Solvent Effects on the Preparation of Novel Amorphous Poly(aryl ether benzil)s

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ABSTRACT: A synthetic approach for the preparation of amorphous poly(aryl ether benzil)s has been developed wherein the generation of the aryl ether linkage is the polymer-forming reaction. Fluoride atoms located at the *para*-position of the benzil moiety were found to be very activated toward nucleophilic aromatic substitution. Facile displacement occurred at these positions since the benzil moiety can accept the negative charge developed in the transition state through a Meisenheimer complex intermediate, analogous to a conventional activating group (i.e., benzophenone). Two synthetic approaches were surveyed to determine the most efficient manner to prepare high molecular weight polymer. The conventional potassium carbonate/dipolar aprotic solvent route was the most effective, but only if dimethyl sulfoxide (DMSO) or sulfolane was used as the solvent. Polymer chain cleavage after initial molecular weight buildup occurred if *N*-methylpyrrolidinone (NMP) or 1,3-dimethyl-3,4,5,6-tetrahydro-2(1*H*)-pyrimidinone (DMPU) was employed. The silylated bisphenol route in NMP containing a catalytic amount of cesium fluoride afforded high molecular weight polymers; however, long reaction times were required. The T_g's of the polymers ranged from 157 to 242 °C depending on the bisphenol utilized, and the thermal stability was comparable to that of other poly(aryl ether)s in air, with decomposition temperatures in the 500 °C range. All of the polymers prepared in DMSO or sulfolane were formed into tough flexible films by solution or melt processing.

Introduction

Poly(aryl ether)s are an important class of commercial polymers and are members of the family of materials referred to as engineering thermoplastics. The synthesis of poly(aryl ether)s usually involves reacting a bisphenol with an activated aryl halide (Figure 1) in a dipolar aprotic solvent in the presence of a weak base.[2] Conventionally, the activating group is an electron-withdrawing group such as a carbonyl (**1**) or a sulfone (**2**), since these functionalities increase the electrophilicity of the halide (e.g., fluorine) bearing carbon. In addition, these activating groups can lower the activation energy for fluorine displacement by stabilizing the Meisenheimer complex intermediate which is formed when the phenate anion attacks the aryl halide.

Several recent reports describing the use of new activating groups to facilitate nucleophilic aromatic substitution reactions in the synthesis of poly(aryl ether)s have appeared. Heterocycle (e.g., benzoxazoles, phenylquinoxaline, phthalazine, and isoquinoline), imide, amide, and azine activation have been utilized. For instance, benzazole activation[3] (**3**) of fluorophenyl groups was pursued as a general route to ether-based poly(aryl ether benzoxazole) and poly(aryl ether benzthiazole)s. The benzoxazole ring exerts a strong electron-withdrawing effect on the pendant fluorophenyl group, analogous to activated halophenyl ketones and sulfones, and as a result aryl halides in the *para*-position are most reactive toward nucleophilic displacement. Similarly, poly(aryl ether quinoxaline)s have been prepared by fluoride displacement of quinoxaline-activated moieties (**4** and **5**). In this case, the fluoride can be attached directly to the quinoxaline ring system[4] (**4**) or it can be situated at the *para*-position of a pendant phenyl group[5] (**5**). While both of these structures provide high molecular weight polymers, the

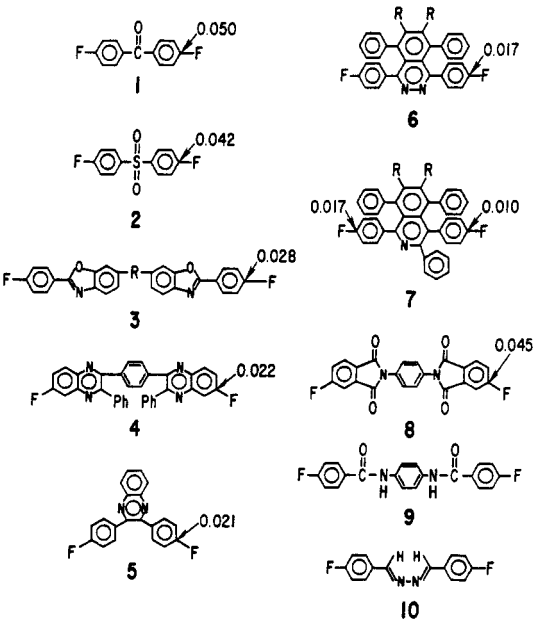

Figure 1. Hückel molecular orbital (HMO) charge density (δ) values for some activated difluorides which are known to form high molecular weight poly(aryl ether)s when reacted with bisphenols.

polymerization reaction of difluoride **4** is more facile, because stabilization via the Meisenheimer complex intermediate appears to occur more readily, since more energy is required to rotate the fluorophenyl group in **5** into an optimal coplanar conformation with the heterocyclic moiety. Poly(aryl ether phthalazine)s[6] and poly(aryl ether isoquinoline)s[7] have also been synthesized from phthalazine (**6**) and isoquinoline (**7**) activated difluorides. The reactivity behavior of **6** and **7** is similar to that of **5**, because the fluorine atom is located on a phenyl group which is pendant to the heterocycle activating group. Finally, it has been demonstrated that imides[8] (**8**), amides[9]

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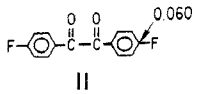


Figure 2. Calculated charge density (δ) value obtained for difluoride 11.

(9), and azines[10] (10) are also effective activating groups and that they provide a facile route to the corresponding poly(aryl ether)s. A unique feature of the poly(aryl ether phthalazine)s and poly(aryl ether isoquinoline)s is that they can be prepared from the same poly(aryl ether ketone) precursor by reaction with hydrazine or benzylamine, respectively. Similarly, it should be possible to transform the poly(aryl ether) derived from azine 10 into a high-temperature polymer analogue by employing an appropriate reactant.

There are two main methods currently employed to predict the potential reactivity behavior of activated aromatic difluorides toward phenoxides in nucleophilic aromatic substitution reactions. One method is computational and utilizes Hückel molecular orbital calculations (HMO)[11] to predict the partial positive charge density (δ) at the carbon bearing fluorine. As expected, the larger the value (δ), the higher is the reactivity. The other method is spectroscopic and involves using ^{1}H-NMR chemical shits of the hydrogens *ortho* to the electron-withdrawing group as an indicator of the activating potential.[12] In general, a downfield shift corresponds to an increase in the reactivity. It is important to realize that these two methods of determining reactivity only consider *inductive* effects of the activating group and do not take into account the extent to which the activating group stabilizes the Meisenheimer complex intermediate. Therefore, the magnitude of the change in the reactivity values obtained in this manner, relative to the actual change in the reactivity, is not linear. Figure 1 shows the calculated charge density (δ) at the carbon bearing fluorine for some of the difluorides which have been shown to be sufficiently reactive. Figures 2 and 3 show that, by applying the two techniques above, it was possible to predict that 4,4′-difluorobenzil (11) is even more activated than ketone and sulfone difluorides 1 and 2 and that it should be possible to incorporate it into a poly(aryl ether) even more readily.

It is of interest to survey the use of a benzil moiety as a possible activating group, since the introduction of such a group into a poly(aryl ether) would provide a *general polymer precursor* from which a series of heterocyclic poly(aryl ether)s could easily be prepared by a subsequent modification reaction. Such a precursor is particularly important for those heterocyclic (e.g., quinoxaline and triazine) containing materials where the formation of high molecular weight polymer is difficult because the heterocycle containing difluoride is weakly activating and as a result requires stringent polymerization conditions. Furthermore, poly(aryl ether)s of the type **5a** (Figure 4) would only be accessible by a modification reaction, since the difluoride analogue of 5 (Figure 1) containing a nitro group at the 5-position of the quinoxaline ring system would be displaced more readily by a phenate than could the fluorides located on the pendant phenyl rings.

Although there has been a report in the patent literature describing the preparation of crystalline poly(aryl ether benzil)s,[13] these materials required very high polymerization temperatures and were difficult to process from solution. In addition, other reports describing the use of a benzil activated nucleophilic aromatic substitution have focused on nitro displacement to prepare bis(α-dicarbonyl) compounds as monomers for poly(phenylquinoxaline) syntheses.[14] In this paper, the use of a benzil activated fluoro-displacement reaction will be discussed as a means of preparing high molecular weight, amorphous, poly(aryl ether benzil)s under mild conditions (e.g., ~150 °C) and short reaction times (1–2 h) using dipolar aprotic solvents.

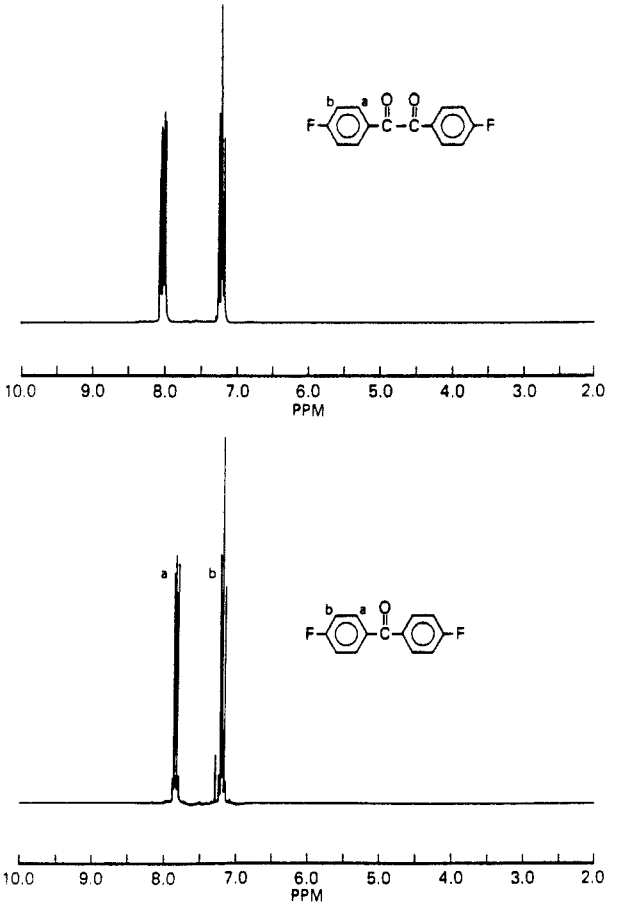
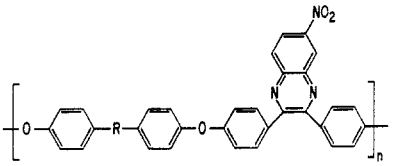


Figure 3. ^{1}H-NMR of difluorides 1 and 11.



5a

Figure 4.

Experimental Section

Characterization. The melting points (T_m) of the monomers and the glass transition temperatures (T_g) of the polymers were measured using a Seiko 220 DSC instrument 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 (heating rate = 10 °C/min), while T_g values were taken from the midpoint of the change in slope of the base line (heating rate = 20 °C). Weight loss data were obtained using a Perkin-Elmer thermogravimetric analyzer (TGA; Model TGS-2) instrument at a heating rate of 10 °C/min in air (50 mL/min). Inherent viscosity (η_{inh}) values were obtained in DMAc (26.5 °C; 0.5 g/dL) with a calibrated Ubbelohde viscometer. A Haake D8 immersion water heater 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 $CDCl_3$. Chemical shifts (δ) are reported relative to $(CH_3)_4Si$ as the internal standard. Microanalyses were obtained from Robertson Microlit Laboratories Inc., Madison, NJ. Mechanical properties were evaluated using thin films of each polymer employing a Polymer Laboratories dynamic mechanical thermal analyzer (DMTA) in the bending mode with a heating rate of 5 °C/min at a frequency of 1 Hz.

Materials. *N,N*-Dimethylacetamide (DMAc; anhydrous, 99+%; packaged under nitrogen in Sure/Seal bottles; Aldrich), 1,3-dimethyl-3,4,5,6-tetrahydro-2(*1H*)-pyrimidinone (DMPU; 99%; Aldrich), and *N*-methylpyrrolidinone (NMP; anhydrous, 99+%; packaged under nitrogen in Sure/Seal bottles; Aldrich) were used as obtained. When higher purity NMP was required, it was stirred with phosphorus pentoxide (P_2O_5) under a nitrogen atmosphere and then distilled under vacuum and stored in a round-bottom flask sealed with a rubber septum. Tetramethylene sulfone (sulfolane; Aldrich) was distilled under reduced pressure. Anhydrous potassium carbonate (Baker) was ground into a fine powder and dried under reduced pressure at 150 °C for 48 h. 3,5-Di-*tert*-butylphenol, 4,4'-difluorodiphenyl sulfone, and 4,4'-(isopropylidene)diphenol were used as obtained from Aldrich Chemical Co. 4,4'-Difluorobenzophenone, 4,4'-biphenol, and 4,4'-(hexafluoroisopropylidene)diphenol were obtained in monomer grade purity from the Ken Seika Corp. 4,4'-Difluorobenzil[5a] was prepared as described previously or purchased from Aldrich. Careful purification by refluxing in ethanol containing activated charcoal (15 min), followed by filtration, recrystallization (2×) from ethanol, and drying at 50 °C under vacuum, gave long light yellow needles; mp = 119.3–120.1 °C. *p*-Benzoquinone (98%; Aldrich) was recrystallized from 95% ethanol and dried under vacuum. Dimethyl(trimethylsilyl)amine was purchased from Petrarch and used without further purification. Cesium fluoride (Aldrich) was heated to 180 °C for 24 h under vacuum prior to use. The bisphenols were silylated with dimethyl(trimethylsilyl)-amine in toluene at 80 °C for 48 h and were purified by distillation.

Synthesis of Model Compound 13. To a 100 mL round-bottom flask equipped with a Dean–Stark trap, condenser, nitrogen inlet, and thermometer was added 0.7 g (2.843 mmol) of 4,4'-difluorobenzil, 1.17 g (5.686 mmol) of 3,5-di-*tert*-butylphenol, 6 mL of toluene, 9.37 mL of DMAc, and 0.471 g (3.408 mmol) of anhydrous potassium carbonate. The resulting mixture was warmed to reflux and toluene removed until the temperature reached 130 °C. After 1.5 h the temperature was increased to 140 °C for 1 h and then 145 °C for 1.5 h. TLC (hexanes:EtOAc, 10:1) indicated that the starting materials (3,5-di-*tert*-butylphenol, R_f = 0.29; 4,4'-difluorobenzil, R_f = 0.35) were completely replaced by the desired disubstituted product (R_f = 0.5). The dark yellow solution was cooled to room temperature and added dropwise to 200 mL of H_2O. The organic layer was extracted with ethyl acetate (EtOAc) (4 × 400 mL). The combined extracts were washed with brine (400 mL) and H_2O (400 mL), dried over $MgSO_4$, filtered, and concentrated to give 1.61 g (yield of crude = 91%) of a white solid. Recrystallization (2×) from ethanol:DMAc (~2:1, respectively) gave white crystals; mp = 155.6–156.7 °C. ^{1}H-NMR ($CDCl_3$): δ 0.52 (s, 36H), 6.13 (s, 4H), 6.21 (d, 6.94 Hz, 4H), 6.49 (s, 2H), 7.15 (d, 6.95 Hz, 4H). Elem anal. Calcd for $C_{42}H_{50}O_4$: C, 81.51; H, 8.14; O, 10.34. Found: C, 81.28; H, 8.42; O, 10.23.

Synthesis of Polymers 16a–d. Typical procedure: To a two-neck round-bottom flask equipped with a Dean–Stark trap, cold water condenser, thermometer, and nitrogen inlet was added 7.417 g (32.489 mmol) of 4,4'-(isopropylidene)biphenol, 8 g (32.489 mmol) of 4,4'-difluorobenzil, 40 mL of toluene, 5.16 g (37.334 mmol) of anhydrous potassium carbonate, and 85.7 mL of sulfolane. This mixture was heated to reflux, and toluene was removed until the temperature reached 135 °C. The temperature was slowly increased to 150 °C over 3 h, then to 155 °C (1 h), and to 160 °C for another hour. The resulting dark yellow viscous solution was cooled to 130 °C, diluted with 40 mL of NMP, and filtered immediately. The resulting solution was precipitated slowly into 3 L of isopropyl alcohol being stirred rapidly in a Waring blender. The light yellow fibrous polymer was filtered, washed with 1 L of isopropyl alcohol, and dried at 80 °C under vacuum for 2 h. To ensure complete removal of residual sulfolane, the polymer was redissolved in 100–150 mL of THF and twice reprecipitated into isopropyl alcohol. Subsequent drying at 100 °C under vacuum for 12 h gave a light yellow fibrous polymer. η_{inh} = 0.55 dL/g. ^{1}H-NMR (250 MHz, $CDCl_3$): δ 1.724 (s, 6H), 7.00 (d, 4H, 7.6 Hz), 7.03 (d, 4H, 7.6 Hz), 7.28 (d, 4H, 8.8 Hz), 7.95 (d, 4H, 8.8 Hz). ^{13}C-NMR (250 MHz, $CDCl_3$): δ 30.98, 42.46, 117.51, 119.94, 127.59, 128.44, 132.33, 147.23, 152.82, 163.61, 192.8.

The synthesis of polymer **16a** (Table 3) done in the presence of a free radical scavenger was run using the following amounts of reagents: 1 g (4.381 mmol) of 4,4'-(isopropylidene)biphenol, 1.079 g (4.381 mmol) of 4,4'-difluorobenzil, ~7 mL of toluene, 0.726 g (5.253 mmol) of anhydrous potassium carbonate, 10.4 mL of NMP, and 0.010 g (~0.5% by weight relative to the monomers) of *p*-benzoquinone.

Synthesis of Polymers 18a, 18b, and 18d. Alternatively poly(aryl ether benzil)s were prepared form 4,4'-difluorobenzil and silylated bisphenols in a dipolar aprotic solvent containing a catalytic amount of CsF according to literature procedure.[18] Typical procedure: To a three-neck round-bottom flask equipped with a nitrogen inlet, Dean–Stark trap, condenser, and thermometer was added 1.505 g (6.112 mmol) of 4,4'-difluorobenzil and 2.937 g (6.112 mmol) of silylated bisphenol AF and CsF. The contents were carefully rinsed into the reaction flask with 11 mL of NMP and 11 mL of CHP. The reaction mixture was slowly heated to 170 °C to effect the polymerization. A significant viscosity buildup was observed in 24 h, and the polymerizations were terminated after 48 h to ensure complete conversion. The polymerization mixture was precipitated into water, rinsed with methanol, and dried under vacuum for 24 h at 80 °C.

Films from Solution Casting. Typical procedure for polymers **16c** (R = $C(CH_3)Ph$) and **16d** (R = fluorene): 0.160 g of polymer **16c** was added to 1 mL of chloroform (or DMAc), and the mixture was stirred until homogeneous and clear. The solution was filtered, placed onto a glass plate, and then covered to allow for slow evaporation of the solvent. The resulting clear yellow–gold film was removed from the glass by immersion in hot water. Subsequent drying at 150 °C (2 h) and 250 °C (1 h) under dynamic vacuum (with a nitrogen bleed) gave a tough creasable film.

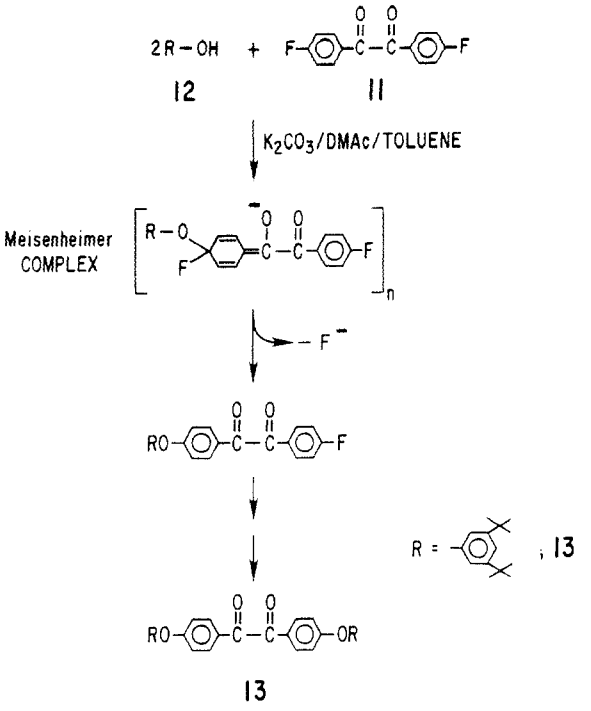
Films from Compression Molding. Typical procedure for polymers **16a** (R = $C(CH_3)_2$) and **16b** (R = $CF_3)_2$): 0.120 g of polymer was heated to 230 °C in a Carver press (Model C), and a pressure of 2000 psi was applied. The sample was cooled to 80 °C and removed to give a clear creasable yellow film (0.170 mm).

Results and Discussion

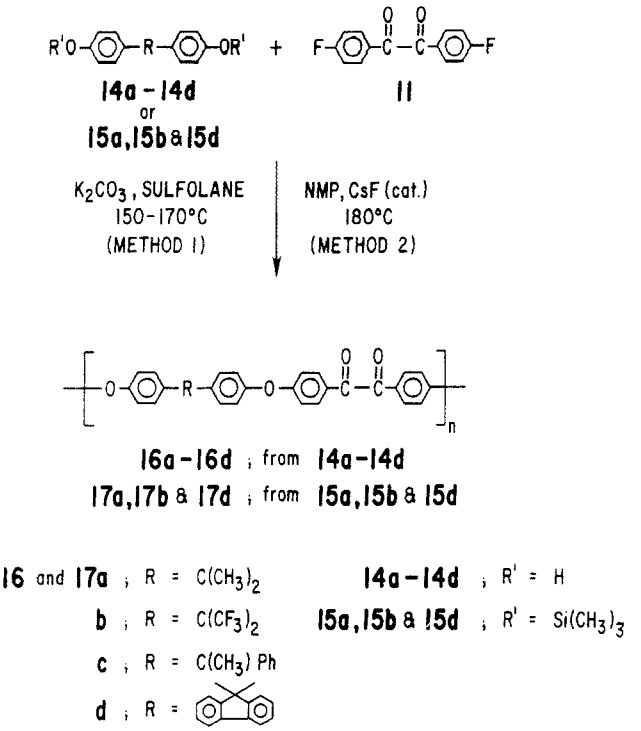
The rationale for choosing 4,4'-difluorobenzil (**11**) as the activated difluoride in nucleophilic aromatic substitution reactions with various bisphenols functioning as nucleophiles was essentially threefold. First, HMO calculations (Figure 2) show that the dicarbonyl group is one of the most powerful carbonyl activating groups, and as a result it dramatically increases the reactivity of the fluorobenzene group toward fluoride displacement by a nucleophile. Second, the benzil moiety can stabilize the negative charge developed upon attack of the phenate anion, through a Meisenheimer complex intermediate, which allows the transformation to proceed with a lower activation energy, analogous to conventional ketone and sulfone activating groups. Third, the incorporation of a dicarbonyl functionality into a poly(aryl ether) gives a *general precursor polymer* which can be converted into a series of different heterocyclic functionalities.

Figure 3 shows and compares the ^{1}H-NMR spectra of 4,4'-difluorobenzil (**11**) and 4,4'-difluorobenzophenone (**1**). If the chemical shifts of the protons *ortho* to the activating group are compared, it is evident that the protons appear 0.3 ppm further downfield for **11**, since they are more deshielded. This suggests that the dicarbonyl moiety is a stronger activating group. Furthermore, we found that when **11** was reacted with 2 equiv of the substituted 3,5-di-*tert*-butylphenol (**12**), in a model reaction (Scheme 1), the fluorines were displaced quantitatively in DMAc in 4 h, as the temperature was gradually increased from 130 to 145 °C to yield the disubstituted product **13**. The enhanced reactivity of the benzil versus the benzophenone structure presents some benefits and some potential problems. The nucleophilic aromatic substitution reaction on 4,4'-difluorobenzil is more facile than that on 4,4'-difluorobenzophenone as the 1,2-dicarbonyl group appears to be more activating than the single carbonyl group. On

Scheme 1



Scheme 2

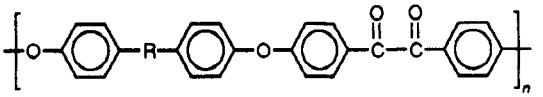


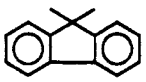
the other hand, other reactions on the benzil 1,2-dicarbonyl group proceed more readily than comparable reactions on the carbonyl of benzophenone. For example, hydroxide reacts with 1,2-dicarbonyl compounds, including benzil, to give benzilic acid (diphenylglycolic acid) via the benzilic acid rearrangement.[15] Furthermore, alkoxides also react with 1,2-dicarbonyl groups to give the corresponding esters of benzilic acid via the benzilic ester rearrangement or a Meerwein–Ponndorf–Verley–Oppenauer (MPVO) reaction in which the benzil is reduced to benzoin and the alcohol is oxidized.[16,17] Fortunately, for the present purpose of polymer formation, the phenoxide anion has little or no reactivity in these rearrangement reactions, since phenoxide reacts so rapidly with the aryl fluoride portion of 11 that the rearrangement reaction with the dicarbonyl group does not appear to occur.

Synthesis of Polymers. Two synthetic routes were evaluated as a means of preparing high molecular weight poly(aryl ether benzil)s; the conventional potassium carbonate/dipolar aprotic solvent route and the method of Kricheldorf,[18] which involves using a silylated bisphenol in a dipolar aprotic solvent and a catalytic amount of CsF. In both cases, nucleophilic aromatic substitution polymerizations were run using a high-boiling dipolar aprotic solvent which contains the activated aryl fluoride and the bisphenol (or silylated bisphenol) in the presence of a base (e.g., potassium carbonate) or another suitable reagent (e.g., cesium fluoride) to generate phenoxide anion *in situ*, at elevated temperatures (155–170 °C). Hydrolytic side reactions with the activated aryl fluoride did not occur in either case, since potassium carbonate is a weak base and the fluoride anion of cesium fluoride is expelled as trimethylsilyl fluoride, and as a result, the generation of the phenoxide anion and polymerization can proceed simultaneously. Dipolar aprotic solvents were used because they effectively dissolve the monomers and solvate the cation which further activates the phenate anion by making it more nucleophilic. They also dissolve the oligomeric polar intermediates which are initially formed in a step growth polymerization and allow reaction to proceed to give high molecular weight polymer. In addition, it is essential that the intermediate to high molecular weight polymer chains are completely soluble to ensure equilibration of chain length in order to provide a polymer with a narrow molecular weight distribution. The solids compositions were maintained at about 20%, which is typical for most poly(aryl ether) syntheses, thereby avoiding side reactions with the fluoride ion by decreasing its solubility[19] and thereby reducing the possibility of polymer cyclic formation. Irrespective of the polymerization solvent(s), toluene was used as a cosolvent to remove water generated by phenoxide formation as a toluene/water azeotrope. The solvent mixtures initially refluxed at about 130–135 °C and could be increased by the incremental removal of toluene to achieve the desired higher temperatures. After bisphenoxide formation and dehydration, the polymerization reactions were typically heated incrementally to ~150 or to 170 °C, depending on the method used to ensure equilibration of polymer chain length even though, in many instances, high molecular weight polymer was already attained as judged by the dramatic increase in viscosity.

Effect of Solvent on the Synthesis of Polymers Using K_2CO_3 as the Base. In this study, high-purity commercial DMAc and NMP were initially utilized as the dipolar aprotic solvents, and the polymerizations were run using an excess of anhydrous potassium carbonate as the base (Scheme 2). Reactions 1, 4, and 10 in Table 1 illustrate that DMAc does not sufficiently solvate the resulting polymer as the molecular weight increases, and as a result the polymers **16a**, **16b**, and **16d** partially precipitate from the *yellow* solution after a few hours. The polymers do not redissolve if the reaction was allowed to proceed overnight at 155 °C, and therefore they are only of intermediate molecular weight, as judged by inherent viscosity (η_{inh}) values in the range 0.25–0.33. Furthermore, if reaction 4 was repeated by progressively diluting with DMAc, as the molecular weight increased (reaction 5, Table 1) and the polymer became less soluble, the highest η_{inh} obtained was 0.34. When NMP (reactions 2, 6, and 12; Table 1) or DMPU (reactions 8 and 11) were used, the solubility was greatly enhanced to give homogeneous polymerization reaction mixtures; however, high molecular weight polymer could not be obtained when reactions were run for 6–9 h at ~160–170 °C. Furthermore, intense *green*

Table 1. Polymers 16a–d Prepared by Method I Using Bisphenols and Anhydrous Potassium Carbonate in Different Dipolar Aprotic Solvents



polymer	R	Reaction	polymn solvent	temp (°C)	time (h)[a]	η_{inh}	T_g (°C)	TGA (°C) (−5%)	DMTA (tan δ)	solubility
16a		1	DMAc	155	15	0.33[c]				
		2	NMP	160–170	6	0.43				
		3	sulfolane	155	5	0.58	157	515	171	$CHCl_3$, THF
16b		4	DMAc	155	9	0.25[c]				
		5	DMAc	155	5	0.34[b]				
		6	NMP	160–170	6	<0.20				
		7	sulfolane	155	5	0.57	162	548	174	$CHCl_3$, THF
16c		8	DMPU	160	9	<0.15				
		9	sulfolane	155	4.5	0.54	177	498	191	$CHCl_3$, THF
16d		10	DMAc	140	5	0.31[c]				
		11	DMPU	160	9	<0.20				
		12	NMP	160–170	6	<0.20				
		13	sulfolane	160–170	4.5	0.65	242	521	250	$CHCl_3$, DMAc

[a] Reaction times include 1–2 h of dehydration at 135–140 °C. [b] Diluted with DMAc progressively from 18% to 10% solids as the molecular weight increased and the polymer began to precipitate. [c] Soluble portion of the polymerization mixture.

colors developed after 0.5–1 h of reaction in NMP and DMPU. Alternatively, polymerizations run in tetramethylene sulfone (sulfolane) showed markedly different behavior. Polymerization of the difluoride monomer 11 with bisphenols **14a–d** was successfully carried out in sulfolane (reactions 3, 7, 9, and 13) in the presence of anhydrous potassium carbonate at 155–170 °C. This general procedure allowed for high molecular weight polymers to be prepared readily, as indicated by the η_{inh} values, which were in the range 0.54–0.65, and the ability to form tough, creasable films. In sulfolane under these conditions the color of the polymerization mixture remained *yellow*, as was the case for DMAc.

The glass transition temperatures (T_g) of these high molecular weight polymers ranged from 157 to 242 °C depending on the bisphenol used in the synthesis, and no evidence of crystallinity was observed by calorimetry measurements in any of the polymers. The thermal stability of the poly(aryl ether benzil)s was assessed by the weight loss in a variable temperature thermogram. The temperature for 5% weight loss (air) ranged from 498 to 548 °C depending on the bisphenol used in the synthesis and the end groups present in the resulting polymer.

These materials could be fabricated from solution or the melt (i.e., compression molding) to yield films which were clear, yellow, tough, and creasable. Films of **16a–c** could be readily redissolved after processing in common organic solvents such as $CHCl_3$ and THF.

Dynamic mechanical analysis of the poly(aryl ether benzil)s **16a–d** (Figure 5) illustrates that the polymers maintain structural integrity to temperatures close to their respective T_g's, and the tan δ values closely resemble the T_g's obtained from differential scanning calorimetry (DSC).

Effect of NMP on the Synthesis of Polymers Using Silylated Bisphenols and CsF. An alternative synthetic approach to prepare poly(aryl ether benzil)s in NMP involved polymerizing silylated bisphenols **15a**, **15b**, and **15d**, instead of bisphenols **14a–d**, with 4,4′-difluorobenzil (11), in the presence of a catalytic amount of cesium fluoride (CsF) (Scheme 2). In contrast to the conventional method described by Kricheldorf and co-workers,[18] which involves running the polymerizations in the melt, NMP was employed as the reaction medium since reduced reaction mixture viscosities and milder temperatures are realized. The solids compositions of the polymerization reaction mixtures were maintained at about 25% and run at approximately 170 °C. Although the polymerizations tended to darken over time, moderately high viscosity solutions were obtained in 48 h. Interestingly, the side reactions precluding high molecular weight polymer observed using bisphenols and anhydrous potassium carbonate in NMP or DMPU were not evident in this synthetic approach. Shown in Table 2 are the characteristics of the poly(aryl ether benzil)s **17a**, **17b**, and **17d**. The η_{inh} values are in the range 0.47–0.62 and are similar to those polymers **16a–d** prepared in sulfolane from biphenols **14a–d** and using an excess of potassium carbonate. However, these polymers were *tan* instead of *yellow*. It should be noted that polymers **16a**, **16b**, and **16d** are structurally equivalent to **17a**, **17b**, and **17d**, but different numbers were assigned to distinguish the method of preparation.

Probing the Effects of Solvent, Free Radical Scavenger, Potassium Carbonate, and Concentration of Phenate Anion. To ascertain why high-purity commercial NMP and DMPU produce intensely *green* polymerization mixtures[20] and only yield low molecular weight poly(aryl ether benzil)s when long reaction times were employed (e.g., 9–12 h), a series of polymerization reactions were run in NMP and DMPU. In the case of NMP, high-purity commercial solvent and an even higher purity form which was distilled from P_2O_5 were both used to determine the importance of small amounts of impurities. The reaction conditions and the results are compiled in Table 3 (entries 1–5). By using only one type of bisphenol (**14a**) and reacting it with the difluoride 11 to prepare only polymer **16a**, the only variables which were altered was the purity of the NMP and the effect of a small amount of radical scavenger (*p*-benzoquinone). Reactions 1 and 2 utilized the very pure commercial grade NMP (99+%) and DMPU (99%) which were also employed in the polymerization reactions 2, 6, and 12 in Table 1. This time portions of the reaction mixture were worked up at 3, 5, 9, and 12 h in order to follow the effect of reaction time on molecular weight. In both cases, the molecular weight *peaked* at ~5 h, as judged by the solution viscosity and the η_{inh} values of the isolated polymers (Table

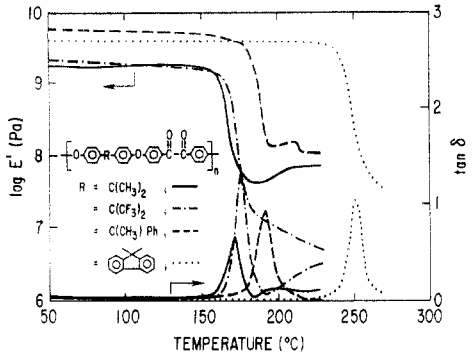
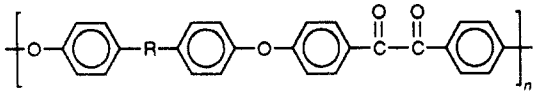
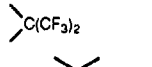


Figure 5. Dynamic mechanical thermal analysis (DMTA) curves of thin films of polymers **16a–d**.

Table 2. Polymers 17a, 17b, and 17d Prepared by Method II Using Silylated Bisphenols and CsF in NMP



polymer[a]	R	polymn solvent	temp (°C)	time (h)	η_{inh}	T_g (°C)
17a		NMP	170	48	0.45	162
17b		NMP	170	48	0.47	155
17d		NMP	170	48	0.62	237

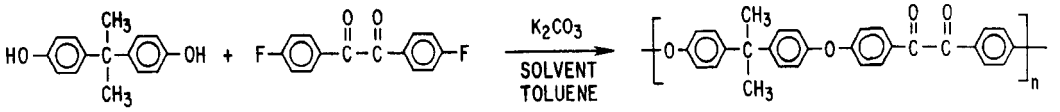
3), and then decreased as the polymerization reaction was continued for longer periods. Furthermore, the optimum reaction time changes with different batches of commercially available NMP and the length of time after which the bottle was initially opened. The reactions also changed color from *green*, to very *dark green*, and finally to *dark red–brown*, as a dramatic reduction in solution viscosity occurred. Figure 6 shows a plot of the η_{inh} values for polymer **16a** isolated at different times during the 12 h reaction in high-purity commercial NMP and in DMPU, run at ~155 °C. Since polymer degradation began to occur *after a buildup in molecular weight* and because it was difficult to predict the optimum time at which to isolate the polymer, without constantly monitoring the reaction, we decided to further purify the commercial NMP[21] by distillation from phosphorus pentoxide (reaction 3) or, alternatively, to add a small amount of the radical scavenger[22] *p*-benzoquinone to the commercial NMP (reaction 4). These two modifications were implemented to determine whether an impurity in the NMP may be responsible for polymer chain cleavage. In both cases, high molecular weight polymers could consistently be prepared in about 4 h, and the molecular weight buildup correlated with reaction time as expected. The *green* color seen in reactions 1 and 2 was *not* visible when distilled NMP (reaction 3) was employed. A tinge of green was visible of reaction 4; however, it was difficult to be certain because reactions run with a catalytic amount of *p*-benzoquinone were brown in color. Furthermore, if distilled NMP and a radical scavenger are both used, then the molecular weight did not improve beyond that obtained in reactions 3 and 4 (Table 3). While it was possible to predict, with more accuracy, the length of the reaction time for the preparation of high molecular weight polymer in reactions 3 and 4, degradation still occurred after molecular weight buildup if the reaction time was extended (e.g., 9–12 h). In addition, the appearance of the isolated polymer was now *off-white to tan*, as was seen for polymers **17a**, **17b**, and **17d** prepared from silylated bisphenols in NMP, instead of *yellow*. When films of **16a** (reactions 3–5) were prepared by compression molding, they were *brown* instead of *yellow*; however, the films were still tough and creasable. These results suggest that very low concentrations of NMP decomposition product(s) have a dramatic effect on molecular weight and that they appear to degrade the polymer *after* molecular weight buildup. These decomposition products may be radical in nature.

To determine whether solvent polarity was a factor in determining the color of the reaction mixture and the rate of polymer chain cleavage, **16a** was prepared in DMSO. In this case, as was seen with DMAc, sulfolane, and distilled NMP, the color of the reaction mixture was *yellow*[23] and *not green*. Furthermore, a buildup in molecular weight occurred very rapidly to give a very viscous solution at 140–150 °C (reaction 6). In fact, the molecular weight of the polymer **16a** became so high that it partially precipitated from the reaction mixture, and the resulting polymer could not be completely dissolved in hot NMP at a concentration of 0.5 g/dL, once it was isolated. If, however, the reaction was run using a 1.5% excess of difluoride **11** relative to the bisphenol **14a** (reaction 7), it was possible to limit the molecular weight by off-setting the stoichiometry to obtain a polymer which was completely soluble in NMP, DMAc, or THF after isolation. However, this polymer also began to precipitate from the polymerization mixture, if the temperature increased to 160 °C, once high molecular weight was attained (20% solids).[24]

Since the only variable in reactions 1–3, 6, and 7 (Table 3) was the type of solvent used, and solvent purity, it is of interest to note that a *green* color develops *only* in reactions which were run in high-purity commercial NMP and DMPU. If the NMP was purified further by distillation or if the solvent was DMSO, DMAc, or sulfolane, then high molecular weight polymers were obtained and the polymerization reactions were *yellow* after ~1 h and remained this color even after a significant buildup in molecular weight occurred. It was not possible to determine whether polymer degradation also occurred in DMSO and sulfolane at long reaction times (e.g., 12 h), because, in the former, polymer **16a** precipitates from the viscous polymerization solution after ~4–5 h and, in the latter, the solution became so viscous that it could not be stirred. Moreover, because the *green* color was not seen for the polymerization reaction when purified NMP (distilled) was used (reaction 3), the color cannot be attributed to a phenate salt (i.e., monomer or oligomer). Further evidence for the latter was seen with the model reaction of 3,5-di-*tert*-butylphenol (**12**) and difluoride **11** outlined in Scheme 1, using commercial NMP as the solvent instead of DMAc. In NMP, the green color formed shortly after the reaction began and persisted, even after all of **12** had reacted to give only the disubstituted product **13**.[25] In DMAc, the color of the model reaction was *yellow* and gradually became *dark yellow* with time. Therefore, it appears that an impurity in the commercially available NMP is responsible for the *green* color.

The anhydrous potassium carbonate also appears to play a role in the formation of the *green* color. If the difluoride **11** was heated in commercial NMP under the polymerization conditions for 2 h at ~130 °C in the absence of the phenol **12** (or biphenol) and potassium carbonate, the solution remained clear and yellow. On the other hand, when the same reaction was run in the presence of base and in the absence of the phenol, a *dark green* color was visible. When the reaction mixture was poured into water, only the starting material **11** could be detected by TLC.

Table 3. Synthesis of Polymer 16a



14a II 16a

reaction	solvent	radical scavenger	reaction time (h)	temp (°C)	η_{inh} (dL/g)	color of reaction after 1 h	color of polymer
1	NMP[a]		3.5	125 → 150	0.38	light green	light yellow
			5	155	0.58		tan
			9	150–170	0.41		dark brown
			12	150–170	0.43		dark brown
2	DMPU		2	125 → 150	0.28	dark green	light yellow
			5	155	0.37		brown
			12	155	0.30		dark brown
3	NMP[b]		3	135 → 140	0.70	yellow	light yellow
			35 min	150 → 155			
4	NMP[a]	*p*-benzoquinone	3	135 → 140			
			1	140 → 155	0.65	*e*	off-white to tan
			50 min	160 → 165			
5	NMP[b]	*p*-benzoquinone	3	135 → 140			
			1	150 → 157	0.68	*e*	off-white to tan
			35 min	158			
6	DMSO		2.5	120 → 150	0.56[c]	yellow	light yellow
7	DMSO		2	120 → 160	0.60[d]	yellow	light yellow

[a] NMP (anhydrous, 99%; Aldrich) packaged under nitrogen in a Sure/Seal bottle. [b] NMP distilled under reduced pressure from P_2O_5 before use. [c] Soluble portion. The remainder of the polymer was too high a molecular weight to dissolve in refluxing DMAc or NMP. [d] Used 1.5% excess of difluoride 11. [e] *p*-Benzoquinone is light brown and turns the polymerization mixture brown immediately upon heating.

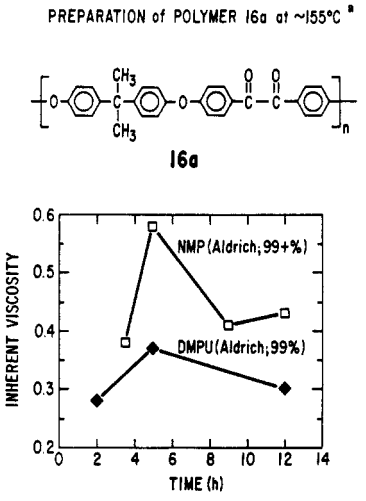


Figure 6. Inherent viscosity values (η_{inh}) of polymer **16a** prepared from bisphenol **14a** and 4,4′-difluorobenzil (**11**) and isolated at different times during the polymerization reaction. High-purity commercial NMP and DMPU were used as the solvents. Anhydrous potassium carbonate was used as base.

This color change was observed for two different ratios of anhydrous potassium carbonate:difluoride **11**: 1.2:1.0 and 0.2:1.0, respectively; therefore, only small amounts of base are required. Since this color change is observed in NMP, and not in DMAc, DMSO, or sulfolane, it appears that the base and NMP interact in some manner. Furthermore, if electron transfer does occur in these reactions to convert the dicarbonyl into a *semidione*,[26] it is unclear whether it occurs from the phenate, from the base, or from NMP degradation product(s). The complexity of the degradation pathway in NMP is similar to the recent observation made by Percec and co-workers,[27c] who illustrated that reductive dehalogenation in polyetherification reactions could proceed in the absence of a phenolate, if NMP was the solvent.

Interestingly, the cleavage reactions which occurred in NMP and DMPU using potassium carbonate as the base, after ~5 h of reaction, did not take place when poly(aryl ether benzil)s were prepared using the method of Kricheldorf and co-workers[18] by utilizing silylated bisphenols (**15a**, **15b**, and **15d**) and a catalytic amount of CsF. In fact, the reaction time could be extended to 48 h at 170 °C and it was still possible to obtain high molecular weight polymers. In this polymerization reaction, the nucleophile does not appear to be a phenoxide anion, as has been described previously in the preparation of xylenyl ether–arylene ether sulfone triblock copolymers[28] but most likely involves a complexation of the fluoride ion (CsF) with the silicon of the silyl ether to give a nucleophile which is considerably weaker than the phenoxide. Second, since only a catalytic amount of CsF was employed, the concentration of the nucleophile was dramatically lower relative to the amount present used in the potassium carbonate route. Third, under these conditions the reaction was *not* run in excess base, as was the case for the reaction condition using anhydrous potassium carbonate.

Possible Polymer Cleavage Site(s). Since very high molecular weight poly(aryl ether ketone)s can be readily synthesized by reacting bisphenol **14a** with 4,4′-difluorobenzophenone (**1**; Figure 1) without using distilled NMP, it was not immediately apparent why and where polymer chain cleavage occurred during the synthesis of poly(aryl ether benzil) **16a** at long reaction times. For example, does cleavage occur at the aryl ether linkage, because the dicarbonyl group is more strongly activating than the ketone, or does it occur at the dicarbonyl moiety? It is known that substituted benzils can accept electrons to form the radical anion called a *semidione*.[26] ^{1}H-NMR was utilized to characterize the type of end groups which are present in the poly(aryl ether benzil) **16a** prepared in DMAc (reaction 1, Table 1) and in NMP and DMPU (reactions 1 and 2, Table 3) after a 12 h reaction at ~155 °C. Figure 7 shows the monomers (**11** and **14a**) and the model compounds (**18**–**20**) whose ^{1}H-NMR spectra were obtained to aid in the assignment of the end group proton resonances of the resulting polymers. In DMAc after 12 h at 155 °C (reaction 1, Table 1), only phenol (**21**) and aryl halide (**24**) end groups could be detected. In NMP and DMPU after 12 h, it appears that end groups attributable to **22** and **23** also appear to be present in addition to **21**

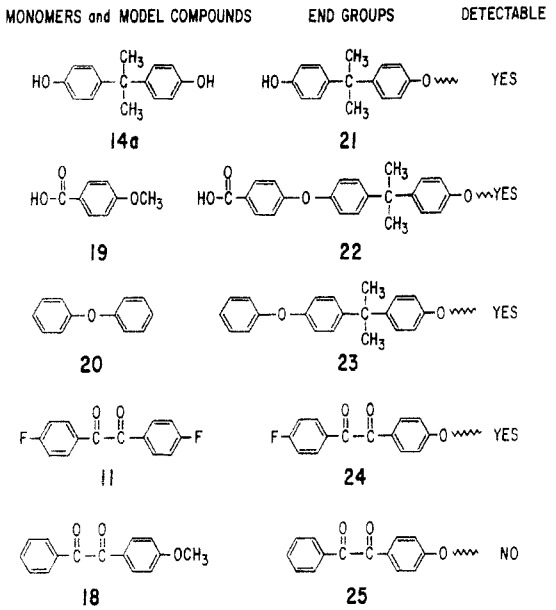


Figure 7. End groups detected by ^{1}H-NMR (250 MHz) for the polymer **16a** prepared using anhydrous potassium carbonate in different dipolar aprotic solvents.

and **24**. Therefore, it appears that in NMP and DMPU, solvent degradation causes cleavage of the dicarbonyl functionality; however, it is difficult to say with certainty whether or not the aryl ether cleavage also occurs, since **21** and **24** are always present to a certain degree depending on the accuracy of bisphenol:activated aryl halide stoichiometry, used to prepare the polymer. In all cases the dehalogenated end group **25** was not detectable.[27]

Summary

A series of novel amorphous poly(aryl ether benzil)s have been prepared by nucleophilic aromatic substitution by generating aryl ether linkages as the polymer forming reaction. It has been demonstrated that the electron-deficient dicarbonyl component of 4,4'-difluorobenzil is strongly activating and allows reaction with a bisphenol to proceed rapidly under mild conditions (~150 °C) in a dipolar aprotic solvent to give high molecular weight polymers using short reaction times. Two synthetic approaches were investigated as a means of preparing high molecular weight polymer; the conventional potassium carbonate/dipolar aprotic solvent route and the use of silylated bisphenols in a dipolar aprotic solvent containing a catalytic amount of cesium fluoride. Under the former polymerization reaction conditions, DMSO and sulfolane proved to be very effective solvents, while NMP or DMPU caused polymer chain cleavage to occur *after a molecular weight buildup*, particularly when long reaction times were implemented. In the silylated bisphenol approach, high molecular weight poly(aryl ether benzil)s could be prepared in NMP; however, long reaction times were required and the resulting polymers were of an inferior quality relative to those prepared in DMSO or sulfolane. Furthermore, it has been shown that the effect of the different solvents, the purity of the solvent, and the polymerization reaction time have a dramatic effect on the quality and the molecular weight of the resulting polymer. The glass transition temperatures ranged from 157 to 242 °C depending on the type of bisphenol used, and the thermooxidative stability was comparable to other poly(aryl ether)s. Furthermore, these high molecular weight polymers all form tough creasable yellow films when cast from solution, and some could also be readily compression molded. These soluble poly(aryl ether benzil)s could potentially serve as generic polymer precursors to provide a route to different heterocyclic containing poly(aryl ether)s such as poly(aryl ether quinoxaline)s, poly(aryl ether imidazole)s, and poly(aryl ether triazine)s by reaction with a diamine (e.g., *o*-phenylenediamine), aromatic aldehyde (e.g., benzaldehyde) and ammonium acetate or a hydrazidine (e.g., 2-pyridylhydrazidine),[29] respectively.

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(23) The reactions remain yellow for DMAc, sulfolane, and DMSO as the molecular weight builds up; however, with the distilled NMP it still eventually becomes brown with time.

(24) It appears that the insolubility is attributable to a molecular weight effect, and not to cross-linking, because the resulting polymer is soluble at lower concentrations, and this solubility behavior is not observable when the reaction is run at the same temperatures in sulfolane.

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