

Thermal Decomposition Kinetics of Thermotropic Liquid Crystalline Polyesterimides

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ABSTRACT: We investigated the thermal decomposition behavior of three groups of polyesterimides that had been synthesized from different compositions of monomers that were added in different. We characterized these polymers with thermogravimetric analysis (TGA) and calculated the apparent activation energy (E_a) associated with the thermal decomposition process by the Ozawa method. The results showed that the E_a of the polyesterimides was correlated with the length of the methylene spacer and the content of the 4,4'-dihydroxybenzophenone monomer. The polyesterimide with four methylene spacers in the main chain had a higher E_a than that with six methylene spacers. The polyesterimide with a higher 4,4'-dihydroxybenzophenone content

provided better thermal stability. The E_a of the polyesterimides also depended on the sequence in which the monomers were added during the copolycondensation process. The E_a of these polyesterimides followed the order: *p*-hydroxybenzoic acid added first > *p*-hydroxybenzoic acid mixed 4,4'-dihydroxybenzophenone adding > 4,4'-dihydroxybenzophenone added first. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 98: 2467–2472, 2005

Key words: liquid-crystalline polymers; thermogravimetric analysis; copolymerization; polyesterimide; adding monomer sequence

INTRODUCTION

Thermotropic liquid crystalline polymers (TLCPs) have been utilized to prepare high-strength, high-modulus, and high-heat-resistant fibers and plastics.^{1–5} Thermal stability of a polymeric material is one of the most important properties for both processing and applications. Elucidation of the thermal stability and decomposition behavior of thermotropic liquid crystalline polymers is a necessary step for developing materials with better balanced processing properties and thermal stability and avoiding thermally induced loss of performance in processing. However, most studies of TLCPs have focused on such characteristics as synthesis, phase transition, morphology, rheology, and mechanical properties; only a few have investigated thermal stability and decomposition behavior.⁶ In the current study we investigated the thermal de-

composition kinetics of thermotropic liquid crystalline polyesterimides.

Thermotropic liquid crystalline polyesterimides have received considerable attention in the past decades. Kricheldorf's group^{7–13} and Lenz's group^{14–16} have reported the synthesis of thermotropic liquid crystalline polyesterimides with various structures. Unfortunately, the thermal decomposition kinetics of the thermotropic liquid crystalline polyesterimides was not well studied. Thermogravimetric analysis (TGA) is the most widely used technique to characterize thermal decomposition of common liquid crystalline polymeric materials because of its simplicity and the useful information afforded from a simple TGA thermogram. In the current study we synthesized a series of polyesterimides by symmetrically varying monomer composition and the sequence of the addition of monomers and investigated the relationship between the apparent activation energy (E_a) and monomer composition along with the sequence of adding monomers.

EXPERIMENTAL

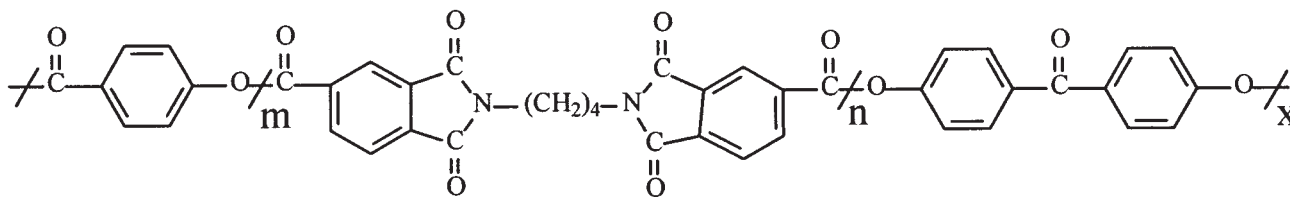
Materials and measurements

The synthesis of polyesterimides has been described in detail previously.¹⁷ Briefly, the polyesterimides were synthesized according to three methods for the

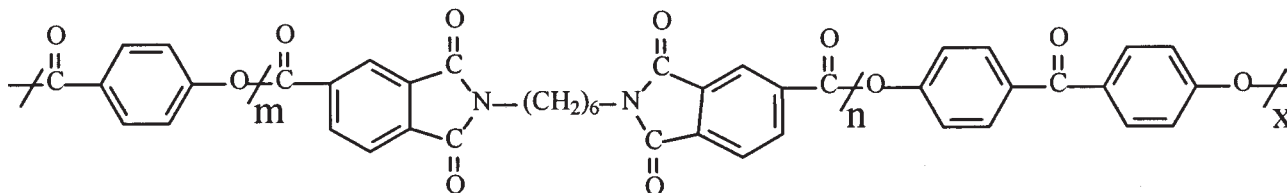
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PIPD4



PIPD6

Scheme 1 Chemical structures of the polyesterimides PIPD4 and PIPD6 (molar ratio $m : n : x = 2 : 1 : 1$).

addition of monomers. The first is the mixed-feeding method. Using this method, *p*-hydroxybenzoic acid (HBA) together with bisphenols [BP; either 4,4'-dihydroxybenzophenone (DHBP) or a combination of DHBP and hydroquinone (HQ)] were dissolved in pyridine. The resulting mixture was then added to imide dicarboxylic acid (IDA), which had been activated in advance by benzenesulfonyl chloride/dimethylformamide/pyridine, in order to proceed to the copolycondensation reaction. The second method is the HBA-first method. According to this method, the pyridine solution of HBA was added to the activated solution of the imide dicarboxylic acid first, and 30 min later the pyridine solution of BP was added. With the third method, the BP-first method, the pyridine solution of bisphenols was added to the activated solution of the imide dicarboxylic acid first, and 30 min later the pyridine solution of HBA was added.

TGA analysis was carried out under an air or nitrogen flow of 25 mL/min in a Shimadzu TGA-50H thermal analyzer. The TGA curves were obtained at various rates of heating per minute: 5°C, 10°C, 15°C, and 20°C.

Ozawa mathematical method

Several methods have been proposed for calculating the kinetic parameters of the thermal decomposition reaction of polymer. The calculation of kinetic energy depends not only on the experimental conditions but also on the mathematical treatment of the data.^{19–28} In the present study, the Ozawa method was used to evaluate the apparent activation energy, E_a , of the

decomposition reaction. A detailed description of the Ozawa method follows.^{28–30}

The degree of conversion (α) in a thermal decomposition process is defined as

$$\alpha = (W_0 - W_t) / (W_0 - W_\infty) \quad (1)$$

where W_t , W_0 , and W_∞ are the actual, initial, and final weights of the samples, respectively.

The rate of decomposition can be expressed as

$$d\alpha/dt = k(T) \cdot f(W) \cdot q(W, T) \quad (2)$$

where t and T are the reaction time and temperature, respectively, and $K(T)$ is generally represented by the Arrhenius equation

$$k(T) = A e^{-E_a/RT} \quad (3)$$

$$f(W) = \left(\frac{W_t - W_\infty}{W_0 - W_\infty} \right)^n = (1 - \alpha)^n \quad (4)$$

where A is the preexponential factor and R is the universal gas constant. The cross term $q(W, T)$ takes into account the interactions between the weight and the reaction arising from factors such as modification of the physical properties of the sample during decomposition. The $q(W, T)$ is generally assumed to be unity. Thus, the rate of decomposition can be also expressed as

$$d\alpha/dt = A e^{-E_a/RT} (1 - \alpha)^n \quad (5)$$

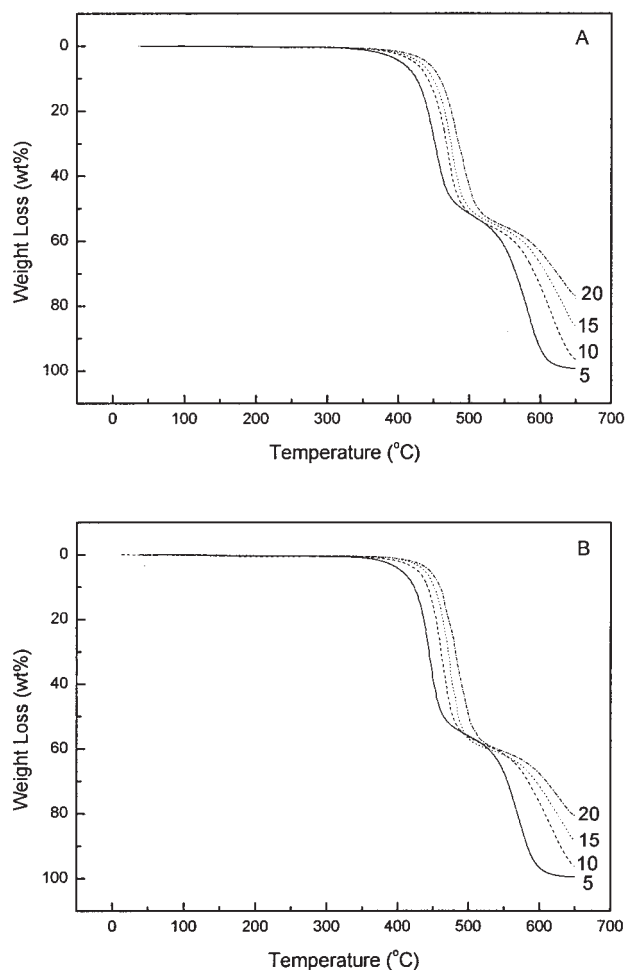


Figure 1 TGA curves of (a) PIPD4 and (b) PIPD6 at different heating rates.

Because the heating rate, β , is equal to dT/dt , the decomposition rate, eq. (5), can be rewritten as

$$d\alpha/dT = A/\beta e^{-E_a/RT} \cdot (1 - \alpha)^n \quad (6)$$

The above equation can be rearranged as

$$f(\alpha) = \frac{A}{\beta} \int_0^T e^{(-E_a/RT)} dT \quad (7)$$

Ozawa²⁸ used Doyle's approximation,³¹ from which he obtained the following equation:

$$\log \beta = \log \frac{AE_a}{Rf(\alpha)} - 2.315 - 0.4567 \frac{E_a}{RT} \quad (8)$$

where A and R are constants. At a specific α or weight loss percentage, $f(\alpha)$ is also constant. Using this equation, the E_a value at a specific weight loss can be

calculated from the linear dependence of $\log \beta$ versus $1/T$ at different heating rates.

RESULTS AND DISCUSSION

Thermal decomposition of polyesterimides with flexible spacers of different lengths in IDA

The chemical structure of two polyesterimides with different lengths of methylene ($-\text{CH}_2-$) spacers that had been synthesized by the HBA-first method are shown in Scheme 1. Their monomer composition was IDA : BP : HBA = 1 : 1 : 2, where BP is DHBP, IDA4 is *N,N'*-butane-1,4-diylbis-(trimellitimides), and IDA6 is *N,N'*-hexane-1,6-diylbis-(trimellitimides). As shown in Scheme 1, the flexible spacers in PIPD4 and PIPD6 corresponded to four and six methylene groups, respectively.

The TGA curves of PIPD4 and PIPD6 in air at different heating rates are illustrated in Figure 1. The curves clearly show two weight-loss stages during the decomposition process for both materials. With the information obtained from the TGA curves, $\log \beta$ was

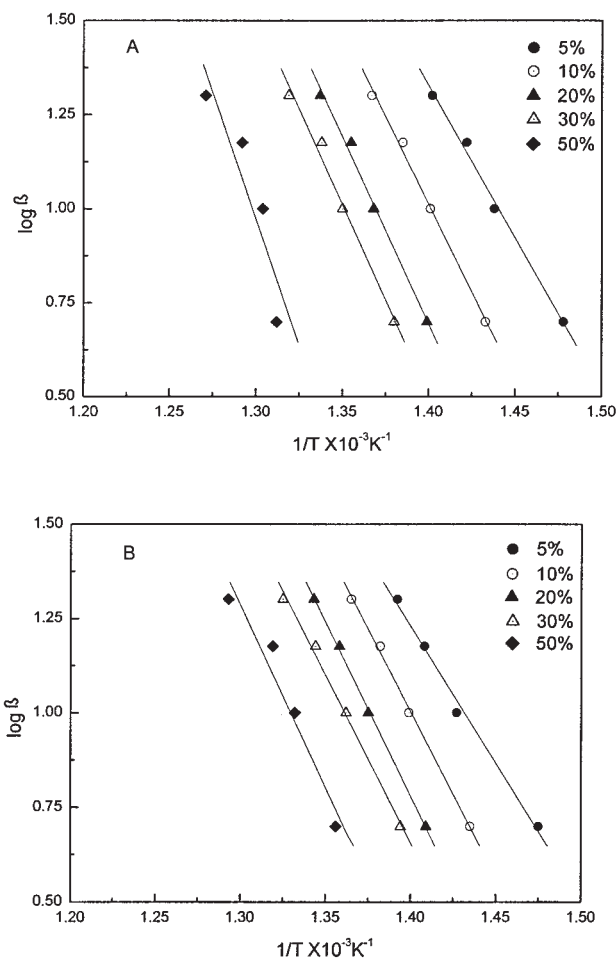


Figure 2 Plots of $\log \beta$ versus $1/T$ for (a) PIPD4 and (b) PIPD6 at different amounts of weight loss.

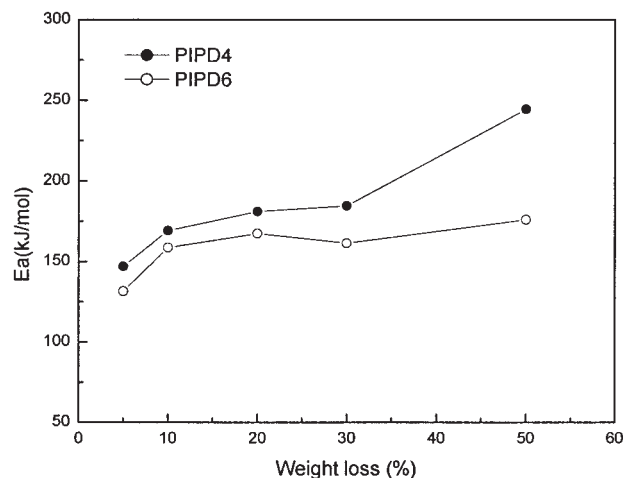


Figure 3 Apparent activation energy, E_a , versus weight loss for PIPD4 and PIPD6.

plotted as a function of $1/T$, as shown in Figure 2, for PIPD4 and PIPD6. Good straight linearity at a given weight loss showed that the experimental data were well described by the Ozawa theory for a weight loss percentage, α , at or below 50%. However, linearity was not good when α was greater than 50%. This suggested that the reaction mechanism of decomposition could vary with the increase of the degree of decomposition.

According to the Ozawa method [eq.(8)], at a specific weight loss percentage, α , the E_a values can be calculated from the linear dependence of $\log \beta$ on $1/T$ at different heating rates. Therefore, from the eq. (8), E_a can be estimated to be $-R \cdot \text{Slop}/0.4567$ (kJ/mol).

From Figure 3, it can be seen that the E_a of the decomposition reaction of PIPD4 was much higher than that of PIPD6 when the weight loss percentage, α , was at or below 50%. The E_a ranged from 146.9 to 244.4 kJ/mol for PIPD4 and from 131.6 to 235.9 kJ/mol for PIPD6 during the decomposition process. This result is probably consistent with the regular pattern of thermal decomposition for commodity polymers such as polyethylene terephthalate (PET) and polybutylene terephthalate (PBT): E_a decreased with an increasing number of methylene groups in the molecular chain.³² In other words, The length of the flexible spacer was responsible for PIPD4 having more improved thermal stability than PIPD6.

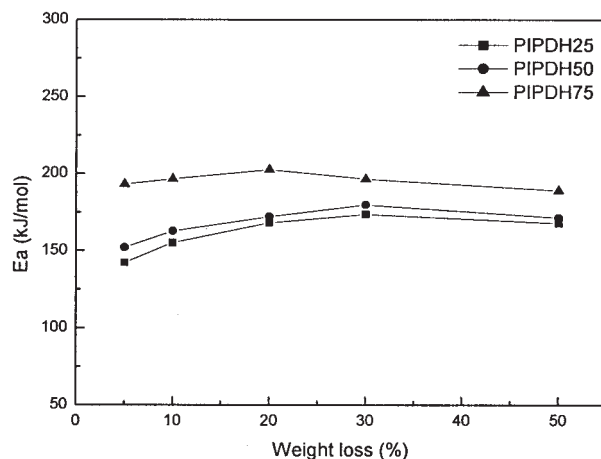
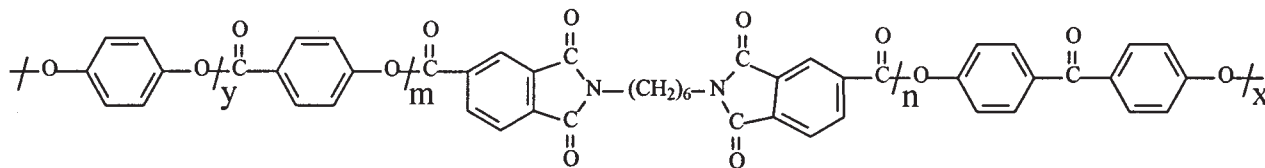


Figure 4 Apparent activation energy, E_a , versus weight loss.

Thermal decomposition of polyesterimides with different relative compositions of two bisphenols

In this section, the influence of the relative composition of two bisphenols, 4,4'-dihydroxybenzophenone (DHBP) and hydroquinone (HQ), on thermal decomposition kinetics is discussed. The three random polyesterimides investigated were synthesized by the mixed-feeding method from HBA, IDA6, DHBP, and HQ with a 2 : 1 : 1 ratio of HBA : IDA6 : (DHBP+HQ). The relative ratios of bisphenols were different: a 1 : 1 ratio of DHBP : HQ for PIPDH50, a 3 : 1 ratio of DHBP : HQ for PIPDH75, and a 1 : 3 ratio of DHBP : HQ for PIPDH25. The general expression of chemical structures for the series of polyesterimide PIPDHs is shown in Scheme 2.

According to the relationship between $\log \beta$ and $1/T$ and the Ozawa method mentioned above [eq. (8)], the calculated activation energy values of PIPDH25, PIPDH50, and PIPDH75 for the decomposition in air plotted with the percentage of weight loss are shown in Figure 4. It can be clearly seen that the E_a for PIPDH75 was the highest of the three samples, for which the order of E_a with the same weight loss percentage was: PIPDH75 > PIPDH50 > PIPDH25. This indicates that the increase in the relative composition of bisphenol monomers in DHBP could improve the thermal stability of the polyesterimide. It was suggested that thermal stability is probably correlated



Scheme 2 Chemical structure of the polyesterimide PIPDH [molar ratio $m : n : (x + y) = 2 : 1 : 1$].

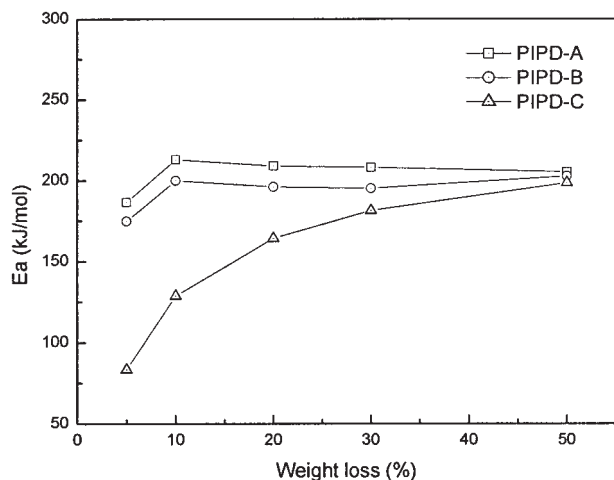


Figure 5 Apparent activation energy, E_a , versus weight loss.

with ketonic group in DHBP. The temperatures at 5% weight loss for PIPDH25, PIPDH50, and PIPDH75 were 421.3°C, 429.1°C, and 440.6°C, respectively.

Dicke and coworkers investigated a series of wholly thermotropic copolyesters and also found that the addition of DHBP could improve processability, the mechanical property, and thermal stability of the copolyesters.^{33–35}

Thermal decomposition of polyesterimides synthesized with different monomer addition sequences

Three polyesterimide samples with the same mole ratio of 1 : 1 : 2 IDA6 : DHBP : HBA were synthesized with different sequences of adding monomers: the HBA-first sequence was labeled as PIPD-A, the mixed-feeding sequence as PIPD-B, and the DHBP-first sequence as PIPD-C.

The activation energy values of the three polyesterimide samples for decomposition in nitrogen (N_2) were calculated according to the Ozawa method mentioned above and plotted with the percentage of weight loss in Figure 5. It can be seen that with the same weight loss percentage the E_a of PIPD-C was much lower than that of PIPD-A and PIPD-B and that the E_a of PIPD-A was very close to and slightly higher

than that of PIPD-B. Thus, the order of thermal stability was: PIPD-A > PIPD-B > PIPD-C. This order probably correlated with monomer addition sequence during synthesis.

According to the polymerization mechanism and monomers ratio in this study, the dicarboxy acid (2 mol —COOH) was activated first. For PIPD-A, when the HBA (2 mol —OH) was added quickly, the —OH was almost condensed with the —COOH, and a new dicarboxy acid was generated, as shown in Scheme 3.

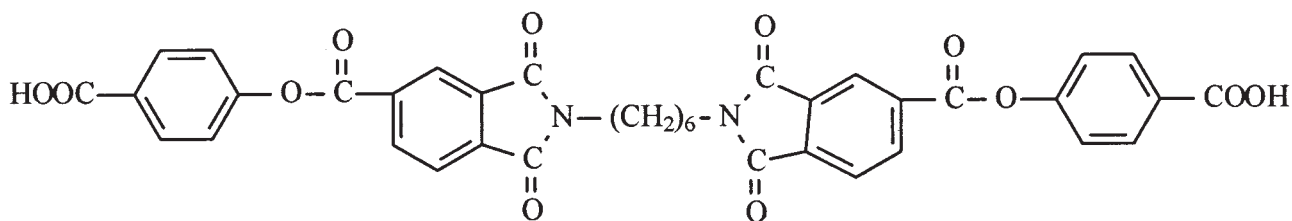
And when the DHBP was added to the new activated dicarboxy acid, the resulting polymer was a bipolymer theoretically. Therefore, with the HBA-first monomer-adding method, the resulting PIPD-A could be considered an alternating copolymer.

When HBA and DHBP were mixed in pyridine and added to the activated dicarboxy acid, the probability of the reaction between the dicarboxy acid and the hydroxyl group in the HBA or in the DHBP was equal. Thus, the resulting PIPD-B could be considered a random copolymer.

With the DHBP-first method, the resulting product had a tendency to form a block copolymer with $-(IDA6-DHBP)_x-(HBA)_y-$ or two independent polymers, $-(IDA6-DHBP)_x-$ and $-(HBA)_y-$.

The sequence of the addition of monomers also affected the solubility of the polyesterimides obtained. The results of the dissolving experiments in trifluoroacetic acid (CF_3COOH) showed that the sample of PIPD-C could not be dissolved by this solvent, but the other two samples could. This suggested that the PIPD-C had a longer HBA block. Because the number of HBA homopolymerizations was more than 3, the dissolvability of the resulting product remarkably decreased until it could not be dissolved in any solvents. Because of the poor dissolvability of the HBA block, the product was prematurely precipitated from $BsCl/Py/DMF$ solution during the polymerization process, resulting in a product with a lower molecular weight. The TGA results showed that the temperature for 5% weight loss of PIPD-C was 399.5°C, which is clearly lower than that of PIPD-A (449.3°C) and of PIPD-B (444.4°C).

As a result, the E_a order was ascribed to the difference in the molecular chain structures formed by different monomer-adding sequences.



Scheme 3 Chemical structure of the new dicarboxy acid.

In addition, it also can be seen from Figure 5 that with an increased degree of decomposition, the E_a of three samples trended toward being close to each other, and at a weight loss of 10%, the E_a for PIPD-A and PIPD-B were at their maximum. In contrast to PIPD-C, no maximum could be observed in the weight loss range of 5%–50%.

The PIPD-A and PIPD6 shown in Figure 3 are the same samples. Comparing Figure 3 to Figure 5, it can be seen that the gas atmosphere had a significant impact on the E_a . For the same weight loss of 5%, the E_a in air was 131.6 kJ/mol in N_2 was 186.5 kJ/mol. In addition, the maximum point of E_a in air, as shown in Figure 3, occurred at a weight loss of 20%; however, in N_2 it moved forward to 10% (Fig. 5).

CONCLUSIONS

We demonstrated that the apparent activation energy of polyesterimides with flexible spacers can be determined using the Ozawa method. Dicarboxy acid with different lengths of flexible spacers affected both the E_a value of thermal decomposition of the resulting polymers and thermal stability. The shorter the length of the flexible spacers, the higher was the thermal stability. The relative content of bisphenols also affected the thermal stability of the resulting polymers, and a high content of 4,4'-dihydroxybenzophenone was advantageous for increasing the thermal stability of the polyesterimide. With the adding monomer sequence during the copolycondensation process, the polyesterimides synthesized by the methods of adding *p*-hydroxybenzoic acid first and of *p*-hydroxybenzoic acid mixed with 4,4'-dihydroxybenzophenone had a higher E_a and greater thermal stability than did that by the method of adding 4,4'-dihydroxybenzophenone first.

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