

Novel Organosoluble and Low-color Poly(ether-imide)s Based on 1,4-Bis(3,4-dicarboxyphenoxy)tritycene Dianhydride and Aromatic Diamines

Ji-Shian Chou (邱繼賢),¹ Hui-Min Wang (王惠民),¹ Sheng-Huei Hsiao (蕭勝輝),^{1*} Chyi-Ming Leu (呂奇明),² Chun-Wei Su (蘇俊璋),² Tzong-Ming Lee (李宗銘)²

¹Department of Chemical Engineering and Biotechnology, National Taipei University of Technology
(國立臺北科技大學化學工程與生物科技系)

²Material and Chemical Research Laboratories, Industrial Technology Research Institute
(工業技術研究院材料與化工研究所)

Tel: +886-2-27712171 ext. 2548; Fax: +886-2-27317117

E-mail: shhsiao@ntut.edu.tw

Abstract

A triptycene-based bis(ether anhydride) monomer, 1,4-bis(3,4-dicarboxyphenoxy)tritycene dianhydride, was synthesized from the nitro-displacement of 4-nitrophthalonitrile with the phenoxide ion of 1,4-dihydroxytritycene, followed by alkaline hydrolysis of the intermediate bis(ether dinitrile) and cyclodehydration of the resulting bis(ether diacid). A series of new poly(ether-imide)s containing three-dimensional triptycene moieties 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 thermal or chemical imidization to the poly(ether-imide)s. The inherent viscosities of the amic acid prepolymers were in the range of 0.44~0.91 dL/g. Most of the resulting poly(ether-imide)s presented a good solubility in many organic solvents and could be solution-cast into transparent and tough films. They also showed good thermal stability with glass-transition temperatures of 238~302 °C and 10% weight loss temperatures in excess of 572 °C. These triptycene-based poly(ether imide)s showed an enhanced optical transparency and decreased color intensity as compared to conventional aromatic polyimides. The poly(ether-imide)s derived from trifluoromethyl-containing bis(ether amine)s could afford highly optically transparent and essentially colorless films, with an UV-visible absorption edge down to 378 nm and a low b^* value (a yellowness index) of 5.9.

1. Introduction

Aromatic polyimides are well known high-performance polymeric materials for their excellent thermal, mechanical and electrical properties.¹ Despite their outstanding properties, most of the conventional aromatic polyimides have high melting or glass-transition temperatures (T_g) and limited solubility in most organic solvents because of their rigid backbones and strong interchain interactions. Thus, polyimide processing is generally carried out via poly(amic acid) precursor, and then converted to polyimide by vigorous thermal or chemical cyclodehydration. However, this process has inherent problems such as emission of volatile by-products and storage instability of poly(amic acid) solution. To overcome these problems, many attempts have been made to the synthesis of soluble and processable polyimides in fully imidized form while maintaining their excellent properties.² It has been generally recognized that aryl-ether linkage imparts properties such as better solubility, melt processing characteristics, and improved toughness in comparison with those polymers without an aryl-ether linkage. However, the decrease in mechanical properties on heating is almost always a consequence of the reduced chain stiffness or T_g s. The introduction of bulky, rigid units in the polymer main chain or as pendent groups can impart an increase in T_g s by restricting the segmental mobility, while providing an enhanced solubility because of decreased packing density and crystallinity. Thus, combining these two structural modifications minimized the trade-off between the processability and the useful/positive properties of aromatic polyimides.

Iptycenes are a class of structurally unique compounds that consist of a number of arene rings joined together to form the

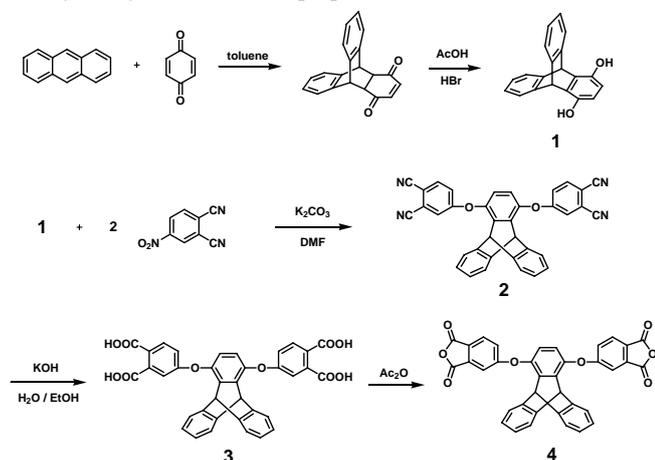
bridges of [2.2.2] bicyclic ring systems.³ The name iptycene originated from the basic unit triptycene, which was first synthesized and named by Bartlett and co-workers in 1942.⁴ The triptycene was named after “the triptych of antiquity, which was a book with three leaves hinged on a common axis.” Later, triptycene has become readily available thanks to the well known work of Wittig⁵ on the preparation of dehydrobenzene (benzyne) and its interaction with anthracene. The chemistry of triptycene has been studied in comparative detail and has been summarized in an earlier review paper reported by the Russian researchers.⁶ Triptycene is a rigid molecular unit with three blades each composed of a benzene ring. Its rigid, three-dimensional framework has been incorporated in molecular rotors, molecular cages, and supramolecular architectures. In addition, triptycene and other iptycene units have been used to design a variety of high performance polymers.⁷ Perhaps the earliest efforts in the study of triptycene polymers were made at Eastman Kodak and DuPont in the late 1960s wherein bifunctional, bridgehead-substituted triptycenes were synthesized and used to prepare a series of triptycene polymers, including polyesters, polyamides, polyurethanes, and a polyoxadiazole.⁸ The use of triptycene moiety as a rigid and shape-persistent component is a method to introduce molecular-scale free volume into a polymer film. Polymers with high triptycene content were found to be interesting low- k dielectric materials owing to the high degree of internal free volume.⁹ Incorporation of triptycene units into polyesters was also found to significantly enhance the mechanical performance of film samples through molecular threading and interlocking. Additionally, it was shown that triptycene-containing polycarbonates displayed improvements in mechanical properties at both low and high strain rates.

Recently, we reported on a series of poly(ether-imide)s based on the bis(ether anhydride)s synthesized from hydroquinone and its derivatives.¹⁰ It was found that the incorporation of larger side groups such as *tert*-butyl and phenyl groups on the poly(ether-imide) backbone could substantially decrease their crystallinity and increase their solubility. In a continuation of these studies, the present study reports the synthesis and basic characterization of a new family of poly(ether-imide)s based on 1,4-bis(3,4-dicarboxyphenoxy)tritycene dianhydride (**4**). The rigid, three-dimensional triptycene units may decrease interchain interactions and hinder close chain packing. Thus, it was expected that the introduction of triptycene structure into the polymer backbone could improve the solubility, decrease the color intensity, reduce the packing efficiency and the crystallinity, and preserve moderately high T_g values of the polyimides.

2. Monomer Synthesis

The new triptycene-based bis(ether anhydride) **4** was synthesized via the synthetic route shown in Scheme 1. According to a reported method,¹¹ the triptycene-hydroquinone (TPHQ) **1** was obtained in a good yield starting from the Diels-Alder reaction of *p*-benzoquinone and anthracene and subsequent rearrangement reaction using acetic acid/HBr as catalyst. The intermediate compound, 1,4-bis(3,4-dicyanophenoxy)tritycene (**2**), was obtained from the nitro-displacement of 4-nitrophthalonitrile with the potassium salt of TPHQ formed *in situ* by treatment of K_2CO_3

in DMF. Alkaline hydrolysis of the bis(ether dinitrile) **2** with aqueous potassium hydroxide in ethanol gave 1,4-bis(3,4-dicarboxyphenoxy)tritycene (**3**), which was subsequently dehydrated with acetic anhydride to generate the target bis(ether anhydride) monomer **4**. The yields in each step were reasonable, and the molecular structures of the synthesized compounds could be affirmed by IR and NMR spectroscopic techniques. Figure 1 illustrates the ^1H NMR and ^{13}C NMR spectra of **4**. These spectra are in good agreement with its proposed molecular structure.



Scheme 1. Synthetic route to target bis(ether anhydride) **4**.

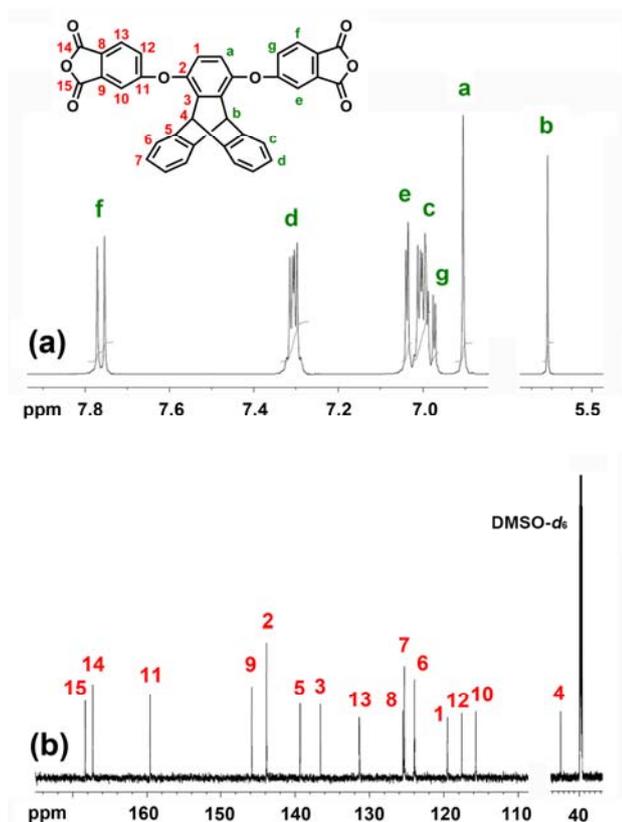
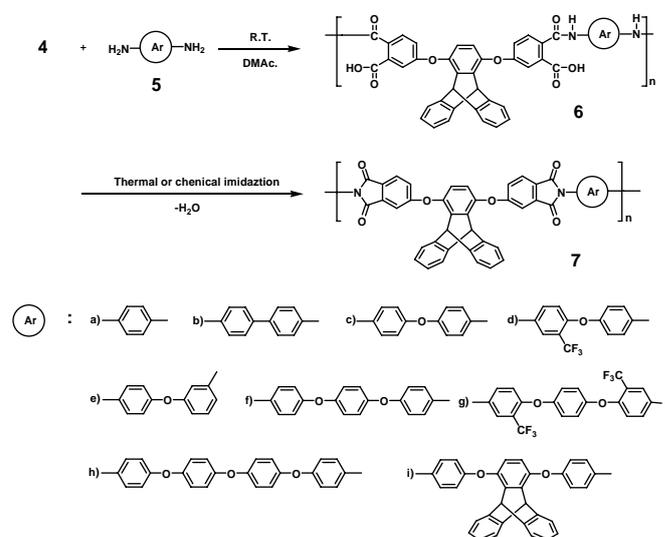


Figure 1. (a) ^1H NMR and (b) ^{13}C NMR spectra of triptycene-based bis(ether anhydride) **4** in $\text{DMSO}-d_6$.

3. Polymer Synthesis

A series of novel poly(ether-imide)s **7a-7i** containing the triptycene unit in the main chain were prepared from bis(ether anhydride) **4** with various aromatic diamines (**5a-5i**) to form poly(amic acids) **6a-6i**, followed by the thermal or chemical cyclodehydration (Scheme 2). In the first step, the viscosities of the reaction mixtures became very high as poly(amic acid)s were

formed, indicating the formation of high molecular weight polymers. As shown in Table 1, the poly(amic acid) precursors had inherent viscosities in the range of 0.44–0.91 dL/g. The resulting viscous poly(amic acid) solutions were poured into a clean glass Petri-dish and dried to form thin solid films. The thermal conversion to polyimides was carried out by step-by-step heating of the poly(amic acid) films to 250 °C. The poly(amic acid) precursors also could be chemically dehydrated to the polyimides by treatment with acetic anhydride and pyridine. All poly(ether-imide)s could afford flexible and tough films via thermal imidization of their poly(amic acid) films. For the organosoluble polyimides such as **7e-7i** could be solution cast to flexible films in the fully imidized form. The poly(ether-imide)s soluble in THF were characterized by GPC, and the relative data are also included in Table 1. The weight-average molecular weights (M_w s) and number-average molecular weights (M_n s) were recorded in the ranges of 27,000–55,500 and 12,000–58,000, respectively, relative to polystyrene standards.



Scheme 2. Synthesis of triptycene-containing poly(ether-imide)s **7a-7i**.

4. Organosolubility and Film Property

The solubility properties of the new triptycene-containing poly(ether-imide)s synthesized by both of thermal and chemical imidization methods are reported in Table 1. The poly(ether-imide)s **7a** and **7b** derived from more rigid diamines such as *p*-phenylenediamine and benzidine are insoluble in all the test solvents. The poly(ether-imide)s **7e-7i** derived from more flexible diamine components exhibited good solubility in organic solvents; they are soluble not only in polar organic solvents such as NMP, DMAc, DMF, and *m*-cresol but also in less polar solvents such as THF and CHCl_3 . The good solubility of these poly(ether-imide)s can be attributed to the presence of three-dimensional triptycene units, together with the flexible segments along the polymer backbone. In addition, the chemically imidized samples generally revealed a higher solubility than those prepared by the thermal imidization method. The less solubility of thermally cured polyimide might be attributed to the presence of partial interchain crosslinking or denser aggregation of the polymer chains during thermal curing process. The WAXD patterns of the poly(ether imide) films are shown in Figure 2. These polymers exhibited an amorphous nature because of the bulky, packing-disruptive triptycene unit along the polymer backbone, which does not favor their close chain packing.

5. Thermal Properties

The thermal properties of all the poly(ether-imide)s were investigated by TGA, DSC, and TMA techniques, and the relevant

thermal behavior data are summarized in Table 2. Typical TGA curves of representative poly(ether-imide) **7d** in both air and nitrogen atmospheres are illustrated in Figure 3-inset. All the polymers exhibited good thermal stability with insignificant weight loss up to 550 °C in both air and nitrogen atmospheres. The decomposition temperatures (T_d) at a 10% weight-loss of the poly(ether-imide)s in nitrogen and air were recorded in the range of 572–634 and 565–618 °C, respectively. The amount of carbonized residue (char yield) of these polymers in nitrogen atmosphere was more than 57% at 800 °C. The high char yields of these polymers can be ascribed to their high aromatic content. The T_g s of all the polymers were measured to be in the range of 238–302 °C by DSC. All the polymers indicated no clear melting endotherms up to the decomposition temperatures on the DSC thermograms. This result also supports the amorphous nature of these polymers. The softening temperatures (T_s) (may be referred as apparent T_g) of the polymer film samples determined by the TMA method with a loaded penetration probe are also listed in Table 2. They were obtained from the onset temperature of the probe displacement on the TMA trace. As a representative example, the TMA trace of poly(ether-imide) **7d** is illustrated in Figure 3. In all cases, the T_s values of the poly(ether-imide)s obtained by TMA are slightly lower than the T_g values measured by the DSC experiments. This may indicate that these polyamides exhibited a higher degree of plasticity near T_g because of the increased free volume caused by the triptycene units in these poly(ether-imide)s. In general, the

thermal analysis results reveal that these poly(ether-imide)s exhibit excellent thermal stability.

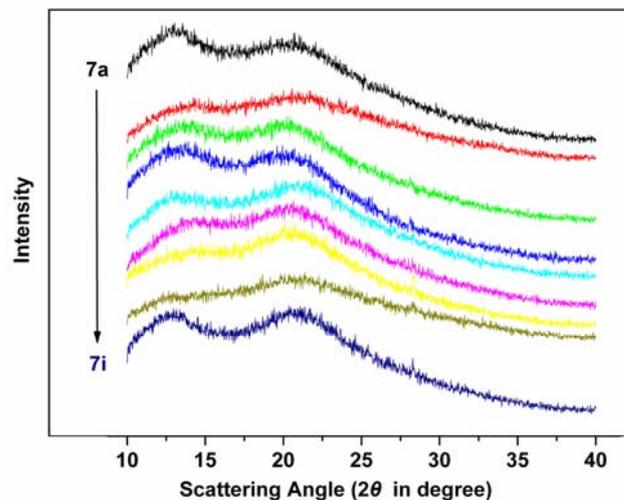


Figure 2. WAXD patterns of poly(ether imide) films.

Table 1. Inherent Viscosity, GPC Data and Solubility Behavior of Poly(ether-imide)s

Polymer code	η_{inh}^b (dL/g)		GPC data of polyimides ^c			Solubility in various solvents ^f							
	PAA	PI	M_w	M_n	PDI	NMP	DMAc	DMF	DMSO	<i>m</i> -Cresol	THF	CHCl ₃	Toluene
7a-T	0.65	— ^d	— ^e	—	—	—	—	—	—	—	—	—	—
7a-C	—	—	—	—	—	—	—	—	—	—	—	—	—
7b-T	0.87	—	—	—	—	—	—	—	—	—	—	—	—
7b-C	—	—	—	—	—	—	—	—	—	—	—	—	—
7c-T	0.74	—	—	—	—	+	—	—	—	+—	—	+—	—
7c-C	—	—	—	—	—	+	+—	+—	+—	+	+—	+—	+—
7d-T	0.64	—	—	—	—	+	+—	+—	+—	+	+—	+—	+—
7d-C	—	—	—	—	—	+	+—	+—	+—	+	+—	+—	+—
7e-T	0.51	0.43	47,000	23,000	2.11	++	++	++	++	+	++	++	—
7e-C	—	0.32	44,000	26,000	1.70	++	++	++	+	+	++	++	—
7f-T	0.91	0.53	53,000	28,000	1.90	++	++	++	++	+	++	++	—
7f-C	—	0.80	80,000	58,000	1.38	++	++	++	+	++	++	++	—
7g-T	0.76	0.25	27,000	13,000	2.18	++	++	++	++	+	++	++	—
7g-C	—	0.44	51,000	29,000	1.77	++	++	++	++	+	++	++	—
7h-T	0.58	0.44	44,000	20,000	2.17	++	++	++	++	+	++	++	—
7h-C	—	0.65	72,000	48,000	1.51	++	++	++	++	+	++	++	—
7i-T	0.44	0.26	29,000	12,000	2.41	++	++	++	+	+	++	++	—
7i-C	—	0.39	42,000	26,000	1.64	++	++	++	+	+	++	++	—

^a T: thermal imidization; C: chemical imidization. ^b Measured at a polymer concentration of 0.5 g/dL in DMAc at 30 °C. ^c Determined in THF relative to polystyrene standards. ^d Insoluble in DMAc. ^e Insoluble in THF. ^f The qualitative solubility was tested with 10 mg of a sample in 1 mL of stirred solvent. ++, soluble at room temperature; +, soluble on heating; +—, partially soluble; —, insoluble even on heating.

Table 2. Thermal Properties of the Poly(ether-imide)s

Polymer code	T_g (°C) ^a	T_s (°C) ^b	T_d at 10% weight loss (°C) ^d		Char yield (wt %) ^e
			In N ₂	In Air	
7a	302	289	606	600	66
7b	295	288	617	598	67
7c	279	273	594	610	63
7d	273	262	634	614	67
7e	262	251	595	606	62
7f	262	252	589	592	62
7g	238	232	620	618	64
7h	247	236	572	588	57
7i	280	270	588	565	65

^a The polymer film samples were heated at 300 °C for 30 min before all the thermal analyses. ^b Midpoint temperature of the baseline shift on the second DSC heating trace (rate = 20 °C/min) of the sample after quenching from 400 to 50 °C (cooling rate = -200 °C/min) in nitrogen. ^c Softening temperature measured by TMA with a constant applied load of 10 mN at a heating rate of 10 °C/min. ^d Decomposition temperature at which a 10% weight loss was recorded by TGA at a heating rate of 20 °C/min and a gas flow rate of 20 cm³/min. ^e Residual weight percentage at 800 °C in nitrogen.

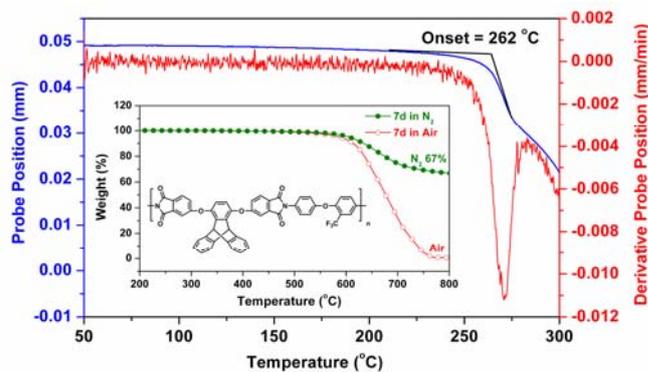


Figure 3. TMA and TGA curves of poly(ether-imide) **7d** with a heating rate 10 and 20 °C/min, respectively.

6. Optical and Colorimetric Properties

The color intensities of the poly(ether-imide)s were elucidated from the yellowness (b^*) or redness (a^*) indices observed by a colorimeter. For comparison, a standard polyimide from PMDA and ODA (the same components to the commercial Kapton film) was also prepared and characterized by its color intensity. The color coordinates of the poly(ether-imide) films are given in Table 3. In general, the cast films of chemically treated polyimide samples showed a lower yellowness index (b^*) of 5.9~28.9. The slightly higher yellowness index of the thermally imidized poly(ether-imide)s films might be a result of thermal oxidation of chain-end amino groups or a denser chain packing. In addition, thin films were measured for optical transparency using UV-Vis spectroscopy. Figure 4 shows the UV-visible transmittance spectra of some representative poly(ether-imide) films, and the cut-off wavelengths

(absorption edge; λ_0) from the UV-Vis spectra are also listed in Table 3. All poly(ether-imide) films exhibited cut-off wavelengths shorter than 400 nm and were entirely transparent and near colorless. Figure 5 shows the photographs of the films of poly(ether-imide)s **7g-C** and **7i-C** and a standard Kapton (PMDA-ODA) polyimide. In general, the films made from the 7 series poly(ether-imide)s exhibited much lighter color than the standard Kapton polyimide film. The low color of these poly(ether-imide)s could be explained by the decreased intermolecular electronic interactions. The bulky and three-dimensional triptycene units in the bis(ether anhydride) component were effective in decreasing charge-transfer complexing (CTC) between the polymer chains through a steric hindrance effect.

Table 3. Color Coordinates and λ_0 's of the Poly(ether-imide)s

Polymer code	Film thickness (μm)		Color coordinates ^a						λ_0 (nm) ^b	
			a^*		b^*		L^*		(T)	(C)
Imidization method	(T)	(C)	(T)	(C)	(T)	(C)	(T)	(C)	(T)	(C)
Blank	—	—	-0.6	—	0.3	—	96.5	—	—	—
7a	45	—	1.4	—	21.0	—	84.5	—	386	—
7b	46	—	-0.7	—	17.4	—	81.4	—	393	—
7c	47	—	1.7	—	17.0	—	81.4	—	390	—
7d	53	—	1.9	—	21.9	—	84.1	—	387	—
7e	50	51	1.6	1.1	18.3	13.3	85.1	86.2	386	382
7f	48	52	4.1	4.7	22.0	19.1	79.4	76.9	388	389
7g	61	42	0.3	-0.5	17.4	5.9	85.2	91.5	383	378
7h	56	46	6.4	0.8	25.2	12.7	78.6	85.1	391	393
7i	58	45	3.6	-0.8	28.9	18.6	74.4	82.5	392	392
Kapton	37	—	0.7	—	99.1	—	82.4	—	462	—

^a The color parameters were calculated according to a CIE LAB equation. L^* is the lightness, where 100 means white and 0 implies black. A positive a^* means a red color, and a negative a^* indicates a green color. A positive b^* means a yellow color, and a negative b^* implies a blue color. ^b Absorption edge from the UV-vis spectra of the polymer thin films.

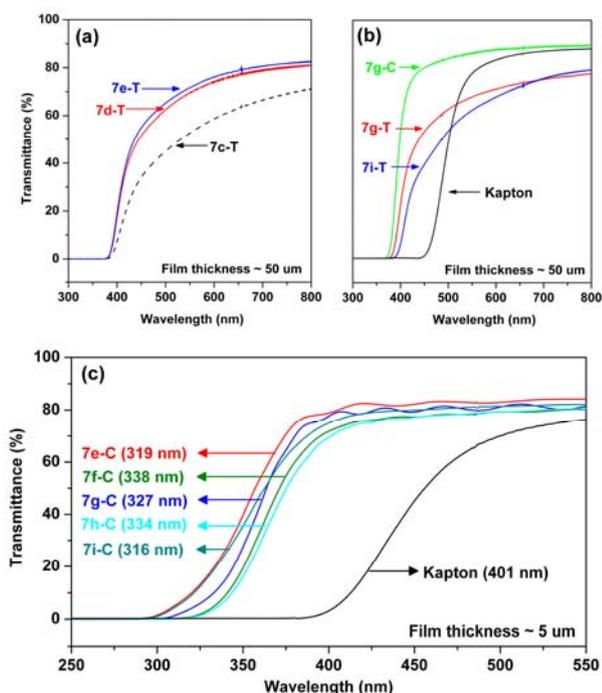


Figure 4. Transmission UV-vis spectra of some poly(ether-imide)s and Kapton films.



Figure 5. Photographs of Kapton film and the cast films obtained from poly(ether-imide)s **7g-C** and **7i-C** (thickness ~50 μm).

7. Conclusions

A series of novel triptycene-based poly(ether-imide)s were synthesized from 1,4-bis(3,4-dicarboxyphenoxy)triptycene dianhydride with various aromatic diamines by two-step thermal or chemical imidization method. All the poly(ether-imide)s afforded transparent, flexible, and strong films. Most of poly(ether-imide)s exhibited very good solubility in organic solvents and could be solution-cast to pale yellow to nearly colorless films directly in their fully imidized form. The enhanced solubility and decreased color intensity in these poly(ether-imide)s have been achieved at little sacrifice in thermal stability, flexibility, or mechanical properties. Thus, these properties suggest the potential usefulness of these novel poly(ether-imide)s in microelectronics and optoelectronics applications.

References

- Wilson, D.; Stenzenberger, H. D.; Hergenrother, P. M., Eds.; Polyimides; Blackie: Glasgow and London, 1990.
- De Abajo, J.; de la Campa J. G. *Adv Polym Sci* 1999, 140, 23-59.
- Yang, J.-S.; Yan, J.-L. *Chem Commun* 2008, 1501-1512.
- Bartlett, P. D.; Ryan, M. J.; Cohen, S. G. *J Am Chem Soc* 1942, 64, 2649-2653.
- Wittig, G.; Ludwig, R. *Angew Chem* 1956, 68, 40.
- Skvarchenko, V. R.; Shalaev, V. K.; Klabunovskii, E. I. *Russ Chem Rev (Engl Transl)* 1974, 43, 951-966.
- Swager, T. M. *Acc Chem Res* 2008, 41, 1181-1189.
- Klanderma B. H.; Faber, J. W. H. *J Polym Sci Part A1 Polym Chem* 1968, 6, 2955-2965
- Long, T. M.; Swager, T. M. *J Am Chem Soc* 2003, 125, 14113-14119.
- (a) Yang, C. P.; Hsiao, S. H.; Yang, H. W. *Macromol Chem Phys* 2000, 201, 409. (b) Hsiao, S. H.; Chung, C.-L.; Lee, M.-L. *J Polym Sci Part A: Polym Chem* 2004, 42, 1008-1017.
- Yang, J.S.; Swager, T. M. *J Am Chem Soc* 1998, 120, 11864-11873.