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Preparation and Properties of Cyano-Containing Polyimide Films Based on 2,6-Bis(4-aminophenoxy)-benzonitrile

Baoping Lin (✉) and Xiaohui Xu

Department of Chemistry and Chemical Engineering, Southeast University, Nanjing 210096,
P. R. China
E-mail: lbp@seu.edu.cn; Fax: (0086) 25-83793171

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Summary

A series of cyano-containing polyimides were synthesized from 2,6-bis(4-aminophenoxy)benzonitrile and some aromatic dianhydride monomers by solution polycondensation. The poly(amic acid) films could be obtained by solution-cast from *N*-methyl-2-pyrrolidinone solutions and thermally converted into tough polyimide films. Structure and physical properties of thin films of those polyimides were measured by FTIR, TGA, dynamic mechanical analysis and LCR hitester et al. Results showed that the polyimides prepared from 2,6-bis(4-aminophenoxy)-benzonitrile and 2,2-bis[4-(3,4-dicarboxyphenoxy)phenyl]propane dianhydride or 4,4'-(hexafluoropropylidene)diphthalic anhydride exhibited more excellent energy-damping characteristic and excellent solubility in NMP, DMF, DMAc, DMSO, THF and $CHCl_3$, whereas the polyimides from 2,6-bis(4-aminophenoxy)benzonitrile and 3,3',4,4'-biphenyltetracarboxylic dianhydride or Pyromellitic dianhydride were insoluble in polar and nonpolar organic solvents. All polyimides indicated higher glass transition temperatures, excellent thermal stability and tensile properties. Incorporating a nitrile group into the polyimide backbone would enhance the dielectric constant of the polyimide films.

Introduction

Aromotic polyimides possess marked thermal stability, and excellent mechanical, electrical and solvent resistance properties. Therefore they can be widely used in the microelectronic industry. Of utmost importance for these applications is that the polyimides have a low dielectric constant [1-3]. With the rapid development of advanced IT technology, the conventional polyimides cannot completely meet the requirements of fine function and further miniaturization of electronic devices. In order to meet these requirements, raising the dielectric constant of polyimides is very necessary [4].

From the point of view of molecular design, introducing strong polar groups or chains into the molecular structure of polyimides can improve its dielectric constant. Owing to the high molar polarization and low molecular volume of the cyano group, that it is introduced into the molecular chain of polyimides appears to be a reasonable selection increasing the dielectric constant of polyimides. In addition, the cyano group at the molecular chain serves as a potential site for crosslinking reaction and can make polymer transform from thermoplastic to thermosetting, which enhances the thermal stability of the polymer [5-9]. Kakimoto et al [4] used 4-[bis(4-aminophenyl)amino]-benzonitrile and 4-[4-(1-cyanopropoxy)phenyl]-2,6-bis-(4-aminophenyl)pyridine as diamine monomers and synthesized a series of novel polyimides with pendant cyano groups on the side chain. The incorporation of cyano groups into macromolecular chain leads to an enhanced thermo-oxidative stability, solubility and dielectric constant when compared with no cyano-containing polymers of analogous structures. Among cyano-containing polyimides, not much work has been done using 2,6-bis(4-aminophenoxy)benzonitrile (APBN) for preparing polyimides. In this article, a series of cyano-containing polyimide films were prepared by APBN reacting with aromatic dianhydride monomers, respectively. The structures, the thermal properties, dynamic mechanical properties, and dielectric properties were investigated.

Experimental

Materials

High purity 2,6-dichlorobenzonitrile (DCBN) and 4-Aminophenol was used as received. 2,2-Bis[4-(3,4-dicarboxyphenoxy)phenyl]propane dianhydride (BPADA), 3,3',4,4'-biphenyl-tetracarboxylic dianhydride (BPDA), benzophenone-3,3',4,4'-tetracarboxylic dianhydride (BTDA) and 4,4'-(hexafluoropropylidene)diphthalic anhydride (6FDA) were recrystallized from acetic anhydride and dried under a vacuum respectively. Pyromellitic dianhydride (PMDA) was purified by sublimation before use. *N*-methyl-2-pyrrolidone (NMP) was purified by distillation under ambient pressure from P_2O_5 prior to use. The rest chemical reagents (all from Shanghai Chemical Reagents Company) were used without further purification.

Synthesis of APBN

APBN was synthesized according to the method of literature [5,6]. 4-Aminophenol (0.2 mol), powdered anhydrous K_2CO_3 (0.15 mol), NMP (150 ml), and toluene (130 ml) were charged into a four-necked flask equipped with a condenser, nitrogen inlet, a thermometer, a Dean-Stark trap and a mechanical stirrer. The reaction mixture was stirred under the purge of N_2 and heated to reflux (about 135°C) and water was removed by azeotropic distillation with toluene. Then, a solution of 2,6-dichlorobenzonitrile (0.1 mol) in NMP (80 ml) was added to the reaction mixture dropwisely. After complete dehydration, the toluene was removed and the temperature was increased to about 195°C for 5 h. After cooling to 60°C, the reaction mixture was poured into ice water. The precipitate was filtered and dried at 100°C *in vacuo*. The precipitate was recrystallized from 1:1 (by volume) toluene/ethanol mixing solvent to obtain tan solid. Yield: 55%, melting temperature: 212-213°C. FTIR (cm^{-1}, KBr): 3468, 3409, 3364, 3335 (NH_2), 2220 (C≡N) and 1250 (C–O–C). ^1H NMR (DMSO-d_6): δ = 5.15 ppm (s, 4H, NH_2), δ = 6.64 ppm due to aromatic proton ortho to amine, 6.88 ppm aromatic proton meta to amine, 6.31 ppm aromatic proton meta to nitrile, 7.38 ppm aromatic proton para to nitrile.

Analysis calculated for $C_{19}H_{15}N_3O_2$: C, 71.92%; H, 4.73%; N, 13.24%. Found: C, 71.90%; H, 4.84%; N, 12.8%.

Preparation of polyimides

The polyimides were synthesized by mixing an equivalence of relevant APBN and an aromatic dianhydride at room temperature in NMP solvent, reacting for 24 h. After reaction, the solution was clarified and coated on glass substrates. When the coats were gently baked at 60°C *in vacuo* for 4 h, with most of the solvent withdrawn, gel films were formed. To evacuate the NMP remaining in the films, polyamic acid gel films were treated at 100°C, 150°C, 200°C and 250°C *in vacuo* for 1.5 h respectively. Finally, the imidization of polyamic acid thin films was performed at 280°C for 0.5 h. The preparation process is described in Figure 1.

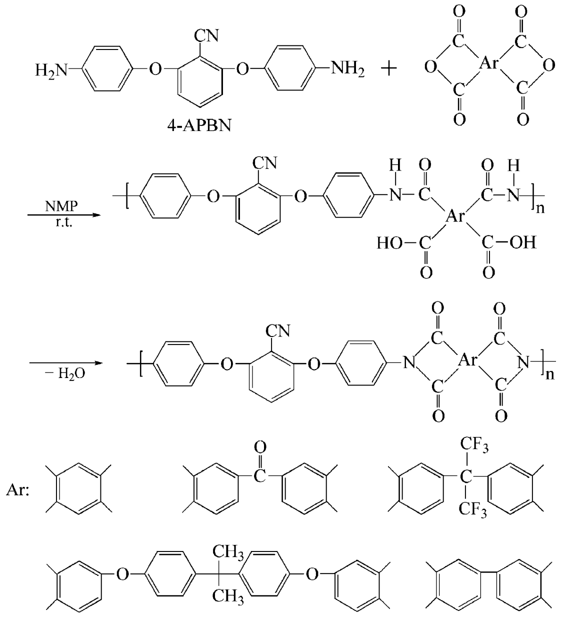

Figure 1. Synthesis scheme of the polyimides

Characterization

The structures of the polyimides were confirmed by Fourier Transform Infrared (FTIR, Nicolet Magna IR650). ^{1}H NMR spectrum was obtained using a Bruker 400 spectrometer operating at 400 MHz. Elemental analyses was made on a Leeman CE440 instrument. The solubility of these polyimides was determined by observing the solubility of the polyimides in several solvents at reflux temperature for 24 h. The thermal stabilities of polyimides were characterized by thermogravimetric analysis (TGA). The TGA spectra were recorded on a TA instruments SDT Q600, under a nitrogen purge or an air purge. The scanning rate was 20°C/min. Dynamic mechanical analysis was performed on a Rheometric Scientific Mark V, Dynamic Mechanical Thermal Analyzer (DMTA). The run conditions were conducted at a frequency of 1Hz and a heating rate of 3°C/ min from –100°C to 350°C in air. Static strain-stress measurements were carried out on polyimide films using strips of the polyimide thin films 20 mm long and 2 mm wide with a Rheometric Scientific Mark V, DMTA. The dielectric constant of the polyimide films were measured in a parallel plate configuration using a Hioki 3532-50 LCR hitester in the range of 10 kHz ~ 5 MHz at 25°C.

Results and discussion

The polyimide synthesized from APBN and BPADA was designated as BPADA-PI. That from APBN and BPDA was designated as BPDA-PI. The rest were designated as BTDA-PI, 6FDA-PI and PMDA-PI respectively.

The ATR-FTIR spectra of polyimide films are shown in Figure 2. The structure of polyimides was illustrated with the IR spectrum of PMDA-PI. The characteristic absorption at 1855 cm^{-1} and 1770 $cm^{-1}$of C=O stretching in aromatic dianhydride monomer and the absorption of O—H in the range of 3100 – 3400 cm^{-1} disappeared, and that the characteristic absorption at 1716 cm^{-1} and 1774 $cm^{-1}$of C=O stretching in imide groups was observed. The absorption of C—N stretching at 1375 cm^{-1} and C—N bending at 737 cm^{-1}, respectively, in imide groups was also observed. The absorption at 1246 cm^{-1} was based on the aromatic ether —O— in PMDA-PI. The characteristic C≡N absorption appeared at 2231 cm^{-1}. The observation of these absorption bands clearly indicated the existence of imide groups and cyano groups, and confirmed the successful synthesis of cyano-containing polyimides.

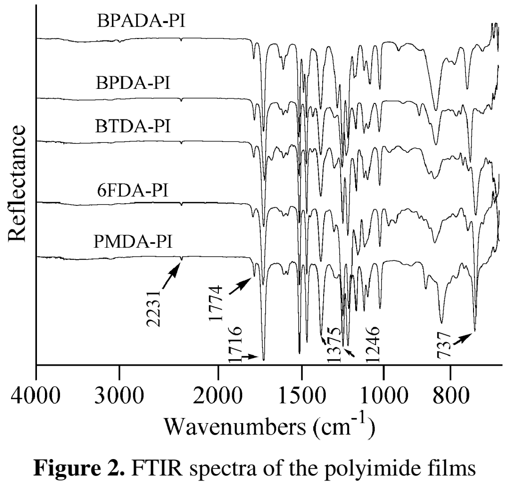

Figure 2. FTIR spectra of the polyimide films

Generally, conventional polyimides are insoluble in many organic solvents [10]. Table 1 lists the solubility behavior of the polyimides prepared from APBN and some aromatic dianhydride monomers in several organic solvents. It was observed that the polyimides prepared from APBN and BPADA or 6FDA were soluble in the test solvents including NMP, *N*,*N*-dimethylformamide (DMF), *N*,*N*-dimethylacetamide

(DMAc), dimethyl sulfoxide (DMSO), tetrahydrofuran (THF) and chloroform ($CHCl_3$). The good solubility was possibly owing to the structural modification through the incorporation of the flexible isopropylidene, hexafluoroisopropylidene, arylene ether groups and cyano groups. The polyimides derived from APBN and BPDA or PMDA showed poor solubility due to the increase of rigidity of the polyimide molecular chains. Furthermore, the polyimide from APBN and BTDA was only soluble in NMP and DMSO. The results clearly showed that introducing flexible groups into the backbone of a polyimide to reduce intermolecular interaction, the solubility of the polyimides could be modified efficiently.

Table 1. Solubility of the polyimide films in several of solvents

Sample code	NMP	DMF	DMAc	DMSO	THF	$CHCl_3$
BPADA-PI	+	+	+	+	+	+
BPDA-PI	-	-	-	-	-	-
BTDA-PI	+	-	-	+	-	-
6FDA-PI	+	+	+	+	+	+
PMDA-PI	-	-	-	-	-	-

+: soluble; -: insoluble.

Table 2. TGA data summary of the polyimide films

Sample code	T_{d1}, N_2 (°C) [1]	T_{d10}, N_2 (°C) [2]	T_{d1}, air (°C)	T_{d10}, air (°C)
BPADA-PI	498	534	473	541
BPDA-PI	491	567	414	571
BTDA-PI	501	562	446	573
6FDA-PI	491	553	414	571
PMDA-PI	493	567	423	563

1 Temperature at 1% weight loss (T_{d1}) determined by TGA in nitrogen or in air at a heating rate of 20°C/min

2 Temperature at 10% weight loss (T_{d10}) determined by TGA in nitrogen or in air at a heating rate of 20°C/min

The thermal stabilities of polyimides were characterized by TGA measurement. The temperatures at 1% weight loss (T_{d1}) and 10% weight loss (T_{d10}) of the polyimides are summarized in Table 2. The 1% weight losses ranged from 414 to 501°C, and the 10% weight losses were in the range of 534 to 573°C. BPADA-PI polyimide exhibited higher degradation rate whether in nitrogen atmosphere or in air. The low thermal stability of BPADA-PI polyimide film was due to the C-C and C-H bonds in the aliphatic portion of the polyimide molecular chain, which were known to possess lower bond dissociation energy than the aromatic C-C and C-H bonds. It was also interesting to find that the polyimides derived from APBN showed an initial weight gain during thermal gravimetric analysis. All polyimide films presented an initial weight gain, which was probably due to oxidation of methyl groups in the polyimides to carbonyl and hydroxyl groups easily or gas adsorption on the surface of the polyimide films. The decomposition temperature of all polyimide films at 1% weight losses was lower in air than in nitrogen. However, the polyimide films derived from APBN with BPADA, BPDA, BTDA and 6FDA respectively had a slightly higher decomposition temperature at 10% weight losses in air than in nitrogen. This phenomenon was similar to other cyano-containing polymers. It indicated that the decomposition pathway was not a thermo-oxidative process, and cyclization of nitrile groups might occur in the initial decomposition stages of cyano-containing polyimides [7].

Dynamic viscoelastic spectra of the polyimide films measured with DMTA are shown in figure 3. The glass transition temperatures (T_g) and dynamic viscoelastic properties of the polyimide films are tabulated in Table 3. Tg of the polyimide films were clearly observed and ranged from 213 – 328°C. The polyimide obtained from APBN and BPADA exhibited the lowest glass transition temperature due to the incorporation of the flexible isopropylidene into the main chain of the polyimide. The rigidity increase in the polyimide main chain would make the region of glass transition of the polyimide films become wider gradually. This phenomenon bore an analogy to that induced by the enhancement of crosslink degree in the crosslink polymers. The magnitude of the storage modulus of all polyimide films was consistent with that of conventional polyimides before glass transition. The magnitude of tan δ at T_g is a measure of the energy-damping characteristic of a material, and is related with the impact strength of a material [11,12]. The flexibility of the polymers increases with the addition of tan δ value at T_g. The results indicated that the introduction of the flexible groups into the main chain of the polyimide would lead to the increase of the polyimide flexibility.

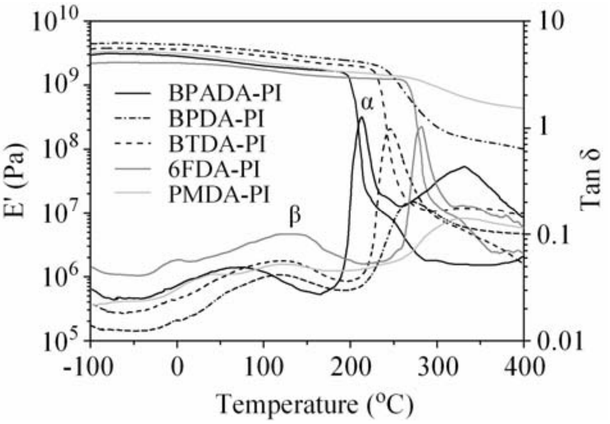

Figure 3. Dynamic viscoelastic spectra of the polyimide films

Table 3. Viscoelastic properties of the polyimide films

Sample code	T_g (°C)	Tanδ (α)	$T_β$ (°C)	Tanδ (β)
BPADA-PI	213	1.3928	64	0.0494
BPDA-PI	271	0.2033	117	0.0420
BTDA-PI	245	1.0087	121	0.0573
6FDA-PI	280	1.2126	130	0.1011
PMDA-PI	328	0.1419	118	0.0528

The beta relaxation, β, occurs below the T_g and is associated with local bond rotations and molecular segment motions along the polymer backbone, and the magnitude of this relaxation is proportional to the concentration of segments contributing to the relaxation. In general, these motions are considered to be primarily a function of the type of dianhydride in the polyimide, and their presence and magnitude have been ascribed to several material properties. In our experiments, β transition temperature (T_β) and tanδ value at T_β varied with the polyimide structure. Fluorine-containing polyimide exhibited the highest β transition temperature (T_β) and tanδ value at T_β. Hence, increasing of the number of 6FDA-PI polyimide segments in motion was evident from the increase of tan δ at β transition as comparing with other polyimides, which indicated that a lower energy barrier in 6FDA-PI polyimide existed for chain segment motions.

The micromechanical characterization of the polyimide films showed that Young's modulus values of the polyimide films were different with varying of the structure (Figure 4). Young's modulus values of the polyimide films ranged from 2.12 – 3.33 MPa. Varying tendency of yield stress was consistent with that of Young's modulus. The polyimide film prepared from APBN and BPDA possessed the highest Young's modulus and yield stress, whereas BPADA-PI polyimide films containing flexible groups presented lower Young's modulus. The polyimide film from APBN and PMDA did not exhibited the highest Young's modulus and yield stress, which might be ascribed to that the intermolecular forces in PMDA-PI polyimide film was lower than that of BPDA-PI and BTDA-PI polyimide films.

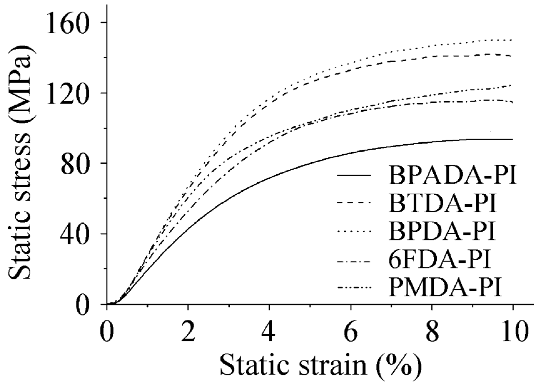

Figure 4. Static stress-strain curves of the polyimide films

The dependence of dielectric constants (ε) of the polyimide films (using aluminum as bottom and top electrodes) on the frequency is shown in Figure 5. It was seen that the dielectric constants decreased with the increase of frequency for all polyimide films. The observed nature of the dielectric constants was due to the inability of the dipoles to orientate in a rapidly varying electric field [13]. Among these polymers, polyimide derived from PMDA exhibited rather high dielectric constant, whereas in contrast, sample from BPADA showed lower values. These results were related with the number and polarization properties of polarity groups in the polyimides.

In comparison with the conventional polyimides, the polyimides with nitrile groups exhibited higher dielectric constant. The increase of their dielectric constant was due to the high molar polarization (P_M = 11.0 cm^3 mol^{-1}) and low molar-specific volume (V_M = 19.5 cm^3 mol^{-1}) of the –CN group [4]. This implied that the introduction of the nitrile group into the polyimide structure would make a large contribution toward increasing dielectric constant.

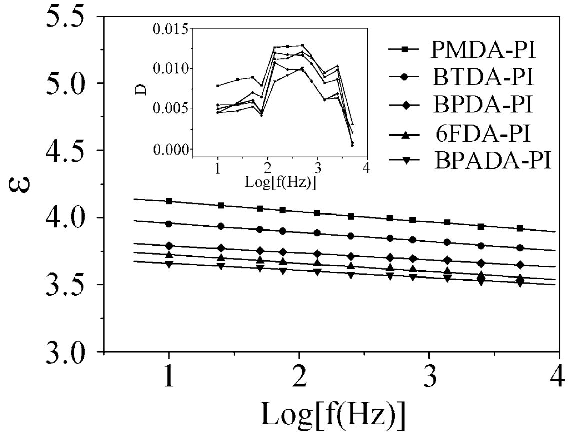

Figure 5. Dependence of dielectric constants on frequency for the polyimide films

Conclusions

Cyano-containing polyimides derived from 2,6-bis(4-aminophenoxy)benzonitrile had been synthesized by solution polycondensation. The polyimides prepared from APBN and BPADA or 6FDA exhibited more excellent energy-damping characteristic and excellent solubility in NMP, DMF, DMAc, DMSO, THF and $CHCl_3$ et al, however the polyimides from APBN and PMDA or BPDA were insoluble in polar and nonpolar organic solvents. All polyimides showed higher glass transition temperatures, excellent thermal stability and tensile properties. In comparison with the corresponding polyimides, incorporating a nitrile group into the polyimide molecular chain would make their dielectric constant increase.

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