

Synthesis and characterization of Functionalized poly (ether imide)s with different pendant groups

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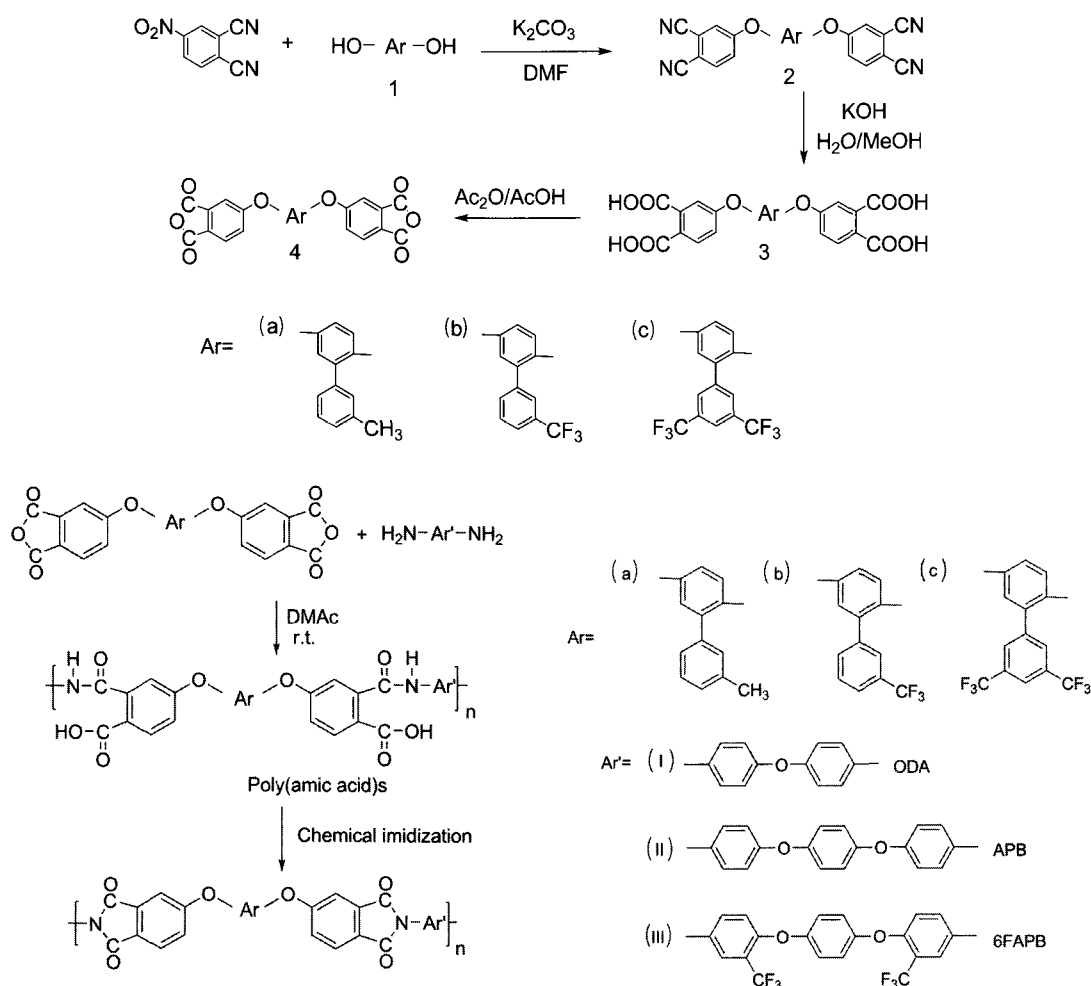
Introduction

High optical transparency is one of the most attractive properties of polyimides materials for a variety of applications such as optical waveguides.^{1,2} However, most of the conventional aromatic polyimide films show considerable coloration from light yellow to dark brown due to their highly conjugated aromatic structures, the formation of intermolecular charge transfer complexes and electronic polarization interactions. In addition, the aromatic polyimides are difficult to be processed because of their poor solubility and high processing temperature, which are caused by their rigid polymer backbones and strong interchain interaction.^{3,4}

The development of soluble polyimides with high optical transparency has been to attract major interest in the research of aromatic polymers. Fortunately, considerable efforts have got good progresses on the processing ability and solubility of polyimides based on structure design and modification of aromatic dianhydride and diamine monomers. Introducing noncoplanar moiety into the backbone of the polyimides, contributed either by the dianhydrides or from the diamines, has been proven to be a successful approach to attain the solubility without sacrificing their excellent properties.⁵⁻⁹ Moreover, it is an effective method to improve high optical transparency through introducing trifluoromethyl into polyimides. It has been demonstrated that the introduction of bulky trifluoromethyl group into polyimide backbones resulted in an enhanced solubility and optical transparency together with a lower dielectric constant, attributed to low polarizability of the C-F bond and the increase in free volume. The fluorinated polyimides also provided other merits such as good thermal and thermo-oxidative stability and low moisture absorption. In addition, the introduction of bulky trifluoromethyl moieties into the polymers could decrease the refractive index and the birefringence effectively.

At present, most dissoluble aromatic polyimides containing fluorine were prepared by using different kinds of aromatic diamine containing fluorine rather than fluorinated aromatic dianhydrides, except for 6FDA, which is currently commercial available. However, the widespread applications and commercialization for 6FDA are also hampered by the difficulty in handling of poisonous gaseous chemicals in the synthetic procedure. As part of our continuing efforts to gain colorless and soluble polyimides with high thermal stability and wide application potentials in optoelectronics, three novel bis(ether dianhydride)s, bis(ether dianhydride) [4,4'-(2-(3'-methylphenyl)-1,4-phenylenedioxy)-diphthalic anhydride (4a)], [4,4'-(2-(3'-trifluoromethylphenyl)-1,4-phenylenedioxy)-diphthalic anhydride (4b)] and [4,4'-(2-(3',5'-ditrifluoromethylphenyl)-1,4-phenylenedioxy)-diphthalic anhydride (4c)] were designed and synthesized. Three series of soluble poly (ether imide)s (PEIs) (4aI-4aIII, 4bI-4bIII and 4cI-4cIII) were prepared by polycondensation of the monomers with various aromatic diamines(see Scheme 1). The present study deals with the synthesis and basic characterization of the PEIs based on bis (ether anhydride)s derived from hydroquinone and its methylphenyl, trifluoromethylphenyl and ditrifluoromethylphenyl pendant derivatives. The

effect of methylphenyl, trifluoromethyl and ditrifluoromethyl groups on solubility, thermal properties, mechanical properties, dielectric constant and optical properties of the PEIs were investigated.



Scheme 1. Synthetic procedures of monomers and PEIs.

Results and Discussion

The thermal behavior data of all the PEIs are also listed in **Table 1**. The T_g values of series 4a, 4b and 4c were, respectively, in the ranges of 208–230 °C, 200–216 °C and 218–226 °C, which increased in the order of ODA > APB > 6FAPB. All the PEIs had excellent thermal stability, and no obvious decomposition was observed below 500 °C, and char yield at 800 °C in nitrogen was in the range of 47–67 wt%. Film samples of polyimides underwent 5% weight losses at 520–590 °C under nitrogen when subjected to TGA with a heating rate of 10 °C/min. It is characterized that the molecular weights (M_w) of the resulting PEIs were in the range of 71,000–162,000 with the M_w/M_n values of 1.4–1.9 and the intrinsic viscosities of the PEIs were in the range of 0.65–0.86 g/dL. (See **Table 1**)

All the PEIs showed excellent solubility in aprotic polar solvents such as DMSO, DMAc, DMF and NMP and were also soluble in less polar solvents such as pyridine and THF at room temperature. The improved solubility is attributed to the introduction of bulky pendant methylphenyl, trifluoromethylphenyl and ditrifluoromethylphenyl groups which could inhibit close packing and reduce the interchain interactions

Table 1. Inherent Viscosity, GPC Data and Thermal Properties of the PEIs

Polymer	Inherent Viscosity $\eta_{inh}(\text{dL/g})^a$	GPC data		DSC		TGA	
		M_w $\times 10^4$	M_w/M_n ^b	T_g ^c (°C)	$T^d_{5\%}$ (°C)	$T^d_{10\%}$ (°C)	Char yield ^e (%)
4aI	0.84	13.5	1.7	230	531	551	57
4aII	0.86	16.2	1.6	211	520	544	58
4aIII	0.82	13.5	1.9	208	536	574	61
4bI	0.65	7.1	1.4	216	590	604	62
4bII	0.71	7.8	1.4	203	575	597	60
4bIII	0.67	8.1	1.5	200	585	603	67
4cI	0.73	13.2	1.4	226	578	602	47
4cII	0.85	17.2	1.6	220	578	602	57
4cIII	0.75	9.3	1.5	218	576	598	50

The mechanical properties of PEI films are summarized in **Table 2**. The PEI films have tensile strength of 88–117 MPa, tensile modulus of 2.14–2.47 GPa, and elongation at breakage of 15–27%. The tensile modulus of the PEIs enhanced with increasing in the imide concentration accompanied polymer backbones. PEI-4aI, 4bI and 4cI, which had the highest imide concentration and the lowest ether concentration, exhibited the highest tensile modulus compared with PEIs from diamine II, III.

Table 2. Mechanical Properties of the PEIs

Polymers	Film thickness (μm)	Tensile strength (MPa)	Elongation at break (%)	Youngs' modulus (GPa)
4aI	91	113	20	2.40
4aII	85	93	25	2.21
4aIII	80	89	27	2.19
4bI	90	117	18	2.47
4bII	85	92	22	2.18
4bIII	87	90	22	2.16
4cI	87	107	15	2.34
4cII	85	88	27	2.15
4cIII	89	92	20	2.14

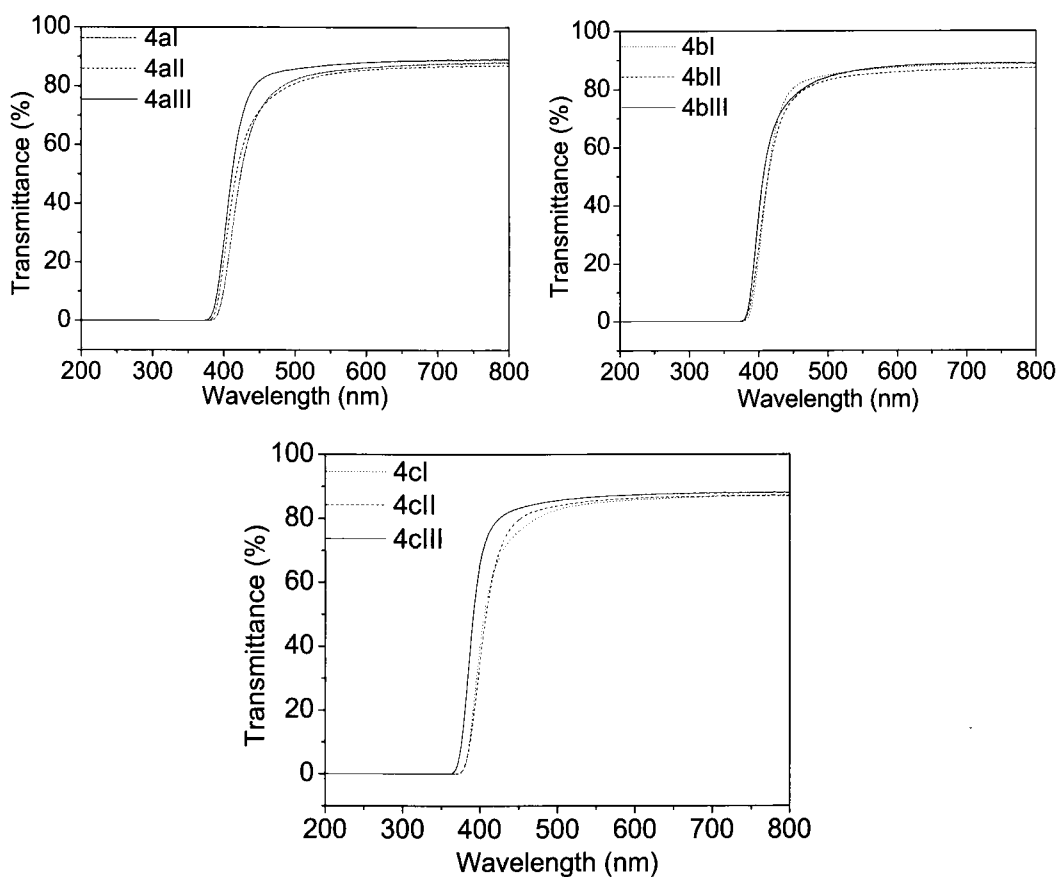


Figure 1. UV-visible spectra of PEI films.

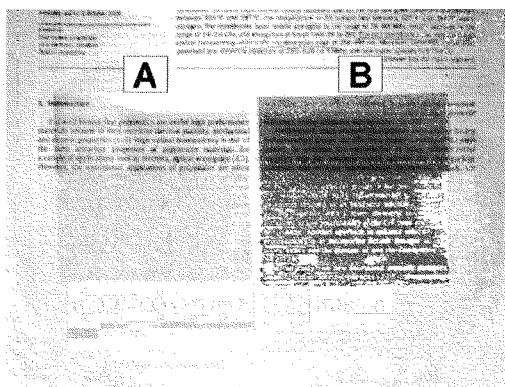


Figure 2. Photographs of a piece of the PEI-4cIII film (89 μm thick) and a piece of the Kapton film (90 μm thick).

Thin films (pale-yellow, $\sim 90 \mu\text{m}$ thick) were measured for optical transparency with UV-visible spectroscopy. Figure 1 shows the UV-visible transmittance spectra of the PEI films. All the PEIs had shorter λ_0 than 380 nm, and exhibited high optical transparency of 87%–89%. Because of the highly conjugated aromatic structures and intermolecular charge-transfer complex (CTC) formation of PI, most polymers between UV and the visible area had strong absorption. However, these PEIs which had flexible group like ether linkage and CF_3 group with bulky side groups in the center of dianhydride reduced the intermolecular CTC between alternating electron-donor (diamine) and electron-acceptor (dianhydride) moieties. Moreover CF_3 group might weaken chain-to-chain cohesive force due to lower

polarizability of the C–F bond. The decrease in intermolecular CTC formation was understandable also from the significant solubility of the PEIs prepared from dianhydrides. A photograph of one piece of the PEI 4cIII is shown in **Figure 2A**. For comparison, another photograph of a commercially Kapton film is shown in **Figure 2B** either. The films were photographed against a special background to highlight the transparency. It is easy to find that PEI 4cIII film exhibited much lighter color than Kapton film.

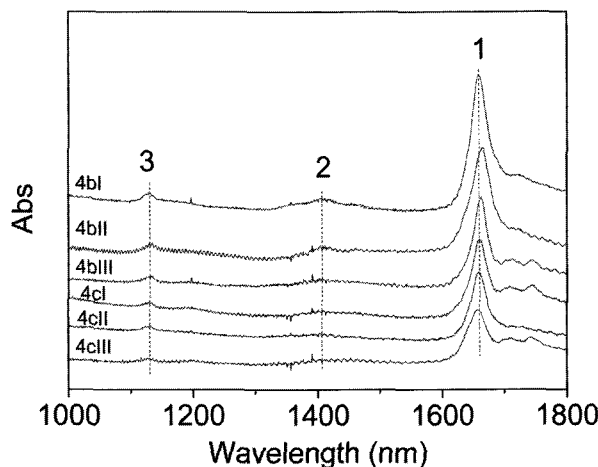


Figure 3. Near-IR spectra of PEIs

The propagation losses of the fluorinated PEIs series 4b and 4c were measured by the near-infrared (NIR) absorption spectra, and the spectra are shown in the **Figure 3**. There were C–H bond vibrational absorbing peaks ($2\nu_{\text{C-H}}$ 1650 nm and $3\delta_{\text{C-H}}$, 1100 nm) and related peak ($2\nu_{\text{C-H}} + \delta_{\text{C-H}}$, 1400 nm). However, it had small light absorptions at telecommunication wavelengths of 1310 and 1550 nm due to high fluorine content. Furthermore, the near-infrared absorption of series 4c was weaker than that of series 4b at the key telecommunication wavelengths of 1310 and 1550 nm because of the presence of two $-\text{CF}_3$ groups. The wavelength of 1310 or 1550 nm will be used for optical telecommunication, so these PEIs are expected to be applicable to optoelectronic materials.

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