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Soluble polyimides from unsymmetrical diamine containing benzimidazole ring and trifluoromethyl pendent group

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ABSTRACT

New unsymmetrical diamine monomer containing both the benzimidazole ring and trifluoromethyl group, 6,4′-diamino-2′-trifluoromethyl-2-phenylbenzimidazole, was prepared from 2-bromo-5-nitrobenzotrifluoride and 4-nitro-1,2-phenylenediamine. The monomer was polymerized with ODPA, BTDA and 6FDA by using one-pot synthetic method to obtain corresponding polyimides. All the prepared polyimides were soluble in aprotic polar solvents. Incorporation of trifluoromethyl groups unsymmetrically in the rigid polyimides improves their solubility without decreasing their physical properties. The polymers showed high glass transition temperature ($T_g = 289$–$352\ ^\circ C$), high thermal stability ($T_{d10} > 500\ ^\circ C$), and relatively low coefficient of thermal expansion (CTE = 26.1–46.4 ppm/°C) because of their rigid-rod like structure. Also, they showed low refractive indexes ($n = 1.46$–1.68) and low birefringence ($\Delta \approx 0.02$) due to the trifluoromethyl pendent groups that interrupt chain packing and increase free volume.

1. Introduction

Aromatic polyimides are well known as highly heat resistant materials and have been widely used in many applications such as electronics, coatings, composite materials, and membranes [1]. Polyimides are often insoluble and infusible in their fully imidized form due to their rigid chain characteristics, leading to processing difficulties. Thus, polyimide processing is generally carried out with poly(amic acid) intermediate, and then converted to polyimide *via* rigorous thermal and/or chemical treatment [2,3]. However, this process has several inherent problems such as emission of volatile by-products (e.g. H_2O) and storage instability of poly(amic acid) intermediate [4]. Also, it is reported that the poly(amic acid) has corrosion problem with copper interconnecting metal [5–8].

To overcome these problems, much of research efforts have been focused on the synthesis of soluble and processable polyimides in fully imidized form without deterioration of their own excellent properties [9–11]. Several successful approaches to synthesize soluble polyimides including insertion of flexible linkage [12–16] or bulky substituents on the main chain [17–24] and utilization of noncoplanar [25–29] or alicyclic [30–34] monomers have been introduced in last decade. Copolymerization with two different diamine or dianhydride monomers is also known as an effective way to improve the solubility of insoluble polyimides [35–37]. Recently, we reported that introducing trifluoromethyl pendent groups unsymmetrically in the polyimide backbone can enhance the solubility of the resulting polymers dramatically [38]. Most of the above approaches for soluble polyimides are aimed at reduction of several types of chain–chain interaction, such as chain packing (e.g. crystallinity) and charge transfer and electronic polarization interactions [2,3,39,40].

Among many diamine monomers for soluble polyimides, 2,2′-bis(trifluoromethyl)-4,4′-diaminobiphenyl (TFDB) has unique structure, rigid but non-planar structure with two bulky trifluoromethyl groups [17–19]. The polymers made from TFDB show relatively low dielectric constant (ε) and low moisture absorption without loosing other physical properties. Since the velocity of pulse propagation is inversely proportional to the square root of the ε of the medium, a reduction of ε of the insulating material translates directly into reduction of delay time [41]. While rigid-rod-like polyimides with planar structure have many desirable properties including low thermal expansion and excellent mechanical strength, they are often insoluble and show poor adhesion properties [42]. It is known that the incorporation of primary or secondary amine groups, which can interact with the metal, in the polymer chain enhances the adhesion to the metal [43]. In our previous study, the soluble polyimide copolymers containing benzimidazole rings and trifluoromethyl groups were prepared

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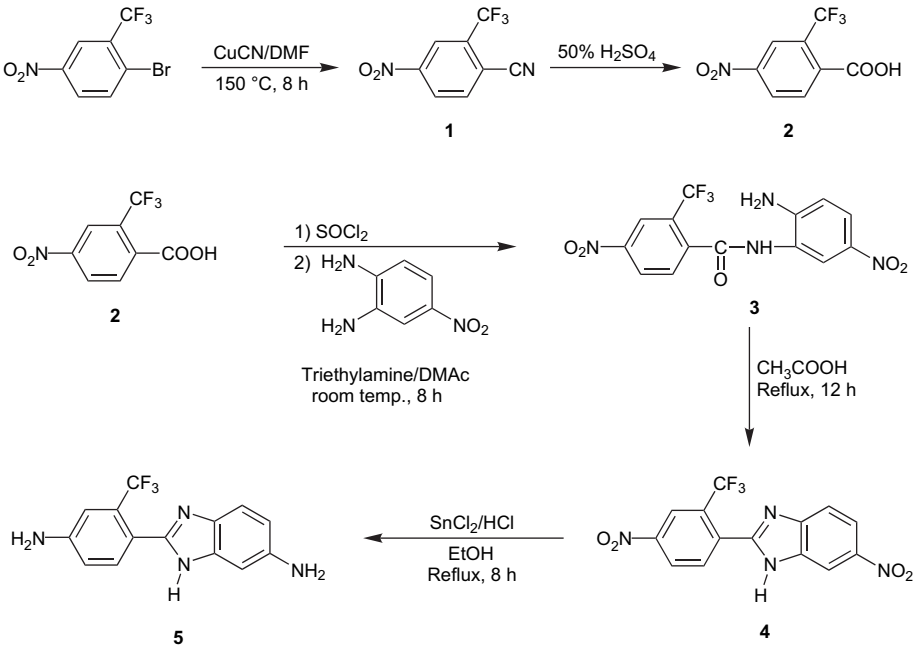


Scheme 1. Synthesis of monomer **5**.

from 6,4′-diamino-2-phenylbenzimidazole (BIA) and 2,2′-bis(trifluoromethyl)-4,4′-diaminobiphenyl (TFDB) with an appropriate aromatic dianhydride (BTDA), and they showed excellent thermal properties, low refractive indexes (RIs) due to the presence of trifluoromethyl groups, and high adhesive force to copper due to the presence of secondary amine in the benzimidazole rings [44–46].

In this study, the new diamine monomer containing both benzimidazole ring and trifluoromethyl group was synthesized and polymerized to make soluble polyimides. The new diamine monomer, 6,4′-diamino-2′-trifluoromethyl-2-phenylbenzimidazole (**5**), was prepared from 2-bromo-5-nitrobenzotrifluoride and 4-nitro-1,2-phenylenediamine according to Scheme 1. Though the monomer has rigid structure without any flexible linking group, it is expected that it can give sufficient solubility due to its unsymmetrical and twisted structure. Because it has both secondary amine group and trifluoromethyl group, the polyimide prepared from the diamine shows many desirable properties such as low dielectric constant and high adhesion properties to the inert metal such as copper.

2. Experimental section

2.1. Materials

2-Bromo-5-nitrobenzotrifluoride (purchased from Marshallton), copper(I) cyanide and 4-nitro-1,2-phenylenediamine (purchased from Aldrich) were used as-received. 4,4′-Oxydiphthalic anhydride (ODPA), 3,3′,4,4′-benzophenone tetracarboxylic dianhydride (BTDA) and 4,4′-(hexafluoroisopropylidene)diphthalic anhydride (6FDA) were recrystallized from acetic anhydride, and then dried *in vacuo* at 150 °C for 24 h. *N*-Methyl-2-pyrrolidinone (NMP) was stirred in the presence of P_2O_5 overnight and then distilled under reduced pressure. Chlorobenzene was stirred in the presence of CaH_2 overnight and then distilled under nitrogen. Other commercially available reagent grade chemicals were used without further purification.

2.2. General measurement

^{1}H NMR and ^{13}C NMR spectra of the synthesized compounds were recorded on Bruker Fourier Transform AVANCE 400 (400.13 MHz for ^{1}H and 100.62 MHz for ^{13}C) nuclear magnetic resonance spectrometers. Chemical shift of NMR was reported in parts per million (ppm) using tetramethylsilane as an internal reference. Splitting patterns designated as s (singlet), d (doublet), dd (doublets of doublet), t (triplet), tt (triplets of triplet) and m (multiplet). FTIR spectra of the compounds were obtained with a Bruker EQUINOX-55 spectrophotometer using KBr pellet or film. Gel permeation chromatographic (GPC) diagrams were obtained with Younglin Autochro-GPC equipped with UV and RI detectors and packing column (Styragel HR 5 μm) using *N*,*N*-dimethylformamide as an eluent at 40 °C. Number and weight average molecular weights of the polymer were calculated on the basis of polystyrene standards. Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) were performed on a TA 2200 thermal analyzer system. Glass transition temperature (T_g) of the polymer was obtained with DSC instrument at a heating rate of 10 °C/min in N_2. TGA measurements were made at a heating rate of 10 °C/min in N_2. The refractive indices of the synthesized polyimides were measured in air with ca. 40% relative humidity using a Metricon 2010 prism coupler. The light source was a He–Ne laser of 632.8 nm wavelength, i.e., 474.08 THz frequency. All measurements were performed using a cubic zirconia prism of $n_{TE} = n_{TM} = 2.1677$. The refractive index (n) of films was measured in transverse electric (TE) and transverse magnetic (TM) modes by choosing the appropriate polarization of the incident laser beam, giving the in-plane refractive index ($n_{TE} = n_{xy}$) and the out-of-plane refractive index ($n_{TM} = n_z$), respectively. The dielectric constant (ε) was estimated from the measured refractive indices by the simple Maxwell equation: $\varepsilon = n^2$.

2.3. Monomer synthesis

2.3.1. 2-Cyano-5-nitrobenzotrifluoride (*1*)

2-Bromo-5-nitrobenzotrifluoride (27.0 g, 100 mmol), CuCN (10.0 g, 112 mmol) and DMF (100 mL) were placed in a 250 mL three-necked round-bottom flask. The solution was heated to 150 °C and refluxed for 8 h under N_2. The reaction mixture was cooled to room temperature and mixed with workup solution ($FeCl_3$ 50 g, conc. HCl 30 mL, water 500 mL). The mixture was extracted with ethyl acetate and collected organic layer was

washed with 10% (v/v) HCl (aq) and dried. After removal of ethyl acetate in a rotary evaporator, dark brownish liquid was obtained. The desired product was separated by vacuum distillation at 80 °C (15.8 g, yield 73.1%). ^{1}H NMR (DMSO-d_6, 400 MHz, ppm): 8.69 (dd, 1H, J = 8.41, 0.98 Hz), 8.63 (s, 1H), 8.50 (d, 1H, J = 8.51 Hz). ^{13}C NMR (DMSO-d_6, 100 MHz, ppm): 149.8, 137.5, 132.4 (q, J_{C-F} = 33.4 Hz), 128.1, 122.0 (q, J_{C-F} = 5.0 Hz), 121.5 (q, J_{C-F} = 272.4 Hz), 114.2.

2.3.2. 4-Nitro-2-trifluoromethyl-benzoic acid (**2**)

A mixture of 2-cyano-5-nitrobenzotrifluoride (**1**) (19.0 g, 87.9 mmol) and 60 mL of 50% H_2SO_4 solution was stirred at 160 °C for 1 h. After 30 min, the solution became homogeneous. The reaction mixture was cooled, poured into cold water, neutralized with NaOH solution and extracted with ethyl acetate, followed by drying over $MgSO_4$ and concentration by a rotary evaporator. Then, the crude product was sublimated in vacuum at 130 °C to give a yellow solid (18.0 g, yield 87.1%). ^{1}H NMR (DMSO-d_6, 400 MHz, ppm): 8.56 (dd, 1H, J = 8.39, 2.00 Hz), 8.50 (d, 1H, J = 1.72 Hz), 8.07 (d, 1H, J = 8.43 Hz). ^{13}C NMR (DMSO-d_6, 100 MHz, ppm): 164.6, 149.5, 135.2, 128.4 (q, J_{C-F} = 4.8 Hz), 126.1, 121.8 (q, J_{C-F} = 33.6 Hz), 121.8 (q, J_{C-F} = 271.7 Hz).

2.3.3. 2′-Amino-2-trifluoromethyl-4,5′-dinitrobenzanilide (**3**)

4-Nitro-2-trifluoromethyl-benzoic acid (**2**) (16.5 g, 70.2 mmol) in thionyl chloride (80 mL) was placed in a one-neck round-bottom flask and then refluxed for 6 h under anhydrous atmosphere. The yellowish reaction mixture was cooled to room temperature and the residual thionyl chloride was removed under reduced pressure. The obtained 4-nitro-2-trifluoromethyl-benzoylchloride was used at the next reaction step without further purification. To a mixture of 4-nitro-1,2-phenylenediamine (10.7 g, 69.9 mmol) and 100 mL of anhydrous NMP was added dropwise 4-nitro-2-trifluoromethyl-benzoylchloride in 90 mL of anhydrous NMP under nitrogen atmosphere at 0 °C. The reaction mixture was stirred overnight at room temperature and then poured into water, filtered and dried in a vacuum oven at 100 °C to give brown solid (24.1 g, yield 92.7%). ^{1}H NMR (DMSO-d_6, 400 MHz, ppm): 10.17 (s, N*H*), 8.65 (dd, 1H, J = 8.44, 2.23 Hz), 8.56 (d, 1H, J = 2.22 Hz), 8.30 (d, 1H, J = 8.44 Hz), 8.25 (d, 1H, J = 2.75 Hz), 7.93 (dd, 1H, J = 9.12, 2.68 Hz), 6.83 (d, 1H, J = 9.16 Hz), 6.57 (s, NH_2). ^{13}C NMR (DMSO-d_6, 100 MHz, ppm): 164.8, 149.6, 148.0, 140.9, 135.5, 131.1, 127.5, 127.3 (q, J_{C-F} = 32.6 Hz), 123.8, 122.6 (q, J_{C-F} = 272.7 Hz), 122.2, 121.7 (q, J_{C-F} = 4.8 Hz), 120.1, 114.1.

2.3.4. 6,4′-Dinitro-2′-trifluoromethyl-2-phenylbenzimidazole (**4**)

2′-Amino-2-trifluoromethyl-4,5′-dinitrobenzanilide (**3**) (18.5 g, 50.0 mmol) and 250 mL of acetic acid were placed in a one-neck round-bottom flask and then refluxed for 12 h. The reaction mixture was cooled, and then poured into cold water, filtered and dried in a vacuum oven at 100 °C to give yellow solid (12.9 g, yield 73.3%). ^{1}H NMR (DMSO-d_6, 400 MHz, ppm): 8.68 (m, 2H), 8.58 (s, 1H), 8.20 (d, 2H, J = 8.39 Hz), 7.87 (d, 1H, J = 8.91 Hz). ^{13}C NMR (DMSO-d_6, 100 MHz, ppm): 151.9, 148.5, 143.3, 142.9, 139.1, 134.7, 134.3, 129.3 (q, J_{C-F} = 32.4 Hz), 127.5, 122.5 (q, J_{C-F} = 272.3 Hz), 122.2 (q, J_{C-F} = 5.4 Hz), 118.5, 115.3, 113.3.

2.3.5. 6,4′-Diamino-2′-trifluoromethyl-2-phenylbenzimidazole (**5**)

A mixture of dinitro compound **4** (12.5 g, 35.5 mmol), anhydrous $SnCl_2$ (41.0 g, 216 mmol), and 160 mL of 95% ethanol was stirred while 80 mL of conc. HCl was added slowly. After addition of HCl was over, the mixture was refluxed for 12 h. Excess ethanol was evaporated and the remaining solution was poured into 300 mL of distilled water. The solution was basified with 10% NaOH solution and the precipitate was filtered off, washed with hot water and cold methanol, and recrystallized from ethanol to give pale brown product (8.49 g, yield 81.7%). ^{1}H NMR (DMSO-d_6, 400 MHz, ppm): 11.79 (br, N*H*), 7.37 (d, 1H, J = 8.30 Hz), 7.23 (d, 1H, J = 8.44 Hz), 7.06 (s, 1H), 6.88 (dd, 1H, J = 8.45, 2.23 Hz), 6.71 (s, 1H), 6.55 (dd, 1H, J = 8.12, 2.03 Hz), 5.58 (s, NH_2), 4.65 (br, NH_2). ^{13}C NMR (DMSO-d_6, 100 MHz, ppm): 149.7, 147.6, 144.5, 135.9, 132.9, 128.3 (q, J_{C-F} = 32.1 Hz), 124.0 (q, J_{C-F} = 273.6 Hz), 118.7, 116.9, 115.9, 111.0, 110.8, 110.7, 94.5.

2.4. Polymerization

2.4.1. General procedure of the polymerization

Polymerization was conducted in a 25 mL three-necked round-bottom flask equipped with a nitrogen inlet, mechanical stirrer, Dean–Stark trap, and a reflux condenser. The flask was charged with **5** (1 mmol), dianhydride monomer (1 mmol) and NMP (16 wt%) and then the reaction mixture was stirred for 4 h. After resulted poly(amic acid) solution was diluted with NMP (8 wt%), temperature was raised up to 190 °C slowly and the reaction mixture was stirred for 12 h at 190 °C. Chlorobenzene was periodically removed from the Dean–Stark trap and replaced with dry chlorobenzene to ensure cyclodehydration. The polymer was precipitated into a 500 mL of vigorously stirred methanol/water mixture and then filtered. The precipitated polymer was washed with hot water and methanol repeatedly, and dried in vacuum oven at 100 °C for 24 h to give pale yellow polyimide.

2.4.2. ***PI-6***

Polymerization of the mixture of **5** (0.7924 g, 2.71 mmol), 4,4′-oxydiphthalic anhydride (ODPA) (0.8410 g, 2.71 mmol) and 10 mL of NMP gave 1.42 g (yield 96.2%) of fibrous **PI-6**. η_{inh} = 0.69 dL/g with a concentration 0.5 dL/g in DMAc at 30 °C. ^{1}H NMR (DMSO-d_6, 400 MHz, ppm): 13.13 (br, N*H*), 8.11 (m, 3H), 8.00 (dd, 2H, J = 20.52, 8.44 Hz), 7.66 (m, 6H), 7.32 (d, 1H, J = 8.52 Hz). ^{13}C NMR (DMSO-d_6, 100 MHz, ppm): 166.6 (d, J = 18.2 Hz), 165.8 (d, J = 13.8 Hz), 160.9 (q, J = 12.1 Hz), 150.1, 134.6 (d, J = 12.8 Hz), 133.5, 133.1, 130.8, 129.2, 128.2 (q, J_{C-F} = 31.3 Hz), 127.3 (q, J = 8.8 Hz), 126.2 (d, J = 30.2 Hz), 125.2 (m), 123.2 (q, J_{C-F} = 272.2 Hz), 113.8 (d, J = 20.1 Hz), 112.2.

2.4.3. ***PI-7***

Polymerization of the mixture of **5** (0.4985 g, 1.71 mmol), 3,3′,4,4′-benzophenone tetracarboxylic dianhydride (BTDA) (0.5496 g, 1.71 mmol) and 6.5 mL of NMP gave 0.82 g (yield 82.9%) of fibrous **PI-7**. η_{inh} = 0.66 dL/g with a concentration 0.5 dL/g in DMAc at 30 °C. ^{1}H NMR (DMSO-d_6, 400 MHz, ppm): 13.15 (br, N*H*), 8.18–8.33 (m, 7H), 8.45 (q, 2H, 8.60 Hz), 7.80 (s, 2H), 7.35 (s, 1H). ^{13}C NMR (DMSO-d_6, 100 MHz, ppm): 193.4 (t, J = 7.7 Hz), 166.7, 165.9, 150.1, 143.3, 141.7 (q, J = 9.1 Hz), 135.8 (d, J = 27.1 Hz), 134.8 (d, J = 23.2 Hz), 134.2, 133.4, 133.1, 131.9 (d, J = 15.9 Hz), 130.8, 129.3, 128.5 (q, J_{C-F} = 31.4 Hz), 125.3, 124.0, 123.8, 123.2 (q, J_{C-F} = 272.3 Hz), 119.1, 111.5.

2.4.4. ***PI-8***

Polymerization of the mixture of **5** (0.7222 g, 2.47 mmol), 4,4′-(hexafluoroisopropylidene)diphthalic anhydride (6FDA) (1.0977 g, 2.47 mmol) and 11.4 mL of NMP gave 1.77 g (95.2% yield) of fibrous **PI-8**. η_{inh} = 0.57 dL/g with a concentration 0.5 dL/g in DMAc at 30 °C. ^{1}H NMR (DMSO-d_6, 400 MHz, ppm): 13.15 (br, NH), 8.25 (m, 2H), 8.15 (s, 1H), 8.01 (m, 4H), 7.81 (m, 4H), 7.35 (d, 1H, J = 7.92 Hz). ^{13}C NMR (DMSO-d_6, 100 MHz, ppm): 166.6 (d, J = 12.4 Hz), 165.7 (d, J = 15.6 Hz), 150.1, 143.5, 137.5 (q, J = 9.1 Hz), 135.9 (m), 133.1 (m), 131.0, 129.5, 128.5 (q, J_{C-F} = 31.2 Hz), 126.1, 125.5, 124.6 (m), 123.2 (q, J_{C-F} = 272.1 Hz), 122.4, 111.82, 111.42.

2.5. Adhesion to copper test

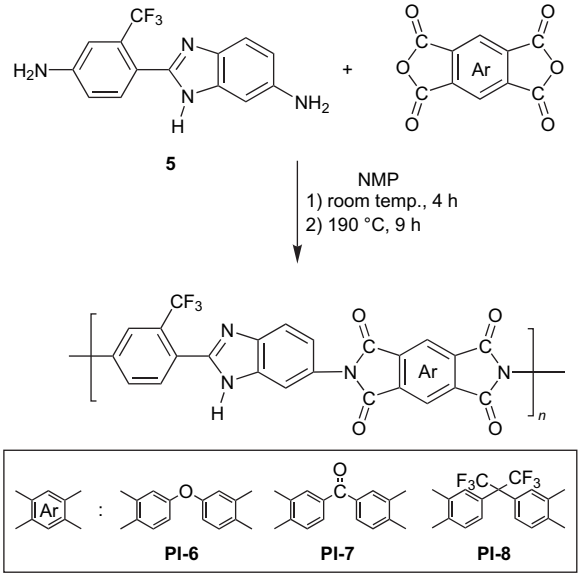
The polyimide solution was coated onto the Cu plates and dried at 80 °C for 3 h and 70 °C in a vacuum for 2 h to prepare 8–13 μm

thick film. The supporting frame was made by epoxy molding with bisphenol-A–(epichlorohydrin) (25g) and triethylenetetramine (3g). The epoxy resin was placed in a silicone molder and cured at room temperature for a day. A 90° peel test was conducted by peeling the Cu plate. The locus of the fracture was the interface of copper and polyimide.

3. Results and discussion

2-Bromo-5-nitrobenzotrifluoride was reacted with copper cyanide in DMF to afford 2-cyano-5-nitrobenzotrifluoride (**1**), which was consequently hydrolyzed with 50% H_2SO_4 solution. The obtained 4-nitro-2-trifluoromethyl-benzoic acid (**2**) was then refluxed in thionyl chloride and, without isolation, reacted with equimolar amount of 4-nitro-1,2-phenylenediamine at room temperature in the presence of triethylamine as an acid acceptor to yield 2′-amino-2-trifluoromethyl-4,5′-dinitrobenzanilide (**3**). This step was found to give only one product, because the nitro group predominantly deactivates the amino group at the *para* position. The amide linkage was formed by the amine group at *meta* position to the nitro group in 4-nitro-1,2-phenylenediamine in the reaction condition employed. The benzanilide **3** was cyclo-dehydrated to the corresponding benzimidazole (**4**) by refluxing at 150 °C in glacial acetic acid. The dinitro compound **4** was hydrogenated with stannous chloride and HCl to give the corresponding diamine monomer **5**. The chemical structure of the monomers was confirmed by spectral analyses.

The polyimides were prepared from **5** and commercially available aromatic dianhydrides, such as ODPA, BTDA and 6FDA in *N*-methyl-2-pyrrolidone (NMP) *via* one-pot synthetic method as shown in Scheme 2. The polymerization was carried out by reacting stoichiometric amounts of diamine monomer **5** with aromatic dianhydrides at a concentration of 16 wt% solids in NMP. The ring-opening polyaddition at room temperature for 4 h yielded poly(amic acid) solutions. After dilution of the solution to 8 wt%, subsequent cyclodehydration by heating at 190 °C for 8 h gave the fully imidized polyimides. Imidization was carried out by azeotropic distillation of chlorobenzene without any catalyst. Because azeotroping agents are non-solvents to the conventional polyimides, the maximum volume of the azeotroping agent in imidization media should be less than 20% (v/v) to prevent premature precipitation. After imidization, precipitation was not occurred and



Scheme 2. Synthesis of polyimides.

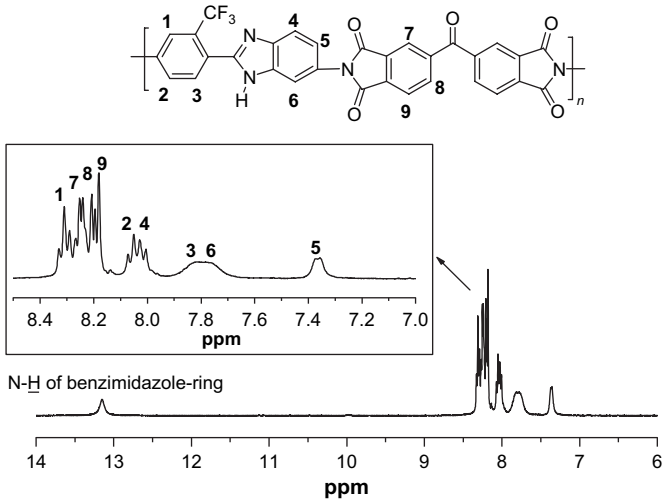


Fig. 1. ^{1}H NMR spectrum of **PI-7** (400 MHz, in DMSO-d_6).

the reaction mixture remained in solution. The inherent viscosities of the polyimides were 0.57–0.69 dL/g.

The structures of the synthesized polyimides, **PI-6**–**PI-8**, were confirmed by FTIR and NMR spectroscopies. ^{1}H NMR spectrum of **PI-7** is shown in Fig. 1. The ^{1}H NMR spectra of the polyimides showed no amide and acid protons, which indicates full imidization. The FTIR spectra of the polyimides showed the absorption bands at 1780 (C═O asymmetric stretching), 1720 (C═O symmetric stretching), 1370 (C–N stretching), and 720 (C═O bending) cm^{-1} corresponding to the characteristic imide bands. Also, TGA and DSC measurements that did not show any transition corresponding to imidization imply that the polyimides prepared by using solution imidization method are fully imidized. The UV–vis spectra of polyimides showed that the cut-off wavelengths for the polyimides are around 400 nm.

The solubility of the synthesized polymers is summarized in Table 1. The synthesized polyimides were well dissolved in aprotic polar solvents such as NMP, DMF, DMAc and DMSO at room temperature, and formed tough and transparent films by solution-casing. Rigid-rod polyimides are often insoluble in organic solvent, but the synthesized polyimides showed good solubilities. The enhanced solubility of the resulting polyimides is attributed not only to the bulkiness of the pendent trifluoromethyl groups but also to the unsymmetrical structure coming from the diamine monomer.

The physical and thermal properties of the synthesized polyimides are summarized in Table 2. The number-average molecular weight of the polymers measured by GPC using DMF as an eluent and polystyrenes as standards was in the range 3.35×10^4–8.64×10^4, indicating that the high molecular weight polymers were synthesized. Thermal properties of the polyimides were evaluated by TGA, DSC, and TMA. Ten percent weight loss temperatures of the polyimides were in the range of 527–541 °C in nitrogen. TGA results indicated that all of the polymers were stable up to around 500 °C in nitrogen. All of the polyimides showed high glass transition temperatures (T_gs) and low thermal expansion

Table 1
Solubility of the synthesized polyimides

PI	NMP	DMAc	DMF	DMSO	*m*-Cresol	THF	$CHCl_3$	CB	Acetone
6	++	++	++	++	+	+	−	−	−
7	++	++	++	++	±	±	−	−	−
8	++	++	++	++	±	±	−	−	−

++: Soluble at room temperature; +: soluble on heating; ±: partially soluble; −: insoluble. NMP, *N*-methylpyrrolidone; DMAc, *N*,*N*-dimethylacetamide; DMF, *N*,*N*-dimethylformamide; DMSO, dimethyl sulfoxide; THF, tetrahydrofuran; $CHCl_3$, chloroform; CB, chlorobenzene.

Table 2
Physical properties of the synthesized polyimides

PI	η_{inh}[a] (dL/g)	M_n[b] ($\times 10^4$)	M_w[b] ($\times 10^4$)	PDI[b]	T_g[c] (°C)	T_{d10}[d] (°C)	CTE[e] (ppm/°C)
6	0.69	3.35	6.63	1.98	289	538	46.4
7	0.66	8.64	21.58	2.50	341	541	26.1
8	0.57	5.16	11.68	2.26	352	527	41.1

[a] Inherent viscosity, measured at a concentration of 0.5 g/dL in DMAc at 30 °C.
[b] Measured by GPC using DMF as an eluent and polystyrenes as standards.
[c] Measured by DSC with a heating rate of 10 °C/min in N_2.
[d] The 10% weight loss temperature measured by TGA with a heating rate of 10 °C/min.
[e] Measured by TMA at a temperature range from 50 to 250 °C with a heating rate of 5 °C/min in N_2.

coefficients (CTEs). The T_gs of these polymers are 289, 341, and 352 °C (Fig. 2) and the CTEs are 46.4, 26.1, and 41.1 ppm/°C for **PI-6**–**PI-8**, respectively. Especially, the glass transition temperature (T_g) of **PI-6** was lower than those of **PI-7** and **PI-8**. It seems that the low T_g of **PI-6** may stem from the overall increasing chain mobility of the polymer backbone because ether linkage of the ODPA increases its chain flexibility. Therefore, the difference of chain rigidity due to the different structure of the dianhydride employed also affected T_g and CTE values of the polyimides. Generally, CTE decreases with increasing T_g for the polymers with similar structures. However, **PI-7** showed lower CTE than **PI-8**, even though the T_g of **PI-8** was higher than that of **PI-7**. It seems that the chain structure of **PI-7** which has more planar shape than **PI-8** containing a kinked hexafluoroisopropylidene group affected the CTE more than the glass transition temperature of the polymer.

Results of in-plane and out-of plane refractive index (n_{xy} and n_z) measurement at 632.8 nm are summarized in Table 3. All the synthesized polyimides had much lower refractive indexes (n) and birefringence (Δ) than the conventional polyimides such as Kapton™. Generally, the polyimides containing trifluoromethyl pendent groups have low refractive index due to the low polarizability of fluorine. The synthesized polyimides show slightly higher n_{xy} than n_z. For most of the polyimides, n_{xy} is higher than n_z because the polarizability along the chain axis is higher than that of normal to the chain axis [47]. All of the synthesized polyimides have low refractive indices (n) and birefringence (Δ) due to the trifluoromethyl pendent groups that interrupt chain packing and increase free volume. Dielectric constants (ε) of the synthesized polyimides were estimated from the measured n values using Maxwell's equation ($\varepsilon = n^2$), and the results are summarized in Table 3. All the synthesized polyimides had relatively low ε and anisotropy.

The adhesion to the interconnecting metal is a factor critical to the interlevel dielectric application, as previously described. Benzimidazole rings are known to promote adhesion to copper, but usually the polymers containing fluorine groups have poor adhesion property to most substrates [48]. Because the synthesized

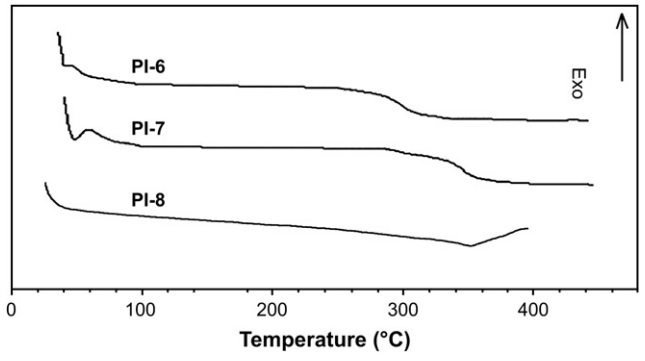


Fig. 2. DSC curves of the polyimides (heating rate, 10 °C/min, in N_2).

Table 3
Optical and dielectric properties of the synthesized polyimides

PI	Optical properties[a]				Dielectric properties[b]				d[c] (μm)
	n_{xy}	n_z	n_{av}	Δ	ε_{xy}	ε_z	ε_{av}	Δ	
6	1.6451	1.6342	1.6415	0.0109	2.71	2.67	2.69	0.04	5.1
7	1.6627	1.6427	1.6575	0.0156	2.76	2.70	2.75	0.06	4.7
8	1.4695	1.4617	1.4656	0.0078	2.16	2.14	2.15	0.02	3.3

[a] Measured at 632.8 nm (474.58 THz).
[b] Estimated from refractive indices using Maxwell's equation.
[c] Film thickness.

polymers have both the benzimidazole ring and the trifluoromethyl group on each repeating unit, it is interesting to see how they affect the adhesion of the polyimides. The adhesion test to copper was conducted by a 90° peel test, as reported in the previous paper [44]. The locus of failure was not the interface of epoxy and polyimides but that of copper and polyimides. The representative polyimide (**PI-7**) shows good adhesion property. When it was utilized as an adhesive layer, it showed the adhesion strength near 325 N/m in the 90° peel test which is somewhat lower than the peel strength of the previously reported polyimide prepared from 6,4′-diamino-2-phenylbenzimidazole (BIA) and TFDB with incorporation of 75 mol% of BIA unit presumably because of its high fluorine content [44]. However, since the peel strength of 300 N/m or greater is acceptable to most microelectronic applications [49], the synthesized polyimides are good candidates for interlevel dielectric applications without any adhesion promoter.

4. Conclusion

New series of soluble polyimides containing both benzimidazole ring and trifluoromethyl groups are prepared from the unsymmetrical diamine monomer and several dianhydrides by using one-pot synthetic method. Incorporation of trifluoromethyl groups unsymmetrically in rigid polyimides improves their solubility without decreasing their physical properties. All of the synthesized polyimides showed similar T_g but somewhat lower thermal stability compared to the polyimides containing benzimidazole rings without trifluoromethyl pendent groups. The polymers showed relatively low coefficient of thermal expansion due to the rigid-rod like structure. Also, they have low refractive indices (n) and birefringence.

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