Synthesis and properties of poly(ether imide)s derived from 4,4'-(1,5-naphthylenedioxy)diphthalic anhydride and various aromatic diamines

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SUMMARY:
   A naphthalene unit-containing bis(ether anhydride), 4,4'-(1,5-naphthylenedioxy)-diphthalic anhydride, was prepared in three steps starting from the nucleophilic nitro-displacement reaction of 1,5-dihydroxynaphthalene and 4-nitrophthalonitrile in *N,N*-dimethylformamide (DMF) solution in the presence of potassium carbonate. High-molar-mass aromatic poly(ether imide)s were synthesized using a two-stage polymerization process from the bis(ether anhydride) and ten aromatic diamines. The intermediate poly-(ether amic acid)s had inherent viscosities of 0,66–1,27 dL/g. The films of poly(ether imide)s derived from some diamines, such as *p*-phenylenediamine, benzidine, and bis[4-(4-aminophenoxy)phenyl] ether, crystallized and embrittled during the thermal imidization process. The other poly(ether imide)s were amorphous materials and could be fabricated into transparent, flexible, and tough films. These poly(ether imide) films had yield strengths of 111–125 MPa, tensile strengths of 96–150 MPa, elongations to break of 10–38%, and initial moduli of 1,6–2,4 GPa. All of these polymers were insoluble in organic solvents, except for that derived from 2,2-bis[(4-aminophenoxy)phenyl]propane. Their T_g's were recorded in the range of 226–265 °C by DSC. Thermogravimetric analysis (TG) showed that all the polymers were stable up to 535 °C in both air and nitrogen atmosphere.

Introduction

   Aromatic polyimides are well known as high-performance polymer materials, for their excellent thermal stability and chemical resistance, together with balanced electric and mechanical properties[1]. Polyimides are mainly used in the aerospace and electronic industries in the forms of films and moldings. Other uses for these polymers such as adhesives, composite matrices, coatings and foams are rapidly increasing. However, aromatic polyimides are difficult to process because of high softening temperatures and limited solubility in commercially available solvents. In fact, they are usually processed via the form of their poly(amic acid) precursors.
   Poly(ether imide)s with the following general structure (A):

(A)
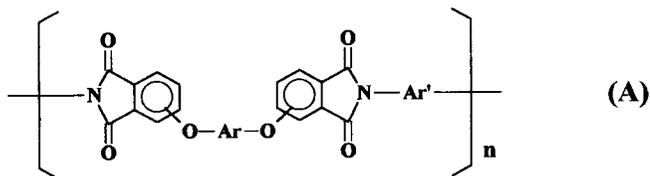
have been receiving much attention because they can provide a compromise between good thermal stability and processability when compared to polyimides. The poly(ether imide)s with the general structure of (A) are usually prepared by the widely utilized two-stage process for the manufacture of polyimides via poly(amic acid)s from bis(ether anhydride)s with general structure (B) and aromatic diamines. The large number of commercially or synthetically available aromatic diols (the source of the Ar moieties) and diamines (the source of the Ar' units) indicates that hundreds of structurally different poly(ether imide)s may be synthesized.
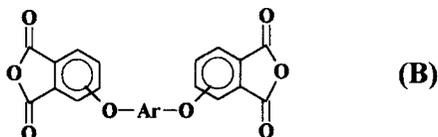
Bis(ether anhydride)s having the structure (B) can be easily prepared using the nucleophilic displacement of a nitro or halide group from a phthalic acid derivative, e.g., 3- or 4-nitrophthalic derivative and 3- or 4-fluorophthalic acid derivative, by reaction with the alkali metal salt of an aromatic diol. The literature depicts two major routes suitable for the synthesis of bis(ether anhydride)s derived from phthalic acid derivatives and various diols; these procedures have been reviewed by Take-koshi[2] and Eastmond et al.[3] The most popular displacement reactions are those between N-phenyl or N-alkyl nitrophthalimides and bisphenolates[4–6]. The bis(ether phthalimide)s so formed are hydrolyzed to tetracarboxylic acids and then dehydrated to yield the bis(ether anhydride)s. The alternative nitrodisplacement reaction is that between nitrophthalonitrile and bisphenolates[7–9]. This reaction produces a tetranitrile which is then converted to the corresponding tetracarboxylic acid and hence to the bis(ether anhydride). In principle, these techniques can be used to synthesize bis(ether anhydride)s from bisphenols (e.g., bisphenol A), benzenediols (e.g., hydroquinone, resorcinol, and catechol), or naphthalenediols. A number of bis(ether anhydride)s have been prepared from bisphenols and benzenediols[2,9]. However, the bis(ether anhydride)s of naphthalenediols are scarcely known.

In a recent publication of Eastmond and Parprotny[9], the synthesis of 4,4'-(1,5-naphthylenedioxy)diphthalic anhydride (4 in Scheme 1) derived from 1,5-di-hydroxynaphthalene has been described; however, no poly(ether imide)s were derived. In our continuing effort to develop high performance, high temperature resistant polymers containing naphthalene moieties, this article deals with the synthesis of bis(ether anhydride) 4 and its derived poly(ether imide)s, and the basic characterization of these polymers as well.

Experimental part

Materials

The materials employed in the synthesis of 4,4'-(1,5-naphthylenedioxy)diphthalic anhydride, including 1,5-dihydroxynaphthalene (Janssen), 4-nitrophthalonitrile (TCI),

potassium carbonate (K$_2$CO$_3$; Fluka), N,N-dimethylformamide (DMF; Fluka), potassium hydroxide (Wako), and acetic anhydride (Janssen), were used without previous purification. p-Phenylenediamine (5a) (Wako) and benzidine (5c) were purified by sublimation. m-Phenylenediamine (5b) (Janssen) was vacuum-distilled prior to use. 4,4'-Bis(4-amino-phenoxy)biphenyl (5h) (m.p. 198–199 °C), bis[4-(4-aminophenoxy)phenyl] ether (5i) (m.p. 112–113 °C), and 2,2'-bis[4-(4-aminophenoxy)phenyl]propane (5j) (m.p. 126 °C) were prepared by the nucleophilic substitution reaction of the corresponding bisphenols, i.e., 4,4'-biphenyldiol, bis(4-hydroxyphenyl) ether, and 2,2-bis(4-hydroxyphenyl)propane (bisphenol A), and p-chloronitrobenzene in the presence of potassium carbonate, giving the bis(p-nitrophenoxy) compounds, and subsequent reduction of the dinitro compounds using hydrazine as the reducing agent and palladium as the catalyst[10, 11]. The other diamines, 4,4'-methylenedianiline (5d) (TCI), 4,4'-oxydianiline (5e) (TCI), 3,4'-oxydianiline (5f), and 1,4-bis(4-aminophenoxy)benzene (5g) (TCI), were used without further purification. N,N-Dimethylacetamide (DMAc) was purified by distillation under reduced pressure over calcium hydride and stored over 4 Å molecular sieves.

4,4'-(1,5-Naphthylenedioxy)diphthalonitrile (2)

In a 300-mL flask, 8,0 g (0,05 mol) of 1,5-dihydroxynaphthalene (1), 17,31 g (0,1 mol) 4-nitrophthalonitrile, and 13,8 g (0,1 mol) of K$_2$CO$_3$ were suspended in 100 mL of DMF. The suspension solution was stirred at room temperature for about 24 h. Then, the reaction mixture was poured into 700 mL of water, and the precipitated brown solid was collected and washed thoroughly with methanol and water. The yield of the product was 19,5 g (95%); m.p. 232–234 °C [245 °C (DSC)].

IR (KBr): 2 230 (C≡N), 1 400–1 600 (arom. C=C), and 1 250 cm^{-1} (C–O).

4,4'-(1,5-Naphthylenedioxy)diphthalic acid (3)

In a 500-mL flask, a suspension of bis(ether dinitrile) 2 (19,5 g; 0,047 mol) in an ethanol/water mixture (200 mL/200 mL) containing dissolved 53,0 g (0,94 mol) of KOH was boiled under reflux. The suspension turned into a clear solution after about 5 days. Reflux was continued for about 1 day until the evolution of ammonia had ceased. The resulting hot, clear solution was filtered to remove any insoluble impurities. The hot filtrate was allowed to cool and acidified by conc. HCl to pH ≑ 3. The brown precipitated product was filtered off, washed repeatedly with water, and dried in vacuum, to give 24,6 g (100%) of bis(ether diacid) 3.

IR (KBr): 2 400–3 600 (O–H), 1 700 (C=O), and 1 250 cm^{-1} (C–O–C).

4,4'-(1,5-Naphthylenedioxy)diphthalic anhydride (4)

In a 1 000-mL flask, bis(ether diacid) 3 (24,6 g; 0,05 mol) was suspended in 300 mL of acetic anhydride and 200 mL of glacial acetic acid. The suspension was boiled under reflux until turning into a clear solution. The resulting hot, clear solution was filtered to remove any insoluble impurities. On cooling, the crystallized brown solid was collected, washed with dry toluene, and dried in vacuo, to give 17,6 g of bis(ether anhydride) 4. Yield 80%; m.p. 252–253 °C [258 °C (DSC)].

IR (KBr): 1 850 (asym. C=O), 1 770 (sym. C=O), 1 400–1 600 (arom. C=C), and 1 280 cm^{-1} (C–O).

C$_{26}$H$_{12}$O$_8$ (452,37)	Calc.	C 69,03	H 2,67
	Found	C 69,07	H 2,64

Syntheses of poly(ether imide)s

A typical polymerization procedure is as follows. 4,4′-Oxydianiline (**5e**) (0.3068 g; 1,532 mmol) was dissolved in 9.5 mL of dried DMAc in a 50-mL flask. After the diamine was dissolved completely, 0.6932 g (1.532 mmol) of bis(ether anhydride) **4** was added in one portion. The mixture was stirred at room temperature for 2.5 h. The inherent viscosity of the resulting poly(ether amic acid) (**6e**) in DMAc was 1.22 dL/g, measured at a concentration of 0.5 g/dL at 30 °C. The polymer solution was poured into a ϕ = 9 cm glass culture dish, which was placed in a 90 °C oven overnight to remove the solvent. The semi-dried poly(ether amic acid) film was further dried and transformed into poly-(ether imide) by sequential heating at 150 °C for 20 min, 180 °C for 20 min, 220 °C for 20 min, and 250 °C for 30 min. By soaking in hot water, a flexible poly(ether imide) film of **7e** self-stripped from the glass surface.

IR of **6e** (film): 2 700–3 400 (N—H and O—H str.), 1 500–1 780 (broad, arom. C=C str. + C=O str. + N—H, O—H bending), 1 200–1 300 cm^{-1} (C—O).

IR of **7e** (film): 1 780 (asym. C=O), 1 730 (sym. C=O), 1 500–1 620 (arom. C=C), 1 380 (C—N), 1 250 (C—O), 1 100, 750 cm^{-1} (imide ring deformation).

All other poly(ether imide)s were prepared by a similar method.
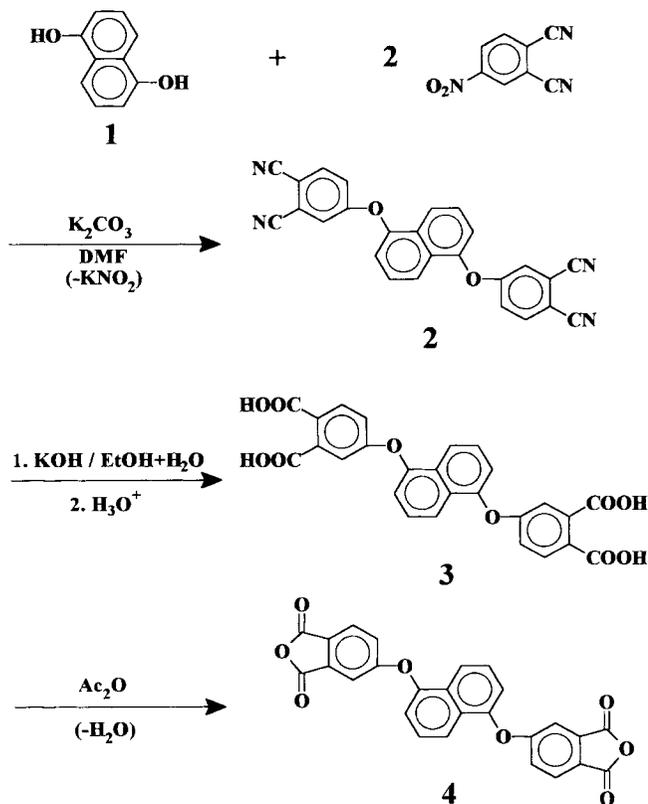
Measurements

IR spectra were recorded on a Jasco FT/IR-7000 Fourier transform infrared spectrometer. Elemental analyses were run in a Perkin-Elmer Model 2400 C, H, N analyzer. The inherent viscosities were measured with an Ubbelohde viscometer thermostated at 30 °C. A Sinku Riko DSC-7000 differential scanning calorimeter equipped with a Sinku Riko TA-7000 analyzer was used to determine the thermal transitions. Heating rate was 20 °C/min. 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. Thermogravimetry (TG) was conducted with a Rigaku thermoflex TG 8110 coupled to a Rigaku TAS-100 thermal analysis station. Experiments were carried out on 9–11 mg samples heated in flowing nitrogen or air (50 cm^3/min) at a heating rate of 20 °C/min. Wide-angle X-ray diffraction measurements were performed at room temperature (about 25 °C) on a Siemens Kristalloflex D5000 X-ray diffractometer, using Ni-filtered CuK$_\alpha$ radiation (40 kV, 15 mA). The scanning rate was 2°/min over a range of 2θ = 5–40°. An Instron universal tester Model 1130 with a load cell 5 kg was used to study the stress-strain behavior of the samples. A gauge of 2 cm and a crosshead speed of 5 cm/min were used for this study. Measurements were performed at room temperature with film specimens (6 cm long, 0.5 cm wide, and about 0.1 mm thick), and an average of at least five individual determinations was used.

Results and discussion

Monomer synthesis

According to a reported method[7-9], the naphthalene unit-containing bis(ether anhydride) **4** was prepared using a three-stage reaction from 1,5-dihydroxynaphthalene (**1**) and 4-nitrophthalonitrile as outlined in Scheme 1. The yield was high, usually above 70% (on the basis of diol **1**). The structure of bis(ether anhydride) **4** was confirmed by element analysis and IR spectroscopy.

The IR spectrum of bis(ether dinitrile) **2** is characterized by a sharp absorption near 2 230 cm^{-1}. The most characteristic bands of bis(ether diacid) **3** are observed

Scheme 1:

HO—(ring)—OH **1**   +   **2** O_2N—(ring)—CN, CN

$\xrightarrow[\text{(-KNO}_2)]{\substack{K_2CO_3 \\ DMF}}$

NC, NC—(ring)—O—(ring)—O—(ring)—CN, CN

2

$\xrightarrow[\text{2. } H_3O^+]{\text{1. KOH / EtOH+}H_2O}$

HOOC, HOOC—(ring)—O—(ring)—O—(ring)—COOH, COOH

3

$\xrightarrow[\text{(-}H_2O)]{Ac_2O}$

4

near 1700 cm^{-1} (C=O stretching) and in the region of 2400–3600 cm^{-1} (O—H stretching). The spectrum of bis(ether anhydride) **4** shows characteristic cyclic anhydride absorbances near 1850 and 1770 cm^{-1}, pointing at the asymmetrical and symmetrical stretching vibrations of C=O.

Synthesis of poly(ether imide)s

All poly(ether imide)s were prepared by the two-stage process outlined in Scheme 2, described above in detail for the polymer (**7e**) derived from bis(ether anhydride) **4** and 4,4′-oxydianiline (**5e**). The diamines used are also listed in Scheme 2. Polymer preparation involved adding the bis(ether anhydride) to a diamine in DMAc solution to form the poly(ether amic acid) (**6**), pouring the poly(ether amic acid) solution onto a glass substrate, slowly evaporating the solvent, and then thermally dehydrating to form the poly(ether imide). As shown in Tab. 1, the inherent viscosities of the intermediate poly(ether amic acid)s are in the 0,66–1,32 dL/g range, indicating the formation of high molar masses. The polymerization results also indicate that the

Scheme 2:

Ar : a, b, c, d, e, f, g, h, i, j
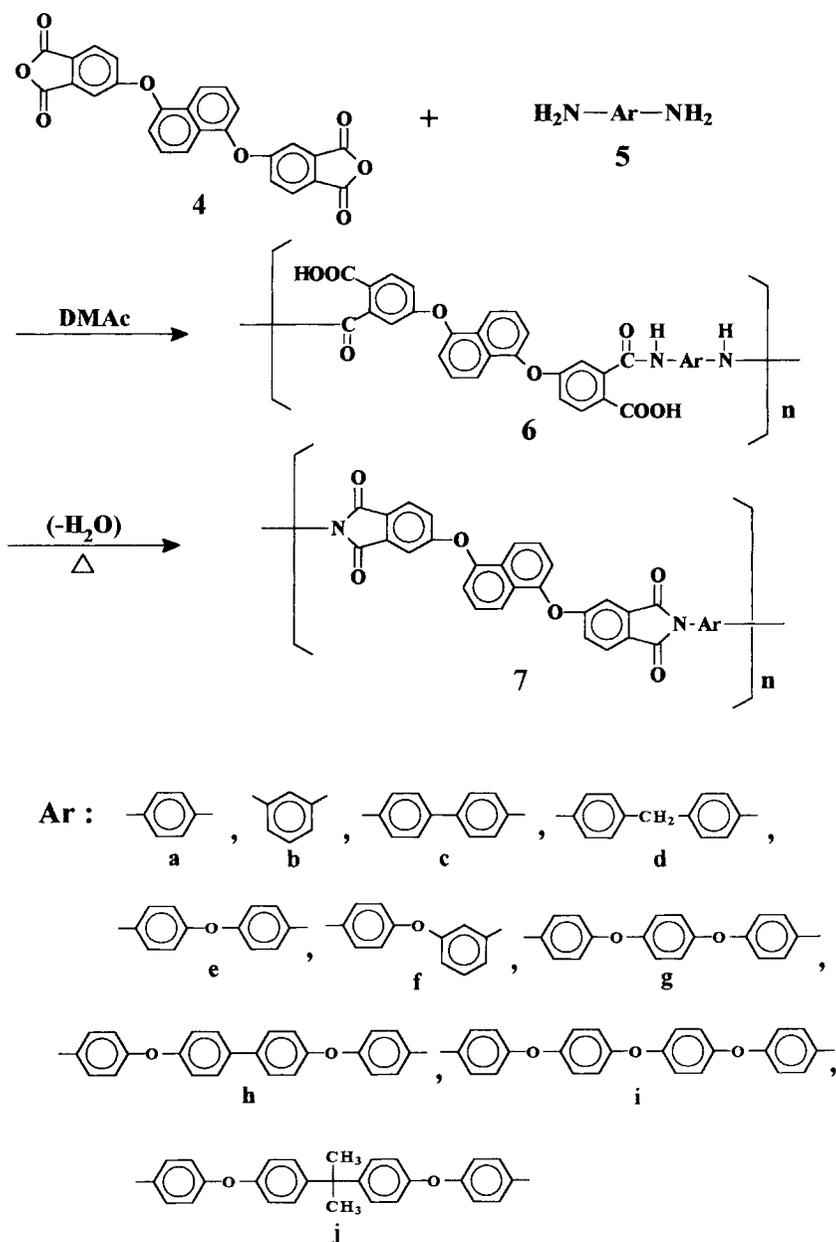
Tab. 1. Characterization of polymers

| Polymer code | η_{inh} [a] dL/g | Tensile properties [b] | | | | T_g [c] in °C | Thermal properties | | Char yield [g] in wt.-% |
		strength at yield point in MPa	strength at break point in MPa	elongation at break point in %	initial modulus in GPa		T_d [f] in °C in air	in N_2	
7a	1,01	–	–	–	–	–[d]	553	570	59,9
7b	0,66	–	136	10	1,9	265	558	563	59,2
7c	1,27	–	–	–	–		570	579	64,7
7d	0,89	–	150	11	2,4	250	546	551	67,2
7e	1,22	125	117	15	2,0	262	566	581	63,5
7f	0,74	–	139	11	2,3	239	558	576	62,4
7g	1,14	119	113	21	1,6	250	559	573	59,1
7h	1,32	115	120	38	1,6	256	565	568	64,5
7i	1,17	–	–	–	–	230 (402)[e]	564	563	54,1
7j	1,04	111	96	19	1,7	226	536	538	58,3

[a] Inherent viscosities of poly(amic acid) precursors, measured in DMAc (0.5 g/dL) at 30 °C.
[b] The poly(ether imide) films were obtained by thermal dehydration of the poly(amic acid) films using the following sequence: 150 °C/20 min, 180 °C/20 min, 220 °C/20 min, 250 °C/30 min. Polymers 7a, 7e, and 7i embrittled during thermal imidization.
[c] From DSC measurement conducted at a heating rate of 20 °C/min; T_g's were read at the middle of the baseline shift on the second DSC heating traces.
[d] No discernible glass transition was observed.
[e] With a sharp endotherm on the first DSC heating scan.
[f] Decomposition temperatures at which 10% weight loss was recorded by TG at a heating rate of 20 °C/min.
[g] Residual weight % at 80 °C in nitrogen.

monomer synthesis is successful. The cast films of poly(ether imide)s **7a** and **7c** derived from rigid diamines, such as *p*-phenylenediamine and benzidine, embrittled during the thermal imidization process. This may be due to a high degree of crystallinity of these poly(ether imide)s. It is unexpected that the cast film of poly(ether imide) **7i**, which was derived from the multi ether-linked flexible diamine **4i**, also revealed a brittle nature. This is also related to its high level of crystallinity, as evidenced by its X-ray diffraction pattern later on. The other films were tough and flexible and could be creased without cracking.

IR spectroscopy allows monitoring of the imide ring formation during cure. When the poly(ether amic acid) was converted into the poly(ether imide), the characteristic absorption bands of amide and carboxyl groups in the regions of $2\,700-3\,400$ cm^{-1} and $1\,500-1\,650$ cm^{-1} disappeared, and those of the imide ring were observed near $1\,780$ (asym. C=O str.), $1\,730$ (sym. C=O str.), $1\,380$ (C—N str.), $1\,100$, and 750 cm^{-1} (imide ring deformation). The aryl ether stretching absorbed near $1\,250$ cm^{-1}.

Properties of poly(ether imide)s

The solubility of poly(ether imide)s was studied qualitatively. Poly(ether imide) **7j** was soluble in polar solvents, such as NMP, DMAc, and DMF, and even in less polar solvents, such as *m*-cresol and chloroform. The other poly(ether imide)s were insoluble in all the solvents tested and only soluble in concentrated sulfuric acid. The high solubility of polymer **7j** may be attributable to the fact that the introduction of the diamine **5j** leads not only to the incorporation of flexible aryl ether and isopropylidene groups, coupling the aromatic portions of the polymer chain, but also to a dilution of the rigid phthalimide units in the polymer backbone. These results imply that the incorporation of 1,5-naphthylenedioxy unit in the poly(ether imide) main chain gives limited improvement in solubility. Unless properly selecting the diamine component, the poly(ether imide)s based on bis(ether anhydride) **4** and conventional diamines usually exhibited limited solubility.

The crystallinity of the prepared poly(ether imide)s was determined by wide-angle X-ray diffraction experiments. Poly(ether imide)s **7a** and **7c**, which embrittled during thermal imidization, showed highly crystalline patterns. This can be attributed to the existence of the following rigid planar imide segments in their polymer backbones:
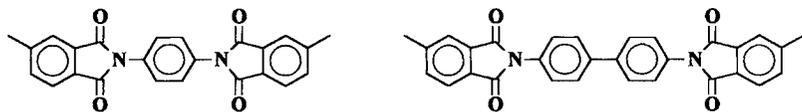
which led to a better packing of polymer chains. On the contrary, the poly(ether imide) **7b** based on *m*-phenylenediamine revealed an almost completely amorphous pattern. Insertion of one or two phenoxy groups into the repeating units of **7a** and **7c** resulted in a significant decrease in crystallinity. For example, polymers **7e**, **7g**, and

7h presented amorphous diffraction patterns. This is reasonable because the presence of kinked *m*-phenylene or ether group induces loose chain packing. However, polymer **7i** showed a partially crystalline pattern, even though the diamine residue exhibits three ether kinks. The reason was not investigated in detail; however, it should be associated with their high chain packing density caused by the flexible symmetric diamine residue. This result also corresponded to the formation of brittle noncreasable film of **7i** during the imidization of its poly(ether amic acid) film.

All the poly(ether imide)s exhibiting amorphous X-ray diffraction patterns could be processed into good-quality and creasable films. These flexible films were subjected to tensile test, and the results are also presented in Tab. 1. All the specimens showed high tensile strengths. Their yield or tensile strengths were usually higher than 111 MPa. Some polymers like **7e**, **7g**, **7h**, and **7j** necked during tensile testing and had a moderate elongation before breaking, indicating high toughness.

Thermal properties of all the poly(ether imide)s were evaluated by thermogravimetry (TG) and differential scanning calorimetry (DSC). All the poly(ether imide)s showed no significant weight loss below 530 °C in air or nitrogen, and more than 54 wt.-% residue remained when heated to 800 °C in nitrogen. The data reported in Tab. 1 show that the 10% weight loss temperatures of these poly(ether imide)s were recorded in the range of 536–570 °C in air and 538–581 °C in nitrogen. Except for the crystalline poly(ether imide)s **7a** and **7c**, all the other polymers showed distinct baseline shifts on their DSC heating traces. Glass transition temperatures (T_g's), defined by the midpoint of baseline shift, of the new polymers stay in the range of 226–265 °C. Poly(ether imide) **7j** has the lowest T_g, 226 °C, which is due to the highest amount of flexible bridges, isopropylidene and ether groups, per elemental unit of the macromolecule. Poly(ether imide) **7i** has a sharp melting endotherm on the first DSC heating trace near 402 °C. Rapid cooling and reheating showed a strong T_g at 230 °C and disappearance of the melting transition, pointing to a low crystallization rate. The large window between T_g and the decomposition temperature makes these polymers attractive for practical processing.

Conclusions

A series of high-molar-mass poly(ether imide)s based on 4,4′-(1,5-naphthylenedioxy)diphthalic anhydride and various aromatic diamines have been prepared as films. Depending on the diamines used, these polymers may be made with high degree of crystallinity or with an amorphous nature. The incorporation of 1,5-naphthylenedioxy units into the polyimide backbone does not seem to lead to a significant increase in solubility. However, several of these polymers exhibited a desired combination of properties that included high strength, excellent thermal stability, and large window between decomposition temperature and T_g.

[1] D. Wilson, H. D. Stenzenberger, P. M. Hergenrother, Eds., *Polyimides*, Chapman and Hall, New York 1990
[2] T. Takekoshi, *Polym. J.* **19**, 191 (1987)
[3] G. C. Eastmond, P. C. B. Page, J. Paprotny, R. E. Richards, R. Shaunak, *Polymer* **35**, 4215 (1994)
[4] T. Takekoshi, J. E. Kochanowshi, J. S. Manello, M. J. Webber, *J. Polym. Sci., Polym. Chem. Ed.* **23**, 1759 (1985)
[5] G. C. Eastmond, J. Paprotny, I. Webster, *Polymer* **34**, 2865 (1993)
[6] H. S.-I. Chao, E. Barren, *J. Polym. Sci., Part A: Polym. Chem.* **31**, 1675 (1993)
[7] U. S. Pat. 3,956,320 (1976), General Electric Co., invs.: D. R. Heath, J. G. Wirth; *Chem. Abstr.* **85**, 62809j (1976)
[8] G. C. Eastmond, J. Paprotny, *Polymer* **35**, 5148 (1994)
[9] G. C. Eastmond, J. Paprotny, *Macromolecules* **28**, 2140 (1995)
[10] K. Suematsu, *Macromolecules* **18**, 2083 (1985)
[11] S.-H. Hsiao, C.-P. Yang, C.-K. Lin, *J. Polym. Res.* **2**, 1 (1995); *Chem. Abstr.* **123**, 287811g (1995)