# Preparation and Properties of Polyimides Based on Bis[3,5-dimethyl-4-(4-aminophenoxy)phenyl]methane

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**ABSTRACT:** A series of polyimide (PI) thin films were synthesized based on bis[3,5-dimethyl-4-(4-aminophenoxy)phenyl]methane and conventional aromatic dianhydrides. The structures and properties of the thin films were measured with Fourier transform infrared, NMR, thermogravimetric analysis, dynamic mechanical analysis, and impedance analysis. The PI films exhibited glass-transition temperatures in the range of 211–300°C and possessed initial thermal decomposition temperature reaching up to 457–482°C in air and 461–473°C in nitrogen. Some PI films had high solubility in organic solvents such as 1-methyl-2-pyrrolidinone, $N,N$-dimethylformamide, $N,N$-dimethylacetamide, dimethyl sulfoxide, $m$-cresol, tetrahydrofuran, and $CHCl_3$. The mechanical properties of these films were also examined. The dielectric constants of the films were in the range of 2.8–3.3 at 25°C. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 104: 1265–1270, 2007

**Key words:** polyimides; property; thin films

## INTRODUCTION

Aromatic polyimides (PIs) are well known as high-performance polymers possessing excellent thermal stability, inert behavior against organic solvents, and good mechanical properties.[1] However, many PIs cannot be processed with conventional methods because of their insoluble and infusible properties. Therefore, much work has been done to synthesize soluble or thermoplastic PIs.

Several approaches are used to improve soluble and fusible properties, such as inserting flexible groups into the main chain to reduce the packing force, introducing bulky pendant groups into the main chain to enhance the free volume, replacing aromatic groups with alicyclic groups, and introducing fluorinated groups.[2] Tamai and Yamaguchi[3] synthesized melt-processable PIs with aromatic ether groups. Great solubility in organic solvents and thermal stability were exhibited. Lu et al.[2] indicated that PIs with good organosolubility and light color were prepared based on 4,4'-diamino-3,3'-dimethyldiphenylmethane (MMDA). All the PIs synthesized from MMDA, even with a rigid dianhydride [pyromellitic dianhydride (PMDA)], presented high organosolubility in aprotonic polar solvents such as 1-methyl-2-pyrrolidinone (NMP), $N,N$-dimethylacetamide (DMAc), and $m$-cresol. Some can even be dissolved in common low-boiling-point solvents such as tetrahydrofuran

(THF) and chloroform. Liaw et al.[1] noted that flexible diamine α,α'-bis[3,5-dimethyl-4-(4-aminophenoxy)phenyl]-1,4-diisopropylbenzene (BDAPD) was used to obtain highly processable PIs. Recently, Yang and Chen[5] claimed that they had already synthesized another kind of PI with good organosolubility based on 1,1-bis[4-(4-aminophenoxy)phenyl]-1-phenylethane. Qian et al.[4] used α,α'-(4-amino-3,5-dimethylphenyl)phenylmethane to prepare PIs that had excellent processable properties.

Although much research has already been performed, due attention is needed to determine the effects of novel PIs. In this study, novel PIs were synthesized with five kinds of conventional dianhydrides and bis[3,5-dimethyl-4-(4-aminophenoxy)phenyl]methane (BDAPM) as a diamine monomer. The solubility, mechanical properties, thermal stabilities, and dielectric properties of the PI films were also examined.

## EXPERIMENTAL

### Materials

2,6-Dimethylphenol, $p$-chloronitrobenzene, anhydrous potassium carbonate, hydrazine monohydrate, and 5% palladium on activated carbon (5% Pd/C) were used as received. 3,3',4,4'-Benzophenonetetracarboxylic dianhydride (BTDA), 3,3',4,4'-biphenyltetracarboxylic dianhydride (BPDA), 4,4'-(hexafluoroisopropylidene)diphthalic anhydride (6FDA), and 4,4'-(4,4'-isopropylidenediphenoxy)bis(phthalic anhydride) (BPADA) were recrystallized from acetic anhydride and dried *in vacuo*. PMDA was purified by sublimation before it

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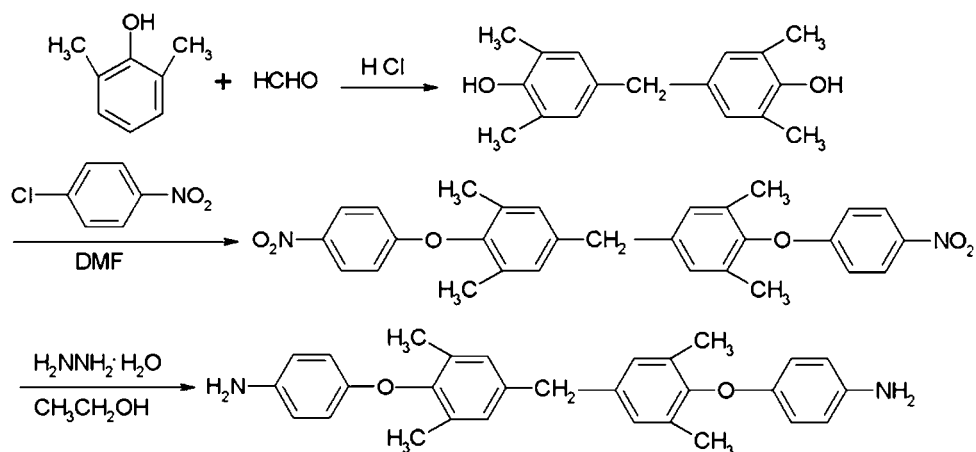
**Scheme 1** Synthesis route for BDAPM.

was used. NMP, *N,N*-dimethylformamide (DMF), DMAc, and *m*-cresol were purified by distillation under reduced pressure before they were used. The other chemical reagents (all from Shanghai Chemical Reagents Co., Shanghai, China) were used as received.

**Synthesis of BDAPM**

First, bis[3,5-dimethyl-4-phenol]methane (BDPM) was synthesized according to a literature method.[2] Then, in the presence of potassium carbonate (28.1 g, 0.2 mol) and DMF (300 mL), bis[3,5-dimethyl-4-(4-
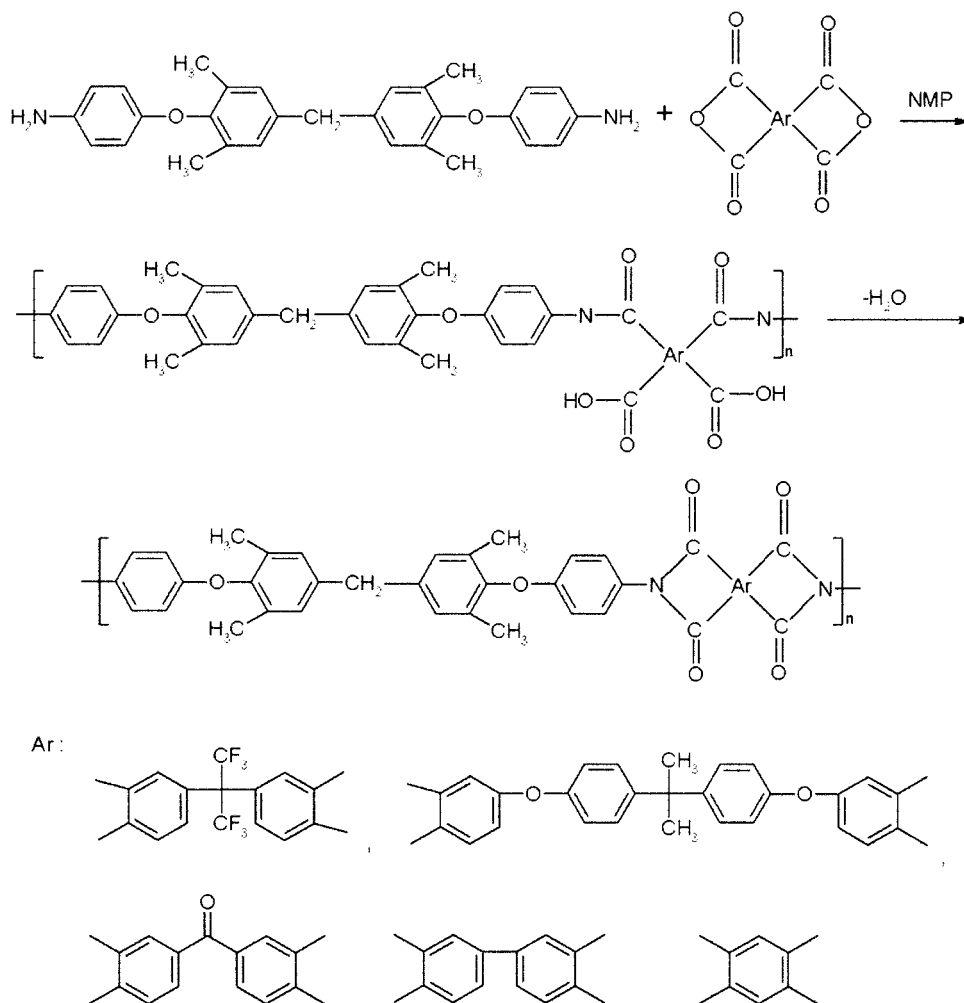


**Scheme 2** Synthesis scheme for the PIs.

nitrophenoxy)phenyl]methane (BDNPM) was synthesized by the reaction of BDPM (25.6 g, 0.1 mol) and *p*-chloronitrobenzene (31.5 g, 0.2 mol) at 150–160°C for 12 h. After it cooled to room temperature, the solution was poured into distilled water. A yellow powder was obtained by filtration and dried at 80°C. In the next stage, 50 mL of hydrazine monohydrate was added dropwise to a mixture containing 25.9 g (0.052 mol) of BDNPM, 3.1 g (0.02 mol) of ferric chloride, 0.3 g of 5% Pd/C, and 200 mL of anhydrous ethanol at 70°C. When the addition was completed, the reaction was continued subsequently at 80–90°C for another 14 h. Finally, the product was filtered and recrystallized with anhydrous ethanol. After the purification, yellow crystals (BDAPM) were obtained.

Yield: 67%. mp: 173–175°C. Fourier transform infrared (KBr, cm$^{-1}$): 3427.3, 3386.8, 3303.9, 3201.7 (N—H), 1380.6 (—CH$_3$), 1224.7 (C—O—C). $^1$H-NMR (dimethyl sulfoxide-$d_6$, δ, ppm): 3.79 (s, 2H), 4.70 (s, 4H), 6.43–6.51 (d, 8H), 6.98 (s, 4H), 2.02 (s, 12H). ANAL. Calcd for C$_{29}$H$_{30}$N$_2$O$_2$: C, 79.42%; H, 6.89%; N, 6.39%; Found: C, 79.06%; H, 6.88%; N, 6.32%.

Scheme 1 presents the synthesis route of BDAPM.

## Preparation of the PIs

The PIs were prepared by a conventional two-step polymerization method, as shown in Scheme 2, involving ring-opening polyaddition forming poly(amic acid) and subsequently thermal imidization. A typical polymerization procedure was as follows. Molar equivalents of diamine and dianhydride were dissolved in dried NMP with a 10% solid concentration under a nitrogen atmosphere at room temperature for 24 h; the solution was then spread on a glass plate, which was placed in an 80°C vacuum oven for 2 h to remove the solvent, and the film was heated sequentially from 80 to 280°C for about 8 h for imidization.

## Characterization

The structures of the PIs were confirmed by IR with a Nicolet Magna IR650 (Madison, WI) and by NMR with a Bruker 400 spectrometer. The thermal stabilities of the PIs were characterized by thermogravimetric analysis (TGA). TGA spectra were recorded on a TA Instruments SDT Q600 under a nitrogen purge and an air purge. The scanning rate was 20°C/min. Dynamic mechanical analysis, including static stress–strain measurements, was performed on a Mark V dynamic mechanical thermal analyzer. The run conditions were a frequency of 1 Hz and a heating rate of 3°C/min from −100 to 350°C in nitrogen. Elemental analysis was performed with a Leeman CE440 instrument. The dielectric constants of the PI films were tested with a Hioki 3532-50 impedance analysis instrument (Ueda, Nagano, Japan). The solubility of these PI films was
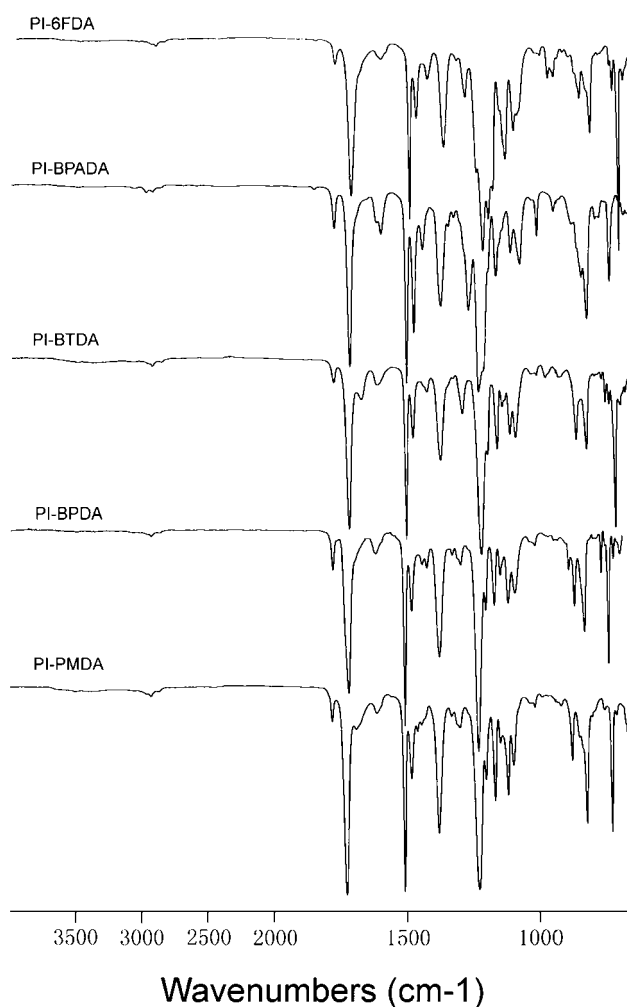


**Figure 1** IR reflectance spectra of the PI films.

determined by the observation of the soluble process of PI thin films of equal quality in different solvents at room temperature and at the reflux temperature for 24 h.

## RESULTS AND DISCUSSION

The PI synthesized from BDAPM and PMDA was designated PI-PMDA; that from BDAPM and BPDA was designated PI-BPDA. The rest were designated PI-BTDA, PI-6FDA, and PI-BPADA.

## IR and $^1$H-NMR spectra of the PIs

Figure 1 shows the IR reflectance spectra of the PI films. The absorption bands at about 1720 and 1780 cm$^{-1}$ represent the stretching of C=O in the imide groups, and those at about 1377 and 725 cm$^{-1}$ represent C—N stretching and C—N bending, respectively, in the imide groups as well. The imide groups are indicated to exist. Figure 2 shows the $^1$H-NMR spectrum of PI-BPDA as a representative example.
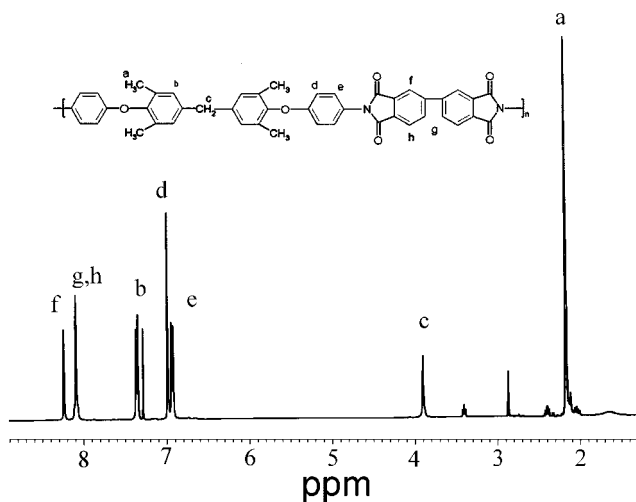
**Figure 2** $^1$H-NMR spectrum of PI-BPDA.

$^1$H-NMR (CDCl$_3$, δ, ppm): 3.90 (s, 2H), 7.35 (s, 4H), 6.99 (s, 4H), 6.93 (d, 4H), 8.09(s, 4H), 8.24 (d, 2H), 2.17 (s, 12H).

The successful synthesis of the PIs was proved.[2]

## Solubility

Table I contains the results of the solubility tests of the PI films. PI-BPADA and PI-6FDA, possessing flexible groups, exhibited excellent solubility after being heated and could be easily dissolved in some organic solvents, such as NMP, DMAc, DMF, dimethyl sulfoxide (DMSO), *m*-cresol, THF, and chloroform. On the contrary, PIs with PMDA containing a rigid phenyl group and BTDA containing a C=O group as dianhydride monomers did not show good solubility as before. PI-PMDA and PI-BTDA could hardly be dissolved in any solvent. However, the spatial symmetry of the PI structure was reduced for the distorted configuration of biphenyl groups and phenyl groups in the main chain. Therefore, PI-BPDA, containing rigid biphenyl groups, showed dramatically excellent solubility in most of the solvents and especially could dissolve in CHCl$_3$ without heating.

**TABLE I**
**Solubility of the PI Films**

| Sample | Solvent | | | | | | |
|---|---|---|---|---|---|---|---|
| | NMP | DMF | DMAc | DMSO | *m*-Cresol | THF | CHCl$_3$ |
| PI-6FDA | + | + | + | + | + | + | + |
| PI-BPADA | + | + | + | + | + | + | + |
| PI-BTDA | − | − | − | − | − | − | − |
| PI-BPDA | + | + | + | − | + | − | ++ |
| PI-PMDA | − | + | − | − | − | − | − |

++ = soluble in room temperature; + = soluble after heating; − = insoluble.

**TABLE II**
**Thermal Properties of the PI Films**

| Sample | $T_{d5}$ (°C)[a] | | Char yield (%) |
|---|---|---|---|
| | In air | In N$_2$ | |
| PI-6FDA | 471 | 473 | 47.64 |
| PI-BPADA | 482 | 473 | 43.35 |
| PI-BTDA | 457 | 461 | 66.78 |
| PI-BPDA | 477 | 468 | 51.56 |
| PI-PMDA | 463 | 469 | 55.09 |

[a] Temperature at 5% weight loss determined by TGA in nitrogen and in air at a heating rate of 20°C/min.
[b] At 800°C in nitrogen.

## Thermal and physical properties

Table II presents the data for the thermal properties of the PI films examined by TGA. The temperatures at 5% weight loss reached up to 461–473°C in nitrogen and 457–482°C in air. This indicated good heat resistance for the PI films. All the PIs gained a little weight in air at the very beginning. That may have been caused by the oxidation of the CH$_3$ group in the polymer chain; carbonyl (C=O) and hydroxyl (O—H) groups formed that made the weight increase.

Figure 3 presents the dynamic mechanical properties of the PI films. Typical behaviors of PIs were exhibited: the storage modulus was lost above the softening point. Below the softening point, the storage modulus of the PI films showed some consistency with conventional PIs in the numerical value. The glass-transition temperatures ($T_g$'s) of the PIs were found in the range of 211–300°C and are presented in Table III. PI-BPADA had the lowest $T_g$ because of the flexible groups. The rigidity increased with increasing intermolecular forces in the PI molecules. Therefore, PI-PMDA possessed the highest $T_g$. The $T_g$ values of the rest of the PI films were between them. As shown in the figure, the magnitude of tan δ at $T_g$ was a mea-
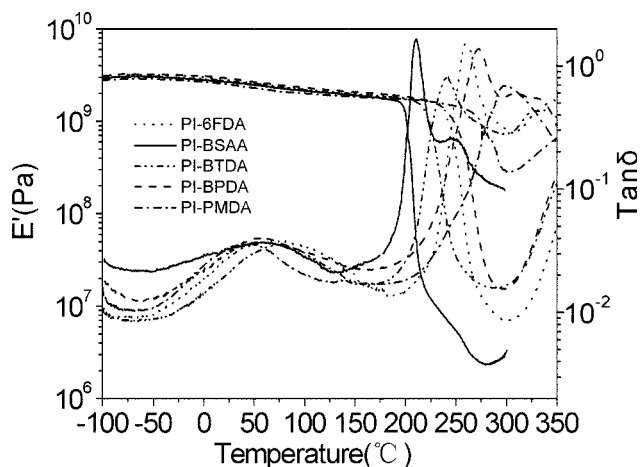


**Figure 3** Dynamic mechanical spectra of the PI films. $E'$ is the storage modulus.

**TABLE III**
**Dynamic Mechanical Analysis of the PI Films**

| Sample | α | | β | |
|---|---|---|---|---|
| | $T_g$ (°C) | Tan δ | $T_\beta$ (°C) | Tan δ |
| PI-6FDA | 259 | 1.53 | 76. 8 | 0.038 |
| PI-BPADA | 211 | 1.66 | 47.6 | 0.037 |
| PI-BTDA | 245 | 0.84 | 74.7 | 0.035 |
| PI-BPDA | 273 | 1.38 | 58.1 | 0.042 |
| PI-PMDA | 300 | 0.70 | 41.1 | 0.036 |

The dynamic mechanical thermal analysis data were collected at 3°C/min in nitrogen at 1 Hz. α, for the amorphous polymer, α relaxation is the glass transition; β, the beta relaxation, occurs below the $T_g$ and is associated with local band rotations and molecular segment motions along the polymer backbone, and the magnitude segments contributing to the relaxation; $T_\beta$, the peak value temperature of the β relaxation.

sure of the energy-damping characteristics for the materials and was related to the impact strength.[20,21] Table III shows that of all five thin films, PI-BPADA had the most excellent energy-damping characteristics. Below $T_g$, the β relaxation, associated with local bond rotations and molecular segment motions along the polymer backbone, was proportional to the concentration of segments.[21] In general, these motions were considered to be primarily a function of the type of diamine in the PI, and their presence and magnitude were ascribed to several material properties.[22] PI films with higher temperatures and lower tan δ values possessed higher energy barriers for molecular motion.

The tensile properties of the PI films are summarized in Figure 4. The Young's modulus depended on the structure of the PI films, and with increasing yield stress, the Young's modulus increased. PI-BTDA exhibited the highest Young's modulus and yield
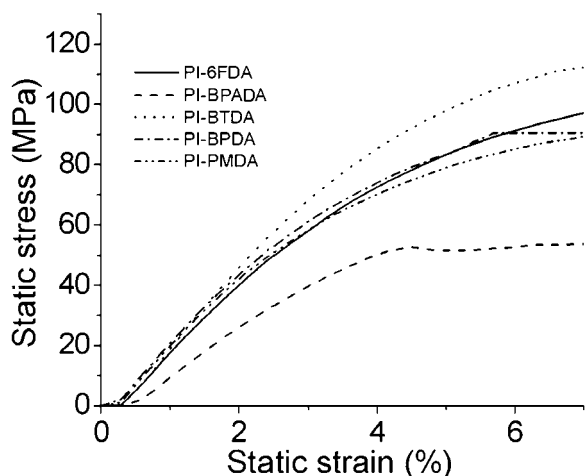


**Figure 4** Static stress–strain curves of the PI films at room temperature.
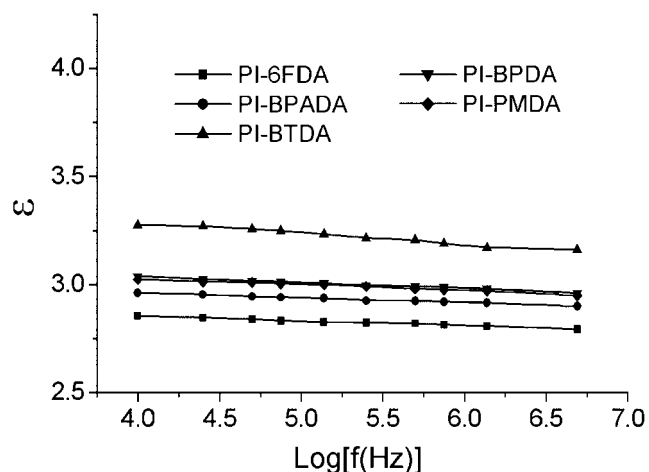


**Figure 5** Relationship between the dielectric constant (ε) and frequency (f) for the PI films at 25°C.

stress, whereas PI-BPADA, possessing flexible groups, presented the lowest Young's modulus and proved to be a thermoplastic material, showing an obvious yield point. The Young's moduli of the rest of the PI films were between those of PI-BTDA and PI-BPADA, and this showed that their intermolecular forces were between them. These results can also be explained by the assumption of crosslinking of PI-BTDA.

**Dielectric properties**

The dielectric constants of the PI films (with aluminum as the bottom and top electrodes) were tested at different frequencies at 25°C. The dielectric waste was controlled in a small range. The dielectric constants of all the PI films were stably reduced with increasing frequency. The PI-BTDA film possessed the highest dielectric constants because of the existence of C=O groups, whereas PI-6FDA had the lowest dielectric constants because of the presence of fluoride groups. The observed nature of the dielectric constants was due to the inability of the dipoles to orient in a rapidly varying electric field.[23] Figure 5 shows that the results depended on the quantity and polarity of the groups in the PI chains.

**CONCLUSIONS**

PI films were prepared with BDAPM as a diamine monomer. Some of the PI films, especially PI-BPADA, PI-6FDA, and PI-BPDA, had high solubility in common organic solvents. The $T_g$ values of the PIs were between 211 and 300°C, and the initial thermal decomposition temperatures reached up to 457–482°C in air and 461–473°C in nitrogen. The films showed strong and tough tensile properties. The dielectric constants of the PI films were in the range of 2.8–3.3 at 25°C.

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