Synthesis and Characterization of Novel Poly(aryl ether pyridyltriazine)s

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ABSTRACT: Poly(aryl ether pyridyltriazine)s were synthesized by two approaches. In the first approach novel pyridyltriazine-containing monomers, 3-(2′-pyridyl)-5,6-bis(4′-fluorophenyl)-1,2,4-triazine and 3-(2′-pyridyl)-5,6-bis(4′-hydroxyphenyl)-1,2,4-triazine, were prepared and reacted with various bisphenols and activated aromatic difluorides, respectively, via a nucleophilic aromatic substitution reaction. A conventional potassium carbonate/dipolar aprotic solvent reaction procedure was employed with the exception of higher temperatures (195–235 °C) and a higher boiling solvent (i.e., *N*-methylcaprolactam). High molecular weight polymers were achieved in reactions with 3-(2′-pyridyl)-5,6-bis(4′-hydroxyphenyl)-1,2,4-triazine. However, for polymers prepared with 3-(2′-pyridyl)-5,6-bis(4′-fluorophenyl)-1,2,4-triazine, evidence of cross-linking accompanying the linear polymerization was detected. The second synthetic approach involved preparing poly(aryl ether benzil)s and then reacting them with (2-pyridyl)hydrazidine to form poly(aryl ether pyridyltriazine)s. The polymer modification reaction was quantitative and proceeded with no detectable backbone cleavage. From a synthetic viewpoint, the latter approach proved to be more advantageous, since difficulties associated with either the stability or reactivity of heterocyclic (e.g., triazine) monomers could be bypassed. All of the poly(aryl ether pyridyltriazine)s were amorphous and exhibited glass transition temperatures in the range 202–277 °C, significantly higher than the glass transition temperatures of the parent benzil polymers (167–242 °C). The thermooxidative stability of the polymers prepared was excellent; 5% weight loss in air occurred in the range 420–447 °C. Some of the polymers were both solution and melt processable, and all formed tough clear creasable films.

Introduction

Polymers that are resistant to chemical degradation and structural deformation at elevated temperatures are well suited as materials for electronic and aerospace components. Many engineering thermoplastics possess these characteristics. One important class of thermoplastics is the poly(aryl ether)s; their unique properties can be attributed to the presence of aryl ether linkages along the polymer backbone, which improves toughness, increases flexibility, and allows for facile processing from solution or the melt. Poly(aryl ether)s are conveniently prepared by reacting a bisphenol with an activated aromatic dihalide in a dipolar aprotic solvent in the presence of a base.[2a–g] The polymerization reaction proceeds by nucleophilic aromatic substitution via the stepwise formation of aryl ether linkages. An activated aromatic dihalide is used to ensure that the Meisenheimer complex intermediate, which is formed upon its reaction with the phenate salt, is sufficiently stabilized to allow for quantitative reaction.

In the last decade, the synthesis of poly(aryl ether)s has been extended to materials containing heterocyclic moieties. The incorporation of such functional groups leads to an enhanced T_g, increased thermooxidative stability, and improved mechanical and adhesive properties. Some examples of heterocyclic moieties which have been incorporated into poly(aryl ether)s are imide,[3–5] quinoxaline,[6–10] phthalazine,[11] isoquinoline,[12] imidazole,[13,14] 1,3,4-oxadiazole,[2a,15a,b] 1,2,4-triazole,[15a] pyrazole,[16,17] benzimidazole,[18] and benzoxazole.[19,20]

There are two synthetic strategies currently employed to introduce heterocyclic functionalities into poly(aryl ether)s. One method involves incorporating the heterocyclic moiety into the bisphenol, while another entails introducing it into the activated aromatic dihalide. The former usually yields poly(aryl ether)s of the general structure A, while the latter provides materials of the type B (Figure 1). In both cases, the synthetic strategy requires preparation of the heterocyclic monomer prior to its incorporation into a polymer.

From a synthetic viewpoint, it would be convenient to utilize a *general amorphous polymer precursor* from which a series of heterocyclic poly(aryl ether)s could be readily prepared. One example of such a material is an amorphous poly(aryl ether benzil). In this case, the benzil functionality could potentially be converted into triazine, quinoxaline, or imidazole moieties by reacting the polymer with the appropriate small molecule. *Such a precursor polymer would be particularly useful for the preparation of poly(aryl ether)s (type A or B) which contain heterocyclic functionalities that are not sufficiently robust to tolerate the polymerization reaction conditions or for the synthesis of polymers (type B) which contain heterocyclic functionalities that are only weakly activating and require stringent conditions for their preparation.* We recently described the synthesis of amorphous poly(aryl ether benzil)s from various bisphenols and 4,4′-difluorobenzil.[21] While polymer modification reactions are generally difficult to run without backbone cleavage, we have been able to convert poly(aryl ether benzil)s into a series of novel amorphous poly(aryl ether pyridyltriazine)s quantitatively and with no detectable backbone degradation.

Experimental Section

Materials. *N*-Methylpyrrolidinone (NMP; Aldrich), *N*-methylcaprolactam (NMC; Aldrich), and tetramethylene sulfone (sulfolane; Aldrich) were distilled under reduced pressure from calcium hydride prior to use and stored over 4 Å molecular sieves under nitrogen. *N*,*N*-Dimethylacetamide (DMAc) and 1,3-dimethyl-3,4,5,6-tetrahydro-2(1*H*)-pyrimidinone (DMPU) were used as obtained from Aldrich. Diphenyl sulfone (Aldrich) and 4,4′-dichlorodiphenyl sulfone (Ken Seika Corp.) were recrystallized from ethanol and dried under

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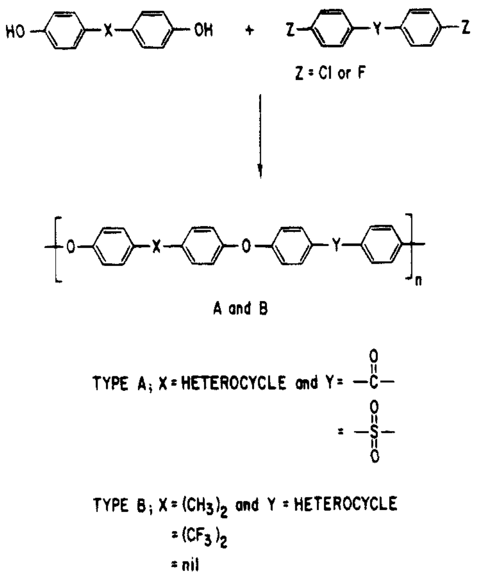


Figure 1. Poly(aryl ether)s of general structure type A and B.

vacuum (nitrogen bleed) for 48 h. Anhydrous potassium carbonate was ground into a fine powder and dried at 150 °C under vacuum (nitrogen bleed) for 48 h. Methanesulfonic acid, 48% aqueous hydrogen bromide, hydrazine monohydrate, 2-cyanopyridine, 3,5-di-*tert*-butylphenol, 4,4′-difluorodiphenyl sulfone, and 4,4′-isopropylidene diphenol were used as received from Aldrich. 4,4′-Dimethoxybenzil (APIN Chemical) was used as obtained. 4,4′-Difluorobenzophenone, 4,4′-biphenol, and 4,4′-(hexafluoroisopropylidene)diphenol were obtained in monomer-grade purity from Ken Seika Corp. Udel [poly(aryl ether sulfone)] was obtained from Scientific Polymer Products. 4,4′-Difluorobenzil[9] and 1,3-bis(4′-fluorobenzoyl)benzene[22] were prepared as described.

Characterization. The melting points of the monomers and the T_g's of the polymers were measured using a Seiko 220 DSC at a heating rate of 20 °C/min under a nitrogen (50 mL/min) atmosphere. The onset of the change in slope to the minimum of the endotherm peak was recorded as the T_m value, while T_g values were determined from the midpoint of the change in slope of the baseline. Weight loss data were obtained by dynamic heating using a Perkin-Elmer thermogravimetric analyzer (TGA; Model TGS-2) instrument at a heating rate of 10 °C/min under a nitrogen (50 mL/min) atmosphere, and the values reported are for 5% weight loss. Inherent viscosity (η_{inh}) data were obtained with a calibrated Ubbelohde viscometer. Measurements were made in NMP at 25 °C or in DMAc at 26.5 °C at 0.5 g/dL. A Haake immersion water heater (Model D8) was employed to control the bath temperature. ^{1}H-NMR and ^{13}C-NMR spectra were recorded at 250 MHz using a Bruker AF250 spectrometer in $CDCl_3$ or DMSO-d_6. Chemical shifts (δ) are reported relative to $(CH_3)_4Si$ as the internal standard. Microanalyses were obtained from Robertson Microlit Laboratories, Madison, NJ. Mechanical properties were evaluated on thin films using a Polymer Laboratories dynamic mechanical thermal analyzer (DMTA) in the bending mode at a heating rate of 5 °C/min and a frequency of 1 Hz.

Hückel Molecular Orbital Calculation. The reactivity difference is based on the calculated partial charge density (δ) at the carbon bearing the fluorine. The values were obtained using the Hückel Molecular Orbital (HMO) program (The Molecular Modelling System, Cambridge Scientific Computing Inc., 875 Massachusetts Ave., Suite 61, Cambridge, MA). The HMO program manual describes that the analyzes of the inputted structure (e.g., difluoride) are done by isolating the atoms that participate in the π-cloud and then inserting suitable atom and bond parameters into the Hückel matrix. The atom and bond parameters used were obtained from Table 3 of Streitwieser's *Molecular Orbital Theory for Organic Chemists* (Wiley: New York, 1961; p 135).

Synthesis. (2-Pyridyl)hydrazidine (2). 2-Cyanopyridine was reacted with an excess of hydrazine in ethanol according to the procedure of Case.[23] The crude product (52.4 g; 77% yield) was purified by recrystallization from toluene to give 42.7 g (63% yield) of white needles. ^{1}H-NMR (250 MHz, $CDCl_3$) δ 5.18 (bs, 4H), 7.33 (m, 1H), 7.76 (m, 1H), 8.1 (m, 1H), 8.58 (m, 1H). ^{13}C-NMR (250 MHz, $CDCl_3$) δ 119.25, 123.21, 135.87, 147.47, 147.56, 150.7.

3-(2′-Pyridyl)-5,6-bis(4′-fluorophenyl)-1,2,4-triazine (9). To a 1 L round bottom (rb) flask containing 14.7 g (59.8 mmol) of 4,4′-difluorobenzil (**8**) and 8.14 g (59.8 mmol) of (2-pyridyl)hydrazidine (**2**) was added 50 mL of NMP. The mixture was heated with stirring to 55 °C to give a clear golden-brown solution. After 1 h the temperature was increased to 85 °C and maintained at this temperature for 3 h. The solution was cooled to room temperature and was slowly poured into 700 mL of H_2O while stirring. The resulting precipitate was filtered, washed with H_2O and hexanes, and dried to give 19.75 g (95% yield) of a yellow solid. Recrystallization from toluene (2×) using activated charcoal gave 17.92 g (83% yield) of yellow crystals, mp = 179.2–180 °C. This dihalide could also be purified in high yield by sublimation at 180 °C under vacuum. ^{1}H-NMR (250 MHz, $CDCl_3$) δ 7.11 (m, 4H), 7.53 (qd, 1H, 1.2 Hz), 7.64 (m, 2H), 7.73 (m, 2H), 7.99 (td, 1H, 1.8 Hz), 8.73 (dt, 1H, 8.7 Hz, 1 Hz), 8.94 (m, 1H). Anal. Calcd for $C_{20}H_{12}N_4F_2$: C, 69.36; H, 3.49; N, 16.18; F, 10.97. Found: C, 69.38; H, 3.30; N, 15.94; F, 10.68.

3-(2′-Pyridyl)-5,6-bis(4′-methoxyphenyl)-1,2,4-triazine (4). To a 1 L rb flask containing 29.8 g (110.3 mmol) of 4,4′-dimethoxybenzil (**3**) and 15.0 g (144.1 mmol) of (2-pyridyl)hydrazidine (**2**) was added 70 mL of NMP. The mixture was stirred for 5 min, 1 mL of methanesulfonic acid was added, and the temperature was increased to 55 °C. After 4 h the temperature was reduced to 23 °C and the reaction mixture was stirred overnight. The contents were added very slowly to 2 L of H_2O, being rapidly stirred in a Waring blender. After filtration and drying, a light green gummy solid was obtained. Recrystallization (3×) from ethyl acetate (EtOAc; 350 mL) gave 19.4 g (48% yield) of yellow crystals, mp = 135–136 °C. ^{1}H-NMR (250 MHz, $CDCl_3$) δ 3.85 (d, 6H, 4 Hz), 6.89 (d, 2H, 9 Hz), 6.93 (d, 2H, 8.9 Hz), 7.51 (qd, 1H, 1.2 Hz), 7.63 (d, 2H, 8.9 Hz), 7.76 (d, 2H, 8.9 Hz), 7.97 (td, 1H, 1.8 Hz), 8.72 (dt, 1H, 7.93 Hz, 1 Hz), 8.95 (m, 1H).

3-(2′-Pyridyl)-5,6-bis(4′-hydroxyphenyl)-1,2,4-triazine (5). To a 500 mL rb flask containing 17 g (45.9 mmol) of **4** were added 100 mL of glacial acetic and 150 mL of 48% aqueous hydrogen bromide. The reaction mixture was heated to reflux and stirred overnight. When cooled, solids precipitated. The solution was neutralized with 3 N aqueous KOH until basic and then acidified with glacial acetic acid. The resulting precipitate was filtered and dried to give 15.2 g of a yellow solid. Recrystallization (2×) from DMAc (180 mL):H_2O (180 mL) gave 11.5 g (73% yield) of a bright yellow solid, mp = 289–290.4 °C. Anal. Calcd for $C_{20}H_{14}N_4O_2$: C, 70.16; H, 4.12; N, 16.36. Found: C, 70.03; H, 4.01; N, 16.18.

3-(2′-Pyridyl)-5,6-bis[4′-(3″,5″-di-*tert*-butylphenoxy)phenyl]-1,2,4-triazine (11). Typical Procedure. To a 100 mL two-neck rb flask equipped with a Dean–Stark trap, cold water condenser, nitrogen inlet, and thermometer were added 0.715 g (3.465 mmol) of 3,5–di-*tert*-butylphenol (**10**), 0.6 g (1.733 mmol) of difluoride **9**, 4 mL of toluene, 0.574 g (4.153 mmol) of anhydrous potassium carbonate, and 6.5 mL of NMP. This mixture was heated to reflux and toluene was removed carefully from the Dean–Stark trap until a temperature of 145–150 °C was reached. This dehydration temperature was maintained for 4 h. The temperature was increased to 160 °C. After 3 h, analysis of an aliquot of the reaction mixture using thin-layer chromatography on silica gel (TLC; 1:1 petroleum ether:EtOAc) indicated that the starting materials had been replaced completely by a new product. The mixture was cooled to 50 °C, poured into 250 mL of water, and neutralized with 1 N aqueous HCl. The organic layer was extracted with EtOAc (3 × 120 mL). The combined extracts were washed with brine (200 mL) and water (300 mL), dried over $MgSO_4$, filtered, and concentrated under reduced pressure to give a light brown solid. This was redissolved in a minimum amount of hot THF, cooled, and added dropwise to 300 mL of water, being stirred rapidly in a Waring blender. Filtration, drying, and purification by flash column chromatography (2:1 hexanes:EtOEt) on silica gel gave 1.13 g (91% yield) of **11** as a white solid, mp = 211–213 °C. ^{1}H-NMR (250 MHz, $CDCl_3$) δ 1.304 (s, 18H), 1.307 (s, 18H), 6.96 (m, 8H), 7.23 (m, 2H), 7.47 (m, 1H), 7.65 (d, 2H, 8.9 Hz), 7.73 (d, 2H, 8.9 Hz), 7.93 (td, 1H, 17 Hz), 8.71 (d, 1H, 7.9 Hz), 8.92 (m, 1H). ^{13}C-NMR (250 MHz, $CDCl_3$) δ 31.5, 34.98, 114.14, 114.22, 114.38, 117.51, 117.77, 118.13, 118.30, 124.02, 125.27, 129.31, 129.37, 131.05, 131.75, 137.04, 150.36, 152.90, 152.95, 155.11, 155.36, 155.48, 155.72, 159.68, 160.34, 161.61. Anal. Calcd for $C_{48}H_{54}N_4O_2$: C, 80.19; H, 7.57; N, 7.79; O, 4.45. Found: C, 80.32; H, 7.52; N, 7.73; O, 4.39.

Polymers 14 and 15 from 3-(2′-Pyridyl)-5,6-bis(4′-fluorophenyl)-1,2,4-triazine (9). Typical Procedure for the Synthesis of Polymer 14. To a two-neck 100 mL rb flask equiped with a Dean–Stark trap, cold water condenser, nitrogen inlet, and thermometer were added 0.645 g (3.46 mmol) of 4,4′-biphenol (**12**), 1.2 g (3.46 mmol) of difluoride **9**, 4 mL of chlorobenzene, 0.527 g (3.81 mmol) of anhydrous potassium carbonate, and 7.28 mL of *N*-methylcaprolactam. The resulting mixture was heated to reflux (~145 °C) while stirring. After 3–4 h of dehydration at 145–150 °C, the temperature was increased to 170 °C (1.5 h), 190 °C (16 h), and 200–205 °C (12 h). The solution was cooled to 155 °C, diluted with 5 mL of NMP, precipitated into methanol, filtered, and dried to give the light brown polymer **14**.

Poly(aryl ether benzil)s 16–19 from 4,4′-Difluorobenzil (8). These compounds were prepared as described previously.[21] IR (cm^{-1}; thin film of polymer **16**) 1670, 1603, 1581, 1502, 1477.

Poly(aryl ether pyridyltriazine)s 15 and 24–26 from Poly(aryl ether benzil)s 16–19 and (2-Pyridyl)hydrazidine (2). Two-Step Procedure: Step 1 (Formation of Intermediate 20). To a 250 mL rb flask containing 4.69 g (10.8 mmol) of polymer **16** and 2.94 g (21.6 mmol) of (2-pyridyl)hydradizine (**2**) was added 58.7 mL chlorobenzene, and the contents were stirred at 23 °C for 4 days. The polymer was then added slowly to 500 mL of EtOH, being rapidly stirred in a Waring blender. Filtration and washing with EtOH, H_2O, and EtOH gave the light yellow polymer intermediate **20**. η_{inh} = 0.53 dL/g. T_g = 211 °C. ^{13}C-NMR (250 MHz, $CDCl_3$) δ 30.98, 42.28, 117.36, 117.94, 118.28, 119.0, 119.78, 121.76, 125.02, 128.15, 128.28, 128.88, 130.54, 131.1, 131.52, 131.78, 136.34, 146.08, 146.24, 146.90, 147.05, 148.08, 150.06, 150.42, 153.07, 154.08, 155.98, 159.63, 160.18, 162.47, 197.53. IR (cm^{-1}; thin film) 1671, 1616, 1591, 1562, 1498, 1470.

Step 2 (Solution Cyclization of Polymer Intermediate 20 To Give Polymer 24). To a 25 mL rb flask equiped with a Dean–Stark trap, cold water condenser, and N_2 inlet were added 0.300 g of polymer **20**, 8 mL of chlorobenzene, and 2 mL of sulfolane. This solution was heated to reflux with stirring. After 5 h the solution was cooled and the resulting polymer was isolated as described above to give a light yellow fibrous polymer **24** (R = $C(CH_3)_2$). η_{inh} = 0.56 dL/g. T_g = 220 °C. ^{13}C-NMR (250 MHz, $CDCl_3$) δ 30.99, 42.27, 117.94, 118.16, 119.16, 119.25, 124.0, 125.29, 128.21, 129.78, 129.89, 131.08, 131.75, 136.99, 146.32, 146.52, 150.40, 152.92, 153.63, 153.86, 155.28, 155.59, 159.23, 160.17, 160.40. IR (cm^{-1}; thin film) 1595, 1500, 1388, 1365. Polymers **15**, **25**, and **26** were prepared as described above.

Polymer **15** (R = $(CF_3)_2$). η_{inh} = 0.64 dL/g. T_g = 224 °C. ^{13}C-NMR (250 MHz, $CDCl_3$) δ 63.84 (t, 118.4, 118.55, 119.03, 119.28, 121.87, 124.11, 125.43, 126.44, 128.37, 128.58, 130.83, 130.96, 131.32, 131.9, 137.05, 150.48, 152.78, 155.22, 155.51, 156.79, 157.01, 157.85, 158.77, 160.62.

Polymer **25** (R = $C(CH_3)Ph$). η_{inh} = 0.51 dL/g. T_g = 232 °C. ^{13}C-NMR (250 MHz, $CDCl_3$) δ 30.76, 51.78, 118.09, 118.33, 118.89, 119.01, 124.03, 125.3, 126.2, 128.02, 128.54, 129.94, 130.06, 130.16, 131.12, 131.78, 136.99, 144.72, 144.93, 148.76, 150.44, 152.95, 153.96, 154.19, 155.24, 155.57, 159.03, 159.98, 160.44.

Polymer **26** (R = fluorene). η_{inh} = 0.54 dL/g. T_g = 277 °C. ^{13}C-NMR (250 MHz, $CDCl_3$) δ 117.96, 118.19, 119.20, 120.23, 123.94, 125.26, 125.95, 127.6, 127.77, 129.5, 129.76, 130.98, 131.65, 136.95, 139.9, 141.4, 141.61, 150.33, 150.92, 152.75, 154.48, 154.70, 155.17, 155.46, 158.81, 159.76, 160.3.

One-Step Procedure. To a 50 mL rb flask containing 0.300 g (0.690 mmol) of polymer **16** (η_{inh} = 0.55 dL/g) was added 0.188 g (1.38 mmol; 2 equiv) of hydrazidine **2**, 7 mL of chlorobenzene, and 1.5 mL of sulfolane. The solution was stirred at 23 °C (1 h), at 40 °C (1 h), and finally at reflux (5 h). The solution became cloudy after 1 h at 23 °C and then became clear again after warming to 40 °C. The mixture was cooled and added dropwise to 2-propanol (~250 mL), being stirred rapidly in a Waring blender. Filtration and drying for 6 h at 80 °C under dynamic vacuum (nitrogen bleed) gave a yellow polymer (η_{inh} = 0.51 dL/g).

Thermal Thin-Film Cyclization of Polymer Intermediate 20 into Poly(aryl ether pyridyltriazine) 24. A thin film (0.100 mm) of polymer **20** was cast from $CHCl_3$ and cured in an oven (nitrogen bleed) under two conditions. Cure cycle A: 150 °C (1 h), 170 °C (1 h), 200 °C (1 h), and 250 °C (1.5 h). This was done under vacuum at −25 mmHg. Cure cycle B: 25 °C (1 h), then heated at 1 °C/min until 285 °C, and then held at 285 °C (15 min). This was done at atmospheric pressure.

Polymers 30–32 from 3-(2′-Pyridyl)-5,6-bis(4′-hydroxyphenyl)-1,2,4-triazine (5). Typical Procedure. To a two-neck 100 mL rb flask equiped with a Dean–Stark trap, cold water condenser, nitrogen inlet, and thermometer were added 0.9 g (2.629 mmol) of bisphenol **5**, 0.847 g (2.629 mmol) of 1,3-bis(4-fluorobenzoyl)benzene (**29**), 4 mL of chlorobenzene, 7 mL of *N*-methylcaprolactam, and 0.400 g (2.891 mmol) of anhydrous potassium carbonate. The resulting mixture was heated to reflux (150 °C) with stirring to give an orange solution. After 4 h of dehydration, the temperature was increased to 180 °C for 2 h and then to 195–200 °C for 17 h. When a small portion of the reaction mixture was added to excess methanol, high molecular weight polymer precipitated. The temperature was decreased to 155 °C, 4 mL of NMP was added to dilute the reaction, and the resulting polymer was precipitated by dropwise addition into 400 mL of rapidly stirred MeOH. Filtration and drying gave a quantitative yield of an off-white precipitate.

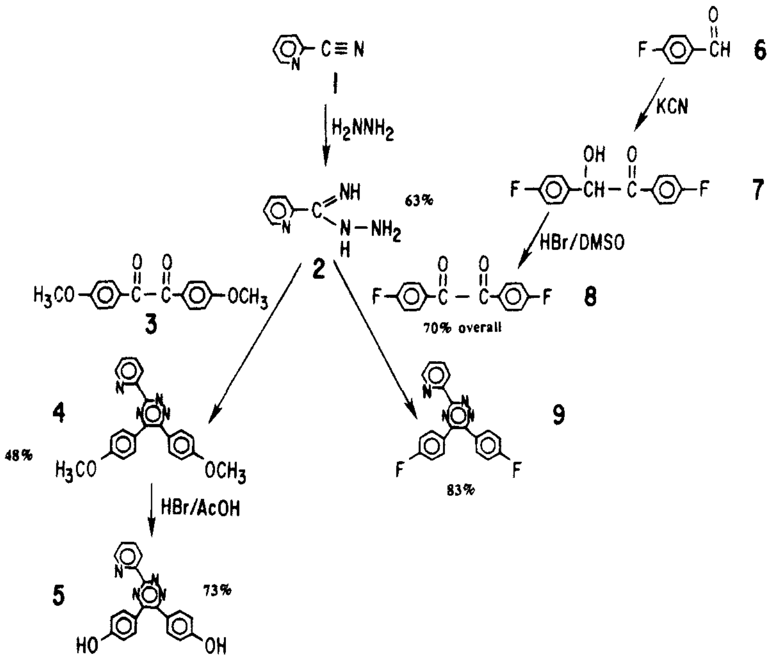
Solution Casting. Typical Procedure for the Preparation of Thin Films Used for Mechanical Testing. To 0.160 g of polymer **24** was added 1 mL of chloroform, and the mixture was stirred until homogeneous and clear. The solution was filtered, placed onto a glass plate, and then covered to ensure slow evaporation of the solvent. The resulting clear yellowish-gold film was placed in hot water until it could be removed. Subsequent drying at 150 °C (2 h) and 250 °C (1 h) under dynamic vacuum (nitrogen bleed) gave a tough creasable film.

Adhesion Measurements. Typical Procedure. To 0.500 g of polymer **16** was added 4–5 mL of $CHCl_3$, and the mixture was stirred until clear. Three to four drops of this solution was placed onto a glass plate and spread slowly using a doctor blade (adjusted to 0.075 mm thick). The solvent was allowed to evaporate overnight at room temperature, and the film was then heated to 100 °C (1 h), 150 °C (2 h), and 250 °C (2 h) under dynamic vacuum (nitrogen bleed) to give a clear film which was almost colorless. The resulting thickness as measured by Dectak was typically ~1 μm. The film was then covered with a mask and coated with a 0.010 mm layer of copper by electron beam evaporation (rate = ~35 Å/s). Adhesion measurements were made by removing (rate = 5 mm/min) copper strips (6 mm × 45 mm) at an angle of 90° using an Instron testing machine (Model 1123) at room temperature.

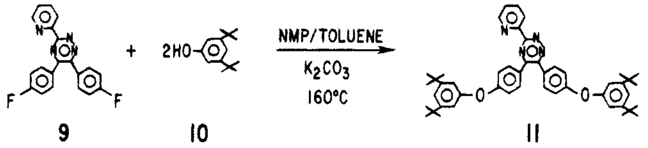
Results and Discussion

Monomer Synthesis. Bisphenol **5** and difluoride **9** were prepared in three and four steps, respectively, from readily available starting materials (Scheme 1). In both cases, (2-pyridyl)hydrazidine (**2**) was used to convert the benzil group into the 1,2,4-triazine functionality. The (2-pyridyl)hydrazidine (**2**) was synthesized from 2-cyanopyridine (**1**) using an excess of hydrazine monohy-

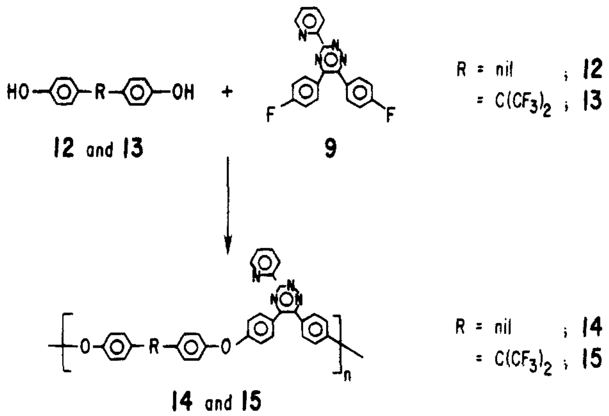
Scheme 1. Synthesis of Monomers 5 and 9



Scheme 2. Synthesis of Model Compound 11



Scheme 3. Synthesis of Poly(aryl ether pyridyltriazine)s 14 and 15

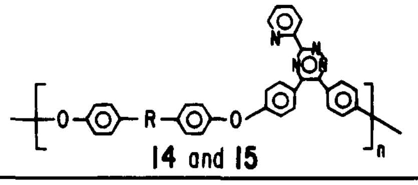


drate in ethanol as described by Case.[23] However, it was determined by careful monitoring of the reaction that the amount of hydrazine employed could be reduced from 6 to 3 equiv. Furthermore, the procedure for the isolation of **2** had to be modified to improve the isolated yield, since extraction with ether or EtOAc, after the addition of water, resulted in a low isolated crude yield (<50%), even though the reaction appeared to be quantitative as monitored by TLC. If the volume of the reaction mixture was reduced and the temperature decreased to 0 °C after completion of the reaction, most of **2** precipitated and could be isolated by filtration to give a substantially improved yield (63%). Presumably, this isolation technique was more efficient than extraction with an organic solvent, because a significant amount of **2** partitions in the aqueous layer due to its polarity. Bisphenol **5** was prepared by the stoichiometric condensation of **2** with 4,4′-dimethoxybenzil (**3**) in NMP at 85 °C (48% yield), followed by conversion of the methoxy groups to hydroxy using hydrogen bromide in acetic acid (73% yield; Scheme 1). Similarly, difluoride **9** was prepared by the stoichiometric reaction of **2** with 4,4′-difluorobenzil (**8**) in NMP at 85 °C (83% yield; Scheme 1). Presumably, 1,2,4-triazine ring formation proceeds more readily with difluoride **8**, because the carbonyl group is activated by the fluorine atoms, making the carbonyl carbon atoms more electrophilic.

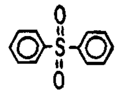
Model Compound Synthesis. To ensure that nucleophilic displacement of fluoride from dihalide **9** by a phenate anion proceeds quantitatively, a model reaction was run in NMP employing 1 equiv of **9** and exactly 2 equiv of 3,5-di-*tert*-butylphenol (**10**) in the presence of anhydrous potassium carbonate under standard conditions (Scheme 2).[2a-g] TLC indicated that complete conversion of **9** into **11** occurred within 3 h at 160 °C, after the mixture was dehydrated for 4 h at 145–150 °C. When this reaction was run at higher temperatures (205 °C) for prolonged reaction times (12 h) after dehydration at 150 °C, the starting materials were converted into four new products instead of one, as determined by TLC. Since simple phenol exchange would not lead to additional products, the result suggests that a side reaction at the heterocyclic functionality accompanies fluoride displacement at elevated temperatures.

Poly(aryl ether pyridyltriazine)s 14 and 15 from 3-(2′-Pyridyl)-5,6-bis(4′-fluorophenyl)-1,2,4-triazine (9). Biphenols **12** and **13** were reacted with the difluoride **9** (Scheme 3) using different solvents and reaction conditions in order to ascertain the optimum polymerization procedure (Table 1). Even though the difluoride **9** reacted quantitatively with 3,5-di-*tert*-butylphenol (**10**) to yield the disubstituted adduct **11** (Scheme 2), it was not possible to prepare high molecular weight poly(aryl ether pyridyltriazine)s under *similar* reaction conditions when **9** was reacted with biphenols **12** and **13**. In fact, reactions 1 and 2 (Table 1) show that when the polymerization temperature was less than 200 °C, only low molecular weight polymers were obtained (η_{inh} < 0.2 dL/g), even if long reaction times (12 h) were utilized. When polymerization temperatures were increased to 200 °C or above (reactions 3–8), significantly higher η_{inh} values were obtained; however, the increase in molecular weight was attributable in

Table 1. Properties of Poly(aryl ether pyridyltriazine)s 14 and 15



14 and 15

REACTION	R	POLYMER	SOLVENT	% SOLIDS	TEMP (°C)	TIME (h)	η_{inh}
1	nil	14	NMP	20	170	12	<0.15
2	"	14	DMPU	20	180	12	0.15
3	"	14	NMC	25	200	40	0.59
4	"	14	SULFOLANE	45	225	4	0.42[a]
5	"	14		25	235	18	0.36
6	$C(CF_3)_2$	15	SULFOLANE	45	225	3	0.58[a]
7	"	15	SULFOLANE	36	225 200	1 2	0.68[a,b]
8	"	15	NMC	25	200	24	<0.15

[a] Soluble portion of reaction mixture. [b] Used 1% excess of difluoride **9**.

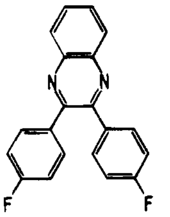
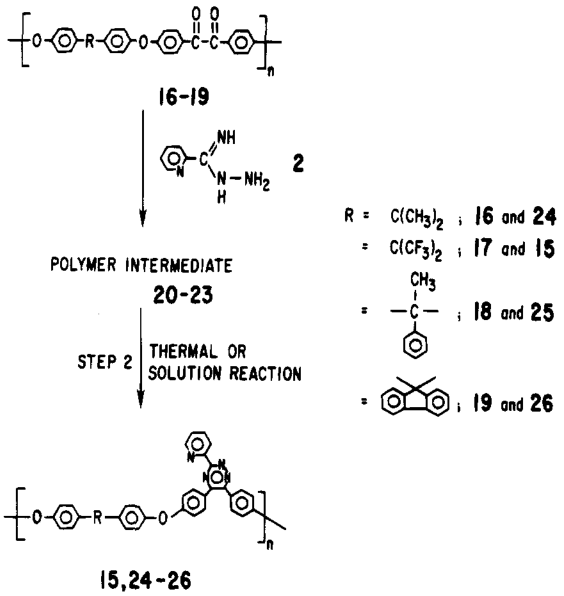


Figure 2. 2,3-Bis(4′-fluorophenyl)quinoxaline.

part to some cross-linking, since partial gel formation and precipitation occurred for some samples. This result was particularly noticeable for reactions 4, 6, and 7. For polymerizations run at 200 °C or above in sulfolane,[24] NMC, or diphenyl sulfone the ratio of the bisphenol to potassium carbonate was 1 to 1.1, respectively. To ensure that gel formation could indeed be attributed to cross-linking and not to the formation of very high moelcular weight polymer, which became insoluble, an end-capping polymerization was run using an imbalance in the stoichiometry of the difluoride **9** relative to the biphenol **13** (reaction 7; 1% excess of **9**). Under these conditions, the resulting polymer began to precipitate again at elevated temperatures as the reaction progressed and partial gel formation occurred. It has been shown that the difluoride 2,3-bis(4′-fluorophenyl)quinoxaline[9,10] (Figure 2) can be polymerized with various bisphenols to give high molecular weight poly(aryl ether quinoxaline)s under similar conditions. Since the difluoride **9** is of similar reactivity, a competing side reaction at elevated temperatures may explain the partial gel formation and polymer precipitation. One possible explanation for this behavior is that thermal decomposition and/or rearrangement of the triazine ring occurs. As was described, running the model reaction (Scheme 2) at elevated temperatures (e.g., 205 °C) for an extended time (12 h) seems to support this type of degradation, since simple ether exchange would not lead to the additional products observed by TLC.

Poly(aryl ether pyridyltriazine)s 15 and 24–26 from Poly(aryl ether benzil)s 16–19. Since it was difficult to prepare linear high molecular weight poly(aryl ether pyridyltriazine)s **14** and **15** directly from the difluoride **9** (Scheme 3) without cross-linking occurring, we decided to synthesize these materials by converting previously prepared poly(aryl ether benzil)s **16–19**[21] into poly(aryl ether pyridyltriazine)s by reaction with (2-pyridyl)hydrazidine (**2**) (Scheme 4). This approach would allow for readily accessible high molecular weight poly(aryl ether benzil)s to serve as potential precursors to various poly(aryl ether pyridyltriazine)s. To determine the optimum transformation conditions which would lead to quantitative conversion and to no detectable polymer chain cleavage, experiments were initially confined to using only poly(aryl ether benzil) **16**, in order to limit the number of variables. The transformation reaction was first run by converting the benzil group of polymer **16** into the stable polymer intermediate **20**,[25] using (2-pyridyl)hydrazidine (**2**). After isolation, polymer **20** was redissolved and cyclized to give the 1,2,4-triazine-containing polymer **24**.

Scheme 4. Synthesis of Polymer Intermediates 20–23 and Poly(aryl ether pyridyltriazine)s 15 and 24–26



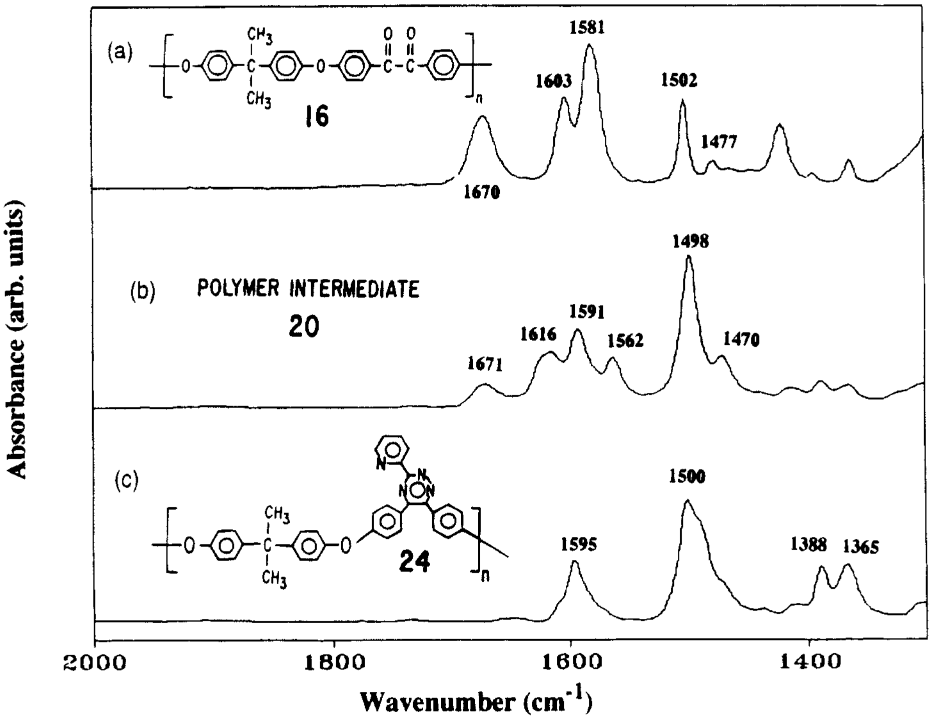


Figure 3. Infrared spectra of poly(aryl ether benzil) **16**, polymer intermediate **20**, and poly(aryl ether pyridyltriazine) **24**.

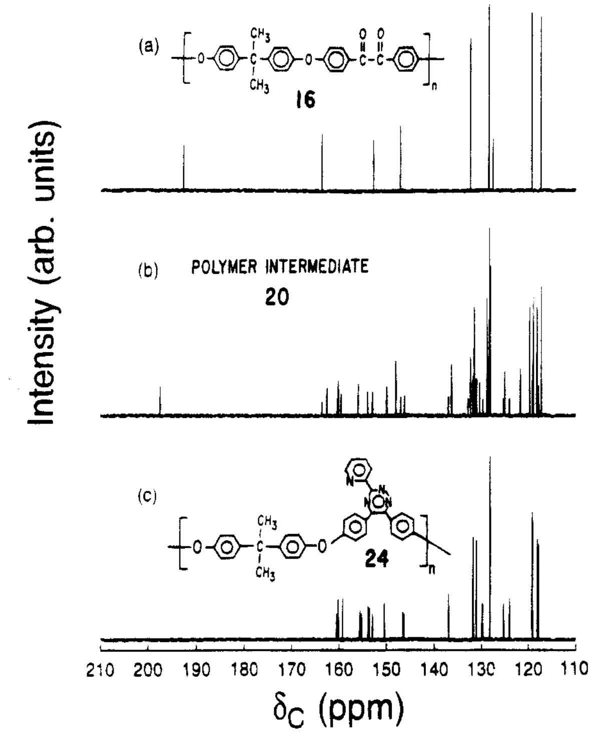


Figure 4. ^{13}C-NMR spectra of poly(aryl ether benzil) **16**, polymer intermediate **20**, and poly(aryl ether pyridyltriazine) **24**.

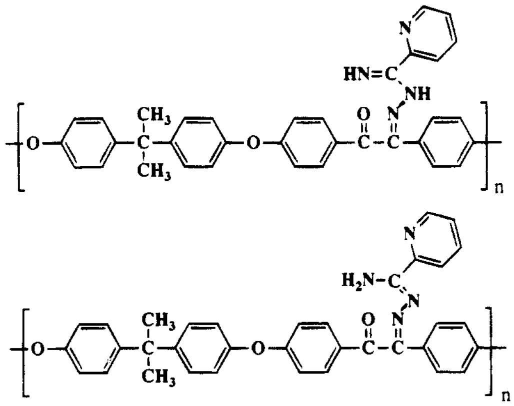
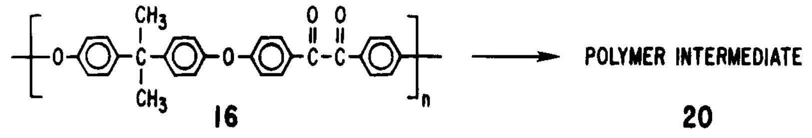


Figure 5. Possible structures of polymer intermediate **20**.

The infrared (IR) and ^{13}C-NMR spectra of polymers **16**, **20**, and **24** are shown in Figures 3 and 4. The IR spectra of polymers **16** and **24** are typical of materials which contain the benzil and 1,2,4-triazine functional groups and are very similar to those of the small molecules 4,4′-dimethoxybenzil[26] and 3-(2′-pyridyl)-5,6-diphenyl-1,2,4-triazine.[27] The ^{13}C-NMR spectra of polymers **16** and **24** contain resonances at positions attributable to a 4,4′-disubstituted benzil[28] and a substituted 3-(2′-pyridyl)-5,6-diphenyl-1,2,4-triazine,[29] respectively. In fact, the triaryltriazine portion of the spectrum of polymer **24** is almost identical to that of the triazine model compound **11** (Scheme 2). While the structure of polymer **20** has not been proven, it is reasonable to assume from the IR and the ^{13}C-NMR spectra that the (2-pyridyl)hydrazidine (**2**) reacts with polymer **16** to form one of the Schiff base tautomers depicted in Figure 5, since it has been established that amines react with benzils to give benzil monohydrazones.[30] Moreover, the ^{13}C-NMR of **20** appears to be remarkably clean. For this reason, ^{13}C-NMR was employed to follow the progress of the reaction from polymer **16**, to the intermediate **20**, and then to the desired poly(aryl ether pyridyltriazine) **24** by monitoring the formation and disappearance of certain distinctive peaks (e.g., 136.3, 137, 162.5, and 197.5 ppm). As is shown for the poly(aryl ether benzil) **16** (Figure 4), the carbonyl carbon peak at 192.8 ppm was replaced by a peak at 197.5 ppm when the intermediate **20** was formed, and when **20** was subsequently converted into the triazine polymer **24**, the peak at 197.5 ppm disappeared (along with peaks at 136.3, 137, and 162.5 ppm).

Table 2 summarizes the reaction conditions which were used to optimize the conversion of poly(aryl ether benzil) **16** into polymer intermediate **20**. Reactions 1–3 illustrate that at least 2 equiv of (2-pyridyl)hydrazidine (**2**) were required to fully transform all of the benzil

Table 2. Conversion of Poly(aryl ether benzil) 16 into Polymer Intermediate 20[a]

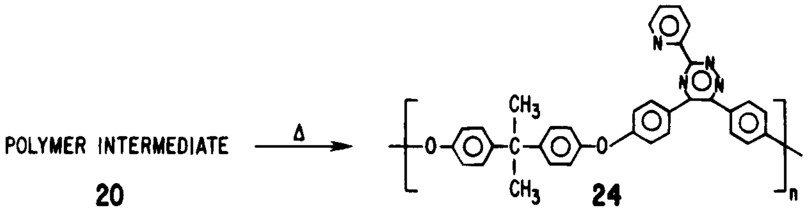


16 → 20

REACTION	REACTION TIME (h)	TEMP (°C)	EQUIV OF 2	SOLVENT	η_{inh}	T_g (°C)	CONVERSION TO 20
1	70	25	1	DMAc	0.39	-	INCOMPLETE
2	70	25	2	DMAc	0.39	-	COMPLETE
3	70	25	5	DMAc	0.40	-	COMPLETE
4	9	95	2	DMAc	0.28	-	COMPLETE
5	70	25	2	⌬-Cl	0.50	211	COMPLETE

[a] Poly(aryl ether benzil) **16**; η_{inh} = 0.55 dL/g.

Table 3. Conversion of Polymer Intermediate 20 into Poly(aryl ether pyridyltriazine) 24



20 → 24

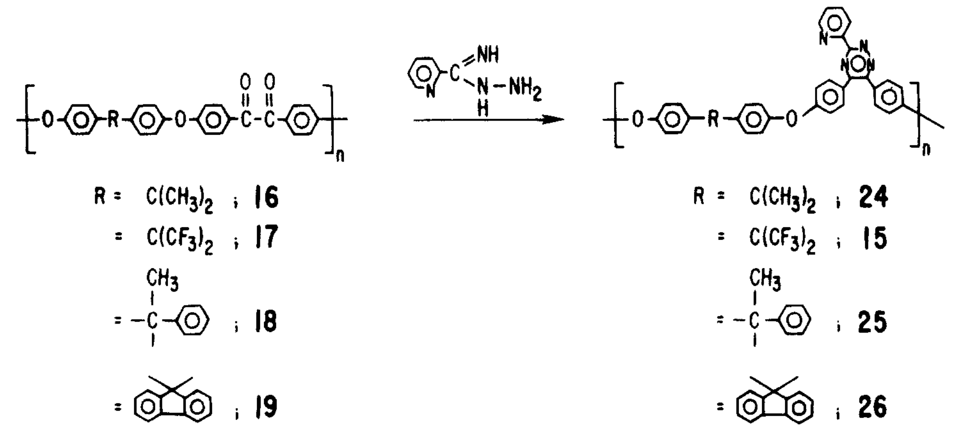
REACTION	REACTION TIME (h)	TEMP (°C)	EQUIV OF 2	SOLVENT	η_{inh}	CONVERSION TO TRIAZINE
1	3	95	-	⌬-Cl	0.59	INCOMPLETE
2	12	95	-	⌬-Cl	0.53	INCOMPLETE
3	3	REFLUX	-	⌬-Cl	0.60	INCOMPLETE
4	5	REFLUX	-	⌬-Cl/SULFOLANE	0.56	COMPLETE

groups into those of the polymer intermediate **20**. The η_{inh} results (Table 2), however, suggested a small amount of chain cleavage in DMAc at room temperature. Increasing the reaction temperature to 95 °C (reaction 4) further increased chain cleavage, confirming this result. Chain scission was almost eliminated, however, when a less polar solvent, chlorobenzene, was employed instead of DMAc (reaction 5). Table 3 outlines the conditions utilized for the solution transformation of polymer intermediate **20** into poly(aryl ether pyridyltriazine) **24**. Interestingly, the reaction progresses very slowly at 95 °C (reactions 1 and 2) with almost no conversion of **20** into **24**. When reflux temperatures were employed (reactions 3 and 4), to azeotrope out the water which was generated during the cyclization, the reaction proceeded quantitatively in 5 h with negligible chain cleavage.[31] However, some sulfolane was required as a cosolvent to completely solubilize the resulting triazine-containing polymer to ensure complete conversion. *Furthermore, it was determined that polymer* ***16*** *could be converted directly into* ***24*** *in one step (without isolating the intermediate) by employing the reaction solvent and conditions described in reaction 4, after initially reacting (2-pyridyl)hydrazidine (****2****) with polymer* ***16*** *under mild conditions [23 °C (1 h) and 40 °C (1 h)].*

Polymer intermediate **20** could also be converted into **24** using a solid-state transformation by first casting a film of **20** and then subsequently slowly heating from 25 to 285 °C to promote ring closure. The resulting films were clear, tough, and flexible; however, some voids were visible in some samples, possibly because water evolved too rapidly during the cyclization reaction, since the procedure was not optimized. Films of polymer **24** prepared in this manner could subsequently be redissolved in chloroform or NMP at room temperature.

The properties of the poly(aryl ether pyridyltriazine)s **15** and **24**–**26** are compiled in Table 4 and are compared to those of the poly(aryl ether benzil)s **16**–**19** prepared previously.[21] As is illustrated from the η_{inh} values and the thin-film properties, polymers **15** and **24**–**26** were all high molecular weight and formed clear flexible films. Polymer **24** could also be compression molded. The glass transition temperatures were higher in all cases for the 1,2,4-triazine-containing polymers (T_g = 220–277 °C), as compared to the parent benzil-containing materials (152–242 °C). This can be attributed to enhanced polymer backbone rigidity, due to a restricted degree of freedom. The thermooxidative stability, however, was lower by 50–100 °C (5% weight loss ~ 430–450 °C). The latter may be explained by the recent result of Chmil and Sherf,[32] who showed that when the functional group 3-methyl-5,6-diphenyl-1,2,4-triazine was incorporated into a polyarylene polymer,[28] it could be converted into diphenylacetylene (by the elimination of nitrogen and acetonitrile) via the well-known thermolytic decomposition reaction at ~400 °C.[33] A similar degradation pathway may be feasible in polymers **15**

Table 4. Comparison of Polymer Properties



POLYMER	η_{inh}	T_g (°C)	TGA (°C)	POLYMER	η_{inh}	T_g (°C)	TGA (°C)	DMTA	FILM CHARACTERISTICS	SOLUBILITY
16	0.58	152	515	**24**	0.56	220	445	227	CLEAR, GREENISH-YELLOW & FLEXIBLE	$CHCl_3$, THF, NMP
17	0.57	162	548	**15**	0.64	224	436	232	"	"
18	0.54	177	498	**25**	0.51	232	447	241	"	"
19	0.65	242	521	**26**	0.54	277	443	282	"	$CHCl_3$, NMP

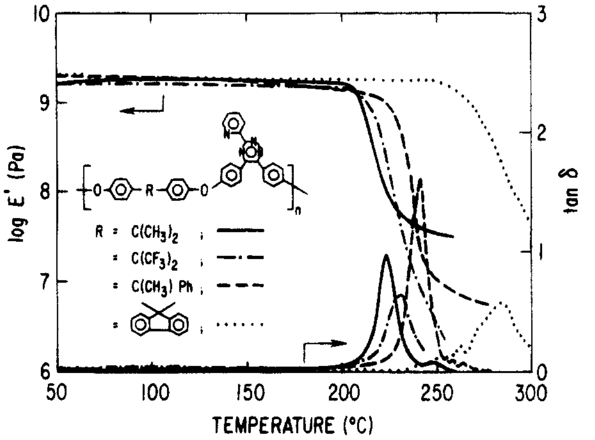
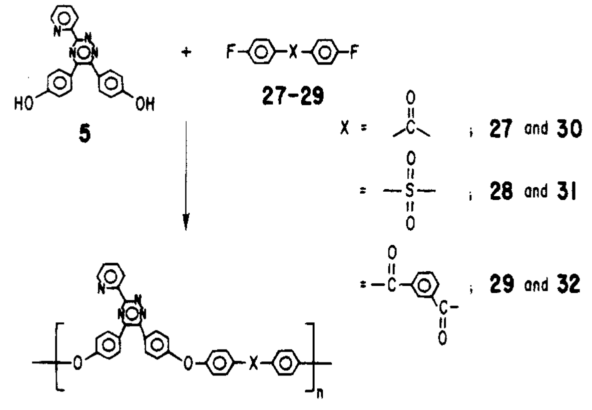


Figure 6. Dynamic thermal analysis of poly(aryl ether pyridyltriazine)s **15** and **24–26**.

and **24–26** with the evolution of nitrogen and 2-cyanopyridine. While polymers **15** and **24–26** were soluble in solvents such as $CHCl_3$, THF, and DMAc, they were less soluble than the corresponding poly(aryl ether benzil)s **16–19**. The mechanical properties of polymers **15** and **24–26** as obtained from thin-film (~0.100–0.140 mm) samples using DMTA are depicted in Figure 6. All of the polymers were robust and maintain Young's moduli typical of engineering thermoplastics to temperatures very close to their T_g's. Furthermore, the tan δ values obtained corresponded closely to the T_g values obtained from DSC.

Poly(aryl ether pyridyltriazine)s 30–32 from 3-(2′-Pyridyl)-5,6-bis(4′-hydroxyphenyl)-1,2,4-triazine (5). When bisphenol **5** was initially reacted with the most activated aromatic difluoride **29** of the series **27–29** (Scheme 5) under standard conditions[2a–g] using DMAc or NMP as the dipolar aprotic solvent and an excess of anhydrous potassium carbonate as the base, it was surprising that oligomers precipitated from the reaction mixture, since the *meta*-substituted difluoride **29** generally yields soluble poly(aryl ether ketone)s, even when rigid bisphenols are employed. Table 5 shows that when the polymerization reaction was run at a higher temperature (195 °C), employing *N*-methylcaprolactam (NMC) as the solvent, the solubility of the oligomers improved sufficiently to obtain high molecular weight polymer. It appeared, however, that the temperature and the solvent polarity were important parameters in allowing the polymerization reaction to proceed to completion, since high molecular weight polymer could not be prepared (η_{inh} = 0.24 dL/g) in diphenyl sulfone at 210 °C, even though the polymers were soluble.

Scheme 5. Synthesis of Poly(aryl ether pyridyltriazine)s 30–32

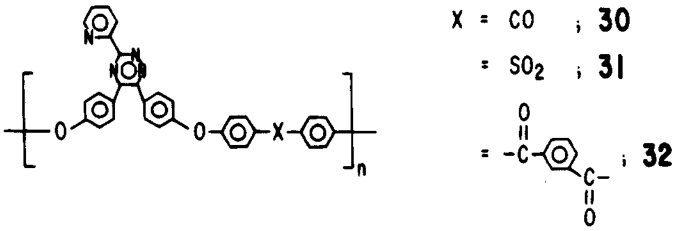


30-32

The reactivity of the dihalide (Figure 7) also seemed to be an important variable, since the more reactive ketone difluorides **27** (δ = 0.050)[9] and **29** (δ = 0.052)[34] yielded high molecular weight polymers, while the sulfone difluoride **33** (δ = 0.042)[9] did not, even though the polymer solubility appeared to be similar. Furthermore, if the less reactive dichloro analogue **33** (δ < 0.040)[34] of sulfone difluoride **28** was employed, reaction with bisphenol **5** yielded even lower molecular weight polymer with η_{inh} values of less than 0.15 dL/g.

Adhesion of Polymers to Copper. Compiled in Table 6 are the average peeling strength values (g/mm)

Table 5. Properties of Poly(aryl ether pyridyltriazine)s 30–32



POLYMER	POLYMERIZATION SOLVENT	TEMP (°C)	TIME	η_{inh}	T_g (°C)	TGA (°C)
30	NMC	195	15h	0.50	223	420 (-5%) 445 (-10%)
31	NMC	195	15h	0.30	265	-
32	NMC	195	15h	0.56	202	425 (-5%) 455 (-10%)

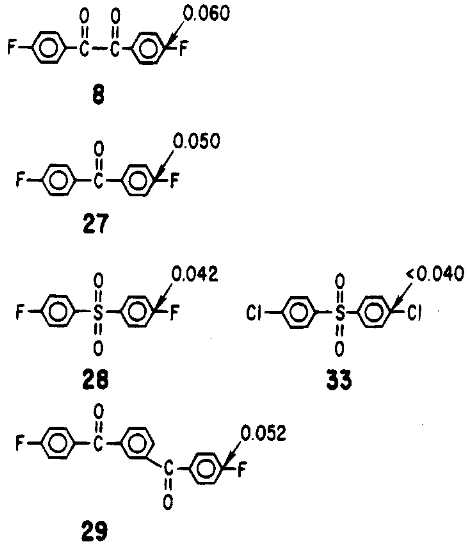
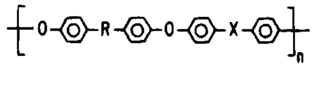
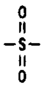
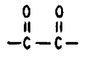
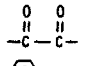


Figure 7. Hückel molecular orbital (HMO) charge density (δ) values.

Table 6. Average Peeling Strength Values for Polymers Udel, 16, 17, and 24



POLYMER	R	X	AVERAGE PEELING STRENGTH (g/mm)
Udel	$C(CH_3)_2$	 $-\mathrm{SO_2}-$	<1
16	$C(CH_3)_2$	 $-\mathrm{C(O)}-\mathrm{C(O)}-$	15.1 ± 1.2
17	$C(CF_3)_2$	 $-\mathrm{C(O)}-\mathrm{C(O)}-$	16.9 ± 2.7
24	$C(CH_3)_2$		36.7 ± 4.0

for polymer thin-film samples coated with a layer of copper metal (0.010 mm). The values correspond to the weight which had to be applied to peel a strip of copper from the polymer film using an Instron tensile testing machine.[35] Commercially available poly(aryl ether sulfone), Udel, was used as a control. As expected, Udel did not adhere to copper, since the sulfone functionality does not interact with the copper surface. When the sulfone group was replaced by dicarbonyl, poly(aryl ether benzil)s **16** and **17** exhibited significantly improved adhesion (16 g/mm), and when the dicarbonyl moiety was replaced with the pyridyltriazine group, the adhesion of polymer **24** was further improved to 37 g/mm.[36] While it has been shown that triazine groups adhere well to copper,[37] there should also be a substantial contribution in this case from the chelation of the bipyridyl portion of the pyridyltriazine group. Interestingly, the location of the 2-pyridine moiety at the 3-position of a 1,2,4-triazine ring system allows the bipyridyl group to be available for chelation from two conformations which are related by a 180° rotation (Figure 8).

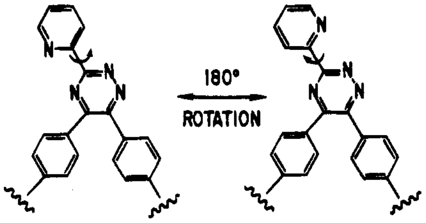
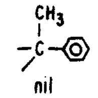
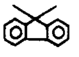
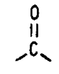
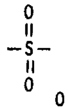
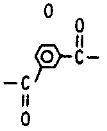


Figure 8.

Polymer Comparison. Table 7 provides a comparison of the T_g values for various poly(aryl ether benzil)s and their corresponding poly(aryl ether pyridyltriazine)s. While all of the 1,2,4-triazine-containing polymers appeared to be amorphous, as indicated by DSC, two of the benzil polymers, **34** and **35**, prepared previously[38] at very high temperatures, are substantially crystalline. These poly(aryl ether benzil)s exhibit poor solubility and would not be practical as potential precursors to heterocyclic-containing poly(aryl ether)s. Therefore, poly(aryl ether pyridyltriazine)s of the type **15** and **24–26** would be very difficult to prepare by this route. Poly(aryl ether benzil)s **16–19**, however, are amorphous and could be readily converted into **15** and **24–26**. Furthermore, **15** and **24–26** are only accessible by modification of the corresponding poly(aryl ether benzil)s, since the triazine-containing difluoride **9** (Scheme 1) undergoes side reactions which led to crosslinking. Moreover, 1,2,4-triazine-containing polymers such as **30** are only conveniently accessible from the bisphenol **5**, because the transformation of the diketone

Table 7. Polymer Comparison

R	POLYMER	η_{inh}	T_g (°C)	POLYMER	η_{inh}	T_g (°C)
$C(CH_3)_2$	16	0.58	157	24	0.56	220
$C(CF_3)_2$	17	0.57	162	15	0.64	224
	18	0.54	177	25	0.51	232
nil	34[a]	1.07	178(272)	14	0.59	230
	19	0.65	242	26	0.54	277
	35[a]	0.37	148(289)	30	0.50	223
	-	-	-	31	0.30	265
	-	-	-	32	0.56	202

[a] Reference 38.

moiety in the poorly soluble crystalline poly(aryl ether benzil) **35** to the (2-pyridyl)triazine group would also be very difficult.

Conclusions

Two new pyridyltriazine-containing monomers, 3-(2′-pyridyl)-5,6-bis(4′-hydroxyphenyl)-1,2,4-triazine and 3-(2′-pyridyl)-5,6-bis(4′-fluorophenyl)-1,2,4-triazine, have been synthesized from the readily available starting materials 4,4,′-dimethoxybenzil and 4,4′-difluorobenzil, respectively, by reaction with (2-pyridyl)hydrazidine. A series of novel linear high molecular weight poly(aryl ether pyridyltriazine)s were prepared by two different methods. The first involved polymerization of 3-(2′-pyridyl)-5,6-bis(4′-hydroxyphenyl)-1,2,4-triazine or 3-(2′-pyridyl)-5,6-bis(4′-fluorophenyl)-1,2,4-triazine with the corresponding activated aromatic difluoride or bisphenol, respectively. While reaction of the former was viable, reaction of the latter was not, due to partial cross-linking during the polymerization reaction at elevated temperatures. The second approach entailed converting various preformed amorphous poly(aryl ether benzil)s into poly(aryl ether pyridyltriazine)s using (2-pyridyl)-hydrazidine. Backbone cleavage was not detectable, and the reaction could be done in a "one-pot" synthesis. The polymers appear to be amorphous and exhibit T_g's and thermooxidative stabilities in the range 202−277 and 420−447 °C (5% weight loss), respectively. To our knowledge this is the first example of such a polymer modification reaction employing poly(aryl ether)s containing benzil groups. Since it can be done efficiently, it should be possible to use such *general amorphous polymer precursors* to prepare a variety of other heterocyclic (e.g., fluoro- or nitro-substituted quinoxaline, imidazole, phenylene, etc.) containing poly(aryl ether)s. This methodology should be particularly useful for preparing poly(aryl ether)s of type B (Figure 1), since many desirable materials of this type are simply not accessible using an activated aromatic difluoride if they contain functionalities which are *not sufficiently inert* (or stable) to withstand the polymerization reaction conditions or if they are *not sufficiently activating* to be converted into high molecular weight polymer in reactions with various bisphenols. Moreover, poly(aryl ether benzil)s are thermally stable and have a long shelf life. The poly(aryl ether pyridyltriazine) prepared from 4,4′-isopropylidenediphenol adheres well to copper as measured by an Instron peel test (37 g/mm). Finally, since these polymers are soluble, have high T_g's, are thermally stable, and can be synthesized readily in few steps, they may be useful as polymer supports for the preparation of thermally stable metal catalysts.[39,40]

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References and Notes

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