

Synthesis and Characterization of Poly(ester-ether-imide)s Derived from 5-(4-Trimellitimidophenoxy)-1-trimellitimido naphthalene

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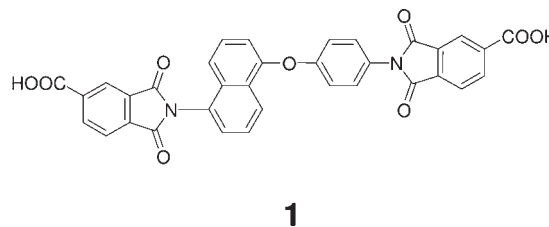
ABSTRACT: A series of novel aromatic poly(ester-ether-imide)s with inherent viscosity values of 0.44–0.74 dL g⁻¹ were prepared by the diphenylchlorophosphate-activated direct polycondensation of an imide ring-containing diacid namely 5-(4-trimellitimidophenoxy)-1-trimellitimido naphthalene (**1**) with various aromatic dihydroxy compounds in the presence of pyridine and lithium chloride. Owing to comparison of the characterization data, an ester-containing model compound (**2**) was also synthesized by the reaction of **1** with phenol. The model compound **2** and the resulted polymers were fully characterized by FT-IR and NMR spectroscopy. The ultraviolet λ_{max} values of the poly(ester-ether-imide)s were also determined. The resulting polymers exhibited an excellent organosolubility in a variety of high polar solvents such as *N,N*-dimethylacetamide, *N,N*-dimethylformamide, dimethyl sulfoxide, and

N-methyl-2-pyrrolidone. They were soluble even in common less polar organic solvents such as pyridine, *m*-cresol, and tetrahydrofuran on heating. Crystallinity of the polymers was estimated by means of wide-angle X-ray diffraction. The resulted polymers exhibited nearly an amorphous nature. From differential scanning calorimetry thermograms, the polymers showed glass-transition temperatures between 221 and 245°C. Thermal behaviors of the obtained polymers were characterized by thermogravimetric analysis, and the 10% weight loss temperatures of the poly(ester-ether-imide)s were found to be over 410°C in nitrogen. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 116: 977–985, 2010

Key words: poly(ester-ether-imide); polycondensation; inherent viscosity; thermal properties

INTRODUCTION

The reaction between aromatic diamines and trimellitic anhydride is a usual manner to prepare imide ring-containing aromatic dicarboxylic acids.^{1–7} This route is widely used in the field of polymeric materials for the synthesis of some copolyimides such as poly(amide-imide)s^{8–12} and poly(ester-imide)s.^{13–17} According to this strategy, 5-(4-aminophenoxy)-1-naphthylamine reacted with two mole equivalents of trimellitic anhydride in refluxing glacial acetic acid to obtain 5-(4-trimellitimidophenoxy)-1-trimellitimido naphthalene (**1**). The addition reaction between the amino and anhydride groups as well as the subsequent thermal cyclodehydration reaction was carried out in a yellow heterogeneous solution. The detailed discussion about this synthesis was reported, previously.¹⁸



The imide ring-containing diacid **1** was then utilized for the preparation of appropriate poly(amide-ether-imide)s using some aromatic diamine comonomers such as 1,4-phenylene diamine, benzidine, 2,6-diaminopyridine, 3,3'-dimethoxybenzidine, 4,4'-oxydianiline, 1,5-diaminonaphthalene, 2,4-diamino-6-phenyl-1,3,5-triazine, and 4-phenyl-2,6-bis(4-aminophenyl)pyridine.

It seems to be predictable that like the previously prepared poly(amide-ether-imide)s, the poly(ester-ether-imide)s potentially resulted from monomer **1** must have some distinguished properties such as good organosolubility, moderate T_g values, and high thermostability. In fact, the ether-containing and naphthalene-based diimide-diacid **1** has so much useful structural aspects that account for its application in the preparation of another class of

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copolyimides namely poly(ester-ether-imide)s in addition to the previous ones. To prepare this class of copolyimides, diphenylchlorophosphate (DPCP)-promoted reactions have been considered. Polyesterification using DPCP in the presence of lithium chloride in pyridine is a well-accepted direct method that will be discussed more about it afterward. Therefore, this study deals with the synthesis of some novel aromatic poly(ester-ether-imide)s derived from imide ring-containing dicarboxylic acid **1** and various kinds of aromatic dihydroxy compounds. Organosolubility in common solvents, crystallinity behavior, DSC plots, and thermal decomposition thermograms of the poly(ester-ether-imide)s prepared herein were investigated and compared with those of the previous poly(amide-ether-imide)s.

EXPERIMENTAL

Materials

Diphenylchlorophosphate (DPCP, purity = 99%) was purchased from Aldrich chemical Co. and used as received. All the other chemicals were purchased either from Merck chemical Co. or Fluka chemical Co. According to the reported method,¹⁹ 5-(4-aminophenoxy)-1-naphthylamine (m.p. = 109–110°C), used to prepare the monomer **1** was synthesized by a two-step reaction starting from 5-amino-1-naphthol and *p*-chloronitrobenzene in dry DMF, followed by the reduction of 5-(4-nitrophenoxy)-1-naphthylamine obtained by means of Pd/C (10%), and hydrazine monohydrate. Aromatic dihydroxy compounds including resorcinol (**3a**), hydroquinone (**3b**), pyrocatecol (**3c**), 2,2'-dihydroxybiphenyl (**3d**), 2,2'-dihydroxy-1,1'-binaphthyl (**3e**), and 1,4-dihydroxyanthraquinone (**3g**) were used as obtained without further purification. Bisphenol A (**3f**) was purified by recrystallization from acetic acid. Trimellitic anhydride (purity, >98%) was used as received. Commercially obtained anhydrous lithium chloride was dried under vacuum at 150°C for 12 h. Phenol was recrystallized from petroleum ether/benzene and stored in a vacuum desiccator. Pyridine was dried with sodium, followed by distillation. Polar aprotic solvents including *N*-methyl-2-pyrrolidone (NMP), *N,N*-dimethylacetamide (DMAc), *N,N*-dimethylformamide (DMF), dimethyl sulfoxide (DMSO), and pyridine were purified by distillation under reduced pressure over calcium hydride and stored over 4 Å molecular sieves. *m*-Cresol was redistilled under a nitrogen atmosphere. Tetrahydrofuran (THF) was dried by sodium and redistilled before use.

Measurements

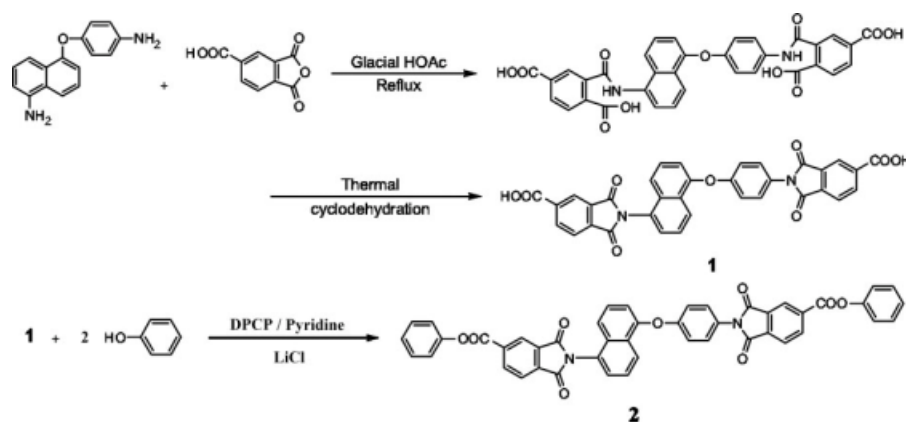
Inherent viscosities results were measured using an Ubbelohde viscometer with polymer solutions in

DMAc at a concentration of 0.5 g dL⁻¹ at 30°C. Melting points were determined in open capillaries with IA 9100 Series Digital Melting Point apparatus (Electrothermal, UK). FT-IR spectra were recorded on a Perkin Elmer RX I FT-IR spectrometer (USA), and the spectra of solids were obtained using KBr pellets. ¹H NMR and ¹³C NMR spectra were recorded on a Bruker Advance 500 NMR (Germany) operated at 500 MHz for proton and 125 MHz for carbon using dimethyl sulfoxide-*d*₆ (DMSO-*d*₆). Thermal gravimetric analysis (TGA/DTG) and differential scanning calorimetry (DSC) were performed on a Mettler TA 5000 system (Columbus, OH) under nitrogen atmosphere at a heating rate of 10°C min⁻¹. The DSC traces were obtained from heating, rapid cooling, and reheating of samples in a range of 50–400°C. Ultraviolet maximum wavelength (λ_{max}) values were determined with a GBC model 916 ultraviolet-visible (UV-vis) instrument (GBC Scientific Equipment, Australia) in DMSO. Wide-angle X-ray diffraction patterns were performed at room temperatures with film specimens on a D8 Advance Bruker X-ray diffractometer with Ni-filtered Cu-K α radiation (30 kV, 25 mA).

Synthesis of the model compound **2**

DPCP (0.05 g), lithium chloride (0.04 g), and pyridine (2.5 mL) were poured in a round-bottomed flask and stirred at room temperature for 45 min. On the other hand, in a two-necked round bottomed flask, a solution consisting of imide-containing diacid **1** (0.299 g, 0.5 mmol) and phenol (0.094 g, 1 mmol) in pyridine (3.0 mL) was prepared and heated at 120°C for 5 min, while stirring. The first prepared mixture was then added dropwise through a dropping funnel over a period of 30 min under reflux and stirring. Next, the final solution was heated at 120°C for 3 h. The diimide-diester solution obtained was trickled into methanol (50 mL), giving rise a yellow crude precipitate, which was washed thoroughly with methanol and hot water, filtered off and dried at 100°C for 5 h under vacuum to afford 0.363 g (97%) of the model compound **2** as a dark-yellow solid having ultraviolet $\lambda_{\text{max}} = 374$ nm in DMSO, m.p. > 300°C.

FT-IR (KBr): 3049 (w, sh), 2923 (w, sh), 1779 (m, sh), 1723 (s, br), 1598 (w, sh), 1534 (w, sh), 1505 (s, sh), 1413 (m, sh), 1384 (m, sh), 1289 (w, sh), 1231 (m, sh), 1168 (w, sh), 1100 (m, sh), 924 (w, sh), 870 (w, sh), 786 (m, sh), 729 (w, sh), 691 (w, sh) cm⁻¹. ¹H NMR (DMSO-*d*₆): 8.48 (d, *J* = 7.7 Hz, 1H), 8.42 (d, *J* = 8.2, 1H), 8.40 (s, 1H), 8.33 (s, 1H), 8.31 (d, *J* = 8.0 Hz, 1H), 8.14 (d, *J* = 7.7 Hz, 1H), 8.08 (d, *J* = 8.2 Hz, 1H), 7.80–7.73 (m, 8H), 7.57–7.51 (m, 8H), 7.26 (d, *J* = 8.8 Hz, 2H), 7.22 (d, *J* = 7.4 Hz, 1H) ppm. ¹³C NMR (DMSO-*d*₆): 167.98, 167.85, 157.21, 153.42, 137.29, 137.25, 137.10, 137.01, 136.72, 136.54, 136.52,



Scheme 1 Synthesis of ester-containing model compound 2.

136.44, 136.22, 134.73, 133.82, 133.39, 133.36, 133.24, 130.34, 130.32, 129.87, 129.46, 128.96, 128.94, 128.49, 128.44, 128.42, 127.12, 125.89, 125.04, 125.02, 124.85, 124.46, 124.33, 124.22, 123.45, 119.09, 119.06, 119.02, 116.24 ppm.

Synthesis of the poly(ester-ether-imide)s 4a-4g

A typical example of polycondensation is as follows: A solution of DPCP (0.05 g), lithium chloride (0.04 g), and pyridine (2.5 mL) was stirred at room temperature for 45 min and then added dropwise over a period of 30 min to a solution containing diimide-diacid **1** (0.299 g, 0.5 mmol) and resorcinol, **3a**, (0.055 g, 0.5 mmol) in pyridine (3.0 mL) under reflux and stirring. The final solution was stirred and heated at 120°C for 3 h. The polymer solution obtained was trickled into methanol (50 mL), giving rise a stringy precipitate, which was washed thoroughly with methanol and hot water, collected by filtration and dried at 100°C for 2 h under vacuum to afford 0.305 g (96%) of the polymer **4a**. The other poly(ester-ether-imide)s were synthesized in a similar manner. Inherent viscosities of the polymers were measured in DMAc at a concentration of 0.5 g dL⁻¹ at 30°C. Ultraviolet λ_{max} values of the samples were determined in DMSO. Furthermore, the obtained IR and NMR spectroscopic data will be discussed in the results and discussion section.

RESULTS AND DISCUSSION

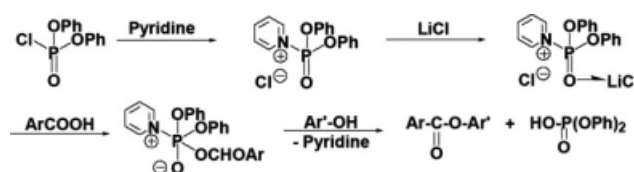
Synthesis

As stated earlier, imide ring-containing and naphthalene-based wholly aromatic dicarboxylic acid **1** having flexible ether linkages (yellow solid, m.p.= 349–351°C) seems to be a good candidate to produce poly(ester-ether-imide)s as copolyimides other than those prepared previously. However, at first a model compound (**2**) possessing both imide heterocyclic

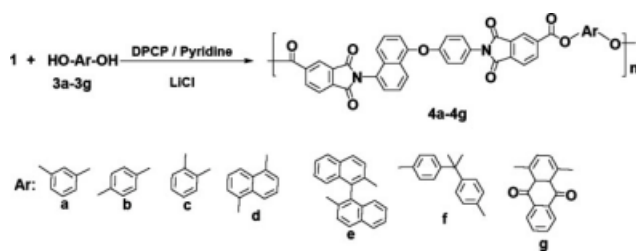
rings and ester linkages was synthesized through the reaction of diimide-diacid **1** with 2 mole equivalents of phenol. Scheme 1 shows the reaction route to prepare the model compound **2** starting from 5-(4-aminophenoxy)-1-naphthylamine.

IR spectrum of the compound **2** exhibited characteristic absorption bands of imide rings at 1779, 1723 (asymmetric and symmetric C=O stretching vibration, respectively), 1384 (C–N stretching vibration), and 729 (imide ring deformation) cm⁻¹. The absorption of ester carbonyl groups appeared at 1723 cm⁻¹, which was overlapped with the symmetrical C=O stretching vibration of the imide ring. The ¹H NMR spectrum of the compound **2** showed some peaks in the region of 7.22–8.48 ppm related to the aromatic protons in the structure. In this spectrum the peaks appeared at above 8 ppm can be attributed to hydrogens of the trimellitimido group.^{20–22}

Within the wide range of phosphorus compounds diphenylchlorophosphate (DPCP) was found to be the most effective and convenient ones.^{23–25} In pyridine solution, DPCP forms *N*-phosphonium salt, which reacts with carboxylic acid and gives the activated acyloxy *N*-phosphonium salt. A favorable effect of lithium chloride on reaction rate and molar masses has been reported and assumed to originate from the formation of a complex with the *N*-phosphonium salt (Scheme 2). This phenomenon decreases the electron density of the phosphorus atom and favors in for the reaction with the aromatic acid. Good results were obtained using pyridine-LiCl solutions of DPCP in polyesterification of



Scheme 2 DPCP-activated direct esterification mechanism.



Scheme 3 Synthesis of poly(ester-ether-imide)s 4a-4g.

aromatic dicarboxylic acids with various kinds of bisphenols.^{26,27}

This method was utilized herein for the preparation of the poly(ester-ether-imide)s **4a-4g** from monomers including imide-containing diacid **1** and various aromatic dihydroxy compounds (**3a-3g**) using the conditions applied for the synthesis of model compound **2**. All the reactions proceeded smoothly with a high yield (above 95%). Scheme 3 shows the reaction route to obtain the poly(ester-ether-imide)s **4a-4g**.

The viscosity measurements provide an approximate estimate about the molecular weights by the Mark-Huwink equation.^{28,29} Molecular weights can be studied viscometrically and generally their measure increases by increasing the viscosity values. In-

herent viscosity values of the resulting poly(ester-ether-imide)s are listed in Table 1. Comparison between the obtained inherent viscosity data with the corresponding values of similar structures showed the polyesterification reactions proceeded satisfactorily. In Table 1 some other results including yield of the reactions, maximum absorbance of the polymers in their UV spectra (λ_{\max}), and apparent color of the polymers are also listed.

The synthesized polymers were characterized by their IR and ¹H NMR spectra. The spectra of the poly(ester-ether-imide)s are similar to the spectra of the model compound **2** because of their structural similarity. All the IR spectra showed the characteristic absorptions of the carbonyl bonds occurred at about 1780 and 1720 cm^{-1} , peculiar to carbonyl stretching of imide and ester groups. All of these polymers exhibited absorption bands at about 1370 and 720–730 cm^{-1} , which show the presence of the imide heterocyclic ring in their chemical structure. Figure 1(a) represents the IR spectrum of poly(ester-ether-imide) **4b**, for example.

In general, the ¹H NMR spectra of all polymers showed a number of distinguished peaks in the range of 7.20–8.45 ppm due to the aromatic protons. In all cases, chemical shift values and surface under the peaks are conformable to the attributed chemical

TABLE I
Synthesis and Some Characteristics of the Resulting Poly(ester-ether-imide)s

Code	Dihydroxy structure	Yield (%)	$\eta_{\text{inh}}^{\text{a}}$ (dL g ⁻¹)	$\lambda_{\text{max}}^{\text{b}}$ (nm)	Color
4a		96	0.47	368	Orange
4b		97	0.44	375	Gray
4c		95	0.55	361	Yellow
4d		95	0.67	387	Brown
4e		96	0.74	380	Brown
4f		96	0.53	389	Brown
4g		95	0.49	373	Yellow

^a Measured in DMAc at a concentration of 0.5 g dL⁻¹ at 30°C.

^b Obtained in DMSO.

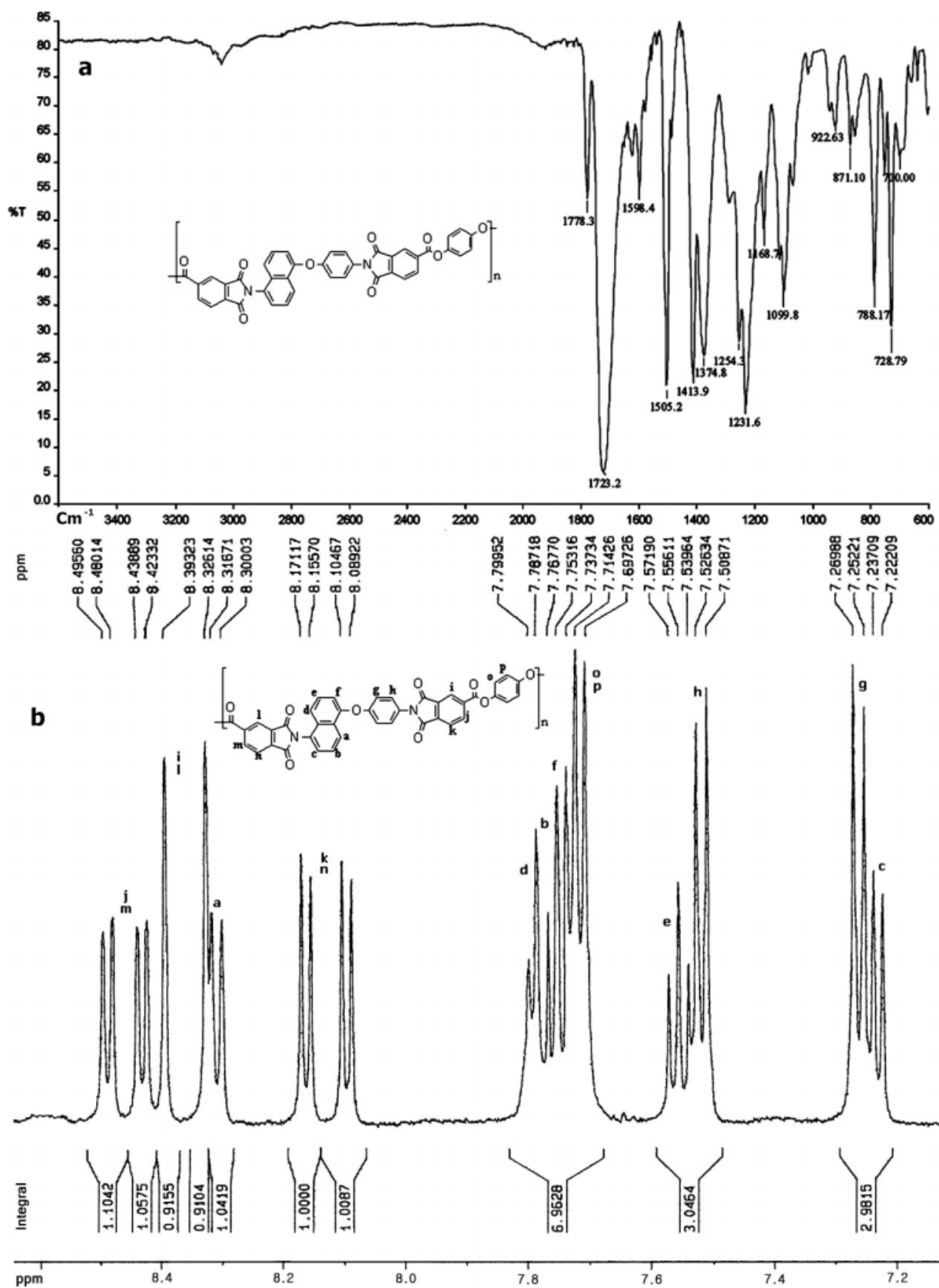


Figure 1 IR (a) and ^1H NMR (b) spectra of poly(ester-ether-imide) 4b.

TABLE II
Solubility of the Resulting Poly(ester-ether-imide)s^a

Code	DMAC	DMF	DMSO	NMP	Pyridine	<i>m</i> -Cresol	THF	Toluene	DCM
4a	+	++	++	±	±	++	±	–	–
4b	±	±	++	±	–	±	±	–	–
4c	±	±	++	++	±	±	–	–	–
4d	++	++	±	++	±	±	++	–	–
4e	++	++	±	++	±	++	±	–	–
4f	++	±	++	±	++	±	++	–	–
4g	±	++	±	++	±	±	±	–	–

^a Solubility: ++, soluble at room temperature; ±, soluble on heating; –, insoluble.

DMAC: *N,N*-dimethylacetamide; DMF: *N,N*-dimethylformamide; DMSO: dimethyl sulfoxide; NMP: *N*-methyl-2-pyrrolidone; THF: tetrahydrofuran; DCM: dichloromethane.

Concentration: 5 mg mL⁻¹.

structure. Figure 1(b) shows a representative ¹H NMR spectrum of the same poly(ester-ether-imide) **4b**.

Properties

Table 2 represents solubility test results of the polymers obtained in some common organic solvents including *N,N*-dimethylacetamide (DMAC), *N,N*-dimethylformamide (DMF), dimethyl sulfoxide (DMSO), and *N*-methyl-2-pyrrolidone (NMP), pyridine, *m*-cresol, tetrahydrofuran (THF), toluene, and dichloromethane (DCM). Although the polymers are insoluble in low polar solvents, they are almost dissolved thoroughly in high polar solvents and even in moderate polar solvents such as pyridine and tetrahydrofuran (THF) at room temperature or on heating. Moreover, the solubility study revealed that all of the resulted polymers have a similar behavior toward the organic solvents used. In fact, the diamine comonomers have no efficient role on the organosolubility behavior since the polarity extent of the structures is mainly determined by the presence of the imide ring-containing aryl ether moieties. On the other hand, the asymmetrical orientation of the polar linkages attached to the central naphthalene ring into the polymer backbone interrupted a good chain packing thus leading to high solubility of the polymers in most of high polar organic solvents.

The crystallinity of some prepared poly(ester-ether-imide)s (**4b**, **4f**, and **4g**) was measured by X-ray diffraction scans at room temperature. Typical diffraction patterns for some representative polymers with 2θ ranging from 5 to 60° were presented in Figure 2.

In general, in X-ray diffractograms of rigid-rod aromatic polymers without bulky pendant groups or twisted structures crystalline patterns can be observed due to a better packing of polymer chains. In our study, however, no remarkable crystal diffraction was detected for the evaluated polymers (**4b**, **4f**, and **4g**). Poly(ester-ether-imide) **4b** showed a further

crystallinity than the other two. This can be attributed to a more compactness of the macromolecular chains. However, insertion of disordered isopropylidene segment into the polymer chains resulted in a significant decrease in crystallinity of polymer **4f**. Moreover, amorphous nature of polymer **4g** is reasonable because the presence of anthraquinone bulky group into the backbone induces looser chain packing. The crystallinity of all polymers was usually reflected in their solubility behavior, which is in agreement with the general rule that the solubility decreases with increasing crystallinity.

The thermal behavior of the poly(ester-ether-imide)s **4a-4g** was evaluated by both thermogravimetric analysis (TGA/DTG) and differential

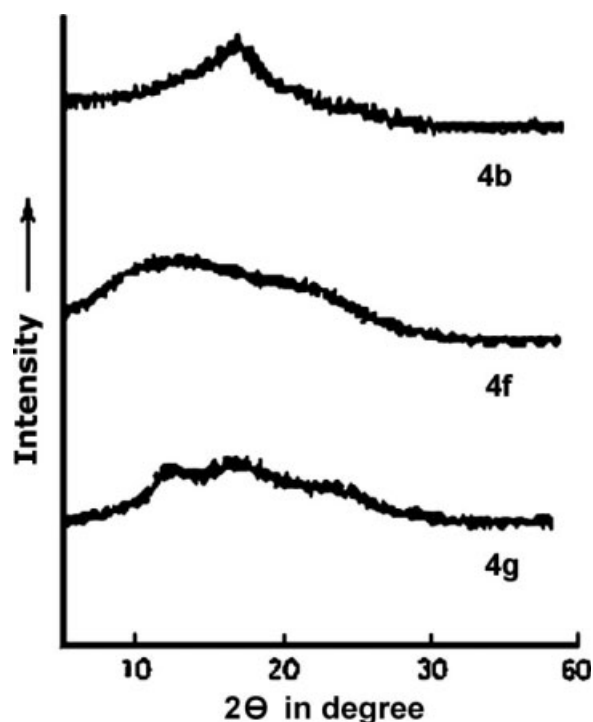


Figure 2 X-ray diffraction patterns of poly(ester-ether-imide)s **4b**, **4f**, and **4g**.

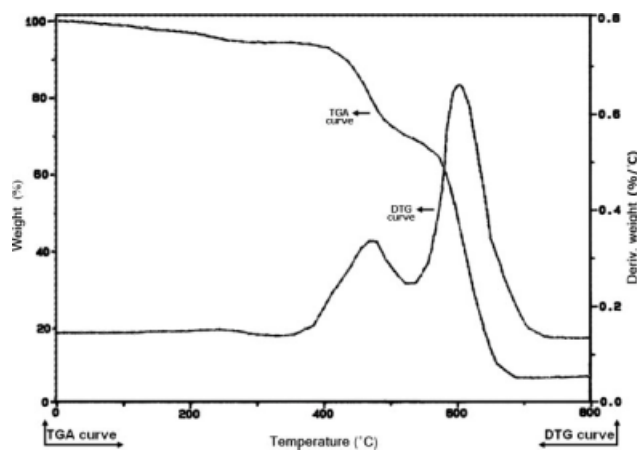


Figure 3 TGA/DTG thermograms of poly(ester-ether-imide) 4d obtained at a heating rate of 10 °C min⁻¹ in a nitrogen atmosphere.

scanning calorimetry (DSC). Thermal stability evaluation of the resulting poly(ester-ether-imide)s was carried out by their TGA/DTG in nitrogen atmosphere at a heating rate of 10 °C min⁻¹. The obtained polymers were thoroughly stable up to 400 °C and lost 10% of their total weight ($T_{d10\%}$) at the temperatures ranged from 410 to 469 °C. This desirable thermal stability of the resulting polymers is ascribed to their wholly aromatic polymer backbone. Here, the presence of the naphthalene-based backbones as well as the incorporation of heat-resistant imide rings causes an improved stability toward heat. A representative TGA/DTG thermogram of the polymer 4d is shown in Figure 3. Furthermore, in order to have a better comparison, temperatures at 10% weight losses ($T_{d10\%}$) are tabulated in Table 3. In general, the thermograms of the resulted polymers were almost similar to each other, and poly(ester-ether-imide)s showed a two-stage decomposition at elevated temperatures. Assuming a different stability of the ester and imide units, the first stage of weight losses may be attributed to the early degradation of the ester groups. Therefore, the 10% weight loss temperatures are mainly caused by the decomposition of ester linkages. Among the polymers, poly(ester-ether-imide) 4e having binaphthylene moieties in its main chain showed the highest $T_{d10\%}$ value, with a higher thermal stability than those of the other ones.

The glass transition temperatures (T_g 's) of the polymers are summarized in Table 3. The order of the data is comparable to the decreasing order of stiffness of the polymer backbones. In the second-heating traces, after cooling from elevated temperatures to room temperature, an obvious base line shift according to glass-transition temperature (T_g) values was observed. In general, the DSC thermograms of the poly(ester-ether-imide)s showed T_g values in the range of 221–245 °C, depending on the structure of

TABLE III
Thermal Properties of the Poly(ester-ether-imide)s

Code	T_g^a (°C)	$T_{d10\%}^b$ (°C)
4a	232	437
4b	236	448
4c	227	425
4d	231	428
4e	245	469
4f	221	410

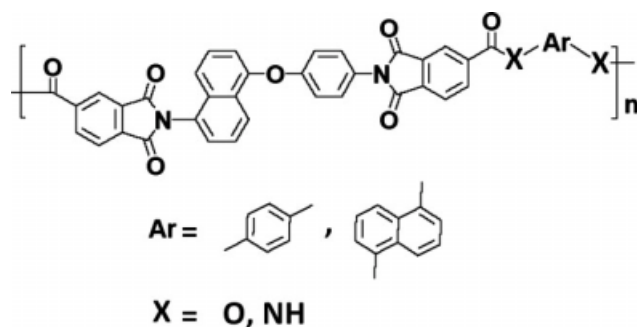
^a From the second-heating traces of DSC measurements with a heating rate of 10 °C min⁻¹ in nitrogen.

^b Temperature at which 10% weight loss was recorded by TGA at a heating rate of 10 °C min⁻¹ in nitrogen.

the dihydroxy component, and decreased with decreasing rigidity of the polymer backbone. Among the poly(ester-ether-imide)s, polymer 4e containing sterically-hindered binaphthylene units showed higher T_g value than the other ones. This could be attributed to the incorporation of bulky and rigid binaphthylene units along the poly(ester-ether-imide)s backbone, which restricted the free rotation of the macromolecular chains leading to an enhanced T_g value. Conversely, polymer 4f derived from bisphenol-A showed the lowest T_g value, attributed to the presence of isopropylidene unit in the polymer backbone. The incorporation of this unit into the polymer backbone lowered the rigidity of the polymer backbone and reduced the T_g value of the polymers.


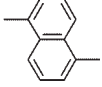

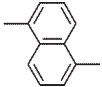
To investigate the structure effect on some properties of two classes of aromatic copolyimides including those previously-prepared poly(amide-ether-imide)s and these poly(ester-ether-imide)s, four polymers having the same aromatic moieties have been considered. The comparative properties are solution viscosity, UV maximum wavelength, T_g and $T_{d10\%}$ values, and the apparent color of polymers. Scheme 4 shows their chemical structure, and Table 4 tabulates the obtained results.

The most important difference between these two blocks of aromatic copolyimides is their thermal decomposition behavior. The two poly(amide-ether-



Scheme 4 Chemical structure of two classes of copolyimides with the same aromatic backbone.

TABLE IV
Some Characteristics of Poly(ester-ether-imide)s and Poly(amide-ether-imide)s with the Same Aromatic Moieties

Polymer class	Aromatic moiety of comonomer (diamine/dihydroxy)	η_{inh}^a (dL g ⁻¹)	λ_{max}^b (nm)	T_g^c (°C)	T_{d10}^d (°C)	Color
Poly(ester-ether-imide) 4b		0.44	375	236	448	Gray
poly(ester-ether-imide) 4d		0.67	387	231	428	Brown
poly(amide-ether-imide)		0.48	364	307	539	Orange
poly(amide-ether-imide)		0.7	383	299	533	Yellow

^a Measured in DMAc at a concentration of 0.5 g dL⁻¹ at 30°C.

^b Obtained in DMSO.

^c From the second-heating traces of DSC measurements with a heating rate of 10 C min⁻¹ in nitrogen.

^d Temperature at which 10% weight loss was recorded by TGA at a heating rate of 10°C min⁻¹ in nitrogen.

imide)s showed obviously a thermal decomposition having a great gradient at elevated temperatures (at about 550°C) attributed to the amide linkages and imide heterocyclic rings decomposition, but as stated earlier, the two poly(ester-ether-imide)s (**4b** and **4d**) showed a two-stage decomposition pattern at elevated temperatures (the first, at about 450°C and the second, at about 550°C) attributed to the ester linkages decomposition and imide heterocyclic rings decomposition, respectively. Therefore, it is revealed that thermal degradation of the two poly(amide-ether-imide)s happens late comparing with the two poly(ester-ether-imide)s (**4b** and **4d**) because of lesser heat stability of ester group in comparison with amide group. Moreover, T_g values of the two poly(amide-ether-imide)s are remarkably greater than those of **4b** and **4d**. This could be attributed to the incorporation of flexible ester units along the poly(ester-ether-imide)s backbone, while the presence of amide groups with H-bond formation ability causes a restriction in free rotation of the macromolecular chains leading to enhanced T_g values.

CONCLUSION

The direct polyesterification of diimide-diacid **1** with a number of aromatic dihydroxylic compounds in the presence of DPCP in pyridine as the reactions solvent resulted in the corresponding poly(ester-ether-imide)s **4a-4g**, satisfactorily. The polymers were highly soluble in common organic solvents particularly those solvents with high polarity. Moreover, comparison between the solubilities of poly(ester-ether-imide)s with those of previously-prepared poly(amide-ether-imide)s revealed a significant solubility enhancement for this new class of copoly-

mides particularly in high polar solvents. No remarkable crystal diffraction was detected for the polymers obtained, and they showed almost an amorphous diffraction patterns. The TGA/DTG thermograms showed obviously two-stage decomposition at elevated temperatures. The effect of chemical structure on T_g values was also investigated by DSC plots of the polymers. The T_g values for the resulted poly(ester-ether-imide)s were up to 240°C, whereas these values for the previously-prepared poly(amide-ether-imide)s with the same aromatic moieties were up to 300°C.

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