

# Structural Effects of Pendant Groups on Thermal and Electrical Properties of Polyimides

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**ABSTRACT:** Two series of aromatic polyimides containing various-sized alkyl side groups were synthesized by thermal imidization of the poly(amic acid)s prepared from the polyaddition of benzophenonetetracarboxylic dianhydride and hexafluoro-isopropylidene bis(phthalic anhydride) with 4,4'-methylenedianiline, 4,4'-methylene-bis(2,6-dimethylaniline), 4,4'-methylene-bis(2,6-diethylaniline), and 4,4'-methylene-bis(2,6-diisopropylaniline). The extent to which alkyl substitutes affect the thermal properties of polyimides was examined by differential scanning calorimetry, thermomechanical analyzer, and thermogravimetric analysis techniques. The analytical results demonstrated that the incorporation of alkyl moieties causes a moderate increase in

the coefficient of thermal expansion and a slight decrease in thermal stability. Notably, all polymers had a decomposition temperature exceeding 500°C. The glass transition temperature increases markedly when hydrogen atoms at ortho positions on aniline rings are replaced with methyl groups, but decreases with growing alkyl side group size. The dielectric measurements show that the polymer possessing a large alkyl side group would have the lower dielectric value. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 100: 4672–4678, 2006

**Key words:** polyimides; thermal properties; dielectric constant

## INTRODUCTION

Aromatic polyimides have found diverse applications in the advanced aerospace, automobile, microelectronic, and printed circuit industries because of their distinguished thermal stability, high chemical resistance, good mechanical strength, and excellent dielectric properties.<sup>1–6</sup> However, conventional polyimides are frequently classified as an insoluble, intractable, and infusible material owing to their rigid backbone structure. These disadvantages make conventional polyimides extremely difficult to process and severely limit their commercial uses. Various attempts have been made to overcome these deficiencies, including the use of noncoplanar or alicyclic monomers<sup>7–10</sup> and the introduction of flexible segments into the polymer backbone.<sup>11–13</sup> Methods for overcoming these deficiencies include reducing chain crystallinity, intermolecular charge-transfer, and electronic polarization interactions. An alternative approach involves incorporating pendant groups onto the rigid polyimide

backbone.<sup>14–18</sup> Aforementioned investigations have shown that the presence of bulky groups can effectively prevent the coplanarity of aromatic rings and reduce the packing efficiency of molecular chains without sacrificing thermal properties. While synthesizing two series of polyimides containing alkyl side groups of different sizes, this study investigates how the molecular structure of pendant groups affects the thermal properties of polyimides.

## EXPERIMENTAL

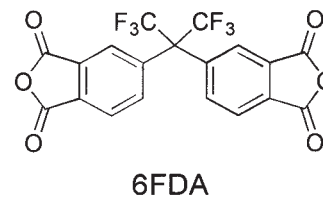
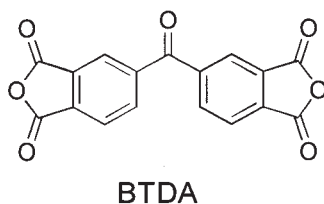
### Materials

Pyromellitic dianhydride (PMDA), 3,3',4,4'-benzophenonetetracarboxylic dianhydride (BTDA), and 4,4'-hexafluoroisopropylidenediphthalic anhydride (6FDA) were recrystallized from acetic anhydride before use. Moreover, 4,4'-Methylenedianiline (MDA), 4,4'-methylene-bis(2,6-dimethylaniline) (MBDMA), 4,4'-methylene-bis(2,6-diethylaniline) (MBDEA), and 4,4'-methylene-bis(2,6-diisopropylaniline) (MBDIA) were purified by recrystallization from a solvent mixture of hexane and toluene (volume ratio 3:1) prior to use. *N*-Methyl-2-pyrrolidone (NMP) were purified and dehydrated by distillation under reduced pressure over calcium hydride and drying over 4 Å molecular sieves. Finally, acetic anhydride was purified by vacuum distillation. Figure 1 shows the chemical struc-

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### Dianhydrides :



### Diamines :

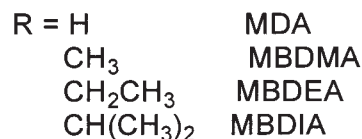
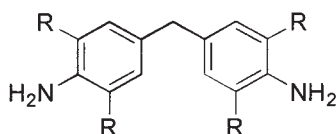


Figure 1 Chemical structures of dianhydride and diamine monomers.

tures of both dianhydride and diamine monomers used in this study.

### Preparation of polyimides

A typical example of polymerization is as follows: In a dry 25 mL round-bottom flask with a magnetic stirring bar, a diamine monomer of MDA (0.88 g, 2.75 mmol) dissolved in NMP (10 mL) was charged under N<sub>2</sub>. The dianhydride monomer of BTDA (0.54 g, 2.75 mmol) was added to this solution and vigorously stirred. The reaction mixture was stirred at ambient temperature under N<sub>2</sub> for 2 days to give a viscous pale yellow solution. The resulting poly(amic acid) solution at a concentration of 15 wt % was then cast onto glass substrates using a microsyringe, and dried at 100°C for 12 h to remove most of the solvents in the polymer film. The soft-baked precursor films were thermally imidized by consecutive heating at 150°C for 30 min and at 350°C for 60 min in a tube furnace under a steady stream of nitrogen with ramping rates of 5.0°C min<sup>-1</sup> and 10.0°C min<sup>-1</sup>, respectively. Following the thermal imidization, the samples were cooled to room temperature at a rate of 2.0°C min<sup>-1</sup>. The films were stripped from the glass substrates by soaking in a dilute HF solution, and then were washed twice with deionized water and dried in a vacuum oven at 80°C for 2 days. All polyimide films had a thickness of 50–100 μm. Glass plate cleaning was performed by immersion in sodium hydroxide aqueous solution overnight, sequential washing with water, acetone, and *n*-hexane in an ultrasonic bath, and finally oven drying at 100°C under N<sub>2</sub> flow.

### Measurements

Fourier transform infrared (FTIR) spectra were recorded on a Nicolet 750 spectrometer. Spectra were obtained by averaging 64 scans at a resolution of 2 cm<sup>-1</sup> in the range 400–4000 cm<sup>-1</sup>. Thermogravimetric analyses (TGA) data were gathered on a thermogravimetric analyzer 2950 of TA Instruments at a heating rate of 10°C min<sup>-1</sup> from 100 to 800°C under N<sub>2</sub> atmosphere. Differential scanning calorimetry (DSC) measurements were conducted using a TA DSC-2910 differential scanning calorimeter under flowing nitrogen at a heating rate of 10°C min<sup>-1</sup>. The glass transition temperatures were taken as the midpoint of the heat capacity change in the DSC thermograms. All samples experienced two heating processes in the DSC measurement and thermograms were taken only for the second run. The in-plane coefficient of thermal expansion (CTE) was measured by a TA TMA-2940 thermo-mechanical analyzer at a heating rate of 10°C min<sup>-1</sup>. Moreover, the CTE values were calculated based on the slope of the expansion–temperature plots over the 100–200°C range.

## RESULTS AND DISCUSSION

### Polymer synthesis

Eight polyimides were synthesized from two aromatic dianhydrides and the diamines MDA, MBDMA, MBDEA, and MBDIA by the conventional two-step process via thermal cyclodehydration, as illustrated in Figure 2. The dianhydride was reacted in 1:1M ratio with a desired diamine in anhydrous NMP at room temperature. To obtain a high molecular weight poly-

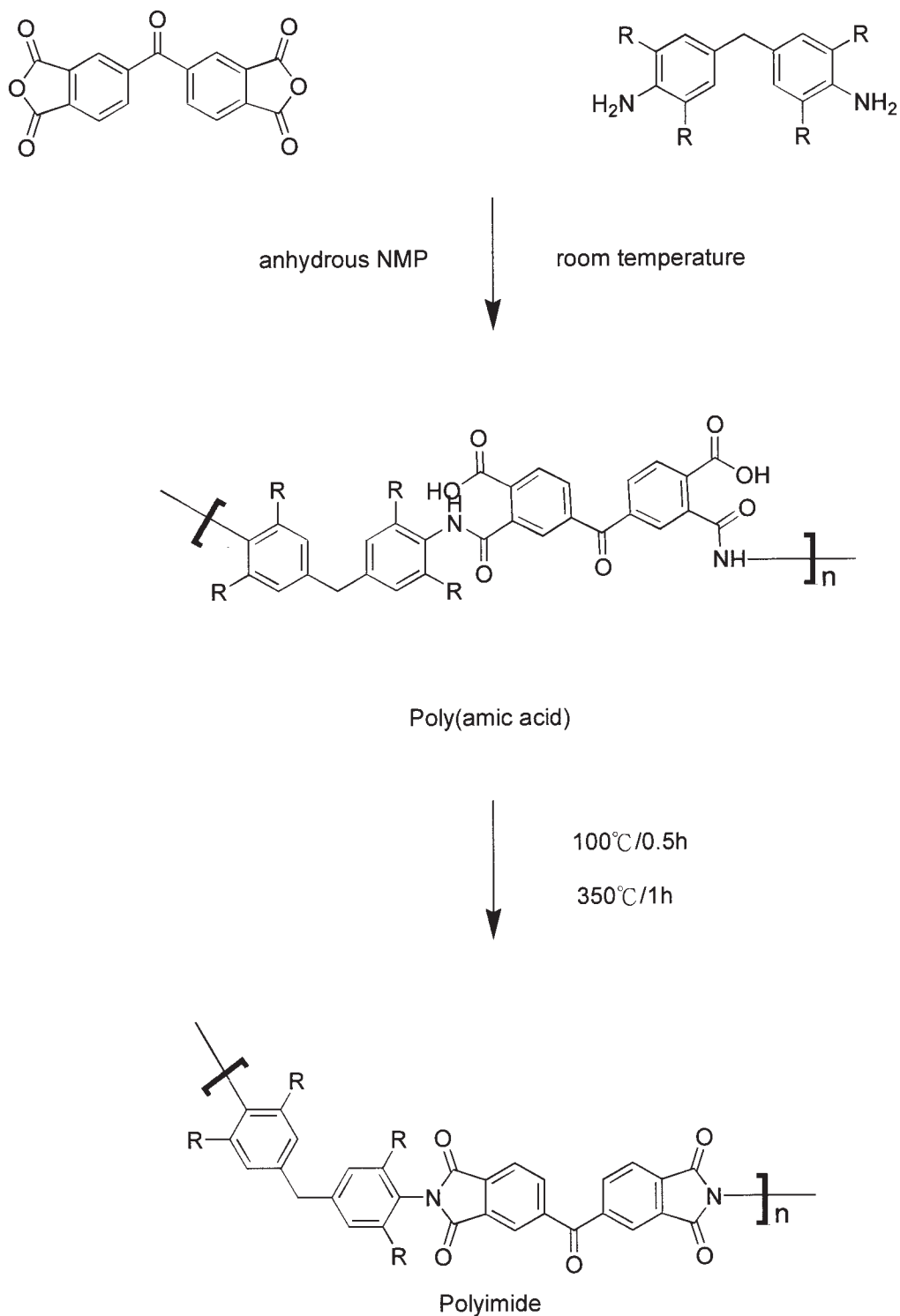


Figure 2 Synthetic scheme of polyimide from BTDA and MDA derivatives.

(amic acid)s, all monomers and solvents were purified by repeated recrystallization and distillation, respectively. Poly(amic acid) viscosity increased rapidly during the early stage of the reaction. As the diamine was varied for a given dianhydride, the increase in viscosity followed the order MDA > MBDMA > MBDEA

~ MBDIA (see Table I). Differences in the rate of viscosity build-up may be attributed to the basicity of diamine monomer and the steric hinderance of the side group. The attachment of electron-donating pendant groups on aniline unit increased the basicity of amine groups, thus providing higher reactivity in the

TABLE I  
Physical, Thermal, and Electrical Properties of Polyimides

Polymer	$[\eta]^a$	$T_g$ (°C)	$T_d^b$ (°C)	Char yield (%)	CTE <sup>c</sup> ( $\mu\text{m}/\text{m}^\circ\text{C}$ )	$\kappa^d$
BTDA-MDA	0.876	302	547	63	37	3.39
BTDA-MBDMA	0.731	331	535	64	52	3.35
BTDA-MBDEA	0.528	296	497	64	46	3.26
BTDA-MBDIA	0.413	263	509	65	50	3.08
6FDA-MDA	0.628	276	527	53	43	3.22
6FDA-MBDMA	0.578	316	525	52	59	3.07
6FDA-MBDEA	0.479	266	494	54	62	3.05
6FDA-MBDIA	0.417	282	504	51	56	2.97

<sup>a</sup> Intrinsic viscosity were measurement at 40°C constant temperature.

<sup>b</sup> Thermal decomposition temperature at 10% weight loss.

<sup>c</sup> The in-plane coefficient of thermal expansion.

<sup>d</sup> Dielectric constants were measured at 1 MHz and at room temperature.

polycondensation reaction. Meanwhile, the bulkiness of alkyl side arms neighboring amine functional groups may reduce monomer reactivity. The experimental results clearly demonstrated that the steric effect dominates in this series of reactions. The formation of poly(amic acid)s was confirmed by IR spectroscopy. Figure 3 shows a typical IR spectra for poly(amic acid) and polyimide. The characteristic absorption bands of an amic acid are located at 3300 (N—H and O—H), 1720 (acid C=O), 1650 (amide C=O), and 1550  $\text{cm}^{-1}$  (N—H, bending). Thermal imidization of the precursor film was carried out by casting poly(amic acid) solutions onto a glass substrate, followed

by consecutive heating at 150 and 350°C in a tube furnace with constant nitrogen flow. During cyclodehydration, the characteristic absorption bands of the imide ring appeared at 1770 (asym C=O), 1720 (sym C=O), 1380 (C—N in imide ring), 1100 and 720  $\text{cm}^{-1}$  (imide ring deformation), while those of the amide and carboxyl groups at 3300 and 1550  $\text{cm}^{-1}$  gradually disappeared. These observations validated the development of imide linkage from the thermal curing of poly(amic acid). Moreover, the band ratio in the FTIR spectra was adopted to monitor the progress of the thermal reaction.<sup>19,20</sup> The degree of imidization was determined as the area ratio of the absorption peak at

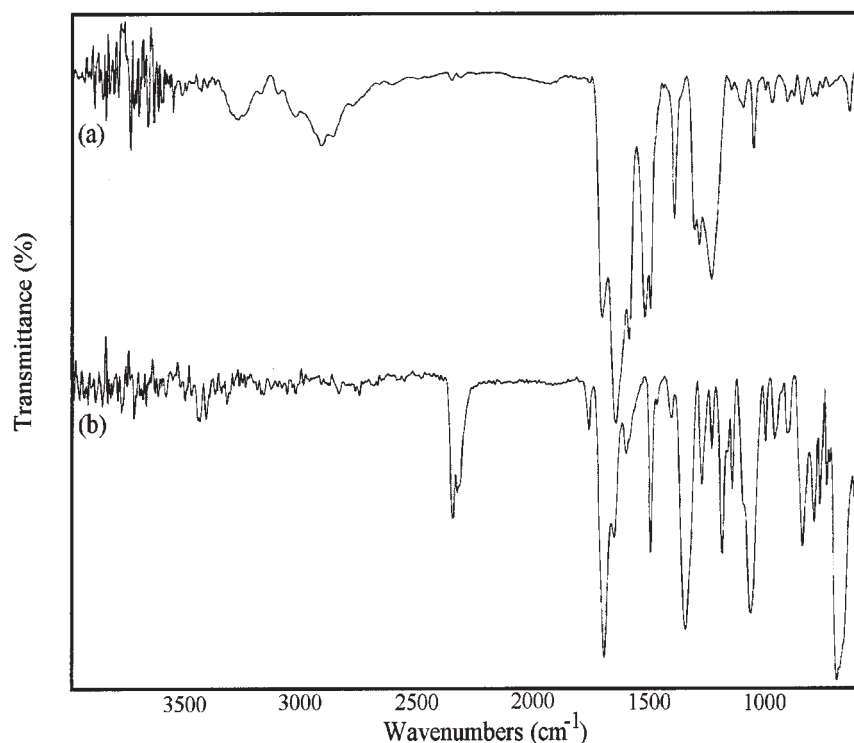
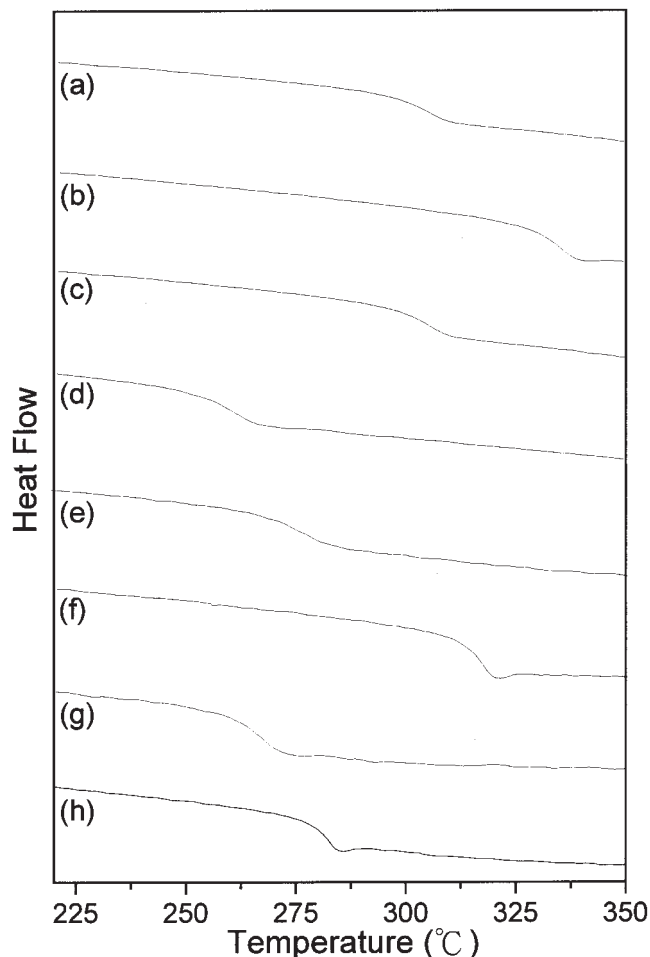


Figure 3 FTIR spectra for (a) poly(amic acid) and (b) polyimide of BTDA-MDA.



**Figure 4** DSC thermograms of (a) BTDA-MDA, (b) BTDA-MBDMA, (c) BTDA-MBDEA, (d) BTDA-MBDIA, (e) 6FDA-MDA, (f) 6FDA-MBDMA, (g) 6FDA-MBDEA, and (h) 6FDA-MBDIA polyimides.

$1770\text{ cm}^{-1}$ , which was normalized with a reference peak at  $1500\text{ cm}^{-1}$  (aromatic stretching) to its initial area. Adequate time and heating temperature were provided to ensure complete curing of the precursor films. All polyimide films obtained were tough and flexible.

### Properties of polyimides

The phase transition properties of polyimides were examined using differential scanning calorimetry. DSC measurements were conducted with two consecutive heating-cooling cycles. The first heating process was employed to rub out the history of thermal annealing, and the second heating run was recorded for data analysis. Figure 4 presented the DSC thermograms for all polyimides synthesized in this work. Only a thermal phase transition was observed. Table I lists the DSC results. In summary, the  $T_g$  values ranged from 260 to 300°C for BTDA-based polyimides

and from 265 to 280°C for 6FDA-based polyimides. The glass transition temperatures ( $T_g$ ) of the polyimide films were all high because of the stiff natures of the polymer backbones. Table I lists the experimental results. Within a given diamine family, the  $T_g$ 's of the BTDA-derived polymers exceeded that of the 6FDA-derived materials. This phenomenon suggested that the carbonyl-bridge is more rigid than the hexafluoroisopropylidene linkage. For the BTDA case, the  $T_g$  values decreased in the order BTDA-MBDMA > BTDA-DMA > BTDA-MBDEA > BTDA-MBDIA. This order clearly indicates that the alkyl pendant groups could be important in glass transition. The bulky alkyl groups have a twofold influence on the  $T_g$  of a polyimide. First, the introduction of bulky alkyl side groups on the polymer backbone reduces intermolecular interactions and chain packing, and thus increases the free volume in polymer systems, thus reducing  $T_g$ . This effect increases with alkyl group size. Second, attaching bulky alkyl groups beside the imide linkage may severely restrict polymer chain thermal rotation, thus significantly increasing chain stiffness and  $T_g$ . From Table I, polymers BTDA-MBDMA displayed 30°C higher  $T_g$ 's than BTDA-MDA. Notably, a similar relation was also observed for polyimides 6FDA-MBDMA and 6FDA-MDA. These results indicated two methyl groups bonded on both ortho positions to the amine group, inducing notable steric hindrance on the bond rotation between the phenyl and imide rings. Additionally, the replacement of methyl groups with larger ethyl or isopropyl groups caused a massive depression rather than further increment in  $T_g$ . This reduction in  $T_g$  is attributed to the increased free volume in the polymer system resulting from the growth of the alkyl group.

In-plane coefficient of thermal expansion was determined by the TMA method. Before measurement, polymer films were heat pretreated at 250°C in  $N_2$  atmosphere for 2 h to remove residual stresses and thermal history. For each polyimide, the measured CTE was averaged over the range of 100–200°C, which is well below its  $T_g$ . Table I lists the calculation results. The CTE values were all positive and in the range 36–56  $\mu\text{m}/\text{m}^\circ\text{C}$ . Polyimides of BTDA-MBDMA, BTDA-MBDEA, and BTDA-MBDIA revealed a higher expansion coefficient than the unsubstituted analogue BTDA-MDA. This revealed that the introduction of massive groups into polyimide as side chains could increase thermal expansion in the film. However, all alkyl-substituted polyimides displayed comparable CTEs, despite the size difference in pendant groups. The chosen dianhydride was noted to have a mild effect on the CTE, with the more rodlike BTDA yielding lower CTEs than the 6FDA.

Figure 5 illustrated the TGA curves for BTDA-derived polyimides. All polymers showed similar single-

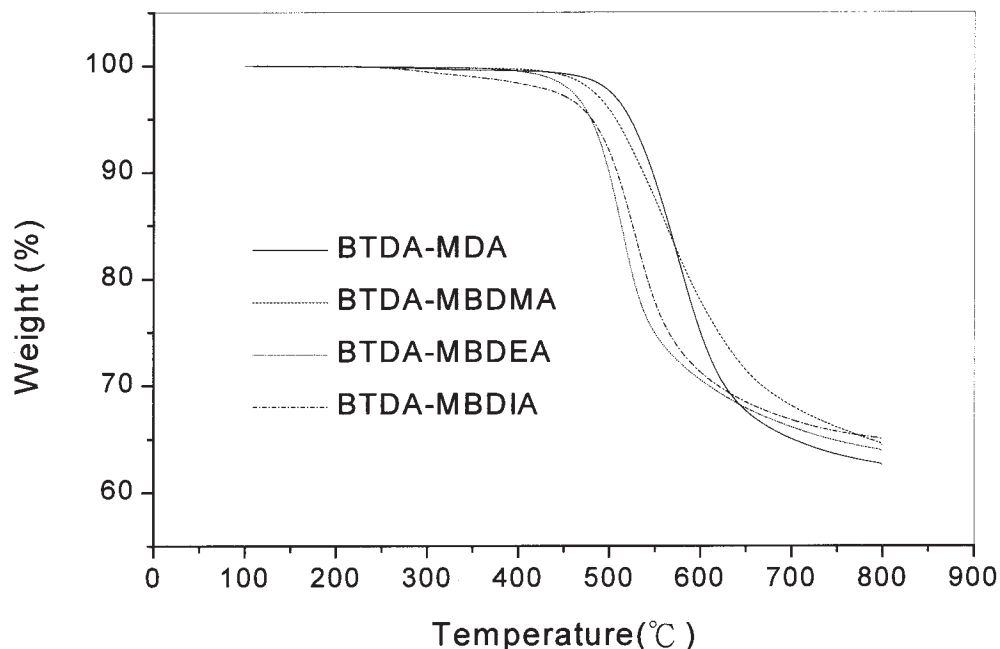


Figure 5 TGA thermograms of BTDA-based polyimides.

stage decomposition behavior, with no significant weight loss up to a temperature of  $\sim 460^\circ\text{C}$  in nitrogen atmospheres. Table I lists summarized results from both series of polyimides based on BTDA and 6FDA dianhydrides. All polyimides displayed excellent thermal stability, and their decomposition temperatures at 10% weight loss exceeded  $500^\circ\text{C}$  in  $\text{N}_2$ . The amounts of carbonized residue at  $800^\circ\text{C}$  for these polyimides exceeded 50%. However, a slight reduction in polymer thermal stability was observed on anchoring pendant groups, because of the alkyl groups being susceptible to thermal degradation. Interestingly, the decomposition temperatures ( $T_d$ ) of BTDA-MBDIA and 6FDA-MBDIA slightly exceeded those for BTDA-MBDEA and 6FDA-MBDEA, respectively, despite the isopropyl group being heavier than the ethyl group. For a given diamine, the  $T_d$  values of 6FDA-based materials were slightly lower than those based on BTDA dianhydride. This difference can be attributed to the thermal weak linkage of the hexafluoroisopropylidene group.

The dielectric constant,  $\kappa$ , of polyimide films was measured by the parallel-plate capacitor method and the experimental data was summarized in Table I. Obviously, the 6FDA-derived polyimides possess lower value of dielectric constant than the corresponding polyimides derived from BTDA dianhydride. Very importantly, the incorporation of alkyl pendant groups into the polymer backbone can effectively decrease the dielectric constant of the material and the  $\kappa$  value decreases with the increasing size of pendant group. This phenomenon reveals that the interactions between polymer chains are

effectively reduced by the presence of pendant groups along the linear backbone.

## CONCLUSIONS

Aromatic polyimides with various sizes of alkyl side-chain were synthesized and characterized. The incorporation of alkyl side chains on the ortho position to the amine group was found to significantly influence polymer thermal properties. Series of polyimides derived from both BTDA and 6FDA dianhydrides exhibited similar glass transition temperature behavior. Both series followed a decreasing order of BTDA-MBDMA > BTDA-MDA > BTDA-MBDEA > BTDA-MBDIA and 6FDA-MBDMA > 6FDA-MDA > 6FDA-MBDIA > 6FDA-MBDEA. These differences in  $T_g$  can be attributed to two opposite factors, namely the restriction of chain rotation caused by the steric hindrance of pendant groups and the increase of free volume resulting from the reduction of intermolecular interaction and ordered chain-packing. Higher CTE values were noted for all alkyl-substituted adducts compared to their parent polyimides. Notably, the CTEs were essentially independent of the pendant group size for these polymers. As expected, the side-group-containing polyimides were thermally less stable than the unsubstituted polymers. However, these materials continued to exhibit single thermal degradation behavior and high decomposition temperature, exceeding  $500^\circ\text{C}$ . Finally, the dielectric measurement also presented the same phenomenon as the thermal properties, which resulted from the different pendant group of the molecules.



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