Polymer 42 (2001) 7993–7998

polymer

www.elsevier.nl/locate/polymer

Synthesis and characterization of new highly organosoluble poly(ether imide)s derived from 1,1-bis[4-(4-dicarboxyphenoxy)phenyl]-4-*tert*-butylcyclohexane dianhydride

Der-Jang Liaw*, Chang-Yu Hsu, Been-Yang Liaw

Department of Chemical Engineering, National Taiwan University of Science and Technology, 43, Section 4, Keeling Road, Taipei 106, Taiwan, ROC

Received 22 January 2001; received in revised form 9 March 2001; accepted 26 March 2001

Abstract

A new bulky pendent bis(ether anhydride), 1,1-bis[4-(4-dicarboxyphenoxy)phenyl]-4-*tert*-butylcyclohexane dianhydride (**3**), was prepared in three steps starting from nitro-displacement of 1,1-bis(4-hydroxyphenyl)-4-*tert*-butylcyclohexane with 4-nitrophthalonitrile to form bis(ether dinitrile) (**1**), followed by alkaline hydrolysis of the bis(ether dinitrile) and subsequent dehydration of the resulting bis(ether diacid). A series of new poly(ether imide)s were prepared from such bis(ether anhydride) (**3**) with various diamines by a conventional two-stage synthesis including the polyaddition and subsequent chemical cyclodehydration. The resulting poly(ether imide)s had inherent viscosities in the range of 0.50–0.79 dl g^{-1}. The GPC measurement revealed that the polymers exhibited number-average and weight-average molecular weight up to 64,000 and 142,000, respectively. All the polymers showed typical amorphous diffraction patterns. All of the poly(ether imide)s showed excellent solubility and were readily soluble in various solvents such as *N*-methyl-2-pyrrolidinone, *N,N*-dimethylacetamide (DMAc), *N,N*-dimethylformamide, pyridine, cyclohexanone, tetrahydrofuran and even in chloroform. These polymers had glass transition temperatures in the range of 227–266°C. Most of the polymers could be dissolved in chloroform of as high as 30 wt% concentration. Thermogravimetric analysis showed that all polymers were stable up to 450°C, with 10% weight loss recorded in the range of 470–515°C in nitrogen. These transparent, tough and flexible polymer films could be obtained by solution cast from the DMAc solution. These polymer films had tensile strength in the range of 79–98 MPa and tensile modulus in the range of 1.8–2.0 GPa.

Keywords: Pendent; *t*-Butyl cyclohexane bis(ether anhydride); Organosoluble

1. Introduction

Aromatic polyimides are thermally stable polymers that exhibit excellent mechanical strength and stability. In the past decade, interest in these polymers has increased in response to increasing technological applications in a variety of fields such as aerospace, automobile, and microelectronics [1]. Aromatic polyimides are normally insoluble in organic solvents, and have extremely high glass transition or melt-temperatures, which preclude melt processing. Hence, a great deal of efforts has been made to improve the processing characteristics of these intractable polyimides. One of the successful approaches to improve solubility and processability of polyimides with minimal detrimental effect on their high thermal stability is the introduction of bulky substituent [2–5] or pendent groups [6–10] along the polymer backbone.

The introduction of cardo (Latin meaning loop) groups into the backbone of polymers is another approach for improving solubility and thereby processability. Cardo polymers exhibit a valuable set of properties: the combination of an increased thermal stability with an increased solubility in organic solvents because of the specific contribution of the cardo group [11–14]. In our previous works, we have found several means for the introduction of cardo groups such as cyclododecylidene [15], adamantane [16], norbornyl [17] and tricyclo[5.2.1.$0^{2.6}$]decane [18] groups in the polymer backbone. In these attempts solubility of polyimide was enhanced while high glass transition temperature and thermal stability were maintained [15–18].

Recently, continuing these studies, we were interested in the potential usefulness of a *tert*-butylcyclohexylidene group as a bulky pendent group in the polymer backbone. *tert*-Butylcyclohexylidene group could be considered as a bulkier pendent group as compared with other pendent

---

* Corresponding author. Tel.: +886-2-27376638/886-2-27335050; fax: +886-2-23781441/886-2-27376644.

E-mail address: liaw@ch.ntust.edu.tw (D.-J. Liaw).

0032-3861/01/$ - see front matter © 2001 Elsevier Science Ltd. All rights reserved.
PII: S0032-3861(01)00287-7

groups mentioned above. The bulkier group possibly may contribute to an enhanced solubility of the polymers [19]. To obtain more insight into the effect of *tert*-butylcyclohexylidene on the properties of the polyimides, a new bis(ether anhydride), 1,1-bis[4-(4-dicarboxyphenoxy)phenyl]-4-*tert*-butylcyclohexane dianhydride (**3**), was synthesized as a monomer in the present study. A series of new poly(ether imide)s were prepared from **3** with various diamines. The general properties such as solubility, crystallinity, thermal and mechanical properties of the obtained polyimides have been investigated.

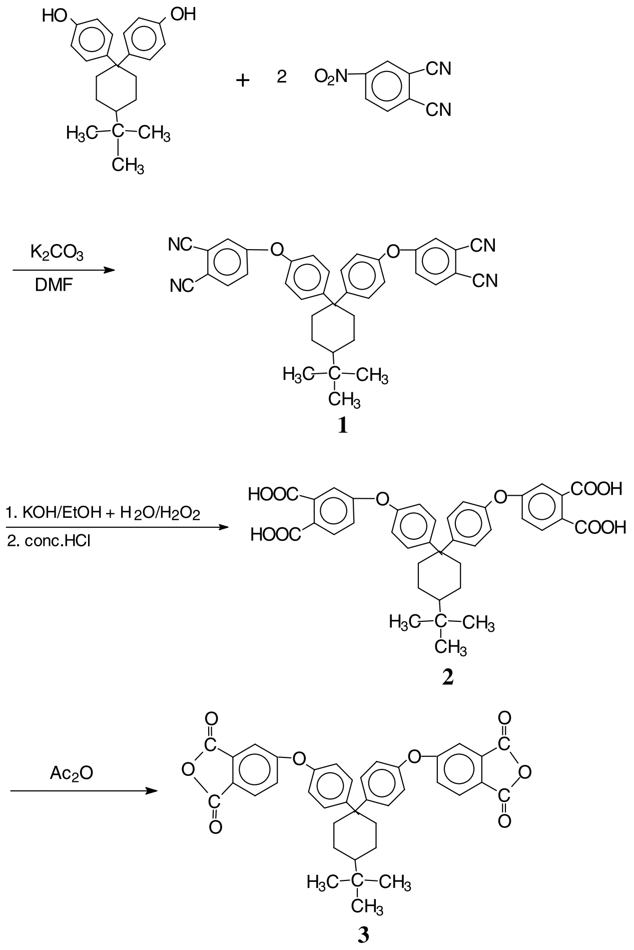
2. Experimental

2.1. Materials

1,1-Bis(4-hydroxyphenyl)-4-*tert*-butylcyclohexane was synthesized according to the procedure given in a previous study [19]. 4-Nitrophthalonitrile (from TCI) was used without further purification. *N,N*-Dimethylformamide (DMF), *N,N*-dimethylacetamide (DMAc) and pyridine were purified by distillation under reduced pressure over calcium hydride before use. Acetic anhydride was purified by vacuum distillation.

2.1.1. Synthesis of monomers (Scheme 1)

*2.1.1.1. 1,1-Bis[4-(4-dicyanophenoxy)phenyl]-4-tert-butylcyclohexane (**1**).* In a 100-ml round-bottomed flask, 5.0 g (16.2 mmol) of 1,1-bis(4-hydroxyphenyl)-4-*tert*-butylcyclohexane and 7.5 g (43.3 mmol) of 4-nitrophthalonitrile were dissolved in 40 ml of dry DMF. Anhydrous potassium carbonate 11.5 g (83.2 mmol) was added and the suspension was stirred at room temperature for 2 days. The reaction mixture was then poured into 500 ml of water to give a pale-yellow solid product which was washed repeatedly with water and methanol, filtered out, and dried. The crude product was then recrystallized twice from acetonitrile to obtain white crystal of bis(ether dinitrile) (**1**) in 86% yield; m.p. 211–212°C. IR (KBr): 2224 ($C\equiv N$) and 1245 cm^{-1} (C–O). ^{1}H NMR (DMSO-d_6): δ (ppm) = 8.10–8.04 (dd, 2H); 7.70 (d, 2H); 7.52 (d, 2H); 7.35–7.28 (m, 4H), 7.14 (d, 2H), 7.04 (d, 2H), 2.82 (d, 2H), 1.82–1.10 (m, 7H), 0.73 (s, 9H); ^{13}C NMR (DMSO-d_6): δ (ppm) = 162.5, 152.8, 149.8, 143.6, 137.6, 137.5, 131.1, 129.2, 123.7, 123.0, 122.9, 121.1, 120.1, 117.7, 117.6, 116.8, 116.3, 109.0, 108.9, 47.2, 45.0, 36.5, 31.9, 27.1, 23.1. Anal. calcd for $C_{38}H_{32}N_4O_2$: C, 79.14%; H, 5.59%; N, 9.72%; found: C, 79.12%; H, 5.51%; N, 9.87%.



Scheme 1.

*2.1.1.2. 1,1-Bis[4-(4-dicarboxyphenoxy)phenyl]-4-tert-butylcyclohexane (**2**).* In a 100-ml round-bottomed flask, 3.5 g (6 mmol) of bis(ether dinitrile) (**1**) was suspended in a solution of 7.24 g (0.17 mol) potassium hydroxide in 55 ml/55 ml of water–ethanol for 1 h and the solid bis(ether dinitrile) had been dissolved within 2 h. Hydrogen peroxide (10 ml) was added dropwise over a period of 0.5 h to the suspension solution. Reflux was continued for 2 days until the evolution of ammonia had ceased. After filtration, the cooled filtrate was diluted with 200 ml of water and acidified by concentrated HCl. The precipitated bis(ether diacid) (**2**) was filtered off and washed thoroughly with distilled water until the filtrate was neutral. The yield was 85%; m.p. 179–181°C. IR (KBr): 2500–3600 (C(O)O–H), 1705 (C=O), and 1225 cm^{-1} (C–O–C). ^{1}H NMR (DMSO-d_6): δ (ppm) = 7.95 (d, 2H), 7.46 (d, 2H), 7.33 (d, 2H), 7.27 (d, 2H), 7.10–7.04 (m, 4H), 6.96 (d, 2H), 2.79 (d, 2H), 1.80–1.07 (m, 7H), 0.73 (s, 9H); ^{13}C NMR (DMSO-d_6): δ (ppm) = 169.7, 169.1, 160.5, 154.2, 148.8, 142.5, 138.3, 134.3, 130.8, 128.9, 128.4, 120.6, 120.3, 120.0, 119.4, 47.3, 44.8, 36.6, 32.0, 27.2, 23.1. Anal. calcd for $C_{38}H_{36}O_{10}$: C, 69.93%; H, 5.55%; found: C, 69.19%; H, 5.34%.

*2.1.1.3. 1,1-Bis[4-(4-dicarboxyphenoxy)phenyl]-4-tert-butylcyclohexane dianhydride (**3**).* In a 100-ml round-bottomed flask, 1.0 g (1.53 mmol) of bis(ether diacid) (**2**) was suspended in 5 ml of glacial acetic acid and 3 ml of acetic anhydride. The mixture was boiled under reflux for

2 days. Then, to the mixture was added 0.5 g of active carbon and stirred for 5 min. The suspension solution was then filtered to remove the active carbon and the filtrate was left to crystallize overnight. The crystal product (**3**) was filtered out and further recrystallized from acetic anhydride. The yellow crystal obtained was filtered out, washed with dry *n*-hexane, and dried at 100°C for 12 h under vacuum to give pure bis(ether anhydride) (**3**). Yield: 85%, m. p. 164–165°C. IR (KBr): 1841, 1768 (C=O), 1278 cm^{-1} (C–O). ^{1}H NMR ($CDCl_3$): δ (ppm) = 7.89–7.84 (m, 2H), 7.44–7.21 (m, 8H), 7.05 (d, 2H), 6.93 (d, 2H), 2.72 (d, 2H), 2.02–1.17 (m, 7H), 0.76 (s, 9H); ^{13}C NMR ($CDCl_3$): δ (ppm) = 166.2, 166.0, 163.6, 163.5, 163.1, 152.7, 152.5, 149.9, 143.7, 134.5, 134.4, 130.8, 128.9, 128.2, 128.1, 125.4, 124.7, 124.6, 120.9, 120.7, 113.0, 112.7, 47.5, 45.0, 37.0, 31.7, 26.7, 22.9. Anal. calcd for $C_{38}H_{32}O_8$: C, 74.00%; H, 5.23%; found: C, 73.45%; H, 5.45%.

2.1.2. Polymerization procedures (Scheme 2)

To a stirred solution of **4a** (0.85 g, 0.524 mmol) in DMAc (5 ml), bis(ether anhydride) (**3**) (0.397 g, 0.85 mmol) was gradually added. The mixture was stirred at room temperature for 2 h under argon atmosphere to form the poly(ether amic acid) precursor. Chemical imidization was carried out by adding extra 3 ml of DMAc, 1 ml of acetic anhydride and 1 ml pyridine into the above-mentioned poly(ether amic acid) solution with stirring at room temperature for 1 h, and then heating at 100°C for 3 h. The homogeneous solution was subsequently poured into methanol and the white stringy precipitate filtered off was washed with methanol and hot water, and then dried at 100°C for 24 h to afford poly(ether imide) **6a**. The inherent viscosity of the polymer in *N,N*-dimethylacetamide (DMAc) was 0.50 dl g^{-1}, measured at a concentration 0.5 g dl^{-1} at 30°C. IR (KBr): 1766, 1718 (imide C=O) and 1367 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ (ppm) = 7.79–7.74 (t,2H), 7.38–7.16 (m,10H), 7.00–6.98 (d,4H), 6.88 (d,4H), 6.79 (d,4H), 2.68–1.13 (m,9H), 0.72 (s,9H); ^{13}C NMR ($CDCl_3$): δ (ppm) = 168.1, 168.0, 164.8, 164.5, 158.5, 158.4, 153.5, 153.4, 149.6, 149.4, 148.4, 143.1, 135.0, 134.9, 131.1, 130.6, 128.7, 128.5, 126.2, 125.8, 125.6, 125.4, 123.5, 120.6, 120.4, 115.6, 112.7, 112.3, 47.7, 45.0, 41.6, 37.1, 31.8, 30.5, 26.8, 23.1, 15.9. All other poly(ether imide)s (**6b–g**) were prepared using a similar procedure.

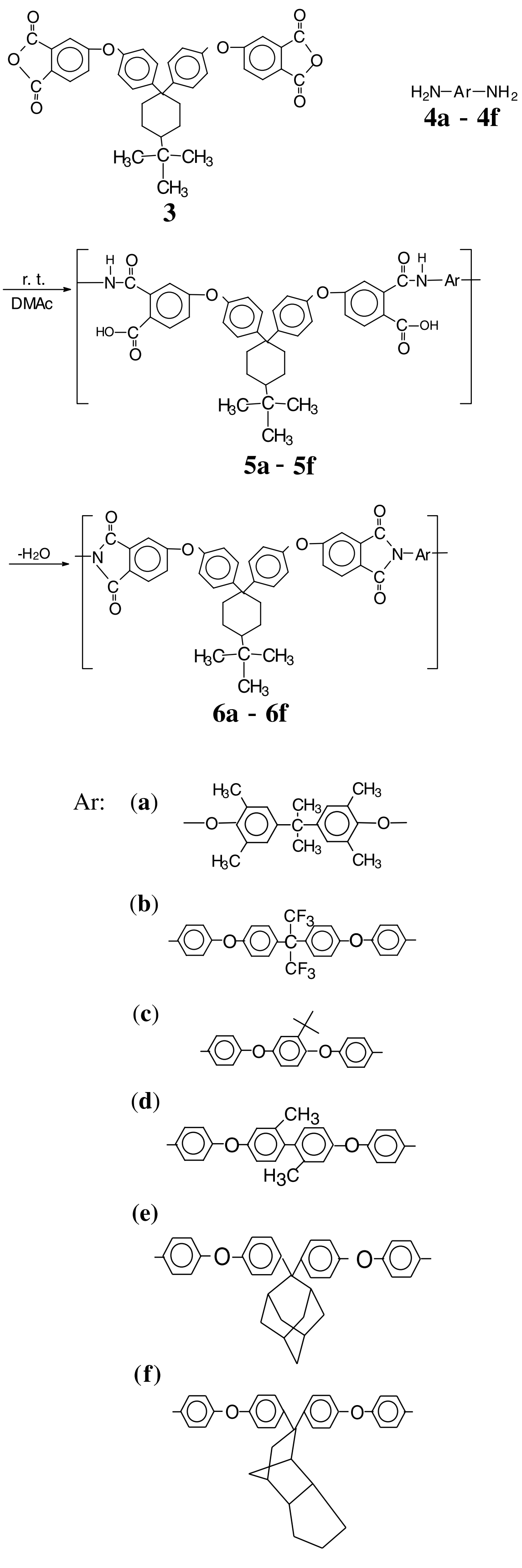
2.1.3. Instruments

Melting points were measured in capillaries on a Büchi apparatus (Model BUCHI 535). IR spectra were recorded in the range 4000–400 cm^{-1} on a JASCO IR-700 spectrometer. ^{13}C and ^{1}H NMR spectra were obtained using a Joel EX-400 operating at 100.40 MHz for carbon and 399.65 MHz for proton. The inherent viscosities of all poly(ether imide)s were measured using Ubbelohde viscometer. Elemental analysis was made (Perkin–Elmer 2400 instrument). Weight-average ($\bar{M}_w$) and number-average molecular weights ($\bar{M}_n$) were determined by gel permeation chromatography (GPC). Four Waters (Ultrastyragel) columns 300 × 7.7 mm^2 (guard, 10^5, 10^4, 10^3, 500 Å in a series) were used for GPC analysis with tetrahydrofuran (THF) (1 ml min^{-1}) as the eluent. The eluents were monitored with a UV detector (Gilson model 116) at 254 nm. Polystyrene was used as the standard. Wide-angle X-ray diffraction patterns were performed at room temperature with film specimens on an X-ray diffractometer (Philips model PW 1710) using Ni filtered Cu-Kα radiation (30 kV, 20 mA). Thermogravimetric data were obtained on a Dupont 2100 in flowing nitrogen or air (60 cm^3 min^{-1}) at a heating rate of 20°C min^{-1}. Differential scanning calorimetry (DSC) analysis was performed on a Dupont 2000 differential scanning calorimeter at a heating rate of 20°C min^{-1}. Tensile properties were determined from stress–strain curves obtained with a 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 (4 mm wide, 5 cm long, and ca. 0.1 mm thick).

3. Results and discussion

3.1. Monomer synthesis

As shown in Scheme 1, the new bis(ether anhydride) was synthesized using a three-step synthetic procedure starting from the nucleophilic nitro-displacement reaction of 1,1-bis(4-hydroxyphenyl)-4-*tert*-butylcyclohexane and 4-nitrophthalonitrile in dry DMF in the presence of potassium carbonate at room temperature. The bis(ether dinitrile) **1** was then hydrolyzed in an alkaline solution ($KOH_{(aq)}$) in the presence of hydrogen peroxide to obtain the bis(ether diacid) (**2**). It was worth noting that nitriles can be hydrolyzed to give either amides or carboxylic acids. Although the amide is formed initially, carboxylic acid is the more common product as amides are hydrolyzed with acid or base. When carboxylic acid is desired, the reagent of choice is aqueous KOH containing about 6–12% hydrogen peroxide, though acid-catalyzed hydrolysis is also carried out frequently [20,21]. The bis(ether diacid) (**2**) was then cyclodehydrated to bis(ether anhydride) **3** using dehydrating agents such as a mixture of acetic anhydride and pyridine. The structure of these synthesized compounds was confirmed by elemental analysis, IR and NMR spectroscopy. The cyano group (C≡N) of compound **1** was evident from the peak at 2224 cm^{-1} in the IR spectrum. In the IR spectrum of **2**, the cyano stretching vibration was absent, but a broad C(O)O–H absorption appeared in the region of 2500–3600 cm^{-1} and a C=O stretching absorption appeared at 1705 cm^{-1}. The IR spectrum of the bis(ether anhydride) **3** shows characteristic cyclic anhydride absorption at 1841 and 1768 cm^{-1} attributing to the asymmetrical and symmetrical stretching vibrations of C=O of the anhydride group. The corresponding ^{13}C and ^{1}H NMR spectra of **1**, **2** and **3** are listed in the Section 2. These results clearly confirm that the dianhydride prepared herein is consistent with the proposed structure.



Scheme 2.

3.2. Preparation of poly(ether imide)s

The poly(ether imide)s (**6a**–**f**) were prepared by the conventional two-step polymerization method, as shown in Scheme 2, which involves ring-opening polyaddition of bis(ether dianhydride) **3** with various diamines (**4a**–**f**) formed poly(ether amic acid) precursors **5a**–**f**. The cyclodehydration of the obtained poly(ether amic acid) solution was carried out by adding dehydrating agents such as a mixture of acetic anhydride and pyridine to produce poly(ether imide)s **6a**–**f**. The resulting poly(ether imide)s had inherent viscosities of 0.50–0.79 $\mathrm{dl\,g^{-1}}$ in DMAc (Table 1). The GPC measurement demonstrated that these polymers exhibited number-average molecular weight ($\bar{M}_n$) and weight-average molecular weight ($\bar{M}_w$) in the range of 31,000–64,000 and 60,000–142,000, respectively. The structure of the polymers was identified by IR and NMR spectroscopy. Specifically, the IR spectra of these poly(ether imide)s revealed that the characteristic bands around 1770 and 1720 $\mathrm{cm^{-1}}$ are commonly attributed to the asymmetric and symmetric stretches of carbonyl group of imide, respectively. The C–N band at 1381 $\mathrm{cm^{-1}}$ verified the formation of the imide structure. The NMR data of the representative polymer **6a** is listed in Section 2. The resonance peaks at 168.1 and 168.0 ppm were ascribed to the carbons of the imides group. The elemental analysis data of these polyimides listed in Table 1 were generally in good agreement with the respective structures for hydrogen and nitrogen, while carbon analysis data were below their theoretical values — a phenomenon common for high-temperature polyimides [3]. All the polymer films could be easily obtained by the solution cast from their DMAc solution. All polymer films showed a transparent, tough and flexible nature. These films were subjected to wide-angle X-ray and mechanical tests.

3.3. Polymer characterization

The crystallinity of these new poly(ether imide)s was estimated by means of wide-angle X-ray diffractograms. All of the cardo poly(ether imide)s exhibited amorphous patterns. The amorphous behavior of the cardo poly(ether imide) is due to the bulky planar substituents, which disrupt the symmetry of their macromolecules and prevent their ordering. In addition, the bulky pendent groups also decreased the intermolecular force between the polymer chains, subsequently causing a decrease in crystallinity.

The solubility behavior of these poly(ether imide)s obtained by the chemical imidization method is summarized in Table 2. It was observed that all of these polymers showed excellent solubility in a variety of solvents, such as NMP, DMAc, *N,N*-dimethylformamide, pyridine, cyclohexanone, THF and even in chloroform at room temperature

Table 1
Inherent viscosity, molecular weight and elemental analysis of various poly(ether imide)s

Polymer code	η_{inh}[a] (dl g^{-1})	$\bar{M}_n \times 10^{-4}$[b]	$\bar{M}_w \times 10^{-4}$[b]		Elemental analysis (%)		
					C	H	N
6a	0.50	6.4	14.2	Calculated	79.13	5.97	2.67
				Found	78.02	6.00	2.71
6b	0.55	4.2	7.9	Calculated	71.03	4.40	2.54
				Found	70.06	4.45	2.54
6c	0.51	3.7	8.5	Calculated	77.57	5.64	3.01
				Found	76.86	5.67	3.05
6d	0.79	4.3	7.6	Calculated	78.67	5.36	2.87
				Found	77.57	5.42	2.83
6e	0.55	3.1	6.0	Calculated	79.83	5.76	2.59
				Found	78.52	5.84	2.54
6f	0.54	5.0	9.6	Calculated	79.83	5.76	2.59
				Found	78.62	5.85	2.59

[a] Measured in DMAc at a concentration of 0.5 g dl^{-1} at 30°C.
[b] Measured by GPC in THF using polystyrene as standard.

or upon heating at 70°C. Most of the polymers could be dissolved in chloroform of as high concentration as 30 wt%. The high solubility of these poly(ether imide)s is due to the presence of the bulky pendent group, which did not allow for dense chain packing and the solvent molecules can penetrate easily to solubilize the polymer chain. The solubility of such new poly(ether imide)s especially, was better than those of the polymers containing cardo groups reported previously [15–18]. For instance, polymers containing cardo groups such as adamantance, norbornane, cyclododecane and methanohexahydroindane in diamine groups showed poor solubility in THF [15–18]. However, polymer derived from 1,1-bis[4-(4-dicarboxyphenoxy)-phenyl]-4-*tert*-butylcyclohexane dianhydride showed excellent solubility in THF and molecular weight could be measured by GPC (Table 1). The thermal behavior data of these poly(ether imide)s are summarized in Table 3.

All of these poly(ether imide)s displayed distinct glass transitions on the second heating DSC traces, whereas endotherms or exotherms are completely lacking. These poly(ether imide)s had glass transition temperatures (T_gs) in the range of 227–266°C, depending on the structure of diamine monomer components. It was observed that polymers **6b** and **6c** containing hexafluoroisopropylidene and *tert*-butyl substituent, respectively, showed relatively lower T_g values than the other poly(ether imide)s. The incorporation of the kink unit such as hexafluoroisopropylidene into the polymer backbone lowered the rigidity of the polymer backbone and reduced the T_g value of the polymers [22]. On the other hand, the presence of the mono-*tert*-butyl substituent in the polymer backbone decreased the order along the polymer chain and reduced the stiffness of the polymer backbones [3,23]. It was noted that polymer **6e** containing rigid adamantane pendent group exhibited the highest T_g value (266°C). In general, introducing rigid and bulky pendent group hindrances the free rotation of the polymer chain and leads to an enhancement of T_g value [24].

Thermogravimetric analysis (TGA) traces revealed that all of the poly(ether imide)s do not decompose around or below 450°C in nitrogen atmosphere. Their decomposition temperatures of 10% weight loss (T_{d10}) were in the range of 470–515°C in nitrogen.

The mechanical property of the tough polyimide films obtained by solution casting is also summarized in Table 3. They have tensile strengths of 79–96 MPa, elongation at break of 6–9%, and tensile modulus of 1.8–2.0 GPa. It demonstrates that most of these poly(ether imide) films are strong materials.

Table 2
Solubility of various poly(ether imide)s (+ + : soluble at room temperature; +: soluble on heating at 70°C; + − : partially soluble on heating at 70°C). Abbreviations: NMP: *N*-methyl-2-pyrrolidinone; DMAc: *N*,*N*-dimethylacetamide; DMF: *N*,*N*-dimethylforamide; THF: tetrahydrofuran

Polymer code	Solvent						
	NMP	DMAc	DMF	Pyridine	cyclohexaone	THF	Chloroform
6a	++	++	++	+	++	++	++
6b	++	++	++	++	++	++	++
6c	++	++	++	++	++	++	++
6d	++	++	++	++	++	++	++
6e	++	++	++	++	++	++	++
6f	++	++	+−	++	++	++	++

Table 3
Thermal and mechanical properties of various poly(ether imide)s

Polymer code	T_g[a] (°C)	T_{d10}[b] (°C)	Tensile strength (MPa)	Elongation at break (%)	Tensile modulus (GPa)
6a	248	470	90	8	1.9
6b	227	515	85	6	2.0
6c	233	504	96	9	2.0
6d	236	507	98	6	1.9
6e	266	513	89	7	2.0
6f	257	494	79	7	1.8

[a] From the second heating trace of DSC measurements conducted at a heating rate of 20°C min^{-1}.

[b] Temperature at 10% weight loss (T_{d10}) determined by TGA in nitrogen at a heating rate of 20°C min^{-1}.

4. Conclusions

A new cardo bis(ether anhydride) bearing bulky pendent *tert*-butylcyclohexyl group was successfully prepared in three steps starting from 1,1-bis(4-hydroxyphenyl)-4-*tert*-butylcyclohexane. A series of poly(ether imide)s were obtained from this bis(ether anhydride) monomer and various diamines. These poly(ether imide)s showed excellent solubility in various organic solvents including chloroform. Most of the polymers could be dissolved in chloroform of as high as 30 wt% concentration. They also showed good thermal stability and mechanical properties. Their T_g and T_{d10} values were as high as 266 and 515°C, respectively. Thus, these new soluble poly(ether imide)s could be considered as new processable high-performance polymeric materials.

Acknowledgements

The authors thank the National Science Council of the Republic of China for supporting this work.

References

[1] Ghosh MK, Mittal KL. Polyimide: fundamentals and applications. New York: Marcel Dekker, 1996.

[2] Jeong HJ, Oishi Y, Kakimoto M, Imai Y. J Polym Sci Part A: Polym Chem 1991;29:39.

[3] Liaw DJ, Liaw BY. Polym J 1996;28:970.

[4] Liaw DJ, Liaw BY, Li LJ, Sillion B, Mercier R, Thiria R, Sekiguchi H. Chem Mater 1998;10:734.

[5] Sun X, Yang YK, Lu F. Macromolecules 1998;31:4291.

[6] Spiliopoulos IK, Mikroyannidis JA. Macromolecules 1998;31:515.

[7] Mikroyannidis JA. Macromolecules 1995;28:5177.

[8] Park KH, Tani T, Kakimoto MA, Imai Y. J Polym Sci Part A: Polym Chem 1998;36:1767.

[9] Kasashima Y, Kumada H, Yamamoto K, Akutsu F, Naruchi K, Miura M. Polymer 1995;36:645.

[10] Yi MH, Huang W, Jin MY, Choi KY. Macromolecules 1997;30:5606.

[11] Jin MY, Choi KY. Macromolecules 1997;30:5606.

[12] Ayala D, Lozano AE, de la Campa JG, de Abajo J. Polym Prepr 1998;39(1):359.

[13] Korshak VV, Vinogradova SV, Vygodski YS. J Macromol Sci, Rev Macromol Chem 1974;C11:45.

[14] Biolley N, Gregoire M, Pascal T, Sillion B. Polymer 1991;32:3256.

[15] Liaw DJ, Liaw BY. Polymer 1999;40:3183.

[16] Liaw DJ, Liaw BY. Macromol Chem Phys 1999;200:1326.

[17] Liaw DJ, Liaw BY. Polym J 1999;31:1270.

[18] Liaw DJ, Liaw BY, Chung CY. J Polym. Sci Part A: Polym Chem 1999;37:2815.

[19] Liaw DJ, Liaw BY, Chung CY. Macromol Chem Phys 2000;201:1887.

[20] March J. Advanced organic chemistry. 4th ed. New York: Wiley, 1992. p. 887–8.

[21] Liaw DJ, Liaw BY, Chen JR, Yang CM. Macromolecules 1999;32:6860.

[22] Park JW, Lee M, Lee MH, Liu JW, Kim SD, Chang JY, Rhee SB. Macromolecules 1994;27:3459.

[23] Heitz W, Niessner N. Makromol Chem 1990;191:225.

[24] Korshak VV, Vinogradova SV, Vygodski YS. J Macromol Sci, Rev Macromol Chem 1974;C11:45.