Poly(arylene ether)s Containing 1,2,4-Triazole and Phthalimide or Naphthalimide Moieties Joined by a N−N Linkage

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ABSTRACT: The synthesis and characterization of new monomers and polymers containing the 1,2,4-triazole group are described. A model reaction of 4-*N*-amino-3,5-diphenyltriazole with phthalic and naphthalic anhydride demonstrated the preparation of the 1,2,4-triazole-imide compounds containing a N−N linkage. From 4-amino-3,5-bis(4-hydroxyphenyl)triazole four new bisphenols with pendent phthalimide or naphthalimide moieties linked through a N−N linkage were prepared in a one-step reaction in high yield. Poly(aryl ether)s were synthesized from these bisphenols, or their carbamate derivatives, by reaction with various activated arylene difluorides. The reactions were carried out in DMSO in the presence of potassium carbonate to yield high molecular weight, amorphous, and thermally stable polymers with pendent imide moieties joined by a N−N linkage. A new bisphenol with a pendent 3,5-diphenyl-1,2,4-triazole was prepared by an imidization reaction of an anhydride bisphenol with 4-amino-3,5-diphenyltriazole. Polymerization with activated difluoro compounds gave poly(aryl ether)s with a pendent 1,2,4-triazole moiety. These polymers had high T_g's, from 222 to 283 °C. Copolymers containing the 1,2,4-triazole in the polymer backbone as well as pendent were also prepared. Using decafluorobiphenyl as coreactant, extremely high molecular weight polymers were obtained at lower polymerization temperature, 90−100 °C, in a shorter reaction time. The polymers formed clear, transparent, flexible, and tough films from DMF solution. Many of the polymers showed strong blue to greenish-yellow fluorescence from 428 to 510 nm in solution and in the solid state under UV, depending upon the monomer composition of the polymer.

Introduction

Poly(arylene ether)s are an important class of engineering thermoplastics and possess useful physical properties such as high modulus, toughness, high thermal, thermooxidative stability, and chemical resistance.[1−3] These polymers have become increasingly important and are used in a variety of applications such as coatings, adhesives, composites, and molded components.[1,2,4]

Earlier work in this laboratory demonstrated the synthesis of high molecular weight poly(ether imide)s and copoly(ether imide)s having a N−N linkage between the imide units in the polymer backbone. The polymers are soluble in organic solvents and have extremely high T_g's and exceptional thermal stability.[5,6] A series of poly(thioether−naphthalimide)s containing the N−N linkage in the polymer backbone that incorporate both a flexible thioether linkage and a rigid naphthalic anhydride moiety have also been prepared.[7] The polymers had high T_g's and excellent thermal stability and were also fluorescent. We have also recently described a new class of poly(arylene ether)s with a N−N linkage obtained by reaction between an anhydride and a bisphenol containing a pendent *N*-aminophthalimide moiety.[8]

In the present investigation we report the synthesis of a new class of bisphenols containing the 1,2,4-triazole moiety with pendent phthalimide and naphthalimide groups attached through a N−N linkage between anhydride and an *N*-amino-1,2,4-triazole. A new bisphenol with a pendent 3,5-diphenyl-1,2,4-triazole group was prepared from an anhydride bisphenol previously prepared.[9−11] A series of high molecular weight poly(arylene ether-1,2,4-triazole)s with pendent phthalimide moieties were obtained. From the monomer with pendent 3,5-diphenyl-1,2,4-triazole groups, a series of blue to greenish-yellow fluorescent, amorphous, thermally stable polymers were prepared.

Experimental Section

Materials. Benzonitrile, *p*-cyanophenol, hydrazine hydrate, hydrazine dihydrochloride, ethylene glycol, bis(4-fluorophenyl)sulfone, 4,4′-difluorobenzophenone, 4,4′-difluorobenzil, decafluorobiphenyl, zinc diacetate, phthalic anhydride, *tert*-butylphthalic anhydride, tetraphenylphthalic anhydride (Aldrich), bis(4-fluorophenyl)phenylphosphine oxide (Triton, Systems Inc. Technology innovators, Cambridge, MA), and *n*-propyl isocyanate (Across) were used as received. The 1,8-naphthalic anhydride (Aldrich) was recrystallized from acetic anhydride. The reagent grade solvents such as *N*-methyl-2-pyrrolidinone (NMP), *N,N*-dimethylacetamide (DMAC), *N,N*-dimethylformamide (DMF), tetramethylsulfolane, *N*-cyclohexyl-2-pyrrolidinone (CHP), *N,N*-dimethylpropyleneurea (DMPU), dimethyl sulfoxide, potassium carbonate, cesium carbonate, magnesium hydroxide, and triethylamine were used as received. 3,8-Bis(4-hydroxyphenyl)-1,2-naphthalic anhydride,[8] 1,3-bis(4-fluorobenzoyl)benzene,[7] 3,5-diphenyl-4-amino-1,2,4-triazole, and 3,5-bis(4-hydroxyphenyl-4-amino-1,2,4-triazole[12,13] were synthesized as per the literature procedures.

Characterization. ^{1}H and ^{13}C NMR spectra were recorded on a Varian Mercury 300 spectrometer using $CDCl_3$ or 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

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apparatus. UV−vis spectra were recorded on a Hewlett-Packard 8452A diode array spectrophotometer. Fluorescent spectra were performed on a Fluoro Max-2 spectrophotometer. Monitoring the progress of the reaction and 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 Seiko 220 DSC at a heating rate of 20 °C/min. The T_g was taken from the midpoint of the change in slope of the baseline, while melting temperature were taken from the onset of the change in slope to a minimum of the endotherm of peak. The weight loss data were obtained from a Seiko 220 TGA/DTA instrument at a heating rate of 20 °C/min in 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.

3,5-Diphenyl-4-(*N*-phthalimide)-1,2,4-triazole (4). A 25 mL three-necked round-bottom flask was equipped with a nitrogen inlet, a magnetic stir bar, a Dean−Stark trap, and a reflux condenser. The flask was charged with **1** (0.5 g, 2.11 mmol), **2** (0.78 g, 5.27 mmol), CHP (8 mL), and toluene (8 mL) and 2 drops of isoquinoline as catalyst. The resulting reaction mixture was heated to 120 °C under N_2 and kept at 120 °C for 12 h to azeotrope off the resulting water with toluene. The toluene was then removed, and the reaction mixture was heated to 200 °C and maintained at this temperature for 12 h. The reaction mixture became dark brown. The reaction mixture was analyzed by HPLC and showed only one peak. The cooled reaction mixture was poured slowly into 150 mL of water with constant stirring, and a faint brown solid separated out. The product was collected by filtration and washed with water (50 × 3 mL) and then dried in a vacuum oven at 80 °C for 12 h. The product **4** was obtained in 86% yield. ^{1}H NMR ($CDCl_3$): δ (ppm) 7.25−7.42 (m, 6H), 7.58−7.63 (m, 4H), 7.70−7.90 (m, 4H). ^{13}C NMR ($CDCl_3$): δ (ppm) 125.50, 128.50, 129, 129.50, 131.50, 135.80, 155.50, 163.20. Mp: 182 °C. MALDI−TOF MS: 366.6 (M^+). HPLC (r.t.; purity): 2.23 (100%).

3,5-Diphenyl-4-(*N*-1,8-naphthalimide)-1,2,4-triazole (5). A 25 mL three-necked round-bottom flask was equipped with a nitrogen inlet, a magnetic stir bar, a Dean−Stark trap, and a reflux condenser. The flask was charged with **1** (0.3 g, 1.26 mmol), **3** (0.287 g, 1.45 mmol), zinc diacetate (0.03 g, 0.16 mmol), NMP (8 mL), and toluene (8 mL). The reaction mixture was heated to 150 °C under nitrogen and refluxed for 5 h to distill off water azeotropically with toluene. Then toluene was removed, and the temperature was raised to 180 °C and maintained there for 20 h. During this period the reaction mixture became dark brown. The TLC analysis indicated the formation of product and disappearance of **1**. The cold reaction mixture was poured into 150 mL of water with constant stirring. The brown product obtained was collected by filtration and washed three times with water (50 × 3 mL) to remove NMP. The product was dried in a vacuum oven and recrystallized from methanol/chloroform (15 + 5 mL, 3:1) solvent. The yield of **5** obtained after recrystallization was 0.13 g (25%). ^{1}H NMR ($CDCl_3$): δ (ppm) 7.24−7.28 (m, 6H), 7.60−7.63 (m, 4H), 7.69−7.74 (t, J = 15.82 Hz, 2H), 8.22−8.25 (d, J = 8.21 Hz, 2H), 8.52−8.55 (d, J = 8.21 Hz, 2H). ^{13}C NMR ($CDCl_3$): δ (ppm) 121.01, 125.76, 127.57, 128.43, 129.13, 130.76, 132.17, 133.49, 136.24, 155.09, 161.69. Mp: >300 °C. MALDI−TOF MS: 416.13 (M^+). HPLC (r.t.; purity): 2.13 (100%).

3,5-Bis(4-hydroxyphenyl)-4-(*N*-phthalimido)1,2,4-triazole (9). A 100 mL three-necked round-bottom flask equipped with a magnetic stir bar, a cold water condenser, and a nitrogen inlet was charged with **6** (4 g, 15 mmol), **2** (2.76 g, 18.6 mmol), and zinc diacetate (0.35 g, 1.92 mmol) and 40 mL of NMP. The resulting reaction mixture was heated gradually to 180 °C with stirring under nitrogen and continued at this temperature for 12 h. On heating to 180 °C, the color of the reaction mixture turned to faint brown and later changed to dark brown. After 12 h of reaction HPLC indicated the absence of **6**. The cold reaction mixture was slowly poured into ice cold water (500 mL) with vigorous stirring. The faint brown compound was separated by filtration. It was dried in a vacuum oven for 12 h. It was dissolved in boiling ethanol (75 mL), and the dark brown solution obtained was treated with charcoal, boiled for a few minutes, and filtered. The solution color was now faint brown. Distilled water (160 mL) was added until slightly turbid, and on heating a clear solution was obtained. On cooling to room temperature a white crystalline compound **9** was obtained; 5.30 g (90%). ^{1}H NMR (DMSO-d_6): δ (ppm) 6.79−6.82 (d, J = 7.62 Hz, 4H), 7.35−7.37 (d, J = 7.62 Hz, 4H), 7.96−8.05 (m, 4H),10.08 (s, 2H). ^{13}C NMR (DMSO-d_6): δ (ppm) 115.67, 116.88, 126, 128.62, 129.67, 137.30, 154.61, 160.49, 163.97. Mp (DTA): 330 °C. MALDI−TOF MS: 398.5 (M^+). HPLC (r.t.; purity): 2.08 (100%).

Synthesis of 10. The reaction was carried out by taking **6** (4.00 g, 14.9 mmol), **7** (3.80 g, 18.6 mmol), and zinc diacetate (0.352 g, 1.96 mmol) in 50 mL of NMP and heated for 12 h at 180 °C under N_2. It was recrystallized from ethanol/water (1:1) solvent to afford **10**. Yield: 85%. ^{1}H NMR (DMSO-d_6): δ (ppm) 1.30 (s, 9H), 6.79−6.82 (d, J = 7.62 Hz, 4H), 7.33−7.36 (d, J = 8.79 Hz, 4H), 7.95−8.04 (m, 3H), 10.07 (s, 2H). ^{13}C NMR (DMSO-d_6): δ (ppm) 31.19, 36.5, 115.72, 116.88, 122.86, 125.86, 125.89, 126.03, 128.83, 129.68, 134.32, 154.73, 160.47, 161.20, 163.86, 164.05. Mp (DTA): 362 °C. MALDI−TOF MS: 461.23 (M^-Li^+). HPLC (r.t.; purity): 2.20 (100%).

Synthesis of 11. The reaction was conducted by taking **6** (2.00 g, 7.5 mmol), **8** (4.21 g, 9.31 mmol), and zinc diacetate (0.176 g, 0.96 mmol) in 30 mL of NMP and heated for 12 h at 180 °C under N_2. The product was isolated by precipitating in 1 L of distilled water, and a white powder was obtained. The product was washed with chloroform (100 × 2 mL) (to remove excess of **8** from the product because it is soluble in chloroform). The analysis by HPLC showed that it was 100% pure. The product was crystallized from ethanol (150 mL) to afford **11**. Yield: 89%. ^{1}H NMR (DMSO-d_6): δ (ppm) 6.83−6.87 (m, 8H), 6.89−6.92 (d, J = 8.79 Hz, 4H), 7.02−7.05 (m, 4H), 7.14−7.16 (m, 8H), 7.32−7. 35 (d, J = 8.79 Hz, 4H), 10.15−10.25 (bs, 2H). ^{13}C NMR (DMSO-d_6): δ (ppm) 115.78, 116.97, 125.11, 127.25, 127.54, 128.12, 128.23, 129.78, 130.16, 130.90, 135.32, 137.85, 141.02, 149.97, 154.83, 160.48, 162.73. Mp (DTA): 386 °C. MALDI−TOF MS: 703.4 (M^-Li^+). HPLC (r.t.; purity): 2.18 (100%).

4-(*N*-Tetraphenylphthalimido)-3,5-bis(*n*-propylcarbamoyl)phenyl-1,2,4-triazole (12). To a 100 mL round-bottomed flask fitted with a magnetic stirrer, a reflux condenser, and a drying tube were added **11** (2 g, 2.84 mmol), *n*-propyl isocyanate (5.33 mL, 5.69 mmol), triethylamine (0.15 mL), and DMF (50 mL). The reaction mixture was stirred at 110 °C for 24 h under N_2. After cooling, the mixture was poured into 500 mL of cold water with vigorous stirring. A white compound separated from water and was isolated by filtration. It was crystallized from ethanol/water (1:1) (60 + 60 mL) to obtain white crystals of **12** to afford 1.98 g (80%). Mp: 224 °C (by DTA). ^{1}H NMR ($CDCl_3$): δ (ppm) 0.93−1.01 (t, J = 14.07 Hz, 6H), 1.61−1.63 (d, J = 6.45 Hz, 4H), 3.25 (bs, 4H), 5.30 (bs, 2H), 6.76−6.88 (m, 8H), 7.03−7.17 (d, J = 8 Hz, 4H), 7.19−7.25 (m, 12H), 7.62−7.65 (d, J = 7.62 Hz, 4H). ^{13}C NMR ($CDCl_3$): δ (ppm) 11.54, 23.29, 43.28, 121.82, 122.35, 125.22, 126.82, 127.32, 127.75, 128.02, 129.91, 130.05, 130.71, 134.77, 137.62, 141.33, 149.90, 153.46, 154.29, 162.44. MALDI−TOF MS: 872.47 (M^+). HPLC (r.t.; purity): 2.18 (100%).

Synthesis of 13. The reaction was carried out by taking **6** (2.00 g, 7.45 mmol), **3** (1.77 g, 8.94 mmol), and zinc diacetate (0.176 g, 0.96 mmol) in 25 mL of NMP and heated for 24 h at 180 °C under N_2. It was recrystallized from ethanol/water (1:1) solvent to afford **13** with a faint yellow color. Yield: 75%. ^{1}H NMR (DMSO-d_6): δ (ppm) 6.70−6.73 (d, J = 8.79 Hz, 4H), 7.33−7.36 (d, J = 8.79 Hz, 4H), 7.91−7.96 (t, J = 15.82 Hz, 2H), 8.59−8.64 (t, J = 15.24 Hz, 4H), 9.99 (s, 2H). ^{13}C NMR (DMSO-d_6): δ (ppm) 116.29, 116.71, 120.33, 127.86, 128.58, 129.54, 132.16, 137.79, 154.13, 160.18, 161.95. Mp: (DTA): 364 °C. MALDI−TOF MS: 448.5 (M^+). HPLC (r.t.; purity): 2.17 (100%).

Synthesis of 14. The compound was prepared by following the procedure adopted for **12**, except the reaction was conducted at 60 °C for 24 h in DMF under N_2. The compound was purified by recrystallization by dissolving in dichloromethane and adding hexane until the solution was turbid. The yield of compound **14** obtained was 85%. Mp: 212 (by DTA). ^{1}H NMR (CDCl$_3$): δ (ppm) 0.81−0.86 (t, J = 14.07 Hz, 6H), 1.45−1.47 (d, J = 7.03 Hz, 4H), 3.07 (bs, 4H), 5.04 (s, 2H), 7.01−7.03 (d, J = 8.21 Hz, 4H), 7.58−7.61 (d, J = 7.62 Hz, 4H), 7.70−7.75 (d, J = 14.07 Hz, 2H), 8.23−8.26 (d, J = 7.61 Hz, 2H), 8.52−8.54 (d, J = 6.45 Hz, 2H). ^{13}C NMR (CDCl$_3$): δ (ppm) 11.43, 23.19, 43.14, 120.96, 122.20, 127.60, 128.41, 129.67, 132.28, 133.71, 136.47, 153.20, 154.08, 154.83, 161.80. MALDI−TOF MS: 624.75(M$^-$Li$^+$). HPLC (r.t.; purity): 2.08 (100%).

Synthesis of 16. The compound was prepared by the reaction of **15** with 10 mol % excess of **1** in NMP and heating the reaction mixture for 20 h at 180 °C. The product was recrystallized from DMF/water (; 1) (100 +100 mL). The yield of the product **16** was 85% and with faint yellow color. ^{1}H NMR (DMSO-d_6): δ (ppm) 6.88−6.91 (d, J = 8.21 Hz, 4H), 7.14−7.16 (d, J = 7.62 Hz, 4H), 7.50−7.56 (m, 10H), 7.75−7.84 (m, 4H), 10.07 (s, 2H). ^{13}C NMR (DMSO-d_6): δ (ppm) 115.86, 120.23, 124.22, 125.13, 127.93, 129.44, 130.18, 131.06, 131.87, 136.19, 142.66, 154.54, 158.66, 162.57, 162.98. Mp: 336 °C (DTA). MALDI−TOF MS: 600.93 (M$^+$). HPLC (r.t.; purity): 2.11 (100%).

General Procedure for the Synthesis of Poly(arylene ether-1,2,4-triazole)s. The synthesis of most of the poly(arylene ether-1,2,4-triazole)s was carried out in DMSO. The polymerization was conducted initially at 135−40 °C for 2−2.5 h to remove the water with toluene using a Dean−Stark trap and then at 170−175 °C to effect the polymerization reaction. Wherever there is change in polymerization conditions, such as final polymerization temperature or use of different solvent, it is noted. A typical procedure is as follows. A 25 mL three-necked round-bottomed flask 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 **9** (0.24 g, 0.6 mmol), bis(4-fluorophenyl)sulfone (0.15 g, 0.6 mmol), K$_2$CO$_3$ (0.165 g), DMSO (4.5 mL), and toluene (5.5 mL). The reaction mixture was heated to 135 °C for 2 h to remove the water generated in the reaction with toluene. The reaction mixture temperature was raised to 175 °C, and the toluene was removed. The reaction mixture was kept at low reflux until a viscous solution was obtained. After cooling, the mixture was diluted with 3 mL of DMSO and poured into 150 mL of methanol containing 5 vol % of hydrochloric acid to precipitate out polymer **17a**. The polymer was collected by filtration, washed with hot water (100 mL) and again with methanol, and dried in a vacuum oven at 80 °C for 12 h; yield 0.34 g (95%).

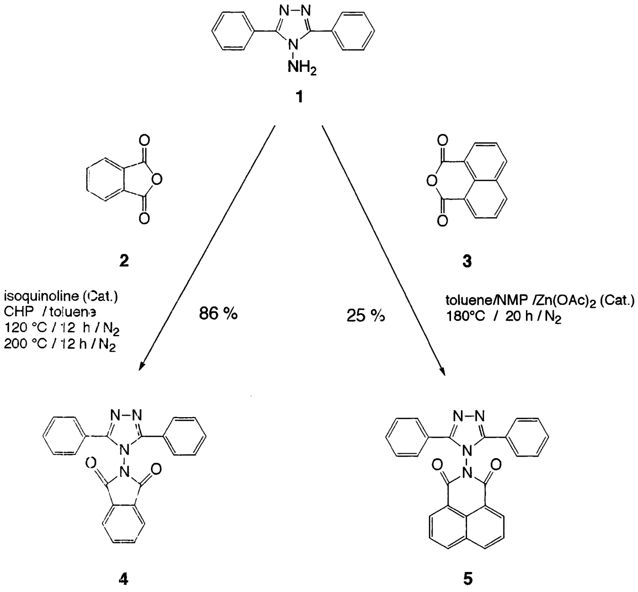
General Procedure for the Synthesis of Poly(arylene ether-1,2,4-triazole)s from Biscarbamates 12 and 14. A typical example is as follows. A 25 mL three-necked round-bottom flask equipped with nitrogen inlet, a magnetic stirrer, and a condenser was flushed with nitrogen and charged with biscarbamate **12** (0.261 g, 0.3 mmol), 4,4′-difluorobenzophenone (0.65 g, 0.3 mmol), K$_2$CO$_3$ (0.096 g), and DMSO (4 mL). The reaction mixture was heated to 165 °C under nitrogen. After 4 h, the reaction mixture became viscous. The cooled reaction mixture was diluted with DMSO (3 mL) and poured into 150 mL of methanol. The polymer was isolated by filtration, washed with hot water, and again washed with 75 mL of methanol. The polymer was dried in a vacuum oven at 80 °C for 12 h. Yield: 0.13 g (51%).

General Procedure for Polymerization with Decafluorobiphenyl. The polymerization reactions were conducted as described above. The reaction temperatures were maintained in the temperature between 90 and 100 °C, and in some cases the final temperature was 120 °C. The polymer was isolated and purified as described above.

Results and Discussion

Synthesis of Model Compounds 4 and 5. The reaction of aliphatic and aromatic amines/diamines with carboxylic acid anhydrides has been extensively studied for the preparation of polyamides and polyimides.[14] Poly(aryl ether)s from bisphenols containing the imidoaryl linkage[9,10] and poly(ether imide)s containing a N−N linkage connecting the imide groups[7] have been synthesized. In this work, our objective was to carry out the imidization reaction of the N-amino group attached to a 1,2,4-triazole ring with acid anhydrides to form 1,2,4-triazole-imide joined through a N−N linkage. The 3,5-disubstituted-4-amino-1,2,4-triazoles, potentially good corrosion inhibitors, were prepared from aromatic nitriles and hydrazine hydrochloride in excellent yield by a one-step reaction as described in the literature.[12,13] Our approach was to carry out the imidization reaction with acid anhydrides in order to study the reactivity of the N-amino group in the 1,2,4-triazole. We initially carried out model reactions between 3,5-diphenyl-4-amino-1,2,4-triazole (**1**) prepared from benzonitrile with hydrazine dihydrochloride in one-step by the reported procedure.[12,13] Our efforts were concentrated on the reaction of **1** with **2** by changing various reaction parameters and initially gave incomplete reactions. When the reaction was conducted for longer times at higher temperatures there was complete imidization forming the N−N linkage between 1,2,4-triazole and anhydride (**4**, Scheme 1, Table 1). This is evident from ^{1}H NMR. Compound **1** showed a characteristic peak at 6.30 δ ppm for the N-amino group, and after imidization it completely disappeared. The reaction of **1** with **2** was slow because of the lower basicity of the amine attached to 1,2,4-triazole compared to aliphatic and aromatic amines. The reaction of **1** with **3** to prepare **5** under the same experimental conditions was unsuccessful.

Scheme 1. Synthesis of 4-(*N*-Phthalimido)-3,5-diphenyl-1,2,4-triazole (4) and 4-(*N*-1,8-Naphthalimido)-3,5-diphenyl-1,2,4-triazole (5)

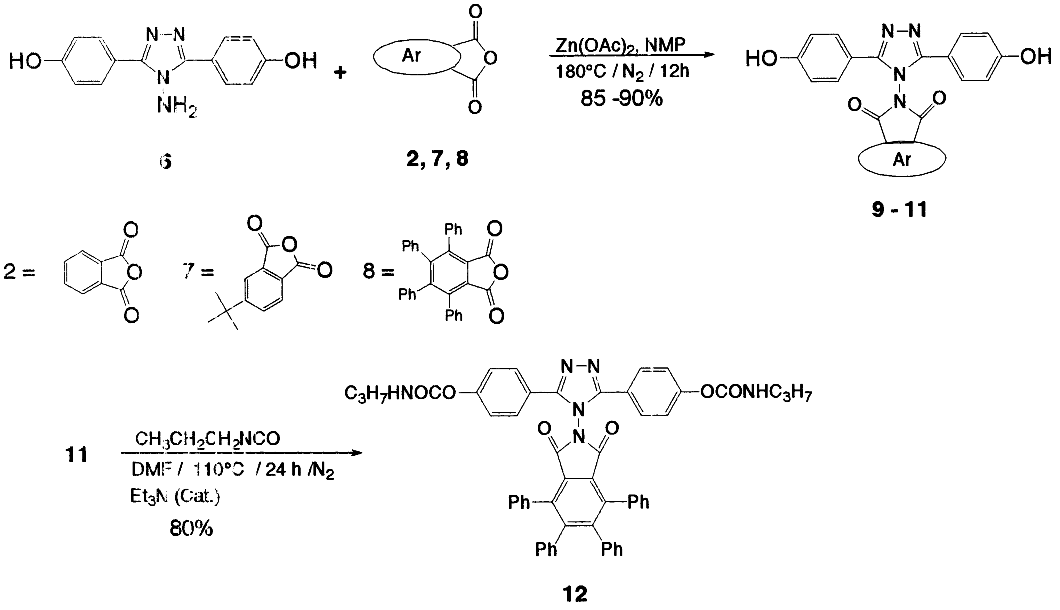


Recently, it has been reported that the direct imidization reaction of aromatic amines with 1,4,5,8-naphthalenetetracarboxylic dianhydride and 3,4,9,10-perylenetetracarboxylic anhydride can be conducted using zinc acetate as a catalyst.[15] The reaction was complete in a shorter reaction time, and good yields of the corresponding imides were obtained. We carried out the reaction of phthalic anhydride **1** with **3** using zinc acetate as imidization catalyst, and the expected product **5** was obtained in low yield (Scheme 1, Table 1). The product was completely characterized.

Table 1. Synthesis and Properties of 1,2,4-Triazole-Imide Model Compounds 5 and 6, Bisphenols 9−11, 13, and 16, and Biscarbamates 12 and 14

compd	yield, %	mp, °C	appearance	solvent	T, °C (t, h)	purification procedure
4	86	182	pale brown	CHP/toluene	120 (12) 200 (12)	from the reaction mixture
5	25	>300	white	NMP/toluene	180 (20)	recrystallization (MeOH/CHCl$_3$)
9	90	330	white	NMP	180 (12)	(EtOH/H$_2$O)
10	85	362	white	NMP	180 (12)	(EtOH/H$_2$O)
11	89	386	white	NMP	180 (12)	(EtOH)
12	80	224	white	DMF	110 (24)	(EtOH/H$_2$O)
13	75	364	faint yellow	NMP	180 (24)	(EtOH/H$_2$O)
14	85	212	white	DMF	60 (24)	(CH$_2$Cl$_2$/hexane)
16	85	336	faint yellow	NMP	180 (20)	(DMF/H$_2$O)

Scheme 2. Synthesis of 4-(*N*-Phthalimido)-3,5-bis(4-hydroxyphenyl)-1,2,4-triazole (9−11) and Biscarbamate of 11



Bisphenol **6** containing the *N*-amino-1,2,4-triazole moiety also reacted with anhydrides to give new bisphenols **9**−**11** with pendent phthalimide, naphthalimide, and 3,5-diphenyl-1,2,4-triazole moieties attached by a N−N linkage for the preparation of poly(arylene ether 1,2,4-triazole)s.

1,2,4-Triazole-Imide Bisphenols (9−11 13, and 16) and Biscarbamates (12 and 14). The compound 3,5-bis(4-hydroxyphenyl)-4-amino-1,2,4-triazole (**6**) was obtained in good yield in a single-step reaction from *p*-cyanophenol and hydrazine dihydrochloride by the reported procedure.[12,13] The reaction of anhydrides **2, 7,** and **8**, with **6** was carried out in NMP at 180 °C by using 20−25 mol % excess of **2, 7,** and **8** based on **6** and 7 mol % of zinc diacetate as an imidization catalyst (Scheme 2). The reactions were followed by HPLC to completion as indicated by the absence of **6** in the reaction mixture. The products were isolated by pouring the reaction mixtures into distilled water, and the resulting solids were purified by recrystallization from a suitable solvent or combination of solvents. The white crystalline compounds **9, 10,** and **11** were obtained in good yields (85−90%). These compounds are high melting with melting points above 300 °C (Scheme 2, Table 1).

Similarly, the reaction of **6** with **3** was carried out using 25 mol % excess of **3** and zinc diacetate as catalyst. As expected, the reaction of **6** with **3** was slow, and hence the reaction was conducted for 24 h in NMP at 180 °C. The yield of the product obtained was 75%. Compound **12** has a melting point of 364 °C and a faint yellow color (Scheme 3, Table 1).

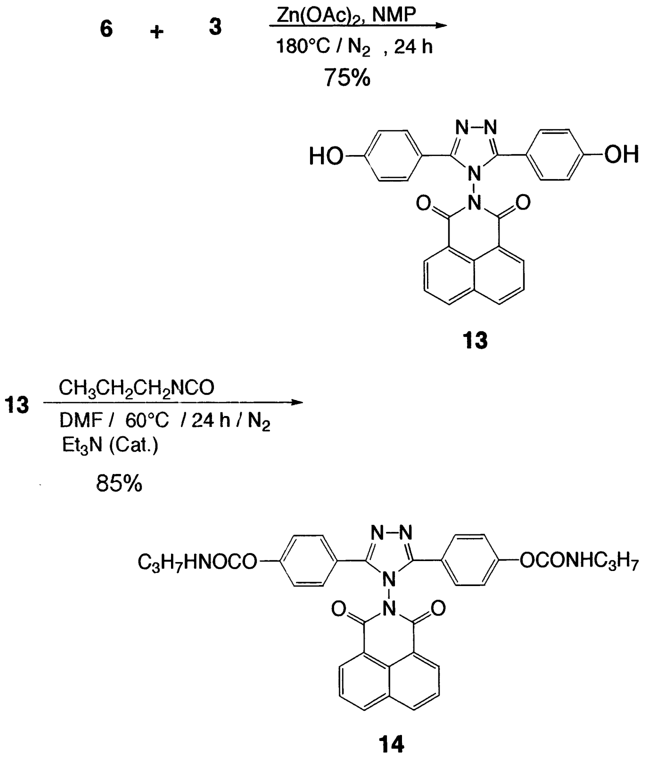
In another effort, a new bisphenol **16**, prepared from a previously synthesized anhydride bisphenol **15**,[8] was condensed with **1**. A 15 mol % excess of **1** was used, and the reaction was conducted for 20 h in NMP. Monomer **16** was purified by recrystallization from DMF/water. The yield of compound **16** was 85%, and it has a faint yellow color (Scheme 4, Table 1).

Compounds **11** and **13** were further reacted with excess of *n*-isopropyl isocyanate in DMF at 110 and 60 °C for 24 h under nitrogen to yield the carbamates **12** and **14**. Compound **12** was purified by recrystallization from ethanol/water (Scheme 2, Table 1). The recrystallization of **14** by the same solvent led to partial conversion to bisphenol **13**. It was purified by dissolving in methylene chloride and adding hexane (Scheme 3, Table 1). The use of biscarbamates **12** and **14** will be discussed in detail in the polymerization section.

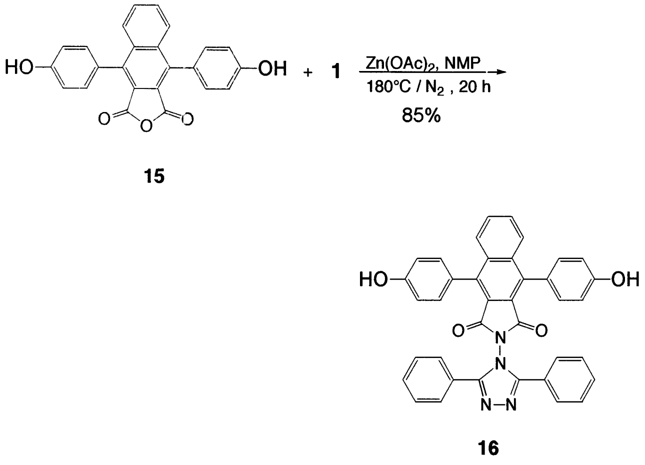
All the compounds were completely characterized, and their spectroscopic data were in complete agreement with their structures. The structures were confirmed from their MALDI−TOF MS data, the purity was checked by HPLC, and all the monomers were 100% pure.

The energy-minimized molecular models of compound **4, 11,** and **16** are shown in Figure 1 (Cache Mopac 2000, Fujitsu Ltd.). The N−N dihedral angles for the pendent imide moieties in **4** and **11** are calculated to be 92.5° and 88.63°, respectively, and 76.6° in **16.** Hence, it is expected that the poly(aryl ether 1,2,4-triazole)s derived from them would be amorphous and thermally stable with high T_g's. Since the structures are rigid and highly unsymmetrical, chain packing would be difficult. Crystal

Scheme 3. Synthesis of 4-(*N*-1,8-Naphthalimido)-3,5-bis(4-hydroxyphenyl)-1,2,4-triazole (13) and Its Biscarbamate 14



Scheme 4. Synthesis of 3,8-Bis(4-hydroxyphenyl)-1,2(naphthalimido)-4(*N*-3,5-diphenyl-1,2,4-triazole) (16)



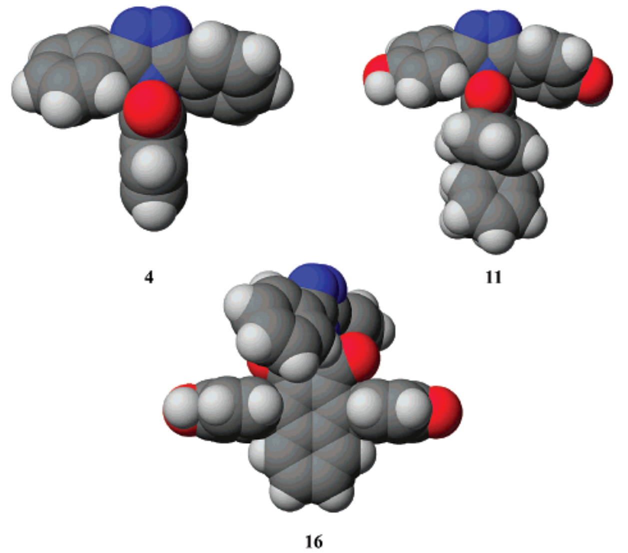


Figure 1. Energy-minimized structures of **4**, **11**, and **16**.

structures have been obtained on a related compound, 3,3′-dimethyl-5,5′-diphenyl-4,4′-bi-4*H*-1,2,4-triazole.[16] The N−N dihedral angle in this molecule was 73°, and MOPAC calculations for this structure give a dihedral angle of 79.5°.

Synthesis and Properties of Poly(aryl ether 1,2,4-triazole)s from 9 and 10. The conventional aromatic nucleophilic substitution polymerization technique was adopted for the synthesis of 1,2,4-triazole containing poly(arylene ether)s with phthalimide pendent moieties from **9** and various activated difluoro compounds **a**−**e** (Scheme 5). The polycondensation was conducted in DMSO by reacting bisphenol and difluoro compounds together in the presence of anhydrous K_2CO_3 as base. The high melting bisphenol **9** dissolved in DMSO on heating and converted to its potassium salt. Initially, the polymerization was carried out for 2 h at 130 °C to remove the water azeotropically with toluene using a Dean−Stark trap. Afterward, the temperature was raised to 170−175 °C for difluoro compounds **a**−**d** to effect the polycondensation. In the case of **e** the polymerization temperature was 150 °C. In the literature high molecular weight poly(aryl ether benzil)s synthesized from difluoro compound **e** have been prepared at 150 °C, and it was demonstrated that the use of higher temperature leads to lower molecular weight polymers due to chain cleavage reactions.[17]

The final polymerization time was varied from 2 to 6 h to a point where a large increase in the solution viscosity of the reaction mixture occurred. The results are summarized in Table 2. The η_{inh} of polymers **17a**−**e** varied from 0.28 to 0.88 dL/g with yields between 83 and 97% depending upon the difluoro monomer. The lowest viscosity polymer was obtained with **e** even though the polymerization was conducted at a lower temperature (150 °C), presumably due to side reactions during polymerization. All the polymers were isolated and purified by precipitation in methanol, collected by filtration, and washed with hot water and finally with methanol. The thermal data for polymers **17a**−**e** are presented in Table 2. The T_g's of the polymers determined by DSC ranged from 201 to 283 °C, depending upon the difluoro monomer used. For these polymers the T_g's were also obtained from DTA except for **17e.** No melting transitions were observed, which clearly indicates that these are amorphous polymers. The T_g's are higher than those of the reported poly(arylene ether)s containing 1,2,4-triazole groups in the chain[18] due to the pendent bulky phthalimide moiety. The polymers are thermally stable and showed 5% weight loss above 400 °C, except polymer **17e** which has a low molecular weight. The polymers are colorless and form clear, transparent and very tough films from DMF solution. All the polymers were soluble in DMF, NMP, DMAC, and DMSO at room temperature and in hot TCE and insoluble in $CHCl_3$, THF, and 1,4-dioxane.

Similarly, the polymerization of **10** with difluoro monomers **a**−**d** (Scheme 5, Table 2) in DMSO was conducted in a single-step polymerization. In this case, the η_{inh} of the products obtained were slightly higher (0.34−1.09 dL/g) than with **9**, and this is attributed to the presence of a *tert*-butyl group on the phthalimide pendent group that increased the solubility of the

Scheme 5. Synthesis of Polymers 17a–e and 18a–d

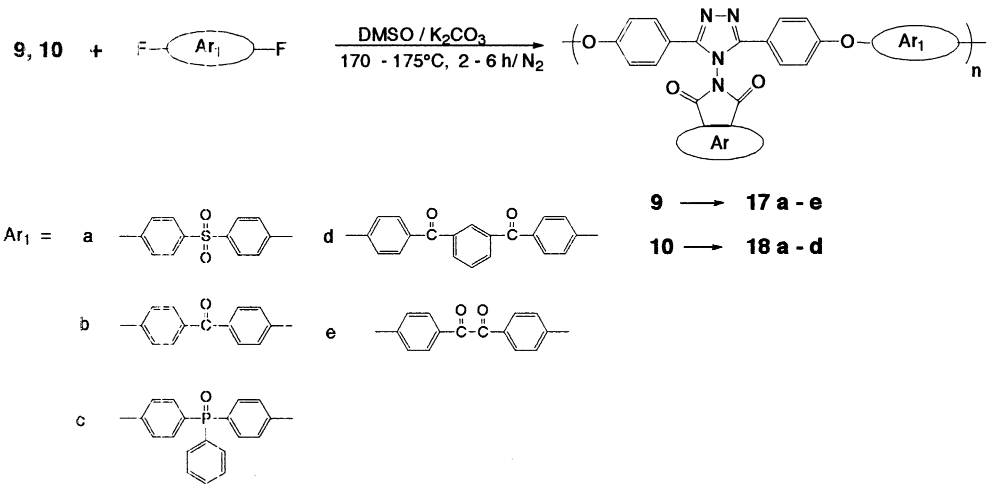


Table 2. Solution Viscosities and Thermal Properties of Polymers 17a–e and 18a–d

polymer	polymerization T (°C)/t (h)	yield (%)	η_{inh} (dL/g)[a]	T_g (°C)	T_d (°C) (−5 wt %)	T_g (°C)[b]
17a	170/2	95	0.64	266	437	267
17b	175/2.5	97	0.88	245	419	235
17c	175/6	90	0.42	283	433	275
17d	175/2	93	0.38	201	437	198
17e	130−40/2, 150/5	83	0.28	208	361	–[c]
18a	170/2	91	0.65	250	411	271
18b	175/2	94	1.09	237	404	244
18c	175/6	94	0.34	270	423	275
18d	175/1	93	0.45	220	424	217

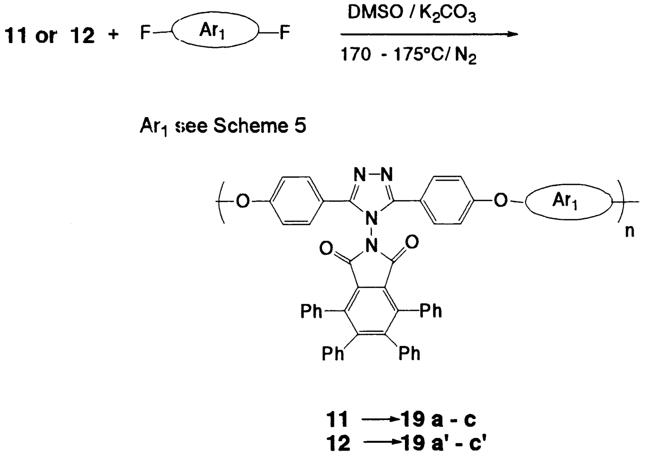
[a] Determined in DMF at 25 °C (0.2 g/dL). [b] Determined by DTA in N_2; heating rate 20 °C/min. [c] Not observed.

Table 3. Solution Viscosities and Thermal Properties of Polymers 19a–c and 19a′–c′

polymer	polymerization T (°C)/t (h)	solvent	yield (%)[a]	η_{inh} (dL/g)[b]	T_g (°C)	T_d °C (−5 wt %)
19a[c]	170/2.5	DMSO	66	0.64	263	416
19a	170/2.5	DMSO	55	0.56	263	423
19b	175/2.5	DMSO	42	0.70	–[g]	–
19b[d]	175/2.5	DMSO	63	0.47	–	–
19c	175/6	DMSO	50	0.53	–	–
19a′[e]	170/5	DMSO	44	0.27	–	–
19b′	165/4	DMAC	51	0.27	–	–
19b′	175/2.5	sulfolane	53	0.43	–	–
19a′[f]	100−150/7	DMSO	85	0.90	268	404
19b′[f]	100−150/7	DMSO	85	0.93	245	406
19c′[f]	100−150/24	DMSO	55	0.50	–	–

[a] **19a–c, 19a′–c′**, and **19c′**[5] contained large amounts of low molecular weight. [b] Determined in DMF at 25 °C (0.2 g/dL). [c] Two-step polymerization. [d] Dehydration carried out for 4 h. [e] Cs_2CO_3/$Mg(OH)_2$ used as base. [f] Polymerization carried out with stepwise increase in temperature with time. [g] Not determined.

Scheme 6. Synthesis of Polymers 19a–c and 19a′–c′



polymer. Polymers **18a–d** had 7–16 °C lower T_g values and 5% weight losses. The polymers formed tough, clear, and transparent films from DMF. These polymers had similar solubility patterns to those of polymers derived from **9**.

Synthesis of Poly(aryl ether 1,2,4-triazole)s from Bisphenol 11 and the Biscarbamate 12. The same polymerization conditions were used to synthesize polymers from bisphenol **11** with difluoro monomers **a** and **b** (Scheme 6). The yields of the polymers were 55 and 42% with $\eta_{inh.}$ of 0.56 and 0.70 dL/g (Table 3). The polymerization reaction was then carried out in a two-step reaction. In the first step, **11** was converted to the dipotassium salt by the dehydration reaction for 2 h followed by the polycondensation with difluoro monomers **a** and **b** for 4 h. The result was a slight increase in the isolated yield of the polymers. It was observed that during the dehydration step the disodium salts separated from the solution, and after addition of difluoro monomer and increasing the temperature they slowly went into solution.

In our earlier work we successfully demonstrated that carbamate masked bisphenols are much more reactive in nucleophilic substitution polymerization reactions to give high molecular weight poly(arylene ether)s in a very short period of time.[19,20] This method is especially useful with bisphenols that are unstable or if the dipotassium salts of the bisphenols are very insoluble in the reaction medium and large amounts of cyclic oligomers are formed. Under these conditions a quasi-high-dilution condition is created. With this approach the formation of cyclic oligomers in the preparation of poly(arylene ether)s can also significantly be suppressed.[18] The biscarbamate **12** was polymerized using a cesium carbonate/magnesium hydroxide combination as base. This combination of bases has been effective in previous preparations of poly(arylene ether)s.[21]

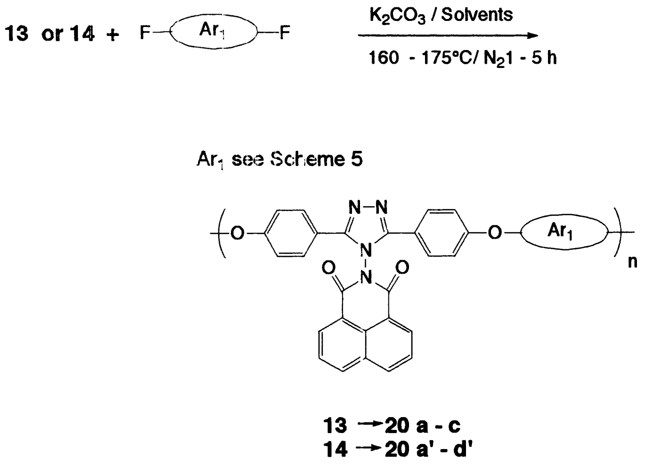
Polymerization of biscarbamate **12** was also conducted in DMAC and the higher boiling sulfolane as solvent. At elevated temperatures it was observed that due to the rapid and complete cleavage of the carbamate **12**, the dipotassium salt separated out from the reaction mixture as previously observed, and again only a low

Table 4. Solution Viscosities and Thermal Properties of Polymers 20a−c and 20a′−d′

polymer	polymerization T (°C)/time (h)	solvent	yield (%)	η_{inh} (dL/g)[a]	T_g (°C)	T_d (°C) (−5 wt %)	color of polymer
20a	175/2.5	DMSO	96	*b*	−[d]	−	brown
20a	175/1	DMSO	82	0.22	273	−	brown
20a	165/1.5	DMPU	90	0.22	−	−	brown (faint)
20a	170/1.5	NMP/CHP	87	0.33	−	−	brown (dark)
20a[c]	160/2	DMAC	70	0.33	−	−	brown
20a	165/2	sulfolane	85	0.28	−	383	brown (faint)
20b	170/1	DMSO	80	*b*	255	389	brown
20c	170/2.5	DMSO	64	0.18	−	390	brown
20a′	175/3	sulfolane	95	0.42	277	393	brown, tough film
20a′	160/3	DMSO	72	0.43	−	383	brown, brittle film
20b′	160/3, 175/1	sulfolane	95	0.27	255	389	brown, brittle film
20c′	175/5	sulfolane	47	0.12	−	390	brown
20d′	170/1.5	sulfolane	92	0.28	222	390	brown, brittle

[a] Determined in DMF at 25 °C (0.2 g/dL). [b] Insoluble in DMF. [c] Polymerization carried out using $CsCO_3$/$Mg(OH)_2$. [d] Not determined.

Scheme 7. Synthesis of Polymers 20a−c and 20a′−d′



yield of polymer with lower viscosity resulted (Scheme 6, Table 3).

To overcome this difficulty, the polymerization was conducted at lower temperature for a longer period of time. Initially, the temperature of the reaction mixture was raised to 100 °C, and later it was slowly increased to 150 °C in a stepwise manner over 7 h time (10 °C/h) (Table 3). Using this approach, the carbamate **12** was slowly cleaved at this temperature, and the phenate ions produced reacted immediately with the difluoro compond, thus avoiding the formation of the insoluble bisphenate salt. Polymer yields up to 85% with inherent viscosities of 0.90−0.93 dL/g were obtained with **a** and **b**. Despite conducting the polymerization at lower temperature for a longer period of time (ca. 100−150 °C, 24 h), the yield of the polymer using **c** as correctant was only 55% with inherent viscosity 0.50 dL/g. This difluoro monomer is much less reactive than **a** or **b**; therefore, at the higher reaction temperatures necessary for the displacement reaction the biscarbamate would be completely cleaved prior to condensation.

Synthesis of Poly(aryl ether 1,2,4-triazole)s from Bisphenol 13 and the Biscarbamate 14. The polymerization of the 1,2,4-triazole bisphenol with a pendent naphthalimide group **13** with difluoro monomer **a** was carried out in DMSO in a single step at 175 °C for 2.5 h (Scheme 7). An insoluble brown polymer was formed (Table 4). When the polymerization was carried out for 1 h, the polymer obtained had η_{inh} of 0.22 dL/g and was brown in color. Therefore, the effect of various solvents on the polymerization was investigated. Table 4 shows the results of the polymerization reactions that were conducted in a variety of polar aprotic media. The maximum η_{inh} obtained was 0.33 dL/g. The yield of isolated polymer varied from 70 to 90%. The polymerization with difluoro monomer **b** at 170 °C in DMSO also resulted in the formation of an insoluble brown polymer. This may be due to hydrolysis of the naphthalimide group and oxidation of the bisphenol due to trace amounts of oxygen.

We therefore carried out the polymerization of biscarbamate **14** in DMSO under the same polymerization conditions. There was an increase in η_{inh} (0.42 dL/g) and yield (95%), and no insoluble polymer was obtained (Scheme 7). The color of the polymer was pale brown. From this polymer a tough and transparent film with slight brownish tinge was cast form DMF solution. Polymerization in sufolane at 160 °C gave the same η_{inh} polymer, but the yield obtained was 72%. Polymerization with difluoro monomers **b** and **d** in sulfolane gave low η_{inh} polymers with yields of 95%. A polymerization reaction with **c** gave very low η_{inh} polymer, and the polymer was obtained in low yield (Table 4). As expected, the T_g of this polymer was higher than the polymers derived from **9**−**11** due to the rigid pendent naphthalimide moiety.

Synthesis and Characterization of Poly(arylene ether)s with 3,5-Diphenyl-1,2,4-triazole Pendent Group 16. In our earlier work,[8] a series of homo- and copoly(arylene ether)s were prepared from bisphenols containing the heterocyclic benzoylenebenzimidazole and phthaloperinone moiety, respectively. The polymerization reaction was conducted in NMP and sulfolane as solvent, and high-T_g and themooxidatively stable polymers with yellow and orange color were obtained. In the present work, the bisphenol **16** was polymerized with difluoro monomers **a**−**d** (Scheme 8, Table 5). The polymerization of **16** with **a** was conducted in different solvents (DMAC, DMSO, and sulfolane), and the final polymerization temperature was 170 °C. The polymerization in sulfolane gave the highest η_{inh} and yield of **21a** (0.5 dL/g, 92%). Polymerization reactions with difluoro monomers **b**−**d** were conducted in sulfolane solvent, and the final polymerization time was varied from 4 to 6 h. The polymer obtained with monomer **c** had a low inherent viscosity and yield. This may be due to the lower reactivity of monomer **c**. Very low molecular weight oligomers were recovered from the mother liquor that accounts for the low yield. The poly(arylene ether)s **21a**−**d** possess the pendent 3,5-diphenyl-1,2,4-triazole moiety linked through a N−N linkage between anhydride and triazole. The thermal properties are listed in Table 5. The T_g's of the polymers are in the range

Scheme 8. Synthesis of Polymers of 21a−d and Copolymers 22−24

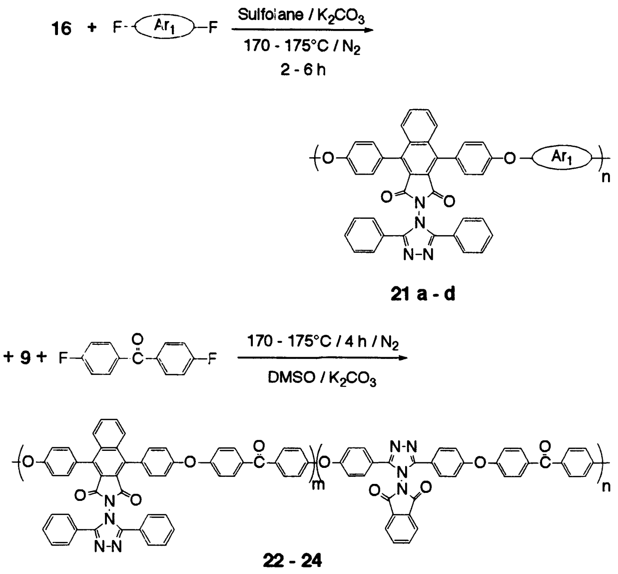


Table 5. Solution Viscosities and Thermal Properties of Homo- and Copolymers 21a−d and 22−24

polymer	polymerization T (°C)/time (h)	yield (%)	η_{inh} (dL/g)[a]	T_g (°C)	T_d (°C) (−5 wt %)
21a[b]	170/2	77	0.48	280	429
21a[c]	170/3	78	0.46	283	407
21a	170/2.5	92	0.50	280	412
21b	170/4	90	0.37	258	426
21c[d]	175/6	45	0.18	242	432
21d	175/4	89	0.37	222	415
22	175/4	81	0.38	253	377
23	175/4	82	0.36	235	389
24	175/4	81	0.40	262	403

[a] Determined in DMF at 25 °C (0.2 g/dL). [b] Polymerization carried out in DMAC. [c] Polymerization carried out in DMSO. [d] Low yield due to low molecular weight oligomers, mainly cyclics.

between 222 and 280 °C. The highest T_g (280 °C) was obtained from monomer **a**. The 5% weight losses obtained for these polymers by TGA are above 400 °C. The polymers are colorless and soluble in dipolar aprotic solvents such as DMAC, NMP, DMSO, DMF, soluble in hot TCE and insoluble in $CHCl_3$, THF, and 1,4-dioxane.

Monomer **16** was copolymerized with **9** in different proportions with difluoro monomer **b** to prepare poly(arylene ether)s containing the 1,2,4-triazole moiety in the backbone of the polymer as well as a pendent moiety (Scheme 8). The polymerization was carried out in DMSO at 175 °C for 4 h. Yields of the polymers were 81−82%, and η_{inh} varied from 0.36 to 0.40 dL/g. The T_g's varied from 235 to 262 °C. These polymers show the same solubility pattern as that of **21a−d**; however, these copoly(arylene ether)s **22−24** are pale yellow in color.

Synthesis and Characterization of Poly(arylene ether 1,2,4-triazole)s Derived from Decafluorobiphenyl f. As described above, 1,2,4-triazole bisphenols **9−11**, **13**, and **16** were polymerized with activated arylene difluoro monomers **a−d** in DMSO or sulfolane, and medium to high molecular weight polymers were obtained. Homo- and copoly(arylene ether)s containing the oxadiazole moiety synthesized with decafluorobiphenyl gave polymers with high T_g's and excellent thermal stability and showed blue light emission.[18] Recently, it has been reported[22,23] that preparation of perfluorinated oligo(*p*-phenylene)s and perfluorinated phenylene dendrimers as effective electron-transporting materials for OLED's because of their low-lying LUMO's and HOMO's, which are important for electron injection and hole blocking, respectively.

1,2,4-Triazole derivatives have been utilized as electron transport materials in electroluminescent cells. The 1,2,4-triazole has a phenyl substituent on the nitrogen atom, and it has been pointed out that it may be bulky enough to prevent formation of exciplexes and charge-transfer complexes.[24]

The triazole monomers **9−11**, **13**, and **16** were polymerized and copolymerized with decafluorobiphenyl as depicted in Scheme 9. Since decafluorobiphenyl is more reactive in the nucleophilic displacement reaction, all the polymerizations were conducted at lower temperatures (90−120 °C) in DMSO solvent using excess of K_2CO_3, and polymerization times varied from 0.75 to 4 h. These polymers were obtained in excellent yields, from 93% to 100%. The polymers were obtained as white fibrous materials, and η_{inh} varied from 0.66 to 3.27 dL/g. The highest viscosity polymer was obtained from monomer **10** perhaps due to greater solubility of the monomer and polymer in the reaction medium due to the presence of the *tert*-butyl group on the pendent phthalimide moiety. The thermal data are depicted in Table 6. The T_g's varied from 209 to 282 °C, and the highest T_g of 282 °C was obtained from the copolymerization of monomer **13** with **16** to give the copolymer with 1,2,4-triazole in the main chain of the polymer and also as a pendant. The lowest T_g of 209 °C was obtained by copolymerizing with BPA (70%) and 30% of monomer **16**. All these polymers show excellent thermal stability with 5% weight loss temperatures above 400 °C. Polymers **17f−18f1** and **20f−26** are soluble in dipolar aprotic solvents such as DMF, NMP, and DMAC and insoluble in THF, 1,4-dioxane, toluene, and chloroform. Polymers **17f−21f** are soluble in hot TCE whereas **25−27** are soluble in TCE at room temperature. Interestingly, polymers **19f** and **19f1** are soluble in THF and 1,4-dioxane but insoluble in chloroform. Polymer **27** was soluble in these solvents and swelled in chloroform due to the larger amount of BPA in the polymer. From all the polymers clear, transparent, and tough films were obtained by casting from DMF solution.

UV Absorbance and Fluorescent Properties of 16, Polymers 21a−d,f, and 21−27. Earlier, we have observed[8] that the anhydride bisphenol **15** shows absorption in the UV at 360 nm. The bisphenol **16**, which is derived from **15** and **1**, is faint yellow in color and shows a UV absorption peak at 267 nm and a small peak at 349 nm. Because of the attached triazole moiety, there is shift in absorption at lower wavelength. The UV absorption and emission data of polymers **21a−f** and **22−27** are tabulated in Table 7, and these data were recorded in DMF solution. Polymers **21a−f** and **25−27** showed absorption peaks at 267−269 nm. Polymers **22−24** and **26** showed additional absorption at higher wavelength (297 and 341, 358 nm). This is attributed to the difluoro monomer **b** and **13** which has a naphthalene moiety. The polymers show strong photoluminescence in DMF solution when excited at their absorption maxima. The maximum emission wavelength (λ_{em}) for polymers **21a−f** and **25−27** ranges from 382 to 450 nm. Polymer **21a** showed additional emission at 510 nm, and this may due to the strong electron-

Scheme 9. Synthesis of Homo- and Copoly(arylene ether 1,2,4-triazole)s 17–21f and 25–27

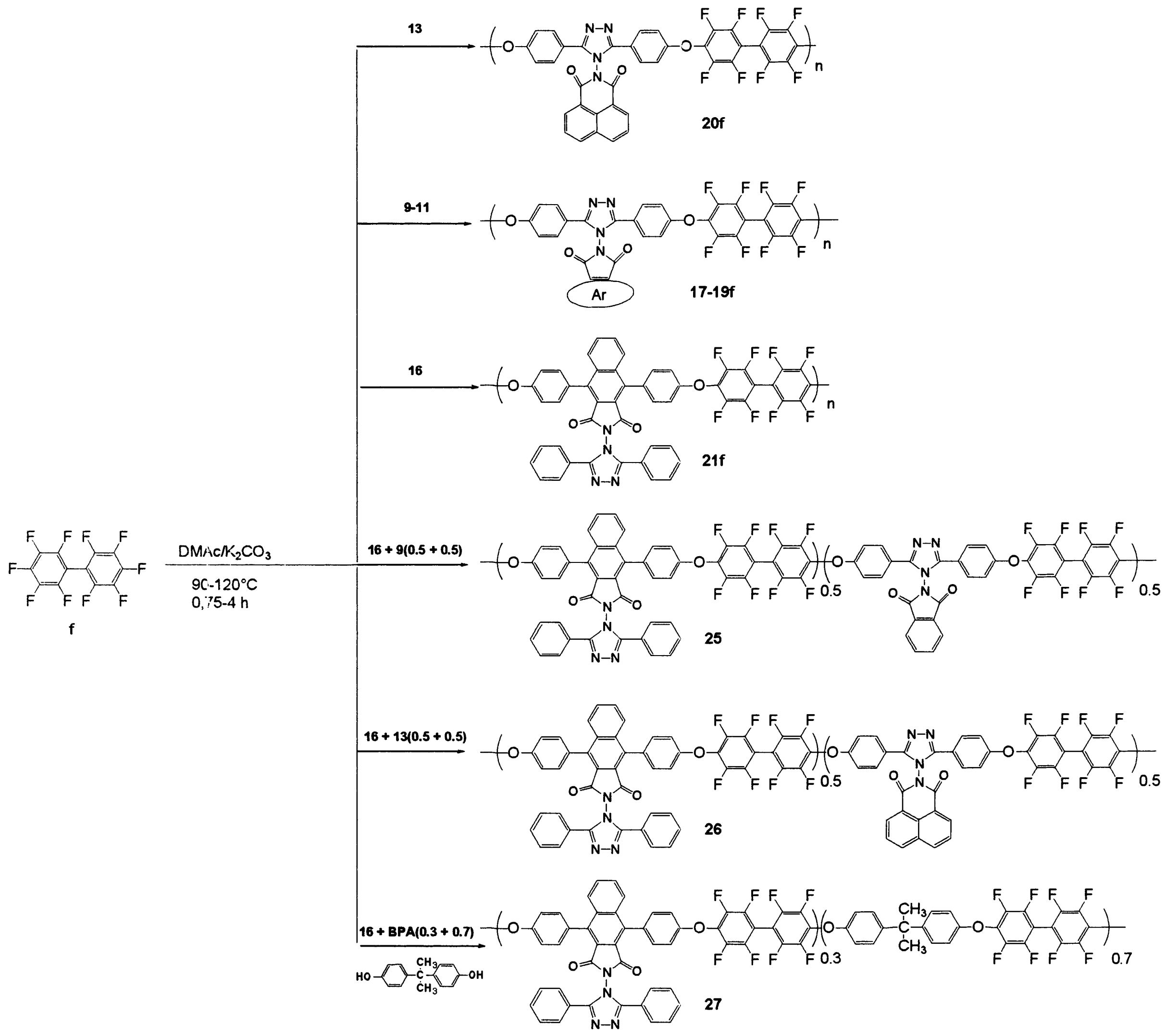


Table 6. Homo- and Copoly(arylene ether 1,2,4-triazole)s with Decafluorobiphenyl f

polymer	bisphenols	polymerization T (°C)/time (h)	yield (%)	η_{inh} (dL/g)[a]	T_g (°C)	T_d °C (−5 wt %)
17f	**9**	90/1.5	98	2.01	254	428
18f	**10**	95/1.5	96	3.27	235	438
18f1	**9** + **10** (0.50 + 0.50)	95/1.5	95	0.88	244	438
19f[b]	**11**	95/4, 110/2, 120/2	93	1.04	246	414
19f1[b]	**9** + **11** (0.50 + 0.50)	95/2	93	0.62	252	429
20f	**13**	90/1, 100/2	97	1.14	259	403
21f	**16**	95/1.5	95	1.48	264	436
25	**16** + **9** (0.50 + 0.50)	95/0.75	100	0.75	263	420
26	**16** + **13** (0.50 + 0.50)	95/0.75	100	1.04	282	437
27[c]	**16** + **BPA** (0.30 + 0.70)	95/1.5	97	2.08	209	498

[a] Determined in DMF at 25 °C(0.2 dL/g). [b] Soluble in THF and 1,4-dioxane, insoluble in $CHCl_3$. [c] Soluble in THF and 1,4-dioxane, swells in toluene and $CHCl_3$.

withdrawing sulfone group. Polymers **21a–f** and **25–27** are colorless and showed blue fluorescence under UV in solution and in the solid state. The copolymers **22–24** showed emission at higher wavelengths (496–504 nm) because of the difluorobenzophenone comonomer. These polymers are yellow in color and showed greenish-yellow fluorescence under UV in the solid state as well as in the solution. Thus, these polymers are potentially useful as electron-transporting materials with fluorescent properties. Further studies are in progress.

Conclusions

The N–N linkage between 1,2,4-triazole and phthalimide or naphthalimide moieties has been demonstrated to be stable under the polymerization conditions without hydrolysis and side reactions.

The reaction of the *N*-aminotriazole **1** with phthalic anhydride **2** and naphthalic anhydride **3** under optimized reaction conditions led to the formation of new compounds **(4, 5)** with phthalimide and naphthalimide pendent groups with a N–N linkage to the 1,2,4-

Table 7. UV Absorption and Fluorescent Properties of 16 and Polymers 21a−d,f and 22−27[a]

compd/ polymer	λ_{uv}, nm[b]	λ_{ex}, nm[b]	λ_{em}, nm[d]	fluorescence under UV
16	267, 349 (s)	320, 370, 392	421	
21a	267	395, 448	453, 510	blue
21b	269	350, 378	457	blue
21c	266	342, 376	458	blue
21d	268	323	382, 450	blue
21f	267	342, 377	412, 457	blue
22	266, 297	382, 395	503	greenish yellow
23	266, 297	291, 326, 379	504	greenish yellow
24	263, 297	324, 375	441, 496	greenish yellow
25	267	290, 333, 374	427	blue
26	341, 358 (s), 267	332, 378	428	blue
27	267	334, 379	433	blue

[a] All measurements were carried out in DMF, s = small shoulder. [b] Maximum absorption wavenumbers. [c] Excitation wavenumber. [d] Emission wavenumber.

triazole. New bisphenols **9−11** and **13** containing the 1,2,4-triazole attached to pendent phthalimide, and naphthalimide groups through a N−N linkage were prepared by a single-step reaction with **6** using zinc diacetate as imidization catalyst in high yield (75−90%). A new class of poly(arylene ether 1,2,4-triazole)s **17a−e** and **18a−d** containing the pendent phthalimide moiety have been prepared by nucleophilic displacement polymerization with activated arylene difluorides **a−d**. High molecular weight polymers with high T_g's (201−283 °C), and excellent thermal stability were obtained. Clear, transparent, and flexible films were cast from DMF solution. A monomer with a tetraphenyl-substituted phthalimide moiety **11** was polymerized to obtain high molecular weight polymers **19a−c** in low yield. This was due to the precipitation of the dipotassium salt of **11** during polymerization. Analysis of product obtained from mother liquor by MALDI−TOF MS showed the presence of linear oligomers up to trimer of **19a**.

Using the carbamate derivatives, with careful control of the polymerization conditions, i.e., slow increase in the reaction temperature with time, avoided the precipitation of the dipotassium salt, and hence high molecular and high yields of polymers **19a,b** were obtained. Monomer **13** and the biscarbamate derivative led to the formation of medium molecular weight polymers. A new monomer **16** with 1,2,4-triazole as pendent moiety was prepared from **15** and **1** by an imidization reaction using zinc diacetate as catalyst. Homo- and copoly(arylene ether)s with 1,2,4-triazole in the polymer backbone as well as a pendent moiety were obtained. The polymers **21a−d** and **21−24** showed T_g's between 222 and 283 °C and are colorless to pale yellow in color. All the bisphenols **9−11, 13**, and **16** were polymerized with decafluorobiphenyl at lower temperature (90−110 °C) and shorter reaction time. The solution viscosity of the polymers varied from 0.62 to 3.27 dL/g depending upon the triazole bisphenol. The polymers are soluble in dipolar aprotic solvents, and clear, transparent, and tough films were cast from DMF solution. Homo- and co(polyarylene ether 1,2,4-triazole)s **21a−d** and **21−27** (obtained from monomer **16**) showed blue to yellow-green fluorescence under UV as well as in solution. The polymers with 1,2,4-triazole in the polymer backbone as well as a pendent group were also fluorescent and are potentially useful as electron-transporting materials in OLED's.

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References and Notes

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