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The Synthesis of Poly(arylene ether)s in Solution at Pilot-Plant Scale with Control over Molecular Weight and End-Group Composition

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Abstract:

The lab-scale optimization and pilot-plant-scale synthesis of a poly(aryl ether ketone) is reported. The polymer produced had the desired properties of low molecular weight ($M_w = 14-15$ kD, $M_n = 6.3-6.5$ kD), reasonable polydispersity (PD = 2.37−2.39), and well-defined controlled end groups. This has been accomplished using a one-step solution polymerization of 4,4′-difluorobenzophenone (DFBP), bisphenol A (BPA), and 4-*tert*-butylphenol (tBP). The presence or absence of a stoichiometric amount of tBP in the polymerization reaction dictated whether the obtained polymer possessed exclusively a halide or a *tert*-butylphenol terminus. Simple variation of the ratio of difluorobenzophenone to BPA controls the molecular weight of the obtained polymer without affecting the polydispersity. Several other factors were examined to completely optimize the polymerization process: the replacement of 4,4′-difluorobenzophenone with 4,4′-dichlorobenzophenone as a cost-saving measure, the effect of temperature, and the effect of the concentration of the reactants.

Introduction

Poly(arylene ether)s are a general class of engineering plastics which include poly(phenylene oxide)s,[1] poly(ether imide)s,[2] poly(ether sulfone)s,[3] and poly(ether ketone)s.[4] While a plethora of academic research has been done on such materials, only a few examples of these materials are currently on the commercial market.[2b] In all cases, commercial materials are intended for applications that necessitate the polymer to be of high molecular weight. However, some new applications such as ultrathin films, photoresist materials, and so forth may require a polymer of lower molecular weight or a lower solution viscosity or both. This can only be done where the obvious loss of mechanical robustness (due to a lower molecular weight) can be traded off against the benefits of a low solution viscosity. It would therefore be of interest to assess the ability to produce, at pilot-plant scale, a poly(aryl ether) where the molecular weight is kept low and the polydispersity is not significantly broad. Moreover, the presence of controlled and predictable end-groups on the polymer chains would be advantageous. For example, in the case of a photoresist derived from the described poly(arylene ether) and developed using photo-initiated free radical-type cure, the presence of halogen endgroups may cause unwanted side reactions, resulting in chain extension.[5]

Typical procedures to make lab-scale quantities of poly-(aryl ether ketone)s and poly(aryl ether sulfone)s involve the polycondensation of an activated dihalide monomer with a bisphenol. These are performed in the presence of a carbonate base and a polar aprotic solvent mixed with a lower-boiling solvent which forms an azeotropic mixture with water (such as toluene or chlorobenzene) to allow for the azeotropic removal of water produced during the polymerization.[3,4] While this method is routine in a laboratory setting, it is not immediately obvious that such a procedure is amenable to the synthesis of poly(aryl ether ketone)s at pilot-plant scale.

Herein we report on the successful development of a pilot-plant scale solution polymerization method for the synthesis of a poly(aryl ether ketone) (PAEK), of low molecular weight with narrow polydispersity and possessing well-defined polymer endgroups (Scheme 1). The molecular weight of the polymer obtained is stoichiometrically controlled and is dictated solely by the starting ratio of monomers. Optimization of the process has made it possible to complete the synthesis in less than 8 h with an optimum reactor yield.

Experimental Section

Materials. 4,4′-Dichlorobenzophenone (DCBP, 99%), 4-*tert*-butylphenol (tBP, 99%), *N,N*-dimethylacetamide (DMAc, 99%), and tetramethylene sulfone (TMS, sulfolane, 99%) were purchased from Aldrich Chemical Canada (Oakville, Ontario, Canada) and used as received. 4,4′-Difluorobenzophenone (DFBP) was purchased in bulk from Oakwood Chemicals (West Columbia, SC) or Honeywell Specialty Chemicals (99.9%, Morristown, NJ) and used as received. 2,2-Bis(4-hydroxyphenyl)propane (BPA, bisphenol A, grade BPA-157) was purchased in bulk from Shell Canada Chemical Co. (Calgary, AB, Canada) and used as received. Methylene chloride, toluene, methanol, and reagents were

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(2) (a) Cotter, R. J. *Engineering Plastics: A Handbook of Polyarylethers*; Gordon and Breach: Basel, Switzerland, 1995; pp 45−49. (b) *Ibid*. pp 289−336. (c) *Ibid*. p 28.

(3) (a) El-Hibri, M. J.; Nazabal, J.; Equiazabal, J. I.; Arzak, A. *Plast. Eng. (N. Y.)* **1997**, *41(Handbook of Thermoplastics)*, 893−930.. (b) Labadie, J. W.; Hedrick, J. L.; Ueda, M. Step-Growth Polymers for High-Performance Materials. *ACS Symp. Ser.* **1996**, *624*, 210−25. (c) Rose, J. B. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1986**, *27(1)*, 480−1.

(4) Cakmak, M. *Plast. Eng. (N. Y.)* **1997**, *41(Handbook of Thermoplastics)*, 931−950.

(5) Xerox Corporation has extensive patent coverage on photoresists derived from the type of poly(arylene ether)s described in this paper: U.S. Patent 6,187,512; U.S. Patent 6,184,263; U.S. Patent 6,139,920; U.S. Patent 6,124,372; U.S. Patent 6,090,453; U.S. Patent 6,087,414; U.S. Patent 6,020,119; U.S. 5,994,425; U.S. Patent 5,958,995; U.S. Patent 5,945,253; U.S. Patent 5,907,001; U.S. Patent 5,863,963; U.S. Patent 5,761,809; U.S. Patent 5,753,783; U.S. Patent 5,739,254.

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Scheme 1. **Synthesis of endcapped poly(aryl ether ketone) used in this study**

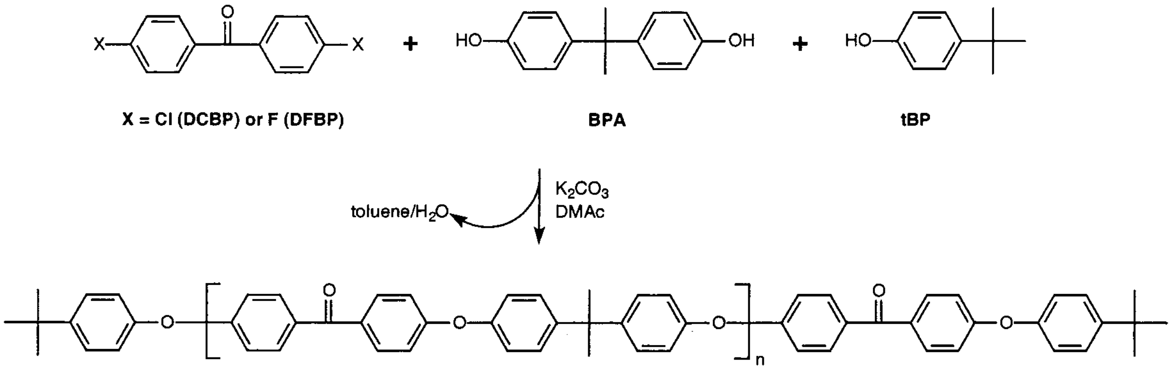

Table 1. **Factors studied for the synthesis of poly(aryl ether ketone) (PAEK-1−PAEK-15)**

PAEK run number	scale mol BPA	halide monomer	monomer concn	tBP	solvent	temp (°C)	monomer ratio	distillate recirculation	M_w (kD)	M_n (kD)	PD	observations
1	0.26	DCBP	low	no	DMAc	160	1.08	yes	2.0	1.2	1.69	
2	0.26	DCBP	high	no	DMAc	160	1.08	yes	1.0	0.8	1.36	
3	0.26	DCBP	low	no	sulfolane	200	1.08	yes	4.3	2.2	2.00	
4	0.26	DCBP	high	no	sulfolane	200	1.08	yes	3.2	1.6	1.92	
5	0.26	DFBP	low	no	DMAc	160	1.08	yes	15.5	6.7	2.31	
6	0.26	DFBP	high	no	DMAc	160	1.08	yes	16.1	6.4	2.53	
7	0.26	DFBP	low	yes	DMAc	160	1.08	yes	14.7	6.8	2.17	
8	0.26	DFBP	low	yes	DMAc	160	1.10	yes	12.2	6.0	2.03	
9	0.26	DFBP	low	no	DMAc	165	1.08	no	15.4	5.9	2.59	
10	0.26	DFBP	low	no	sulfolane	200	1.08	yes	8.8	4.1	2.15	gelled after 1.5 h
11	0.26	DFBP	low	yes	sulfolane	200	1.08	yes	12.0	5.1	2.34	gelled after 2.0 h
12	1.32	DFBP	low	yes	DMAc	160	1.08	yes	14.4	5.9	2.42	
13	8.76	DFBP	low	yes	DMAc	160	1.08	yes	14.9	6.3	2.37	
14	8.76	DFBP	low	yes	DMAc	160	1.08	no	14.7	6.2	2.38	
15	8.76	DFBP	low	yes	DMAc	160	1.08	no	15.4	6.5	2.39	

[a] BPA: bisphenol A; DCBP: dichlorobenzophenone; DFBP: difluorobenzophenone; tBP: 4-*tert*-butylphenol; DMAc: *N*,*N*-dimethylacetamide; monomer ratio [moles DCBP/moles BPA] or [moles DFBP/moles BPA]; M_w: weight-average molecular weight; M_n: number-average molecular weight; kD: kilodaltons; PD: polydispersity [M_w/M_n];

purchased from Caledon Laboratories (Georgetown, Ontario, Canada) and were of ACS grade and used as received.

Characterization. Gel-permeation chromatograms were acquired using a Waters 2690 GPC with five in-series columns using THF as the eluent, at 1.0 mL min^{-1}, using RI detection and were calibrated against narrowly dispersed polystyrene standards. Typical acquisition times were 1 h. ^{1}H (TMS internal reference) and ^{19}F (TFA internal reference) NMR were acquired using a Bruker 300 MHz spectrometer with the samples in solution in $CDCl_3$.

Typical Lab Scale Synthesis. *Typical Procedure for Halide-Terminated PAEK (**PAEK-5**, Table 1, 0.26 mol scale).* K_2CO_3 (87.5 g, 0.634 mol), BPA (60.6 g, 0.265 mol), DFBP (62.6 g, 0.287 mol), toluene (34.6 g, 40.0 mL), and DMAc (374.8 g, 400.0 mL) were added to a three-necked 1-L Morton flask, fitted with a Claisen adaptor, nitrogen bubbler, a submersible thermometer, and a 25-mL Dean−Stark trap topped with a water-jacketed condenser. The reaction mixture was agitated mechanically at 500 rpm using an IKA RW 20 DZM.n overhead stirrer with glass stir rod and Teflon blade. The reaction mixture was refluxed for 6 h under a slow nitrogen purge while the distillate was allowed to recirculate into the reaction flask and the produced water was periodically drained. After air-cooling to room temperature, the reaction mixture was diluted with THF or DMAc (260 mL) and poured slowly into vigorously stirred methanol (2 L). The precipitated polymer was isolated by vacuum filtration through no. 54 Whatman filter paper, redissolved in methylene chloride (2 L), and stirred with Celite 521 (50 g) for 1 h. The solution was filtered through no. 54 Whatman filter paper and added slowly to vigorously stirred methanol (4 L). The precipitate was isolated by vacuum filtration through no. 54 Whatman filter paper, followed by vacuum-drying (30 °C, 7 mTorr) to yield a white, free-flowing powder (100.5 g, 1.48% volatiles, 83.8% yield).

*Typical Procedure for tBP-Terminated PAEK (**PAEK-12**, Table 1, 1.32 mol scale).* K_2CO_3 (437.7 g, 3.167 mol), BPA (302.9 g, 1.327 mol), DFBP (312.9 g, 1.434 mol), tBP (32.4 g, 0.216 mol), toluene (173.0 g, 200.0 mL), and DMAc (1894.0 g, 2021.3 mL) were added to a three-necked, 5-L Morton flask fitted with a Claisen adaptor, nitrogen bubbler, a submersible thermometer, and a 500-mL Dean−Stark trap containing toluene (370 mL) topped with a water-jacketed condenser. The reaction mixture was agitated mechanically at 500 rpm using an IKA RW 20 DZM.n overhead stirrer

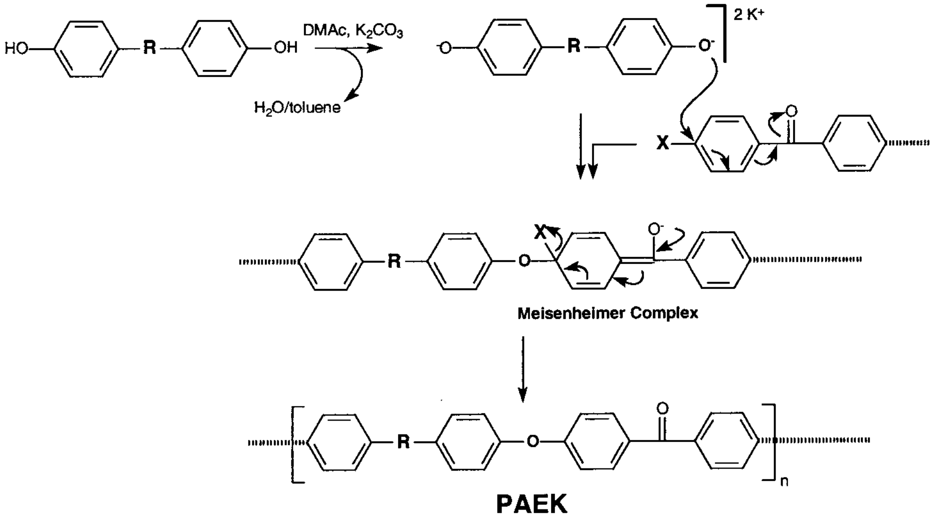

Figure 1. **Synthesis of poly(aryl ether ketone) by $S_{N,Ar}$ reaction (X = Cl or F).**

with glass stir rod and Teflon blade. The reaction mixture was refluxed for 6 h under a slow nitrogen purge while the distillate was allowed to recirculate into the reaction flask and the produced water was periodically drained. After air-cooling to room temperature, the reaction mixture was diluted with DMAc (1 L) and vacuum-filtered through no. 4 Whatman filter paper and added gradually to vigorously stirring methanol (30 L). The precipitate was isolated by vacuum filtration through no. 1 Whatman filter paper, followed by stirring in deionized water (5 L) for 1 h, refiltering and then stirring in methanol (5 L) for 1 h, and then a final filtration. The preciptitate was dried in a vacuum oven (60 °C, 7 mTorr) for 3 days to yield a white, free-flowing powder (100.5 g, 3.00% volatiles, 90.0% yield).

Typical Pilot-Plant Scale Synthesis. A 5-gal (20 L) stainless steel reactor is equipped with a distillation condenser, an external piping loop to act as a water separator, an electrically driven agitator, a means to purge with nitrogen, and a means to draw samples (Figure 6). There is a return line from the separator to the reactor to recirculate the distillate back into the reactor. The reactor is purged with nitrogen and the agitator started at minimum speed. Then the nitrogen purge is stopped, and a standard batch charge is added through the loading port in the following sequence: DMAc (13 kg), toluene (4 kg), tBP (0.214 kg), DFBP (2.064 kg), BPA (1.999 kg), and K_2CO_3 (2.60 kg). The loading port is closed, and the reactor is purged for 5 min with nitrogen and then switched to the vent line for the remainder of the reaction. Heat is applied to the reactor using a 60-kW hot oil system with the hot oil temperature being controlled in automatic mode using a slave controller (hot oil setpoint 175 °C). Time zero for the process is set to the time at which distillation begins (reaction temperature 150 °C). Over the first 1 h, removal of the denser phase of distillate (a total of 4 L is collected) is performed as the hot oil temperature is gradually increased to 190 °C. Once the internal temperature of the reactor is 165 °C, all subsequent distillate is returned to the reactor. Sampling of the reaction for analysis by GPC is done using vacuum to draw a sample into a small vessel connected to a dip-tube. The reaction is run for 6 h after achieving 150 °C, and then the reactor is cooled to 25 °C. The product mixture is pressure-filtered (to remove insoluble salts contains KF and K_2CO_3) through a bag filter attached to the bottom valve. The solid collected in the bag filter is rinsed with fresh DMAc charged to the reactor. The DMAc solution is then precipitated into highly agitated MeOH (10 vol equiv relative to DMAc). The resulting powder is isolated by vacuum filtration (in a Büchner-type apparatus) and washed with water (20 kg) and methanol (20 kg) in the filter. The resulting cake is dried in a tray drier at 60 °C under vacuum until a constant weight is achieved (yield 3.1 kg (81%), theoretical yield 3.8 kg).

Results and Discussion

Lab-Scale Optimization of Synthesis (PAEK-1−PAEK-11). An experiment matrix was constructed whereby the choice of dihalide monomer, the effect of temperature and of concentration, and the presence or absence of endcapping agent could be studied (Table 1). In all cases, except one, an 8% excess of dihalide monomer was used (1.08 equiv of dihalide monomer relative to BPA), and in all cases potassium carbonate was used as a base. No other carbonate bases were tried, and as such, the effect of base on the described process was not determined. It is known that the reactivity of carbonate bases in this type of polymerization increases on the order Li < Na < K < Cs. Although cesium carbonate would be an appropriate substitute for potassium carbonate, its use is seen as economically prohibitive on a large scale.

Choice of Monomer. Poly(aryl ether sulfone)s (PAES) and poly(aryl ether ketone)s (PAEK) can be made by an aromatic nucleophilic substitution reaction ($S_{N,Ar}$ reaction) of a bisphenolic compound with an activated bishalide compound, which is shown mechanistically in Figure 1 (X = Cl or F) for the case of a PAEK. In the synthesis of poly(aryl ether ketone)s, the use of activated fluoride ketone monomers (such as 4,4′-difluorobenzophenone, DFBP) is preferred because of the well-established increase in reactivity over activated chloride ketone monomers (such as 4,4′-dichlorobenzophenone, DCBP).

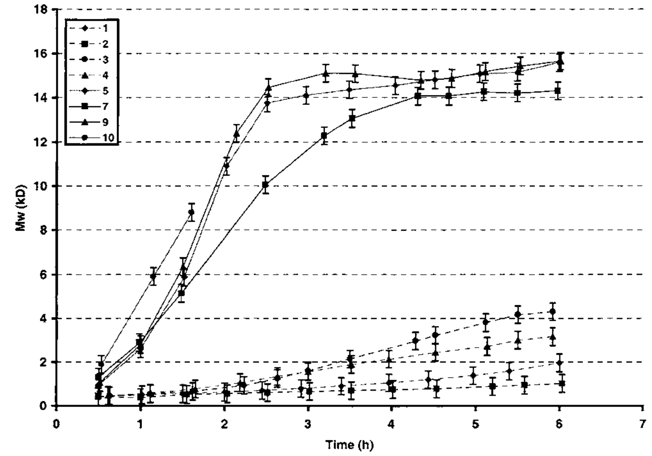

Figure 2. **Plot of molecular weight (kD) with time (h) for PAEK-1−PAEK-5, PAEK-7, and PAEK-9−PAEK-10 (legend shown on plot).**

This is due to the ease of which the hard fluoride ion is released from the intermediate Meisenheimer complex over the softer chloride ion (Figure 1).

For research-scale quantities of materials, the use of DFBP is appropriate. However, for large-scale production of PAEK, the replacement of DFBP with the less expensive DCBP would be economically beneficial, from a raw materials cost (RMC) point of view. Balanced against the RMC are the reaction time and the associated allocation of resources. In this study, we have set a limit of one working day on the process time. As such, the polymerization reaction must reach its desired molecular weight and be discharged from the reactor within 6−8 h.

It can be clearly seen that the use of DCBP as the dihalide monomer for the synthesis of PAEK under any conditions (**PAEK-1**−**PAEK-4**) did not reach the maximum molecular weight within 6−8 h (Figure 2). In fact we have found that a total reaction time of 30−40 h is required to reach the desired molecular weight when using DCBP as the monomer. While the use of tetramethylene sulfone (TMS) and accessibility to a higher reaction temperature did produce a polymer having a molecular weight of 4 kD versus 2 kD for DMAc, it still did not accelerate the reaction enough to reach the desired molecular weight within the allotted time.

Switching from DCBP to DFBP had the expected pronounced effect on the rate of polymerization. Within 1 h the molecular weight obtained with DFBP already exceeded the molecular weight obtained after 6 h of reaction with DCBP. For all lab-scale runs using DFBP (**PAEK-5**−**PAEK-9**, **PAEK-12**) the polymerization reached its stoichiometrically dictated molecular weight within 3−4.5 h (Figure 2).

The relative rate of reaction of DFBP to DCBP has been reported to be 100 to 1, through the study of model reactions.[2c] How this relative rate translates into a rate of molecular weight growth is unclear. However, under our reactions conditions, it seems that the rate of polymer growth is at least 10 times greater with DFBP (**PAEK-5**) than with DCBP (**PAEK-1**).

Control of Molecular Weight. To obtain PAEK of the desired molecular weight, an excess of dihalide monomer is used (1.08 or 1.10 equiv relative to BPA, Table 1). Experience and experimentation has shown that a monomer offset ratio of 1.08 gives a polymer of $M_w = 14.5-16.0$ kD with $M_n = 5.9-6.8$ kD that possess halide terminal groups. It is worth noting that the absolute molecular weight of the polymer as calculated using a monomer offset ratio of 1.08 using the Carother's equation[6] is $M_n = 5.1$ kD. However, the molecular weights quoted in this work are relative to polystyrene standards and, as such, are unreliable as an indication of absolute molecular weight of the obtained PAEK.

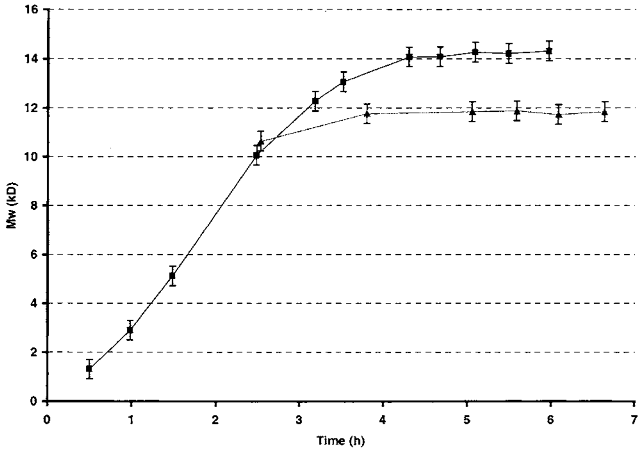

Figure 3. **Plot of molecular weight (kD) with time (h) for PAEK-7 (■) and PAEK-8 (▲).**

To illustrate the versatility of the described approach, the monomer offset ratio was changed from the usual 1.08 (**PAEK-7**) to 1.10 equiv of DFBP relative to BPA (**PAEK-8**, Figure 3). The molecular weight of the obtained PAEK in run **8**, reached a maximum of 12 kD instead of 14 kD, as expected, and within approximately 3.5 h instead of 4.5 h. Furthermore, **PAEK-8** had a measured polydispersity (PD) that was even smaller than that measured for **PAEK-7**.

Selection of Polymer Endgroups. Offsetting the monomer stoichiometry to have an excess of dihalide monomer should result in a PAEK with terminal halide groups (as is the case in run **PAEK-1**−**PEAK-6**). However, it would be of interest to know whether this process is amenable to the modification of the PAEK end groups by addition of a monofunctional phenolic compound into the original polymerization mixture. The addition of such a monofunctional monomer should have little effect on both the PAEK molecular weight and the obtained PD.

To study this, a stoichiometric amount of 4-*tert*-butylphenol (tBP) was added to the polymerization reaction (**PAEK-7**). 4-*tert*-Butylphenol was chosen because of its similar reactivity to that of BPA and its ease of detection within the PAEK structure by ^{1}H NMR. By direct comparison between

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(6) Using Carother's equation:

$$1.08 = \frac{(n+1)}{n}$$

$$\therefore n = \frac{1}{1.08:\ 1} = 12.5 \textit{ repeat units}$$

(*repeat unit molecular weight* 406.48 *D*)

$$M_n = 12.5 \times 406.48 = 5.1\ kD \text{ (ref 6)}$$

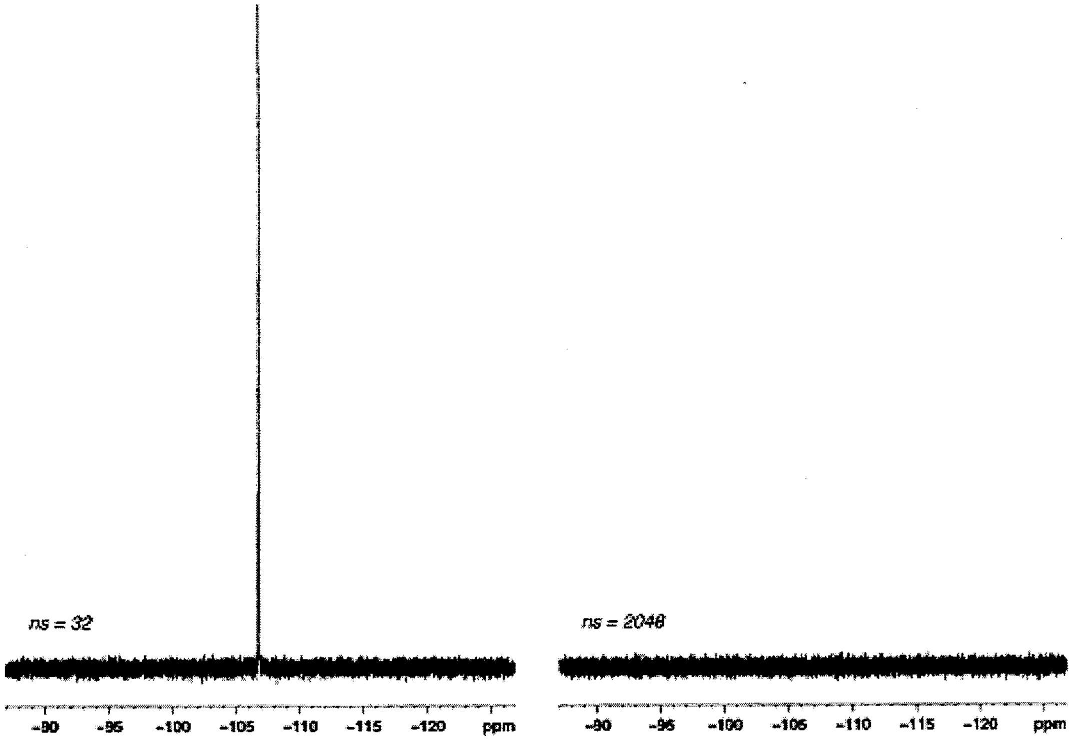

Figure 4. **^{19}F NMR of poly(aryl ether ketone) produced without tBP (PAEK-5, left) and with tBP (PAEK-7, right).**

PAEK-5 and **PAEK-7**, addition of tBP to the polymerization resulted in a PAEK with slightly lower molecular weight and a slightly narrower PD. The absence of fluoride endgroups within **PAEK-7** can be confirmed using ^{19}F NMR (Figure 3), which shows a clear and sharp resonance from the terminal fluoride group at δ 106.5 ppm that is totally undetectable in **PAEK-7** even after 64 times as many scans (at the same concentration). The presence of 4-*tert*-butylphenyl endgroups in **PAEK-7** can be confirmed using ^{1}H NMR (Figures 4 and 5), by the appearance of a sharp singlet at δ 1.3 ppm. The resonances at 2.1 ppm and 3.0 ppm indicate residual DMAc is present in both **PAEK-5** and **PAEK-7**.

Method for Removal of Water from the Reaction and Increasing the Concentration of the Polymerization Reaction. Toluene is used to azeotropically remove the water produced during the polymerization. In the lab, a Dean−Stark trap is typically used to separate the water and toluene before allowing the toluene to recirculate back into the reaction vessel. While our pilot-plant reactor is equipped to allow the separation of the water from the toluene and recirculation of the toluene back into the reaction vessel (Figure 6), it would be of interest to see whether such a setup is necessary. If such a setup is not necessary, there would be a piping and space savings. The alternative would be the use of straight distillation to remove the water and toluene. During **PAEK-9**, the water and toluene were removed together by straight distillation. As a result, the reaction temperature increased slightly from 160 to 165 °C (the boiling point of DMAc). The effect of concentration was also examined for this polymerization reaction (**PAEK-6**). To accomplish this, the relative amounts of reagents were kept the same, but the mass of DMAc was decreased.

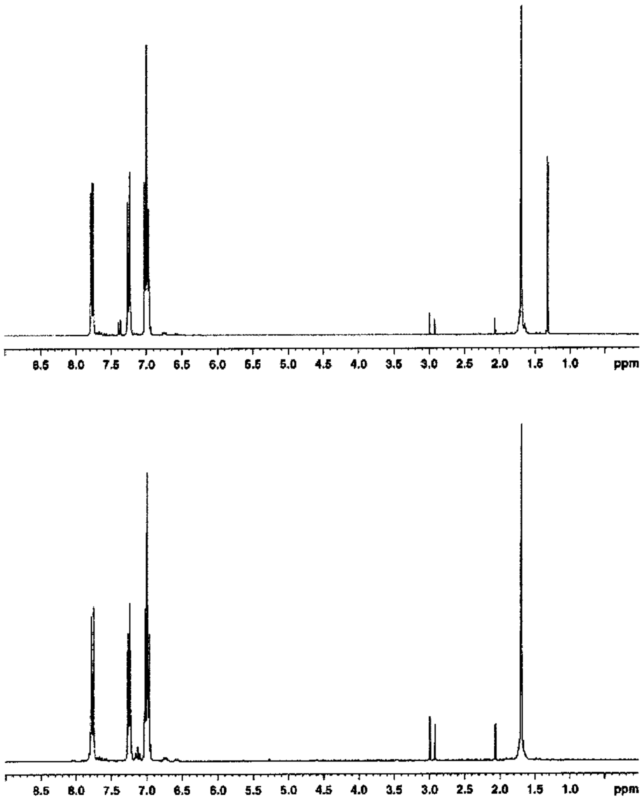

Figure 5. **^{1}H NMR of PAEK produced with tBP (PAEK-7, top) and without tBP (PAEK-5, bottom).**

Although independent variables, both distillation of the water/toluene and increasing the concentration of the polymerization reaction resulted in PAEKs with slightly higher molecular weights and slightly broadened PDs. As the goal of this research was to produce PAEKs with the narrowest

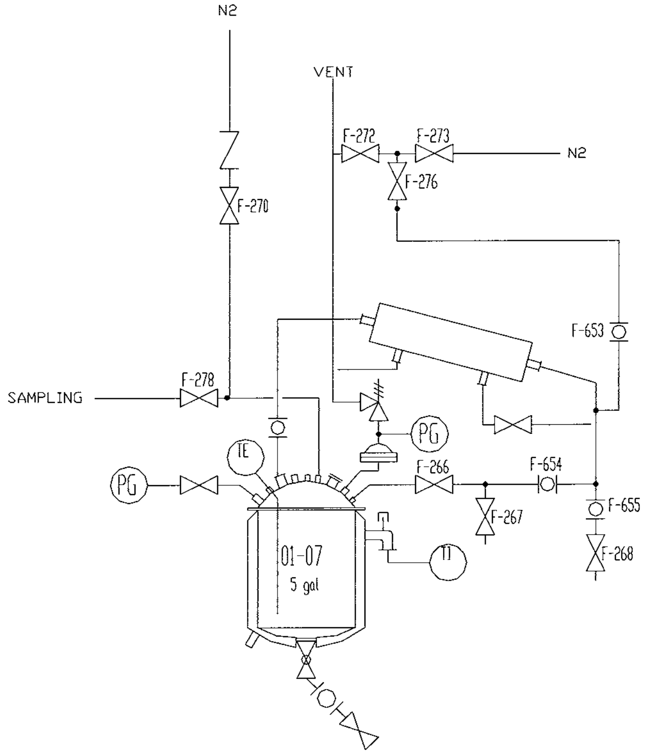

Figure 6. **Reactor setup used for pilot-plant scale synthesis. (Legend) PG: pressure gauge; TI: temperature indicator for hot oil system; TE: temperature element; site glass positions for the Dean−Stark trap section of the reactor are labeled as F-655, F-654, and F-653; distillate is removed through valve F-268.**

possible PD, both of these were taken as negative changes, and as such, our optimized lab-scale reaction conditions did not include them.

Choice of Solvent and Temperature. A way to increase the rate of the polymerization is to increase the temperature. However, the maximum temperature attainable under the described conditions is 165 °C, the boiling point of DMAc under atmospheric pressure. Since the polymerization requires the use of a polar aprotic solvent and we did not want to pressurize the reactor, a solvent is needed that has a higher boiling point than DMAc. Tetramethylene sulfone (TMS, sulfolane) has a boiling point of 285 °C and therefore provides a medium to study the effect of increasing the temperature on the polymerization rate.

Although a comparison between **PAEK-5** (DMAc) and **PAEK-10** (TMS) shows that the initial rate increases when TMS is used as the solvent at a temperature of 200 °C (**PAEK-10**, Figure 2), gelation of the polymerization solution occurred after 1.5 h. Gelation presumably occurred because the polymer reached a molecular weight high enough to attain its solubility limit in TMS. Gelation occurred no matter if tBP was present (**PAEK-11**) or not (**PAEK-10**).

Pilot-Plant-Scale Synthesis of PAEK. *Optimized Synthesis (PAEK-12).* On the basis of the factors discussed, **PAEK-7** was chosen as the procedure for further scale-up. In this case, both the reaction time and the polydispersity (PD) were minimized. Furthermore, the presence of *tert*-butylphenyl endgroups within the PAEK was desirable. The polymerization giving **PAEK-12** was done at 5-times scale compared to **PAEK-7** (1.32 mol BPA vs 0.26 mol BPA) and produced a polymer with slightly wider polydispersity and slightly lower molecular weight. However, these undesirable effects were small in magnitude, and as such, these exact conditions were used to carry out the polymerization at a scale of 8.76 mol BPA in our pilot plant (**PAEK-13**−**PAEK-15**).

Pilot-Plant Synthesis (*PAEK13-15*). At a lab scale, toluene is used to azeotropically remove water produced during the polymerization and drive the reaction to completion. A Dean−Stark trap is typically used to phase-separate water from the toluene before allowing toluene to recirculate back into the reaction vessel. The denser water layer is collected at the bottom of the Dean−Stark trap, and its volume is indicative of the progress of the reaction. The apparatus is normally glass, allowing for easy observation of the distillation, phase-separation, and recirculation processes.

At a pilot-plant scale, the stainless steel reactor was initially outfitted with external piping from the condenser to allow separation of water from the toluene and recirculation of toluene back into the reactor, mimicking a Dean−Stark trap (Figure 6). However, due to the relatively small volume of reactor being used (5 gal) compared to the large volume of external piping required, much more toluene was needed to fill the external piping in this case. Even with the additional toluene added, it was found that a significant amount of DMAc was distilled along with the toluene and water mixture, rendering the entire mixture miscible so that attempted recirculation returned all three back to the reactor. As a consequence, during the first pilot-plant reaction (**PAEK-13**), alternate removal and return of the distillates was performed. After the distillates were collected, ^{1}H NMR was used to determine what the composition was of each portion of collected distillate as the reaction progressed. It was found that the expected amount of water was removed from the reaction and contained in the initial portion of distillate (4 L). The distillate was collected during the first hour while the reactor had an internal temperature of less than 155 °C.

During the second plant process (**PAEK-14**), the distillation rate was slowed, and all of the distillate was collected without returning to the reactor over a 2 h period. Contrary to the results obtained on a lab scale, the PAEK obtained under these conditions did not have an increased polydispersity. This run demonstrated that a simple, slow distillation of water, toluene, and DMAc allowed the reaction to proceed to completion. As a consequence, future reactor setups will not require an external recirculation loop. After 2 h and every subsequent hour thereafter, the progress of the polymerization was determined by removing a sample (using a standard vacuum sampling setup connected to the dip-tube) for analysis by GPC. After 5 h at 160−165 °C (6 h after reaching 150 °C) a PAEK with the desired M_w of about 15 kD and PD of 2.3−2.4 was obtained. On cooling, the reaction mixture can easily be filtered through a bag filter to remove any insoluble materials. The resulting clear solution is added to 10 vol. equiv of vigorously stirred methanol. The precipitated polymer is recovered by vacuum filtration. After the sample was dried, NMR was used to confirm the absence of DMAc and fluorine endgroups and the presence of *tert*-butylphenyl endgroups. Furthermore, ^{1}H NMR could be used to determine the molecular weight of the polymer obtained by relative integration of the *tert*-butyl resonance with the isopropylidene resonance. The values obtained were in good agreement with the ones measured by GPC.

Pilot-Plant Safety and Waste Disposal. The polymer obtained is a free-flowing, fine white powder and as a result represents an inhalation hazard. *Care should be taken not to inhale this powder as its effects on the respiratory system are not known*.

The main waste products of this reaction are an inorganic salt filter cake [presumably composed of potassium fluoride (KF), potassium hydrogen carbonate ($KHCO_3$), and potassium carbonate (K_2CO_3)] and DMAc/methanol wastes containing trace amounts of the PAEK product. No special disposal precautions out of the ordinary were taken.

Conclusions

We have demonstrated a method for the synthesis of controlled molecular weight poly(aryl ether ketone)s (PAEKs) from 4,4′-difluorobenzophenone (DFBP) and bisphenol A (BPA) at a pilot-plant scale within one working day (6−8 h). The isolated PAEKs were white, free-flowing powders, having a weight-average molecular weight (M_w) of approximately 15 kD and a polydispersity (PD) of 2.3−2.4. The control over the molecular weight comes from controlling the ratio of the two monomers, and it has been shown on a lab scale that the molecular weight of the final PAEK can be tailored on the basis of the monomer ratio.

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