Synthesis of 1,2,4-Triazole Poly(aryl ethers) via Heterocyclic-Activated Displacement Polymerization

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ABSTRACT: The synthesis and characterization of new monomers and polymers containing the 1,2,4-triazole unit are discussed. The monomers were synthesized via a route that allowed the preparation of a variety of 3,5-bis(4′-fluorophenyl)-4-aryl-1,2,4-triazoles. ^{1}H, ^{13}C, and ^{19}F NMR have proved to be valuable in the evaluation of the degree of activation in these weakly activated fluoro monomers. Model reactions with *m*-cresol were performed on these new monomers to ascertain that they were indeed good candidates in a poly(aryl ether) synthesis. Reaction times, temperatures, and solvent systems had to be adjusted to optimize conditions for these weakly activated systems. The monomers were polymerized with various bisphenols in high-boiling polar aprotic solvents in the presence of potassium carbonate to yield high molecular weight, amorphous polymers which were thermally stable and amenable to common processing conditions. The polymers had T_g's ranging from 185 to 230 °C, had intrinsic viscosities between 0.40 and 1.45 dL/g, and showed dynamic mechanical behavior consistent with other high-temperature thermoplastics.

Introduction

The development of high-temperature polymers for use as matrix resins for high-performance composite structures as well as thermally stable microelectronic materials is one area of active interest. It is well known that aromatic polymers containing heterocyclic rings are among the most thermally stable polymers available. Examples of thermally stable heterocycles successfully incorporated into aromatic polymers include imides, quinoxalines, benzoxazoles, benzothiazoles, etc. In these systems, the heterocycle ring is typically generated in the polymer-forming reaction.

Another potentially interesting heterocycle is the 1,2,4-triazole unit. Early efforts to incorporate the 1,2,4-triazole unit in the structural backbone of various polymers gave materials that showed excellent thermal stability, with polymer decomposition temperatures in excess of 500 °C.[1] These polymers, however, suffered from low solubility in common organic solvents, and in spite of their high thermal stability, they were not easily processed in the melt due to their high softening temperatures. Additionally, the synthesis often required the derivatization of polymeric precursors which, in many cases, resulted in low molecular weight materials with poor film-forming properties.

An alternative method for the incorporation of preformed heterocyclic units into a polymer is through the utilization of a poly(aryl ether) synthesis, where the generation of an aryl ether linkage is the polymer-forming reaction. Using this approach, the heterocyclic unit is employed as a comonomer in a polyether synthesis. This allows the retention of some of the favorable properties of heterocyclic polymers such as high thermal stability and good mechanical properties, while the aryl ether linkages increase the solubility and lower the glass transition temperature, facilitating both synthesis and processing.[2,3] Some heterocycles incorporated into poly(aryl ethers) by this method include imidazoles,[4] phenylquinoxalines,[5,6] benzazoles,[7-9] pyrazoles,[10] and triazoles.[11,12] In these cases, the heterocycle was functionalized as either a bishalide or a bisphenol monomer and polymerized with the appropriate comonomer to give the desired poly(aryl ether). Connell et al. reported the first poly(aryl ether triazoles) in which the bisphenol 3,5-bis(4′-hydroxyphenyl)-4-phenyl-1,2,4-triazole was polymerized with various activated aromatic dihalides.[11] We have focused our efforts on the preparation of aryl difluoride monomers in which the heterocyclic ring acts as an electron-withdrawing group, thus activating the aryl halides toward nucleophilic substitution displacement polymerization. In this paper, several new examples of poly(aryl ethers) containing 1,2,4-triazole units prepared via heterocyclic-activated displacement will be discussed. In all of the earlier triazole polymers, only the 4-phenyl- or 4-hydro-1,2,4-triazole substituents were incorporated. Our synthetic procedure allows the incorporation of a variety of substituted 4-aryl-1,2,4-triazoles into the backbone of high molecular weight poly(aryl ethers).

Experimental Section

Materials. All materials were commercially available and used as received unless otherwise noted. *N*-Cyclohexyl-2-pyrrolidinone (CHP) (Aldrich) and 1,3-dimethyl-3,4,5,6-tetrahydro-2(1*H*)-pyrimidinone (*N*,*N*′-dimethylpropyleneurea, DMPU) (Aldrich) were vacuum distilled over calcium hydride. The monomer 2,2-bis(4′-hydroxyphenyl)propane, Bisphenol A (**17a**) (Aldrich), was recrystallized from toluene, and 2,2-bis(4′-hydroxyphenyl)hexafluoropropane, Bisphenol AF (**17b**) (Aldrich), was purified by recrystallization from toluene/ethyl acetate (95:5).

Analyses and Instrumentation. NMR spectra were recorded on either an IBM WP 250 spectrometer operating at 250.1 (^{1}H) or 62.9 MHz (^{13}C) or an IBM WP 300 spectrometer operating at 282.3 MHz (^{19}F). Tetramethylsilane (Me_4Si) was used as a reference for ^{1}H and ^{13}C NMR measurements, while $CFCl_3$ was used as an internal standard for the ^{19}F NMR measurements, with the reference peaks being assigned at 0.0 ppm. Chemical shifts upfield of the reference are assigned a negative sign and are reported in ppm, while the coupling constants are reported in hertz. Elemental analysis and mass spectra were performed by Oneida Research Services. Glass transition temperatures, taken as the midpoint of the change in the slope of the baseline, were measured on a DuPont DSC 1090 instrument at a heating rate of 10 °C/min. Thermal gravimetric analyses (TGA) on the polymer samples were conducted at a heating rate of 10 °C/min in a nitrogen atmosphere. Dynamic mechanical behavior was assessed on a Polymer Laboratories dynamic mechanical thermal analzyer (DMTA) in the tension mode with a heating rate of 10 °C/min (10 Hz). Intrinsic viscosity measurements were determined by using a Cannon Ubbelohde dilution viscometer in *N*-methyl-2-pyrrolidinone (NMP, 25 °C).

1,4-Bis(4′-fluorophenyl)-2,3-diaza-1,3-butadiene (1). A 250-mL round-bottomed flask fitted with a magnetic stirring

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bar and reflux condenser was charged with 20.40 g (0.158 mol) of *p*-fluorobenzaldehyde and 175 mL of absolute ethanol. To this slurry was added 4.0 g (0.099 mol) of $H_2NNH_2 \cdot H_2O$ while the reaction mixture was rapidly stirred. The mixture became warm and yellow crystals formed. The reaction was heated to 60 °C for 12 h, after which the mixture was cooled and filtered. The yellow crystals were washed (3×) with ethanol and dried under vacuum to give 17.58 g (91% yield) of **1**: mp 180–182 °C; ^{1}H NMR (DMSO-d_6) δ 8.72 (s, 2 H), 7.97–7.91 (m, 4 H), 7.39–7.32 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ 164.49 (d, J_{FC} = 255.1), 160.70 (s), 130.24 (s), 130.20 (s), 115.89 (d, $^2J_{FC}$ = 22.1); ^{19}F NMR (DMSO-d_6) δ −107.99. Anal. Calcd for $C_{14}H_{10}F_2N_2$: C, 68.84; H, 4.13; N, 11.47. Found: C, 68.74; H, 4.10; N, 11.43.

1,4-Bis(3′-fluorophenyl)-2,3-diaza-1,3-butadiene (2). The preparation of this compound was the same as for **1** except 3-fluorobenzaldehyde (Aldrich) was substituted and the procedure yielded the desired product in 83% yield: mp 132–134 °C; ^{1}H NMR ($CDCl_3$) δ 8.62 (s, 2 H), 7.62 (d, 2 H), 7.60 (d, 2 H), 7.48–7.25 (m, 2 H), 7.18 (dd, 2 H); ^{13}C NMR ($CDCl_3$) δ 162.88 (d, J_{FC} = 247.1), 161.11 (s), 136.01 (s), 130.33 9s), 124.75 (s), 118.22 (d, $^2J_{FC}$ = 21.7), 114.42 (d, $^2J_{FC}$ = 22.6); ^{19}F NMR (DMSO-d_6) δ −112.06.

1,4-Dichloro-1,4-bis(4′-fluorophenyl)-2,3-diaza-1,3-butadiene (3). A 250-mL three-necked flask fitted with a magnetic stirrer, reflux condenser, thermometer, and glass bubbler tube was charged with 17.7 g (0.073 mmol) of **1** and 200 mL of glacial acetic acid. The slurry was stirred and Cl_2 was slowly bubbled into the reaction mixture, which spontaneously warmed and became homogeneous. The flask was heated to maintain an internal temperature of 50 °C, and the addition of Cl_2 was continued for 5 h. After the addition, the mixture was cooled to room temperature while under a N_2 purge. The resulting yellow crystals were filtered, rinsed repeatedly with water, and vacuum dried overnight. The filtrate was diluted with 200 mL of CH_2Cl_2, transferred to a separatory funnel, and washed successively with aqueous sodium bicarbonate solution and water. The organic layer was dried over magnesium sulfate and filtered. The CH_2Cl_2 was allowed to evaporate to give yellow crystals which were added to the filtered precipitate for a total yield of 17.5 g (77%) of **3**: mp 124–126 °C; ^{1}H NMR ($CDCl_3$) δ 8.18–8.12 (m, 4 H), 7.17 (dd, 4 H); ^{13}C NMR ($CDCl_3$) δ 164.95 (d, J_{FC} = 253.9), 143.65 (s), 130.65 (s), 129.71 (s), 115.62 (d, $^2J_{FC}$ = 22.3).

1,4-Dichloro-1,4-bis(3′-fluorophenyl)-2,3-diaza-1,3-butadiene (4). The synthesis of **4** was identical to that of **3** using **2** as the starting material to give the desired product in 77% yield: mp 97–98 °C; ^{1}H NMR δ 7.93 (d, 2 H), 7.84 (d, 2 H), 7.50–7.42 (m, 2 H), 7.26 (dd, 2 H); ^{13}C NMR ($CDCl_3$) δ 162.50 (d, J_{FC} = 247.2), 143.18 (s), 135.54 (s), 130.09 (s), 124.23 (s), 118.84 (d, $^2J_{FC}$ = 21.6), 115.42 (d, $^2J_{FC}$ = 24.6).

4′-(Methylsulfonyl)aniline (5). A 250-mL three-necked round-bottom flask fitted with a reflux adapter and magnetic stirring bar was charged with 16.60 g (0.065 mol) of *p*-acetaminobenzenesulfonic acid sodium salt (TCI), 6.18 g (0.065 mol) of chloroacetic acid, and 50 mL of water. The pH of the mixture was adjusted to ~8.0 with a 50% NaOH solution. The solution cleared with stirring. The mixture was heated to reflux (~140 °C) for 40 h and allowed to slowly cool over a period of 48 h to give white crystals which were ground and washed repeatedly with water. The crystals at this point consisted of a mixture of protected and unprotected product. The crude product was heated to reflux for 2 h with 4 M HCl solution. The mixture contained only the desired product as determined by TLC analysis. The solution was neutralized with a 5 M sodium hydroxide solution and extracted with CH_2Cl_2 which was washed several times with water. The solvent was evaporated to give 6.7 g (61% yield) of **5**: ^{1}H NMR ($CDCl_3$) δ 7.85 (d, $^3J_{HH}$ = 7.75, 2 H), 7.68 (d, $^3J_{HH}$ = 7.75, 2 H), 4.25 (s, 2 H), 3.01 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 151.28, 129.34, 128.57, 118.86, 113.97, 44.88.

4-(Perfluorohexylfulonyl)aniline (6). Into a 250-mL flask stirred magnetically and equipped with a reflux condenser were placed 2.35 g (4.4 mmol) of (4-perfluorohexyl)thiotrifluoroacetamide, 3.02 g (30 mmol) of CrO_3, and 60 mL of glacial acetic acid. The mixture was heated to 115 °C for 2.5 h. After cooling, 125 mL of ice water was added, and the mixture extracted two times with 75 mL of CH_2Cl_2. The organic layer was washed with water and saturated sodium bicarbonate and dried. After removal of the CH_2Cl_2, the residue was dissolved in a mixture of 45 mL of ethanol and 8.6 mL of water containing 3.02 g (22 mmol) of K_2CO_3 and heated for 2 h at reflux. The ethanol was removed by evaporation, water was added, and the mixture was extracted with CH_2Cl_2. The extract was dried over Na_2SO_4. Evaporation of the solvent yielded 1.3 g of crude product (63%), which was recrystallized from toluene–hexane (2:1): mp 126 °C; ^{1}H NMR (acetone-d_6) δ 7.62 (d, J = 8.9, 2 H), 6.79 (d, J = 8.9, 2 H), 5.80 (br s, 2 H); ^{13}C NMR (acetone-d_6) δ 157.0 (s), 134.3 (s), 115.7 (s), 113.9 (s).

3,5-Bis(4′-fluorophenyl)-4-phenyl-1,2,4-triazole (7). A 50-mL three-necked flask fitted with an overhead stirrer was charged with 5.10 g (0.016 mol) of **3**, 4.55 g (0.049 mol) of freshly distilled aniline, and 10 mL of xylene. The flask was fitted with a reflux condenser and heated with stirring to 140 °C. The mixture started to solidify after 3 h and was allowed to react for a total of 5 h. After cooling and dilution with 50 mL of $CHCl_3$, the solution was washed successively with dilute HCl, aqueous sodium bicarbonate, and water. The organic layer was dried over magnesium sulfate with activated charcoal and filtered. The crude product was purified by repeated recrystallization from 4:1 methanol–acetone to give 4.27 g (78% yield) of **7**: mp 246–247 °C; ^{1}H NMR ($CDCl_3$) δ 7.51–7.45 (m, 3 H), 7.40–7.37 (m, 4 H), 7.14 (d, 2 H), 7.0 (dd, 4 H); ^{13}C NMR ($CDCl_3$) δ 163.38 (d, J_{FC} = 251.8), 153.86 (s), 130.75 (s), 130.59 (s), 130.11 (s), 129.85 (s), 127.63 (s), 122.91 (s), 115.60 (d, $^2J_{FC}$ = 21.8); ^{19}F NMR (DMSO-d_6) δ −110.49. Anal. Calcd for $C_{20}H_{13}F_2N_3$: C, 72.06; H, 3.94; N, 12.60. Found: C, 71.70; H, 3.96; N, 12.49. Mass spectrum (*m/e*): 333 (M^+); calcd for M^+ = 333.

3,5-Bis(4′-fluorophenyl)-4-[3′-(trifluoromethyl)phenyl]-1,2,4-triazole (8). The preparation of **8** was similar to that of **7** except the flask was charged with 4.013 g (0.0128 mol) of **3**, 6.51 g (0.038 mol) of 3-(trifluoromethyl)aniline (Fluka), and 10 mL of xylene. The crude product was purified by flash chromatograhy[13] using 4:1 CH_2Cl_2–acetone as the eluent, and fractions were checked for purity of TLC. The product was recrystallized twice from an acetone–hexane mixture to give 3.72 g (72.3% yield) of **8**: mp 199–201 °C; ^{1}H NMR ($CDCl_3$) δ 7.77 (d, $^3J_{HH}$ = 7.5, 1 H), 7.61 (t, $^3J_{HH}$ = 7.5, 1 H), 7.34 (m, 6 H), 7.02 (dd, $^3J_{FH}$ = 12.5, 4 H); ^{13}C NMR ($CDCl_3$) δ 163.53 (d, J_{FC} = 251.5), 153.73 (s), 130.41 (s), 132.67 (d, $^2J_{FC}$ = 33.8), 130.95 (s), 130.85 (s), 130.79 (s), 130.72 (s), 124.59 (s), 124.40 (d, J_{FC} = 254.2), 115.85 (d, $^2J_{FC}$ = 21.9); ^{19}F NMR (DMSO-d_6) δ −60.83, −110.50. Anal. Calcd for $C_{21}H_{12}F_5N_3$: C, 62.85; H, 3.01; N, 10.47. Found: C, 62.67; H, 3.06; N, 10.43. Mass spectrum (*m/e*): 401 (M^+); calcd for M^+ = 401.

3,5-Bis(4′-fluorophenyl)-4-(4′-methylphenyl)-1,2,4-triazole (9). The preparation of **9** was carried out using *N,N*-diisopropylethylamine as the HCl acceptor. A 100-mL round-bottomed flask fitted with a mechanical stirrer was charged with 4.457 g (0.0142 mol) of **3**, 1.52 g (0.0142 mol) of 4-toluidine, 4.23 g (0.0327 mol) of *N,N*-diisopropylethylamine, and 15 mL of xylene and heated to 125 °C for 20 h. The resulting slurry of brown crystals was dissolved in 100 mL of $CHCl_3$, and the organic solution was washed successively with dilute HCl, aqueous sodium bicarbonate, and water. The $CHCl_3$ layer was dried over $MgSO_4$ and activated charcoal and filtered. The resulting light tan crystals were recrystallized twice from acetone–hexane to give white crystals, 2.33 g (47.0% yield), of **9**: mp 252–254 °C; ^{1}H NMR ($CDCl_3$) δ 7.43 (m, 4 H), 7.24 (d, $^3J_{HH}$ = 8.3, 2 H), 6.99 (dd, $^3J_{FH}$ = 9.0, 4 H); ^{13}C NMR ($CDCl_3$) δ 163.32 (d, J_{FC} = 250.7), 153.89 (s), 130.66 (s), 130.57 (s), 127.32 (s), 115.54 (d, J_{FC} = 21.8); ^{19}F NMR (DMSO-d_6) δ −110.50. Anal. Calcd for $C_{21}H_{15}F_2N_3$: C, 72.61; H, 4.35; N, 12.10. Found: C, 72.54; H, 4.42; N, 12.14.

3,5-Bis(4′-fluorophenyl)-4-[4′-(methylsulfonyl)phenyl]-1,2,4-triazole (10). The preparation of **10** was similar to that of **9** using 3.73 g (0.0119 mol) of **3**, 2.04 g (0.012 mol) of **5**, 3.20 g (0.025 mol) of *N,N*-diisopropylethylamine, and 15 mL of xylene. The crude product was purified by flash chromatography using 1:1 CH_2Cl_2–acetone as the eluent, and fractions were checked for purity by TLC. The product was recrystallized twice from an acetone–hexane mixture to give 3.5 g (71% yield) of **10**: mp 216–218 °C; ^{1}H NMR ($CDCl_3$) δ 8.03 (d, $^3J_{HH}$ = 8.3, 2 H), 7.36 (m, 6 H), 7.05 (dd, $^3J_{FH}$ = 8.5, 4 H); ^{13}C NMR ($CDCl_3$) δ 163.61 (d, J_{FC} = 251.8), 153.66 (s), 141.82 (s), 138.36 (s), 130.95 (s), 130.81 (s), 129.28 (s), 128.61 (s), 116.00 (d, $^2J_{FC}$ = 21.9), 44.21 (s); ^{19}F NMR

(DMSO-d_6) δ -110.10. Anal. Calcd for $C_{21}H_{15}F_2N_3O_2S$: C, 61.30; H, 3.68; N, 10.21. Found: C, 60.84; H, 3.67; N, 10.14. Mass spectrum (m/e): 411 (M^+); calcd for M^+ = 411.

3,5-Bis(4′-fluorophenyl)-4-[4′-(phenylsulfonyl)phenyl]-1,2,4-triazole (11). The preparation of 11 was similar to that of 9 using 2.15 g (0.0069 mol) of 3, 1.60 g (0.0069 mol) of 4-(phenylsulfonyl)aniline, 1.77 g (0.014 mol) of *N,N*-diisopropylethylamine, and 15 mL of xylene. After refluxing for 24 h, the reaction mixture was dissolved in $CHCl_3$ and filtered, and the solution was washed successively with dilute HCl, aqueous sodium bicarbonate, and water. The $CHCl_3$ layer was dried over $MgSO_4$ and activated charcoal and filtered. The resulting light tan crystals were twice recrystallized from acetone to give white crystals, 2.62 g (81% yield), of 11: mp 270–271 °C; ^{1}H NMR ($CDCl_3$) δ 7.97 (m, 4 H), 7.63 (d, $^3J_{HH}$ = 9.5, 1 H), 7.58 (t, $^3J_{HH}$ = 7.0, 2 H), 7.31 (m, 6 H), 6.98 (dd, $^3J_{FH}$ = 8.4, 4 H); ^{13}C NMR ($CDCl_3$) δ 163.54 (d, J_{FC} = 251.8), 153.60 (s), 143.15 (s), 138.80 (s), 133.82 (s), 130.86 (s), 130.73 (s), 129.47 (s), 129.40 (s), 128.49 (s), 127.73 (s), 122.26 (s), 115.88 (d, $^2J_{FC}$ = 21.95); ^{19}F NMR (DMSO-d_6) δ -110.06. Anal. Calcd for $C_{26}H_{17}F_2N_3O_2S$: C, 65.95; H, 3.62; N, 8.87. Found: C, 65.74; H, 3.65; N, 8.82.

3,5-Bis(4′-fluorophenyl)-4-[4′-(perflurohexylsulfonyl)-phenyl]-1,2,4-triazole (12). The preparation of 12 was similar to that of 9 using 1.32 g (0.0042 mol) of 3, 2.00 g (0.0042 mol) of 6, 1.17 g (0.009 mol) of *N,N*-diisopropylethylamine, and 15 mL of xylene. After refluxing for 24 h, the reaction mixture was dissolved in $CHCl_3$ and filtered, and the solution was washed successively with dilute HCl, aqueous sodium bicarbonate, and water. The $CHCl_3$ layer was dried over $MgSO_4$ and activated charcoal and filtered. The resulting light tan crystals were recrystallized twice from acetone–hexanes to give white crystals, 2.62 g (60% yield), of 12: ^{1}H NMR ($CDCl_3$) δ 8.12 (d, $^3J_{HH}$ = 8.6, 2 H), 7.42 (d, $^3J_{HH}$ = 8.6, 2 H), 7.31 (m, 4 H), 7.04 (dd, $^3J_{FH}$ = 8.6, 4 H); ^{13}C NMR ($CDCl_3$) δ 163.68 (d, J_{FC} = 251.7), 153.45 (s), 141.97 (s), 132.81 (s), 130.94 (s), 130.80 (s), 129.00 (s), 124.98 (d, $^2J_{FC}$ = 31.6), 124.47 (d, $^2J_{FC}$ = 32.3), 121.81 (s), 116.06 (d, $^2J_{FC}$ = 21.8); ^{19}F NMR (DMSO-d_6) δ -79.73, -110.28, -111.96, -119.23, -121.08, -122.04, -125.28. Anal. Calcd for $C_{26}H_{12}F_{15}N_3O_2S$: C, 43.65; H, 1.69; N, 5.87. Found: C, 43.49; H, 1.63; N, 5.82.

3,5-Bis(4′-fluorophenyl)-4-(4′-fluorophenyl)-1,2,4-triazole (13). The synthesis was accomplished in an analogous manner as for 7, using 4-fluoroaniline to give white crystals of 13 which were recrystallized from acetone–hexanes to give the desired product in 70% yield: mp 218–219 °C; ^{1}H NMR ($CDCl_3$) δ 7.40 (m, 4 H), 7.14 (m, 4 H), 7.03 (dd, 4 H); ^{13}C NMR ($CDCl_3$) δ 163.44 (d, J_{FC} = 251.6), 162.94 (d, J_{FC} = 257.9), 153.92 (s), 130.76 (s), 130.62 (s), 129.51 (s), 122.67 (s), 117.28 (d, $^2J_{FC}$ = 23.3), 115.73 (d, $^2J_{FC}$ = 21.9); ^{19}F NMR (DMSO-d_6) δ -110.37, -110.40. Anal. Calcd for $C_{20}H_{12}F_3N_3$: C, 68.37; H, 3.44; N, 11.96. Found: C, 68.74; H, 3.41; N, 11.97.

3,5-Bis(4′-fluorophenyl)-4-(3′-fluorophenyl)-1,2,4-triazole (14). The synthesis was accomplished in an analogous manner as for 7, using 3-fluoroaniline to give white crystals of 14 which were recrystallized from acetone–hexanes to give the desired product in 74% yield: mp 259–261 °C; ^{1}H NMR ($CDCl_3$) δ 7.47 (m, 1 H), 7.41 (m, 4 H), 7.23 (t, 1 H), 7.02 (dd, 4 H), 6.98 (m, 1 H), 6.88 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ 163.49 (d, J_{FC} = 251.6), 162.78 (d, J_{FC} = 251.6), 153.75 (s), 136.09 (s), 131.43 (s), 130.70 (s), 123.62 (s), 122.53 (s), 117.17 (d, $^2J_{FC}$ = 20.8), 115.76 (d, $^2J_{FC}$ = 21.8), 115.34 (d, $^2J_{FC}$ = 23.9); ^{19}F NMR (DMSO-d_6) δ -110.28, -110.83. Anal. Calcd for $C_{20}H_{12}F_3N_3$: C, 68.37; H, 3.44; N, 11.96. Found: C, 68.32; H, 3.43; N, 11.92.

3,5-Bis(3′-fluorophenyl)-4-phenyl-1,2,4-triazole (15). The synthesis was accomplished in an analogous manner as for 7, using 4 to give light tan crystals of 15 which were recrystallized from acetone–hexanes to give the desired product in 78% yield: mp 194–196 °C; ^{1}H NMR ($CDCl_3$) δ 7.49 (m, 3 H), 7.18 (center of complex multiplet, 10 H); ^{13}C NMR ($CDCl_3$) δ 162.24 (d, J_{FC} = 246.9), 153.77 (s), 134.54 (s), 130.19 (s), 130.09 (s), 129.97 (s), 128.52 (s), 124.28 (s), 116.71 (d, $^2J_{FC}$ = 20.9), 115.64 (d, $^2J_{FC}$ = 23.8); ^{19}F NMR (DMSO-d_6) δ -111.99. Anal. Calcd for $C_{20}H_{13}F_2N_3$: C, 72.06; H, 3.94; N, 12.60. Found: C, 71.83; H, 3.87; N, 12.55.

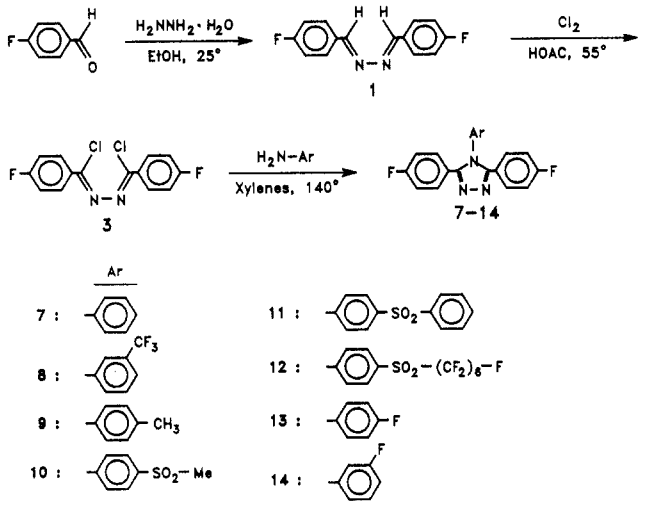
3,5-Bis[4′-(3-methylphenoxy)phenyl]-4-phenyl-1,2,4-triazole (16). A 15-mL three-neck flask fitted with an overhead stirrer and a Dean–Stark trap was charged with 991.3 mg (2.974 mmol) of 7, 649.7 mg (5.945 mmol) of *m*-cresol, 1.7 g of K_2CO_3, and 6.2 mL of DMPU. A small amount of toluene was added to effect the azeotropic removal of water. This mixture was stirred and heated to 140 °C, at which point toluene was collected and removed from the system. The temperature was maintained for 5 h, and more toluene was added periodically and subsequently collected and drained from the trap. The mixture was then heated to 170 °C for 48 h. The reaction mixture, which contained one product detected by TLC, was cooled, diluted with 100 mL of $CHCl_3$, and washed successively with 10% HCl solution, saturated $NaHCO_3$ solution, and water. The organic layer was dried over $MgSO_4$ and filtered. The solvent was removed in vacuo to give a white solid which was recrystallized twice from methanol–water to yield 890 mg (74.5%) of 16: mp 221–223 °C; ^{1}H NMR ($CDCl_3$) δ 7.47 (m, 3 H), 7.37 (d, 4 H), 7.21 (m, 4 H), 6.95 (d, 2 H), 6.85 (m, 8 H), 2.34 (s, 6 H); ^{13}C NMR ($CDCl_3$) δ 158.85, 155.79, 154.18, 140.03, 135.22, 130.17, 129.91, 129.54, 129.47, 127.78, 124.79, 121.20, 120.28, 117.73, 116.61, 21.25. Anal. Calcd for $C_{34}H_{27}N_3O_2$: C, 80.13; H, 5.34; N, 8.25. Found: C, 80.64; H, 5.31; N, 8.24.

Polymer Synthesis. The various poly(aryl ether) syntheses were conducted in a similar manner as described here for the poly(aryl ether) derived from 7 and Bisphenol A (17a). A 15-mL three-neck flask equipped with a nitrogen inlet, mechanical stirrer, and Dean–Stark trap fitted with a condenser was charged with 0.7859 g (2.357 mmol) of 7 and 0.5382 g (2.357 mmol) of 17a. The monomers were carefully washed into the flask with 5.0 mL of DMPU. An excess of K_2CO_3 (1.31 g, 9.48 mmol) and approximately 6 mL of dry toluene were added. The reaction mixture was heated to 145 °C, at which point the toluene began to reflux. Collected toluene was removed from the Dean–Stark trap, and more deoxygenated toluene was periodically added and then subsequently collected and drained from the trap. The reaction mixture was maintained at this temperature for 4–6 h to ensure complete dehydration of the system. The temperature was increased to 180 °C, and the mixture was allowed to react for approximately 35 h. Completion or near completion was qualitatively estimated by the point where the reaction mixture viscosity increased dramatically. The polymer was precipitated into 500 mL of a methanol–water (1:1) solution followed with vigorous stirring prior to filtering. The precipitated polymer, 18a, was washed several times with methanol and vacuum dried to a constant weight, 1.22 g (>99% yield). The yields were essentially quantitative for all of the polymerizations.

Results and Discussion

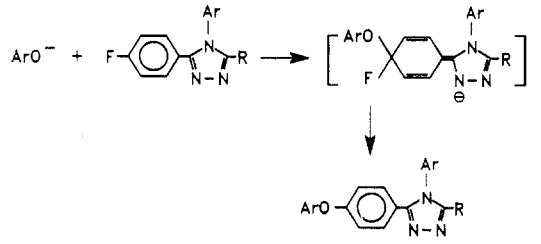
There are a number of known synthetic routes to 1,2,4-triazoles.[14] To make the desired fluorinated monomers, we first tried the technique described by Connell et al. for the synthesis of 3,5-bis(4′-hydroxyphenyl)-4-phenyl-1,2,4-triazole. In this synthesis, a 1,2-bis(4′-hydroxybenzoyl)-hydrazide intermediate was reacted with aniline hydrochloride at 250 °C for 2 h. Cyclocondensation occurred which gave the expected 1,2,4-triazole in 37% yield. We have previously reported the synthesis of 1,4-bis(4-fluorophenyl)hydrazide, which was used as the precursor to 2,5-bis(4-fluorophenyl)-1,3,4-oxadiazole.[15] All attempts to convert the hydrazide with aniline hydrochloride failed to generate the desired compound, 7, but produced instead mainly the oxadiazole contaminated by small amounts of the triazole. We found the most successful route to the triazole to be a three-step synthesis similar to that reported fy Stollé et al.[16] As shown in Scheme I, the appropriate fluorobenzaldehyde was reacted with hydrazine hydrate to give 1 or 2 in ~90% yield, which could subsequently be chlorinated in glacial acetic acid to produce the chlorinated azines 3 or 4. The chlorinated azines reacted with a variety of substituted anilines to give the desired products (7–15) via a facile cyclocondensation reaction. In these reactions, it is necessary to remove the HCl generated during the reaction. Usually, the most convenient method is to use an excess of the desired arylamine, but in cases where only small amounts of arylamine were

Scheme I



Scheme II

Triazole Activation



available, (10–12), *N,N*-diisopropylethylamine was added as a HCl scavenger. The amine hydrochloride is removed from the product during the workup. The synthesis of 3,5-bis(3′-fluorophenyl)-4-phenyl-1,2,4-triazole (15) was analogous to the other triazoles except that 3-fluorobenzaldehyde is used to generate the bis(phenylazine) (4). The triazoles were easily recrystallized and isolated in good yields. They are thermally and atmospherically stable.

It has been shown that nucleophilic aromatic substitution reactions between bifunctional activated-halide monomers and bisphenols can lead to aryl ether polymers, and there are several commercial polymers that are made via this process (e.g., poly(aryl ether ketone) (PEEK, ICI) and polysulfone (UDEL, Amoco)).[17] In these reactions, an aryl halide (fluorides are more reactive than chlorides) is activated by an electron-withdrawing group (conventionally either a ketone or sulfone group) toward substitution by an anionic phenoxide nucleophile (Scheme II). This activating group serves two purposes. First, the electron-withdrawing group decreases the electron density at the site of substitution and second, it lowers the energy of the transition state for the reaction by stabilizing the anionic intermediate. Certain heterocycles function similarly, and reports of the use of these nonconventional activating groups in polymer-forming reactions have appeared recently.[12,18,19] We anticipated that the 1,2,4-triazole ring would activate the aromatic ring toward substitution by functioning both as an electron-withdrawing substituent and as a stabilizing substituent for the anionic intermediate (Scheme II).

We have found that NMR is a valuable tool for evaluating the electron-withdrawing effect of substituents in potential monomers. When a resonance electron-withdrawing group is present on a phenyl ring, a partial positive charge develops at the ortho and para positions through resonance interactions. NMR chemical shifts are very sensitive to electron density at the particular nuclei

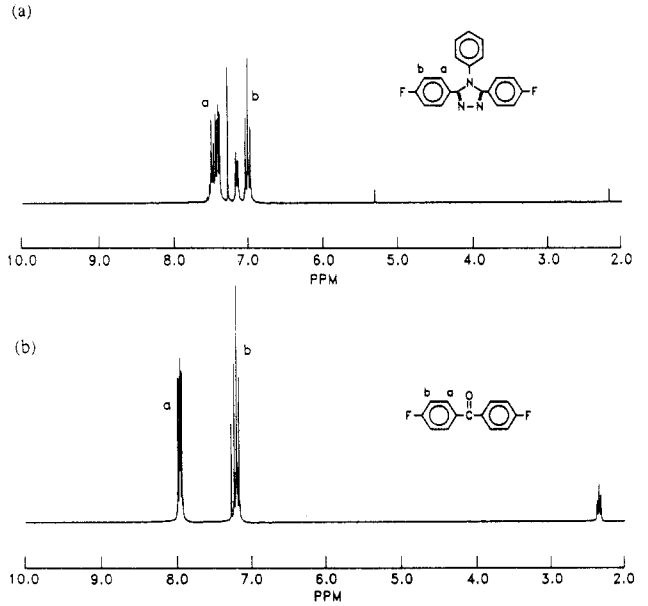


Figure 1. (a) ^{1}H NMR spectrum of 3,5-bis(4′-fluorophenyl)-4-phenyl-1,2,4-triazole. (b) ^{1}H NMR spectrum of 4,4′-difluorobenzophenone.

of interest, and in the case of the aryl fluorides there are three NMR probes that can be utilized: ^{1}H, ^{13}C, and ^{19}F. Previously we have reported the predictive use of ^{1}H NMR chemical shift data for the protons ortho to the electron-withdrawing group.[20] In these examples, the ortho proton resonances of potential monomers were compared with those of conventional activating groups (i.e., ketones or sulfones). For example, the ortho protons of 2,3-diphenyl-6-fluoroquinoxaline appear at δ 8.1, which is similar to those of 4,4′-difluorobenzophenone at δ 7.9.[5] In contrast, those of fluorobenzene, which is not activated, are observed at δ 7.3. The ^{1}H NMR of the fluorotriazole monomer 7 is shown in Figure 1 together with that of 4,4′-difluorobenzophenone. The protons ortho to the triazole ring appear around δ 7.4, which when compared with other systems would suggest that this monomer is only weakly activated. Since ^{1}H NMR shielding can vary significantly due to anisotropy and ring effects, and surveys the ortho positions rather than the actual site of reaction, other NMR probes were investigated.

Both ^{13}C and ^{19}F NMR can be used to probe the electron density at the actual site of nucleophilic reaction. The ^{13}C NMR chemical shifts of carbons para to electron-withdrawing groups in monomers which successfully polymerize were found to range from δ 164.5 to 166.2 while that of the unreactive model, fluorobenzene, occurs at δ 162.8 ppm. The relevant ^{13}C NMR chemical shifts for the fluorine-substituted carbons of the 1,2,4-triazoles are listed in Table I. They all cluster around δ 163.5, also suggesting that the triazole moiety is a less effective electron-withdrawing substituent than those systems examined previously. ^{19}F NMR chemical shifts proved to be the most sensitive probe of reactivity, with a chemical shift range spanning 9 ppm (560 Hz) between the most activated monomers (fluorophenyl sulfones) and nonactivated fluorobenzene. The ^{19}F shifts of the triazole monomers were upfield from those of other polymerizable monomers (Table I). Additionally, ^{19}F chemical shifts of *m*-fluorophenyl (14, 15) and *p*-fluorophenyl (7, 13) derivatives have been related to π-electron densities yielding the Taft reactivity parameters σ_I and σ_R^0. These parameters are a relative measure of σ-inductive and σ-resonance effects in substituted aryl rings.[21] The value of σ_R^0 is of greater importance here as it is a measure of conjugative inter-

Table I
NMR Substituent Chemical Shifts of Selected Fluorinated Compounds[a]

compound	^{13}C chem shift[b]	^{19}F chem shift[c]
4,4′-difluorophenyl sulfone	165.31	−104.08
4,4′-difluorobenzophenone	165.27	−106.01
[(phenylsulfonyl)phenyl]triazole	163.54	−110.06
[(methylsulfonyl)phenyl]triazole	163.61	−110.10
[*m*-(trifluoromethyl)phenyl]triazole	163.53	−110.19
[(perfluorohexylsulfonyl)phenyl]triazole	163.83	−110.28
phenyltriazole	163.38	−110.49
(methylphenyl)triazole	163.32	−110.50
fluorobenzene	162.82	−112.77

[a] ^{13}C chemical shifts are reported in ppm relative to TMS = 0.0 ppm. ^{19}F chemical shifts are reported in ppm relative to CCl_3F = 0.0 ppm. [b] Performed on dilute solutions in $CDCl_3$. [c] Performed on dilute solutions in DMSO-d_6.

Table II
Taft Resonance and Inductive Parameters

substituent[a]	σ_R^0	σ_I
NO_2	+0.20	+0.56
COPh	+0.18	+0.19
SO_2Ph[b]	+0.14	+0.52
CF_3	+0.10	+0.38
3,5-triazole positions[c]	+0.05	+0.17
H	0.00	+0.08
4-triazole position[c]	−0.02	+0.49
CH_3	−0.15	−0.08
$N(CH_3)_2$	−0.54	+0.10

[a] Data found in ref 21b except where stated. [b] Data from ref 21c. [c] This work.

actions between the phenyl ring and the substituent. A comparison of these parameters calculated for the 3,5-diphenyl and the 4-phenyl rings of the triazole heterocycle is shown in Table II. It can be seen that the conjugative electron withdrawal by the triazole ring from the 3,5-diphenyl substituents is small, ranging somewhere between that of CF_3 and H. The triazole is actually observed to be weakly donating to the 4-phenyl ring, an anticipated result since the substituent is directly attached to the trisubstituted nitrogen atom of the heterocycle. All of the NMR data thus suggested that the triazoles, at best, would be very weakly activated toward nucleophilic displacements.

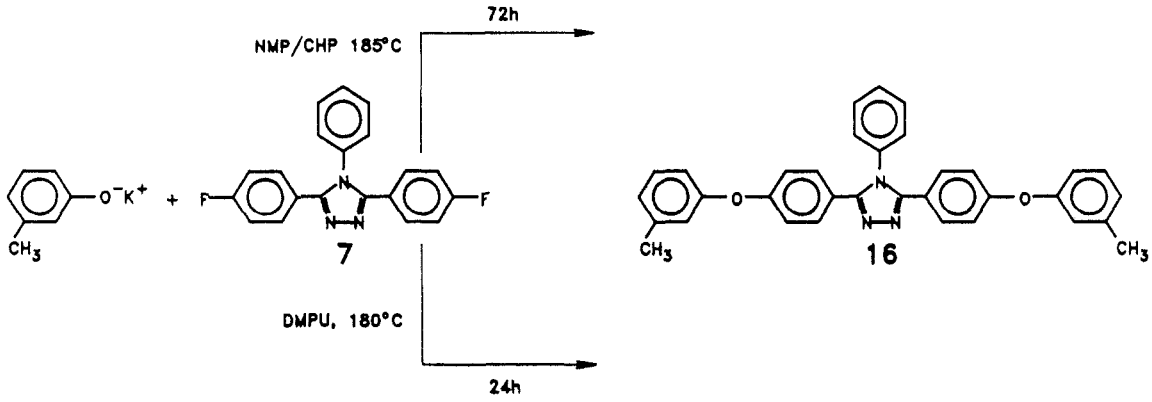
Nucleophilic aromatic substitution polymerizations are typically performed in a high-boiling aprotic polar solvent with the difluoride monomer being reacted with a bisphenol in the presence of a base, potassium carbonate, at elevated temperatures (ca. 180 °C). The potassium carbonate is used to convert the bisphenol into the more reactive anion. Since K_2CO_3 is a weak base, no hydrolytic side reactions with the bis(fluorophenyl)-1,2,4-triazoles were observed. Aprotic dipolar solvents are used in these poly(aryl ethers) syntheses, since they effectively dissolve the monomers and solvate the polar intermediates formed. It is also important that these solvents solvate the polymer formed. In this study, we have investigated two solvent systems: NMP/CHP (50/50) mixture and DMPU. NMP and CHP allow high reaction temperatures, 200 and 260 °C, respectively, and these high temperatures are required to maintain solubility of rigid or stiff-chain poly(aryl ethers). Although NMP alone tends to be a better solvent and is easier to handle, NMP/CHP solvent mixtures are often used since CHP is immiscible with water at temperatures above 100 °C. Thus, nonpolar cosolvents are not required to azeotrope the water generated during the polymerization. Alternatively, DMPU has been shown to be an excellent solvent for polyether syntheses, particularly for those polymers which are only marginally soluble in other dipolar aprotic solvents.[22] Furthermore, DMPU allows higher reaction temperatures (260 °C). We have observed that DMPU, when used in conjunction with toluene as a dehydrating agent, accelerates many nucleophilic substitution reactions. The increased activity of DMPU is probably due to its effectiveness in solvating the polar reagents and intermediates.

To survey the utility of the 1,2,4-triazole monomers in nucleophilic substitution reactions, model reactions between **7** and *m*-cresol were performed under conditions identical to those employed in polymerization reactions (Scheme III). In the model reaction, **7** and *m*-cresol were added in equimolar proportions and heated in the presence of 100% molar excess of anhydrous K_2CO_3 in a 1:1 NMP/CHP solvent mixture. Small aliquots were taken periodically and evaluated by HPLC. The reaction was deemed complete when no starting material was detected and a single product, **16**, was produced. As expected by the NMR studies, the reaction times were significantly longer when performed at 185 °C in NMP/CHP than with other previously examined systems, with complete conversion taking up to 72 h. This result was not encouraging, since our experience has shown that polymerizations requiring extended reaction times (>48 h) at high temperatures do not often lead to high molecular weight polymer, probably due to competitive side reactions and degradation. Alternatively, when the model reaction was studied in DMPU, it was complete in 24 h and gave the desired methoxyphenyl product **16** in essentially quantitative yield. The model reactions demonstrated that the fluoride substituents para to the triazole ring were cleanly displaced by phenoxides. The high selectivity and yield observed in this displacement demonstrated that the triazole-activated transformation is suitable as a polymer-forming reaction.

Polymerization of the triazole monomers with various bisphenols was carried out either in a NMP/CHP solvent mixture or in DMPU containing potassium carbonate (Scheme IV). The solids compositions were maintained at 20%, which is typical for most poly(aryl ether) syntheses, thereby avoiding side reactions with the fluoride ion. Irrespective of the polymerization solvent(s), toluene was used during the initial stages of the polymerizations to remove water generated by phenoxide formation as a toluene azeotrope. The solvent mixtures gave a reflux temperature between 150 and 165 °C. In an effort to keep the mixture anhydrous, the toluene was periodically removed through the Dean–Stark trap and replaced with more deoxygenated dry toluene. After bisphenoxide formation and dehydration, the polymerization mixtures were heated to 180–190 °C to effect the displacement reaction. In each case, high molecular weight polymer was attained within 48 h as judged by the dramatic increase in viscosity. The polymers were isolated in excess methanol and boiled in water to remove any remaining salts.

The 1,2,4-triazole monomers (**7–12**) were reacted with Bisphenol A (**17a**) and Bisphenol AF (**17b**) under conditions similar to those used in the model reactions to generate a new series of poly(aryl ethers) via the triazole-activated ether synthesis. Initially, the polymerizations of both **7** and **8** with **17a** and **17b** were carried out in NMP/CHP containing K_2CO_3. Though polymers were obtained after 72 h, in each case they precipitated from solution and were isolated as brown powders. These polymers could not be redissolved in a variety of organic solvents, and the use of either methanesulfonic acid or sulfuric acid for the determination of intrinsic viscosities resulted in degra-

Scheme III



Scheme IV

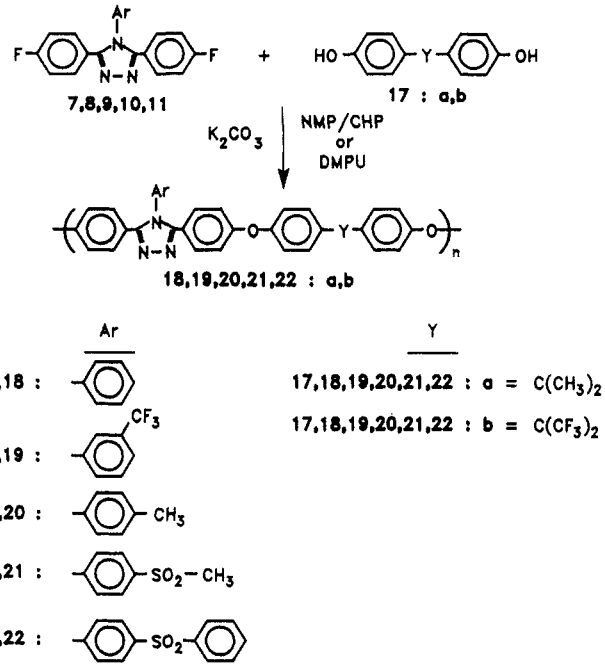


Table III
Properties of 1,2,4-Triazole Poly(aryl ethers)

polymer	reaction solvent	$[\eta]$ (dL/g)	T_g (°C)	PDT[a] (°C)
18a	NMP/CHP	*b*	185	
18a	DMPU	0.43	207	460
18b	NMP/CHP	*b*	200	
18b	DMPU	0.55	203	
19a	NMP/CHP	*b*		
19a	DMPU	0.49	190	
19b	NMP/CHP	0.33	185	
20a	DMPU	0.40	205	
20b	DMPU	0.43	213	
21a	DMPU	*b*	230	420
21b	DMPU	0.42	226	430
22a	DMPU	1.45	198	440
22b	DMPU	0.70	211	440

[a] Polymer decomposition temperature. [b] Polymer precipitated from solution and did not redissolve.

dation of the polymers. Calorimetric measurements of these two powders showed high T_g's, which are listed in Table III. Alternatively, the same reactions performed in DMPU yielded high-viscosity solutions from which the polymers were precipitated to give off-white powders. Calorimetric measurements on these polymers show that these materials have high T_g's similar to those prepared in NMP/CHP and consistent with those reported by Connell et al. for related polymers.[11] All of the monomers, with the exception of 12, successfully polymerized to give

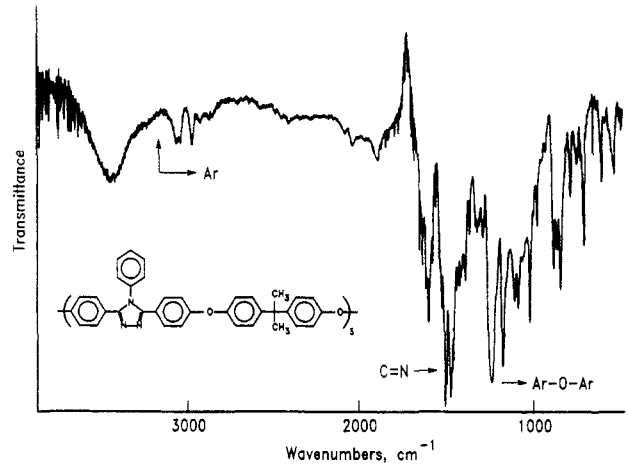


Figure 2. FT-IR of poly(aryl ether triazole) **18a**.

high molecular weight polymers (**18a,b–22a,b**). The unsuccessful attempts to polymerize **12** led us to study model reactions with this monomer which showed that secondary displacement reactions involving the perfluorohexylsulfonyl group take place competitively with the nucleophilic displacement of fluoride. The precipitated polymers were soluble in NMP, except for **21a**. This material rod-climbed during polymerization, but the precipitated polymer could not be redissolved, most likely due to slight cross-linking of the high molecular weight polymer. The FT-IR spectrum of **18a** is shown in Figure 2, and the characteristic absorption bands are noted, including those due to the aryl ether linkage that is generated in the polymer-forming reaction. The measured intrinsic viscosities were high and ranged from 0.40 to 1.45 dL/g (Table III).

It is interesting to note that the relative rates of reaction, as estimated by the time needed to form high molecular weight polymer, were consistent with the predictions based on the ^{19}F NMR chemical shifts of the monomers. Although actual kinetic rates were not measured, the relative reactivity of the triazole monomers was in the order shown in Table I, with the 4-phenyl and 4-(4′-methylphenyl) being the least reactive and the 4-[(phenylsulfonyl)phenyl] reacting the fastest. Similarly, the molecular weights of the polymers derived from the more activated triazoles appear to be higher than those from less activated monomers. This suggests that ^{19}F NMR spectroscopy may be a sensitive predictive tool in regards to the nucleophilic aromatic substitution of aryl fluorides. In the present study, creditable predictions were possible even though the spread of chemical shifts in the triazole monomers was very small ($\Delta\delta$ = 0.44 ppm, ~125 Hz). We are currently conducting relative reactivity studies on a wider variety of aryl fluoride monomers to assess the utility

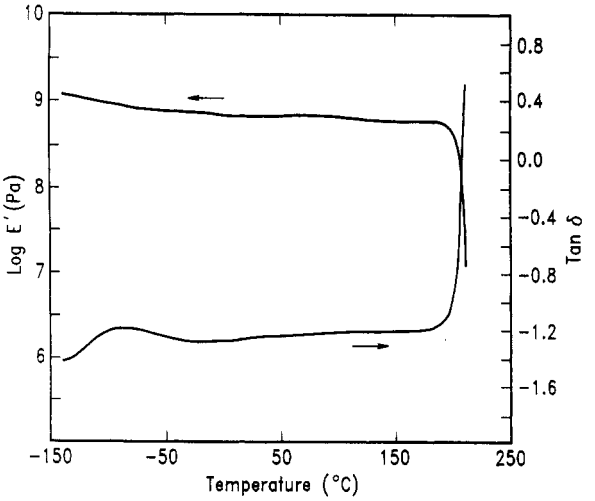


Figure 3. Storage tensile modulus and tau δ as a function of temperature for poly(aryl ether triazole) **18a**.

of ^{19}F NMR spectroscopy as a direct probe of monomer reactivity.

The T_g's of the poly(aryl ether triazoles) ranged from 185 to 230 °C depending on the particular bisphenol and activated difluoride used in the synthesis. The substituted triazoles generally showed T_g's 20–30 °C higher than those of the unsubstituted systems, except for polymers **19a** and **19b**. A plot of the dynamic mechanical behavior for the polymer **18a** is shown in Figure 3. These data, which are consistent with the calorimetry results, clearly show the high T_g and good dimensional stability exhibited by these materials. In contrast to many polyimides and other rigid rod heterocycle-containing structures that do not have a detectable T_g, the poly(aryl ether triazoles) all manifest a measurable T_g, indicative of an amorphous morphology. Although the calorimetric and dynamic mechanical measurements showed no evidence of true melting points, several of the samples appeared somewhat opaque, perhaps indicative of some low level of crystallinity. The T_g's of these polymers are among the highest reported for poly(aryl ethers) prepared by nucleophilic aromatic substitution and are comparable to those reported by Connell et al.[11] for similar structures.

The poly(aryl ether triazoles) behave in many respects as engineering thermoplastics with characteristics similar to those of polysulfones, poly(ether imides), etc. In contrast to conventional polytriazoles which decompose at or close to their softening temperature, the 1,2,4-triazole poly(aryl ethers) can be thermoformed by compression molding approximately 50 °C above their respective T_g's. The good thermal stability, as evidenced by the high polymer decomposition temperatures (430 °C), allows for high-temperature processing (Table III). These materials also have a number of mechanical characteristics typical of many other engineering thermoplastics, including tough ductile properties. Furthermore, many of the poly(aryl ether triazoles) that show these ductile deformation processes have a majority secondary relaxation (transition) in their dynamic mechanical spectra, analogous to those observed for polysulfone, polycarbonate, and other ductile polymers. Both the origin of theis relaxation and its effects on the ductile behavior are somewhat controversial even though this phenomenon has been investigated by many mechanical and NMR techniques.[23]

Summary

A new class of poly(aryl ether 1,2,4-triazoles) have been prepared by heterocyclic-activated displacement polymerization. In these reactions, the aryl ether linkages are generated in the polymer-forming reaction. We have demonstrated that the 1,2,4-triazole heterocyclic unit is sufficiently electron withdrawing to activate, albeit weakly, aryl fluorides toward nucleophilic displacement by a variety of nucleophiles. The appropriate bis(fluorophenyl)-substituted 1,2,4-triazoles were prepared and NMR studies were performed to assess their usefulness in nucleophilic displacement. Model reactions with *m*-cresol in aprotic polar solvents in the presence of K_2CO_3 were performed to first optimize reaction conditions, and the monomers were subsequently polymerized with various bisphenols yielding new poly(aryl ethers). Higher polymer molecular weights were achieved and structural variety attained through the use of different comonomers. The polymers could be processed either from NMP or from the melt (compression molding). The polymer T_g's ranged from 185 to 230 °C, depending on the monomers, and the polymers were thermally stable with decomposition temperatures in the 420–460 °C range. As expected, the incorporation of the aryl ether linkage induced ductile mechanical behavior, and the materials often showed a major secondary relaxation, characteristic of many engineering thermoplastics. The 1,2,4-triazole ring is one of most weakly activating substrates to be successfully polymerized by nucleophilic substitution, and the predictive spectral techniques used for these materials should be useful in identifying other potential monomers.

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