

Nonfluorinated Copolymerized Polyimide Thin Films with Ultralow Dielectric Constants

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ABSTRACT: A series of copolymerized polyimide (PI) thin films with low dielectric constants were prepared with different molar ratio of bis[3,5-dimethyl-4-(4-aminophenoxy)phenyl]methane and 9,9-bis[4-(4-aminophenoxy)phenyl]fluorene as diamines and 4,4'-(4,4'-isopropylidenediphenoxy)bis(phthalic anhydride) as a dianhydride. Some films possessed good dielectric properties with an ultralow dielectric constant of 2.3 at 1 MHz. The structures and properties of the thin films were measured with Fourier transform infrared and NMR spectroscopy, thermogravimetric analysis, and dynamic

mechanical analysis. The PI films exhibited glass-transition temperatures in the range 223–243°C and possessed initial thermal decomposition temperatures reaching up to 475–486°C in air and 464–477°C in nitrogen. All of the PI films exhibited excellent solubility in organic solvents. The mechanical properties of these films were also examined. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 110: 1515–1519, 2008

Key words: copolymerization; dielectric properties; films; polyimides

INTRODUCTION

Polyimides (PIs), as high-performance polymers, have received more and more attention from academic and industrial research groups.¹ Particularly, low-dielectric-constant PIs have gradually become a focal point for excellent thermal stability and good mechanical properties in the microelectronics, aerospace, electrical insulation, and semiconductor industries (e.g., replacing silicon dioxide with dielectric constant (κ) = 3.9–4.2 as the interlevel dielectric in integrated circuit productions).^{2,3} Usually, the dielectric constants of most nonfluorinated PIs are in the range 2.9–3.5. Several approaches have been used to reduce the dielectric constants.⁶ The introduction of fluorinate groups could obviously decrease the dielectric constant, ranging from 2.5 to 3.2. Hsiao and Chang⁷ indicated that PIs with trifluoromethyl possessed good dielectric properties. However, their dielectric constants were still not low enough for application in developing microelectronics industry. Although nanoporous PI is another significant kind of PI with a low dielectric constant, its mechanical properties do not seem good enough. Wang et al.⁸ claimed that they had already synthesized another kind of nanoporous PI with a low dielectric constant. By 2003, Kohei et al.⁹ noted that a diamine or dianhydride monomer with a fluorene group could be used to reduce the dielectric con-

stants of PIs. Recently, PIs based on bis[3,5-dimethyl-4-(4-aminophenoxy)phenyl]methane (BDAPM) were prepared with dielectric constants ranging from 2.8 to 3.3.⁴

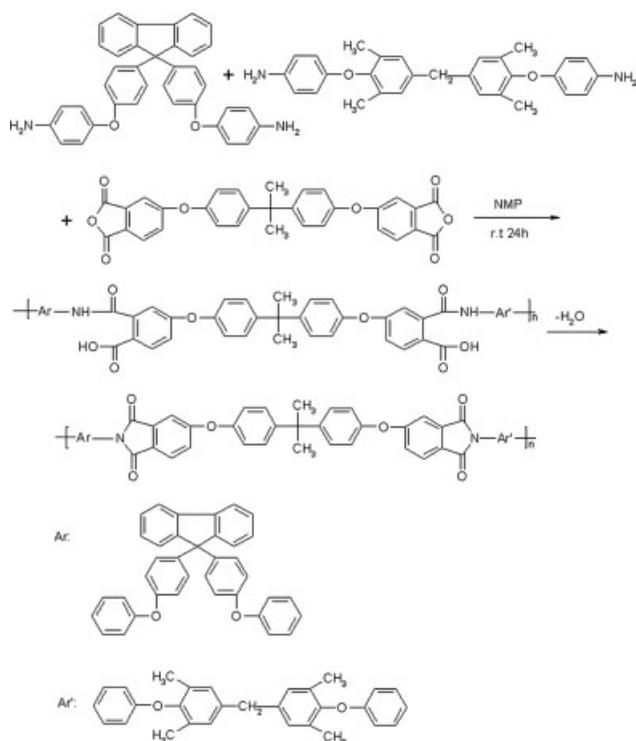
In this article, we report on a series of copolymerized PI thin films with ultralow dielectric constants and good mechanical properties. A series of novel PI thin films were synthesized with 9,9-bis[4-(4-aminophenoxy)phenyl] fluorene (BAOFL) and BDAPM in different molar ratios as diamines and 4,4'-(4,4'-isopropylidenediphenoxy)bis(phthalic anhydride) (BDAPA) as a dianhydride. The dielectric properties, mechanical properties, thermal stabilities, and solubility of the PI films were also examined.

EXPERIMENTAL

Materials

2,6-Dimethylphenol, 9,9-bis(4-hydroxyphenyl) fluorene, *p*-chloronitrobenzene, anhydrous potassium carbonate, hydrazine monohydrate, and 5% palladium on activated carbon (5% Pd/C) (Sinopharm Chemical Reagents Co., Ltd., Shanghai, China) were used as received. BPADA (Shanghai, China) were recrystallized from acetic anhydride and dried *in vacuo*. 1-Methyl-2-pyrrolidinone (NMP), *N,N*-dimethylformamide (DMF), *N,N*-dimethylacetamide (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.

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Scheme 1 Synthesis scheme of the PIs.

Preparation of the PIs

In a previous article, we proposed a processing method of PIs with low dielectric constants on the basis of BDAPM from the literature.⁴ According to literature,⁵ the other diamine monomer, BAOFL, was used to prepared thermally stable PIs with low dielectric constants. With different molar ratios (1 : 1–1 : 4) of diamine monomers and BPADA as a dianhydride, the PIs were prepared by a conventional two-step polymerization method, as shown in Scheme 1. 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 240°C for about 8 h for imidization.

Characterization

The structures of the PIs were confirmed by IR with a Nicolet Magna IR650 instrument (Madison, WI) and by NMR with a Bruker 300 spectrometer (Karlsruhe, Germany), whereas differential scanning calorimetry (DSC) measurements were deduced from a TA Instruments Q20 instrument (New Castle, DE) under a nitrogen purge at a heating rate of 10°C/min from 30 to 350°C. The thermal stabilities of PIs were recorded on a TA Instruments SDT Q600 instrument (New Castle, DE) under a nitrogen purge

and an air purge. The scanning rate was 20°C/min. Dynamic mechanical analysis 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 300°C in nitrogen. The low κ values were tested with a Hioki 3532-50 impedance analysis instrument (Hioki E. E. Corp., Nagano, Japan) with the films plated with aluminum on both surfaces at 25°C. The solubility of these PI films was determined by the observation of the soluble process of the PI thin films in different solvents at room temperature and at the reflux temperature for 24 h. The three-dimensional (3D) structures of the chain segment were determined with Chem 3D software (Cambridge, MA).

RESULTS AND DISCUSSION

The PI synthesized from BDAPM and BAOFL with a molar ratio of 1:1 was designated PI-1; that with a molar ratio of 2:1 was designated PI-2. The rest were designated PI-3 and PI-4, and the PI synthesized from BDAPM and BPADA was designated PI-5.

IR and ¹H-NMR spectra of the PIs

Figure 1 shows the IR reflectance spectra of the PI films. As a representative example, from the IR reflectance spectra of PI-2, the absorption bands at about 1720 and 1780 cm⁻¹ represented the stretching of C=O in the imide groups, and those at about

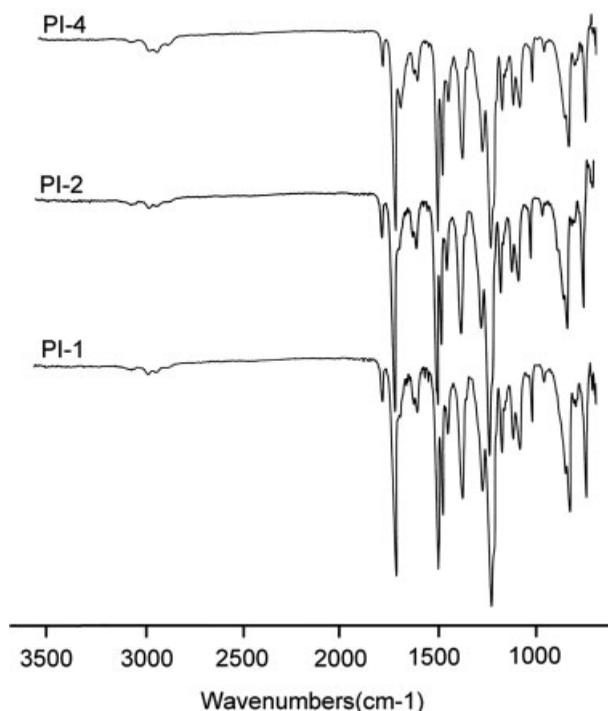


Figure 1 IR reflectance spectra of the PI films.

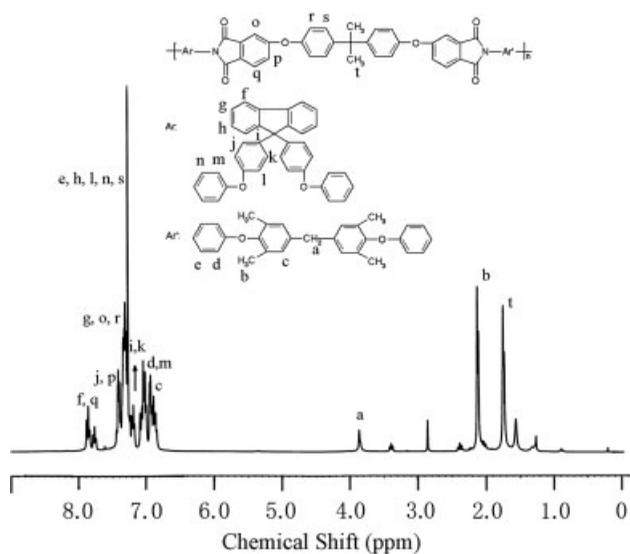


Figure 2 $^1\text{H-NMR}$ spectrum of PI-2.

1377 and 725 cm^{-1} represented the C—N stretching and C—N bending, respectively, in the imide groups as well. This indicated the existence of the imide groups. There were no obvious absorption bands of —OH between 3000 and 3500 cm^{-1} , which proved that the PI precursors were almost fully imided.

Meanwhile, Figure 2 shows the $^1\text{H-NMR}$ spectrum of PI-2.

PI-2 $^1\text{H-NMR}$ (300 MHz, CDCl_3 , δ , ppm): 1.74 (s, 18H), 2.11 (s, 24H), 3.86 (s, 4H), 6.87 (d, 8H), 6.99 (d, 12H), 7.19 (d, 4H), 7.30 (s, 30H), 7.32–7.38 (d, 20H), 7.44 (d, 8H), 7.80–7.91 (d, 8H).

The successful synthesis of the PIs was thus proven.

Dielectric properties

The dielectric constants of the PI films were tested at different frequencies from 1 kHz to 1 MHz at 25°C . The dielectric loss tangent value was controlled in a small range from 0.001 to 0.009. Figure 3(a) presents the relationship between the dielectric constant and frequency. The dielectric constants of all of the PI films were stably reduced with increasing frequency. As shown in Figure 3(b), it was obvious that with increasing content of BAOFL, the dielectric constants of these films first decreased gradually and then stably gained enhancement at 1 MHz. The PI films PI-3 and PI-2 exhibited the lowest dielectric constant values at about 2.3. The change in the free volume of the polymer molecular chains was the main reason for the alteration of the dielectric constants. With

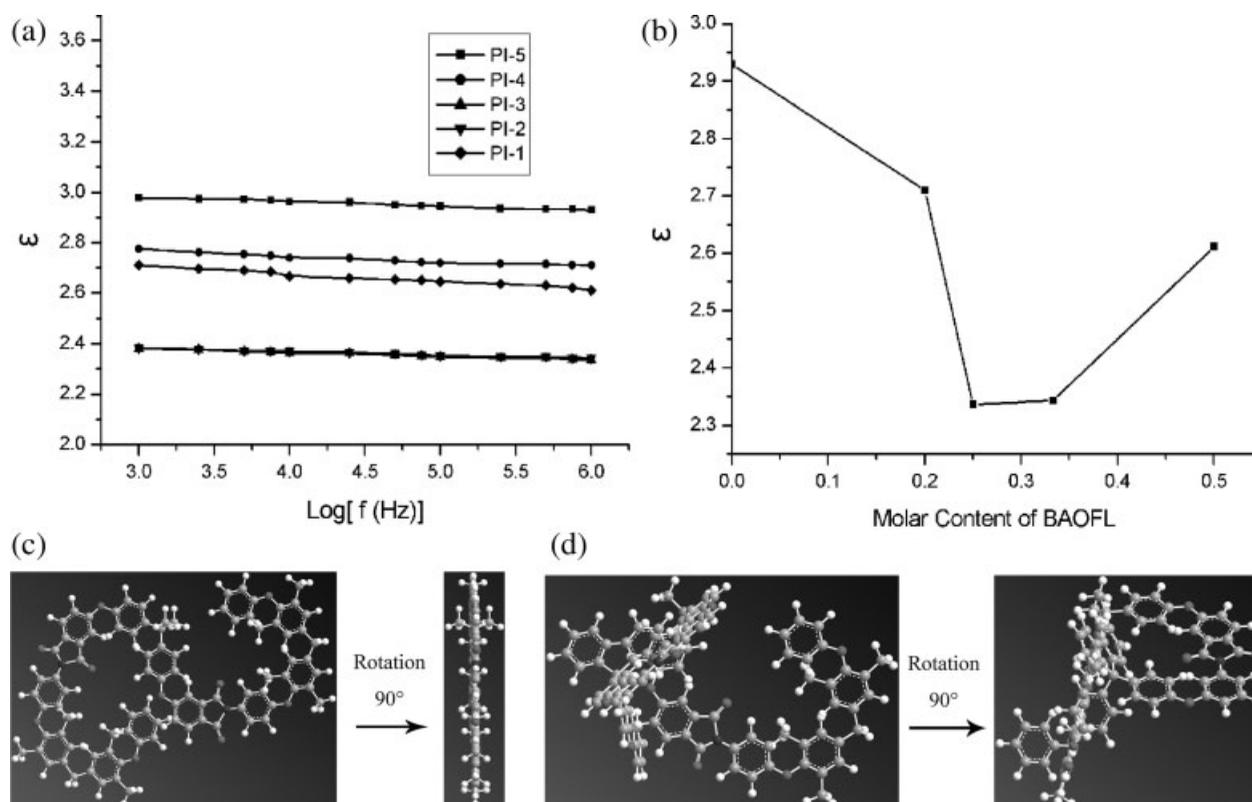


Figure 3 (a) Relationship between the dielectric constant (ϵ) and frequency (f) for the PI films at 25°C . (b) Relationship between ϵ and molar content of BAOFL for the PI films at 25°C . (c) 3D structures of the chain segment for PI-5. (d) 3D structures of the chain segment for PIs with fluorene groups.

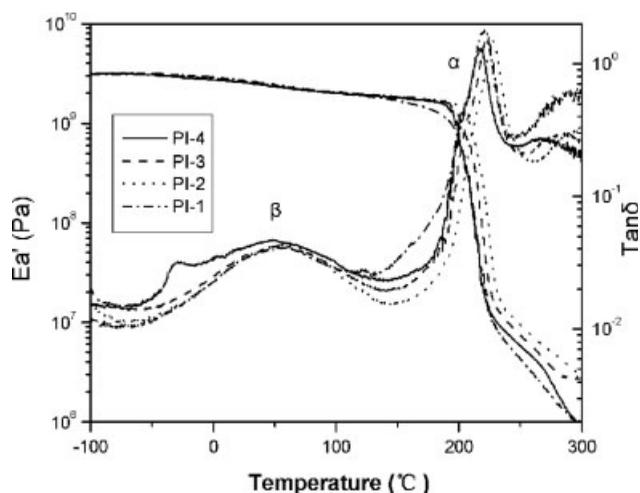


Figure 4 Dynamic mechanical spectra of the PI films (E'_a = storage modulus).

increasing free volume, the dielectric constants decreased. On the contrary, the decreasing free volume led to the enhancement of the dielectric constants.^{10–13}

Figure 3(c,d) shows the 3D structures of the chain segment for PI-5 and PIs with fluorene groups. It was clear that the configuration of PI-5 without fluorene groups was in a plane. The distance between the PI chains was short, whereas PIs with fluorene groups contained the distorted configuration. In addition, the distance between the PI chains increased, especially between the layers. The dielectric constants decreased for the free volume of polymer molecular chains enhanced by the induction of fluorene groups. However, with increasing fluorene groups between the layers, the free volume of the chains decreased. So the dielectric constants grew bigger.^{14,15} Obviously, the results were in accord with the experimental data.

Mechanical and thermal properties

Figure 4 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 was consistent with conventional PIs. The glass-transition temperatures (T_g 's) of the PIs were found in the range 217–227°C. The T_g 's improved because of the increase in rigid fluorene groups. However, the T_g of PI-1 decreased as the polymerization degree of PI-1 decreased. The magnitude of $\tan \delta$ at T_g was a measure of the energy-damping characteristics for the materials and was related to the impact strength. PI-3, possessing the lowest dielectric constants, 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. In general, local bond rotations of the fluorene groups were considered to be the primary reason, and with their presence, PI films at higher temperatures and with lower $\tan \delta$ values possessed higher energy barriers for molecular motion.

Table I contains the data for the thermal properties of the PI films examined by DSC and SDT. The temperatures at 5% weight loss showed values reaching up to 464–477°C in nitrogen and 475–486°C in air. This showed that the PI films containing rigid fluorene groups possessed good thermostability. The static T_g 's were in the range 223–243°C, which was a bit higher than the dynamic T_g 's mentioned previously. In the same way, with the increasing of the rigid fluorene groups, PI-2 possessed the highest static T_g .¹⁶ Also, there were various factors, such as the shape and the way of piling, that could have led to the irregular char yield results in nitrogen.¹⁷

Solubility

All of the PI films exhibited excellent solubility after they were heated and were easily dissolved in common organic solvents, such as NMP, DMAc, DMF, dimethyl sulfoxide (DMSO), *m*-cresol, and tetrahydrofuran, and were easily dissolved in chloroform without heating. This resulted in the presence of the fluorene groups. With increasing fluorene groups, the spatial symmetry of the PI structure was reduced for the distorted configuration of biphenyl groups and phenyl groups in the main chain. Meanwhile, BDAPA, as a dianhydride monomer, inserted flexible groups into the main chain and reduced the packing force.^{18,19} Therefore, the PI films, containing rigid biphenyl groups, showed dramatically excellent solubility in the common solvents. Table II shows the solubility of the PI films.

TABLE I
Thermal Properties of PI Films

Sample	T_g (°C) ^a	T_{d5} (°C) ^b		Char yield (%) ^c
		In air	In N ₂	
PI-1	235	479	471	44.3
PI-2	243	486	477	47.7
PI-3	235	484	469	44.3
PI-4	230	475	464	50.0
PI-5	223	482	473	45.1

^a T_g as determined by DSC in nitrogen at a heating rate of 10°C/min.

^b Temperature at 5% weight loss as determined by thermogravimetric analysis in nitrogen and in air at a heating rate of 20°C/min.

^c Char yield at 700°C in nitrogen.

TABLE II
Solubility of the PI Films

Sample	Solvent						
	NMP	DMF	DMAc	DMSO	<i>m</i> -Cresol	Tetrahydrofuran	CHCl ₃
PI-1	+	+	+	+	+	+	++
PI-2	+	+	+	+	+	+	++
PI-3	+	+	+	+	+	+	++
PI-4	+	+	+	+	+	+	+
PI-5	+	+	+	+	+	+	+

++, soluble in room temperature in 24 h; +, soluble after heating.

CONCLUSIONS

In summary, nonfluorinated ultralow-dielectric-constant copolymerized PI thin films were prepared. The ultralow dielectric constant ($\kappa_{1\text{MHz}} = 2.3$) of the films, required for the applications mentioned in the Introduction, is the most important property we want to stress. These films had good mechanical properties under the T_g . Moreover, all of the films possessed good thermal stabilities and excellent solubilities in common organic solvents (e.g., NMP, DMF, DMAc, DMSO, chloroform).

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