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Synthesis and Polymerization of a Partially Fluorinated Monomer

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Introduction

Poly(aryl ether)s are an important subclass of polymers that are part of a family known as engineering plastics. Engineering plastics have certain properties such as a high resistance to heat, flame retardancy, resistance to chemicals, and impact strength that make them highly useful in manufacturing.¹ These properties are extremely important when engineering parts that need to have a high level of performance compared to regularly produced commodity plastics. With recent advances and new techniques in polymer chemistry, it has become more efficient to work on and produce new polymers.¹ One example of an already commercialized engineering plastic is polyether ether ketone (PEEK), which is used to fabricate bearings, pistons, compressor plate valves, and cable insulators.¹ The most common method used to synthesize poly(aryl ethers) is the use of nucleophilic aromatic substitution (S_NAr).¹ This reaction requires a monomer that has a strong activating group between two aromatic rings that is used to stabilize the negatively charged intermediate, formed by the substitution.¹ The nucleophile of the S_NAr reaction is another diol monomer, and in our research it is a bisphenol that can be treated with a base to convert to a bisphenolate salt. The activating group must be an electron withdrawer in order to make the substitution occur. Popular activating groups have been ketones and sulfones that stabilize the negative charge by forming an extra pi bond through intermediate resonance structures.¹ Recently, there has been research on using new activating groups, such as fused-heterocycle, perfluoroalkyl, and carboxylic acid derivative groups because their strong electronegativity will still activate the ring.^{1,2}

Materials and Methods

Preparation of 4,4'-(bisfluorophenyl)difluoromethane (BFPDF)

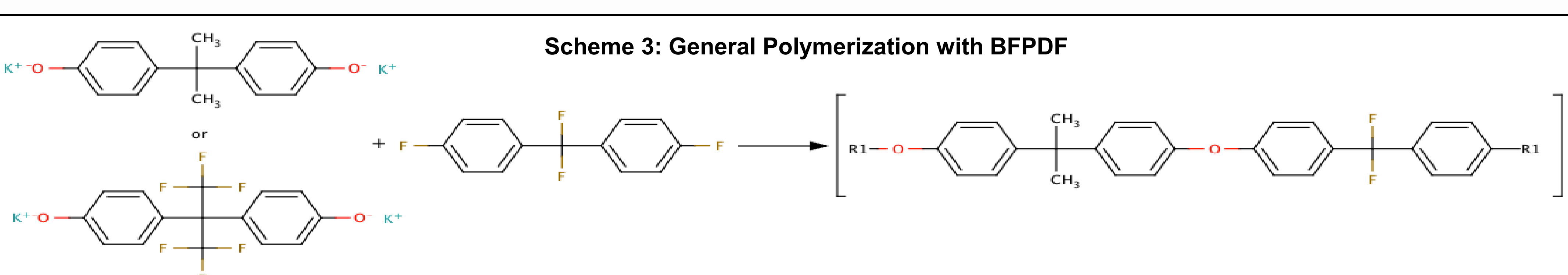
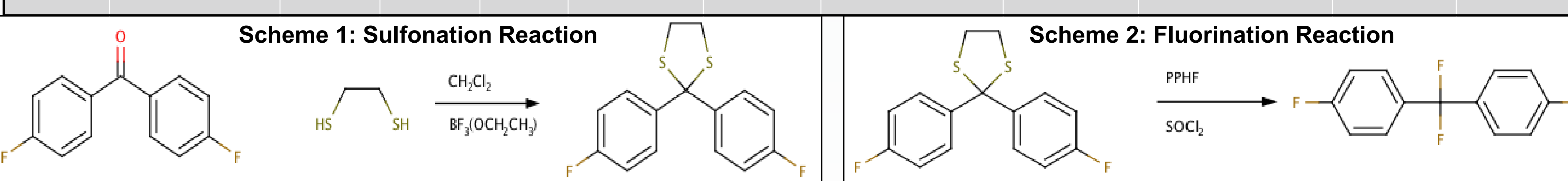
The central carbonyl of 4,4'-difluorobenzophenone was converted to a bridged dithiolane derivative by a sulfonation reaction with 1.5 equivalents of 1,2-ethanedithiol in the presence of 2.2 equivalents of boron trifluoride etherate using methylene chloride as a solvent as shown in Scheme 1. Using the dithiolate derivative, a fluorination reaction was run to remove the reactive dithiol bridge and replace it with two fluorine atoms on the central carbon as shown in Scheme 2. Ratios of 0.5mLSOCl₂, 4mL PPHF, 5mL methylene chloride per 3mmols dithiolate derivative were used under completely anhydrous conditions, with oven dried glassware. The fluorinated monomer (BFPDF) produced by this reaction was purified using column chromatography with a stationary silica phase and a mobile phase solvent of 2.5% ethyl acetate in hexanes. Purity was verified by GC-MS.

Polymerization of BFPDF

Polymerization with BFPDF was carried out with two diol monomers, bisphenol A and bisphenol AF in the presence of potassium carbonate base. Both diol monomers were recrystallized to reach necessary purity levels. Two solvents, n-methylpyrrolidone (NMP) and N,N'-dimethylpropyl urea (DMPU), were used to compare solvent effects on the polymerizations. Both solvents were purified prior to polymerization by distillation and stored over molecular sieves. All glassware was oven dried for 24 hours and cooled under nitrogen prior to use. The diol monomer and potassium carbonate were refluxed in 13 mL of toluene and 3 mL of either solvent for 4 hours at 145 C to collect any water via a dean-stark trap. After 4 hours, the toluene was boiled off through the dean-stark trap, and the BFPDF monomer was added to the reaction by dissolving in 2 mL of solvent and adding via glass syringe. The flask was rinsed with an additional 2 mL of solvent and added. The temperature was increased to 180 C, and the reaction was allowed to run for 6 days. After 6 days, the contents of the reaction flask were precipitated into rapidly spinning water, vacuum filtered, and extracted via a soxlet extractor with water for 24 hours, and methanol for 24 hours. Scheme 3 shows a general polymerization reaction of BFPDF with a diol monomer. The polymer was dried in a vacuum oven and viscosity was measured by dissolving 100mg in 20mL of DMF. 3 trials with each polymer were completed and the inherent viscosity was obtained as shown below in Table 1. Gel Permeation Chromatography with Multi Angle Light Scattering (GPC-MALS) was used to determine molecular weights and was done on a Waters 150-CV Gel Permeation Chromatograph with Wyatt Optilab rEX refractive index (RI) detector and miniDAWN TREOS multi-angle light scattering (MALS) detector.

Table 1: Polymerization Results

Sample	Monomers	Solvent	Base	Temp (C)	Scale (g BFPDF)	Duration	Product Mass (grams)	Recovery	Inherent Viscosity (dL/g)	M _n (g/mol)	M _w (g/mol)
ZS-16	BFPDF BA	NMP	K ₂ CO ₃	180	0.508	6 d	0.575	58.1%	0.310	94,600	148,000
ZS-17	BFPDF HFBA	NMP	K ₂ CO ₃	180	0.484	6 d	0.579	49.9%	0.270	90,200	155,000
ZS-18	BFPDF BA	DMPU	K ₂ CO ₃	180	0.487	6 d	0.558	61.9%	0.150	35,300	56,200
ZS-19	BFPDF HFBA	DMPU	K ₂ CO ₃	180	0.511	6 d	0.786	64.2%	0.204	18,700	51,500
PH-32	BFPDF BA	DMPU	CsF	180	0.484	5 d 19.5 h	0.825	95.8%	0.204	34,770	NR
PH-39	BFPDF BA	DMPU	CsF	180	0.515	6 d 2 h	0.695	75.8%	0.085	NR	NR
PH-47	BFPDF BA	NMP	CsF	170	0.500	6 d 2 h	0.575	64.6%	0.025	NR	NR



Results and Conclusions

From the results shown in Table 1 below, comparisons can be made regarding key reaction conditions. One of the main questions that this work has provided evidence for is whether potassium carbonate can function as a suitable base for this reaction, and how will the polymers produced relate to the polymers produced in previous work using cesium fluoride as a base. By comparing ZS-16 with PH-47, the use of potassium fluoride as a base is clearly seen to increase the inherent viscosity more than 10-fold. It can be observed in the overall results of ZS samples and PH samples that inherent viscosity increases with respect to molecular weight. Following this observation, it can be concluded that potassium carbonate contributes to higher molecular weight polymers than cesium fluoride. This observation is also demonstrated by comparing ZS-18 with PH-32 and PH-39. PH-39 had a very low viscosity and a molecular weight was not reported, but it can be inferred by trends mentioned previously that the molecular weight would be much less than PH-32. Furthermore, ZS-18 actually had a lower inherent viscosity than PH-32, but both samples reported a molecular weight and it was seen that the ZS-18 sample that was run with potassium carbonate had a slightly higher molecular weight relative to PH-32.

Another aspect that was important to investigate was the effect of solvent on the polymers produced. Comparison of ZS-16 with ZS-18 indicates that NMP contributes to higher molecular weight polymers by a large margin. In contrast, this pattern is opposite to what PH samples demonstrated in that greater polymerization activity and molecular weights were observed when DMPU was used. The only change between reaction conditions that could have caused this switch would have been the base, indicating that different bases may actually have different preference of solvent. The overall recovery data indicates that cesium fluoride is more efficient in terms of producing the most product per mole of reactant, but this calculation does not take into account molecular weights and loss of atoms during substitution.

Future Work

Due to time constraints, only few properties were reported for each sample and there is still much characterization to be done in order to fully compare the solvents and bases effects on polymerization. Determination of the glass transition temperature (T_g) will be completed using differential scanning calorimetry (DSC). Determination of decomposition temperature will be done using thermogravimetric analysis (TGA). ¹H NMR and ¹⁹F NMR will also be run to confirm the structure of the synthesized polymers. In addition, more polymerizations will need to be completed and the resulting polymers characterized fully in order to support the conclusions made up to this point. Along with reproducing results using bisphenol A and bisphenol AF, polymerizations can also be done using other aromatic diols for comparison.

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