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Low dielectric constant and organosolubility of polyimides derived from unsymmetric phthalic-thioether-naphthalic dianhydrides

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Abstract A series of polyimides (PIs) with low dielectric constant were synthesized via a polycondensation from two new unsymmetric phthalic-thioether-naphthalic dianhydride isomers which were synthesized from 3- or 4-chlorophthalic anhydride by a four-step procedure. The introduction of the unsymmetric phthalic-thioether-naphthalic dianhydride into polymer backbone is regarded as an effective way to increase the free volume and decrease the intermolecular force and packing ability of the resulting polymers. Thus, the novel PIs exhibit low dielectric constant, low moisture absorption good solubility, high modulus, and high glass transition temperature. The polyimides show good solubility in phenol, dipolar aprotic solvents, and other common organic solvents. In addition, the isomeric effect of 3- and 4-thioether-linked phthalic anhydride on the properties of PIs was discussed.

Introduction

Based on their unique properties, such as outstanding thermal stability and chemical resistance, as well as excellent mechanical and electrical insulation properties, polyimides have been used in many areas, for example, aerospace, membrane separation, and microelectronics [1, 2]. However, most aromatic polyimides have high melting temperature and poor solubility in most organic solvents because of their rigid backbones and strong between-chain interactions, which may restrict their application in some fields. Thus, several modifications of the chemical structure have been made to enhance their processability and solubility with reservation of other advantageous polymer properties. Typical approaches include the introduction of flexible or kinked linkages [3–6], bulky substituents or cardo groups [7–14], noncoplanar structures [15], and spiro-skeletons [16, 17] into the polymer backbone. Besides, it has been demonstrated that the polyimides derived from isomeric dianhydrides and diamines have broad processing windows and good solubility without loss of thermal properties, as evidenced by examples such as mellophanic dianhydride (MPDA) [18], 2,2′-bis(trifluoromethyl)-4,4′,5,5′-biphenyltetracarboxylic dianhydride (6FBPDA) [19], isomeric 3,3′-, 3,4′-, and 4,4′-oxydiphthalic anhydrides (ODPA) [20], isomeric 3,3′-, 3,4′-, and 4,4′-diphenylthioether dianhydrides (TDPA) [21, 22]. Recently, one attractive method for improving processability and solubility is incorporating geometrically unsymmetric diamine or dianhydride into polyimide backbones [23–32].

Five-membered phthalic and six-membered naphthalic dianhydrides are two main kinds of variations in structure for aromatic dianhydride monomers. Previous studies have shown that polyimides derived from bis(phthalic anhydride)s possess excellent processability and solubility in organic solvents, such as Ultem poly(ether imide)s which can polymerize by the one-step displaced polymerization in solution expediently; on the contrary, polyimides derived from bis(naphthalic anhydride)s display superior chemical property, thermal property, and fire resistance to the analogous polyimides derived from bis(phthalic anhydride)s [33, 34]; however, a two-step polymerization of bis(naphthalic anhydride)s is difficult to proceed since the reaction between naphthalic anhydride and primary amine could directly yield isoimide but not via amic acid, and then the

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isoimide converts to imide by heating [35–37]. At the same time, most of polyimides based on bis(naphthalic anhydride)s have poor processability and low solubility in organic solvents, which limits the one-step polymerization in solution. Consequently, the polyimide based on a new dianhydride monomer containing both phthalic anhydride and naphthalic anhydride into the same molecule may integrate the excellent processability and solubility of polyphthalimides with the good chemical property, thermal property, and fire resistance of polynaphthalimides.

In addition to the above property improvements, it is also found that the introduction of the geometric asymmetry in the polymer backbone can obtain significantly lower dielectric constant [27, 38–41], which is very important to the interlayer dielectric materials because of rapid advancement of tightly packed circuitry in the microelectronic industry. It is apparent that geometric asymmetry of the polymer will result in less efficient chain packing and an increase in the free volume of the polymer, thus decreasing the dielectric constant [42, 43]. Therefore, compared to symmetric dianhydride, an unsymmetric dianhydride having phthalic anhydride and naphthalic anhydride into the same molecule is supposed to obtain lower dielectric constant polyimides.

To date, little is known about unsymmetric polyimides derived from a dianhydride monomer containing phthalic anhydride and naphthalic anhydride in the same molecule (Fig. 1). Zheng and Wang [44] once reported unsymmetric polyimides derived from 1-benzoylnaphthalene-3′,4,4′,5-tetracarboxylic dianhydride (BNTDA) and found these polymers possess good solubility and high T_g. However, in that article the authors did not show the dielectric properties of corresponding unsymmetric polyimides. To the best of our knowledge, no previous reports about polyimides derived from dianhydrides such as TNTDA containing flexible thioether linkage or ENTDA containing flexible ether linkage have appeared in the literature. Ether or thioether linkages are the most popular, flexible linkages which could be introduced into polymer backbones and endowed polymer combined properties. It is generally recognized that an aryl–ether or aryl–thioether linkage will impart advantageous properties such as better solubility and melt-processing characteristics and improved toughness in comparison with those of polymers without an aryl–ether or aryl–thioether linkage.

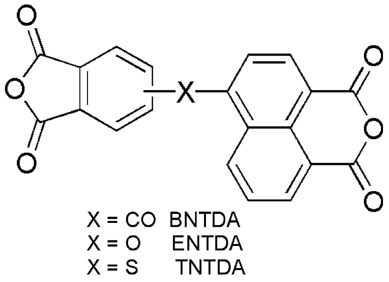


Fig. 1 Three structures of unsymmetric dianhydrides

Herein, we report two kinds of PIs derived from newly synthesized unsymmetric dianhydride isomers, 1-thionaphthalene-2′,3′,4,5-tetracarboxylic dianhydride (3-TNTDA) and 1-thionaphthalene-3′,4,4′,5-tetracarboxylic dianhydride (4-TNTDA). Because the two new dianhydride monomers are molecularly unsymmetric; the resulting PIs are supposed to exhibit good solubility and retain other desirable properties such as high glass transition temperatures and low dielectric constant compared with the polyimides derived from bis(naphthalic anhydride)-based or bis(phthalic anhydride)-based polyimides.

Experimental

Materials

N-methyl-3-chlorophthalimide **1**(**3**) (mp: 101–102 °C) and *N*-methyl-4-chlorophthalimide **1**(**4**) (135 °C) were prepared according to the literature procedures [20, 45]. 4-Bromo-1,8-naphthalic anhydride was purchased from Aldrich Chemical Co., and purified by recrystallization from acetic anhydride. Sodium hydrosulfide hydrate was purchased from Aldrich Chemical Co., and used as received. 4,4-Oxydianiline (ODA) and *p*-phenyldiamine (PDA) were purified by sublimation in vacuum. 1,4-Bis(4-aminophenoxy) benzene (TPEQ) and 1,3-bis(4-aminophenoxy) benzene (TPER) were obtained from Shijiazhuang Tianheng Institute of Medical and Chemical and used as received. Other starting materials were analytical grade and used as received.

Instrumentation

The ^{1}H NMR spectra were measured at 400 MHz on a Bruker 400 AVANCEIII spectrometer, using dimethyl sulfoxide-d_6 (DMSO-d_6) or $CDCl_3$ as solvent. Melting points were determined on an XT4-100B melting point apparatus (Beijing Keyi Elec-opti instrument) and were uncorrected. The Fourier transform infrared spectra (FTIR) were obtained with a Thermo Nicolet 6700 FTIR spectrometer, where the sample was prepared with KBr pellets. Elemental analyses were carried out on a PerkinElmer model 2400II C, H, N, S analyzer. The inherent viscosities were measured with an Ubbelodhe viscometer at 30 ± 0.1 °C in *m*-cresol at a concentration of 0.5 g/dL. Thermogravimetric analysis (TGA) was recorded on a Perkin-Elmer Diamond TG/DTA instrument at a heating rate of 10 °C/min under nitrogen atmosphere (flow rate of 50 mL/min). Differential scanning calorimetry (DSC) was carried out using Mettler Toledo DSC at a heating rate of 20 °C/min under nitrogen atmosphere with 50 mL/min gas flow, and T_g was reported as temperature at the middle of the thermal transition from the second heating scan. The tensile measurements were tested for five PI film samples by an Instron model 5567 at room temperature, and the results were averaged. Dielectric property of the polymer films was tested by the parallel-plate capacitor method using a HP-4194A Impedance/Gain Phase Analyzer at 1 MHz frequency. Silver electrodes were fired on both surfaces of the 15–20 μm thick, 2 × 2 cm dried films, followed by measuring at room temperature at 70% relative humidity. The equilibrium water absorption was determined by the weighing of the changes in vacuum-dried film specimens before and after immersion in deionized water at 25 °C for 100 h.

Synthesis of *N*-methyl-3-mercaptophthalimide **2**(**3**)

Sodium hydrogen sulfide hydrate (28.8 g, 0.36 mol) and *N*,*N*-dimethylacetamide (DMAc) (150 mL) were charged into a 500-mL three-neck round-bottom flask equipped with a magnetic stirrer, condenser, and nitrogen inlet. The mixture was stirred at 60 °C for about 2 h. After the sodium hydrosulfide hydrate was completely dissolved in the DMAc, *N*-methyl-3-chlorophthalimide **1**(**3**) (23.47 g, 0.12 mol) were added into the flask, and the resulting mixture was allowed to stir at 120 °C for 2 h under an atmosphere of nitrogen (Caution: H_2S, which must be trapped and oxidized by passing through a 30% NaOH solution and a bleach solution (NaOCl), is produced during the reaction). The dark brown reaction mixture was cooled and then diluted with ice water (2000 mL), filtered, and slowly acidified with a 5% HCl solution to a pH ~2. An off-white precipitate was formed immediately upon acidification. The crude product was dissolved in 5% K_2CO_3 (800 mL) aqueous solution, filtered, and the filtrate was reprecipitated by adding 5% HCl solution. This purification process was repeated one time and the white granular product was collected, washed well with deionized water, and vacuum-dried at 40 °C for 24 h. Yield: 15.14 g (65.3%). mp: 109–110 °C. IR (KBr): 2548, 1764, 1704, 1604, 1379 cm^{-1}.^{1}H-NMR ($CDCl_3$): δ 7.58 (d, $J =$ 7.2 Hz, 1H), 7.52 (t, $J = 7.6$ Hz, 1H), 7.44 (d, $J = 7.6$ Hz, 1H), 6.16 (s, 1H, SH), 3.19 (s, 3H, CH_3).

Synthesis of *N*-methyl-4-mercaptophthalimide **2**(**4**)

This compound was prepared from *N*-methyl-4-chlorophthalimide **1**(**4**) and sodium hydrosulfide hydrate through similar procedure to **2**(**3**). The product was as pale crystals. Yield: 10.20 g (44.0%). mp: 152–156 °C. IR (KBr): 2559, 1770, 1689, 1607, 1379 cm^{-1}. ^{1}H-NMR ($CDCl_3$): δ 7.71–7.69 (m, 2H), 7.54 (dd, $J = 8.0$ Hz, 1.6 Hz, 1H), 3.82 (s, 1H, SH), 3.18 (s, 3H, CH_3).

Synthesis of *N*-methyl-3-[(4,5-naphthalenedicarboxylic anhydride) thioether]-phthalimide **3**(**3**)

N-methyl-3-mercaptophthalimide **2**(**3**) (7.73 g, 0.04 mol), 4-bromo-1,8-naphthalic anhydride (11.10 g, 0.04 mol), and sodium carbonate (2.94 g, 0.044 mmol) were added into a 500-mL three-necked flask fitted with an overhead mechanical stirrer, a condenser, and a nitrogen inlet; and DMF (280 mL) was added. The reaction mixture was stirred at 120 °C under N_2 atmosphere for 4 h. After cooling to room temperature, the reaction mixture was poured into deionized water (1500 mL), and filtered off. After recrystallization from DMAc, a yellow crystal was obtained. Yield: 15.40 g (98.8%). mp: 368 °C (DSC). IR (KBr): 1774, 1733, 1708, 1588, 1383, 1025 cm^{-1}. ^{1}H NMR (DMSO-*d6*): δ 8.67 (d, $J = 8.8$ Hz, 1H), 8.61 (d, $J = 7.2$ Hz, 1H), 8.51 (d, $J = 7.6$ Hz, 1H), 8.07 (d, $J =$ 7.6 Hz, 1H), 7.96 (t, $J = 7.8$ Hz, 1H), 7.71 (d, $J = 7.2$ Hz, 1H), 7.56 (t, $J = 7.6$ Hz, 1H), 6.96 (d, $J = 8.4$ Hz, 1H), 3.31 (s, 3H, CH_3). Anal. Calcd for $C_{21}H_{11}NO_5S$: C, 64.78; H, 2.85; N, 3.60; S, 8.23. Found: C, 64.66; H, 2.79; N, 3.68; S, 8.28.

Synthesis of *N*-methyl-4-[(4,5-naphthalenedicarboxylic anhydride) thioether]-phthalimide **3**(**4**)

This compound was prepared from *N*-methyl-4-mercaptophthalimide **2**(**4**) and 4-bromo-1,8-naphthalic anhydride through similar procedure to **3**(**3**). The product was as yellow crystals. Yield: 14.68 g (94.2%). mp: 285–290 °C. IR (KBr): 1770, 1728, 1706, 1586, 1374, 1007 cm^{-1}. ^{1}H-NMR (DMSO-*d6*): δ 8.68 (d, $J = 8.4$ Hz, 1H), 8.58 (d, $J = 7.2$ Hz, 1H), 8.43 (d, $J = 7.6$ Hz, 1H), 7.96 (t, $J =$ 8.4 Hz, 1H), 7.87–7.84 (m, 2H), 7.76 (dd, $J = 8.0$ Hz, 1.6 Hz, 1H), 7.68 (d, $J = 1.6$ Hz, 1H), 3.32 (s, 3H, CH_3). Anal. Calcd for $C_{21}H_{11}NO_5S$: C, 64.78; H, 2.85; N, 3.60; S, 8.23. Found: C, 64.67; H, 2.89; N, 3.54; S, 8.28.

Synthesis of 1-thionaphthalene-2′,3′,4,5-tetracarboxylic dianhydride **4**(**3**)

N-methyl-3-[(4,5-naphthalenedicarboxylic anhydride) thioether]-phthalimide **3**(**3**) (14.17 g, 0.036 mol), KOH (25.0 g), and deionized water (150 mL) were charged into a 500-mL three-neck round-bottom flask fitted with a condenser. Then, the mixture was heated to reflux with magnetic stirring about half an hour, and then become colorless solution. After refluxing for 30 h and cooling to room temperature, the light yellow solution was dropped into dilute HCl (1500 mL, pH = 2) slowly and filtered off. After recrystallization from the mixed solvents of acetic anhydride and DMAc (10/1, v/v), pale crystals were obtained. Yield: 10.53 g (76.46%). mp: 267 °C. IR (KBr): 1850, 1772, 1739, 1589, 1020 cm^{-1}. ^{1}H NMR (DMSO-*d*6): δ 8.66 (d, $J = 8.8$ Hz, 1H), 8.61 (d, $J = 7.2$ Hz, 1H), 8.53 (d, $J = 7.6$ Hz, 1H), 8.14 (d, $J = 7.6$ Hz, 1H), 7.96 (t, $J = 7.8$ Hz, 1H), 7.90 (d, $J = 7.6$ Hz, 1H), 7.70 (t, $J = 7.8$ Hz, 1H), 7.10 (d, $J = 8.0$ Hz, 1H). ^{13}C-NMR (DMSO-d6): δ 163.12, 162.30, 160.68, 160.60 137.13, 136.78, 136.53, 135.12, 134.67, 133.55, 133.40, 132.61, 132.45, 131.75, 131.00, 129.42, 128.35, 123.71, 120.99, 120.63. Anal. Calcd for $C_{20}H_8O_6S$: C, 63.83; H, 2.14; S, 8.52. Found: C, 63.95; H, 2.16; S, 8.39.

Synthesis of 1-thionaphthalene-3′,4,4′,5-tetracarboxylic dianhydride **4**(**4**)

This compound was prepared from *N*-methyl-4-[(4,5-naphthalenedicarboxylic anhydride) thioether]-phthalimide **3**(**4**) through similar procedure to **4**(**3**). The product was as yellow crystal. Yield: 11.14 g (82.2%). mp: 246–247 °C. IR (KBr): 1854, 1773, 1735, 1588, 1017 cm^{-1}. ^{1}H-NMR (DMSO-d6): δ 8.69 (d, $J = 8.8$ Hz, 1H), 8.61 (d, $J = 7.2$ Hz, 1H), 8.52 (d, $J = 7.6$ Hz, 1H), 8.07 (d, $J = 7.6$ Hz, 1H), 8.02 (d, $J = 8.0$ Hz, 1H), 7.98 (t, $J = 8.0$ Hz, 1H), 7.83 (s, 1H), 7.81 (dd, $J = 8.0$ Hz, 1.6 Hz, 1H). ^{13}C-NMR (DMSO-d6): δ 162.94, 162.92, 160.75, 160.62, 145.29, 138.13, 136.21, 133.97, 133.50, 133.29, 132.51, 132.18, 131.47, 131.02, 130.03, 129.43, 126.78, 125.11, 120.92, 120.77. Anal. Calcd for $C_{20}H_8O_6S$: C, 63.83; H, 2.14; S, 8.52. Found: C, 63.68; H, 2.32; S, 8.32.

Representative synthesis procedure for the preparation of polyimides (**5**)

As shown in Scheme 2, the polyimides were prepared from monomer **4** with four diamines. One-step polymerizations of dianhydride **4** with various aromatic diamines **a**–**d** were then carried out in *m*-cresol in the presence of a small amount of isoquinoline at 203 °C. The synthetic procedure for all polyimides **5** except two polyimides derived from **b** is described as a typical example. The diamine **c** (0.2923 g, 1 mmol), 3-TNTDA **4**(**3**) (0.3763 g, 1 mmol), and *m*-cresol (12.0 mL) were added to a three-necked flask equipped with a magnetic stirrer, a nitrogen inlet, and a distillation head. Isoquinoline (two drops) was added to the flask. After the mixture was heated at 60 °C until all solids were dissolved completely, it was heated to 203 °C for 20 h. Water was continuously distilled from the reaction mixture. The solution was cooled to room temperature and subsequently poured into methanol (300 mL). The polymer that precipitated was collected, filtered, and then extracted using methanol in a Soxhlet extractor overnight. After drying under a high vacuum at 150 °C for 24 h polyimide **5**(**3c**) was obtained as a white powder (0.6067 g, yield: 95.9%). The inherent viscosity of **5**(**3c**) was 0.40 dL/g, as measured at a concentration of 0.5 g/dL in *m*-cresol at 30 °C. IR (KBr): 1772, 1714, 1665, 1566, 1381, 1014 cm^{-1}.

Synthesis of polyimides **5**(**3b**) and **5**(**4b**)

The synthetic procedure for polymer **5**(**3b**) is described as a typical example. The diamine **b** (0.2002 g, 1 mmol), 3-TNTDA **4**(**3**) (0.3763 g, 1 mmol), benzoic acid (0.0244 g, 0.2 mmol), and *m*-cresol (12.0 mL) were added into a three-necked flask equipped with a magnetic stirrer, a nitrogen inlet, and a distillation head. After the mixture was heated at 60 °C until all solids were dissolved completely, it was then heated to 203 °C for 5 h. The solution was cooled to room temperature, and then two drops of isoquinoline was added into the flask. The solution was heated to 203 °C again and kept for 20 h. Water was continuously distilled from the reaction mixture. The solution was poured into 300-mL methanol. The precipitated polymer was collected, filtered, and then extracted using methanol in a Soxhlet extractor overnight. After dried at 150 °C under high vacuum for 24 h polyimide **5**(**3b**) was obtained as a white powder (0.4973 g, yield: 92.0%). The inherent viscosity of **5**(**3b**) was 0.47 dL/g, as measured at a concentration of 0.5 g/dL in *m*-cresol at 30 °C. IR (KBr): 1771, 1713, 1668, 1567, 1382, 1016 cm^{-1}.

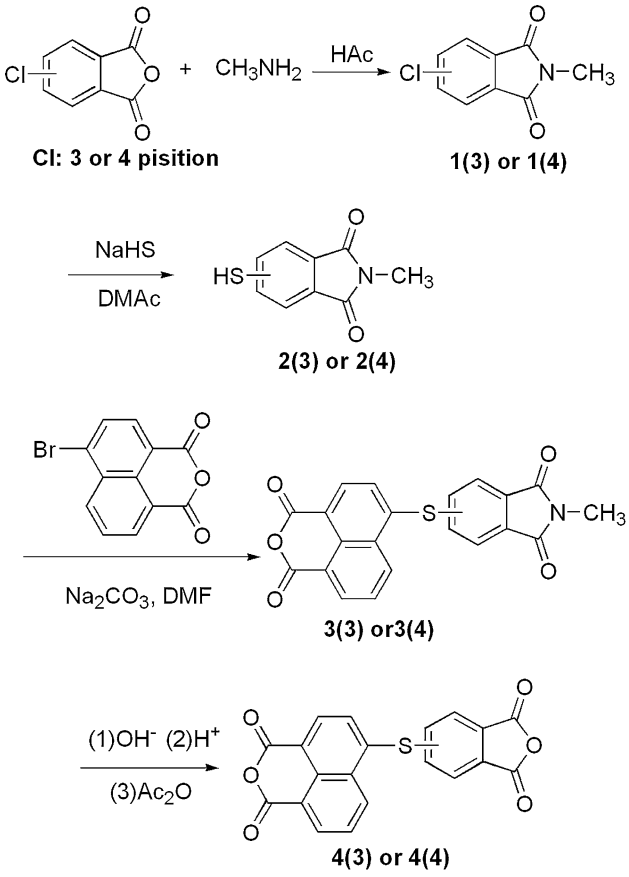
Film casting

All the polymer films were cast from *m*-cresol solutions. A typical procedure for film casting was as follows. The purified and dried polymer (0.8–1 g) was dissolved in 15–18 mL of *m*-cresol (some of the polymers needed to be heated to dissolve rapidly). The solution was cast on a leveled clean glass plate. The casting films were dried in an oven at 130 °C for 6 h, 180 °C for 1 h, 230 °C for 1 h, and last at 300 °C for 1 h. The film was removed from the glass by immersion in water and then dried at 100 °C for 6 h.

Results and discussion

Monomer synthesis

Two new unsymmetric dianhydride isomers were synthesized by a four-step procedure, as shown in Scheme 1. First, two mercaptophthalimides **2**(**3**) and **2**(**4**) were prepared from corresponding chlorophthalimides **1**(**3**) and **1**(**4**) and sodium hydrosulfide hydrate. The amount of sodium hydrosulfide



Scheme 1 Synthesis of TNTDAs

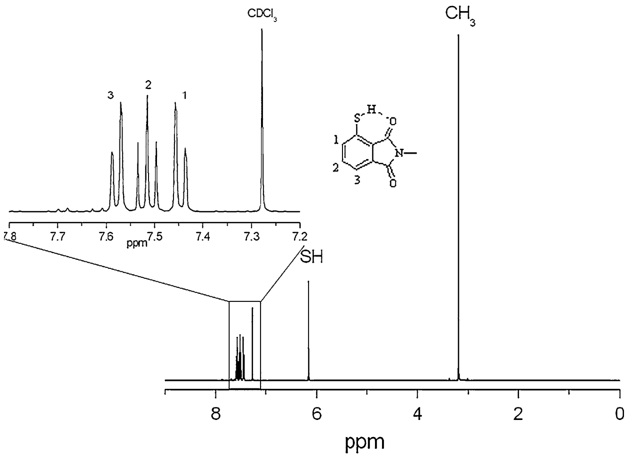


Fig. 2 ^{1}H NMR spectrum of **2**(**3**) in CDCl$_3$

hydrate should be more than chlorophthalimides **1** exceedingly. The reaction proceeded very fast for high electron deficiency of the carbon connecting to chlorine atom and strong reactivity of the sodium hydrosulfide hydrate. There is no *N*-methyl-4-chlorophthalimide **1**(**4**) in the reactive mixture by TLC after one and a half hours. It should be noted that the mercaptophthalimides are easily oxidized by air to form disulfide compounds over 80 °C, so the product can not be dissolved into NaOH solution. To avoid the oxidation, all of the mercaptophthalimides were dried lower than 40 °C under vacuum. The whole process can refer to arenedithiols synthetic procedures by Hay [46]. The structure and purity of mercaptophthalimides are identified by ^{1}H-NMR, IR, and melting point. Interestingly, in the ^{1}H spectrum of compound **2**(**3**), the proton signals of SH appeared in the farthest low-field at 6.16 ppm (Fig. 2) compared with the peak signal for the majority of SH in the upfield (2–4 ppm), which may be on account of deshielding effect caused by the intramolecular hydrogen bonds between the SH and its neighboring carbonyl group. Second, naphthalic anhydride-thioether-phthalimides **3**(**3**) and **3**(**4**) were synthesized by the nucleophilic substitution reaction of 4-bromo-1,8-naphthalic anhydride and corresponding mercaptophthalimides **2**(**3**) and **2**(**4**) in the presence of sodium carbonate with high yield. Both of the reactions took place successfully in DMF at 120 °C and atmospheric pressure for the strong activation of the two carbonyl group of 4-bromo-1,8-naphthalic anhydride and the intense nucleophilicity of mercapto. Finally, two unsymmetric dianhydrides (TNTDAs) were obtained from naphthalic anhydride-thioether-phthalimides **3**(**3**) and **3**(**4**) by hydrolysis, acidification, and recrystallization. Elemental analysis, melting point, IR, ^{1}H NMR, and ^{13}C NMR spectroscopic techniques were used to identify structures of the target unsymmetric dianhydride monomers **4**(**3**) and **4**(**4**). The ^{1}H NMR spectra of TNTDAs are presented in Fig. 3 with assignments of all the peaks. In the ^{13}C NMR spectrum, sixteen aromatic carbon signals and four carbonyl carbon signals are observed, which are consistent with the expected structure. In addition, the measured elemental compositions of the C, H, and S elements agree well with the calculated values. These results clearly support the structure of TNTDAs.

Synthesis of polyimides

The polyimides were prepared by the one-step polymerization in *m*-cresol at 203 °C in the presence of a small amount of isoquinoline (Scheme 2). The formation of PIs was confirmed by IR (Fig. 4). The polymerization of TNTDAs and diamines is difficult for the difference of the reactivity of the two kinds of anhydride group in TNTDAs. Five-membered phthalic dianhydrides can react with diamines readily in dipolar aprotic solvent such as DMAc, dimethyl sulfoxide (DMSO), and *N*-methyl pyrrolidone (NMP) to obtain high molecular weight poly(amic acid)s (PAAs); PAAs then dehydrated to the polyimide via chemical imidization or thermal imidization. Besides, five-membered phthalic dianhydrides can polymerize with diamines in phenolic and other solvents in the presence of

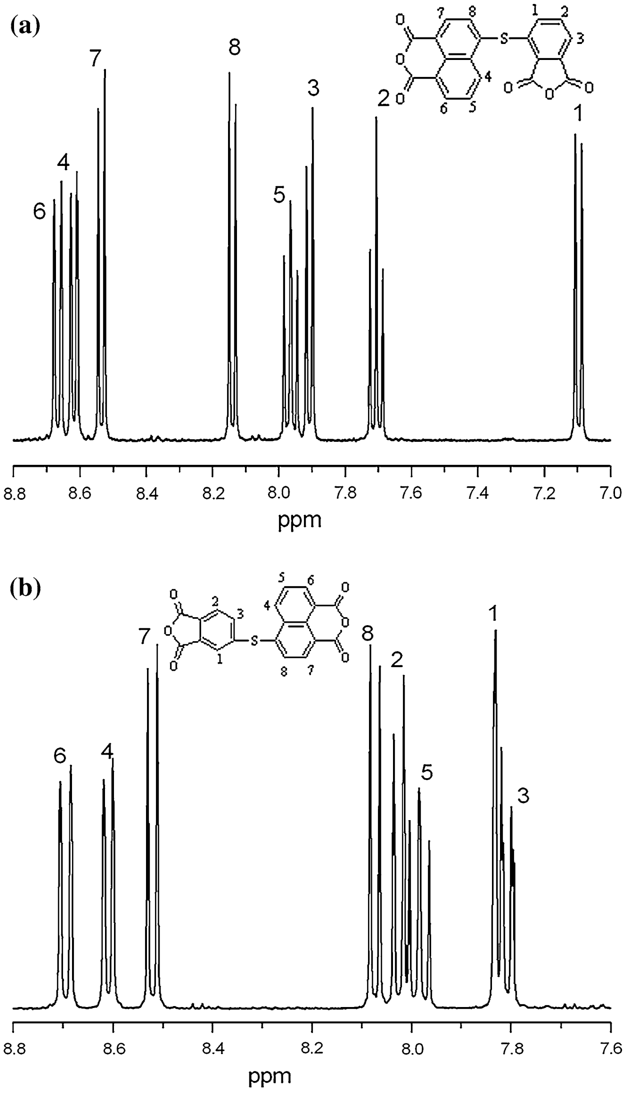
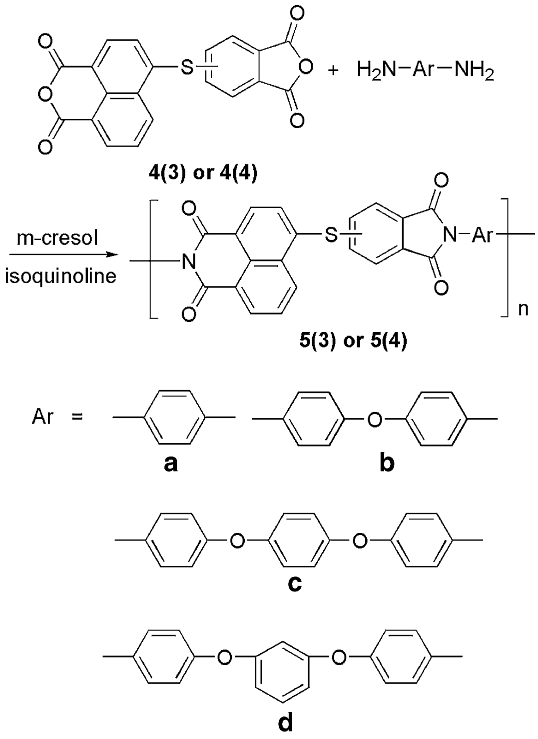


Fig. 3 ^{1}H NMR spectrum of **a** **4**(**3**) and **b** **4**(**4**) in DMSO-d_6



Scheme 2 Preparation of polyimides

catalysts at elevated temperature [1]. However, naphthalic anhydride can not react with amines to afford imides in DMAc [44]. Interestingly, Sek. et al. [36, 37, 47, 48] found that naphthalic anhydride is able to react with amines in *m*-cresol or hexamethylphosphoric triamide (HMPT) to get isoimide without any catalysts, excluding the probability of the reaction to proceed via amic acid and confirming the direct reaction of the carbonyl groups with the amine groups; they also confirmed that the formation of trans isoimide only occurred in the presence of acidic catalysts and only the trans isoimides can isomerize to imide structure in the presence of basic catalysts during heating or UV irradiation, whereas the cis isoimide can not convert into imide. Thereby, the unsymmetric dianhydrides (TNTDAs) can only be polymerized in the phenolic solvents. Polyimides **5b–d** with high molecular weight were readily formed in 20 h, except for polyimide **5a** which precipitated out during polymerization. Possibly due to the rigidity of the polyimides **5**(**3b**) and **5**(**4b**), high molecular weight polymer can not be obtained by the polymerization of monomers of **4** and ODA without acidic catalysts. On the contrary, if acidic catalysts used in the polymerization together with basic catalysts, higher molecular weight polymers were attained.

The structures and codes of the prepared polymers are shown in Scheme 2. As shown in Table 1, the inherent viscosities of novel polyimide **5b–d** derived from unsymmetric phthalic-thioether-naphthalic dianhydrides **4** were 0.39–0.53 dL/g in *m*-cresol indicating the formation of high molecular weight polymers. All the polyimides **5b–d** could be cast into flexible and tough film.

The formation of polyimides was confirmed with FTIR (Fig. 4) and elemental analysis. The IR spectrum of monomer **4**(**3**) showed three peaks at 1850, 1772, and 1739 cm^{-1} for the naphthalic and phthalic anhydrides, while the IR spectra of the polyimide **5**(**3b**) displayed three imide peaks at 1771, 1713, and 1668 cm^{-1} similar to that of diimide prepared by Zheng and Wang [44]. The results of the elemental analysis of all the polyimides are listed in Table 2. The values are generally in good agreement with the calculated values of the proposed structures.

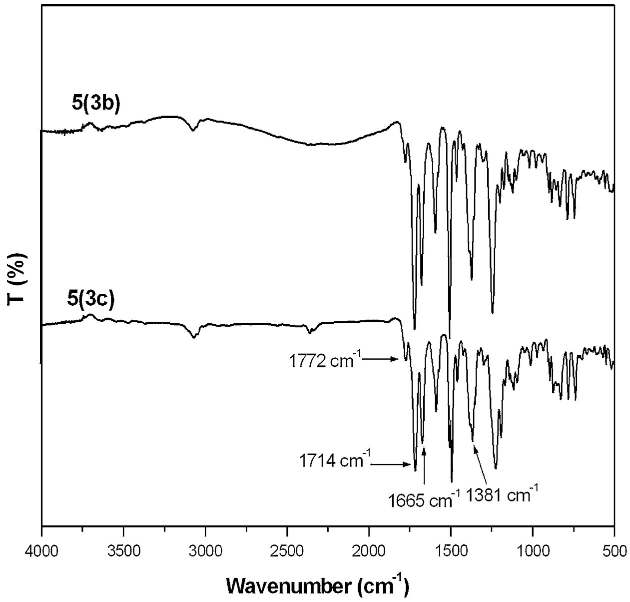


Fig. 4 FTIR spectrum of 5(**3b**) and 5(**3c**)

Properties of the polyimides

Organosolubility

The solubility behavior of the polyimides derived from TNTDAs was tested qualitatively in various organic solvents, and the results are also reported in Table 1. The organosolubility behavior of the polyimides generally depends on their chain packing density and intermolecular interactions, which are affected by the rigidity, symmetry, and regularity of the molecular backbone. Thus, the polyimide derived from unsymmetric phthalic-thioether-naphthalic dianhydride **4**(**4**) and ODA can be dissolved in NMP readily, but the corresponding analogous polyimide derived from 4,4-TDPA and ODA can only be dissolved partially in NMP; and all the polyimides derived from unsymmetric phthalic-thioether-naphthalic dianhydride can be dissolved in chloroform partially, whereas the polyimide derived from 4,4-TDPA and ODA can not. Apparently, such an improvement in solubility can be attributed to the unsymmetric structure of TNTDAs and the resulting three possible diad microstructures within the polyimide backbone. Similarly, the polyimides derived from more flexible diamines such as ODA, TPER, and TPEQ generally displayed a better solubility in *m*-cresol, NMP, and TCE (1,1,2,2-tetrachloroethane) than those obtained from more rigid components such as PDA. Surprisingly, the polyimide derived from unsymmetric phthalic-thioether-naphthalic dianhydride **4**(**4**) and TPEQ can be readily dissolved in chloroform. This may be attributed to the slightly lower viscosity of the polyimide **5**(**4c**) than the others. Of course, compared with the polyimide derived from 4,4′-binaphthyl-1,1′,8,8′-tetracarboxylic dianhydride and ODA prepared by Gao and Wang [34], which only dissolved in *m*-cresol and TCE, the polyimides derived from unsymmetric phthalic-thioether-naphthalic dianhydrides (TNTDAs) and ODA can be not only dissolved readily in *m*-cresol, TCE, but also dissolved readily in NMP, and partially dissolved in DMAc, DMF, and chloroform. Additionally, the polyimide **5**(**4d**) showed better solubility than the polyimide derived

Table 1 Inherent viscosity (η_{inh}), film properties, and solubility behavior of the polyimides

Polymers	η_{inh}^{a}	Solubility[b]							
		m-cresol	NMP	DMAc	DMF	TCE	$CHCl_3$	THF	CH
5(**3a**)	N/M	±	±	±	±	±	±	−	−
5(**4a**)	N/M	±	±	±	±	±	±	−	−
5(**3b**)	0.47	+	+	±	±	+	±	−	−
5(**4b**)	0.39	+	+	±	±	+	±	−	−
5(**3c**)	0.40	+	+	±	±	+	±	−	−
5(**4c**)	0.32	+	+	+	±	+	+	±	±
5(**3d**)	0.36	+	+	+	±	+	±	−	−
5(**4d**)	0.53	+	+	+	±	+	±	−	−
Ref [1][c]	0.48	+	±	±	±	+	−	−	−
Ref [2][d]	0.56[e]	NO	+	±	NO	+	±	NO	NO

[a] Inherent viscosity measured in *m*-cresol at 30 °C. *N/M* not measured due to low solubility in organic solvents listed in the table

[b] Qualitative solubility was tested with 20 mg of a sample (powder) in 2 mL of the solvent. + Soluble; ± partially soluble on heating; − insoluble even at elevated temperatures. *CH* Cyclohexane

[c] Made from 4,4-TDPA and ODA

[d] Made from BNTDA and TPER by Zheng and Wang [44]. *NO* not measured

[e] Inherent viscosity measured in NMP at 30 °C

Table 2 Elemental analysis of the polyimides

Polymers	Calculated (%)				Found (%)			
	C	H	N	S	C	H	N	S
5(3a)	69.64	2.70	6.25	7.15	69.93	3.10	6.44	6.86
5(4a)	69.64	2.70	6.25	7.15	69.32	3.05	6.60	6.83
5(3b)	71.10	2.98	5.18	5.93	70.86	3.02	5.52	5.88
5(4b)	71.10	2.98	5.18	5.93	70.72	3.13	5.43	5.69
5(3c)	72.14	3.19	4.43	5.07	72.02	3.50	4.75	4.98
5(4c)	72.14	3.19	4.43	5.07	72.20	3.47	4.71	4.84
5(3d)	72.14	3.19	4.43	5.07	71.96	3.51	4.75	4.82
5(4d)	72.14	3.19	4.43	5.07	72.41	3.53	4.81	4.80

from BNTDA and TPER probably because the thioether linkage is more flexible than ketone linkage [44].

Tensile properties

The tensile properties of the polyimides derived from TNTDAs measured with an Instron model 5567 analyzer are tabulated in Table 3. All of the polyimides were able to be cast as transparent, flexible, and tough films and had good mechanical strength. These films had tensile strengths of 104.7–127.5 MPa, elongations at break of 4.1–5.8%, and tensile modulus of 2.95–4.37 GPa, which indicated excellent mechanical properties. The tensile strengths of the polyimides derived from unsymmetric phthalic-thioether-naphthalic dianhydrides is close to those derived from TDPA [49]. However, the values of tensile modulus are far larger than those derived from TDPA and are within the range of those derived from 4,4′-binaphthyl-l,1′,8,8′-tetracarboxylic dianhydride [34]. Evidently, the increase in tensile modulus is attributed to the large and rigid naphthalimide unit in the polymer backbone causing chain stiffness to increase [34]. Through increasing the free volume and decreasing the intermolecular force and packing ability of polymers generally decreases modulus and glass transition temperature, may be the large and rigid naphthalimide unit in the polymer backbone can partially compensates the disadvantage.

Electrical properties

As shown in Table 3, the polyimides films derived from TNTDAs show good dielectric properties, and possess low dielectric constants of 2.66–2.86 at a wider frequency range from 1 kHz to 1 MHz at room temperature and 70% relative humidity, which is significantly lower than that ($\varepsilon = 3.46$) of PI film prepared from BTDA and 4,4′-oxidianiline (ODA). Figure 5 gives the dependence of dielectric constants of PI films as a function of frequency. The polyimides **5** with unsymmetric phthalic-thioether-naphthalic dianhydride groups reveal a decreased dielectric constant in comparison with that of the corresponding analogues of the polyphthalimide such as BTDA/ODA. The low dielectric constant is attributed to the fact that the

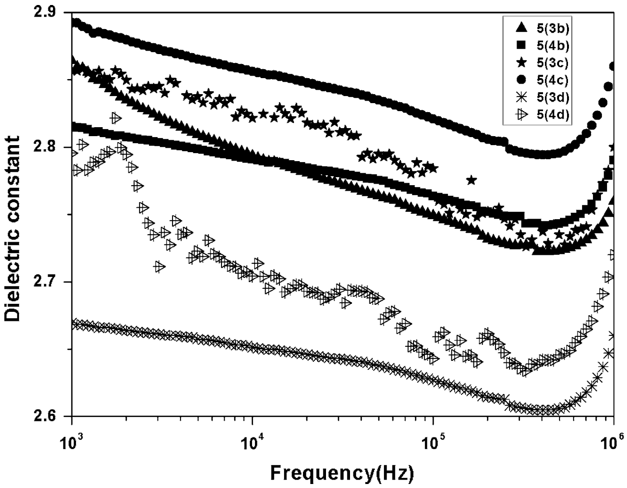


Fig. 5 The dependence of dielectric constants of PI films as a function of frequency

Table 3 Physical properties of polyimide films

Polymers	Initial modulus (GPa)	Strength at break (MPa)	Elongation at break (%)	H_2O% absorption[a]	Dielectric constant (10 kHz)	Dielectric constant (100 kHz)	Dielectric constant (1 MHz)
5(3b)	3.62	127.5	5.4	0.30	2.79	2.75	2.76
5(4b)	4.37	104.7	3.4	0.54	2.79	2.76	2.79
5(3c)	2.95	119.5	5.8	0.42	2.82	2.78	2.80
5(4c)	3.20	111.5	5.5	0.76	2.86	2.82	2.86
5(3d)	3.17	108.7	5.1	0.51	2.65	2.63	2.66
5(4d)	3.34	108.1	4.8	0.42	2.70	2.64	2.72
Ref [3][b]	3.42	146.0	11	2.16	3.53	3.50	3.46

[a] Moisture absorption of polyimide films were measured by immersing the films of these polyimides in distilled water at 25 °C for 100 h

[b] A poly(ether imide) was synthesized from 4,4′-oxydianiline and benzophenone tetracarboxylic dianhydride in our laboratory. The inherent viscosity of its poly(amic acid) precursor was 1.39 dL/g

introduction of the unsymmetric phthalic-thioether-naphthalic dianhydride groups leads to the formation of configuration isomers of repeat units in the polymer backbone and causes the decrease in the intermolecular force and packing ability of the resulting polymers. These results suggest that the PIs containing unsymmetric groups loosen the polymer packing and increased the free volume, subsequently leading to reducing dielectric constant [27, 40, 41, 50]. Interestingly, the dielectric constants of all the polyimides **5**(**3**) were slightly lower than the corresponding polyimides **5**(**4**), which may be attributed to the fact that the polyimides with 3-linked phthalimide units had larger free volume [49]. It was found that polyimides **5** also had low moisture absorption of 0.30–0.76% in distilled water at 25 °C for 100 h. The low moisture absorption is attributed to the fact that the polyimides **5** contained the water proofing effect probably because of the asymmetric phthalic–naphthalimide groups which were more effective than symmetric phthalimide groups [51]. The low water uptakes ensured that the PIs had stable dielectric constants. These results indicate that introducing asymmetric phthalic–naphthalimide groups into the polyimide structure is effective to loosen the polymer packing, subsequently leading to reduce the moisture absorption and stabilize the dielectric constant. The stability of the dielectric constant is important for interlayer dielectrics in microelectronic devices.

Thermal properties

The DSC and TGA were used to investigate the thermal properties of the polyimide films, and some of the thermal behavior data are tabulated in Table 4. The glass transition temperatures (T_g) were determined by DSC (Fig. 6). Glass transition temperatures (T_g) are defined as the temperature at the midpoint of the baseline shift; all PIs based on TNTDAs had high T_g (>259 °C). In comparison with the T_g (263 °C) of the polyimide derived from 4,4-TDPA and ODA, the T_g value of 4-TNTDA-based analogue **5**(**4b**) increased by 66 °C. Evidently, the increase in T_g is attributed to the large and rigid naphthalimide unit in the polymer main chain causing chain stiffness to increase. The T_g values of the polymers derived from 3-TNTDA displayed higher than that of the polymers derived from 4-TNTDA, which may be resulted from *ortho*-positioned larger rigid phthalic imide groups. The steric hindrance effect of *ortho*-positioned larger rigid phthalic imide groups is much larger than that of *meta*-positioned phthalic imide groups. Dynamic thermogravimetry showed the relatively good thermal stability of the polyimides derived from TNTDAs. As shown in Fig. 7, the polyimides based on TNTDAs exhibit good thermal stability of up to 500 °C. Residual weights ranging from 52 to 55% are observed at 800 °C in air. Their 5% weight-loss temperatures ($T_{5\%}$) in nitrogen were recorded at 487–520 °C, which is similar to the thermal stability of polyimides based on bis(phthalic anhydride)s, such as the polyimides derived from 4,4′-TDPA and ODA (whose $T_{5\%}$ is 525 °C in nitrogen atmospheres) [49].

Table 4 Thermal properties of the polyimides

Polymers	T_g (°C)[a]	$T_{5\%}$ (°C)[b]	Char yield (%) (°C)[c]
5(3a)	350	491	55
5(4a)	347	520	55
5(3b)	337	487	54
5(4b)	329	502	53
5(3c)	300	499	52
5(4c)	292	504	53
5(3d)	272	506	52
5(4d)	259	499	54
Ref [1][d]	263	525	56

[a] Temperature at which the middle of change of the heat capacity occurred from the second DSC heating scan at heating rate of 20 °C/min

[b] Temperature at which 5% weight loss recorded by thermogravimetry at a heating rate of 10 °C/min

[c] Residual weight percentage at 800 °C in nitrogen

[d] Made from 4,4-TDPA and ODA

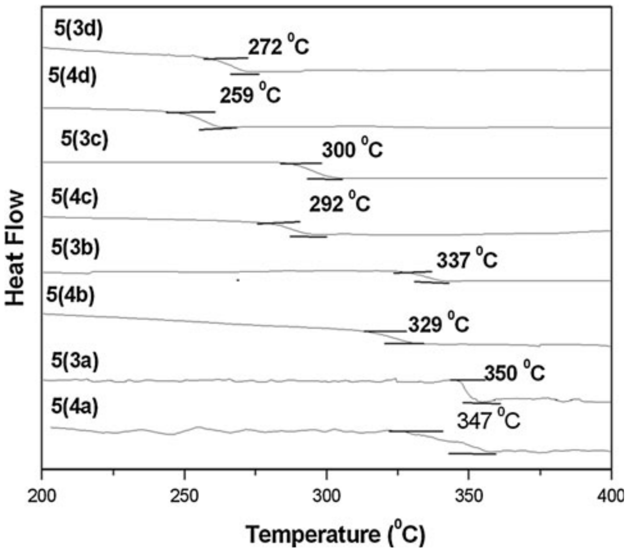


Fig. 6 DSC curves of PI films (in nitrogen atmosphere, 20 °C/min)

Conclusions

Two novel geometric unsymmetric dianhydride isomers integrated phthalic anhydride with naphthalic anhydride into the same molecules were designed and synthesized.

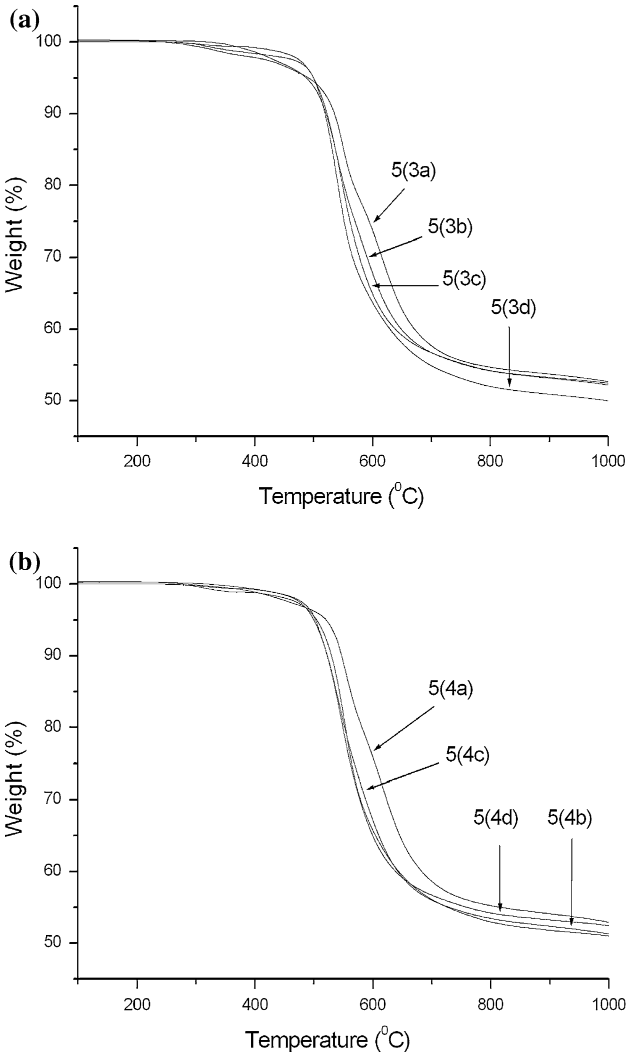


Fig. 7 **a** and **b**. TGA curves of polyimides **5** at a scan rate of 10 °C/min in N_2

A series of PIs were prepared by the polycondensation of TNTDAs and PDA, ODA, TPEQ, and TPER in *m*-cresol. The polyimides based on TNTDAs show a lower dielectric constant (2.66–2.86) than symmetric polyimides derived from bis(naphthalic anhydride)s and/or bis(phthalic anhydride)s owing to the introduction of the unsymmetric naphthalic/phthalic groups and thus resulting in less efficient chain packing and an increase in the free volume of the polymer. The polyimides derived from TNTDAs show good solubility, low moisture absorption (0.30–0.76%), high modulus, and relatively high glass transition temperatures (259–349 °C) compared to the polyimides-based bis(phthalic anhydride)s.

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