) may have the highest molecular weight and rigidity, which could also result in the largest E_a and n values.

TABLE VI
Average Kinetic Parameters Calculated by Friedman, Freeman-Carroll, and Chang Techniques for the First Thermal Degradation Stage PHB/PHC Copolyesters at a Heating Rate of 20°C/min

PHB/PHC	T_d (°C)	T_{dm1} (°C)	T_{dm2} (°C)	Friedman			Freeman-Carroll			Chang			Average		
				E_a^a	n	$\ln(Z)^b$	E_a^a	n	$\ln(Z)^b$	E_a^a	n	$\ln(Z)^b$	E_a^a	n	$\ln(Z)^b$
40/60	310	436	595	298	6.8	48	460	7.0	75	442	6.9	72	400	6.9	65
45/55	313	436	604	295	6.8	47	457	6.7	74	421	6.8	68	391	6.8	63
50/50	321	440	604	334	7.2	54	510	8.2	84	490	7.7	80.0	445	7.7	73
55/45	335	442	633	313	6.6	50	479	7.2	77	455	6.9	73	416	6.9	67
60/40	350	443	637	297	6.8	47	498	8.9	81	431	7.8	69	419	7.8	66
Average	326	440	615	304	6.8	49	474	7.4	77	453	7.1	71	412	7.2	67

^a E_a (kJ/mol).

^b $\ln(Z)$ (min^{-1}).

CONCLUSIONS

PHB/PHC copolyesters show two distinct steps of the weight loss during degradation in nitrogen and their thermostability increases slightly with the increase of the PHB content. Higher $(d\alpha/dt)_m$, E_a , and $\ln(Z)$ values were obtained for the first stage, whereas higher T_{dm} and higher n values were gained for the second stage. In accordance with the dynamic TG, the T_d , T_{dm} , and $(d\alpha/dt)_m$ values, as well as E_a and $\ln(Z)$ values derived from single heating-rate techniques increase significantly with the increase of heating rates, and the E_a value derived from the Flynn–Wall technique decreases steadily with the weight-loss fraction more than 20%. Among copolyesters with different molar feed ratios, the PHB/PHC (50/50) copolyester shows the largest E and n values, indicating the highest thermostability. In the case of single heating-rate techniques, Freeman–Carroll could provide the most reliable E_a , n , and $\ln(Z)$ values, the Friedman technique may offer a little lower values, and the Chang technique can only be used to validate the out-comes from other techniques; nevertheless, the second Kissinger technique cannot give the trustworthy E_a and $\ln(Z)$ values. Additionally, the results given by two of the multiple heating-rate techniques, the first Kissinger and Kim–Park techniques are in good agreement with each other, whereas these results deviate significantly from those given by single heating-rate techniques.

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