Thermal Characterization and Thermal Degradation of Copolyimides Containing Fluorine and Phosphine Oxide

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ABSTRACT: A series of copolyimides containing different ratios of fluorine and phosphine oxide were synthesized. The copolymers were characterized with Fourier transform infrared, differential scanning calorimetry, and thermogravimetric analysis measurements. The copolymers were thermally stable up to 700 K and exhibited glass-transition temperatures in the range of 495–562 K. The glass-transition temperatures of the copolymers decreased with an increase in the phosphine oxide content. The thermal decomposition behavior of the copolymers was investigated. The copolymers with higher phosphine oxide contents displayed lower onset decomposition temperatures and char yields. A new method involving the multiple-rate isotemperature was used to define the most possible mechanism [$G(\alpha)$] for the reactions. The overall kinetic model function of the thermal decomposition of these copolymers obeyed the Avrami–Erofeev model equation, $G(\alpha) = [-\ln(1 - \alpha)]^{1/m}$, where α is the conversion degree. The apparent kinetic parameters of the degradation processes were also obtained. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 98: 2139–2143, 2005

Key words: activation energy; degradation; differential scanning calorimetry (DSC); polyimides

INTRODUCTION

Aromatic polyimides, a class of high-performance polymers,[1,2] are attractive for high-temperature applications as matrix resins because of their excellent thermal, mechanical, adhesive, dielectric, and optical properties, along with their good chemical resistance and high dimensional stability. They have, therefore, been excellent candidates for electronic packaging applications for the past decade. As the electronic devices have become smaller and lighter, the demand has increased for a new class of polyimides with low dielectric constants and excellent solubility that retain their good thermal properties. This has led to considerable research being carried out to improve the dielectric properties of polyimides through methods including fluorination.[3,4] Fluorination is also known to enhance the solubility of polyimides in chloroform, toluene, or tetrachloroethane, even with full imidization. However, fluorinated polyimides also have drawbacks, such as poor adhesion, low mechanical strength, and a high coefficient of thermal expansion. Although polyimides have good adhesive properties, much more effort has been directed toward the further improvement of adhesion to enhance the reliability of electronic devices, especially for fluorinated polyimides. Polyimides containing phosphine oxide are known to have excellent adhesive properties, with the added benefits of excellent thermal stability and miscibility, because of strong hydrogen bonding.[5] Therefore, polyimides containing both fluorine and phosphine oxide will exhibit better integrated properties than those containing only fluorine or phosphine oxide. The thermal properties are some of the most important properties of polyimides. Therefore, this work was undertaken to determine the effect of the copolymer composition on the thermal properties and stabilities in a nitrogen atmosphere.

Numerous ways of investigating the thermal behavior of polyimides have been reported in the literature.[6] Thermogravimetric analysis (TGA)/differential scanning calorimetry (DSC) techniques may be some of the most convenient methods for carrying out this research.[7] The results from TGA data can also suggest a possible degradation mechanism. The objective of this study was to examine a series of novel synthesized copolyimides containing various ratios of fluorine and phosphine oxide. The assigned glass-transition temperatures (T_g's) were determined by DSC. The thermal degradation of the copolyimides was investigated with dynamic TGA under nitrogen at different heating rates. The apparent activation energy (E) values for their degradations were evaluated by an iterative method.[8,9] In addition, a thermal degradation mecha-

TABLE I
Relationship of the ODA–mDA6FPPO–6FDA Copolyimide Molar Ratios and Characteristic Temperatures

Copolymer	Molar ratio			Characteristic temperature (K)		
	ODA	mDA6FPPO	6FDA	DSC T_g	5% mass loss	10% mass loss
PI-A	4.0	0	4.0	562.5	771.5	786.6
PI-B	3.0	1.0	4.0	540.2	766.5	782.3
PI-C	2.0	2.0	4.0	526.3	763.6	776.4
PI-D	1.0	3.0	4.0	501.5	754.5	770.1
PI-E	0	4.0	4.0	495.5	757.5	771.4

nism for these copolyimides is proposed, and a new method involving the multiple-rate isotemperature[10] was used.

EXPERIMENTAL

We synthesized the copolyimides used for this study from 4,4'-diaminodiphenylether (ODA), 2,2'-bis(3,4-dicarboxyphenyl) hexafluoropropane (6FDA), and bis(3-aminophenyl)-3,5-bis(trifluoromethyl)phenylphosphine oxide (mDA6FPPO) with different molar ratios (Table I). The copolymers were prepared by a two-step procedure. In the first step, copoly(amic acid)s were prepared by the stoichiometric addition of various monomers. Then, they were thermally imidized under a nitrogen purge at 150°C for 1 h. Their chemical structures are depicted in Figure 1 and have been characterized with Fourier transform infrared (FTIR). DSC analysis was performed on a Mettler–Toledo (Switzerland) DSC 822^e. The temperature was recorded from room temperature to 573 K at a heating rate of 5 K/min under a nitrogen flow of 50 mL/min. TGA measurements were carried out on a PerkinElmer (Norwalk, CT) TGS-2 thermogravimetric analyzer in a nitrogen flow at 80 mL/min from 300 to 1120 K. The sample size was 3.00 ± 0.20 mg. Dynamic experiments were performed at several heating rates: 5, 10, 15, and 20 K/min.

RESULTS AND DISCUSSION

FTIR characterization

FTIR was run to confirm the completion of imide formation, and the FTIR spectrum is shown in Figure

2. The complete imidization of these copolymers is indicated by the absence of a broad, overlapping band of vNH and vOH at 3436 cm^{-1}, vCO of the amide at 1648 cm^{-1} of the poly(amic acid), and vCO of the anhydride at 1850 cm^{-1}. Moreover, a new band around 1782 and 1728 cm^{-1} due to the imide C=O stretching vibration and imide C—N stretching at 1381 cm^{-1} can be observed for the final copolymers.

DSC measurements

DSC is a convenient method for determining the thermal properties of polymers. In this study, all samples were preheated at a scanning rate of 10 K/min over a temperature range of 300–373 K and maintained at 373 K for 10 min to ensure the complete removal of the residual solvent. The DSC curves of the copolymers are shown in Figure 3. DSC analysis of the copolyimides (Fig. 3) showed that the copolyimides exhibited no crystallization or melting transition in the temperature range of the measurements. A single T_g in DSC traces was presented, which indicated that all the copolyimides were assumed to be random copolymers. The T_g values are summarized in Table I. The sequence of the T_g values is PI-A > PI-B > PI-C > PI-D > PI-E, and this can be explained by the presence of ODA and mDA6FPPO moieties in the backbone. It is interesting at this stage to compare the T_g values of the copolymers shown in Table I. The copolyimides containing the ODA unit (PI-A) in the polymer backbone exhibited higher T_g's than the analogous copolyimide containing the mDA6FPPO unit (PI-E). It is also expected that increasing the ratio of mDA6FPPO and decreasing the ratio of ODA will reduce T_g. This could
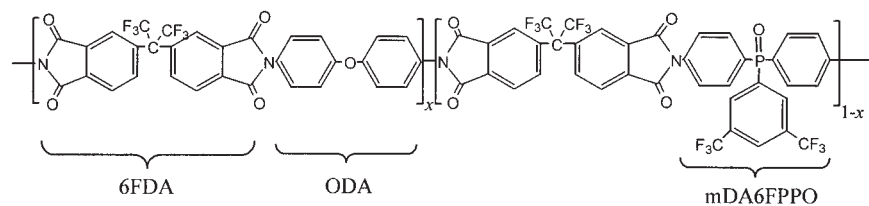

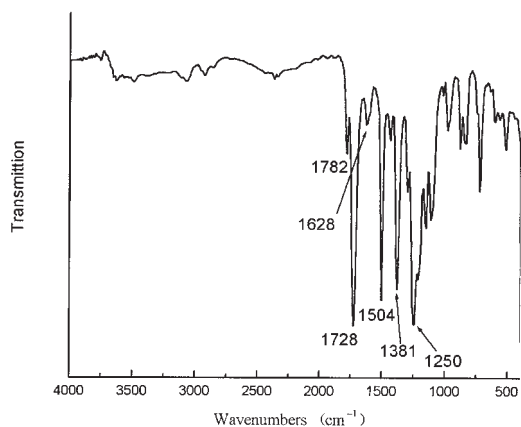**Figure 1** Structure of the 6FDA–ODA–mDA6FPPO copolyimides.

Figure 2 FTIR spectrum of the 6FDA–ODA–mDA6FPPO copolyimides.

Figure 4 TG/DTG curves for the thermal degradation of PI-A at a heating rate of 10 K/min under an atmosphere of N_2.

be attributed to the high free volume present in mDA6FPPO because of the bulky CF_3 moieties and noncoplanarity of mDA6FPPO, whereas ODA is a rigid unit and has a smaller free volume than mDA6FPPO.

Thermal stability

The thermal stability of the copolyimides was evaluated by TGA in a nitrogen atmosphere. Thermogravimetry/differential thermogravimetry (TG/DTG) curves for the thermal degradation of PI-A at a heating rate of 10 K/min under N_2 were recorded and are shown in Figure 4. In general, the degradation of all the copolyimides occurs in three steps. As shown in Figure 4, the first step, from room temperature to ~700 K, represents the volatilization of volatile matter. The second step, starting at ~750 K and ending at ~1000 K, represents the main thermal degradation of copolyimide chains. The third step, starting at ~1000
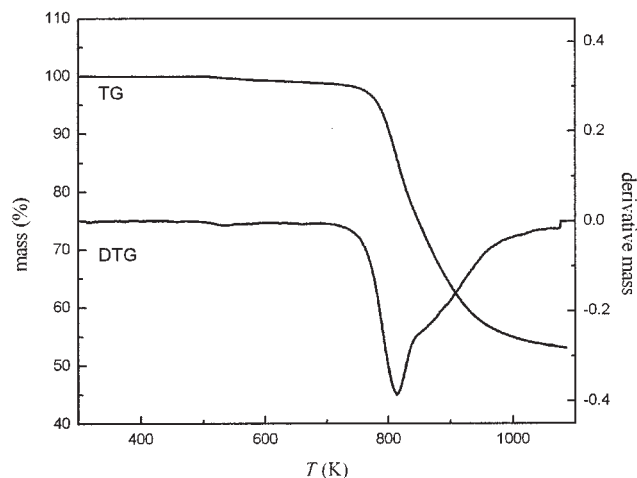
K, symbolizes the carbonization of the degraded products to ash. These three steps represent the thermal degradation of the copolyimides. The char yields at 1100 K were in the range of 48–53% for all the copolymer series. Furthermore, the thermal stability of the copolyimides was obviously modified by the presence of ODA and mDA6FPPO moieties in the backbone. The characteristic temperature for the thermal degradation of the copolymers is summarized in Table I. The 5% weight loss temperature in N_2 of these polymers was in the range of 771–750 K. In general, high thermal stability is due to the presence of rigid backbone structures, as expected for copolyimides. The order of the 5% weight loss temperatures was PI-A > PI-B > PI-C > PI-D $\approx$ PI-E, and this may be due to the fact that the ODA unit is more thermally stable than the mDA6FPPO unit.
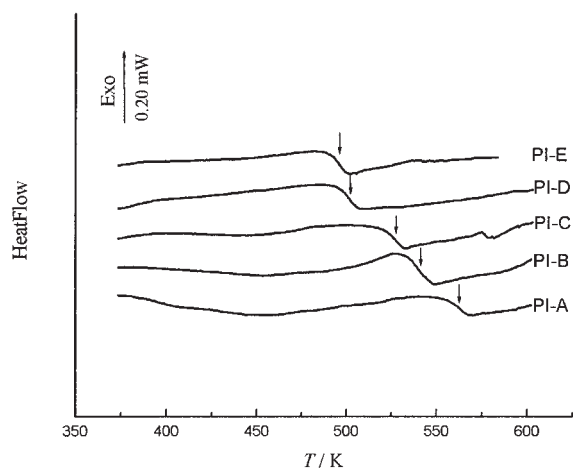
Thermal degradation kinetics

Determination of the activation energies by an iterative procedure

Numerous kinetic methods are available in the literature to characterize the degradation of polymeric materials. In this study, an iterative method[8,9] was used to evaluate the degradation activation energies of the copolyimides.

The thermal decomposition of solid-state materials is subjected to the following equation:

$$d\alpha/dT = (A/\beta) \exp(-E/RT)f(\alpha) \qquad (1)$$

where α is the conversion degree, β is equal to dT/dt, A is the pre-exponent, R is the gas constant, and T is the absolute temperature. In most experiments, the

Figure 3 DSC curves for various copolyimides at a heating rate of 5 K/min under an atmosphere of N_2.
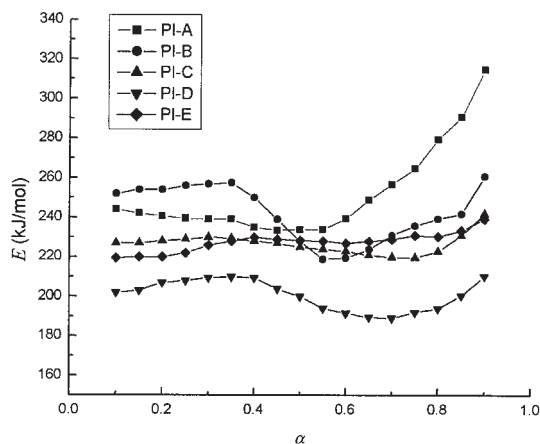
Figure 5 Relationship of E and α for the thermal degradation of the copolyimides.

heating rate is kept constant. Integrating both sides of eq. (1), we obtain the following equation:

$$G(\alpha) = \int_{T_0}^{T} (A/\beta) \exp(-E/RT) \, dT \approx \int_{0}^{T} (A/\beta) \exp$$

$$(-E/RT) \, dT = (AE/\beta R)P(u) \quad (2)$$

where $G(\alpha)$ is the integral expression of the kinetic model function; u is equal to E/RT; and $P(u)$ is the temperature integral function, which can be replaced by an approximation formula.[11]

From eq. (2), an iterative procedure is used to approach the exact values of E. The equation is

$$\ln [\beta/h(u)T^2] = \ln [AE/G(\alpha)R] - E/RT \quad (3)$$

where $h(u)$ is equal to $\exp(u)P(u)x^2$. Iterative calculations by means of plots of $\ln[\beta/h(x)T^2]$ versus $1/T$ give the exact value of the activation energy. The values of the activation energy corresponding to different conversions are shown in Figure 5. The values of E depended on α, and this indicates that the overall degradation reaction preceded a complex kinetic scheme. The average values of E for the thermal degradation of PI-A, PI-B, PI-C, PI-D, and PI-E in the main range of degradation, $0.2 \leqslant \alpha \leqslant 0.8$, were 260.22, 245.75, 231.91, 197.70, and 228.26 kJ/mol, respectively. Comparing the results, we found that PI-D and PI-E exhibited lower values of E, and this was consistent with the conclusions drawn from Table I.

Determination of the kinetic mechanism

A method involving the multiple-rate isotemperature[10] was used to define the most probable mechanism of thermal degradation of the copolyimides. Following eq. (2), we obtained the following:

$$\ln G(\alpha) = \ln [AE \times P(u)/R] - \ln \beta \quad (4)$$

In the main range of degradation, we randomly chose several temperature to calculate the slope, intercept, and correlation coefficient r of 31 types of mechanism functions[12] by plotting $\ln G(\alpha)$ versus $\ln \beta$. We found a very interesting phenomenon: the most probable kinetic mechanisms of the five copolyimides all obeyed the same kinetic model, the Avrami–Erofeev function A_m $\{G(\alpha) = [-\ln(1-\alpha)]^{1/m}\}$, for the description of the degradation of the copolyimides because their slopes were most adjacent to 1.0000 and r was better. The expression of A_m was introduced into eq. (4), and we got eq. (5):

$$\ln \beta = \ln [AE \times P(u)/R] - (1/m) \ln [-\ln(1-\alpha)] \quad (5)$$

The exponent m was determined by the plotting of $\ln \beta$ versus $\ln[-\ln(1-\alpha)]$ at the assigned temperature. Also, A was determined from the intercept. The values of E, $\ln A$, and accommodated m for the thermal degradation of different copolyimides are listed in Table II. Comparing the results, we found that the kinetic parameters for the thermal degradation of the copolyimides showed the same trend as their thermal stability.

CONCLUSIONS

TGA and DSC techniques were used to study the thermal properties of copolyimides containing different ratios of fluorine and phosphine oxide. The T_g values of the copolyimides decreased with a decrease in the molar percentage of ODA in the copolyimide series, whereas the thermal stability of the copolyimides increased with an increase in the ODA ratio in the copolyimide series. The activation energies for their thermal degradation process were determined by an iterative method. The overall thermal degradation mechanism was determined by a new method involving the multiple-rate isotemperature, which was best described by the Avrami–Erofeev function, $G(\alpha) = [-\ln(1-\alpha)]^{1/m}$. Meanwhile, E and $\ln A$ for the thermal degradation of these copolyimides decreased with an increase in the molar percentage of mDA6FPPO.

TABLE II
E and $\ln A$ for the Thermal Degradation of ODA–mDA6FPPO–6FDA Copolyimides in Nitrogen

Copolyimide	E (kJ/mol)	$\ln A$ (1/s)	$1/m$
PI-A	260.22 ± 14.14	31.61	1.37–3.50
PI-B	245.75 ± 14.43	29.87	1.52–1.92
PI-C	231.91 ± 3.65	28.06	1.37–1.97
PI-D	197.70 ± 8.41	23.26	1.29–1.69
PI-E	228.26 ± 3.20	27.84	1.35–1.95

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