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Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

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To cite this Article Li, Xiuhua and Hay, Allan S.(2006) 'Fluorescent Poly(Arylene Ether)s with a 3,5-Dipyridyl-1,2,4-triazole Pendent Group Joined by a N-N Linkage', *Journal of Macromolecular Science, Part A*, 43: 9, 1279 – 1291

To link to this Article: DOI: 10.1080/10601320600814598

URL: <http://dx.doi.org/10.1080/10601320600814598>

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Fluorescent Poly(Arylene Ether)s with a 3,5-Dipyridyl-1,2,4-triazole Pendent Group Joined by a N-N Linkage

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The synthesis and characterization of novel biphenol monomer 3,8-bis(4-hydroxyphenyl)-1,2(naphthalimido)-4(N-3,5-dipyridyl-1,2,4-triazole) and homopolymers and copolymers containing this novel monomer moiety are described. The new bisphenol with a pendent 3,5-dipyridyl-1,2,4-triazole was prepared by an imidization reaction of an anhydride bisphenol with 4-amino-3,5-dipyridyl-1,2,4-triazole. Polymerization with activated difluoro compounds gave poly(arylene ether)s with a pendent 1,2,4-triazole moiety. These polymers had high glass transition temperatures (T_g 's), from 245 to 315°C. The polymers formed clear, transparent, flexible, and tough films from a CHCl_3 solution. Using 4,4'-isopropylidenediphenol (BPA) as comonomer, high molecular weight polymers were obtained in a shorter reaction time. The copolymers showed regular increases in glass transition temperatures as the content of the novel biphenol increased. All the polymers containing the novel biphenol moiety showed strong blue fluorescence in solution under UV irradiation.

Keywords 3,5-dipyridyl-1,2,4-triazole, poly(arylene ether), fluorescence

Introduction

Since the discovery of electroluminescent (EL) light-emitting devices (LEDs) (1), many polymers with EL properties have also been synthesized in the past several years. Polymers have several advantages over inorganic materials, such as low cost, easy processability, flexibility and ease of coating over large areas. Therefore, polymer LEDs exhibit considerable potential in display applications (2–4). Polymer light emitting diodes (PLEDs) require not only good physical properties, but also efficient luminescent properties in devices. The luminescent wavelength of OLEDs can be changed by molecular design. Modified poly(arylene ether)s can be potentially used in organic electroluminescent (EL) devices (5, 6). We have previously described the synthesis of several types of fluorescent polymers. A series of poly(thioether-naphthalimide)s were synthesized containing the N-N linkage in the polymer backbone that incorporate both a flexible thioether linkage and a rigid naphthalic anhydride moiety. They have high T_g 's and excellent thermal stability and were highly fluorescent (7). High molecular weight

Received and Accepted April 2006.

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poly(ether imide)s and copoly(ether imide)s with a N-N linkage between the imide units in the polymer backbone have also been synthesized. These polymers have good solubility in organic solvents, extremely high T_g 's, and excellent thermal stability with red fluorescence (8, 9). A series of stable, highly blue fluorescent poly(isoindole)s were synthesized by treating the respective *o*-dibenzoylbenzenes with substituted anilines at 200°C in the presence of a catalytic amount of *p*-toluenesulfonic acid (10). Poly(arylene ether)s containing the 1,3,5-triphenylbenzene moiety showed blue and red fluorescence (11). Colored and fluorescent poly(arylene ether)s containing benzoylenebenzimidazole, phthaloperinone and phthalocyanine moieties (12) and poly(imidoaryl ether)s with bulky pendent groups, blue light emitting poly(arylene ether)containing 3,6-dialkoxypthalimide moieties were studied (13). A series of blue to greenish-yellow fluorescent, amorphous, thermally stable polymers were also prepared from a monomer with pendent 3,5-diphenyl-1,2,4-triazole groups (14).

Here, we report the synthesis of a new bisphenol with a pendent 3,5-dipyridyl-1,2,4-triazole group. The novel bisphenol was prepared by an imidization reaction of 4-amino-3,5-dipyridyl-1,2,4 triazole with an anhydride bisphenol previously prepared (13, 15, 16). A series of high molecular weight, amorphous, thermally stable poly(aryl ether)s with the pendent 1,2,4-triazole moiety were obtained. Copolymers, using BPA as coreactant, showed high glass transition temperatures that increased as the novel biphenol increased. All the polymers containing this biphenol moiety showed strong blue fluorescence in solution under UV irradiation.

Experimental

Materials

2-Cyanopyridine, hydrazine dihydrochloride, hydrazine monohydrate, diethylene glycol, bis(4-fluorophenyl)phenylphosphine oxide (Triton, Systems, Inc. Technology innovators, Cambridge, MA), 1,3-Bis(4-fluorobenzoyl)benzene, bis(4-fluorophenyl)-sulfone, 4,4-difluorobenzophenone and zinc diacetate were used as received. Reagent grade solvents *N*-methyl-2-pyrrolidinone (NMP), *N,N*-dimethylacetamide (DMAC), *N,N*-dimethylformamide (DMF), sulpholane, potassium carbonate, were used as received. BPA was recrystallized from toluene.

Characterization

^1H - and ^{13}C -NMR spectra were recorded on a Varian Mercury 300 spectrometer using CDCl_3 or $\text{DMSO-}d_6$ as solvent and tetramethylsilane as reference. Matrix assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectra were recorded on a Kratos Kompact MALDI-III TOF mass spectrometer with the instrument set in positive reflection mode to get higher resolution. The melting points were taken on a Fisher-Johns melting point apparatus. UV-Vis spectra were recorded on a Varian Cary 300 Bio UV-Visible Spectrophotometer. Fluorescent spectra were obtained on a Fluoro Max-2 spectrophotometer. Monitoring the purity of the isolated monomers was done by high-performance liquid chromatography (HPLC, Milton Roy, CM 4000) with methanol as an eluent and a UV detector set at 254 nm. The T_g 's of the polymers were obtained using a TA DSC Q1000 instrument at a heating rate of 20°C/min with a heating cooling heating circle scanning method. The T_g was taken from the midpoint of the change in slope of the baseline in the second heating plot. The weight loss data were obtained from

a TA TGA Q500 instrument at a heating rate of 20°C/min under nitrogen. Inherent viscosity data were obtained with a calibrated Ubbelohde suspended viscometer. A water bath with a Julabo (Model type PC) heater was employed to control the temperature.

Synthesis of 3,5-Dipyridyl-1,2,4-triazole 1

The synthesis of 3,5-dipyridyl-1,2,4-triazole was similar to a literature procedure for 3,5-diphenyl-1,2,4-triazole (17). A 250 mL three-necked round-bottom flask was equipped with a nitrogen inlet, magnetic stir bar, and reflux condenser. The flask was charged with 2-cyanopyridine 1 (0.1 mole), hydrazine dihydrochloride (0.1 mole) and hydrazine monohydrate (0.3 mole) and diethylene glycol (100 mL). The reaction mixture was heated at 130°C with stirring under nitrogen for 5–6 h. After cooling, the reaction mixture was diluted with water (100 mL). The precipitate thus obtained was filtered, washed with water, dried in a vacuum oven at 80°C for 12 h and recrystallized from ethanol. The product was obtained as a white powder. The product was obtained in 54% yield. ¹H-NMR (DMSO-*d*₆): Aromatic signals δ (ppm) 7.50–7.60 (m, 2H), 8.00–8.04 (m, 2H), 8.18–8.22 (m, 2H), 8.70–8.75 (m, 2H). Triazole NH₂ signal δ (ppm) 7.79 (s, 2H). Mp: 185–186°C. MALDI-TOF MS: 238.48 (M⁺). TLC indicated 100% purity.

Synthesis of 3,8-Bis(4-hydroxyphenyl)-1,2(naphthalimido)-4(N-3,5-dipyridyl-1,2,4-triazole) 3

Compound 3 was prepared by the reaction of 3,8-bis(4-hydroxyphenyl)-1,2(naphthalic anhydride) 2 with 10 mol% excess of 3,5-dipyridyl-1,2,4-triazole 1 in NMP and heating the reaction mixture for 24 h at 180°C. The product was recrystallized from DMF/water (1/1) (100 + 100 mL). The yield of faint yellow-green colored 3 was 85%. ¹H-NMR (DMSO-*d*₆): δ (ppm) 6.80–6.90 (s, 4H), 7.19–7.23 (s, 4H), 7.45–7.50 (m, 2H), 7.77–7.81 (m, 2H), 7.86–7.93 (m, 2H), 7.97–8.02 (m, 2H), 8.24–8.29 (m, 2H), 8.40–8.45 (m, 2H), 9.70 (s, 2H). Mp: 410°C (DTA). MALDI-TOF MS: 609.31 (M⁻Li⁺). HPLC (r.t.; purity): 2.48 (100%).

General Procedure for the Synthesis of Poly(arylene ether)s 5a-d with a Pendant 3,5-Dipyridyl-1,2,4-triazole Group

The synthesis of most of the polymers was carried out in sulpholane. Wherever there is change in polymerization conditions, such as final polymerization temperature or use of different solvent, it is noted in Table 1. The polymerization was conducted initially at 135–40°C for 2 h to remove the water with toluene using a Dean-Stark trap and then at 170–175°C to effect the polymerization reaction. A typical procedure is as follows. A 25 mL three-necked round-bottomed flask was equipped with a nitrogen inlet, magnetic stirrer, Dean-Stark trap, and a condenser. Initially, the flask was flushed with nitrogen and charged with bisphenol monomer (0.4 mmol), bifluoro monomer (0.4 mmol), K₂CO₃ 0.11 g, sulpholane 4.5 mL and toluene 10 mL. The reaction mixture was heated to 140°C for 2 h to remove water generated in the reaction with toluene. The reaction mixture temperature was raised to 175°C, and the toluene was removed. The reaction mixture temperature was kept at that temperature for 4 h. After cooling, the mixture was diluted with 5 mL DMF and poured into 150 mL of methanol containing 5 vol% of hydrochloric acid to precipitate out polymer. The polymer was collected by

Table 1
Synthesis and thermal properties of poly(arylene ether)s with a 3,5-dipyridyl-1,2,4 triazole pendent group

Polymer	Polymerization T (°C)/time (h)	Solvent	Yield (%)	η_{inh}^a (dl/g)	Tg ^c (°C)	Td(-5wt%) ^d (°C)	Color of polymer
5a	170–175/4	Sulpholane	74.3	0.67	315.1	419.2	Brown
5b	170–175/4	Sulpholane	88.9	1.36	276.9	422.9	Brown
5c	170–175/4	Sulpholane	75.6	0.81	244.8	413.9	Brown
5d	170–175/4	Sulpholane	68.9	0.22 ^b	312.5	388.6	Brown

^aInherent viscosity was measured at a concentration of 0.2 g/dL in CHCl₃ at 25°C.

^bIn DMF at 25°C.

^cTg was determined by DSC at a heating rate of 20°C/min under nitrogen flow rate 80 mL/min, the values were reported from the second scan.

^dReported for 5% weight loss at a heating rate 20°C/min under nitrogen flow rate 60 mL/min.

filtration, washed with 100 mL hot water and again with methanol, and dried in a vacuum oven at 80°C for 12 h.

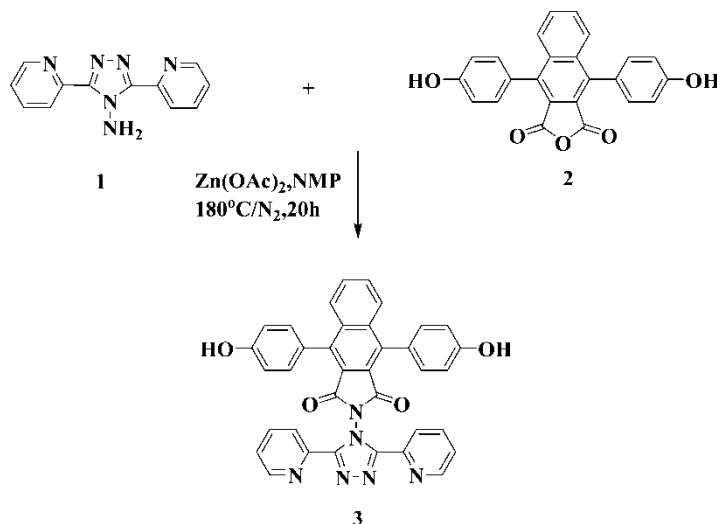
General Procedure for the Synthesis of Copoly(arylene ether)s 7–11 with a Pendent 3,5-Dipyridyl-1,2,4-triazole Group

The synthesis of the copolymers was carried out in DMAC. Wherever there is change in polymerization conditions, such as final polymerization temperature or use of different solvent, it is noted in Table 3. The polymerization was conducted initially at 135–40°C for 2 h to remove the water with toluene using a Dean-Stark trap and then at 170–175°C to effect the polymerization reaction. A typical procedure is as follows. A 25 mL three-necked round-bottomed flask was equipped with nitrogen inlet, a magnetic stirrer, a Dean-Stark trap, and a condenser. Initially, the flask was flushed with nitrogen and charged with bisphenol monomer 3 (0.3 mmol), BPA 6 (0.7 mmol), bifluoro monomer (1.0 mmol), K₂CO₃ 0.11 g, DMAC 4.5 mL and toluene 10 mL. The reaction mixture was heated to 140°C for 2 h to remove water generated in the reaction with toluene. The reaction mixture temperature was raised to 175°C, and the toluene was removed. The reaction mixture temperature was kept at that temperature until the reaction mixture turned very viscous and was difficult to stir. After cooling, the mixture was diluted with 5 mL DMAC and poured into 150 mL of methanol containing 5 vol% of hydrochloric acid to precipitate the polymer. The polymer was collected by filtration, and dried in vacuum oven at 80°C for 12 h. The product was dissolved in 10 mL CHCl₃, filtered through a thin layer of Celite, precipitated into methanol, filtered and dried.

Results and Discussion

Synthesis of 3,8-Bis(4-hydroxyphenyl)-1,2(naphthalimido)-4(N-3,5-dipyridyl-1,2,4-triazole) 3

The reaction of aliphatic and aromatic amines/diamines with carboxylic acid anhydrides has been extensively studied for the preparation of polyamides and polyimides (18). Poly(ether imide)s containing a N-N linkage connecting the imide groups (7) and poly(aryl ether)s from bisphenols containing the imido aryl linkage (15, 16) have been synthesized. Recently, it has been reported that the direct imidization reaction of aromatic amines with 1,4,5,8-naphthalenetetracarboxylic dianhydride and 3,4,9,10-perylenetetracarboxylic anhydride can be conducted using zinc acetate as a catalyst. The corresponding imides were obtained with good yields in a short reaction time (19). The imidization reaction of the N-amino group attached to a N-3,5-diphenyl-1,2,4-triazole ring with acid anhydrides to form 1,2,4-triazole-imide joined through a N-N linkage has been successfully run with zinc acetate as a catalyst (14). N-3,5-Dipyridyl-4-amino-1,2,4-triazole 1 and N-3,5-diphenyl-1,2,4-triazole were prepared from aromatic nitriles and hydrazine hydrochloride in excellent yield by a one-step reaction as described in the literature (17). It is well known that the activity of functional groups is affected by the adjacent groups. The pyridyl group has higher electron withdrawing power than the phenyl group, therefore, the amino group of N-3,5-dipyridyl-4-amino-1,2,4-triazole is less active than the corresponding N-3,5-diphenyl-1,2,4-triazole. The imidization reaction of N-3,5-dipyridyl-4-amino-1,2,4-triazoles was successfully run under reaction conditions similar to those for N-3,5-diphenyl-1,2,4-triazole except for longer reaction time (Scheme 1). The compound was characterized and the spectroscopic data are in



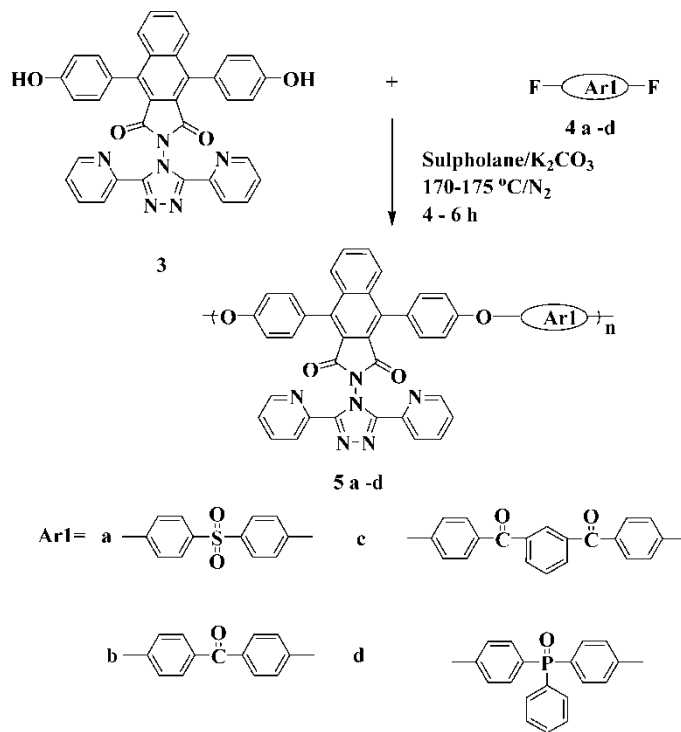
Scheme 1. Synthesis of 3,8-bis(4-hydroxyphenyl)-1,2(naphthalimido)-4(*N*-3,5-dipyridyl-1,2,4-triazole) 3.

agreement agreed with the proposed structure. The $^1\text{H-NMR}$ spectrum of *N*-3,5-dipyridyl-4-amino-1,2,4-triazoles 1 showed a characteristic peak at δ 7.79 ppm for the *N*-amino group, and after imidization this completely disappeared. Novel biphenol 3,8-bis(4-hydroxyphenyl)-1,2(naphthalimido)-4(*N*-3,5-dipyridyl-1,2,4-triazole) 3 was purified by recrystallization from a mixture of NMP/water and DMF/water. When NMP/water was used, the crystals contained a high boiling point solvent that was difficult to remove. From DMF/water, high purity materials were obtained. The yield of faint yellow green color compound 3 was 85%. MALDI-TOF MS and the HPLC showed 100% purity.

Synthesis and Characterization of Poly(arylene ether)s containing 3,5-Dipyridyl-1,2,4-triazole Pendent Group

We previously prepared thermooxidatively stable homo- and copoly(arylene ether)s polymers with high-T_gs from bisphenols containing the heterocyclic benzoylenebenzimidazole and phthaloperinone moieties. The polymerization reactions were conducted in NMP and sulpholane as solvent (12). A series of blue to greenish-yellow fluorescent poly(arylene ether)s with 3,5-diphenyl-1,2,4-triazole pendent group were synthesized with various activated difluoro monomers. The polymerization reactions were conducted in different solvents (DMAC, DMSO, and sulpholane). Polymerization in sulpholane gave the highest inherent viscosities and yields (14).

In the present work, the polymerization reactions with 3 and difluoro monomers 4a-d (Scheme 2) were conducted in a sulpholane solvent. There were no GPC data obtained for these polymers because they contain highly basic groups and the polymers were adsorbed strongly on the GPC column. The poly(arylene ether)s 5a-d possess the pendent 3,5-dipyridyl-1,2,4-triazole moiety linked through a N-N linkage between anhydride and triazole. The thermal properties are listed in Table 1. Typical DSC curves for poly(arylene ether)s with the pendent 3,5-dipyridyl-1,2,4-triazole group are shown in Figure 1. The T_g's of the polymers are in the range between



Scheme 2. Synthesis of poly(arylene ether)s with a 3,5-dipyridyl-1,2,4-triazole pendent group.

244 and 315°C. The highest T_g (315°C) was obtained from monomer 4a. The 5% wt losses obtained for these polymers by TGA are all above 410°C, except polymer 5d with a lower 5% wt loss temperature of 380°C. This can be attributed to the lower molecular weight of polymer 5d. The polymers are light brown in color and soluble

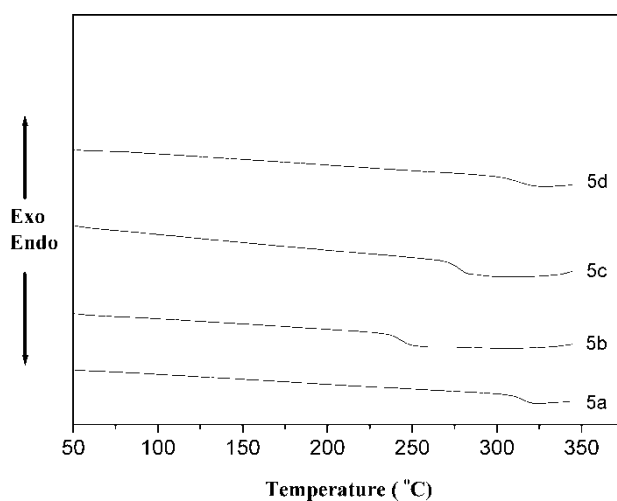


Figure 1. DSC curves for poly(arylene ether)s with a pendent 3,5-dipyridyl-1,2,4-triazole group.

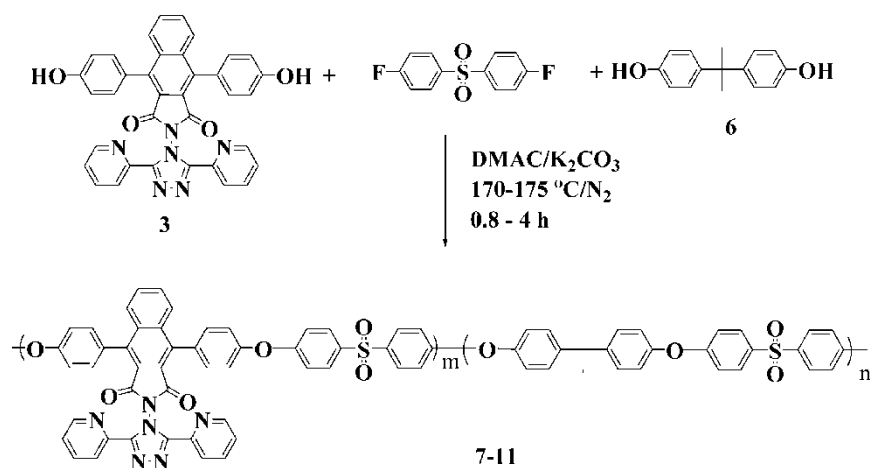
in dipolar aprotic solvents such as DMAC, NMP, DMSO, and DMF. They are also soluble in CHCl_3 except for polymer 5d. These poly(arylene ether)s with a pendent 3,5-dipyridyl-1,2,4-triazole moiety have better solubility than the those previously prepared with 3,5-diphenyl-1,2,4-triazole that do not dissolve in CHCl_3 .

Synthesis and Characterization of Copoly(arylene ether)s with 3,5-Dipyridyl-1,2,4-triazole Pendent Group with BPA as Comonomer

It has been reported (20, 21) that perfluorinated oligo(*p*-phenylene)s and perfluorinated phenylene dendrimers are effective electron-transporting materials for OLEDs because of their low-lying LUMO's and HOMO's. Homo- and copoly(arylene ether)s containing the oxadiazole moiety synthesized with decafluorobiphenyl as a comonomer gave polymers with high T_g 's and excellent thermal stability and showed blue light emission (22).

1,2,4-Triazole derivatives have also been widely applied as electron transport materials in electroluminescent cells. It has been reported that the 1,2,4-triazole group with a phenyl substituent on the nitrogen atom may be bulky enough to prevent formation of exciplexes and charge transfer complexes (23). We synthesized a series of triazole-containing monomers and polymerized with decafluorobiphenyl to obtain polymers with excellent thermal properties with 5% wt loss temperatures above 400°C . These polymers are yellow in color and showed blue to greenish-yellow fluorescence under UV in the solid state as well as in solution and are potentially useful as electron-transporting materials with fluorescent properties (14).

A series of copolymers 7–11 were synthesized from 3 with bis(4-fluorophenyl)sulfone as depicted in Scheme 3. Since BPA is more reactive in the nucleophilic displacement reaction, all the polymerization reactions were finished at shorter reaction times in DMAC solvent using an excess of K_2CO_3 with polymerization times from 0.8 to 4 h. One copolymerization experiment was run with the same solvent, sulfolane, used in the homopolymerization experiment for comparison. The color of the copolymer obtained in



Scheme 3. Synthesis of copoly(arylene ether)s with a 3,5-dipyridyl-1,2,4-triazole pendent group derived from BPA as comonomer.

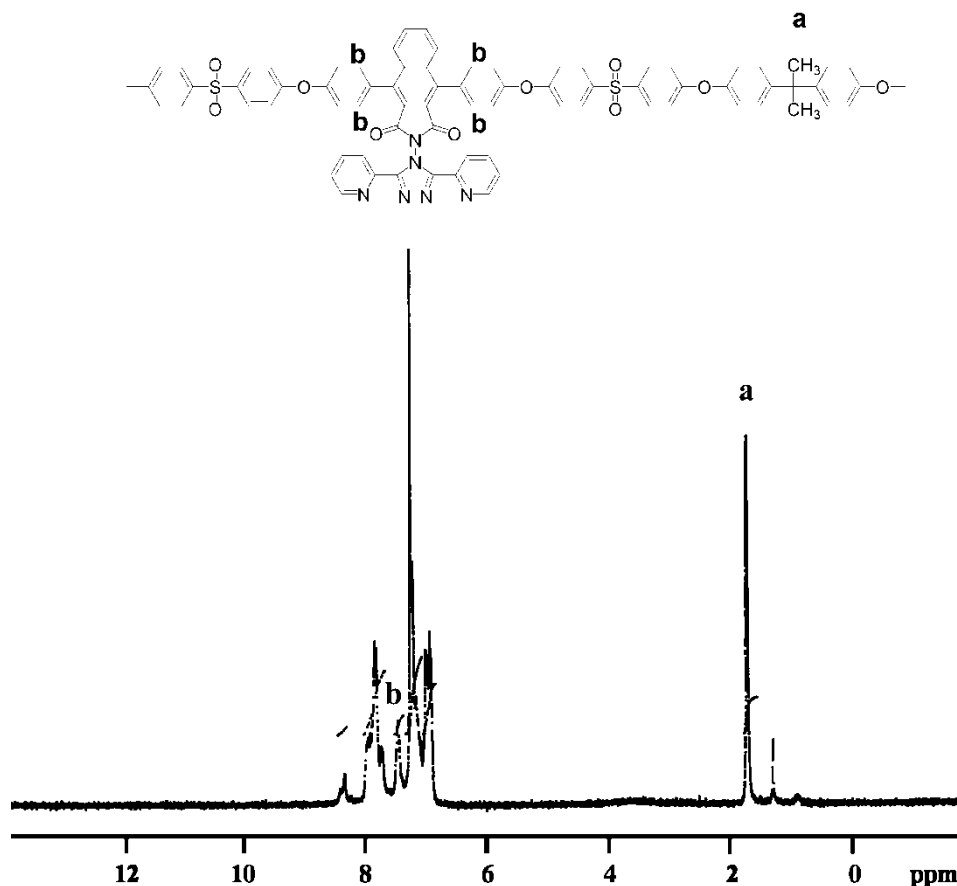


Figure 2. The $^1\text{H-NMR}$ spectrum of copoly(arylene ether) with a feed ratio of 3,8-bis(4-hydroxyphenyl)-1,2(naphthalimido)-4(*N*-3,5-dipyridyl-1,2,4-triazole) 50 mol%.

sulpholane was darker in color than that of the copolymer synthesized in DMAC under the milder conditions, however, the molecular weights of copolymers prepared in various solvents are similar. The polymers were obtained as fibrous materials, and η_{inh} varied from 0.24 to 1.22 dL/g. For the same reason mentioned above, no GPC data were

Table 2

The calculation of the backbone structure of copoly(arylene ether)s with 3,5-dipyridyl-1,2,4 triazole pendent groups by $^1\text{H-NMR}$

Polymer	Feed ratio of monomer 3 mol%	Calculated ratio of monomer 3 mol%
7	0	0
8	30	28
9	50	45
10a	70	68
11	100	100

Table 3
Synthesis and thermal properties of copoly(arylene ether)s with 3,5-dipyridyl-1,2,4 triazole pendent group

Polymer (mol% of 3)	Polymerization T (°C)/time (h)	Solvent	Yield (%)	η_{inh}^a (dl/g)	Tg ^b (°C)	Td(-5wt%) ^c (°C)	Color of polymer
7 (0)	170–180/0.8	DMAC	77.9	1.22	194.8	499.1	White
8 (30)	170–180/2.8	DMAC	69.0	0.38	221.4	435.6	Yellow
9 (50)	170–180/1.0	DMAC	63.2	0.24	239.8	417.9	Yellow
10a (70)	170–180/2.2	DMAC	86.2	0.27	261.3	412.3	Yellow
10b (70)	170–175/4	Sulpholane	74.9	0.24	259.0	438.9	Brown
11 (100)	170–175/4	Sulpholane	74.3	0.66	315.1	419.2	Brown

^aInherent viscosity was measured at a concentration of 0.2 g/dL in CHCl₃ at 25°C.

^bTg was determined by DSC at a heating rate of 20°C/min under nitrogen flow rate 80 mL/min, the values were reported from the second scan.

^cReported for 5% wt loss at a heating rate 20°C/min under nitrogen flow rate 60 mL/min.

available. The copolymers were characterized by $^1\text{H-NMR}$. Figure 2 shows the $^1\text{H-NMR}$ spectrum for the copolymer with 3,8-bis(4-hydroxyphenyl)-1,2(naphthalimido) -4(*N*-3,5-dipyridyl-1,2,4-triazole) 3 with feed ratio of 50 mol%. Peak a and peak b are attributed to the BPA moiety and 3, respectively, as noted. The calculated backbone structure from the $^1\text{H-NMR}$ spectra of the copolymers is listed in Table 2 and these values fit well with the designed structures. The thermal data are depicted in Table 3. The T_g 's varied from 194 to 315°C with T_g increasing with increasing amounts of the 3 moiety as expected. Figure 3 shows the TGA plots for the copolymers. The homopolymer 11 of 3 with bis(4-fluorophenyl)sulfone shows lower 5% wt loss temperature, probably because of the weak binding of N-N linkage between the naphthalimido group and the triazole group. However, all these polymers show excellent thermal stability with 5% wt loss temperatures above 410°C. These copolymers are soluble in dipolar aprotic solvents such as DMF, NMP, DMAC and chloroform. From all the polymers, clear, transparent, and tough films were obtained by casting from CHCl_3 solution.

UV Absorbance and Fluorescent Properties of Poly(arylene ether)s and Copoly(arylene ether)s with 3,5-Dipyridyl-1,2,4-triazole Pendent Group

We have previously reported that the anhydride bisphenol 2 shows absorption in the UV at 360 nm (12). Bisphenol 3, derived from 2 and 3,5-dipyridyl-1,2,4-triazole 1, is faint yellow in color and shows a UV absorption peak at 264 nm and 286 nm with a small shoulder peak at 344 nm in DMF solution. The UV absorption and emission

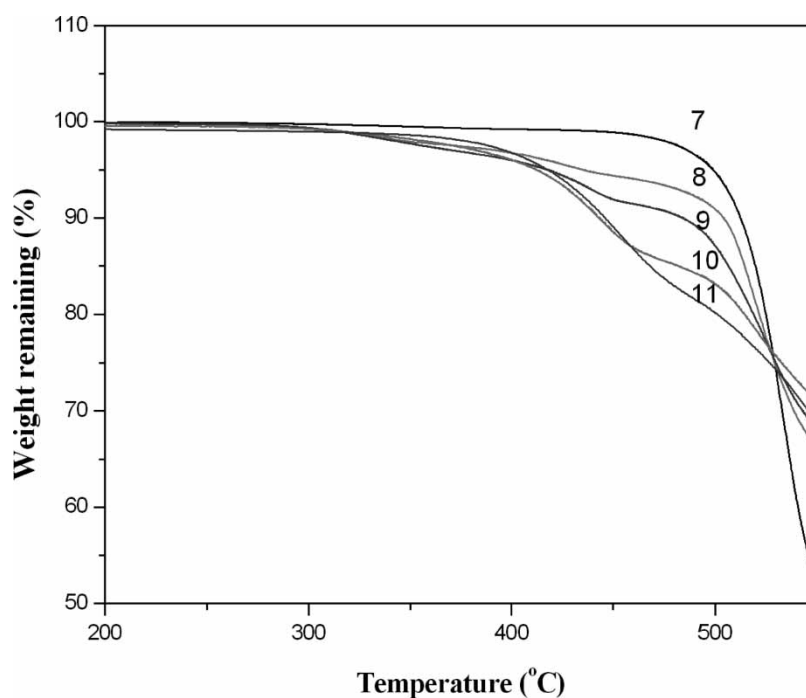


Figure 3. TGA curves for copoly(arylene ether)s with a pendent 3,5-dipyridyl-1,2,4-triazole group.

Table 4
UV absorption and fluorescent properties of poly(arylene ether)s with 3,5-dipyridyl-1,2,4 triazole pendent groups^a

Polymer	λ uv, nm ^b	λ em, nm ^d	Fluorescence under UV light at 365 nm
5a	283,367(s)	439	Blue
5b	264,291,366(s)	438	Blue
5c	264,295,366(s)	436	Blue
5d ^c	266,372(s)	435	Blue
7	No	No	No
8	266,372(s)	433	Blue
9	264,370(s)	433	Blue
10a	264,372(s)	433	Blue
10b	263,370(s)	435	Blue
11	283,367(s)	439	Blue

^aAll measurements were carried out in CHCl₃, s = small shoulder.

^bMaximum absorption wavenumbers.

^cAll measurements were carried out in DMF.

^dEmission wavenumber.

data of polymers and copolymers are tabulated in Table 4. Homopolymers 5a and 5d showed strong absorption peaks at 283 and 266 nm, respectively, with additional absorption at higher wavelengths (367 and 372 nm). Homopoly(ether ketone)s 5b and 5c showed a strong absorption peak at 264 nm. They displayed additional shoulder absorptions at 291–295 and 366 nm. These polymers show strong photoluminescence in solution when excited at their absorption maxima. The maximum emission wavelengths (λ_{em}) for polymers are around 433–439 nm. All these polymers containing a 3,5-dipyridyl-1,2,4-triazole pendent group showed blue fluorescence under UV in solution. Thus, these polymers are potentially useful as electron-transporting materials with fluorescent properties.

Conclusions

A novel biphenol monomer 3,8-bis(4-hydroxyphenyl)-1,2(naphthalimido)-4(*N*-3,5-dipyridyl-1,2,4-triazole) was successfully synthesized by an imidization reaction of an anhydride bisphenol with 4-amino-3,5-dipyridyl-1,2,4 triazole. Polymerization with activated difluoro compounds gave poly(aryl ether)s with a pendent 1,2,4-triazole moiety. These polymers have high glass transition temperatures (T_g 's), from 245 to 315°C. The polymers formed clear, transparent, flexible, and tough films from CHCl₃ solution. High molecular weight copolymers with bis(4-fluorophenyl) sulfone and BPA, together with the novel biphenol as starting materials, were obtained in shorter reaction times. The glass transition temperatures of the copolymers increased with increasing amounts of the novel biphenol molar. All the polymers containing the novel biphenol moiety showed strong blue fluorescence in solution under UV.

Acknowledgements

This research was supported by a Collaborative Research and Development Grant from the Natural Sciences and Research Council of Canada and General Motors, Canada. We thank Ms. Antisar R. Hlil for the preparation of 3,8-bis(4-hydroxyphenyl)-1,2(naphthalic anhydride) 2.

References

1. Tang, C.W. and VanSlyke, S.A. (1987) *Appl. Phys. Lett.*, 51: 913–917.
2. Kraft, A., Grimsdale, A.C., and Holmes, A.B. (1998) *Angew. Chem. Int. Ed.*, 37 (4): 402–428.
3. Brown, A.R., Bradley, D.D.C., Burroughes, J.H., Friend, R.H., Greenham, N.C., Burn, P.L., Holmes, A.B., and Kraft, A. (1992) *Appl. Phys. Lett.*, 61: 2793–2795.
4. Gmeiner, J., Karg, S., Meier, M., Riess, W., Strohrriegel, P., and Schwoerer, M. (1993) *Acta Polym.*, 44: 201–205.
5. Kido, J., Harada, G., and Nagai, K. (1996) *Polymers for Advanced Technologies*, 7 (1): 31–34.
6. Yamamori, A., Adachi, C., Koyama, T., and Taniguchi, Y. (1998) *Appl. Phys. Lett.*, 72: 2147–2149.
7. Sugioka, T. and Hay, A.S. (2001) *J. Polym. Sci., Chem.*, 39: 1040–1050.
8. Ghassemi, H. and Hay, A.S. (1993) *Macromolecules*, 26: 5824–5826.
9. Ghassemi, H. and Hay, A.S. (1994) *Macromolecules*, 27: 4410–4412.
10. Ding, Y. and Hay, A.S. (1999) *J. Polym. Sci., Part A: Polym. Chem.*, 37: 3293–3299.
11. Shaikh, Abbas-Alli, G., and Hay, A.S. (2002) *J. Polym. Sci., Part A: Polym. Chem.*, 40: 496–510.
12. Meng, Y.Z., Abu-Yousef, I.A., Hlil, A.R., and Hay, A.S. (2000) *Macromolecules*, 33: 9185–9191.
13. Meng, Y.Z., Hill, A.R., and Hay, A.S. (2001) *Polym. Adv. Technol.*, 12: 206–214.
14. Shaikh, Abbas-Alli, G., Hlil, A.R., Shaikh, P.A., and Hay, A.S. (2002) *Macromolecules*, 35: 8728–8737.
15. Strukelj, M. and Hay, A.S. (1991) *Macromolecules*, 24: 6870–6871.
16. Strukelj, M. and Hay, A.S. (1992) *Macromolecules*, 25: 4721–4729.
17. Bentiss, F., Lagrenee, M., Traisnel, M., Mernari, B., and Elattari, H.J. (1999) *Heterocycl. Chem.*, 36: 149–152.
18. Ghosh, M.K. and Mittal, K.L., Eds. (1996) *Polyimides: Fundamentals and Applications*. In *Plast. Eng. (N.Y.)*; Marcel Dekker: New York; Vol. 36.
19. Mackinnon, S.M. and Wang, Z.Y.J. (2000) *Polym. Sci., Part A: Polym. Chem.*, 38: 3467–3475.
20. Sakamoto, Y., Suzuki, T., Miura, A., Fujikawa, H., Tokito, S., and Taga, Y.J. (2000) *Am. Chem. Soc.*, 122: 1832–1833.
21. Heidenhain, S.B., Sakamoto, Y., Suzuki, T., Miura, A., Fujikawa, H., Mori, T., Tokito, S., and Taga, Y.J. (2000) *Am. Chem. Soc.*, 122: 10240–10241.
22. Lu, J., Miyatake, K., Hlil, A.R., and Hay, A.S. (2001) *Macromolecules*, 34: 5860–5867.
23. Kido, J., Ohtaki, C., Hongawa, K., Okuyama, K., and Nagai, K. (1993) *Jpn. J. Appl. Phys., Part 2*, 32: L917–L920.