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# Novel Poly(ether imide)s Utilizing Hydrazine as the Diamine

**Hossein Ghassemi and Allan S. Hay***

*Department of Chemistry, McGill University, Montreal, Quebec, Canada H3A 2K6*

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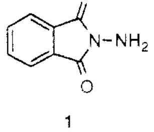
**Introduction.** Polyimides are a class of high-temperature polymers which have gained considerable importance in many engineering applications due to their excellent electrical, thermooxidative, and mechanical properties at elevated temperatures.[1–3] Among the many different types of high-temperature polyheterocycles that have been synthesized, only aromatic polyimides are fabricated on a large commercial scale. Major uses for polyimides are as films, wire enamels, coatings, molding resins, and matrix resins in composites used in the aerospace, transportation, and electrical and electronic industries.[1,2,4] Polyimides are well accepted as highly thermally stable materials; however, applications for polyimides are often limited due to their intractability and insolubility as well as high melting temperatures, which cause a variety of processing problems.[5] Moreover, aromatic diamines which are commonly used in preparation of polyimides are light- and air-sensitive materials and therefore difficult to purify and handle. Furthermore, some aromatic diamines have been found to be carcinogenic, and special care must be taken in handling these materials. Considerable effort has been devoted to the synthesis of new diamines and dianhydrides to improve the solubility and processibility of polyimides without unduly sacrificing thermal stability.[6–8]

Hydrazine and its derivatives have been known for almost a century. It was reported many years ago that hydrazine readily reacts with phthalic anhydride to give two products, *N*-amino imide **1** and phthalhydrazide **2**.[10] When six-membered-ring anhydrides such as naphthalic anhydride are used, the *N*-amino imide **4** is the only product.[9] *N*-Amino imides **1** and **4** are very reactive and readily condense with anhydrides to form bisimides **3** and **5** in quantitative yield.[10] Our interest in soluble polyimides with high $T_{\rm g}$s has been directed toward the synthesis of new types of bis(*N*-amino imide)s which act as diamines when reacted with aromatic dianhydrides. These bis(*N*-amino imide)s were prepared from 4-chloronaphthalic anhydride, hydrazine, and bisphenates in a two-step reaction. We have found that they readily react with aromatic dianhydrides to form high molecular weight polymers.



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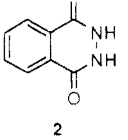

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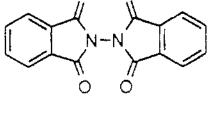

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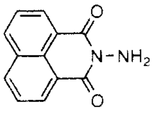

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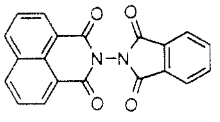

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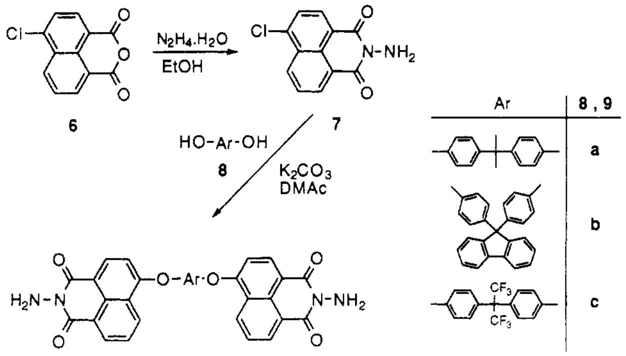
Scheme I



**Results and Discussion.** The monomers 2,2-bis[4-((*N*-aminonaphthalimid-4-yl)oxy)phenyl]propane (**9a**), 9,9-bis[4-((*N*-aminonaphthalimid-4-yl)oxy)phenyl]fluorene (**9b**), and 2,2-bis[4-((*N*-aminonaphthalimid-4-yl)oxy)phenyl]hexafluoropropane (**9c**) were synthesized using the method described for the preparation of Bisphenol A dianhydride (BPADA) with some modifications[11,12] (Scheme I). 4-Chloronaphthalic anhydride (**6**) reacts with hydrazine in ethanol as solvent to give *N*-amino-4-chloronaphthalimide (**7**) in excellent yield. The product crystallized from the reaction mixture in the form of yellow needles and was pure enough to be used in the next step. There was no indication of any chlorine displacement reaction even though a slight excess of hydrazine was used. Bisphenates **8** were generated in *N,N'*-dimethylacetamide solution in the presence of potassium carbonate with removal of the water of the reaction as an azeotrope using toluene as a cosolvent. Under these conditions the displacement of chlorine is quantitative, forming bis(*N*-amino imide)s **9a–c**. The purity of the resulting compounds **9a–c** after recrystallization from *o*-dichlorobenzene (*o*-DCB) or chlorobenzene was very high according to TLC and $^1$H NMR. Compounds **9a–c** are yellow powders and are slightly soluble in chloroform. Compound **9b** was more soluble than the others. They are quite stable at their melting points (280–300 °C) and, unlike aromatic amines, are stable on exposure to light and air. The IR spectra of the bis(*N*-amino imide)s, exhibit C═O absorptions around 1651–1774 cm$^{-1}$ characteristic of the imide ring and around 3260–3344 cm$^{-1}$ for the amino (N–H) stretching vibration.

Soluble high molecular weight poly(ether imides) **10a–f** and **11a–d,f** were prepared by reacting **9a–b** with dianhydrides in a mixture of *m*-cresol and *o*-DCB (Scheme II). The water produced in the polymer synthesis was removed by azeotropic distillation. All the polymers were soluble in their reaction mixtures and were isolated by precipitation in methanol. Inherent viscosities of **10a–f** were in the range of 0.36–0.58 dL/g at a concentration of 0.1 g/dL in NMP at 60 °C. Similar results were obtained for **11a–d,f**, which had inherent viscosities of 0.34–0.46 dL/g. These results indicate that all the polymers are high molecular weight polymers, and this was also confirmed by solution casting of the polymers from *o*-DCB to form clear, tough, and creasable films. In the case of **10a–f** and **11a–d,f** the addition of a few drops of *m*-cresol to the *o*-DCB was necessary to make a clear solution. The IR spectra of the polymers revealed characteristic absorption bands around 1700–1770 cm$^{-1}$ due to the imide carbonyl and around 1108 cm$^{-1}$ due to N–N stretching. No N–H absorption for a hydrazide was detected.

The glass transition temperatures ($T_{\rm g}$s) reported were measured by differential scanning calorimetry (DSC) (Table I) and thermomechanical analysis (TMA) (Table III). Poly(ether imide)s **10a–f** and **11a–d,f** showed very high $T_{\rm g}$s (307–436 °C). Poly(ether imide)s **11a–d,f**, which contain the bulky fluorene group, had higher (23–54 °C)

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**Scheme II**

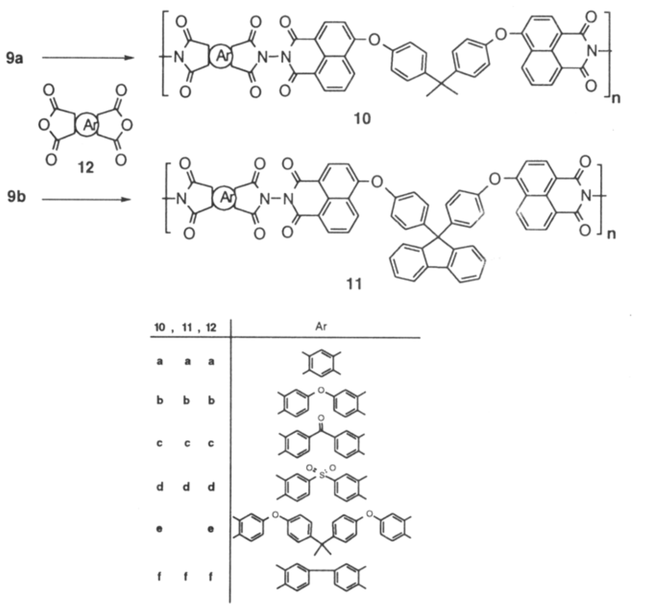

**Table I. Physical Properties of Poly(ether imide)s**

| polymer | $\eta_{inh}$[a] (dL/g) | $T_g$ (°C) | polymer | $\eta_{inh}$[a] (dL/g) | $T_g$ (°C) |
|---|---|---|---|---|---|
| **10a** | 0.47 | ND | **11a** | 0.46 | 436 |
| **10b** | 0.58 | 357 | **11b** | 0.44 | 386 |
| **10c** | 0.54 | 360 | **11c** | 0.45 | 404 |
| **10d** | 0.37 | 362 | **11d** | 0.34 | 385 |
| **10e** | 0.36 | 307 | **11f** | 0.42 | 429 |
| **10f** | 0.47 | 375 | | | |

[a] Inherent viscosities were measured at a concentration of 0.5 g/dL in NMP at 60 °C.

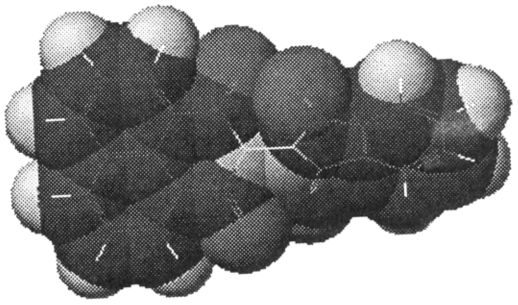

**Figure 1.** 3D structure of the unsymmetric bisimide **5**.

**Table II. Thermal Properties of Poly(ether imide)s 11a–d,f**

| polymer | TGA[a] (°C) | | polymer | TGA[a] (°C) | |
|---|---|---|---|---|---|
| | $N_2$ | air | | $N_2$ | air |
| **11a** | 506 | 507 | **11d** | 500 | 510 |
| **11b** | 510 | 520 | **11f** | 515 | 515 |
| **11c** | 509 | 521 | | | |

[a] Reported for 5% weight loss.

**Table III. Thermomechanical Properties of Poly(ether imide)s**

| polymer | modulus (GPa) at | | tan δ (max) (°C) | polymer | modulus (GPa) at | | tan δ (max) (°C) |
|---|---|---|---|---|---|---|---|
| | 25 °C | 200 °C | | | 25 °C | 200 °C | |
| **10a** | 2.22 | 1.92 | 380 | **11a** | 2.39 | 2.01 | 448 |
| **10b** | 1.81 | 1.48 | 340 | **11b** | 2.31 | 1.92 | 401 |
| **10c** | 2.06 | 1.67 | 345 | **11c** | 2.46 | 2.13 | 401 |
| **10d** | 2.52 | 2.03 | 352 | **11d** | 2.96 | 2.46 | 406 |
| **10e** | 0.72 | 0.68 | 291 | **11f** | 2.45 | 2.01 | 439 |
| **10f** | 2.08 | 1.81 | 366 | | | | |

$T_g$s compared to **10a–f**, which contain the BPA moiety. The lowest $T_g$ value (307 °C, measured by DSC) belongs to **10e**, which has two flexible BPA groups in every repeating unit, and the highest $T_g$ values are obtained for poly(ether imide)s **10a,f** and **11a,f**, which contain the more rigid BPDA and PMDA units. A $T_g$ for poly(ether imide) **10a** was not detectable by DSC. The rigid structure of the bisimide moiety (Figure 1) along with the noncoplanarity of the two aromatic rings and lack of free rotation around the N–N bond are probably responsible for the high $T_g$ values of these poly(ether imide)s. Thermal stabilities of the poly(ether imide)s were determined by thermogravimetric analysis (TGA). As one would expect, poly(ether imide)s **11a–d,f** possess higher thermal stability in air and nitrogen compared to poly(ether imide)s **10a–f**, which contain the isopropylidene group. The TGA results indicated 5% weight losses at 507–521 °C in air for **11a–d,f** (Table II).

Thermomechanical analysis/stress–strain (TMA/SS) measurements were carried out on thin films that were cast from chloroform (**10e**), *o*-DCB (**10b–d** and **11b–d**), or a mixture of *o*-DCB and a small amount of *m*-cresol (**10a–f** and **11a,f**). All the samples were dried at 300 °C under vacuum for 2–3 h before measurements were made. The tensile moduli of all the samples, which should be considered as relative rather than absolute values, were generally in the range of 1.3–3 GPa at 25 °C (Table III). All of the films of poly(ether imide)s of **10a–f** maintained their mechanical properties up to at least 200 °C as indicated by tensile moduli of 1.0–2.0 GPa at this temperature. They start to lose their mechanical properties rapidly around 220 °C for **10e**, which has the lowest $T_g$, and 340 °C for **10a**, which has the highest $T_g$. Poly(ether imide)s **11a–d,f** show slightly higher values of tensile moduli (2–3 GPa) at 25 °C than the corresponding polymers **10a–d,f**. When they were heated to 200 °C, only a small change was observed in their tensile moduli due to their high glass transition temperatures, and they kept most of their mechanical properties, even at 300 °C.

Thus, a new class of bis(*N*-amino imide)s which act as diamines has been prepared in two steps and high yield from readily available compounds. They were reacted with a series of dianhydrides to give high molecular weight novel poly(ether imide)s in one step. All the polymers show extremely high glass transition temperatures and exceptional thermal stability. They are soluble in organic solvents such as NMP, *m*-cresol, and *o*-DCB. Thermomechanical studies show that all the polyimides maintain their properties up to temperatures as high as 200–300 °C. Further work is in progress utilizing bis(*N*-amino imide)s prepared from 1,4,5,8-naphthalenetetracarboxylic dianhydride and 3,4,9,10-perylenetetracarboxylic dianhydride for the preparation of polyimides. High molecular weight polymers and copolymers have been synthesized which are intensely colored and fluorescent.

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