# Synthesis, Characterization, and Studies of Heat-Resistant Poly(ether benzimidazole)s

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The present necessity to use heat-resistant materials in electronics justified the scientific interest in different heterocyclic polymers. This paper is especially concerned with the preparation of novel heat-resistant materials having benzimidazole moieties in the main chain. The poly(ether benzimidazole)s were prepared by the nucleophilic displacement reaction of 1,6-hexanediol with activated aliphatic and aromatic bis(nitrobenzimidazole) compounds in *N*-methylpyrrolidone at 190 °C in the presence of anhydrous potassium carbonate. All polybenzimidazoles were obtained in high-to-quantitative yields and with varying molecular weights (inherent viscosities from 0.24 to 0.77 dL/g), which in some cases were in the fiber-forming range. The polymers exhibited glass transition temperatures ranging from 150 to 300 °C.

## Introduction

Polybenzimidazoles (PBIs) are a class of high-temperature/high-performance polymers that have been commercialized.[1] PBIs are heterocyclic polymers that have been attractive because of their outstanding mechanical and dielectric properties at high temperatures.[2] They also have properties suitable for producing nonflammable fibers and fabrics, which have excellent moisture regain. For example, fabric woven from sulfonated PBI fibers was used in garments for fire fighters. Ion-selective resins have been prepared recently from PBI beads functionalized with chelating agents.[3] In addition, polybenzimidazoles have been successfully used for sea water desalination as reverse osmosis membranes or hollow filaments.[4] PBIs are generally prepared via melt polymerization of aromatic bis(*o*-diamine)s with aromatic dicarboxylic acid derivatives.[5] However, the reactions must be carried out at very high temperatures. Solution polymerizations were performed in poly(phosphoric acid),[6] sulfolane,[7] and diphenyl sulfone.[7] Other synthetic routes used to prepare PBIs included the alkoxide-catalyzed reaction of aromatic bis(*o*-diamine)s with dinitriles[8] and the reaction of the bis(bisulfite adduct)s of aromatic dialdehydes with aromatic bis(*o*-diamine)s.[9] PBIs have only limited solubility[10] 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.[11] Other approaches to modify the properties of PBIs are to make PBI copolymers,[12] to make mixed polymers such as PBI−polyimides[13] or PBI-polyamides,[14] or to blend them with other polymers such as polyimides.[15] The PBI's precursors as aromatic bis-

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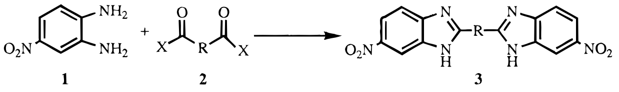
**Scheme 1. Synthesis of Bis(nitrobenzimidazolyl) Compounds**



R and X : see Table 1

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

This work reported the synthesis and physicochemical properties of PBI copolymers. Poly(ether benzimidazole)s (PEBIs) were synthesized via the nucleophilic displacement reaction of activated aromatic bis(nitrobenzimidazole) monomers with 1,6-hexanediol in the presence of anhydrous potassium carbonate.

## Experimental Section

**Materials**. 4-Nitro-1,2-phenylenediamine was recrystallized from absolute ethanol. Dicarboxylic acid derivatives and polyphosphoric acid (Aldrich) were used as received. Potassium bicarbonate was dried under vacuum at 180 °C.

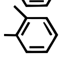
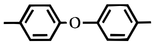
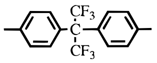
**Purification of Solvents**. Dimethyl sulfoxide (DMSO) was distilled over sodium chloride and calcium hydride using a column packed with glass helixes. 1-Methyl-2-pyrrolidinone (NMP) was purified by vacuum distillation over phosphorus pentoxide. *N*,*N*-Dimethylacetamide (DMAc) was purified by vacuum distillation over calcium hydride. Toluene was washed twice with sulfuric acid, water, 5% aqueous bicarbonate, and then with water. It was dried over calcium sulfate and then phosphorus pentoxide and distilled over sodium.

**Analytical Equipment and Techniques.** Melting points are uncorrected and were measured with a Büchi capillary melting point apparatus. IR 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. $^1$H (200 MHz) and $^{13}$C (50.3 MHz) NMR spectra were obtained with a Bruker ACE 200 spectrometer. Chemical shifts are given in parts per million from tetramethylsilane at 0 ppm. The structures of compounds were confirmed by elemental analysis (Analytical Department of the University of Pierre and Marie Curie, Paris, France). Viscosity was measured at 30 °C using a Canon Ubbelohde type viscometer. Thermogravimetric analysis (TGA) was performed under air atmosphere on a Mettler DSC 30 at a heating rate of 10 °C/min.

**Synthesis of Monomers (Scheme 1).** *Preparation of 2,2′-Aliphatic−bis(5-nitrobenzimidazole) Derivatives.* To a well-stirred solution of 2 mol of 4-nitro-1,2-phenylenediamine (**1**) in 4 N HCl (1 L) was added the appropriate diacid **2** (1 mol). The solution was heated to reflux for 48 h and then concentrated to give a dark brown solid. The pure desired product was obtained by repeated recrystallizations from hot ethanol. Analogous compounds (**3c**−**f**; Table 1) were prepared by this method. The compounds in this series such as **3a** and **3b** were prepared from **1** and diamide derivatives in refluxing ethylene glycol for 12 h, then the solution was poured into water, and the crude monomer was filtered and was purified by column chromatography (silica gel) using petroleum ether/ethyl acetate (1/1) as eluent.

*Preparation of 2,2′-Aromatic−bis(5-nitrobenzimidazole) Derivatives.* A mixture of 2 mol of 4-nitro-1,2-phenylenediamine (**1**) and 1 mol of terephthalic acid (**2**) in poly(phosphoric acid) (PPA) gave a thick paste, and extra PPA was added to give a smooth slurry. It was heated slowly to 220−230 °C and kept at this temperature for 6 h. The reaction mixture was slowly cooled to 100 °C and poured into ice-cold water with rapid stirring. The stirring was continued for 1 h, and the resulting suspension was filtered. The filtrate on neutralization (pH 7.5) with dilute NaOH gave a solid which was filtered and washed with water. The dark brown powder was dissolved in ethanol and treated with charcoal until the solution was pale yellow. The solution was evaporated to dryness to give a precipitate, which was dried and recrystallized twice from ethanol to give 2,2′-phenylbis(5-nitrobenzimidazole) (**3g**, Table 1). Compounds **3h**−**j** were prepared by following the same procedure as described for **3 g**. All of the procedures were carried out under dry nitrogen or argon to avoid ambient moisture.

**Table 1. Preparation Conditions of Bis(nitrobenzimidazolyl) Compounds**

| Compound | X | R | Reaction Conditions<br>Temperature (°C) | Time (h) | Solvent | Yield (%) |
|---|---|---|---|---|---|---|
| 3a | $NH_2$ | nil | 197 | 12 | ethylene glycol | 40 |
| 3b | $NH_2$ | $-CH_2-$ | 197 | 12 | ethylene glycol | 36 |
| 3c | OH | $-(CH_2)_2-$ | 100 | 48 | 4N HCl | 60 |
| 3d | OH | $-(CH_2)_4-$ | 100 | 48 | 4N HCl | 85 |
| 3e | OH | $-(CH_2)_8-$ | 100 | 48 | 4N HCl | 90 |
| 3f | OH | -CH = CH- | 100 | 48 | 4N HCl | 53 |
| 3g | OH |  | 220 | 6 | PPA | 69 |
| 3h | OH |  | 220 | 6 | PPA | 72 |
| 3i | OH |  | 220 | 6 | PPA | 80 |
| 3j | OH |  | 220 | 6 | PPA | 70 |

The characterization of these bis(nitrobenzimidazolyl) compounds was achieved by $^1$H and $^{13}$C NMR and IR spectroscopies and elemental analysis.

*2,2′*-Bis(5-nitrobenzimidazole) (**3a**): mp >300 °C, $^1$H NMR spectrum could not be taken due to insolubility in the proper solvents; IR (KBr) $\nu$ 1615 (*C*═N); 1342 (*N*═O); 3250 cm$^{-1}$ (NH). Anal. Calcd for $C_{14}H_8N_6O_4$: C, 51.86; H, 2.49; N, 25.92. Found: C, 51.48; H, 2.27; N, 25.83.

*2,2′*-Methylenebis(5-nitrobenzimidazole) (**3b**)*:* mp >300 °C, $^1$H NMR spectrum could not be taken due to poor solubility in proper solvents; IR (KBr) $\nu$ 1612 (*C*═N); 1515 (*N*═O); 1342 (*N*═O) and 3250 cm$^{-1}$ (NH). Anal. Calcd for $C_{15}H_{10}N_6O_4$: C, 53.26; H, 2.98; N, 24.84. Found: C, 52.85; H, 2.76; N, 24.06.

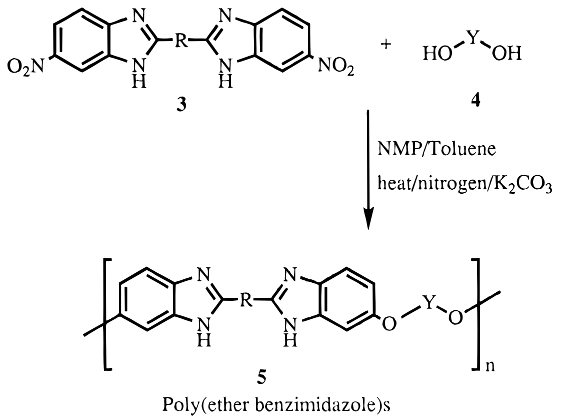
*2,2′*-Ethylenebis(5-nitrobenzimidazole) (**3c**): Recrystallization from ethanol gave a yellow powder, mp 286−288 °C, $^1$H NMR (DMSO-$d_6$) $\delta$ 8.43 (s, 2H, ArH), 8.12 (d, 2H, ArH), 7.72 (d, 2H, ArH), 3.57 (s, 4H, −CH$_2$−); $^{13}$C NMR (DMSO-$d_6$) C2, 158.46; C4, 111.83; C5, 143.88; C6, 118.12; C7, 114.64; C8, 142.31; C9, 139.60; C10, 27.61; IR (KBr) $\nu$ 1615 (*C*═N); 1517 (*N*═O); 1342 (*N*═O); 3250 cm$^{-1}$ (NH). Anal. Calcd for $C_{16}H_{12}N_6O_4$: C, 54.55; H, 3.43; N, 23.85. Found: C, 54.47; H, 3.36; N, 23.82.

*2,2′*-Butylenebis(5-nitrobenzimidazole) (**3d***)*: Recrystallization from ethanol gave a light yellow material; mp 264−266 °C; $^1$H NMR (DMSO-$d_6$) $\delta$ 13 (2H, imidazole N−H), 8.43 (s, 2H, ArH), 8.10 (d, 2H, ArH), 7.72 (d, 2H, ArH), 3.04 (s, 4H, −CH$_2$−), 1.98 (s, 4H, −CH$_2$−); $^{13}$C NMR (DMSO-$d_6$) C2, 160.56; C4, 111.90; C5, 142.98; C6, 118.02; C7, 114.67; C8, 143.61; C9, 139.80; C10, 29.14; C11, 27.59; IR (KBr) $\nu$ 1620 (*C*═N); 1516 (*N*═O); 1342 (*N*═O); 3250 cm$^{-1}$ (NH). Anal. Calcd for $C_{18}H_{16}N_6O_4$: C, 56.84; H, 4.24; N, 22.09. Found: C, 55.4; H, 4.2; N, 21.8.

*2,2′*-Octamethylenebis(5-nitrobenzimidazole) (**3e**): Recrystallization from ethanol gave a light brown material; mp 220−222 °C; $^1$H NMR (DMSO-$d_6$) $\delta$ 8.16 (s, 2H, ArH), 7.83 (d, 2H, ArH), 7.45 (d, 2H, ArH), 2.66 (t, 4H, −CH$_2$−), 1.57 (q, 4H, −CH$_2$−), 1.10 (s, 8H, −CH$_2$−); $^{13}$C NMR (DMSO-$d_6$) C2, 161.23; C4, 112.22; C5, 142.90; C6, 117.94; C7, 114.65; C8, 143.64; C9, 139.81; C10, 29.39; C11, 28.03; IR (KBr) $\nu$ 1626 (*C*═N); 1516 (*N*═O); 1342 (*N*═O); 3250 cm$^{-1}$ (NH). Anal. Calcd for $C_{22}H_{24}N_6O_4$: C, 60.54; H, 5.54; N, 19.25. Found: C, 59.83; H, 5.42; N, 19.15.

*2,2′*-Vinylenebis(5-nitrobenzimidazole) (**3f**): Recrystallization from ethanol gave a yellow material; mp >300 °C; $^1$H NMR (DMSO-$d_6$) $\delta$ 8.43 (s, 2H, ArH), 8.12 (d, 2H, ArH), 7.72 (d, 2H, ArH), 7.70 (s, 2H, CH═CH); $^{13}$C NMR (DMSO-$d_6$) C2, 154.14; C4, 115.45; C5, 143.55; C6, 119.13; C7, 124.68; C8, 142.98; C9, 141.90; C10, 112.88; IR (KBr) $\nu$ 1625 (*C*═N); 1516 (*N*═O); 1342

### Scheme 2. Synthesis of Poly(ether benzimidazole)s



(*N*=O); 3250 cm$^{-1}$ (NH). Anal. Calcd for $C_{16}H_{10}N_6O_4$: C, 54.86; H, 2.88; N, 23.99. Found: C, 54.64; H, 2.54; N, 23.75.

*2,2′-p*-Phenylenebis(5-nitrobenzimidazole) (**3g**): Recrystallization from ethanol gave a brown material; mp >300 °C; $^1$H NMR (DMSO-$d_6$, TFA) $\delta$ 8.67 (s, 2H, ArH), 8.53 (s, 4H, ArH), 8.31 (d, 2H, ArH), 7.97 (d, 2H, ArH); $^{13}$C NMR (DMSO-$d_6$, TFA) C2, 156.17; C4, 111.30; C5, 146.11; C6, 120.05; C7, 124.99; C8, 147.53; C9, 145.13; C10, 128.29; C11, 130.28; IR (KBr) $\nu$ 1630 (*C*=N); 1513 (*N*=O); 1342 (*N*=O); 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, 59.52; H, 2.72; N, 20.69.

*2,2′-o*-Phenylenebis(5-nitrobenzimidazole) (**3h**): Recrystallization from ethanol gave a light yellow powder; mp >300 °C; $^1$H NMR (DMSO-$d_6$, TFA) $\delta$ 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) $\nu$ 1626 (*C*=N); 1512 (*N*=O); 1342 (*N*=O); 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.

*2,2′*-(4,4′-Oxybisphenylene)bis(5-nitrobenzimidazole) (**3i**): Recrystallization from ethanol gave a light brown material; mp 210−212 °C; $^1$H NMR (DMSO-$d_6$) $\delta$ 8.44 (s, 2H, ArH), 8.13 (d, 4H, ArH), 8.01 (d, 2H, ArH), 7.69 (d, 2H, ArH), 7.24 (d, 4H, ArH); $^{13}$C NMR (DMSO-$d_6$) C2, 153.09; C4, 110.99; C5, 136.66; C6, 121.47; C7, 114.98; C8, 145.79; C9, 132.49; C10, 118.90; C11, 131.41; C12, 120.46; C13, 160.83; IR (KBr) $\nu$ 1636 (*C*=N); 1515 (*N*=O); 1342 (*N*=O); 3250 cm$^{-1}$ (NH). Anal. Calcd for $C_{26}H_{16}N_6O_5$: C, 63.41; H, 3.27; N, 17.07. Found: C, 63.38; H, 3.20; N, 17.05.

*2,2′*-(4,4′-Hexafluoroisopropylidenebisphenylene)bis(5-nitrobenzimidazole) (**3j**): Recrystallization from ethanol gave a yellow needles; mp 238−240 °C; $^1$H NMR (DMSO-$d_6$) $\delta$ 8.51 (s, 2H, ArH), 8.40 (d, 4H, ArH), 8.12 (d, 2H, ArH), 7.82 (d, 2H, ArH), 7.74 (d, 4H, ArH); $^{13}$C NMR (DMSO-$d_6$) C2, 155.21; C4, 113.14; C5, 143.56; C6, 118.82; C7, 115.46; C8, 143.89; C9, 140.41; C10, 131.07; C11, 131.27; C12, 128.05; C13, 135.08; C14, 53.19; C15, 126.93; IR (KBr) $\nu$ 1627 (*C*=N); 1518 (*N*=O); 1342 (*N*=O); 3250 cm$^{-1}$ (NH). Anal. Calcd for $C_{29}H_{16}N_6O_4F_6$: C, 55.60; H, 2.57; N, 13.41. Found: C, 55.47; H, 2.43; N, 13.40.

**Synthesis of Poly(ether benzimidazole)s (Scheme 2).** The following procedure was used for the synthesis of poly(ether benzimidazole)s via nucleophilic aromatic substitution in a polar aprotic solvent. 1,6-Hexanediol (29.5 mg, 25 × $10^{-4}$ mol) and potassium carbonate (51 mg, 37 × $10^{-4}$ mol) were dissolved in 25 mL of NMP in a 250 mL four-neck flask equipped with a stirrer, Dean Stark trap, condenser, nitrogen inlet, and thermometer. Toluene (5 mL) was added as an azeotropic agent. The reaction mixture was heated to 140 °C for 3 h to dehydrate the solution then to 190 °C. At this temperature, 1000 mg (25 × $10^{-4}$ mol) of **3g** was added, and the solution was stirred 18 h at 190 °C. The solution was then cooled to room temperature and diluted with 50 mL of tetrahydrofuran. The polymer **5g** was precipitated into methanol/water (80/20 by volume), filtered, and dried in vacuum. The polymer **5g**, obtained as a powder, yield 90%, is insoluble in water at any pH and in most organic solvents. It can be dissolved to a small extent in dimethylformamide and is completely soluble in 100% sulfuric acid; the polymer is recovered unchanged by dilution with water. Polymers **5b** and **5h** were also more difficult to dissolve, sulfuric acid or DMAc with 1% LiCl being necessary. Compounds **5h**−**j** were prepared from **3h**−**j**, respectively, by the same procedure. The characterization of the resulting polymers was realized by the comparison with bis(nitrobenzimidazolyl) compounds. The nitro absorption peak at 1342 cm$^{-1}$ was used as a criterion for the degree of substitution.

## Results and Discussion

**Monomer Synthesis.** Bis(nitrobenzimidazolyl) compounds are easily prepared because the raw materials, 4-nitro-1,2-phenylenediamine and dicarboxylic acids, are either commercially available or easy to prepare and they are readily converted to stable bis(nitrobenzimidazolyl) compounds **3** as indicated in Scheme 1.

Synthesis of bisbenzimidazole from dibasic acids or esters was not successful in the case of malonic acid or esters, which with *o*-phenylenediamine form *o*-phenylenemalonamide, whereas oxalic acid or its esters with *o*-diamines give 2,3-dihydroxyquinoxalines. However, malonamide with *o*-phenylenediamine gives methylenebis-2-benzimidazole. This synthesis proceeds readily when the *o*-diamine or its salts and the diamide were heated in bulk or preferably in a high-boiling solvent, e.g., ethylene glycol or glycerol. The results are listed in Table 1.

Of the compounds described herein, some have been reported previously in the literature,[16,17] but we offer either greatly improved yield (e.g., **3d**) and greater synthetic convenience (e.g., **3c**) or more complete characterization of compounds reported in relatively inaccessible literature (e.g., **3a**). Compounds **3e**−**j** are novel. Fairley et al.[16] prepared by a different way 1,2-bis(nitrobenzimidazolyl)ethane (**3c**). In their synthesis, 1,2-diamino-4-nitrobenzene was heated under reflux with an imidate hydrochloride of succinonitrile for 10 h to afford **3c** in 45% yield.

The structures of bis(nitrobenzimidazolyl) compounds were identified by $^1$H NMR spectra and were further confirmed by a $^{13}$C NMR spectrum. The chemical shift values were obtained from a spin-decoupled spectrum. By making use of the splitting pattern of the off-resonance spectrum, the values were assigned. Strong solvation of some of the benzimidazoles in the solid state is noted, presumably occurring because of their affinity for H-bonding. The elemental analysis of the compound **3d** does not agree with the theoretical amount of carbon, presumably because of its nature.

Earlier work[18] on nitro-substituted phthalimides, in which the nitro group is displaced by a phenoxide, suggested that bis(nitrobenzimidazolyl) compounds might undergo such a reaction. Although Nunno and Florio[19] noted that sodium methoxide in methanol does not give any displacement of the nitro group on 4-nitro-2,1,3-

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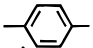
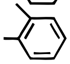
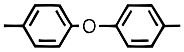
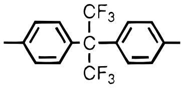
benzothiadiazole. Labadie and Hedrick[20] demonstrated that quinoxaline, benzazole, amide, and perfluoroalkyl groups activate fluoro and, in some cases, nitro displacements from aromatic rings. The imidazole ring in these monomers **3** activates the nitro groups for nucleophilic displacement by the alcoholate ion as shown in Scheme 2.

**Polymer Synthesis.** The polycondensation of bis(nitrobenzimidazolyl) compounds with phenolates and diols was studied in different solvents. The solvent has an important effect, the preferred solvents are polar and aprotic, such as DMSO and NMP, which are good solvents for both reactants and polymers and give a greater enhancement of the reaction rate than other solvents.[21] The polycondensations are carried out in NMP solution, using a slight excess of a weak base (potassium carbonate) catalyst combined with an azeotropic compound (toluene). The best results are obtained with the couple $K_2CO_3$/NMP. When the reaction is carried out without $K_2CO_3$ catalyst, no polymer is obtained. The nucleophilic aromatic displacement of nitro in aromatic compounds is activated by the strongly electron-withdrawing imidazole group, which leads to variable molecular weights (viscosities between 0.24 and 0.77 dL/g), the higher gave a fiber-forming polymer. These products are always soluble in sulfuric acid, which indicates that our technique of polymerization does not give any trace of cross-linked polymer. In particularly, a polycondensation using **3f** carried out in NMP with 1,6-hexanediol and $K_2CO_3$ as a catalyst does not produce impurities such as a cross-linked polymer. This technique allows us to eliminate a number of side reactions and is useful when an accurate dialcohol: bisnitro stoichiometry has to be maintained.

The brown powdery polymers are soluble in DMSO and other solvents; they are characterized by infrared spectroscopy (IR). The PEBIs spectral region between 3500 and 2500 $cm^{-1}$ was analyzed in detail. In particular, the relatively sharp peak at 3415 $cm^{-1}$ was attributed to the stretching vibration of isolated, non-hydrogen-bonded N−H groups, and the very broad, asymmetric absorption, approximately centered at 3145 $cm^{-1}$, was assigned to self-associated, hydrogen-bonded N−H groups. A third low-intensity peak at 3063 $cm^{-1}$ was attributed to the stretching modes of the aromatic C−H groups. The region near 1660−1480 $cm^{-1}$ is very characteristic of benzimidazoles.[21] The C=C/C=N stretching vibrations (1630 $cm^{-1}$) are observed in this region, as well as ring modes which are characteristic of the conjugation between the benzene and the imidazole rings (1590 $cm^{-1}$). Strong absorptions due to in-plane ring modes are found at 1458 and 1438 $cm^{-1}$, whereas an imidazole ring-breathing mode gives rise to a rather broad peak at 1280 $cm^{-1}$. The in-plane C−H deformations, characteristic of substituted benzimidazoles, are found in the region 1230−1090 $cm^{-1}$, and two typical benzene ring modes are found at 1011 and 980 $cm^{-1}$. There were in addition C−O−C stretching bands, the aryl ether band is shown near 1250 and a second band occurs in the 1150−1060 $cm^{-1}$ region which is probably due to the aliphatic ether $CH_2$−O− vibration. Finally, the rings can be observed in the range 900−800 $cm^{-1}$, whose behavior resembles that observed for low-molecular-weight benzene-like compounds.

**Table 2. Poly(ether benzimidazole)s Characterization**

| Compound | Y | R | $\eta_{inh}$[a] (dL/g) | $T_g$[b] (°C) |
|---|---|---|---|---|
| **5a** | -$(CH_2)_6$- | nil | 0.55 | 239 |
| **5b** | -$(CH_2)_6$- | -$CH_2$- | 0.42 | 220 |
| **5c** | -$(CH_2)_6$- | -$(CH_2)_2$- | 0.39 | 185 |
| **5d** | -$(CH_2)_6$- | -$(CH_2)_4$- | 0.37 | 170 |
| **5e** | -$(CH_2)_6$- | -$(CH_2)_8$- | 0.24 | 150 |
| **5f** | -$(CH_2)_6$- | -CH = CH- | 0.51 | 190 |
| **5g** | -$(CH_2)_6$- |  | 0.77 | 250 |
| **5h** | -$(CH_2)_6$- |  | 0.69 | 232 |
| **5i** | -$(CH_2)_6$- |  | 0.57 | 276 |
| **5j** | -$(CH_2)_6$- |  | 0.43 | 244 |

[a] Inherent viscosity measured in NMP at 30 °C, C = 1 g/dL. [b] Transition temperature obtained from DSC with heating rate = 10 °C/min.

Polymer characterization is presented in Table 2. Glass transition temperatures, taken as the midpoint of the change in a slope of the baseline, ranged from 150 to 300 °C for the as-isolated poly(ether benzimidazole)s powders. The inherent viscosities ranged from 0.24 to 0.77 dL/g.

**Thermal Stability.** Thermal stability has been determined for poly(ether benzimidazole)s by weight loss measurements in air atmospheres. The results of thermogravimetric analysis (TGA) given in Figure 1 show that poly(ether benzimidazole)s as a class possess outstanding thermal stability. The degradation temperature $T_d$ of the polymers is situated near 380 °C and the weight loss is about 65% at 800 °C. Characterization of **5e** is given as a typical example for thermogravimetric behavior.

A small weight loss in the temperature range from 100 to 300 °C and a large weight loss at over 420 °C were also observed. The former is due to residual solvent evaporation (NMP) and water (PBIs are known to absorb water because of hydrogen bonding with the benzimidazole ring), and the latter is due to heat decomposition of the polymers backbone. The weight loss in the region 100−300 °C is approximately 10% for **5e**. The poly(ether benzimidazole)s 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)s named Celazole[23] for 10% weight loss was 465 °C in air and 530 °C in nitrogen, respectively. To prepare aromatic polymers with greater flexibility, and therefore with greater solubility, the incorporation of aliphatic ether group has been investigated. Unfortunately, when the solubility increased the thermal stability lowered.

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[21] Johnson, R. N.; Farnham, A. G.; Glendenning, R. A.; Hall, W. F.; Merriam, C. N. *J. Polym. Sci. A1* **1967**, 5, 2375.

[22] Cordes, M. M.; Valter, J. L. *Spectrochim. Acta A* **1968**, *24*, 1421.

[23] Charlotte, NC Celazole PBI Technical Bulletins, Hoeschst Celanese Specialty Operations.

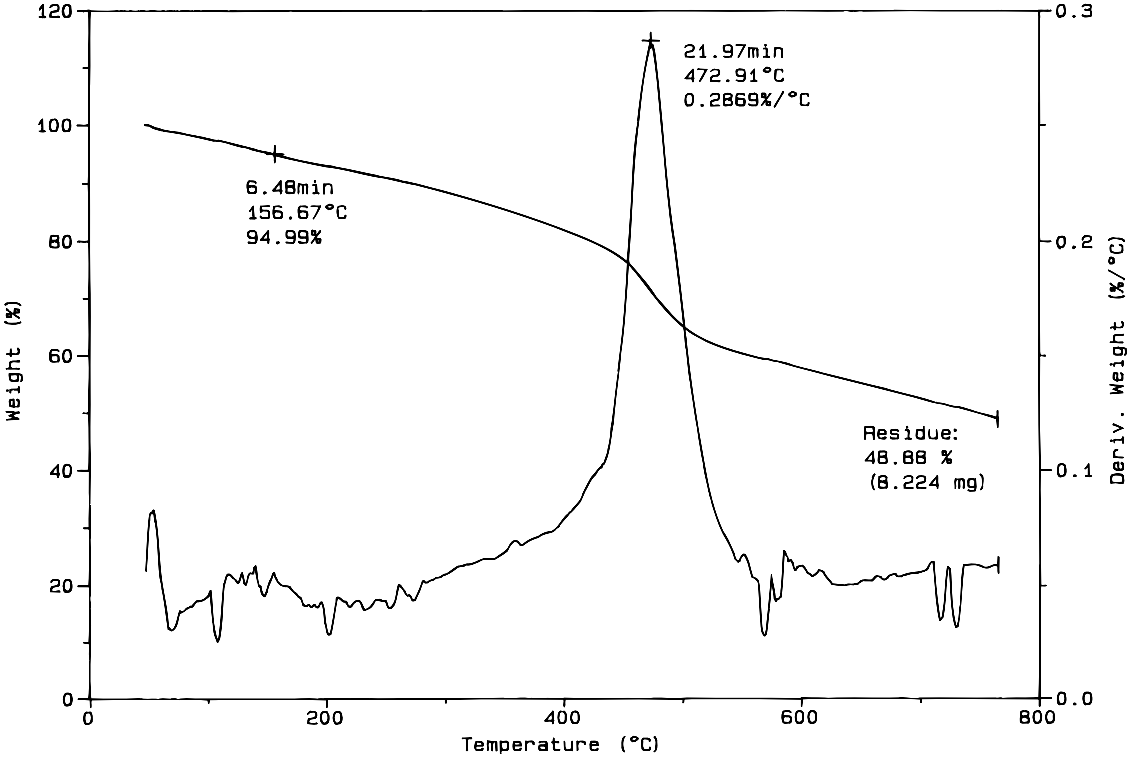

**Figure 1.** Thermograms of Poly(ether benzimidazole)s **5e**

## Conclusions

We have successfully prepared a series of poly(ether benzimidazole)s by the aromatic nucleophilic displacement reaction of 1,6-hexanediol with activated aromatic bis(nitrobenzimidazolyl) compounds. The imidazole ring in these monomers activated the nitro groups for nucleophilic displacement by the alcoholate ion. Moderately high molecular weight polymer was readily achieved, and structural variety could be introduced through the use of different bis(nitrobenzimidazolyl) derivatives. The resulting polymer showed $T_g$'s in the 150−300 °C range, depending on the monomers used in the synthesis. This represents another example of the synthesis of poly(aryl ethers) based on a heterocyclic activated nitro displacement. Moreover, the heterocyclic-activated nucleophilic displacement chemistry povides a general methodology to high-temperature, high-$T_g$ poly(aryl ethers). Using our precursors, we can develop other new copolymers such as poly(imide benzimidazole)s, poly(amide benzimidazole)s, or poly(urea benzimidazole)s by reduction of the nitro groups of **3** to obtain diamine, followed by the condensation reaction with dianhydride, dicarboxylic acids, or diisocyanate, respectively. The new results presented here open access to a new class of interesting polymers. It also allows the design of soluble benzimidazole-containing polymers that are suitable for the processing of advanced materials. The incorporation of aromatic ether groups, unoriented thin-film properties, and carbon fiber unidirectional composite properties are now under study.

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