Polyimides from *N,N'*-Diamino-1,4,5,8-naphthalenetetracarboxylic Bisimide

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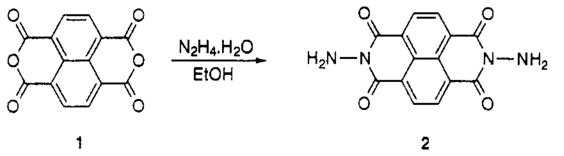
Introduction. Polyimides are the most important commercially available high-temperature polymers. They have found many applications in the electronics and aerospace industries due to their excellent electrical, mechanical, and thermal properties.[1-6] Polyimides are synthesized by the condensation of aromatic diamines and aromatic dianhydrides. Several diamines and dianhydrides have been prepared, but only a few of them are commercially available. High-temperature polymers such as polyimides are basically composed of aromatic and heteroaromatic rings. The rigid and polar structures associated with such aromatic ring systems are responsible for the high use temperatures, as well as the general lack of solubility and difficult processability of these polymers. Insertion of aromatic ether linkages in the main chains of heteroaromatic polymers was found to be an effective approach toward improving processability.[7] This type of modification, generally, leads to lower glass transition temperatures (T_g) and crystalline melting temperatures (T_m). It also improves solubility and other processing characteristics of the polymers. Poly(ether imide)s, for example, are soluble polyimides which can be processed by conventional melt extrusion techniques. The monomers are generally synthesized by an aromatic nucleophilic displacement reaction, and the polymers are made from aryl ether dianhydrides and aromatic diamines.[7-9]

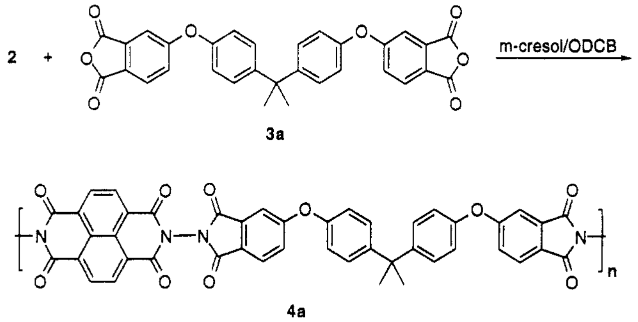
An increasing need for polymers with various specific properties such as high glass transition temperature, improved processability, and long-term thermal stability is still a major driving force for the development of new monomers. The synthesis of a variety of new aromatic diamines and dianhydrides which contain one or more stable flexible linkages between aromatic rings has been reported recently.[10,11] These modifications allow the incorporation of higher aromatic groups such as naphthalene moieties into the polymer chains while maintaining solubility. 1,4,5,8-Naphthalenetetracarboxylic dianhydride reacts with diamino or tetraamino compounds to form polyimides or ladder-type polymers, respectively, which are only soluble in concentrated acids.[12,13] Some dianhydride monomers containing naphthalene units have been recently prepared in low yield via multistep reactions using relatively expensive reagents as starting materials. They form soluble polyimides in a solution polymerization reaction.[14]

Reaction of 1,4,5,8-naphthalenetetracarboxylic dianhydride with hydrazine to form *N,N'*-diamino-1,4,5,8-naphthalenetetracarboxylic bisimide was reported by Dine-Hart.[15] He attempted to make polymers by reacting this diamino compound with pyromellitic dianhydride and 1,4,5,8-naphthalenetetracarboxylic dianhyride. These attempts failed, and only low molecular weight materials were obtained due to the intractability of the resulting products which were only slightly soluble in concentrated sulfuric acid.[16] They were not completely characterized, but the early studies on these low molecular weight materials and some model compounds indicated that they should have high thermal stability at elevated temperatures.[17] We recently reported[18] the synthesis of bis(*N*-aminoimide)s containing naphthalene groups using hydrazine, which upon reaction with aromatic dianhydrides gave high molecular weight poly(ether imide)s with very high glass transition temperature. These polyimides showed very good solubility in many organic solvents. We decided to reinvestigate the polymerization of *N,N'*-diamino-1,4,5,8-naphthalenetetracarboxylic bisimide with more flexible dianhydrides in order to make soluble polyimides and further study their thermal, mechanical, and physical properties. The successful polymerization of *N,N'*-diamino-1,4,5,8-naphthalenetetracarboxylic bisimide with different dianhydrides was carried out in a one-step solution reaction[19] using *m*-cresol or *p*-chlorophenol (PCP) and *o*-dichlorobenzene (ODCB) as solvents, and high molecular weight polymers were formed. The resulting polymers were isolated as yellow fibers, and solution casting of the materials from chloroform, *sym*-tetrachloroethane (TCE), OCDB, or *m*-cresol gave flexible yellow films.

Scheme 1



Scheme 2



Results and Discussion. The monomer *N,N'*-diamino-1,4,5,8-naphthalenetetracarboxylic bisimide (**2**) was synthesized (Scheme 1) by a method similar to that described in our previous paper.[15] 1,4,5,8-Naphthalenetetracarboxylic dianhydride (**1**) slowly dissolved in boiling ethanol over a few hours. Addition of a slight excess of hydrazine monohydrate resulted in the precipitation of a yellow material in a few seconds. Hot filtration of the mixture gave crude product which contained compound **2** and probably some uncyclized hydrazide which was converted to bis(*N*-aminoimide) **2** upon dehydration in vacuum at 80 °C. The yield of the reaction was more than 95%. Monomer **2** was polymerized with Bisphenol A dianhydride (BPADA) (**3a**) in a solution polymerization reaction using *m*-cresol and ODCB as solvents (Scheme 2). Attempts to make polymers from **2** and other aromatic dianhydrides via the one-step method failed due to insolubility of the oligomers which formed in the early stages of the polymerization reaction. Employing the two-step polymerization method giving poly(amic acid) in the first step using NMP as solvent also failed presumably because of insolubility of compound **2** in NMP at ambient temperature. However, high molecular weight copolyimides **4b–e** were successfully prepared (Scheme 3) from **2**, **3a**, and different dianhydrides **3b–e** in a one-step solution polymerization reaction using *m*-cresol/ODCB (1:1) as solvent with a solids concentration of 18%. The

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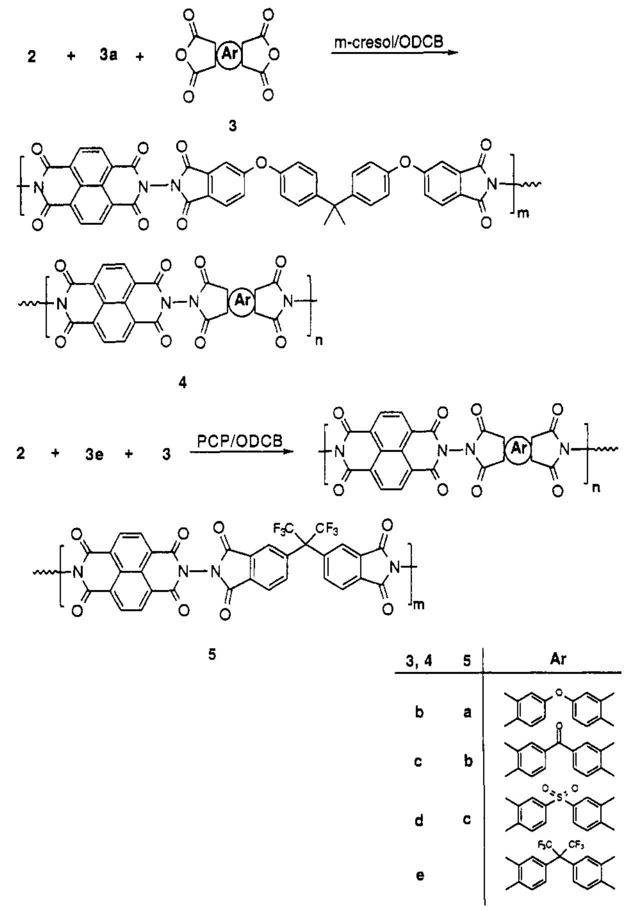
Scheme 3



mole ratio of BPADA to the other dianhydrides was 2:1. Decreasing the relative amount of BPADA affected the solubility of the resulting copoly(ether imide)s in all cases, and low molecular weight polymers precipitated during the polymerization. High molecular weight copoly(ether imide)s **5a–c** were also synthesized (Scheme 3) from **2**, 2,2′-bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride (6FDA) (**3e**), and other dianhydrides as comonomers using the one-step method in a PCP/ODCB (3:1) solvent system with a solids concentration of 8%. Reaction temperatures were in the range of 190–220 °C, depending on the solvent system used in the polymerization. Poly(ether imide) **4a** was readily soluble in chloroform at room temperature, but copolymers **4b–e** were soluble in *m*-cresol or a mixture of ODCB and *m*-cresol and copolymers **5a–c** were soluble in PCP or a mixture of PCP and ODCB at room temperature. All the poly(ether imide) and copoly(ether imide)s except **5a–c** could be readily cast from solution to give flexible, yellow or light-brown transparent films. In the case of copolymers **5a–c**, removal of the PCP from the films was difficult and the films were opaque and after drying at 300 °C under reduced pressure became brittle. Inherent viscosities of the polymers **4a** and other copolymers were in the range of 0.41–1.51 dL/g. To determine the absolute number-average molecular weight of poly(ether imide) **4a**, an end-capped polymer was prepared with a degree of polymerization *n* of 50. The reaction was run using monomers **2** and **3a** in the presence of 4-*tert*-butylphthalic anhydride as an end-capping agent to give poly(ether imide) **4f** with 4-*tert*-butylphthalimide terminal groups (Scheme 4). The number-average molecular weight was determined for the capped materials by ^{1}H NMR studies which gave a degree of polymerization of 51.

Table 1. Physical Properties of Poly(ether imide)s

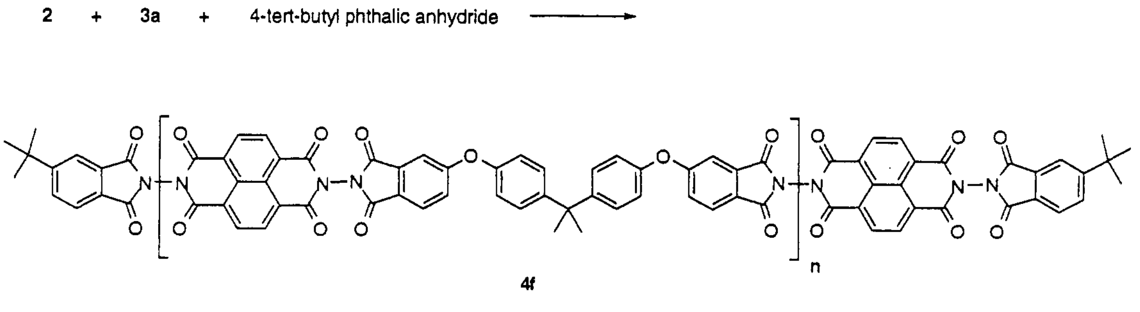
polymer	η_{inh}[a] (dL/g)	T_g[b] (°C)	polymer	η_{inh}[a] (dL/g)	T_g[b] (°C)
4a	0.41	340	**4g**	0.44	288
4b	0.66	360	**5a**	0.65	438
4c	0.52	367	**5b**	0.56	ND
4d	0.70	ND	**5c**	0.41	ND
4e	1.51	ND			

[a] Inherent viscosities were measured at a concentration of 0.5 g/dL in *m*-cresol at 50 °C except for **4a** and **4g**, which were measured in chloroform at 25 °C, and **5a–c**, which were measured in PCP at 50 °C. [b] ND stands for "not detectable".

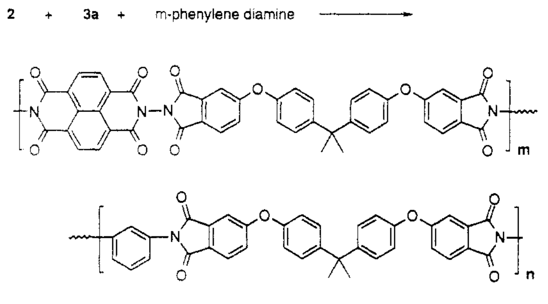
Glass transition temperatures of the polymers **4a–e** are listed in Table 1. All the T_g values are above 340 °C. Poly(ether imide)s **4d,e** and **5b,c** have no detectable T_g by differential scanning calorimetry (DSC) measurement. The T_g of **5c** was determined (456 °C) from tan δ(max) measured by thermomechanical analysis (TMA). The rigid structure of the naphthalene bisimide moiety in the backbone of the polymer and restriction in rotation along the N–N bond are presumably responsible for the high T_g values of the polymers, while BPA groups and ether linkages introduce flexibility and hence solubility to the polymer. T_g values for the more rigid copolymers **5a–c** exceed 400 °C and are close to their degradation temperature.

ULTEM, which is a commercial polymer made from BPADA and *m*-phenylenediamine, has a T_g of 215 °C. Replacement of 50% of *m*-phenylenediamine with **2** (Scheme 5) raised the T_g of the resulting polymer **4g** to 288 °C without decreasing the solubility of the polymer. TGA studies (Table 2) on polymer **4a** and copolymer **4b–e** show high thermooxidative stability with 5% weight losses around 445–465 °C in both air and nitrogen. Copolymers **5a–c**, however, show higher thermooxidative stability (495–526 °C for 5% weight loss). As one would expect, higher glass transition temperatures and replacement of BPADA with 6FDA are the main reasons for the higher thermostability. In the IR spectra of all copolymers, absorption bands characteristic of aromatic polyimides in the range of 1606–1618, 1710–1719, and 1739–1753 cm^{-1} were observed. A weak absorption band is observed around 1101–1112 cm^{-1}, which is characteristic of the N–N bond. Naphthalene-containing polymers **4a–e** show UV absorption bands below 400 nm ($\lambda_{\max}$ = 375 nm, ϵ = 39 000 L

Scheme 4



Scheme 5



4g

Table 2. Thermal and Mechanical Properties of Poly(ether imide)s

	TGA (°C)[a]		modulus (GPa) at		
polymer	N_2	air	25 °C	200 °C	tan δ(max) (°C)
4a	450	456	2.3	2.0	347
4b	444	462	2.4	1.4	365
4c	446	456	1.9	1.2	371
4d	446	459	2.7	1.9	380
4e	451	465	1.5	1.4	390
4g	435	453	2.0	1.7	283
5a	500	506			
5b	495	526			
5c	497	515	1.1	1.1	456

[a] Reported for 5% weight loss.

mol^{-1} cm^{-1} for **4a**), and the fluorescence spectra of films of the polymers show a fluorescence band around 470 nm. Thermomechanical analysis/stress–strain (TMA/SS) measurements were carried out on thin films that were cast from chloroform (**4a**), a mixture of ODCB and *m*-cresol (**4b**,**e**), or PCP (**5a**–**c**) solutions. All the samples were dried at 300 °C under vacuum for 2–3 h before use. The tensile moduli of all the polymers are in the range 1.5–2.4 GPa at 25 °C (Table 2). At 200 °C the samples have tensile moduli of 1.2–2.0 GPa, and due to their high glass transition temperatures they maintain most of their mechanical properties even at temperatures above 300 °C. The low tensile modulus value (1.1 GPa) for polymer **5c** is probably due to the presence of remaining solvent in the film which acts as a plasticizer.

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