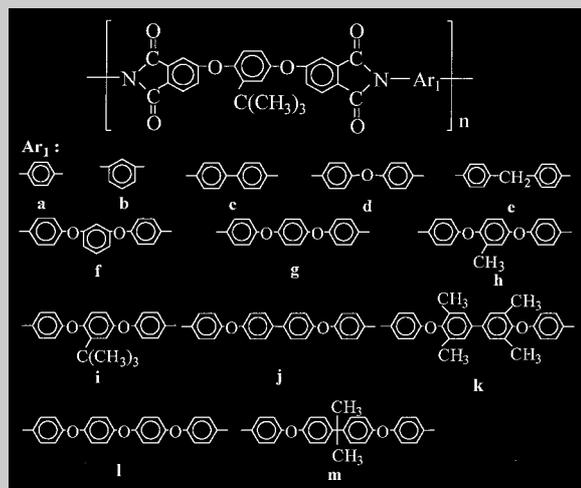


Full Paper: A novel bis(ether anhydride) monomer, 1,4-bis(3,4-dicarboxyphenoxy)-2-*tert*-butylbenzene dianhydride, was synthesized from the nitro displacement of 4-nitrophthalodinitrile by the phenoxide ion of *tert*-butylhydroquinone, followed by alkaline hydrolysis of the intermediate bis(ether dinitrile) and dehydration of the resulting bis(ether diacid). A series of colorless and organosoluble poly(ether imide)s (PEIs) bearing pendent *tert*-butyl groups were prepared from the bis(ether anhydride) with various aromatic diamines via a conventional two-stage process that included ring-opening polyaddition to form the poly(amic acid)s followed by chemical or thermal cyclodehydration to the PEIs. The inherent viscosities of these PEIs are in the range of 0.70–1.44 dL/g. Most PEIs show excellent solubilities in amide polar solvents, *m*-cresol and chlorohydrocarbons. The glass transition temperatures (T_g) of these PEIs were recorded between 217–278 °C, and the decomposition temperatures at 10% weight loss are all above 460 °C in air or nitrogen atmosphere. The PEIs obtained from long chain diamines exhibit high extension to break.



Organosoluble optically transparent poly(ether imide)s based on a *tert*-butylhydroquinone bis(ether anhydride)

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Introduction

Aromatic polyimides are well-known as high performance polymeric materials due to their excellent thermal stability and due to their balanced mechanical and electric properties^{1–6}. They are used for interlayer dielectric for semiconductor devices, e.g. wire coating materials, or as substrates for flexible printed circuits. However, aromatic polyimides are difficult to process because of high softening temperatures and a limited solubility in commercially available solvents. Consequently, the search of new polyimides with better processability, while maintaining their thermal stability, should result in new materials for many applications. On the one hand, the incorporation of ether groups or other flexibilizing linkages into the main chain generally leads to lower glass transition temperatures (T_g) as well as to a significant improvement of the solubility and the thermoplasticity of the polymers^{7–10}. On the

other hand, the introduction of bulky groups^{11–18} into the polymer main chain or the attachment of bulky pendent groups^{19–21} can impart a significant increase in T_g by restricting the segmental mobility, while providing a good solubility due to decreased packing and crystallinity. Combining these two structural modifications minimizes the trade-off between the processability and the properties of aromatic polyimides.

Optical transparency of polyimide films is of special importance for some applications such as flexible solar radiation protectors, orientated films in liquid crystal display devices, optical waveguides for communication interconnectors, and optical half-waveplates for planar lightwave circuits. However, most of the conventional polyimide films always show considerable coloration from pale yellow to deep brown due to charge-transfer complexing between alternating electron-donor (diamine)

and electron-acceptor (dianhydride) moieties²²). St. Clair et al.^{23,24} have shown that polymer backbone alternations which result in a lowering of the charge-transfer complexing generally lead to polyimides with lower a color intensity. A number of very lightly colored to colorless, transparent polyimide films have been synthesized and characterized²⁵). Recently a fluorinated dianhydride monomer, i.e. (hexafluoroisopropylidene)-2,2-diphthalic anhydride (6FDA), has been extensively investigated because the highly soluble polyimides are obtained while maintaining their good thermal stability. The fluorinated polymers are also colorless, which is advantageous for applications such as photopolymers and optoelectronics^{26,27}). An alternating effective approach for lowering color has been to use diamines or dianhydrides that contain alkyl groups that not only eliminate electronic interactions, but also tend to break up extended conjugation along the chain^{28–30}).

It has been reported in our previous publications^{31,32}) that aromatic polyamides and polyarylates having pendant *tert*-butyl group showed higher T_g s and a better solubility than their analogues without *tert*-butyl group, and these polymers form almost colorless, tough films. The polymers were based on 5-*tert*-butylisophthalic acid and its acid chloride derivative. It is well-known that *tert*-butyl group on the aromatic ring is highly resistant to oxidation due to the lack of benzylic hydrogens. Hence, these materials also exhibit high thermo-oxidative stability. Recently, Liaw and Liaw^{33,34}) studied a series of polyimides derived from *tert*-butylhydroquinone- and di-*tert*-butylhydroquinone-based ether-linked diamines. For the former polyimide a relative decrease of the T_g and the crystallinity and some enhancement in solubility were observed due to its non-symmetric nature. Additionally the structure alternation in the dianhydride moiety of polyimides may also have consequences. Modifications in the dianhydride moiety may decrease the charge transfer complexing by separating the aromatic rings and reducing the co-planarity. For example, Eastmond et al.³⁵) studied a series of poly(ether imide)s with alkyl-substituted ether-linked dianhydrides. The linkage groups were based on some hydroquinone derivatives, such as trimethylhydroquinone and di-*tert*-butylhydroquinone. These materials showed an enhanced solubility and acceptable thermal properties. More recently, we reported on a series of poly(ether imide)s based on the bis(ether anhydride)s synthesized from hydroquinone and its methyl-, chloro-, and phenyl-derivatives³⁶). It was found that the incorporation of larger side groups such as chloro or phenyl group on the poly(ether imide) backbone could substantially decrease their crystallinity and could increase their solubility.

In the present article, a new family of poly(ether imide)s derived from the *tert*-butylhydroquinone-based bis(ether anhydride), i.e. 1,4-bis(3,4-dicarboxyphenoxy)-

2-*tert*-butylbenzene dianhydride (**III** in Scheme 1), has been synthesized. The solubility in organic solvent, the tensile properties, and the optical and thermal properties of the polyimides were examined. Several pyromellitic dianhydrides (PMDA) and 6FDA polyimides and polyimides based on 1,4-bis(4-aminophenoxy)-2-*tert*-butylbenzene were also examined for comparison. It was hoped that the incorporation of the hindered ether-linked dianhydride would decrease polymer inter- and intramolecular interactions and would generally disrupt the co-planarity of aromatic units to reduce the packing efficiency and the crystallinity. This should promote the solubility and decrease the color intensity while maintaining high a T_g through controlled segmental mobility.

Experimental part

Materials

tert-Butylhydroquinone (*t*-BHQ) (TCI), 4-nitrophthalodinitrile (TCI), acetonitrile (Alps), *N,N*-dimethylformamide (DMF) (Fluka), acetic anhydride (Ac_2O) (Fluka) were used as received. *p*-Phenylenediamine (**IV_a**) (Wako) and *m*-phenylenediamine (**IV_b**) (TCI) were vacuum-distilled, and benzidine (**IV_c**) (TCI) was crystallized prior to use. Some diamines such as 4,4'-oxydianiline (**IV_d**) (TCI), 4,4'-diaminodiphenylmethane (**IV_e**) (TCI), 1,3-bis(4-aminophenoxy)benzene (**IV_f**) (TCI), 1,4-bis(4-aminophenoxy)benzene (**IV_g**) (TCI), 4,4'-bis(4-aminophenoxy)biphenyl (**IV_j**) (Chriskev), and 2,2-bis[4-(4-aminophenoxy)phenyl]propane (**IV_m**) (Chriskev) were used as received. According to a literature procedure^{37–40}), 1,4-bis(4-aminophenoxy)-2-methylbenzene (**IV_h**) (m.p.: 101–102 °C), 1,4-bis(4-aminophenoxy)-2-*tert*-butylbenzene (**IV_i**) (m.p.: 129–130 °C; lit.³³) 134 °C), 4,4'-bis(4-aminophenoxy)-3,3',5,5'-tetramethylbiphenyl (**IV_k**) (m.p.: 225–226 °C), bis[4-(4-aminophenoxy)phenyl] ether (**IV_l**) (m.p.: 109–110 °C) were prepared from corresponding bisphenol precursors, i.e. methylhydroquinone (TCI), *t*-BHQ (TCI), 3,3',5,5'-tetramethyl-4,4'-biphenol (TCI), and 4,4'-oxybisphenol (TCI). *N*-Methyl-2-pyrrolidone (NMP, Fluka) and *N,N*-dimethylformamide (DMF, Fluka) were purified by distillation under reduced pressure over calcium hydride and stored over 4 Å molecular sieves.

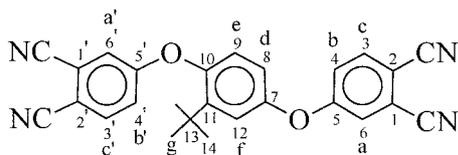
Monomer synthesis

1,4-Bis(3,4-dicyanophenoxy)-2-*tert*-butylbenzene (I): In a 250-mL flask, 6.23 g (37.5 mmol) of *t*-BHQ, 12.98 g (75 mmol) of 4-nitrophthalodinitrile and 10.4 g (37.6 mmol) of K_2CO_3 were suspended in 110 mL of DMF. The suspension solution was stirred at room temperature for about 24 h. Then, the reaction mixture was poured into 600 mL of water, and the precipitated white solid was collected and washed thoroughly with methanol and water. The yield of the product was 15.68 g (100% yield) (m.p.: 209–227 °C). The crude product was purified by recrystallization from acetonitrile to obtain colorless crystals (12.8 g, 82% yield) (m.p.: 231–233 °C).

IR (KBr): 2232 (C≡N), 1243 cm⁻¹ (C—O).

¹H NMR (400 MHz, DMSO-*d*₆): δ = 8.11 (d, 2H, H_c + H_{c'}), 7.79 (dd, 2H, H_b + H_{b'}), 7.50 (d, 2H, H_a + H_{a'}), 7.23 (s, 1H, H_f), 7.11 (s, 2H, H_d + H_e), 1.33 (s, 9H, H_g).

¹³C NMR (100 MHz, DMSO-*d*₆): δ = 162.26 (C⁴, C^{4'}), 151.83 (C⁷), 151.14 (C¹⁰), 145.25 (C¹¹), 137.33, 137.26 (C⁶, C^{6'}), 124.52 (C⁹), 123.21, 123.09, 123.03, 122.75 (C⁸, C¹², C⁵, C^{5'}), 121.04, 120.71 (C³, C^{3'}), 117.79, 117.65 (C², C^{2'}), 116.60, 116.16 (—CN), 109.03, 109.00 (C¹, C^{1'}), 34.46 (C¹³), 29.54 (C¹⁴).



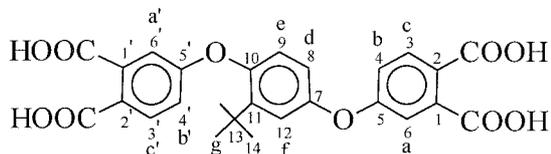
C₂₆H₁₈O₂N₄ (418.45) Calc. C 74.63 H 4.34 N 13.39
 Found C 74.59 H 4.43 N 13.12

1,4-Bis(3,4-dicarboxyphenoxy)-2-tert-butylbenzene (II): In a 500-mL flask, a suspension of bis(ether dinitrile) **I** (12.5 g, 30 mmol) in an ethanol/water mixture (110 mL/110 mL) containing dissolved 27 g (0.48 mol) of KOH was boiled under reflux. Reflux was continued for about 30 h until the evolution of ammonia had ceased. The resulting, clear solution was filtered hot to remove any possible insoluble impurities. The filtrate was allowed to cool and was then acidified by concentrated HCl to pH = 1–2. The white precipitated product was filtered off, washed with water until neutral, and dried under vacuum (100 °C, 6 h) · 14.3 g (98%) of bis(ether diacid) **II** were obtained.

IR (KBr): 2500–3600 (O—H), 1710 (C=O), 1221 cm⁻¹ (C—O—C).

¹H NMR (400 MHz, DMSO-*d*₆): δ = 7.96 (d, 2H, H_c + H_{c'}), 7.39 (dd, 2H, H_b + H_{b'}), 7.16 (s, 1H, H_f), 7.10 (d, 2H, H_a + H_{a'}), 6.99 (s, 2H, H_d + H_e), 1.31 (s, 9H, H_g).

¹³C NMR (100 MHz, DMSO-*d*₆): δ = 169.77, 169.73 (—COOH), 160.97, 160.60 (C⁴, C^{4'}), 152.85 (C⁷), 151.50 (C¹⁰), 144.57 (C¹¹), 138.40, 138.36 (C⁶, C^{6'}), 134.34 (C², C^{2'}), 128.33, 128.00 (C¹, C^{1'}), 124.06 (C⁹), 120.10, 119.86, 119.62, 119.52, 119.34, 119.04 (C⁸, C¹², C⁵, C^{5'}, C⁵, C^{5'}), 34.56 (C¹³), 29.70 (C¹⁴).

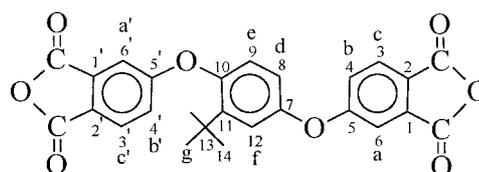


1,4-Bis(3,4-dicarboxyphenoxy)-2-tert-butylbenzene dianhydride (III): In a 200-mL flask, bis(ether diacid) **II** (14 g, 28.3 mmol) was suspended in 35 mL of acetic anhydride and 35 mL of glacial acetic acid. The suspension was boiled under reflux until turning into a clear solution. The resulting, clear solution was filtered hot to remove any insoluble impurities. During cooling, the crystallized white crystals were collected, washed with dry toluene, and dried in vacuum. 10.4 g (80%) of bis(ether anhydride) **III** were obtained; m.p.: 211–213 °C.

IR (KBr): 1848 (asym. C=O str.), 1780 (sym. C=O str.), 1478–1615 (arom. C=C), 1258 cm⁻¹ (C—O—C).

¹H NMR (500 MHz, DMSO-*d*₆): δ = 8.00, 7.98 (d, 2H, H_c + H_{c'}), 7.50 (m, 4H, H_a + H_{a'} + H_b + H_{b'}), 7.25 (s, 1H, H_f), 7.00 (s, 2H, H_d + H_e), 1.37 (s, 9H, H_g).

¹³C NMR (125 MHz, DMSO-*d*₆): δ = 164.81, 164.66 (carbonyl carbons), 162.43, 162.38 (C⁴, C^{4'}), 151.13 (C⁷), 150.62 (C¹⁰), 145.15 (C¹¹), 134.06, 133.95 (C², C^{2'}), 127.86, 127.73 (C¹, C^{1'}), 125.14 (C⁶, C^{6'}), 124.81, 124.54 (C⁵, C^{5'}), 123.23 (C⁹), 120.62 (C⁸), 119.51 (C¹²), 112.98, 112.53, (C³, C^{3'}), 35.08 (C¹³), 29.97 (C¹⁴).



C₂₆H₁₈O₈ (458.45) Calc. C 68.12 H 3.96
 Found C 67.82 H 4.01

Synthesis of poly(ether imide)s

Typical procedures for the syntheses of poly(ether imide)s **C-VI_i** and **VI_i** are described below.

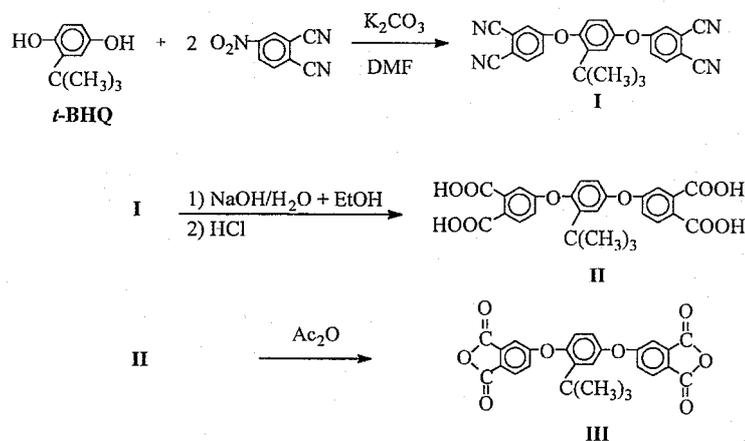
Chemical cyclodehydration: 1,4-Bis(4-aminophenoxy)-2-tert-butylbenzene (**IV_i**) (0.348 g, 1 mmol) was dissolved in 6.29 mL of dried DMAc in a 50-mL flask. After the diamine was dissolved completely, 0.458 g (1 mmol) of bis(ether anhydride) **III** was added in one portion. The mixture was stirred at room temperature for 1 h. The inherent viscosity of the resulting poly(ether amic acid) (PAA) (**V_i**) in DMAc was 1.31 dL/g, measured at a concentration of 0.5 g/dL at 30 °C. Then, a mixture of acetic anhydride (1.0 mL) and pyridine (0.5 mL) was added to the PAA solution, and the reaction mixture was stirred at 80–100 °C for 1 h. The resulting solution was poured into methanol, and the white precipitate was collected by filtration, washed thoroughly with methanol, and dried. The inherent viscosity of the chemically-imidized poly(ether imide) **C-VI_i** in DMAc at a 0.5 g/dL concentration at 30 °C was 1.27 dL/g.

Thermal cyclodehydration: By a similar procedure described as above, a PAA solution of **V_i** in DMAc was prepared (about 6.5 mL, concentration = 10 wt.-%, η_{inh} = 1.30 dL/g). The PAA solution was poured into a glass culture dish (φ = 9 cm), which was placed in a 80 °C oven for 1 h to remove the solvent. The semi-dried PAA film was further dried and imidized by sequential heating at 120 °C for 30 min, 160 °C for 15 min, 210 °C for 15 min, and 250 °C for 30 min. By being soaked in water, a flexible PEI film of **VI_i** was self-stripped off the glass surface.

IR of PAA **V_i** (film): 3500–3000 (O—H and N—H str.), 1717 (C=O, carboxylic acid), 1604 (C=O, amide), and 1211 cm⁻¹ (C—O—C).

IR of PEI **VI_i** (film): 1779 (asym. C=O str.), 1724 (sym. C=O str.), 1607–1480 (arom. C=C str.), 1379 (C—N), and 1227 (C—O), 1080 and 745 cm⁻¹ (imide ring deformation).

Scheme 1:



Measurements

Elemental analyses were run in a Perkin-Elmer Model 2400 C, H, N, analyzer. ^1H and ^{13}C NMR spectra were recorded on a Jeol EX-400 FT-NMR spectrometer or a Bruker DMX-500 MHz FT-NMR spectrometer. IR spectra were recorded on a Jasco FTIR-7000 Fourier-transform Infrared Spectrometer. The inherent viscosities were measured with a Cannon-Fenske viscometer at 30°C . DSC traces were measured on a Sinku Riko 7000 differential scanning calorimeter coupled to a basic component TA 7000 thermal analyzer at the rate of $10^\circ\text{C}/\text{min}$ in flowing nitrogen ($30 \text{ cm}^3/\text{min}$). Thermogravimetry analysis (TGA) measurements were conducted with a Rigaku thermoflex TG 8110 coupled to a Rigaku TAS-100, the experiments were carried out on $10 \pm 2 \text{ mg}$ samples heated in flowing nitrogen ($50 \text{ cm}^3/\text{min}$) at a heating rate of $20^\circ\text{C}/\text{min}$. An Instron universal tester Model 1130 with a load cell of 5 kg was used to study the stress-strain behavior of the polymer films. A gauge length of 2 cm and a strain rate of 5 cm/min were used for this study. The measurements were performed at room temperature with film specimens (0.5 cm wide, 6 cm long, and about 0.5 mm thick) and an average of at least five individual determinations was used. The color intensity of the polymers was evaluated by a Macbeth Color-eye colorimeter. Measurements were performed with films of about 0.05 mm in thickness, using an observational angle of 10° and a CIE (Commission International de l'Eclairage)-D illuminant. A CIE LAB color difference equation was used.

Results and discussion

According to a well-developed method^{8,9}, the bis(ether anhydride) monomer **III** containing the *tert*-butyl group was prepared by a three-step reaction sequence as shown in Scheme 1 starting from the nitro displacement of 4-nitrophthalodinitrile with *t*-BHQ. The yield in each step was satisfactory, and the structure of bis(ether anhydride) **III** was confirmed by elemental analysis and infrared, ^1H NMR, and ^{13}C NMR spectroscopy. The satisfactory

Tab. 1. Synthesis of poly(ether imide)s

PAA ^{a)}	$\eta_{\text{inh}}^{\text{b)}$ dL/g	PEI ^{c)}	$\eta_{\text{inh}}^{\text{b)}$ dL/g
V_a	1.04	C-VI_a	0.90 ^{d)}
V_b	0.72	C-VI_b	0.70
V_c	1.05	C-VI_c	0.99 ^{d)}
V_d	0.99	C-VI_d	0.94
V_e	1.07	C-VI_e	1.00
V_f	1.51	C-VI_f	1.44
V_g	1.32	C-VI_g	1.29
V_h	1.10	C-VI_h	1.07
V_i	1.31	C-VI_i	1.27
V_j	1.20	C-VI_j	1.08
V_k	1.02	C-VI_k	1.00
V_l	1.08	C-VI_l	1.05
V_m	1.10	C-VI_m	1.05

a) Polymerization was carried out with 1 mmol of each monomer in DMAc at a concentration of about 10 wt.-% at room temperature for 1 h.

b) Measured at a concentration of 0.5 g/dL in DMAc at 30°C .

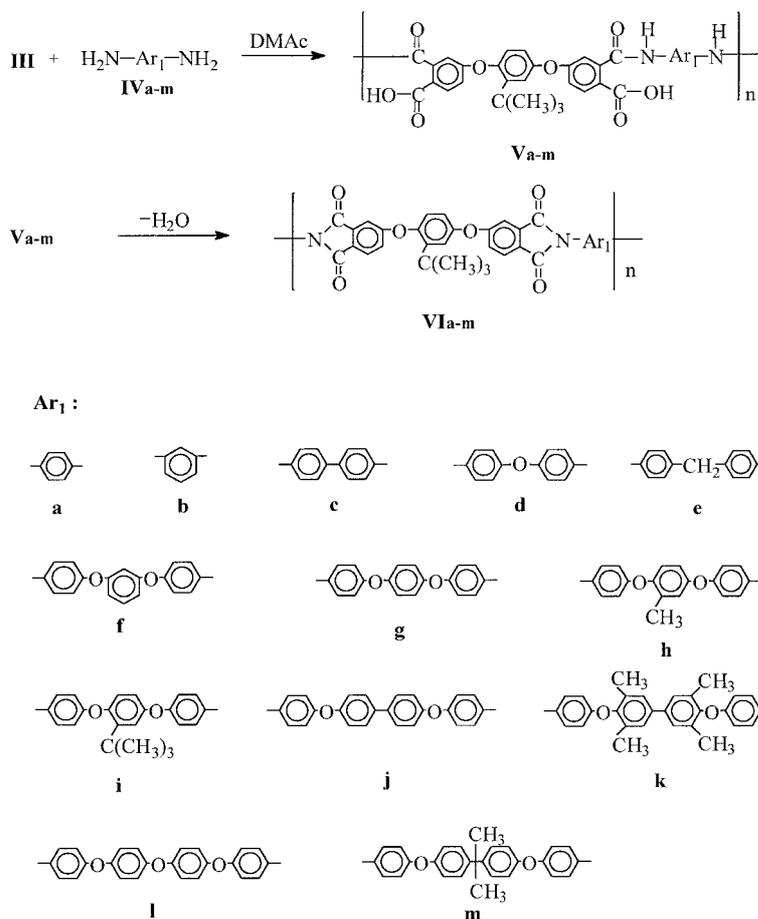
c) Poly(ether imide)s were prepared by the chemical cyclodehydration method.

d) Measured at a concentration of 0.5 g/dL in concentrated sulfuric acid at 30°C .

synthesis of high molecular weight polymers is also a good proof that the pure bis(ether anhydride) **III** has been prepared.

The poly(ether imide)s **VI_{a-m}** were synthesized from bis(ether anhydride) **III** with various aromatic diamines **IV_{a-m}** by the conventional two-stage process as shown in Scheme 2. The intermediate poly(amic acid)s (PAAs) **V_{a-m}** were prepared by adding solid **III** into the DMAc solutions of various aromatic diamines (**IV_{a-m}**) at room temperature. As shown in Tab. 1, the inherent viscosities of the resulting PAAs were in the range of 0.72–1.51 dL/g, indicative of the formation of high molecular weight. All PAAs have adequate molecular weights to permit the casting of flexible and tough films.

Scheme 2:



The thermal conversion to poly(ether imide)s (PEI) was carried out by sequential heating the PAA films to 250 °C. The completion of the imidization by the heating program was confirmed by IR spectroscopy and dynamic thermogravimetry. All the thermally converted PEI films were fairly transparent (almost colorless), flexible, and tough. Alternatively, the PAAs could be converted to the corresponding PEIs by means of chemical imidization using acetic anhydride and pyridine. Except for those derived from more rigid diamines such as *p*-phenylenediamine and benzidine, all the PEIs remained in solution, and thus might reach high levels of imidization. PEIs **VI_a** and **VI_c** were only soluble in strongly acidic media such as concentrated sulfuric acid, and the other PEIs were readily soluble in polar organic solvents like DMAc. Therefore, the characterization of inherent viscosity was carried out without any difficulty, and the inherent viscosities of these PEIs were in the range of 0.70–1.44 dL/g. All the chemically treated PEIs (designated as **C-VI**) except for the organic-insoluble **VI_a** and **VI_c** also could be solution-cast into almost colorless, creasable films from their polymer solutions in DMAc.

IR spectroscopy allows the monitoring of the imide ring formation during thermal curing or chemical treat-

ment. As the PAA was converted into the PEI, the characteristic absorption bands of the imide ring were observed near 1780 (asym. C=O str.), 1720 (sym. C=O str.) 1390 (C–N str.), 1100 and 720 cm⁻¹ (imide ring deformation), and those of amide and carboxyl groups in the regions of 3000–3500 and 1500–1720 cm⁻¹ disappeared. The elemental analysis data of the PEIs listed in Tab. 2 were generally in good agreement with the respective structures for hydrogen and nitrogen, while the carbon analysis data were slightly lower than the theoretical values, a phenomenon common for high-temperature polyimides.

The solubility of these PEIs was tested qualitatively, and the results are summarized in Tab. 3. With the exception of PEIs **VI_a** and **VI_c**, all PEIs of the **VI** series obtained via either thermal or chemical cyclization were readily soluble in polar aprotic solvents such as NMP, DMAc, and DMF, in phenolic solvents like *m*-cresol, in basic solvents like pyridine, and even in halogenated hydrocarbons like dichloromethane. As compared to the analogous counterparts without the pendent *tert*-butyl groups³⁶, these PEIs revealed a dramatic increase in solubility. This can be due to the presence of the hindered *tert*-butyl group, which decreases polymer inter- and intra-chain interactions and disturbs the co-planarity of

Tab. 2. Elemental analysis of poly(ether imide)s^{a)}

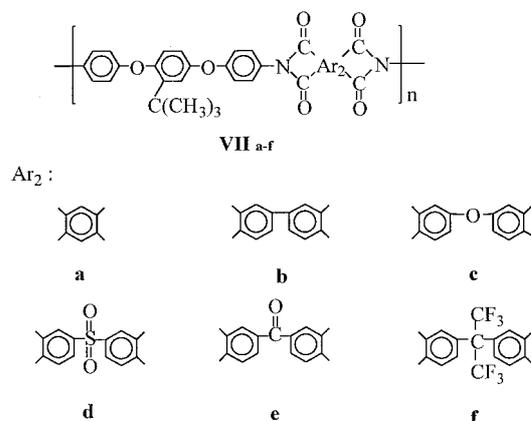
PEI	Formula (formula weight)		Elemental analysis (%)		
			C	H	N
VI_a	(C ₃₂ H ₂₂ O ₆ N ₂) _n (530.54) _n	calcd	72.45	4.18	5.28
		found	71.10	4.19	5.42
VI_b	(C ₃₂ H ₂₂ O ₆ N ₂) _n (530.54) _n	calcd	72.45	4.18	5.28
		found	70.76	4.27	5.51
VI_c	(C ₃₈ H ₂₆ O ₆ N ₂) _n (606.63) _n	calcd	75.24	4.32	4.62
		found	74.10	4.48	4.64
VI_d	(C ₃₈ H ₂₆ O ₇ N ₂) _n (622.63) _n	calcd	73.30	4.21	4.50
		found	72.35	4.30	4.82
VI_e	(C ₃₉ H ₂₈ O ₆ N ₂) _n (620.66) _n	calcd	75.47	4.55	4.51
		found	74.22	4.55	4.56
VI_f	(C ₄₄ H ₃₀ O ₈ N ₂) _n (714.73) _n	calcd	73.94	4.23	3.92
		found	73.16	4.21	3.97
VI_g	(C ₄₄ H ₃₀ O ₈ N ₂) _n (714.73) _n	calcd	73.94	4.23	3.92
		found	73.11	4.16	3.94
VI_h	(C ₄₅ H ₃₃ O ₈ N ₂) _n (729.77) _n	calcd	74.06	4.56	3.84
		found	73.43	4.36	3.86
VI_i	(C ₄₈ H ₃₉ O ₈ N ₂) _n (771.85) _n	calcd	74.69	5.09	3.63
		found	73.80	5.01	3.64
VI_j	(C ₅₀ H ₂₆ O ₈ N ₂) _n (790.83) _n	calcd	75.94	4.33	3.54
		found	75.07	4.45	3.61
VI_k	(C ₅₄ H ₄₆ O ₈ N ₂) _n (850.97) _n	calcd	76.22	5.45	3.29
		found	75.40	5.05	3.40
VI_l	(C ₅₀ H ₃₄ O ₉ N ₂) _n (806.83) _n	calcd	74.43	4.25	3.47
		found	74.03	4.44	4.67
VI_m	(C ₅₃ H ₄₀ O ₈ N ₂) _n (832.91) _n	calcd	76.43	4.84	3.36
		found	75.70	4.87	3.38

^{a)} Thermally-imidized samples.

aromatic units to reduce the packing efficiency and the crystallinity. Poor solubility of PEIs **VI_a** and **VI_c** indicates either strong intermolecular interactions or a good packing ability. Most of the chemically cyclized PEIs were soluble in hot DMSO and cold THF; however, all the thermally imidized PEIs were insoluble in DMSO and THF even at higher temperatures. The difference in the solubility of the PEIs prepared by two different cyclization methods may be attributed to the formation of some intermolecular links of poly(amic acid)s during the thermal imidization.

For comparison, six related polyimides **VII_{a-f}** shown in Scheme 3 were prepared from 1,4-bis(4-aminophenoxy)-2-*tert*-butylbenzene (**IV_i**) and conventional tetracarboxylic dianhydrides including PMDA, 3,3',4,4'-biphenyltetracarboxylic dianhydride (BPDA), 3,3',4,4'-oxydiphthalic anhydride (ODPA), 3,3',4,4'-diphenylsulfonetetracarboxylic dianhydride (DSDA), 3,3',4,4'-benzophenonetetracarboxylic dianhydride (BTDA), and 6FDA. The qualitative solubility behavior of these polyimides is also summarized in Tab. 3. The results revealed that only the polyimides (**VII_d** and **VII_f**) from DSDA and 6FDA showed comparable solubilities in contrast to the **VI** series PEIs. The relatively higher solubility of the PEIs based on the *t*-BHQ bis(ether anhydride) **III** may be

Scheme 3:



explained by the incorporation of more flexible oxygen-bridged phthalimide units along the polyimide backbone. In addition, the incorporation of an —O— linking atom between two phenyl groups in the dianhydride **III** reduces the electron affinity of the dianhydride, causing a reduction in the overall interchain interaction.

Conventional aromatic polyimides are sparingly soluble in organic solvents, while they are generally soluble in strongly acidic media such as concentrated sulfuric acid. As mentioned above (Tab. 1), the PEIs **VI_a** and **VI_c** obtained by the chemical conversion method have inherent viscosities of 0.90 and 0.99 dL/g, respectively, in concentrated sulfuric acid, indicating little molecular chain scission during the imidization process and during the viscosity determination. This also indicates that these PEIs have a good acid-resistance. On the contrary, Ultem® PEI, containing the isopropylidene group, and most PEIs containing cardo units such as 1,1-cyclohexylidene were decomposed simultaneously during the dissolution process in sulfuric acid, as indicated by the very low inherent viscosity values (near zero). In our unpublished results, we also found that many PEIs bearing cardo groups were organo-soluble and could be cast into almost colorless and tough films; however, they did not exhibit a good acid-resistance like the **VI** series PEIs.

The color intensities of the polyimides are elucidated from the yellowness or redness indices observed by a Macbeth Color-eye colorimeter. For comparison, some corresponding polyimides based on 6FDA (**VIII**) and PMDA (**IX**) were also prepared and characterized by their color intensity, where the —Ar₁— used in the structures of **VIII** and **IX** are the same in Scheme 2. The color coordinates of these polyimides are given in Tab. 4. These parameters are generally used by the industry to describe the color, color intensity, and color difference of paints. In Tab. 4, *L*^{*} is lightness, and the color is quantitatively described by the parameters *a*^{*} and *b*^{*}. For instances, a red sample has a positive *a*^{*}, a green sample

Tab. 3. Solubility behavior of polyimides^{a)}

PEI	Solvents ^{b)}								
	NMP	DMAc	DMF	DMSO	<i>m</i> -cresol	Py	THF	CH ₂ Cl ₂	H ₂ SO ₄
C-VI _a	-	-	-	-	-	-	-	-	+
C-VI _b	+	+	+	+h(-) ^{c)}	+	+	s (-)	+ (±)	+
C-VI _c	-	-	-	-	-	-	-	-	+
C-VI _d	+	+	+	+h (-)	+	+	+ (-)	+	+
C-VI _e	+	+	+	+h (-)	+	+	+ (-)	+	+
C-VI _f	+	+	+	+h (-)	+	+	+ (-)	+	+
C-VI _g	+	+ (+h)	+	+h (-)	+	+	+ (-)	+	+
C-VI _h	+	+	+	+h (-)	+	+	+ (-)	+	+
C-VI _i	+	+	+	+h (-)	+	+	+	+	+
C-VI _j	+	+	+ (+h)	+h (-)	+ (-)	+	s (-)	+	+
C-VI _k	+	+	+ (+h)	+h (-)	+	+	+ (±)	+	+
C-VI _l	+	+	+	+h (-)	+	+	+	+	+
C-VI _m	+	+	+	+h (-)	+	+	+	+	+
C-VII _a	-	-	-	-	-	-	-	-	+
C-VII _b	-	-	-	-	+ (-)	-	-	-	+
C-VII _c	+ (s)	-	-	-	+ (-)	+	-	+	+
C-VII _d	+	+	+	+	+	+	+ (-)	+	+
C-VII _e	+ (s)	-	-	-	+ (-)	+ (-)	-	-	+
C-VII _f	+	+	+	+	+	+	+	+	+

^{a)} Measured at a concentration of about 0.5 wt.-%; +: soluble at room temperature; -: insoluble; ±: partially soluble; s: swelling; +h: soluble on heating and then precipitated at room temperature.

^{b)} NMP: *N*-methyl-2-pyrrolidone; DMAc: *N,N*-dimethylacetamide; DMF: *N,N*-dimethylformamide; DMSO: dimethyl sulfoxide; Py: pyridine.

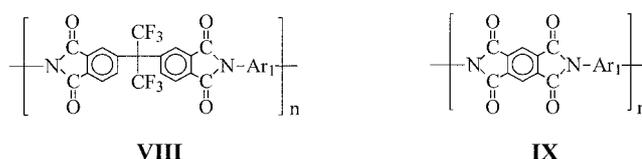
^{c)} The thermally imidized PEIs showed the same solubility behavior as those obtained by chemical imidization, unless otherwise indicated in the parentheses.

Tab. 4. Color coordinates of polyimide films^{a)}

PEI	<i>b</i> *	<i>a</i> *	<i>L</i> *
VI _f	4.30	-2.67	91.17
VI _g	9.85	-5.25	92.32
VI _h	7.38	-3.93	92.28
VI _i	6.43	-4.16	92.74
VI _k	21.20	-8.39	91.33
VI _l	14.43	-2.61	88.82
VI _m	15.37	-2.01	88.57
VIII _f	22.29	-6.13	88.96
VIII _g	25.14	-11.05	92.34
VIII _h	35.50	-6.22	86.27
VIII _i	27.41	-11.39	91.66
VIII _k	28.31	-11.83	91.99
VIII _l	31.61	-4.32	86.45
VIII _m	33.38	-3.92	87.23
IX _h	47.63	21.81	61.01
IX _i	79.06	10.46	78.88
IX _k	69.42	21.60	72.17
IX _m	71.95	16.69	76.76
paper	-8.02	0.94	93.06

^{a)} The color parameters were calculated according to a CIE LAB equation, using paper as a standard. *L** is lightness; 100 means white, while 0 implies black. A positive *a** means red color, while a negative *a** indicates green color. A positive *b** means yellow color, while a negative *b** implies blue color.

has a negative *a**. Similarly, a positive *b** means yellow color, while a negative *b** implies blue color. The results shown in Tab. 4 indicate that all the VI series polyimides showed a lower *b** (a yellowness index) and *a** (a redness index) values by contrast with the corresponding VIII and IX series polyimides. On the whole, the PEIs VI showed comparable or higher transparency than the polyimides derived from 6FDA and were much lighter in color than those from PMDA. The light colors of the PEIs having *tert*-butyl groups in their dianhydride moieties can be explained from the decreased intermolecular interactions. The bulky *tert*-butyl group in the bis(ether anhydride) III is effective in preventing the charge transfer complex (CTC) formation between polymer chains through steric hindrance. The low polarity of the *tert*-butyl group also weakens the intermolecular interactions. The decrease of intermolecular CTC formation is also understandable from the significant solubility of the PEIs prepared from III.



Tab. 5. Thermal properties of polyimides

PEI ^{a)}	T_g ^{b)} °C	T_{10} ^{c)} /°C		Char yield ^{d)} %
		in N ₂	in air	
VI _a	— ^{e)}	484	477	49
VI _b	257	469	462	42
VI _c	278	542	529	57
VI _d	247	542	541	52
VI _e	250	487	477	55
VI _f	217	544	538	54
VI _g	230	547	538	50
VI _h	232	496	505	50
VI _i	240	529	515	41
VI _j	245	540	538	54
VI _k	265	504	502	52
VI _l	225	538	531	48
VI _m	229	542	530	48
VII _a	303	540	527	46
VII _b	268	545	538	52
VII _c	245	520	534	41
VII _d	278	509	508	40
VII _e	255	538	530	53
VII _f	266	540	534	54

- a) Obtained by the thermal cyclodehydration method.
 b) Baseline shift in the second heating DSC traces, with a heating rate of 10 °C/min.
 c) Decomposition temperatures at which 10% weight loss were recorded by TG at a heating rate of 20 °C/min.
 d) Residual weight % when heated to 800 °C in nitrogen.
 e) Difficult to judge.

The thermal properties of all the PEIs were evaluated by thermogravimetry (TG) and differential scanning calorimetry (DSC). The thermal behavior data of all polymers are listed in Tab. 5.

DSC measurements were conducted with a heating rate of 10 °C/min in nitrogen. Quenching from the elevated temperatures (approximately 400 °C) to room temperature in air gave predominantly amorphous samples so that the glass transition temperatures (T_g) of most PEIs could be easily measured in the second heating traces of DSC. The T_g values of the PEIs V_{a-m} were in the range of 217–278 °C, depending on the structure of diamine component and following with increasing stiffness of the polymer backbones. Insertion of flexible linkages such as an ether group or a less symmetrical *m*-phenylene unit increased the overall flexibility of the polymer chain and, thus, generally resulted in a decrease in T_g , as evidenced by some T_g orders shown in Tab. 5: VI_d (247 °C) > VI_g (230 °C) > VI_l (225 °C), VI_b (257 °C) > VI_f (217 °C), VI_c (278 °C) > VI_j (245 °C), and VI_g (230 °C) > VI_f (217 °C). The insertion of alkyl substituents on a ring unit at *ortho* positions to the ether linkage generally increased the T_g of the polymers, due to the hindrance effect of the chain rotation. For example, VI_i (240 °C) > VI_h (232 °C) > VI_g (230 °C) and VI_k (265 °C) > VI_j (245 °C). The T_g values of the VII series polyimides are also listed in Tab. 5. They were recorded in the range of 240–268 °C. As expected, the polyimide (VII_c) derived from ODPA showed the lowest T_g because of the presence of a flexible ether bridge between the phthalimide units, and the polyimide (VII_a) derived from PMDA exhibited the highest T_g due to the rigid pyromellitimide unit.

The thermal stability of the PEIs was characterized by TG analysis conducted at a heating rate of 20 °C/min. The temperatures of 10% weight loss (T_{10}) in nitrogen and air atmospheres were determined from original thermograms and are also tabulated in Tab. 5. The T_{10} values of these

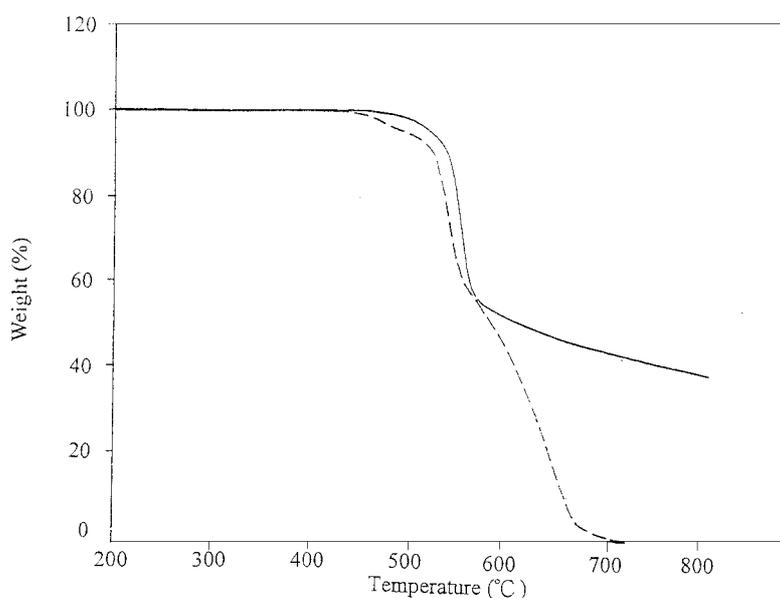


Fig. 1. TG curves for PEI VI_i, in nitrogen (—) and in air (---) with a heating rate of 20 °C/min

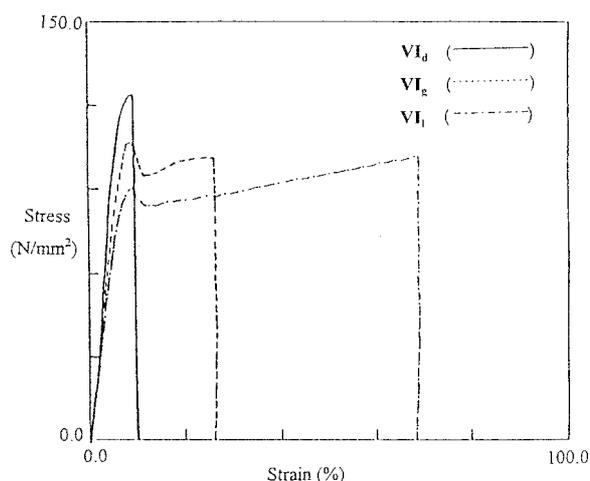


Fig. 2. Stress-strain curves for **VI_a**, **VI_g**, and **VI_i**; the load cell is 500 N; a gauge of 2 cm and a crosshead speed of 5 cm/min

PEIs stayed in the range of 469–547 °C in nitrogen and in the range of 462–541 °C in air, respectively. They left more than 40% char yield at 800 °C in nitrogen. Fig. 1 shows typical TG curves for the representative PEI **VI_i** in nitrogen and air atmospheres. In general, the **VII** series polyimides showed similar TG behavior compared to those of the **VI** series, and their TG data are also summarized in Tab. 5.

All the PEIs could afford good-quality, creasable films by solution-casting. These films were subjected to a tensile test, and their tensile properties are summarized in Tab. 6. They showed an ultimate tensile strength of 96–134 MPa, an elongation to break of 6–68%, and an initial modulus of 1.9–3.1 GPa. Except for PEI **VI_c**, the PEIs derived from short chain diamines such as **IV_{a-d}** revealed low elongations to break, indicative of brittle fracture. The relatively higher initial moduli of **VI_{a-c}** than the other PEIs may be due to the rigidity of the unit consisting of the rigid diamine residue and its adjacent phthalimide moieties. Almost all PEIs derived from long chain diamines such as **IV_{f-m}** showed distinct yield points in their stress-strain curves and moderate elongations to break, indicating high toughness. It may be due to the fact that the long chain diamine residues adopt a conformation that causes the polymer chain to coil strongly, through the disposition of the aromatic units adjacent to the ether linkages, but that under stress these conformations are modified to give a more linear inchain unit; the effective uncoiling of the long chain diamine units at their ether linkages could provide a mechanism for considerable chain extension. Typical stress-strain curves for representative PEIs **VI_a**, **VI_g**, and **VI_i** are illustrated in Fig. 2. The trend to enhance toughness by inserting more phenoxy units in the diamine is very clear.

The tensile properties of the cast films of polyimides **VII** are also summarized in Tab. 6. Their tensile

Tab. 6. Tensile properties of polyimide films^{a)}

PEI	Strength at yield	Strength at break	Elongation to break	Initial modulus
	MPa	MPa	%	GPa
VI_a	–	134	6	3.0
VI_b	–	126	9	2.9
VI_c	126	122	23	3.1
VI_d	–	127	11	2.7
VI_e	110	104	11	2.4
VI_f	108	102	42	2.4
VI_g	108	103	25	2.5
VI_h	117	133	34	2.7
VI_i	119	109	35	2.5
VI_j	–	131	66	2.2
VI_k	99	108	61	1.9
VI_l	90	105	68	2.1
VI_m	100	96	42	2.0
VII_a	–	124	72	2.4
VII_b	–	116	39	2.6
VII_c	112	104	15	2.4
VII_d	–	106	6	2.6
VII_e	–	114	7	2.6
VII_f	–	103	8	2.1

^{a)} PEI films obtained by the thermal cyclodehydration method.

strengths, elongations to break, and initial moduli were recorded in the range of 104–124 MPa, 6–72%, and 2.1–2.6 GPa, respectively. However, in contrast to the observations in PEIs **VI**, the polyimides **VII_a** and **VII_b**, obtained from more rigid dianhydrides such as PMDA and BPDA showed a higher extensibility. The reason is not very clear.

Conclusions

High-molar-mass poly(ether imide)s have been obtained from 1,4-bis(3,4-dicarboxyphenoxy)-2-*tert*-butylbenzene dianhydride and aromatic diamines. These polymers are characterized by high solubility even in the fully imidized form, good film-forming ability, high transparency, a wide temperature range between T_g and decomposition temperature, and good thermal stability together with good mechanical properties. Thus this series of polymers demonstrates a good combination of properties and processability.

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