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Preparation and characterization of new soluble benzimidazole–imide copolymers

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The present necessity to use heat-resistant materials in electronics justifies the scientific interest in different heterocyclic polymers. This paper is especially concerned with the preparation of novel heat-resistant polyimides having bisbenzimidazole moieties in the main chain and their applications as dielectric films. A soluble copolyimide was prepared by a two-step synthesis from aromatic dianhydrides and aromatic diamines. The bisbenzimidazole diamine was prepared by reduction of the corresponding dinitro compound. The diamine was reacted with various aromatic dianhydrides to prepare a series of alternating benzimidazole–imide copolymers *via* the poly(amic acid) precursors and thermal or chemical imidization. Monomers and polymers were characterized by conventional methods and their physical properties such as solution viscosity, solubility properties, thermal stability and thermal behaviour were studied. All copolymers were obtained in high yields having inherent viscosities η_{inh} that ranged from 0.60 to 0.98 dL g^{-1}. Thin films of the copolymer were tough and flexible, having tensile strengths as high as 100 MPa. Glass transition temperatures were observed between 275 and 328 °C. Thermogravimetric analyses indicated that the thermal degradation of poly(benzimidazole–imide) occurs around 530 °C, which is *ca.* 80 °C higher than polyimide, confirming that the introduction of the bisbenzimidazole component improved the thermal stability of polyimide.

1. Introduction

Polybenzimidazoles and polyimides are classes of high-temperature/high-performance polymers already commercialized.[1] They are heterocyclic polymers that are attractive because of their outstanding mechanical and dielectric properties at high temperatures.[2] They have been widely used for high temperature aerospace applications (Fig. 1).

Polyimides (PIs) are well known for their outstanding mechanical properties and thermal stability. Several polyimides have been developed that are suitable as adhesives, coatings and matrix resins, and have found a wide range of applications as high-performance materials in the aerospace and electronics industries.[3–5] However, further development of polyimides is required to meet the increasing demands on high-performance materials. In advanced polymer composites, PIs are just one of a number of resin families currently in use. There is a well-established need to produce polyimide resins that are processable and cost-effective, and can withstand temperatures of 316–371 °C for extended periods of time.[6] Polyimides are commonly synthesized from dianhydrides and diamines in a two-stage process: a soluble, high-molecular weight poly(amic acid) is generated at low or ambient temperatures in the first stage, and is subsequently converted *via* bulk, chemical or solution processes to fully cyclized polyimide during the second stage.[7,8]

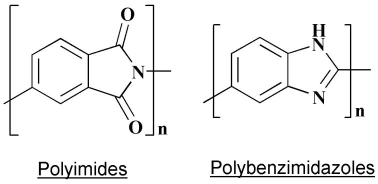

Fig. 1 Aromatic polybenzimidazoles and polyimides.

Polybenzimidazoles (PBIs) are a class of high-performance polymers that have received considerable attention in recent years because of their outstanding ability to withstand extreme conditions without an extensive loss of properties. They have, for example, been widely used in the aerospace industry, where thermal stability is a primary requirement. However, whereas in inert atmospheres the total weight loss of polybenzimidazoles is negligible up to 600 °C, a much more pronounced effect has been observed for the same temperature range in oxidizing environments. PBIs are generally prepared *via* melt polymerization of aromatic bis(*o*-diamine)s with aromatic dicarboxylic acid derivatives.[9] However, the reactions must be carried out at very high temperatures. Solution polymerizations were performed in poly(phosphoric acid),[10] sulfolane and diphenyl sulfone.[11] Other synthetic routes used to prepare PBIs include the alkoxide-catalyzed reaction of aromatic bis(*o*-diamine)s with dinitriles[12] and the reaction of the bis(bisulfite adduct)s of aromatic dialdehydes with aromatic bis(*o*-diamine)s.[13] PBIs have only limited solubility[14] and are intractable and infusible and consequently difficult to process. Several approaches currently are being pursued to improve the processability of PBI polymers. Putting units in the polymer that provide more flexibility can overcome this problem. For example, O, CH_2O, SO_2, and CMe_2 units have been used for this purpose.[15] Other approaches to modify the properties of PBIs are to make PBI copolymers,[16] to make mixed polymers such as PBI-polyimides[17] or PBI-polyamides,[18] or to blend them with other polymers.[19] As co-monomers for PBI synthesis, the aromatic

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bis(*o*-diamines) are also expensive and difficult to purify. Therefore, there is incentive to develop new alternative synthetic routes to these materials.

The present work is especially focused on the development of processable and fully cyclized poly(benzimidazole–imide)s copolymers with very high glass transition temperatures to meet many of these demands (Fig. 2).

To date, the preparation of copolymers based on aromatic benzimidazoles and imides is not well known.[20–25] This deficiency is partly due to the experimental difficulties encountered in the synthesis of benzimidazoles. In the past, we have shown that incorporation of the benzhydrol tetracarboxylic dianhydride (BHTDA) along with the utilization of molecular weight control and solution cyclization methods result in processable, thermally stable polyimides.[26] Using these techniques, we have incorporated novel diamine monomers based on bisbenzimidazole in polyimides.

The present paper describes some recent investigations on the synthesis of poly(benzimidazole–imide)s copolymers that are performed to enhance the thermal properties of conventional polyimides. The route to these copolymers involved the synthesis of 2,2′-alkylene- or arylene-bis(5-nitrobenzimidazole)s,[27] which are then reduced into the corresponding bis(5-amino) compounds. The latter are condensed with aromatic tetracarboxylic anhydrides[28,29] to yield benzimidazole–imide copolymers. An unsubstituted 2,2′-(1,2-phenylene)-bisbenzimidazole (*o*-PBI), is obtained by condensation of 1,2-phenylene diamine with phthalic anhydride. The nitration of *o*-PBI followed by the reduction of the dinitro compound leads to the 2,2′-(1,2-phenylene)-bis(5-aminobenzimidazole), (*o*-P5ABI). When condensed either with aromatic dianhydrides or with phthalic anhydride, the *o*-P5ABI gives respectively alternating copolymers or a model compound. The thermal properties of these copolymers were determined by DSC and TGA.

2. Experimental methods

2.1. Materials

1,2-Phenylene diamine was recrystallized from absolute ethanol. Phthalic anhydride was purified by sublimation and polyphosphoric acid (Aldrich) was used as received. The aromatic dianhydrides, 4,4′-oxydiphthalic anhydride (ODPA), 4,4′-(hexafluoroisopropylidene)diphthalic anhydride (6FDA) and benzophenone tetracarboxylic dianhydride (BTDA), were obtained from Merck and used without further purification. Benzhydrol tetracarboxylic dianhydride (BHTDA) was prepared as reported by Berrada *et al.*[30] and purified by Soxhlet extraction with diethyl ether and dried in a vacuum to give the product in 75% yield, mp 183 °C; ^{1}H NMR (dimethylsulfoxide-d$_6$) δ 8.1–8.4 ppm (m, Ar H, 6H), 6.81 ppm (d, OH, 1H), 6.23 ppm (d, –CH–, 1H); ^{13}C NMR (DMSO-d$_6$) δ 163.17, 162.97, 153.21, 134.01, 131.93, 130.43, 125.79, 122.81, 72.66; IR (KBr) ν 3517 cm^{-1} (s, OH), 1858 and 1784 cm^{-1} (s, CO). Anal. Calcd. for $C_{17}H_8O_7$: C, 62.96; H, 2.46. Found: C, 62.75; H, 2.68.

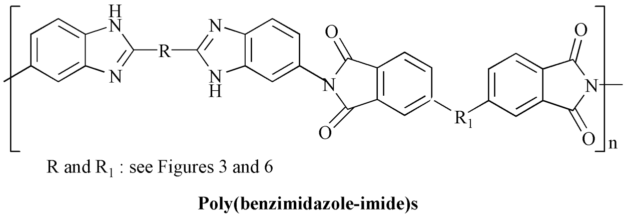


Fig. 2 Novel class of high-temperature/high-performance polymers.

2.2. Purification of solvents

Dimethyl sulfoxide (DMSO) was distilled over sodium chloride and calcium hydride using a column packed with glass helices. 1-Methyl-2-pyrrolidinone (NMP) was purified by vacuum distillation over phosphorus pentoxide. *N*,*N*-dimethylacetamide (DMAc) was distilled over calcium hydride. Toluene was washed twice with sulfuric acid, water, 5% aqueous bicarbonate then with water. It was dried over calcium sulfate, then phosphorus pentoxide and distilled over sodium. The other reagents and solvents were used after appropriate purification in the normal manner.

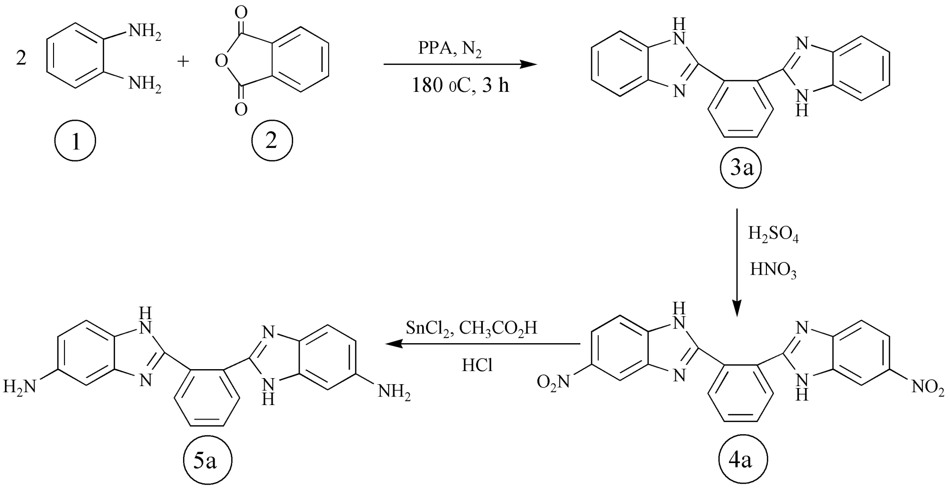
2.3. Analytical equipment and techniques

Melting points were measured in capillaries on a Büchi apparatus (Model BUCHI 535). Infrared spectra were recorded on a Bruker IFS 45 infrared Fourier transform spectrometer. The FT-IR samples were prepared by casting films of the materials on KBr plates. The FT-IR spectrometer acquired 4 complete IR spectra with a spectral resolution of 4 cm^{-1}. ^{1}H (200 MHz) and ^{13}C (50.3 MHz) NMR spectra were obtained with a Bruker ACE 200 spectrometer. Chemical shifts were given in parts per million from tetramethylsilane at 0 ppm. The structures of compounds were confirmed by elemental analysis (Analytical Department of ICSN–CNRS 91198 Gif sur Yvette, France). Viscosity was measured in NMP at 30 °C using a Canon Ubbelohde type viscometer. Differential scanning calorimetry (DSC) analysis was performed with a Mettler 12E at a heating rate of 10 °C min^{-1}. The apparatus was calibrated with Indium and Zinc standards, at 10 °C min^{-1}. The lag between the sample and pan holder temperatures was also taken into account. Glass transition temperatures (T_g's) were read at the middle of the change in the heat capacity and were taken from the second heating scan after quick cooling. Thermogravimetric analysis (TGA) was performed under air atmosphere on a DuPont 9900 at a heating rate of 10 °C min^{-1}. The temperature and the weight scales were calibrated using high-purity standards (nickel and iron) at the specific heating rate with a calibration parameter of their respective Curie points. The high-resolution mass spectra were recorded on a MAT 311 Varian Spectrometer with C.P.G. couplage (Analytical Department of the University of Rennes 1, France). Dielectrical measurements were carried out in the temperature range 30–350 °C and at frequencies 1–200 kHz with an Analyzer 2970 TA Instrument. Tensile properties were determined from stress–strain curves obtained by an Orientec Tensilon with a load cell of 10 kg. A gauge of 3 cm and a strain rate of 2 cm min^{-1} were used for this study. Measurements were performed at room temperature with film specimens (0.4 cm wide, 6 cm long, and *ca.* 0.05 mm thick).

2.4. Synthesis of monomers

2.4.1. Total synthesis of 2,2′-(1,2-phenylene)-bis(5-aminobenzimidazole), 5a (Scheme 1). *1- 2,2′-(1,2-Phenylene)-bisbenzimidazole, **3a** (o-PBI).* 1,2-Phenylene diamine, **1**, (10.8 g, 0.1 mol) was added under N_2 to poly(phosphoric acid) (PPA, 90 g). Phthalic anhydride, **2**, (7.4 g, 0.05 mol) was added under N_2 to the well-stirred mixture, then the solution was heated to 180 °C for 3 h. The solution was cooled to 100 °C and poured into ice–water (60 mL). The precipitate in suspension in water was neutralized with solid sodium carbonate (2 g), filtered, and then washed several times with water. The crude product was refluxed in absolute ethanol (500 mL), the insoluble fraction was filtered, dried and sublimed to give pure white crystals.

Yield 85%, mp 114–116 °C; ^{1}H NMR (DMSO-d$_6$) δ 8.13 (m, 2H, ArH), 8.02 (m, 2H, ArH), 7.62 (m, 4H, ArH), 7.50 (m, 4H, ArH); ^{13}C NMR (DMSO-d$_6$) C2, 146.96; C4, 101.53; C5, 114.72; C8, 133.85; C9, 132.69; C10, 123.89; C11, 126.92; C12, 133.87.



Scheme 1 Synthesis of 2,2′-(1,2-phenylene)-bis(5-aminobenzimidazole).

2-2,2′-(1,2-Phenylene)-bis(5-nitrobenzimidazole), ***4a*** *(*o*-P5NBI).* This compound was obtained by nitration of *o*-PBI, **3a**. Thus, 4 g (0.013 mol) of **3a** were dissolved into concentrated H_2SO_4 (11 mL), and the solution was cooled in an ice–water bath to maintain the temperature below 50 °C. A mixture of fuming HNO_3 (1.385 mL) and concentrated H_2SO_4 (1.184 mL) was added dropwise in *ca.* 10 min. Then the solution was stirred for 1 h and poured into an ice–water mixture. The raw product was filtered, washed with water, neutralized with sodium carbonate until pH 9, and washed with water to give raw **4a**. The solid was then refluxed twice in ethanol and filtered. The recrystallization from tetrahydrofuran (THF) gave pale yellow crystals.

Yield 60%; mp $>$ 300 °C; ^{1}H NMR (DMSO-d$_6$, TFA) δ 8.44 (s, 2H, ArH), 8.18 (d, 2H, ArH), 8.07 (m, 2H, ArH), 7.89 (m, 2H, ArH), 7.72 (d, 2H, ArH); ^{13}C NMR (DMSO-d$_6$, TFA) C2, 150.79; C4, 111.38; C5, 135.65; C6, 122.14; C7, 115.45; C8, 146.46; C9, 131.76; C10, 122.56; C11, 133.43; C12, 134.63; IR (KBr) ν 1626 (CN); 1512 (NO); 1342 (NO) and 3250 cm^{-1} (NH). Anal. Calcd. for $C_{20}H_{12}N_6O_4$: C, 60.00; H, 3.02; N, 20.99. Found: C, 59.82; H, 2.92; N, 20.85 (Calcd. for $C_{20}H_{12}N_6O_4$ 400.031, Found 400.030).

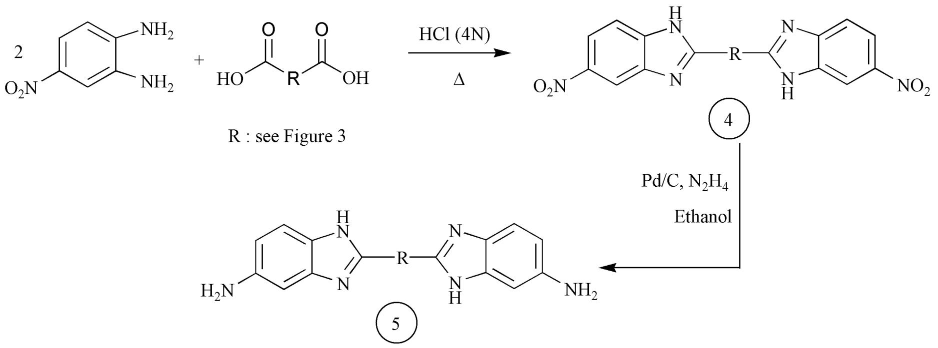
3-2,2′-(1,2-Phenylene)-bis(5-aminobenzimidazole), ***5a*** *(*o*-P5ABI).* Compound **4a** (1 g, 0.025 mol) was dissolved into glacial acetic acid (100 mL). Tin chloride (7 g, 0.0037 mol) was dissolved into concentrated hydrochloric acid (8 mL); both solutions were heated to boiling, then the acetic acid solution was added dropwise to the tin chloride solution in *ca.* 30 min. The mixture was cooled to 5 °C and a bright orange precipitate was filtered, washed with water and dried for 3 h at 50 °C under vacuum. The crude product was then refluxed in ethanol containing active charcoal. The recrystallization from ethanol gave pale yellow crystals.

Yield 78%; mp $>$ 300 °C; ^{1}H NMR (DMSO-d$_6$, TFA) δ 8.14 (m, 2H, ArH), 7.94 (m, 2H, ArH), 7.73 (d, 2H, ArH), 7.63 (s, 2H, ArH), 7.37 (d, 2H, ArH); ^{13}C NMR (DMSO-d$_6$, TFA) C2, 149.99; C4, 108.26; C5, 134.97; C6, 119.29; C7, 115.57; C8, 130.02; C9, 133.11; C10, 125.55; C11, 131.39; C12, 131.88; IR (KBr) δ 1626 (CN) and 3250 cm^{-1} (NH). Anal. Calcd. for $C_{20}H_{16}N_6$: C, 70.57; H, 4.74; N, 24.69. Found: C, 70.47; H, 4.70; N, 24.65. High-resolution MS *m*/*z*: found 340.1441 (Calcd. for $C_{20}H_{16}N_6$, 340.14364).

2.4.2. Synthesis of other bisbenzimidazole diamines, 5c–h (Scheme 2). The synthesis and characterization of dinitro compounds, **4b–h** (see Fig. 3), were previously described.[31] Other diamines were prepared by reduction of the corresponding dinitro compound using the above procedure.

2,2′-(4,4′-Oxybisphenylene)-bis(5-aminobenzimidazole), ***5c*** *(Ox5ABI). The recrystallization from ethanol gave a white-orange solid.* mp $>$ 300 °C, ^{1}H NMR (DMSO-d$_6$) δ 8.25 (d, 4H, ArH), 7.52 (d, 2H, ArH), 7.35 (d, 4H, ArH), 6.86 (s, 2H, ArH), 6.72 (d, 2H, ArH); ^{13}C NMR (DMSO-d$_6$) C2, 149.35; C4, 97.08; C5, 145.70; C6, 112.64; C7, 117.93; C8, 135.02; C9, 139.30; C10, 127.25; C11, 128.61; C12, 119.97; C13, 157.87; IR (KBr) ν 1636 (CN) and 3250 cm^{-1} (NH). Anal. Calcd. for $C_{26}H_{20}N_6O$: C, 63.41; H, 3.27; N, 17.07. Found: C, 63.38; H, 3.20; N, 17.05.

2,2′-(4,4′-Hexafluoroisopropylidene)-bis(5-aminobenzimidazole), ***5e*** *(H5ABI). The recrystallization of the crude product from ethanol gave a yellow solid.* mp $>$ 300 °C; ^{1}H NMR (DMSO-d$_6$) δ 8.17 (d, 4H, ArH), 7.49 (d, 4H, ArH), 7.32 (d,



Scheme 2 Synthesis of bis(aminobenzimidazolyl) compounds.

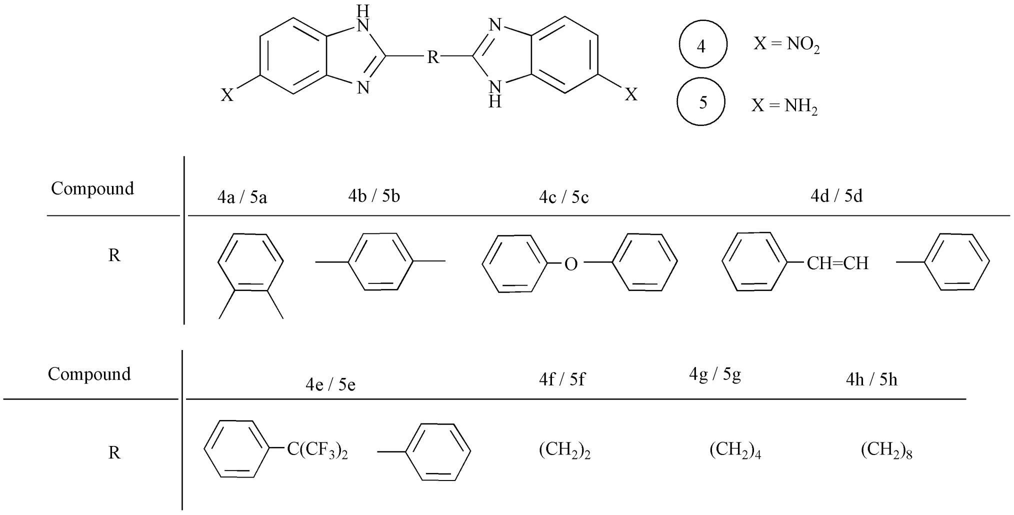


Fig. 3 Dinitro compounds and their corresponding diamines used for the synthesis of the copolymers.

2H, ArH), 6.77 (s, 2H, ArH), 6.60 (d, 2H, ArH); ^{13}C NMR (DMSO-d$_6$) C2, 153.42; C4, 97.46; C5, 148.60; C6, 98.31; C7, 113.28; C8, 131.97; C9, 145.27; C10, 129.03; C11, 130.90; C12, 126.55; C13, 133.51; C14, 53.19; C15, 144.15, 142.13, 121.82, 118,11; IR (KBr) ν 1627 (CN) and 3250 cm^{-1} (NH). Anal. Calcd. for $C_{29}H_{20}N_6F_6$: C, 55.60; H, 2.57; N, 13.41. Found: C, 55.47; H, 2.43; N, 13.40.

2,2′-Ethylene-bis(5-aminobenzimidazole), ***5f*** *(E5ABI). The recrystallization of the crude product in ethanol gave a white solid.* mp 194–196 °C; ^{1}H NMR (DMSO-d$_6$) δ 7.32 (d, 2H, ArH), 6.85 (s, 2H, ArH), 6.62 (d, 2H, ArH), 3.45 (s, 4H, -CH$_2$-); ^{13}C NMR (DMSO-d$_6$) C2, 152.17; C4, 97.63; C5, 144.33; C6, 111.59; C7, 116.79; C8, 133.58; C9, 138.68; C10, 27.64; IR (KBr) ν 1615 (CN) and 3250 cm^{-1} (NH). Anal. Calcd. for $C_{16}H_{16}N_6$: C, 54.55; H, 3.43; N, 23.85. Found: C, 54.47; H, 3.36; N, 23.82.

2,2′-Butylene-bis(5-aminobenzimidazole), ***5g*** *(B5ABI). The recrystallization from ethanol gave a white solid.* mp 224–226 °C; ^{1}H NMR (DMSO-d$_6$) δ 11.82 (2H, imidazole N–H), 7.31 (d, 2H, ArH), 6.77 (s, 2H, ArH), 6.59 (d, 2H, ArH), 4.94 (4H, amine NH$_2$), 2.92 (s, 4H, –CH$_2$–), 1.96 (s, 4H, –CH$_2$–); ^{13}C NMR (DMSO-d$_6$) C2, 153.85; C4, 97.90; C5, 144.25; C6, 111.97; C7, 116.87; C8, 133.61; C9, 138.70; C10, 28.54; C11, 27.95; IR (KBr) ν 1620 (CN) and 3250 cm^{-1} (NH). Anal. Calcd. for $C_{18}H_{20}N_6$: C, 56.84; H, 4.24; N, 22.09. Found: C, 55.4; H, 4.2; N, 21.8.

2,2′-Octamethylene-bis(5-aminobenzimidazole), ***5h*** *(O5ABI). The recrystallization from ethanol gave a white solid.* mp > 300 °C; ^{1}H NMR (DMSO-d$_6$) δ 7.08 (d, 2H, ArH), 6.57 (s, 2H, ArH), 6.38 (d, 2H, ArH), 4.94 (4H, amine NH$_2$), 2.67 (t, 4H, –CH$_2$–), 1.66 (q, 4H, –CH$_2$–), 1.30 (s, 8H, –CH$_2$–); ^{13}C NMR (DMSO-d$_6$) C2, 152.49; C4, 96.59; C5, 143.70; C6, 110.34; C7, 115.56; C8, 132.41; C9, 137.89; C10, 28.59; C11, 27.59; IR (KBr) ν 1626 (CN) and 3250 cm^{-1} (NH). Anal. Calcd. for $C_{22}H_{28}N_6$: C, 60.54; H, 5.54; N, 19.25. Found: C, 59.83; H, 5.42; N, 19.15.

2.5. Synthesis of model benzimidazole–imide compound, 6 (Scheme 3)

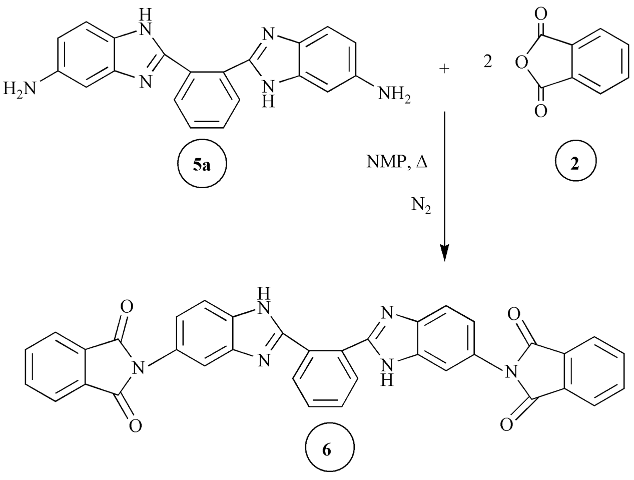
An amine solution was prepared by dissolving 2,2′-(1,2-phenylene)-bis(5-aminobenzimidazole) **5a** (0.50 g, 0.00147 mol) in NMP (25 mL) in a 250 mL four necked flask equipped with a stirrer, Dean Stark trap, condenser, nitrogen inlet, and thermometer. Phthalic anhydride (0.435 g, 0.00294 mol) was gradually added to the amine solution under a nitrogen atmosphere. The reaction mixture was stirred at room temperature, and then toluene (5 mL) was added as an azeotropic agent. The solution was heated to 140 °C for 3 h to dehydrate it then to 190 °C and kept at this temperature for 4 h. The solution was cooled to room temperature, and the model compound **6** was precipitated into methanol (50 mL). It was washed with distilled water then with methanol to remove occluded reagents such as phthalic anhydride. The crude product was recrystallized from acetone, and dried under high vacuum for 16 h at 150 °C to yield the pure model compound **6** as a yellow powder.

Yield 87%; mp > 300 °C; ^{1}H NMR (DMSO-d$_6$) δ 7–8.10 (m, ArH), 13.49 (s, 2H, NH imidazole); ^{13}C NMR (DMSO-d$_6$) C2, 153.51; C4, 116.33; C5, 140.17; C6, 122.81; C7, 115.77; C8, 139.60; C9, 130.59; C10, 126.91; C11, 132.28; C12, 130.87; C13, 168.33; C14, 132.48; C15, 135.40, C16, 124.15; IR (KBr) ν 1765, 1717 (s, CO imide), 1625 cm^{-1} (s, CN) and 1380 cm^{-1} (s, C–N imide). Anal. Calcd. for $C_{36}H_{20}N_6O_4$: C, 71.99; H, 3.36; N, 13.99. Found: C, 71.42; H, 3.57; N, 13.71.

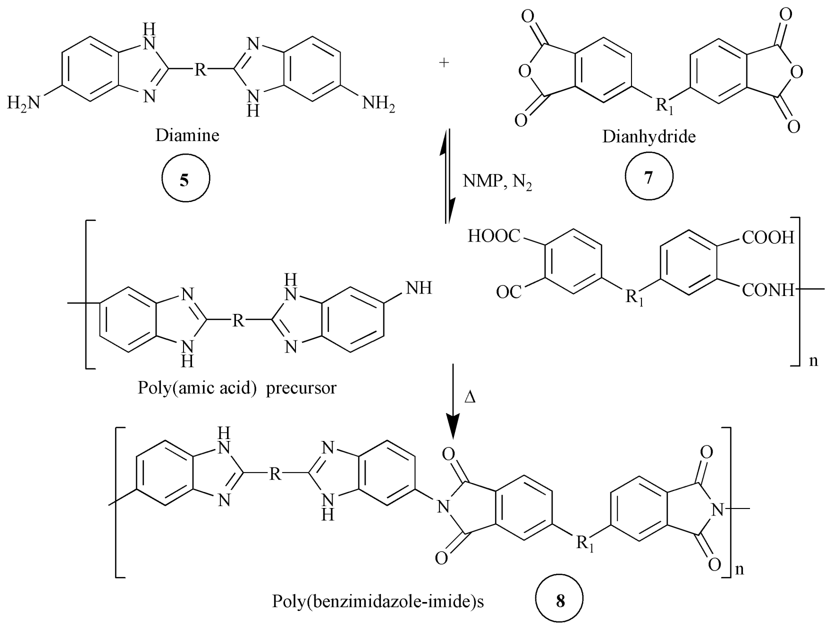
2.6. Synthesis of alternating poly(benzimidazole–imide)s, 8 (PIBI) (Scheme 4)

The synthesis of the PIBI **8**, that is prepared from BHTDA/*o*-P5ABI **8a** (Fig. 4) is given as a typical example.

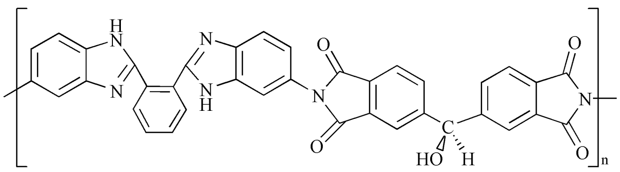
BHTDA (0.48 g, 0.00147 mol) was added to a solution of *o*-P5ABI **5a** (0.50 g, 0.00147 mol) in NMP (70 wt%) in a 250 mL four necked flask equipped with a stirrer, Dean Stark, condenser, nitrogen inlet, and thermometer. The reaction



Scheme 3 Synthesis of model benzimidazole–imide compound.



Scheme 4 Synthesis of poly(benzimidazole–imide)s.



8a

Fig. 4 Copolymer based on BHTDA–*o*-P5ABI or **7b/5a**.

mixture was stirred overnight at room temperature. Toluene (5 mL) was added as an azeotropic agent. The solution was heated to 140 °C for 3 h then to 190 °C and kept 4 h at this temperature for imidization. The solution was cooled to room temperature and added drop wise to methanol (250 mL) to precipitate the copolymer PIBI **8a**. The isolated polymer was a beige powder, it was dried under vacuum for 16 h at 150 °C.

Yield 95%; IR (KBr) v 1774, 1715 (*s*, CO imide), 1625 cm^{-1} (*s*, CN); inherent viscosity: 0.85 dL g^{-1} in NMP (c = 1 g dL^{-1}) at 30 °C. The molecular weight obtained by GPC (10 mg mL^{-1} THF solution, polystyrene standards) is $M_n = 5.7 \times 10^4$, $M_w = 8.6 \times 10^4$.

All of the procedures were carried out under dry nitrogen gas or argon or in a vacuum to avoid ambient moisture because of the hydrolytic instability of the anhydride groups.

3. Results and discussion

3.1. Synthesis and characterization of arylene- and alkylene-bis(5-aminobenzimidazole)s

These diamines (R or Ar-5ABI) are obtained *via* the reduction of dinitro precursors (listed in Table 1). The reduction of nitro compounds to amines is a very useful route to a large range of reagents already developed.[32,33]

From 2,2′-(1,2-phenylene)-bisbenzimidazole, **3a** (*o*-PBI), to 2,2′-(1,2-phenylene)-bis(5-aminobenzimidazole), **5a** (*o*-P5ABI), a complete synthesis was carried out from 1,2-phenylene diamine, **1**, and phthalic anhydride, **2**, as indicated in Scheme 1.

The dinitro compound, **4a** (*o*-P5NBI), was prepared by direct nitration of the unsubstituted *o*-PBI, **3a**. It is significant to note that the nitration of *o*-PBI leads to virtually quantitative substitution in position 5. It seems that the strong conjugation due to *o*- or *p*-phenylene rings bridging the benzimidazole cycles, prevents the nitration on them, whereas a

Table 1 Synthesis and properties of dinitro compounds **4** and the corresponding diamines **5**

		Reactions conditions[a]				
Compound	R	T/°C	Time/h	Solvent	Yield (%)	Melting/°C
4a	1,2-C_6H_4	41	1	Conc. H_2SO_4	60	>300
5a	1,2-C_6H_4	118	0.5	Acetic acid	78	>300
4b	1,4-C_6H_4	220	6	PPA	69	>300
5b	1,4-C_6H_4	118	0.5	Acetic acid	56	>300
4c	1,4-C_6H_4–O–C_6H_4	220	6	PPA	80	210
5c	1,4-C_6H_4–O–C_6H_4				90	>300
4d	1,4-C_6H_4–CHCH–C_6H_4	100	48	4 M HCl	53	>300
5d	1,4-C_6H_4–CHCH–C_6H_4				40	>300
4e	1,4-C_6H_4–$C(CF_3)_2$–C_6H_4	220	6	PPA	70	238–240
5e	1,4-C_6H_4–$C(CF_3)_2$–C_6H_4				85	>300
4f	$(CH_2)_2$	100	48	4 M HCl	60	286–288
5f	$(CH_2)_2$				83	194–196
4g	$(CH_2)_4$	100	48	4 M HCl	85	264–266
5g	$(CH_2)_4$				88	224–226
4h	$(CH_2)_8$	100	48	4 M HCl	90	220–222
5h	$(CH_2)_8$				91	>300

[a] Same reaction conditions from **5a** to **5h**.

m-phenylene ring is nitrated to a significant extent. In addition, some dinitro compounds described herein have been previously reported in literature,[34,35] but we obtained an improved yield (**4g**) or greater synthetic convenience (**4f**).[31] The raw materials, 1,2-diamino-4-nitrobenzene and the dicarboxylic acids are either commercially available or easy to prepare and they are readily converted to stable alkylene- or arylene-bis(5-nitrobenzimidazole)s as indicated in Scheme 2.

A number of new bis(5-nitrobenzimidazoles) and the corresponding bis(5-aminobenzimidazoles) have been prepared and are shown in Fig. 3:

The stannous chloride reduction is known to be acid catalyzed. Thus, during almost a century, all reductions with stannous chloride have been carried out in the presence of water. Recently, Satoh *et al.*[36] proposed the system sodium borohydride–stannous chloride for the selective reduction of aromatic nitro compounds in ethanol. In our search for a mild, selective and general method, we chose $SnCl_2.2\ H_2O$ in glacial acetic acid to reduce a wide variety of substituted nitro compounds in almost quantitative yields.

The reduction of alkylene-bis(5-nitrobenzimidazole)s could be also achieved using hydrazine method (see Scheme 2). The dinitro compound was dissolved in ethanol and the solution was heated under reflux with 10% palladium–activated carbon (Pd/C). Hydrazine hydrate (100%) was added dropwise to the above solution. Then, the mixture was refluxed until the solution became colourless. The mixture was cooled, filtered and the insoluble material washed with ethanol. The ethanol solvent was then removed under vacuum. The resulting residue was recrystallized from ethanol to give pure alkylene-bis(5-aminobenzimidazole)s.

3.2. Synthesis and characterization of model compound 6

The one-step synthesis of benzimidazole–imide, **6**, that is also bisimide compound, is used as a reaction model for the preparation of poly(benzimidazole-imide)s. The model is prepared by reacting phthalic anhydride compound with a bis(5-aminobenzimidazole) derivative in NMP solution under a dry nitrogen atmosphere to avoid the hydrolysis of anhydride groups. After complete reaction, the amic acid is imidized by heat.

Anhydrides are very reactive with aromatic diamines even at room temperature. We prepared the bisimide model **6** to verify if the anhydrides could or not react with the amine of the imidazole ring, which would lead to crosslinked polymer. The characterization of the resulting model compound shows clearly that only primary amines can react with the aromatic anhydrides to produce the model compound as shown in Scheme 3.

The characterization of the model compound was achieved by NMR and IR spectroscopy, (see Experimental section). The infrared spectrum shows the presence of CO imide bands at 1765 and 1717 cm^{-1}, CC and CN stretching vibrations at 1625 cm^{-1} and C–N imide at 1380 cm^{-1}. This model is soluble in usual NMR solvents, which allows NMR spectra to be recorded (see Fig. 5), unlike the copolymers which are insoluble in conventional NMR solvents.

3.3. Synthesis and characterization of poly(benzimidazole–imide) 8

New soluble poly(benzimidazole–imide) copolymers **8** were prepared by polycondensation of these dianhydrides **7** with

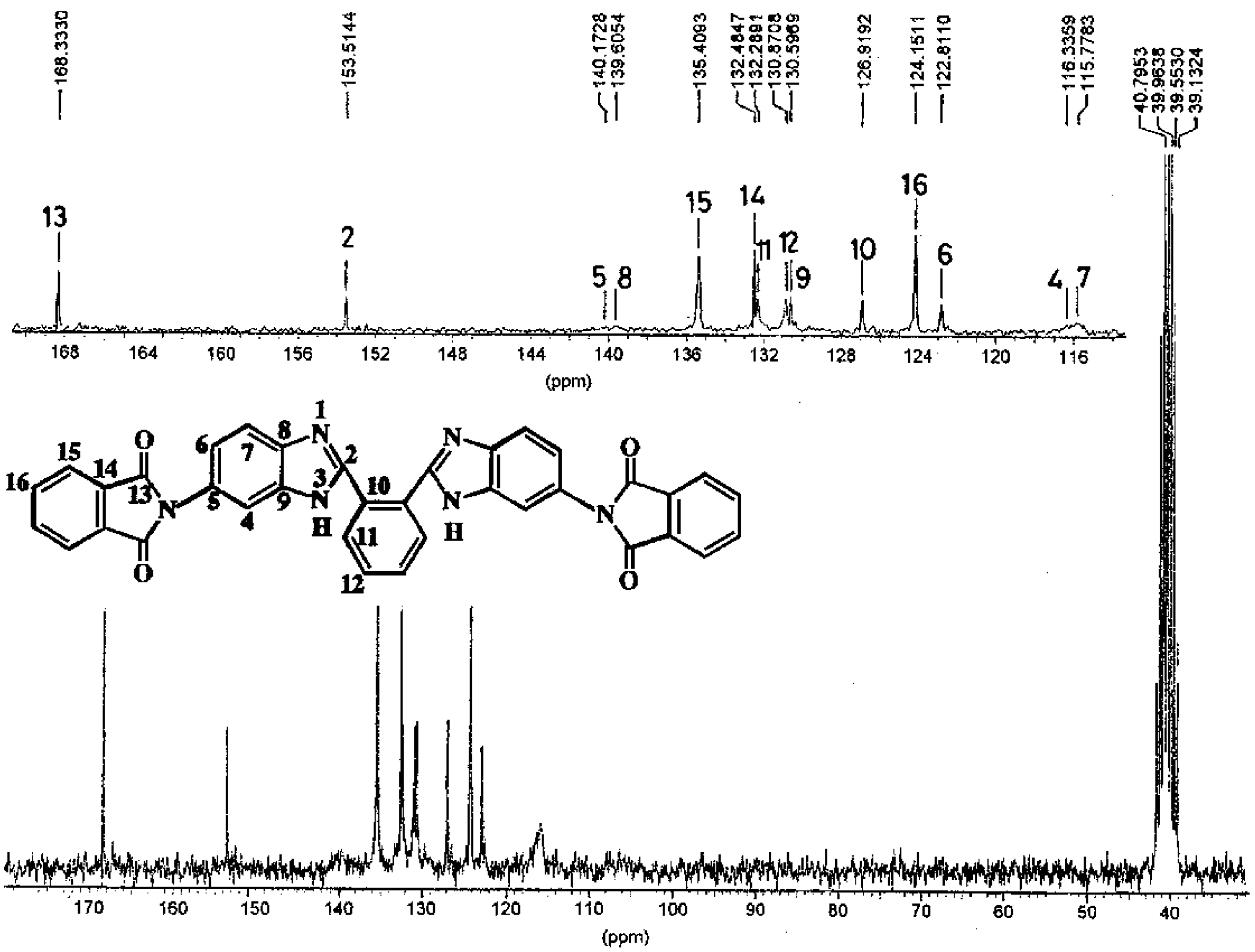


Fig. 5 ^{13}C NMR spectra of model compound **6**. Using DMSO-d_6 as solvent.

aromatic diamines **5** in solution in NMP under dry conditions to avoid the hydrolysis of the dianhydride groups, which affects strongly the molecular weight, followed by thermal imidization method as shown in Scheme 4.

Alternating poly(benzimidazole–imide) copolymers are obtained by condensation of dianhydrides and aromatic diamines carrying benzimidazole groups as shown in Scheme 4.

This technique eliminates a number of detrimental side reactions and has proved to be useful if a rigorous dianhydride:diamine stoichiometry was maintained. The viscosity increases gradually by the polycondensation reaction, and viscous solutions suitable for thick coatings were obtained. The characterization of the resulting polymers was realized with the help of bis(benzimidazole–imide) model. The amide absorption peak at 1650 cm^{-1} served as a criterion for the degree of imidization, and complete cyclization to imide was achieved under the above-described conditions.

The fully cured alternating benzimidazole–imide copolymers reported here are designated by taking the symbols for diamines and combined them with the symbols of the dianhydrides (see Fig. 6): ODPA **7a**, for diphenyloxy tetracarboxylic dianhydride; BHTDA **7b**, benzhydrol tetracarboxylic dianhydride; 6FDA **7c**, hexafluoro tetracarboxylic dianhydride; BTDA **7d**, benzophenone tetracarboxylic dianhydride.

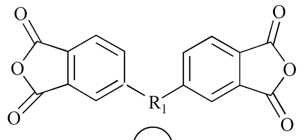
Thus, the 2,2′-(1,2-phenylene)-bis(5-aminobenzimidazole) moiety can be represented either by *o*-P5ABI or by its number **5a**. Therefore, the polymer **8a** can be designed as BHTDA/*o*-P5ABI or **7b/5a**.

The IR amide *I* absorption at 1650 cm^{-1} served as a criterion for the degree of imidization, and a complete cyclization to imide was achieved as described above. However, it was easier to dissolve the bis(5-aminobenzimidazole)s bridged by *o*-phenylene rings than the similar diamines bridged for example by *p*-phenylene rings. In the former case, the diamines are readily soluble in NMP to give 70% solution whereas a diamine of the latter case is soluble only to an extent of 8% of the solid. In this case, high polymer solutions can be obtained since the poly(amic acid) formed is rather soluble and the insoluble diamine enters into solution as the polymer is formed. This is an inconvenient aspect of processing when using the poly(amic acid) as a precursor.

3.4. Properties of poly(benzimidazole–imide)s

Polyimides and polybenzimidazoles are known to be hygroscopic. The poly(benzimidazole–imide)s take up water from the air. Therefore, the thermostable products were kept in dry boxes. Most of the water can be released again by means of an additional drying treatment under vacuum. However, for polyimides this process is not totally reversible. Some of the water can be consumed irreversibly by hydrolysis reactions of the imide groups. Water uptake has an effect on the mechanical properties and can cause stress relaxation.

Poly(benzimidazole–imide)s showed excellent to medium solubility in a variety of polar aprotic solvents such as *N*-methyl-2-pyrrolidinone, *N*,*N*-dimethylacetamide, *N*,*N*-dimethylformamide and dimethylsulfoxide. The good solubility was possibly governed by the structural modification through the incorporation of flexible moieties as hexafluoroisopropylidene and arylene ether groups into the poly(benzimidazole–imide) structure. The polymerization of benzimidazole diamines with aromatic dianhydrides gave moderate-to-high inherent viscosities of 0.60–0.98 dL g^{-1}. The molecular weight of the soluble copolymers were measured by GPC (10 mg mL^{-1} tetrahydrofuran solution as an eluent) after calibration with the standard polystyrenes, except for polymer **7d/5b**, which was insoluble in tetrahydrofuran. These polymers had number-average molecular weight (M_n) in the range from 3.7 × 10^4 to 11.8 × 10^4. All of the polyimide films could be obtained by casting from their NMP solutions and also showed a transparent and flexible nature.



7

Dianhydride

Compound	7a	7b	7c	7d
R$_1$	- O -	- CHOH -	- C(CF$_3$)$_2$ -	- CO -

Fig. 6 Dianhydrides used for the copolymer synthesis.

3.4.1. Electrical properties. Dielectric measurements were carried out in the temperature range 30–350 °C and at frequencies of 1–200 kHz. The values of dielectric constants ε are particularly constant over the corresponding range of temperature. The dielectric constant ε of Polymer **7b/5h** was evaluated as 4.8. This value is higher than those of commercially available polyimides (ε < 3.5), which is probably due to the lower rigidity of the chain and the greater polarity of benzimidazole group.

3.4.2. Mechanical properties. Poly(benzimidazole–imide) was dissolved in NMP to give a 5% solution. Then, polymer solution was cast on a glass plate, and solvent (NMP) was evaporated under vacuum at 50 °C for 16 h. The cast films were then thermally treated at 100 °C and 200 °C for 1 h each. The polymer films showed excellent thermal resistance and were transparent and colourless, desirable characteristics for practical applications in the field of polymer engineering.

The tensile properties of the copolymer films prepared by thermal treatment are summarized in Table 2. The films had tensile strength of 77–95 MPa, elongation at break of 7.2–10.6%, and initial modulus of 2.0–2.4 GPa. Furthermore, the films were strong and tough. The extensive delocalization of π electrons is well known to be responsible for the array of remarkable characteristics that polybenzimidazoles tend to exhibit. These properties include non-linear optical behavior, electronic conductivity, and exceptional mechanical properties such as tensile strength and resistance to harsh environments.

3.4.3. Thermal stability. Thermal stability has been determined for poly(benzimidazole–imide)s by weight loss measurements in an air atmosphere. The results of thermogravimetric analysis (TGA) given in Fig. 7 show that poly(benzimidazole–imide)s as a class possess outstanding thermal stability. The polymers exhibited a one-step pattern of decomposition with no significant weight loss below 420 °C. The degradation temperature T_d of the polymers is situated in the temperature range 420–600 °C. Characterizations of **7b/5a**, **7b/5c**, **7c/5e**, **7c/5g** and **7d/5a** are given as typical examples for thermogravimetric behaviour. Thermogravimetric analyses indicated that the thermal degradation of poly(benzimidazole–imide) occurs

Table 2 Mechanical properties of poly(benzimidazole–imide)s, **8**

Polymer code	Tensile strength/ MPa	Elongation at break (%)	Initial modulus/ GPa
7b/5a	86	7.2	2.1
7b/5c	92	8.7	2.1
7c/5e	95	10.6	2.4
7c/5g	81	10.6	2.0
7d/5a	77	9	2.1

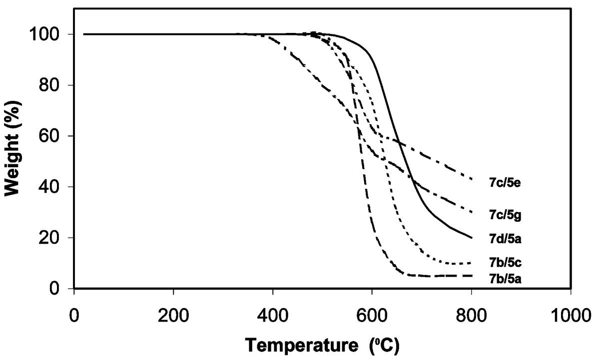


Fig. 7 Thermograms of poly(benzimidazole–imide)s, **8**.

at *ca.* 530 °C, except for **7c/5g**, which is *ca.* 80 °C higher than the conventional polyimide, confirming that the introduction of bisbenzimidazole component improved the thermal stability of polyimide.

The poly(benzimidazole–imide) **7c/5g** with an aliphatic chain as part of the main chain are not as thermally stable as the fully aromatic polymer. The degradation temperature of the commercially aromatic poly(benzimidazole) named Celazole®[37] for 10% weight loss was 465 °C in air and 530 °C in nitrogen respectively. The degradation trends in **7b/5a**, **7b/5c**, and **7d/5a** are similar but the residues left behind after decomposition are different. The TGA curves for **7c/5e** and **7c/5g** also exhibit similar profiles with high char yields, which is probably due to the nature of the dianhydride and the possible degradation mechanism that the copolymers might undergo. Some polymers listed in Table 3 have about 5% of weight loss at about 420 °C. At 600 °C, the residue is about 26% for copolymer **7b/5a**; 73% for **7b/5c**; 90% for **7d/5a**; 54% for **7c/5g**; and 63% for **7c/5e**. The residue left at 800 °C is about 42% for **7c/5e**, and it is found to be 20% for **7d/5a**. These values are remarkably high and they vary according to the structure of the copolymers. However, decomposition under air left negligible residues for both polymers **7b/5c** and **7b/5a**.

The glass transition temperatures, T_g, have values ranging from 275–328 °C. No melting endotherm peak was observed from DSC curves. Thus DSC measurements also revealed the amorphous nature of the poly(benzimidazole–imide)s. When the copolymers are heated up to 400 °C then cooled to 25 °C and reheated, the DSC curves for both heating are very similar. These results confirm the TGA values, which show that the degradation begins only above 500 °C, except for **7c/5g**. These copolymers had glass transition temperatures (T_g) between 275 and 328 °C, which were higher than the T_g value of the commercialized polyimide Ultem1000 (215 °C). As can be expected, the benzophenone containing copolymer **7d/5a** exhibited the highest T_g due to its higher intermolecular force. Polymer **7c/5e** having the most flexible backbone structure gave relatively higher T_g value. This may be attributed to its higher molecular weight. Introducing flexible units, bulky substituents, non-coplanar biphenylene moieties, and kinked units, can be employed to modify the polymer properties, either by lowering the interchain interactions or by reducing the stiffness of the polymer chain. Depending on the type and amount of structural modifications, the transition temperatures can be lowered and the solubilities improved, resulting in processable materials.

Table 3 Thermal properties of polymers, **8**, prepared by condensation of bis(5-diaminobenzimidazole)s, **5**, with dianhydrides, **7**, in NMP solution

Polymer code[a]	Yield (%)	T_g/°C[b]	T_d/°C[c]	Residue (%)[d]
7b/5a	95	288	530	26
7b/5c	85	307	560	73
7c/5e	94	275	530	63
7c/5g	90	296	420	54
7d/5a	92	328	580	90

[a] For example, polymer **7b/5a** could be also called BHTDA/*o*-P5ABI. [b] DSC, 10 °C min^{-1}. [c] Starting of degradation in air, TGA, 10 °C min^{-1}. [d] Percentage of residue at 600 °C, TGA, 10 °C min^{-1}.

4. Conclusions

Polyimides can be used for extended periods of time but have only acceptable thermal performance when compared to polybenzimidazoles that possess excellent thermal performance but can be used only for short time. A novel class of copolymer based on alternating aromatic benzimidazole and aromatic imide moieties was prepared, which enhanced the properties of conventional polyimides and improved the processability of polybenzimidazoles. While the synthesized poly(benzimidazole–imide)s do not necessarily have high temperature stability when compared with the conventional polybenzimidazoles, they do have much more desirable handling characteristics which would allow them to be used in different applications.

A new family of polyimides with desirable properties for manufacturing has been prepared by condensation of dianhydrides and aromatic diamines carrying benzimidazole groups, and alternating poly(benzimidazole–imide) copolymers were obtained. Highly processable thermostable copolymers having high-molecular weight and containing *o*-phenylene ring bridging bis(5-aminobenzimidazole) have been prepared by condensation of these diamines with aromatic dianhydrides. The arylene- or alkylene-bis(5-aminobenzimidazole)s were prepared by reduction of the corresponding dinitro compound. These diamines were polycondensed in solution in NMP with various dianhydrides to yield poly(amic acid) precursors that gave rise to alternating imide–benzimidazole copolymers *via* thermal cyclodehydration.

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