Polyimides Derived from 3,3′-Bis(*N*-aminophthalimide)

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ABSTRACT: A novel diamine, 3,3′-bis(*N*-aminophthalimide) (BAPI), was prepared from 3,3′-bis(*N*-phenylphthalimide). Its structure was determined via IR, ^{1}H NMR, ^{15}N NMR, elemental analysis, and single-crystal X-ray diffraction analysis. A series of homo- and copolyimides were synthesized by a conventional one-step method in *p*-chlorophenol. The characteristic IR absorption bands of hydrazine-based imide groups were near 1780, 1750, 1350, 1100, and 730 cm^{-1}. The polymers showed good solubility in polar aprotic solvents and phenols at room temperature. The temperatures of 5% weight loss ($T_{5\%}$) of the polyimides ranged from 495 to 530 °C in air. DMTA analyses indicated that the glass-transition temperatures (T_gs) of the polyimides were in the range 371−432 °C. These polymers had cutoff wavelengths between 350 and 400 nm. The polyimide films of 6FDA/BAPI and 4,4′-HQPDA/BAPI were colorless; other films were pale yellow or yellow.

1. Introduction

Aromatic polyimides are a class of polymers that have unique high temperature stability, excellent mechanical and electrical properties, and outstanding chemical resistance. Therefore, they are widely used in the aerospace, transportation, and electrical and microelectronic industries. However, because of their chain rigidity and strong interchain interaction, most polyimides are insoluble in common organic solvents and intractable in their imide forms.[1−3] In addition, most polyimides have strong absorption in the visible region due to the existence of charge-transfer complexes, so most polyimides show coloration from pale yellow to deep brown. Poor processability and deep coloration limit the applications of polyimides, especially in the fields that require good optical transparency.[4] To solve these problems, many efforts have been made to design and synthesize polyimides with good processability and optical transparency while maintaining their other excellent properties. The focus is the fluorine-containing or alicyclic polyimides; however, the high cost of the fluorine-containing monomers or the poor thermal stability greatly limits the application of these materials.[5,6]

The incorporation of rigid but noncoplanar moieties, such as 2,2′-disubstituted biphenyl units, is an effective approach to enhance the solubility and optical transparency and reduce the coloration of polyimides. It has been reported that 2,2′-substituted benzidine produced polyimides with good optical transparence, high birefringence, and enhanced solubility.[7−11] Polyimides based on 2,2′-substitued BPDA showed lighter coloration, better solubility, and higher T_gs compared with the corresponding polyimides based on 4,4′-BPDA.[12,13] The steric repulsion of the substitutions in the 2,2′-positions of biphenyl units makes the two phenyl rings out-of-plane, which would inhibit chain packing and crystallization, break the conjugation along the backbone, and hinder the formation of intermolecular charge-transfer complexes. However, the synthesis of these monomers is usually involved in expensive starting materials, multistep procedures, and harsh reaction conditions.

Hydrazine is the simplest diamine, and its reactions with phthalic anhydride and its derivatives have been reported for many years.[14,15] In the 1960s, Dine-hart successfully prepared *N*,*N*′-diaminonaphthalene-1,4,5,8-tetracarboxydiimide and *N*,*N*′-diaminopyromellitimide, but high-molecular-weight polyimides could not be obtained due to the lower reactivity of the monomers and poor solubility of the resulted polymers.[16] In the 1990s, Hay and co-workers prepared high-molecular-weight polyimides from monomers with six-member-ring *N*-amino imide by the introduction of flexible moieties or copolymerization with other diamine monomers. These polyimides showed very high T_gs, excellent thermal stability, and good solubility.[17−23] However, only a few reports on five-member-ring, hydrazine-based polyimides appeared up to now,[16,23] and all of these polyimide could not be cast into flexible films. In this paper, we present the synthesis and properties of five-member-ring, hydrazine-based polyimides derived from 3,3′-bis(*N*-aminophthalimide) and aromatic dianhydrides, some of which can be cast into flexible and colorless films. It has been reported that *N*,*N*′-biphthalimide possesses rigid but noncoplanar structure.[24] Furthermore, the electron-donating property of hydrazine is very weak, which would decrease the formation of charge-transfer complexes. In fact, the hydrazine-based polyimides are wholly aromatic, the properties of hydrazine-based polyimides were characterized, and the results proved that they possessed very high T_gs, good solubility in common organic solvents, excellent optical transparency, and high thermooxidative stability.

2. Experimental Section

2.1. Materials. 3-Chlorophthalic anhydride (97%), 1,4-bis(3,4-dicarboxyphenoxy)benzene dianhydride (4,4′-HQPDA), and 1,4-bis(2,3-dicarboxyphenoxy)benzene dianhydride (3,3′-HQPDA) were synthesized in our laboratory.[25] 3,3′,4,4′-Biphenyltetracarboxylic acid dianhydride (4,4′-BPDA), 3,3′,4,4′-benzophenonetetracarboxylic acid dianhydride (4,4′-BTDA), 3,3′,4,4′-oxy(diphthalic anhydride) (4,4′-ODPA), 4,4′-(hexafluoroisopropylidene)diphthalic anhydride (6FDA), and hydrazine hydrate (80)% were purchased from Aldrich Chemical Co. The other reagents used in this study were purchased from Shanghai Chemical Reagent Plant. 4,4′-BPDA, 4,4′-BTDA, 4,4′-ODPA, and 6FDA were purified by sublimation in vacuo. *N*,*N*-Dimethylacetamide (DMAc) was dried over phosphorus pentoxide and then distilled under reduced pressure and stored over

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4 Å molecular sieves. *p*-Chlorophenol was used after distillation under reduced pressure. 3-Chloro-*N*-phenylphthalimide was prepared from 3-chlorophthalic anhydride and aniline and then recrystallized in ethanol. Other reagents were of analytical grade and used as received.

2.2. Characterization. Fourier transform infrared (FTIR) spectra were determined with a Bio-Red Digilab Division FTS-80 spectrometer. ^{1}H NMR (tetramethylsilane as an internal standard) and ^{15}N NMR (nitrocarbol as the internal standard) spectra were recorded on a Varian Unity spectrometer at 400 Hz. Elemental analyses were performed on an elemental analyzer MOD-1106 (Italyd). The X-ray crystallographic data were collected on a Bruker SMART APEX CCD diffractometer. Melting points were determined on an XT-4 melting point apparatus (Beijing Taike Apparatus, Inc.) and were uncorrected. Inherent viscosities were determined at 30 °C with an Ubbelodhe viscometer, and the concentration was 0.5 g/dL in DMAc. Molecular weight measurements were determined by gel permeation chromatography (GPC) using a multiangle laser light scattering (MALLS) detector. Polymer samples were dissolved in DMF (10 mg/mL) and filtered through a 0.20 μm Telflon filter. Thermogravimetric analyses were obtained at a heating rate of 10 °C/min in air with a Perkin-Elemer TGA-2 thermogravimetric analyzer. Dynamic mechanical thermal analysis (DMTA) was performed on dynamic mechanical thermal analyzer (Rheometric Scienfific, Inc.) using film samples (length: 10 mm) in a tensile mode (strain: 0.1%; initial static force: 0.2 N; static > dynamic force by 10.0%; minimum static force: 0.01 N; maximum autotension displacement: 3.0 mm) at a heating rate of 3 °C/min and a frequency of 1 Hz from room temperature to 300 °C. The tensile measurements were carried out on an Instron model 1122 at room temperature with 50 × 20 mm film samples. UV−vis spectra were measured with a Shimadzu UV-2550 spectrometer in the transmittance mode.

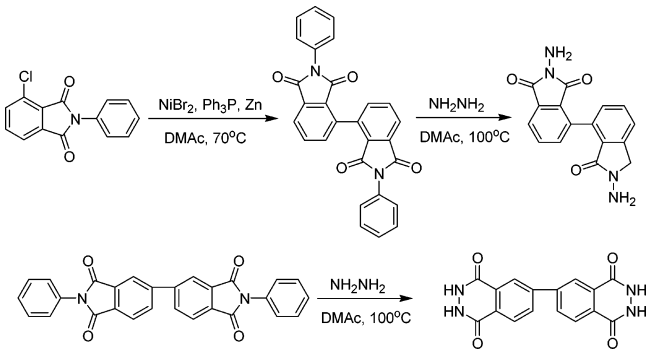
2.3. Synthesis of Monomer. *3,3′-Bis(N-phenylphthalimide).* 3-Chloro-*N*-phenylphthalimide (51.53 g, 0.20 mol), Zn dust (19.62 g, 0.30 mol), nickel(II) bromide (2.19 g, 0.01 mol), triphenylphosphine (20.16 g, 0.076 mol), and DMAc (300 mL) were placed in a three-necked, round-bottomed, 500 mL flask equipped with a magnetic stirrer and nitrogen inlet and outlet. The mixture was heated to 70 °C and stirred for 12 h in a nitrogen atmosphere. After cooling to room temperature, the dark mixture was poured into 2 L of ethanol. The resulting yellow precipitate was filtered and washed with ethanol three times. After sublimation, 3,3′-bis(*N*-phenylphthalimide) (35.55 g, 80%) was obtained as colorless crystals; mp 275−278 °C (lit.[26] 277−279 °C).

3,3′-Bis(N-aminophthalimide) (BAPI). 3,3′-Bis(*N*-phenylphthalimide) (22.22 g, 0.05 mol), hydrazine hydrate (6.25 g (80%), 0.10 mol), and DMAc (150 mL) were placed into a round-bottomed, 250 mL flask equipped with a magnetic stirrer. The mixture was heated to 100 °C and stirred for 6 h. 3,3′-Bis(*N*-phenylphthalimide) was dissolved in DMAc to afford a dark solution at first, and then a yellow precipitate appeared after 10 min. After cooling, the resulting yellow precipitate was collected by filtration, washed with DMAc and then aqueous ammonium (0.25 mol/L), and dried in air to afford 3,3′-bis(*N*-aminophthalimide) (11.28 g, 70%) as a pale-yellow solid. It was further purified by recrystallization from DMF; mp 293−295 °C. A single crystal of BAPI was grown by slow crystallization of its DMF solution (0.75% g/mL) at room temperature.

IR (KBr): 3366 (asym N−H stretching), 3333 (sym N−H stretching), 1783 (asym C═O stretching), 1712 (sym C═O stretching), 1406 (C−N stretching), 1103 (N−N stretching), 725 (C═O bending). ^{1}H NMR (400 MHz, DMSO): δ (ppm) 7.94−7.92 (d, d, 2H), 7.91−7.88 (t, 2H), 7.78−7.75 (d, d, 2H), 4.91 (s, 4H). ^{15}N NMR (400 MHz, DMSO): δ (ppm): 61.0, 180.2. Elem. Anal. Calcd for $C_{16}H_{10}N_4O_4$: C, 59.63%; H, 3.13%; N, 17.38%. Found: C, 59.69%; H, 3.13%; N, 17.41%.

2.4. Reaction of 4,4′-Bis(*N*-phenylphthalimide) with Hydrazine. 4,4′-Bis(*N*-phenylphthalimide) was prepared from 4,4′-BPDA and aniline in DMAc via a conventional two-step method. 4,4′-Bis(*N*-phenylphthalimide) (22.22 g, 0.05 mol), hydrazine hydrate (6.25 g (80%), 0.10 mol), and DMAc (150 mL) were placed into a round-bottomed, 250 mL flask equipped with a magnetic stirrer. The mixture was heated to 100 °C and stirred for 6 h. After cooling to the room temperature, the mixture was poured into 1 L of hydrochloric acid (1 mol/L), and then a yellow precipitate appeared. The precipitate was collected by filtration, dissolved in 0.25 mol/L ammonia, and then acidified with 1 mol/L hydrochloric acid. 6,6′-Bis(phthalaz-1,4-dione) was obtained with a yield of 80%; mp 339−342 °C.

Scheme 1. Reactions of Bis(*N*-Phenylphthalimide) and Hydrazine



IR (KBr): 3020 (N−H stretching), 1670 (C═O stretching), 1340 (C−N stretching), 1080 (N−N stretching). ^{1}H NMR (400 MHz, DMSO): δ (ppm) 11.71 (s (broad), 4H), 8.36−8.20 (m, 6H). Elem. Anal. Calcd for $C_{16}H_{10}N_4O_4$: C, 59.63%; H, 3.13%; N, 17.38%. Found: C, 59.83%; H, 3.20%; N, 17.22%.

2.5. Synthesis of Polymers. All polyimides studied in this work were prepared via conventional one-step procedure in *p*-chlorophenol. An equimolar amount of dianhydride and diamine monomers was used in all cases. The representative polymerization procedures are described as following: 3,3′-Bis(*N*-aminophthalimide) (0.6445 g, 0.002 mol), 4,4′-HQPDA (0.8046 g, 0.002 mol), *p*-chlorophenol (2.5 g), and a catalytic amount benzoic acid were placed into a three-necked, 50 mL flask equipped with a mechanical stirrer. The mixture was heated at 100 °C for 4 h in a nitrogen atmosphere and then at 190 °C for 24 h. The water formed during imidization was removed with a slow stream of nitrogen passing through the solvent. After cooling to 50 °C, the viscous mixture was poured slowly into 100 mL of ethanol. The fiberlike precipitate was collected by filtration and extracted with ethanol in a Soxhlet extractor for 24 h and dried under reduced pressure at 200 °C for 4 h to afford powder of polyimide 4,4-HQPDA/BAPI; yield 97%. The films were cast from the corresponding DMAc solutions of polyimides and then dried at 60 °C for 4 h and 250 °C for 4 h in vacuo.

3. Results and Discussion

3.1. Synthesis of Monomer. The reactions of hydrazine with aromatic anhydrides and their derivatives have been known for many years.[14,15] Hydrazine reacts with phthalic anhydride and its derivatives to give two products: *N*-aminophthalimide and phthalhydrazide. *N*-Aminophthalimdes can also be prepared from phthlimides and hydrazine. The ratios of *N*-aminophthalimide and phthalhydrazide are determined by the positions and amount of substitutions. 3-Substituted phthalimide would give both *N*-aminophthalimide and phthalhydrazide, while 4-substituted phthalimide would only give phthalhydrazide. Dine-Hart reported the synthesis of *N*,*N*′-diaminopyromellitimide which was unstable; therefore, the attempt to prepare high-molecular-weight polyimide failed. As shown in Scheme 1, 3,3′-bis(*N*-aminophthalimide) was prepared successfully from 3,3′-bis(*N*-phenylphthalimide) and hydrazine in high yield. On the other hand, when 4,4′-bis(*N*-phenylphthalimide) reacted with hydrazine at the same conditions, 6,6′-bis(phthalaz-1,4-dione) was the main product, and no 4,4′-bis(*N*-aminophthalimide) was

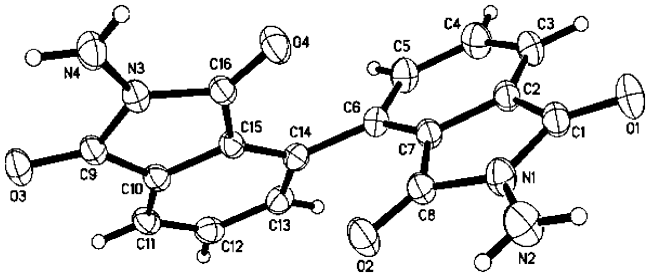


Figure 1. Molecular structure of 3,3′-bis(*N*-aminophthalimide) (BAPI).

separated. The structure of the BAPI was confirmed by IR spectra, ^{1}H NMR, ^{15}N NMR, and elemental analysis. The ^{15}N NMR exhibited the peak assigned to nitrogen atom of amino groups at around 61.0 ppm, suggesting the slightly lower reactivity of the monomer. The structure features of BAPI were further detailed by single-crystal X-ray diffraction. As shown in Figure 1, BAPI had a bent, rigid but noncoplanar structure. It adopted the syn conformation, and the dihedral angle of the two phthalimide plane was 57.1°. It could not be converted into the corresponding phthalhydrazide by heating below its melting point, which is beneficial to purification and polymerization. The steric hindrance resulted in the high yield and stability of 3,3′-bis(*N*-aminophthalimide). This diamine was also stable on exposure to light and air.

3.2. Synthesis of Polymers. As shown in Scheme 2, the polyimides are synthesized via a conventional one-step method in *p*-chlorophenol. The resulting polymers were isolated by the precipitation of the reaction mixture into ethanol and were purified by extract with ethanol in a Soxhlet extractor. The films were cast from the DMAc solution of polymers and then dried at 60 °C for 4 h and 250 °C for 4 h in vacuo. The molecular weights, yields, inherent viscosities, and elemental analysis data are summarized in Table 1. The molecular weights of these polyimides were measured by GPC (10 mg/mL DMF solution) with a multiangle laser light scattering detector after calibration with the standard polystyrens, except for polymer BPDA/BAPI, which was partially soluble in DMF at room temperature. M_n, M_w, and M_n/M_w values of these polymers were in the range of $2.1 \times 10^4 - 5.1 \times 10^4$, $2.2 \times 10^4 - 8.2 \times 10^4$, and 1.1−1.6, respectively. Inherent viscosities of the polymers were in the range of 0.18−0.50 dL/g in DMAc at 30 °C. The films of polyimides based on BPDA, BTDA, and ODPA were brittle, while those based on 6FDA, 4,4′-HQPDA, and 3,3′-HQPDA were flexible. The copolyimides based on BPDA, BTDA, and ODPA were also prepared using ODA as the comonomer. When the ratios of ODA were 20% (BTDA and ODPA) or 30% (BPDA) in two diamines, moderate-molecular-weight polyimides could be obtained, and their films were flexible. It is assumed that the peculiar molecular structure (shown in Figure 1) of BAPI is responsible for the lower molecular weights. The steric hindrance of the two phthalimide units would decrease the reactivity of the diamine. Furthermore, the syn conformation of the monomer made the formation of cyclic oligomer more favorite, which has been discussed in the previous paper.[26]

The structures of the polymers were determined by IR spectra and elemental analysis. The absorption bands near 1780 cm^{-1} (asym C═O str), 1750 cm^{-1} (sym C═O str), 1350 cm^{-1} (C−*N*

Scheme 2. Synthesis of Homo- and Copolyimides

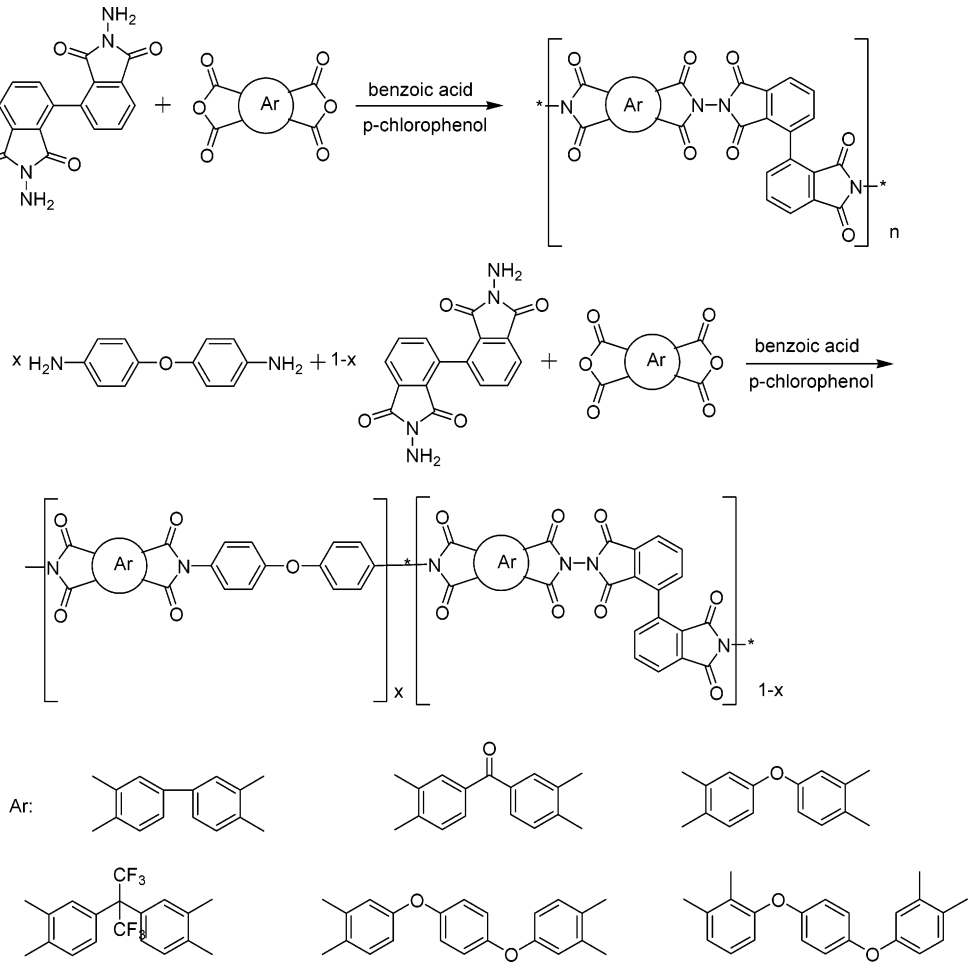


Table 1. Molecular Weights, Yields, Inherent Viscosities, and Elemental Analysis Data of Polyimides Based on BAPI

						elemental analysis data					
						C		H		N	
polymer	M_n (g/mol)	M_w (g/mol)	M_w/M_n	η_{inh}[a] (dL/g)	yield (%)	calcd	found	calcd	found	caldd	found
BPDA/BAPI[b]				0.18	93	66.21	66.83	2.08	2.00	9.65	9.52
BTDA/BAPI	21 000	22 180	1.1	0.19	92	65.14	65.27	1.99	1.96	9.21	9.36
ODPA/BAPI	20 710	23 260	1.1	0.20	94	64.44	64.56	2.03	2.09	9.39	9.27
6FDA/BAPI	30 370	32 910	1.1	0.35	98	57.55	57.63	1.66	1.70	7.67	7.65
4,4′-HQPDA/BAPI	23 440	27 200	1.2	0.37	97	66.28	66.38	2.34	2.36	8.14	8.19
3,3′-HQPDA/BAPI	42 080	55 670	1.3	0.38	95	66.28	66.42	2.34	2.36	8.14	8.09
BPDA/BAPI/ODA	42 020	58 090	1.4	0.49	95	68.96	68.72	2.38	2.40	8.59	8.50
BTDA/BAPI/ODA	51 210	82 240	1.6	0.50	98	66.43	66.82	2.17	2.13	8.52	8.41
ODPA/BAPI/ODA	31 630	35 040	1.1	0.36	96	65.73	65.96	2.22	2.09	8.69	8.42

[a] Inherent viscosity measured with 0.5% g/dL at 30 °C in DMAc. [b] Not measured because of its poor solubility in DMF at the room temperature.

Table 2. Thermal and Mechanical Properties of Polyimides from BAPI

polymer	T_g (°C)[a]	$T_{5\%}$ (°C)[b]	tensile strength(MPa)	modulus (MPa)	elongation (%)
BPDA/BAPI	*c*	523			
BTDA/BAPI		514			
ODPA/BAPI		505			
6FDA/BAPI	431	495	88	1780	9.5
4,4′-HQPDA/BAPI	378	516	106	1950	6.5
3,3′-HQPDA/BAPI	375	497	94	2772	5.0
BPDA/BAPI/ODA	432	530	117	1770	10.3
BTDA/BAPI/ODA	400	515	132	2470	7.2
ODPA/BAPI/ODA	391	519	85	2390	7.0

[a] Obtained from DMTA at a heating rate of 3 °C/min at 1 Hz. [b] Five percent weight loss obtained from TGA at a heating rate of 20 °C/min in air. [c] Not measured because their films were brittle.

str), 1080 (N−N str), and 730 cm^{-1} (imide ring deformation) were assigned to the characteristic absorption bands of hydrazine-based imide groups. It can be concluded that the IR absorption bonds of hydrazine-based imide groups were different from those of common imide groups. In hydrazine-based imide groups, one imide ring was attached another directly. The electron density of imide group was lower than that of conventional group because of the withdrawing of the other imide group, which caused the blue shift in the absorption band of C−N. The lone electron pair in oxygen atom shifted from oxygen to C═O, which caused the red shift in the absorption band of C═O. The elemental analysis data agreed with the proposed structures in general.

3.3. Properties of the Polymers. *3.3.1. Solubility.* The polymers based on BAPI showed good solubility in polar aprotic solvents and phenols at room temperature, and furthermore, polyimides based on 6FDA and 4,4′-HQPDA were soluble in chloroform and TCE. Copolymers showed similar solubility compared with the corresponding homopolymers. The enhanced solubility was contributed to the continuous twisted, rigid but noncoplanar structure. It has been reported that *N*,*N*′-biphthalimide adopted a twisted conformation, and the dihedral angle of the halves was 78°, which is due to the steric repulsion of the four C═O groups.[24] As shown in Figure 1, the 3,3′-biphenyl unit also showed a noncoplanar conformation.[26,27] Both of them formed continuous twisted, rigid but noncoplanar structure with a length of four phthalimide units, which inhibited chains packing, broke up the conjugation along the backbone, and hindered the formation of changed-transfer complexes.

The solubility of polyimide derived from 4,4′-HQPDA and BAPI was better than that from 3,3′-HQPDA and BAPI. This result is contrary to that previously reported on the solubility of the isomeric polyimides.[28−30] In this case, the twisted and noncoplanar structure in the backbone becomes the main factor in determining the behavior in solubility of the polymers. Actually, the difference in solubility of the isomeric polyimides is not as obvious as that of the others.

3.3.2. Thermal and Mechanical Properties. The thermal and mechanical properties of homo- and copolyimides from BAPI are summarized in Table 2. The representative TGA curves of homo- and copolyimides are shown in Figure 2. The temperatures of 5% weight loss ($T_{5\%}$) of the polyimides ranged from 495 to 530 °C in air. The thermooxidative stability of copolymers was slightly higher than that of homopolymers.

The tensile strengths at break of homo- and copolyimides, the modulus, and the elongations at break were 85−132 MPa, 1.77−2.77 GPa, and 5.0−10.3%, respectively. The films of homopolyimides from BPDA, BTDA, and ODPA were highly brittle, while their copolyimides showed excellent mechanical properties because of higher molecular weights and lower chain stiffness.

Figure 3 displays the DMTA curves of polymer 4,4′-HQPDA/BAPI and 3,3′-HQPDA/BAPI. Regarding the peak temperature in the tan δ curves as the glass transition temperature (T_g), the polymer 4,4′-HQPDA/BAPI exhibited a T_g at 378 °C and 3,3′-

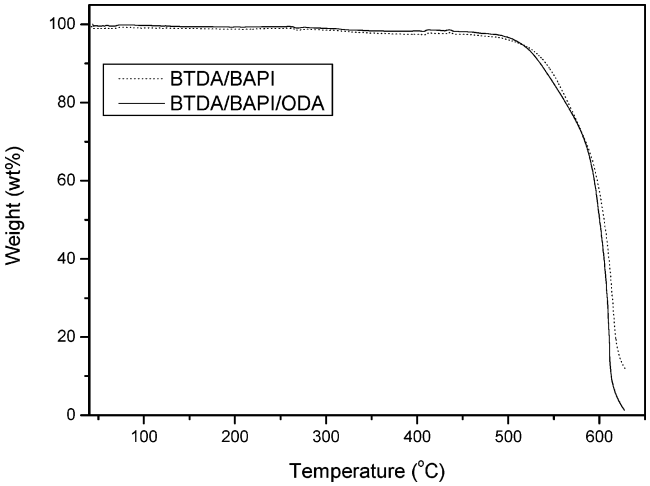


Figure 2. TGA curves of polyimides BTDA/BAPI and BTDA/BAPI/ODA.

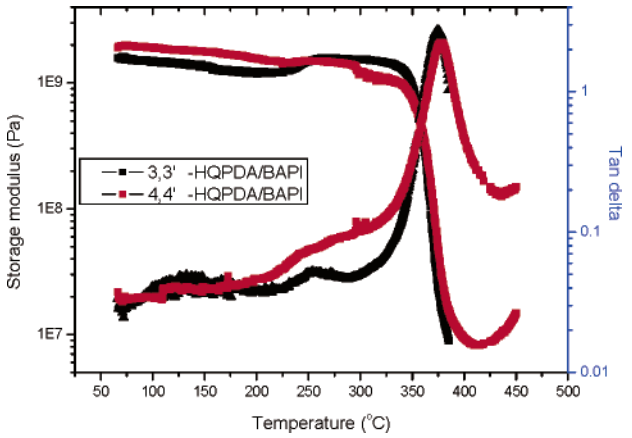


Figure 3. DMTA curves of polyimide 3,3′-HQPDA/BAPI and polyimide 4,4′-HQPDA/BAPI.

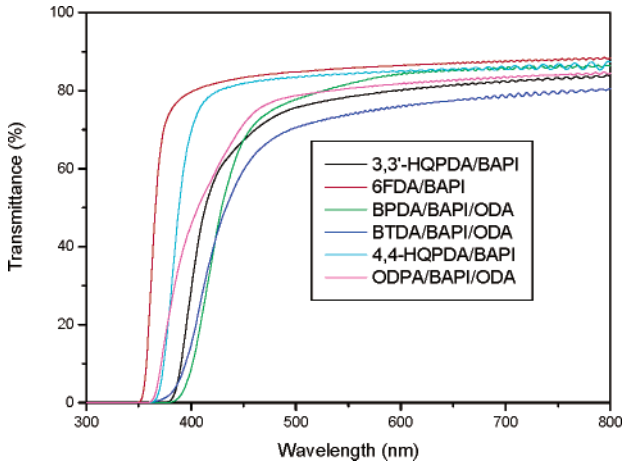


Figure 4. UV−vis spectra of polyimide films (about 15−20 μm thickness).

HQPDA/BAPI at 371 °C. This result was not consistent with previous reports on the T_g's of isomeric polyimides.[25,27,28,31−37] It is also assumed that the BAPI unit dominated the conformation of the polymers, the isomeric effect, e.g., the rotation between phthalimide and oxygen of ether linkage in this case became the minor fact to affect the T_gs.

The T_gs of the other hydrazine-based polyimides are illustrated in Table 2. The high T_gs of hydrazine-based polyimides is due to the continuous rigid and rotation-restricted structures in the backbone.

3.3.3. Optical Properties. UV−vis transmission spectra of polyimide films are shown in Figure 4. The cutoff wavelength of the absorption in polyimide 6FDA/BAPI was lowest, and its transmittance was highest among the polyimides. It must be pointed out that polyimide film based on 4,4′-HQPDA/BAPI, which is nonfluorinated and wholly aromatic, possessed excellent optical properties, with a cutoff wavelength at 368 nm and high transmittance in the visible region. The films of homopolyimides from BPDA, BTDA, and ODPA were brittle, and therefore their optical properties were measured in in DMAc solution with a concentration of 0.5 wt %. The colorations of the polyimide films are compared in Figure 5. Polyimide films of 6FDA/BAPI and 4,4′-HQPDA/BAPI were colorless, and other films were pale yellow or yellow. There are two reasons responsible for the light coloration of hydrazine-based polyimides. First, the electron-donating property of hydrazine unit was very poor, which prevented the formation of both intra- and intermolecular charge-transfer complexes. Second, the continuous, twisted, nonplanar structure in the backbone loosened chains packing and prevented the formation of intermolecular charge-transfer complexes.

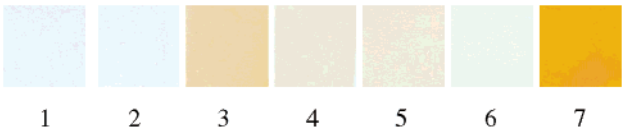


Figure 5. Photographs of polyimides based on BAPI [(1) 6FDA/BAPI, (2) 4,4′-HQPDA/BAPI, (3) 3,3′-HQPDA/BAPI, (4) BPDA/BAPI/ODA, (5) BTDA/BAPI/ODA, (6) ODPA/BAPI/ODA, (7) Kapton].

Polyimide based on 4,4′-HQPDA/BAPI possessed lower cutoff wavelength, higher optical transmittance, and light coloration. Combined with the difference in their solubility, it is supposed that the chain packing in polyimide 4,4′-HQPDA/BAPI is looser than that of 3,3′-HQPDA/BAPI. However, no proof can be found to support our hypothesis.

4. Conclusions

3,3′-Bis(*N*-aminophthalimide) (BAPI) was prepared from inexpensive starting materials via a simple procedure. The single-crystal X-ray diffraction analysis of this monomer indicated that it adopted twisted, syn conformation with a dihedral angle of 57.1°. A series of homo- and copolyimides were obtained via the conventional one-step method in *p*-chlorophenol. M_n, M_w, and M_n/M_w values of these polymers were in the range of $2.1 \times 10^4 - 5.1 \times 10^4$, $2.2 \times 10^4 - 8.2 \times 10^4$, and 1.1−1.6, respectively. The films of homopolyimides based on BPDA, BTDA, and ODPA were brittle, while those of homopolyimides based on 6FDA, 4,4′-HQPDA, and 3,3′-HQPDA as well as copolyimides based on BPDA, BTDA, and ODPA were transparent and flexible. The introduction of continuous, twisted, and rigid but nonplanar structures resulted in dramatic changes on the properties of the resulting polymers. These polymers can be soluble in polar aprotic solvents and phenols. The polyimides from 6FDA and 4,4′-HQPDA were even soluble in chloroform and TCE. These polyimides showed very high T_gs in the range of 371−432 °C and excellent optical properties. The cutoff wavelength of the absorption for 6FDA/BAPI and 4,4-HQPDA/BAPI was 353 and 368 nm, respectively, and their films were colorless. Therefore, the two polyimides are promising in some fields, such as LCD and solar cell. Copolymers based on BPDA, BTDA, and ODPA have very high T_gs combined with good solubility in polar aprotic solvents, such as DMF, DMAc, and NMP. The isomer effect for the polyimides from 4,4′-HQPDA and 3,3′-HQPDA was not as obvious as that for the other polyimides based on isomeric dianhydrides. It is assumed that the couple of the continuous, twisted, and rigid but nonplanar structure becomes the main factor to dominate the properties of the polyimides.

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