Studies Toward Highly Fluorinated Polyphenylenes by Diels-Alder Polymerization

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In
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Abstract

Diels-Alder polyphenylenes (DAPPs) are chemically and thermally stable polymers, used for dielectric resins, gas separation membranes, and fuel cell proton exchange membranes. Highly fluorinated DAPPs are expected to have better thermal stability and chemical resistance, higher glass transition temperatures, improved compatibility with other fluorinated polymers (like Nafion^{TM}), and better adhesion to certain surfaces such as some metals. This thesis proposes a synthesis of highly fluorinated DAPPs by reacting novel, fluorinated bis-cyclopentadienone (CPD) monomers with known aromatic dialkynes.

This thesis starts with an introduction to DAPP synthesis, properties, and applications. The second chapter focuses on the synthesis of 4,4'-bis[1,2,4-tris(perfluoro-4-tolyl)cyclopentadien-5-one-3-yl]octafluorobiphenyl (CPD monomer). In the first step, disodiumbis(cyclopentadieny)octafluorobiphenyl was combined with 6 equivalents of octafluorotoluene in HMPA to give 4,4'-bis[1,2,4-tris(perfluoro-4-tolyl)cyclopentadiene-3-yl]octafluorobiphenyl. Oxidation to the corresponding diketone was effected using selenium dioxide. The synthesis of CPD monomer presented several unexpected challenges that were ultimately overcome. The third chapter describes a series of initial polymerization experiments as well as some model reactions that were carried out to understand monomer reactivity. Finally the future research plan of synthesizing different polymers by Diels-Alder reaction and nucleophilic substitution reaction has been discussed.

Acknowledgements

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Finally, I am most grateful to my parents for their support and endless love over the years, they have been a source of encouragement to me. I dedicate this work to my parents, Mr Ashok Sen and Mrs Sutapa Sen. It would not been possible without their support.

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Chapter 1. Introduction

Polymers formed by the catenation of benzene rings are known as *polyphenylenes* (Figure1.). Any organic chemistry student would predict that polymers made from benzene rings would be chemically and thermal stable. Anyone would also guess that polyphenylenes could have interesting properties because of their aromatic conjugation or because of their stiff, rod-like chains. The early synthetic approaches led directly to highly conjugated but intractable poly(*p*-phenylene) or PPP.[1] An alternative synthesis based on Diels-Alder chemistry, gave polyphenylenes with more flexible backbones, tailorable substitution, lower conjugation lengths, and much higher overall molecular weights.[2] PPP attracted attention in the semiconductor area, while the more flexible, soluble polyphenylenes showed commercial utility as spin-on dielectric coatings.[3] Since those early days, many selective and efficient methods of connecting aromatic rings together have been reported, and many of these have evolved into platforms for polyphenylene synthesis,[4] including hyperbranched and dendritic systems.[5] This thesis chapter describes some of the most important methods of preparing polyphenylenes and the key relationships among synthetic methods, polymer structure, properties, and applications.

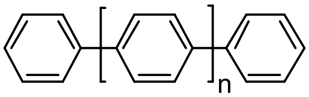


FIGURE 1. Poly(*p*-phenylene)

1.1. Literature Review (Synthesis of Polyphenylenes)

This section summarizes the various synthetic approaches to polyphenylenes and describes their advantages and disadvantages. Diels-Alder polyphenylenes (DAPPs) are emphasized because that is the area where our research group is involved. It is possible that fluorinated

DAPPs will have offer improvements in certain applications such as gas-separation membranes and fuel cell PEMs.

1.1.1. Overview. There are three major synthetic pathways to polyphenylenes. Metal-mediated couplings (Section 1.1.2) offer the broadest range of chemistries, including reactions that will tolerate many different functional groups and structural features. The biggest disadvantage of these reactions is that there are always some residual metal salts or oxides, colloidal metals, or catalyst fragments (ligands, etc.) in the polymeric product. Those impurities are not necessarily easy to remove, and they can degrade properties significantly. Three minor approaches (Section 1.1.3) include electropolymerization (which is specialized for the growth of PPP films on surfaces), Bergman cyclization, and post-aromatization of poly(cyclohexadiene)s. The second major pathway is Diels-Alder (DA) polymerization (Section 1.1.4). One important advantage of the DA approach is that propagation follows a clean polycondensation mechanism by [4+2] cycloaddition, so that metal catalysts are not needed. The biggest disadvantage of the DA approach is the synthesis of the monomers, which can be difficult and expensive. As a result, there are fewer monomers available.

1.1.2. Metal-Mediated Couplings. Metal-mediated polyphenylene synthesis can be divided into two groups. *Stoichiometric* coupling reactions include the Kovacic Synthesis[1] (Section 1.1.1.1) and Ullmann Coupling[4] (Section 1.1.1.2). The metallic reagents in stoichiometric coupling processes are usually consumed as either oxidants or reductants. These reactions are very simple and use cheap commodity chemicals, but the reactive intermediates in the mechanisms lead to side reactions and a lack of control. Among the many types of *catalytic* coupling reactions (Section 1.1.1.3), the Pd-catalyzed Suzuki[6] and Stille[7] reactions have seen the most use in polyphenylene synthesis. The lower cost and improved selectivity of catalytic reactions are balanced against the greater cost and toxicity of the boron- and tin-containing monomers.

1.1.2.1. Kovacic Polymerization and PPP. In 1963 Kovacic reported the synthesis of brown colored poly(*p*-phenylene) (PPP) from benzene using a strong Lewis-acidic catalyst (aluminum chloride, antimony pentachloride, or molybdenum pentachloride) and a one-electron oxidant (Figure 2.).[1]

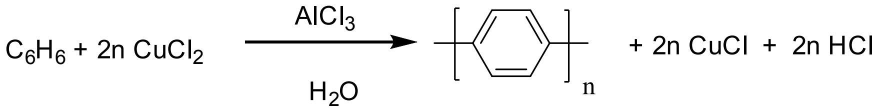


FIGURE 2. Kovacic synthesis of PPP

Copper (II) chloride worked the best for the oxidant, but iron (III) chloride was also investigated briefly. The ratio of catalyst to oxidant dictates the approximate molecular weight of the oligomeric product, and a 2:1 ratio of $AlCl_3$ and $CuCl_2$ was found to be optimum for the polymerization.[8] A small amount of water is required to initiate the reaction, although too much water significantly poisons the reaction. In a similar way, biphenyl can be trimerized to *p*-sexiphenyl, but interestingly the reaction of biphenyl does not readily proceed to higher polymers.[9] The mechanistic details of Kovacic Synthesis are given in Figure. 3 but all its aspects are still not clear.

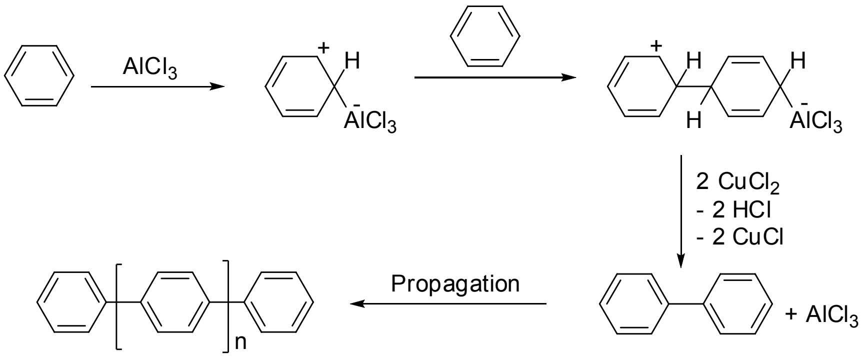


FIGURE 3. Mechanism of Kovacic Synthesis

Although polyphenylenes may adopt all three regiochemistries, only the all-*para* isomer can be prepared using the Kovacic method. The other isomeric forms can be obtained by Diels-Alder polymerization, but PPP has attracted by far the most attention of any polyphenylene because of its simple, rod-like, highly conjugated structure. By appropriate doping, the conductivity of PPP can be varied from the native insulator up to 500 S/cm.[10, 11] PPP is suitable for the preparation of polymer light-emitting diodes (PLED),[12] sensing devices, semiconductors, electro or photo-luminescent materials, and so on.[12-14] Unfortunately, the rod-like structure also makes PPP highly insoluble in common solvents. Addition of alkyl side groups ("lateral" substituents) increases solubility, but the challenge for PPP is to retain the conductive properties that depend on co planarity of adjacent phenylene units.[15] This particular challenge remains largely unmet, and PPP has fallen out of favor as other related polymers like poly(thiophene) have emerged.[16]

1.1.2.2. Ullmann Reaction. In 1901, Ullmann discovered that aryl halides couple to form biaryls in the presence of finely divided metallic copper at 200 – 220 °C (Figure. 4).[4] Electron withdrawing *ortho* substituents (nitro, carbomethoxy) retard the reaction while electron donating groups (amino, hydroxyl) accelerate the reaction. Aryl iodides work better than aryl chlorides too. The reaction has reasonable synthetic yields (70%), but on the other hand, a 70% conversion is not usually considered good enough to be the basis of a polymerization method. Also, harsh conditions were required for the coupling. One interesting trick is to use nitrogen or sulfur groups (specially a Schiff base) at the *ortho* position of the arene. The heteroatom coordinates the copper and speeds up the coupling reaction.[17]

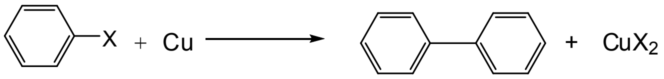


FIGURE 4. Ullmann Coupling

1.1.2.3. Palladium-Catalyzed Coupling. Generally, the most useful type of metal-catalyzed aryl couplings follow the same mechanism (Figure. 5). First there is oxidative addition of the aryl halide (the monomer), which attaches the first aryl group to the transition metal (usually Pd). Then transmetalation from boron (Suzuki, M = B) or tin (Stille, M = Sn) introduces the second aryl group onto Pd. Finally reductive elimination of the two aryl groups gives the new CC sigma bond, propagating the polyphenylene and returning the catalyst to its resting state.

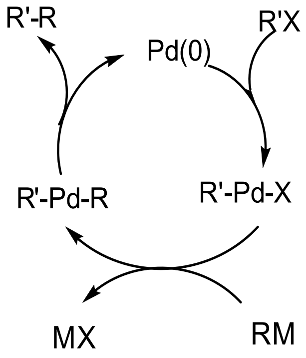


FIGURE 5. Pd-catalyzed sigma coupling mechanism

In the Suzuki reaction, halide reactivity follows the order I>Br>Cl. Pd(0) phosphine complexes perform well as catalysts but unfortunately they are expensive and sensitive, and they are so reactive that they can attack the C-P bonds of the triarylphosphine.[18] Other palladium "precatalyts" generally involve a palladium(II) salt such as $Pd(Ph_3P)_2Cl_2$ and added phosphine ligands. The choice of ligand is highly empirical. The oxidation states visited by Pd in the catalytic cycle remain somewhat controversial.[19, 20]

One other recent development is the use of water as the Suzuki reaction solvent together with microwave heating or water-soluble catalysts.[21] Of course it is best if all of the starting materials are soluble in water, but good results using insoluble aryl halides have been achieved using phase transfer catalysts such as ammonium salts. Based on the synthesis of the small molecules in aqueous medium with microwave radiation Wallow and Novak showed that high molecular weight polymer can also be obtained by using a water-solubilizing ligand like sulfonated triphenylphosphine and monomers with appreciable water solubility (Figure 6.).[21]

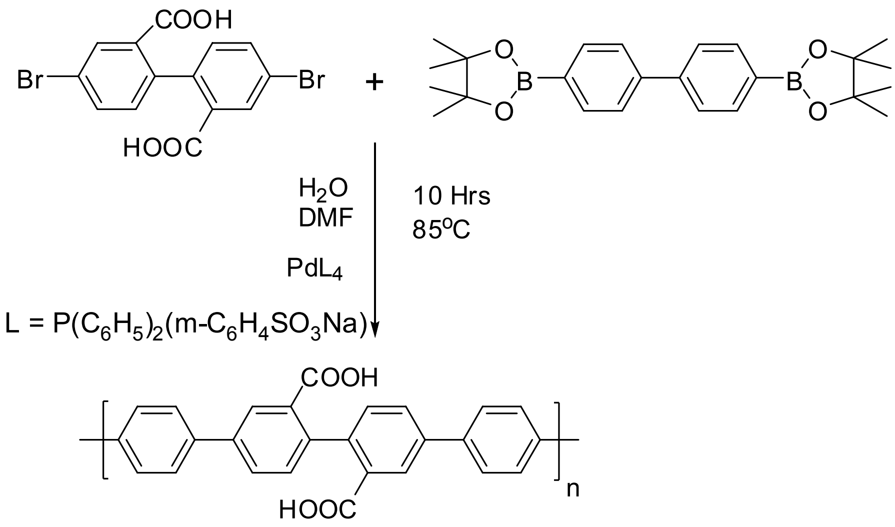


FIGURE 6. Suzuki Coupling polymerization in water medium

If the arylboron reagent of the Suzuki reaction is replaced with an arylation compound, the reaction is known as the Stille Coupling. Stille reactions have found the most use in making poly(phenylene thienylene)s and poly(phenylene vinylene)s which are somewhat outside the scope of this review.

1.1.3. Minor Synthetic Approaches

1.1.3.1. Electropolymerization. The minor methods of preparing polyphenylenes are included here because of the close relationship between electropolymerization and the Kovacic synthesis. In electropolymerization, benzene (and other aromatics such as thiophene) oligomerizes with removal of electrons using an electrode rather than a chemical oxidant (Figure 7.). Again, solubilityof the product limits molecular weight and the scope of the method overall.

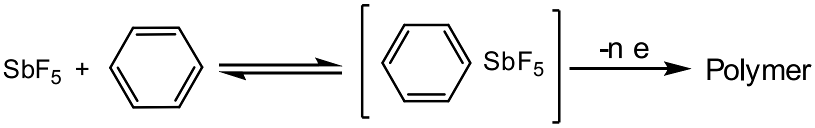


FIGURE 7. Electropolymerization of benzene

However, the method is particularly well-suited to the growth of PPP (or polythiophene) films on surfaces for electronic or electro-optic device applications. Aeiyach and coworkers[22] reported the synthesis of PPP by the anodic polymerization of benzene and biphenyl in liquid sulfur dioxide medium. As in the Kovacic synthesis, a strong Lewis acid such as SbF_5 or $BF_3(OEt_2)$ or even sulfuric acid is added to bring the oxidation potential of benzene into a practical range.[22] In a novel variant, Adenier polymerized benzenediazaonium salts on carbon, metal and silica supports.[23] Improvements in the electropolymerization technique have also been achieved using ionic liquid solvents.

Because PPP films are surface-bound, they are somewhat challenging to characterize. Okuzaki and Kubota measured the absorption of C-H out-of-plane (OOP) bending of the *para* di-substituted and mono-substituted phenyl rings and concluded that the degree of polymerization decreased with the increase of the temperature or the electrode potential.[24] TGA studies showed that the main chain of the polymer degrades only at or above about 600 ^{o}C, but with increasing temperature the PPP films do become brittle and hard. One more successful method of characterizing electrode-bound PPP is cyclic voltammetry.[25] In fact, the progress of the reaction may be monitored this way, but the details are beyond the scope of this review.

1.1.3.2. Bergman Cyclization. The valence tautomerization of enediynes to arylene biradicals shows promise for making polyphenylenes (Figure 8.).[26] Tour[26] found a system that works, but there are a lot of defects in the polymers and molecular weight distributions are very broad. Also, enediynes are expensive and unstable.

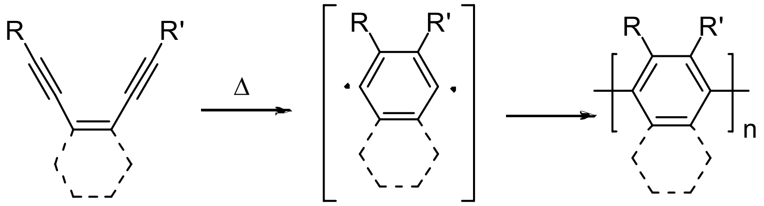


FIGURE 8. Polymerization by Bergman Cyclization

1.2.3.3. Poly(cyclohexadiene) Aromatization. Cyclohexadienes are easy to polymerize, and if they contain two acetoxy groups (OAc), then these can be eliminated after polymerization to make a polyphenylene (Figure. 9). Grubbs showed that this method could give PPP films but there is no good way to include other substituents. The PPP films made by this approach are not as good as those made by electropolymerization, so the whole idea was eventually abandoned.[27, 28]

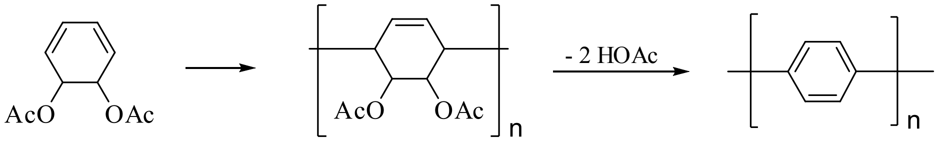


FIGURE 9. (Polycyclohexadiene) aromatization

1.1.4. Diels-Alder Polymerization

The Diels-Alder reaction is a cycloaddition of a conjugated diene and either an alkene or alkyne (called the dienophile). The attractive features of the Diels-Alder reaction include its concerted mechanism, which preserves certain regio- and stereochemical features of the starting materials, and its exothermicity (two pi bonds are replaced with new sigma bonds). However because the Diels-Alder reaction is a simple cycloaddition rather than a condensation, it is disfavored entropically. The initial polymers made by Stille in the early 1960s (Figure 10.) had a tendency to revert to monomer above about 120 ^{o}C.[2] Stille quickly adapted by utilizing Diels-Alder schemes that *do* involve condensation and are therefore irreversible. This section focuses on these more practical systems.[29]

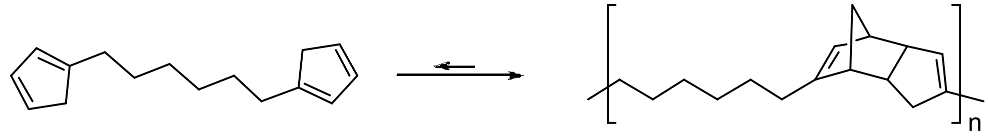


FIGURE 10. Diels Alder polymerization

1.1.4.1. Stille's Irreversible DA Polymerization Systems. Stille chose to base his irreversible Diels-Alder polymerizations on cycloadditions of cyclopentadienones (CPDs), alpha-pyrones, and thiophene oxides, which proceed with extrusion of a small molecule (CO, CO_2, or SO_2, respectively) (Figure 11.).[2, 29] These model reactions, especially the CPD and pyrone reactions, were converted to polymerization systems by constructing phenylene-linked bis-CPD and bis-pyrone monomers and reacting them with dialkynylbenzenes. A schematic of the bis-pyrone system is shown in (Figure 12.). The polymerization temperatures are high – often as high as 250

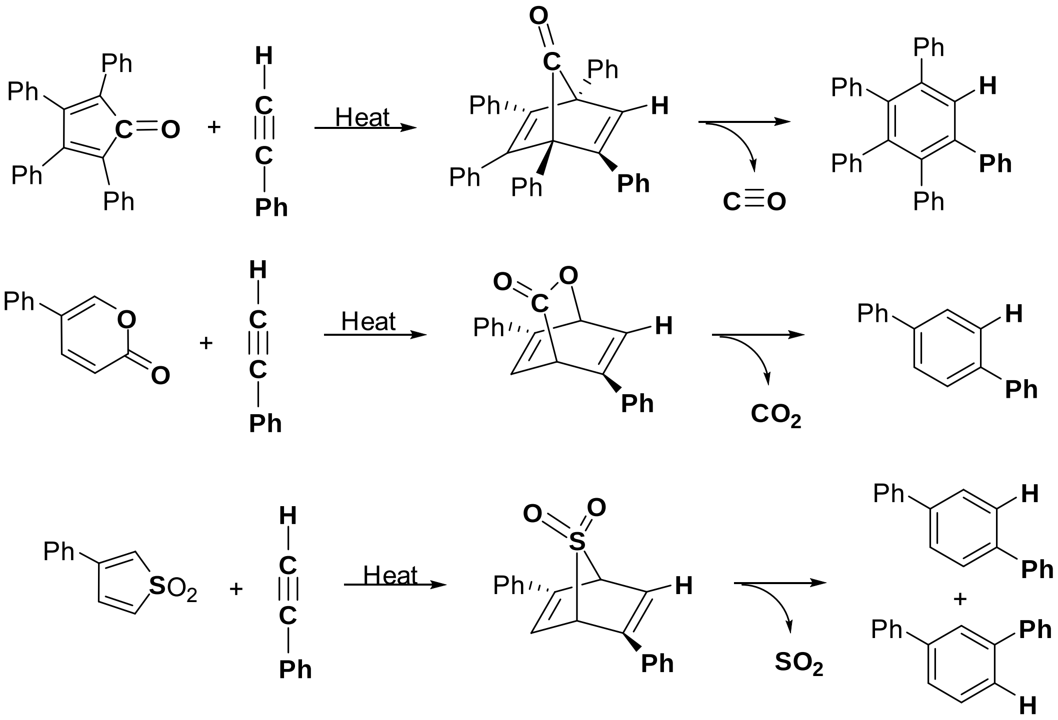


FIGURE 11. Irreversible DA polymerization

^{o}C – in solvents like diphenyl ether, 1,2,4-trichlorobenzene, or 1-methylnaphthalene. This particular reaction is interesting because it produces PPP, which means that the cycloaddition itself must be highly regioselective.[2] Stille used this feature of pyrone cycloadditions to synthesize a family of polyphenylenes having various regioregular structures. The regiochemistry of the starting monomers was within his synthetic control, while the cycloadditions remained intrinsically selective.

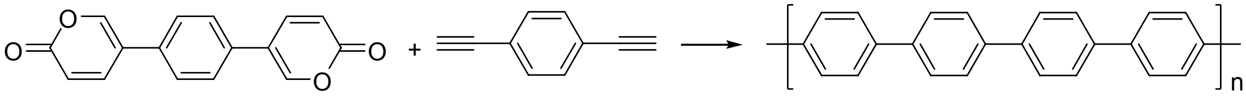
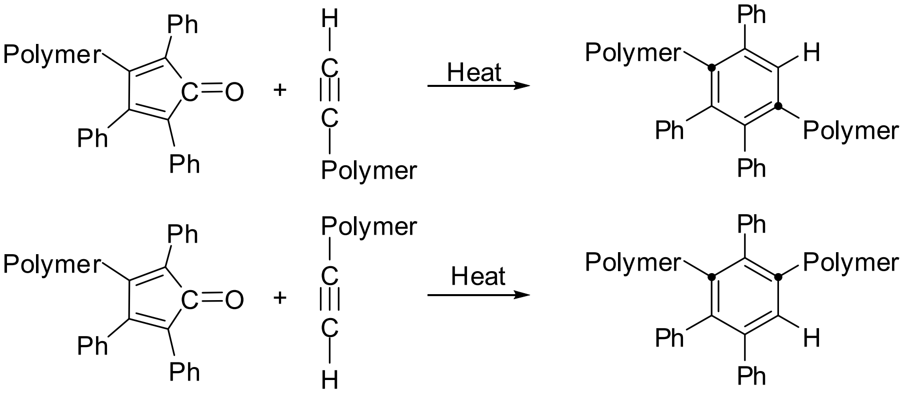


FIGURE 12. Polymerization of bispyrone

The CPD systems readily accessible to Stille were only stable with three or preferably four aromatic substituents. Less fully substituted CPDs can undergo Diels-Alder reactions with themselves, which would lead to defects in the resulting polymers. So, the *CPD polymerizations characteristically give polyphenylenes having lateral aryl substituents*. Stille became interested in these polymers when he discovered that, unlike PPP, they are quite soluble in common solvents like toluene or chloroform and colorless. Solubility is brought about by the lateral phenyl groups, which prevents inter chain arene stacking and decreases the crystalline property of the polymer.[30]



FIGUR 13. Para or meta catenation

Unlike the pyrone system, the regioselectivity of alkyne addition in the CPD system is poor. An all-*para* isomer is shown in the above figure 11, but both *para* and *meta* linkages can be formed during the formation of the bicyclic intermediate (dots in Figure 13.). As expected for a Diels-Alder polymerization, the reaction proceeds under second-order kinetics. The degree of polymerization (DP) is linear with time, and activation parameters are typical of a cycloaddition ($\Delta S^{\#} = -48\ J\ K^{-1}\ mol^{-1}$; $\Delta H^{\#} = 12.4\ kcal\ mol^{-1}$).[31]

Stille[31] also prepared polymers having poly(methylene) spacers (Figure. 14) in the chain by condensation of an α,ω-bis-CPD-*n*-alkane as the dienophile, and either *p*- or *m*-diethynylbenzene. Light colored polymers are formed by this method.

As the methylene group containing bistetracyclones have a lower degradation temperature (300 °C) than the tetraphenylcyclopentadieneone (410 °C), polymerization is best carried out at 225 °C. Once polymerized, however, the system is quite stable. IR spectra taken before and after heating shows the loss of all the methylene groups and some phenyl groups

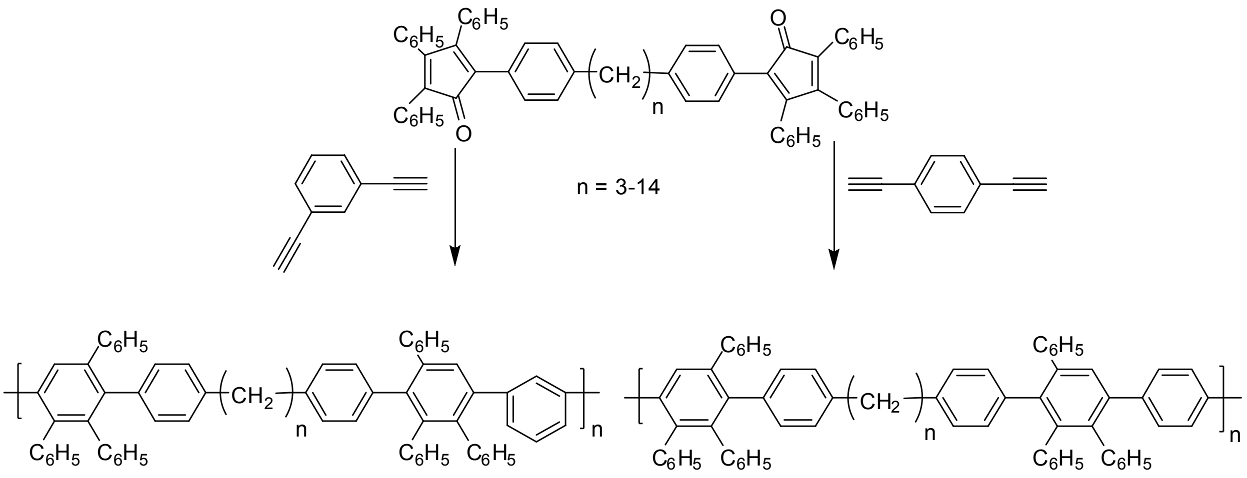


FIGURE 14. Methylene group separated polyphenylene

above 465 °C and formation of cross-linked polynuclear structures. The decrease in the intensity of the C-H stretching peaks after heating proves the loss of methylene group. The solubility of the polymer increases slightly with the increase of the alkyl groups in between. This is because of the destruction of the crystalline structure of the polymer. Clear films of these polymers can be cast from chloroform.[31]

Stille's phenylated CPD-based polyphenylenes have relatively stiff chains, which gives them high glass transition temperatures (T_g). This feature might be an advantage in some

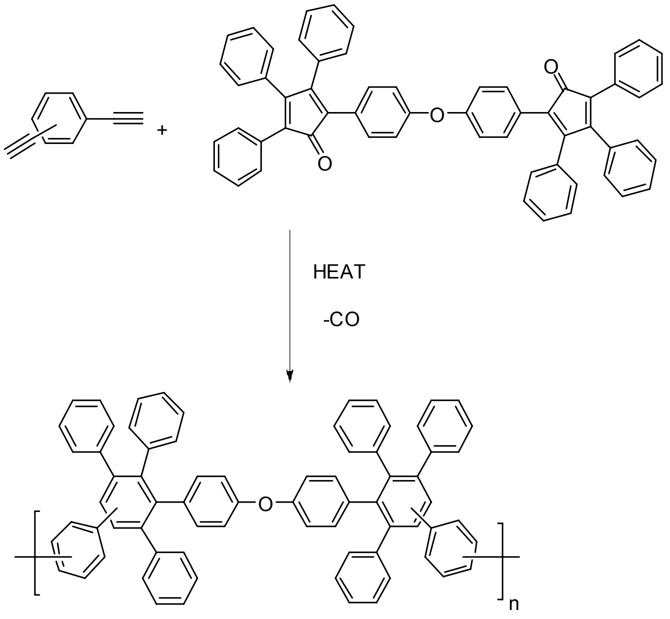


FIGURE 15. Polymer with oxybistetracyclone

applications, but very high molecular weights are needed to achieve film-forming resins. To make the chains more flexible and processable, Stille introduced a diaryl ether moiety in the linker, giving an oxybis(tetracyclone) monomer (Figure 15.).

On the other hand the T_g could be increased again by cross-linking of the polymer chains. For this purpose the polymer formed by the reaction of oxybistetracyclone and *p*-diethynylbenzene was end capped with *m*-hydroxyethynylbenzene (Figure 16.).[32] Generally a low molecular weight pre-polymer is synthesized first (M_n = 4000). The hydroxy groups are then converted to cyanates with cyanogen bromide (confirmed by IR). Upon heating the heating the cyanato-terminated oligomers at 200 °C for 6 h, trimerization of the cyanato groups gives a three-dimensional polymer network.[32]

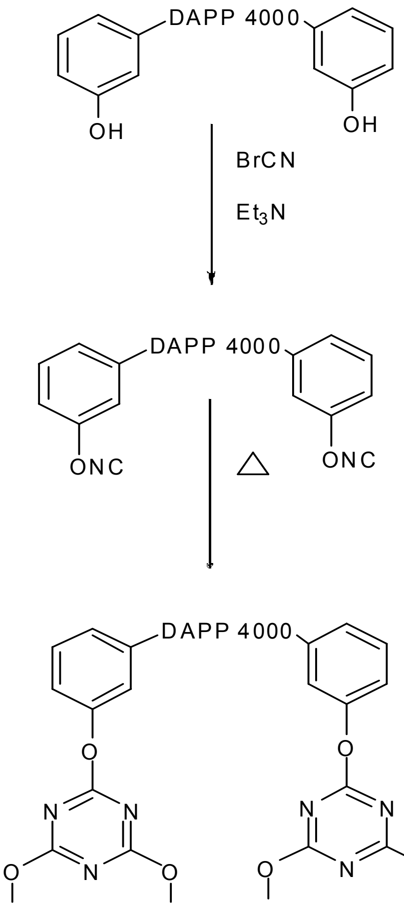
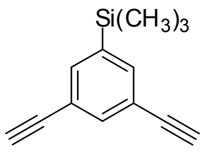


Figure 16. Crosslinking of polyphenylene

Kumar and Neenan used Stille's method to prepare DAPPs from substituted dialkynes and substituted CPDs.[33] Again they found that the presence of the oxygen in the CPD monomer makes the polymer more flexible. This feature, along with the mixed *para-meta* catenation, made the polymer soluble in common organic solvents like THF, chlorobenzene, toluene, chloroform etc. Neenan's polymer was found (using GPC with viscometric detection) to have higher molecular weight (200,000) than Stille's polymer (40,000-100,000). Neenan attributed this increase to a decrease in steric hindrance of the terminal ethynyl groups.[34] Also, better chain flexibility makes it easier for the CPD and the ethynyl groups to interact; alignment is important in Diels-Alder reactions because two bonds are formed at once (strongly negative entropy of activation). The molecular weight of Neenan's DAPPs depended much more upon the substituted diethynylbenzene monomer than the CPDs. Bromine, amide and silicon substituted diethynylbenzenes give lower molecular weight than either the fluorinated or unsubstituted monomers. These functional groups might simply be unstable at the high polymerization temperatures, decreasing the total conversion. On the other hand, T_g depended upon both the CPD and diyne structures. Tetracyclones lacking substitution at the pendent phenyl groups gave higher T_g values due to the rigid structure.

Dialkyne monomers



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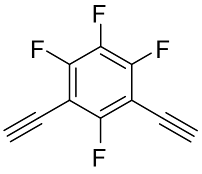

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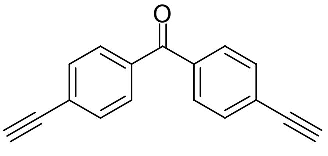

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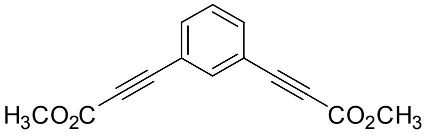

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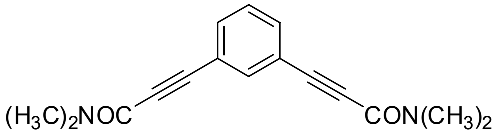

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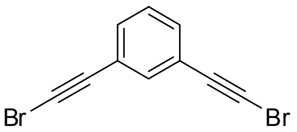
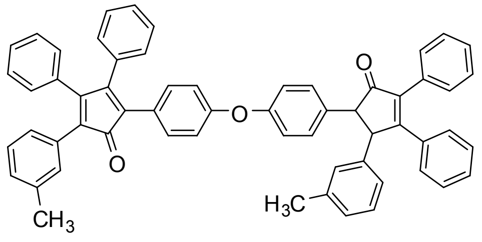


F

CPD monomers



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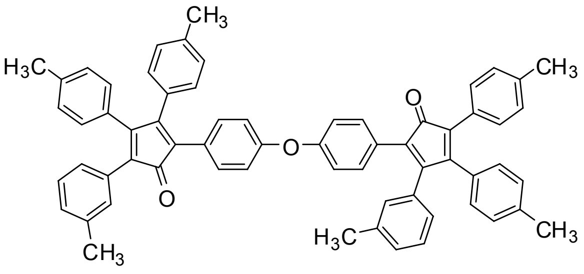

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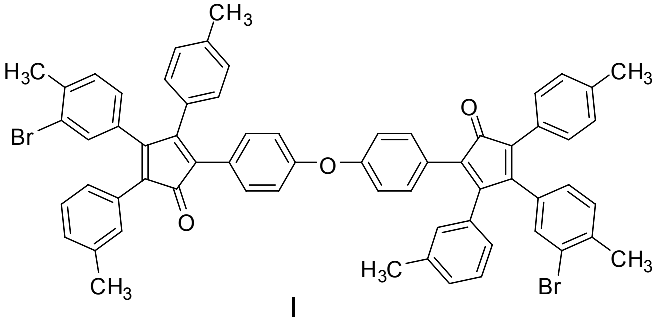


I

TABLE 1. Properties of different Neenan's Diels-Alder polymers

Dialkyne	CPD	T_g ^oC	Mol wt. (M_w) X 10 ^{3}
A	G	280	38-72
B	G	285	109 (at higher monomer conc.)
B	H	-----	350
C	G	270	91-185 (depending on monomer conc.)
C	H	245	185-327 (depending on monomer conc.)
D	G	300	91-94
D	I	270	27-68 (depending on monomer conc.)
E	G	285	17-21
F	G	260	10-14

Many dendritic and hyperbranched polymers can also be synthesized by DA polymerization procedure following Stille's general approach.[5, 35-38] In the dendritic systems the CPD monomer bears two *protected* alkynyl groups (Figure. 17). After reaction of this "branching" CPD with a polyalkynlated "core" molecule, the terminal alkynyl groups are deprotected, and the overall result is a twice larger number of alkynyl groups. Müllen has succeeded in building monodisperse, soluble, shape-persistent dendrimers up to the 5th generation by this approach. In some cases asymmetrical functionality in the core molecule leads to dendrons that can be attached to surfaces or dyes for sensing applications.

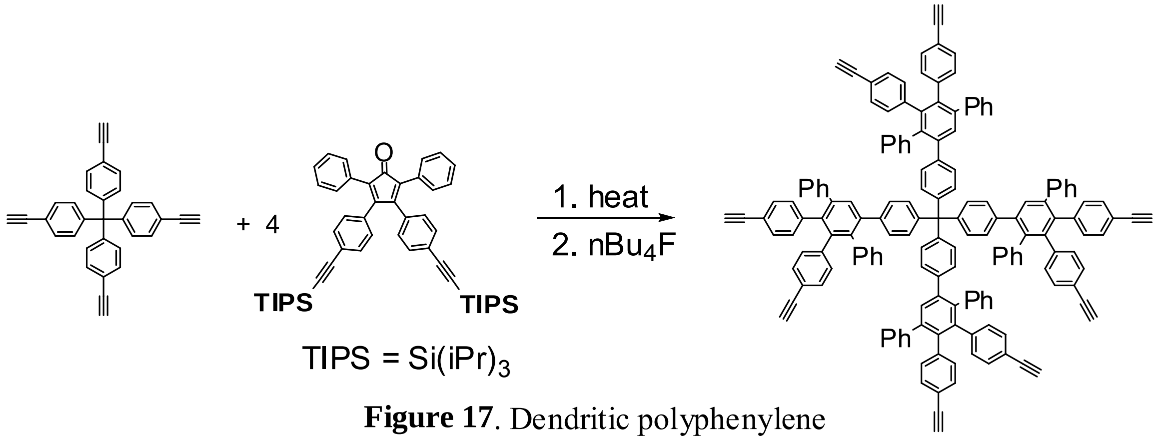


Figure 17. Dendritic polyphenylene

1.2. Applications

Polyphenylenes are useful for several applications – including dielectric resins (1.2.1), proton exchange membranes (1.2.2) and gas separation membranes (1.2.3).

1.2.1. Dielectric Resins. Dow commercialized the Stille-Neenan[3] type polyphenylenes as low-k spin-on dielectric coatings under the trade-name "**SiLK**." According to Professor Dennis Smith, who worked on the Dow Silk program for several years, IBM used Dow SiLK to make integrated circuits for 10-12 years. The product is "b-staged," which means it is only partially polymerized. The low molecular weight ($M_n < 10{,}000$) and the low concentration (5-20%) of the polymer ensure a less viscous solution so that it can fill all the gaps on the wafer. After preparing the surface (often with a silicone-type adhesion promoter according to Dow sales literature), the resin is spun on to the chip wafer and then cured at a high temperature, which drives off any solvent and completes the polymerization. According to Prof. Smith, Dow's main innovation (their patentable invention) was the use of trialkynylbenzene cross-linking agents in the resin formulation, which ensured good thermal stability and mechanical strength in the resulting cured films without adding undesirable functionality as in the case of Stille's polymer.

1.2.2. Fuel Cell Proton Exchange Membranes. In a hydrogen fuel cell, the anodic and cathodic compartments are separated by a *proton-exchange membrane* (PEM), which selectively transports *only* hydrogen ions (H^+). H_2 diffuses to catalyst particles embedded in the anode and dissociates into protons and electrons (eq 1). Protons travel through the PEM to the cathode, where they combine with oxygen to form water (eq 2),[39-44] while charge-balancing electrons pass through the outer circuit with sufficient voltage and current to power a device (Figure 18.).

$$2\,H_2 = 4\,H^+ + 4\,e^- \quad \text{(anode)} \tag{1}$$

$$4\,H^+ + O_2 + 4\,e^- = 2\,H_2O \quad \text{(cathode)} \tag{2}$$

$$2\,H_2 + O_2 = 2\,H_2O \quad \text{(overall)} \tag{3}$$

Fuel cells could replace batteries, grid-based electrical power, and even internal combustion engines, for many applications. Hydrogen or methanol is used as the fuel.[42, 45, 46] The big advantage in the case of hydrogen is that the only byproduct is water (eq 3). CO_2, NO_x, SO_x, CO, and the hydrocarbon emissions, especially from cars and trucks, could be shifted to central plants where primary fuel (coal) could be burned more cleanly.

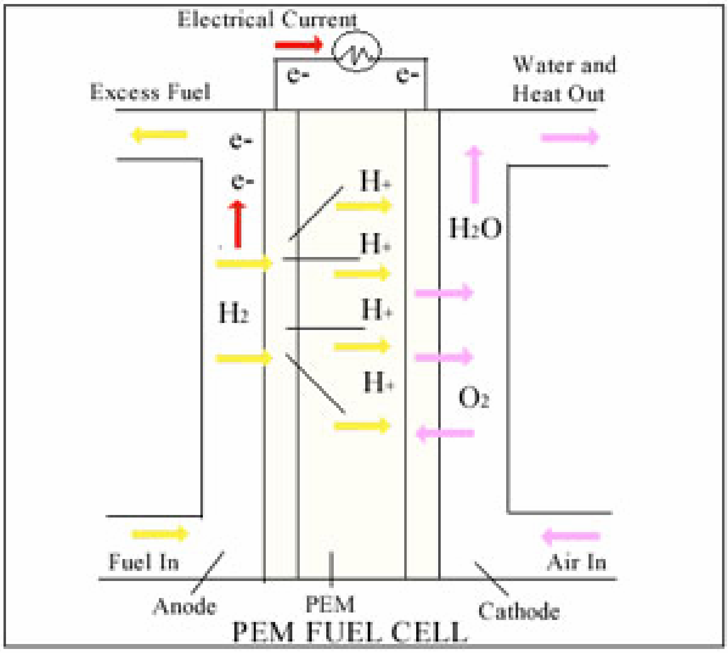


FIGURE 18. Schematic diagram of PEM fuel cell

Improvements in tank-to-wheel efficiency (e.g., within the automobile) require advances in the materials science of fuel cells (and of hydrogen storage). A good PEM has several ideal characteristics.[42] *Low electronic conductivity* prevents the passage of electrical current as electrons, forcing them instead to pass through the external circuit or load. *High proton* *conductivity* avoids resistive voltage losses within the cell. *Low fuel permeability* prevents direct combustion with loss of energy to heat. *Low water transport* helps manage the moisture content so that the cell does not dry out and stop working. *Oxidative/hydrolytic stability* ensures that the PEM will not break down under acidic, aqueous conditions. *Mechanical properties* should be maintained over wide ranges of temperature and humidity. *Ready fabrication* allows the PEM to be incorporated into membrane-electrode assemblies (MEAs). *Low cost* is always a desirable "bottom line" feature.

The best-known PEM polymer is Dupont's Nafion™ (Figure 19.). Like other fluoropolymers, Nafion has excellent chemical resistance.[47]

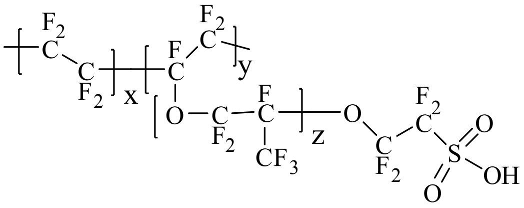


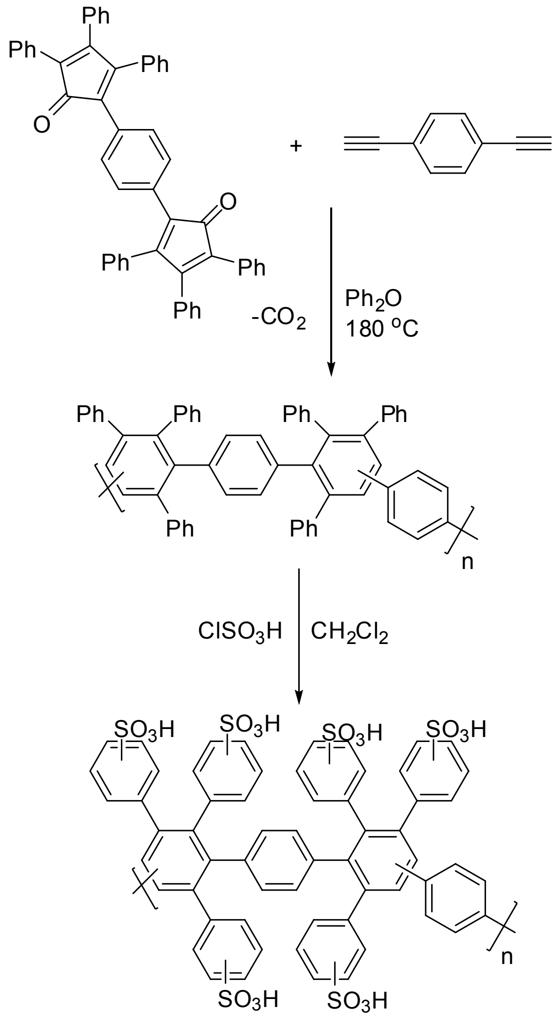
FIGURE 19. Nafion, Commonly used polymer for PEMs

Weakly basic perfluoroalkanesulfonate groups transmit protons easily. Unfortunately Nafion suffers from high temperature instability and processing difficulties. It is expensive too. As one might expect, there is a wide variety of research underway worldwide to prepare superior proton exchange membrane film materials. In fact some of the most promising work is underway at Virginia Tech in Professor McGrath's laboratories. Sulfonated polyamides,[42] poly(aryl ether sulfones),[43] phenol-formaldehydes,[46] polyphenylene oxides, poly-(*p*-phenoxybenzoyl-1,4-phenylene),[48] and poly(benzimidazole) are the most promising materials for this purpose right now.

Fujimoto and coworkers (Sandia National Laboratories) recently reported the synthesis of a

Stille-type phenylated polyphenylenes (Scheme 1) that show promise as PEM materials. The Sandia innovation was post-sulfonation of the lateral phenyl groups (selectivity is thought to be steric in origin) using chlorosulfonic acid in dichloromethane solution.[49] Again the remarkable solubility of the polymer come from the lateral phenyl group substitution along with of *meta* and *para* linkages. Films can be cast from toluene solution on a mesoporous alumina support. It has been found that most of the non fluorinated materials used for the fuel cell membrane are cost-competitive with Nafion, but they suffer from low oxidative resistance and poor thermal stability at higher temperature.

SCHEME 1



1.2.3. Gas separation membranes (GSMs). Polymer membranes offer promising technologies for the separation of industrial gas mixtures, such as natural gas (Figure 20.).[50, 51] Permeability of a gas through the membrane is dependent on both diffusivity and solubility of that particular gas in the polymer. Therefore gas separation through a polymer membrane is not only a function of chemical structure of the polymer but also is determined by the free volume, morphology, and domain structure formed by the polymer in the membrane.[51-54]

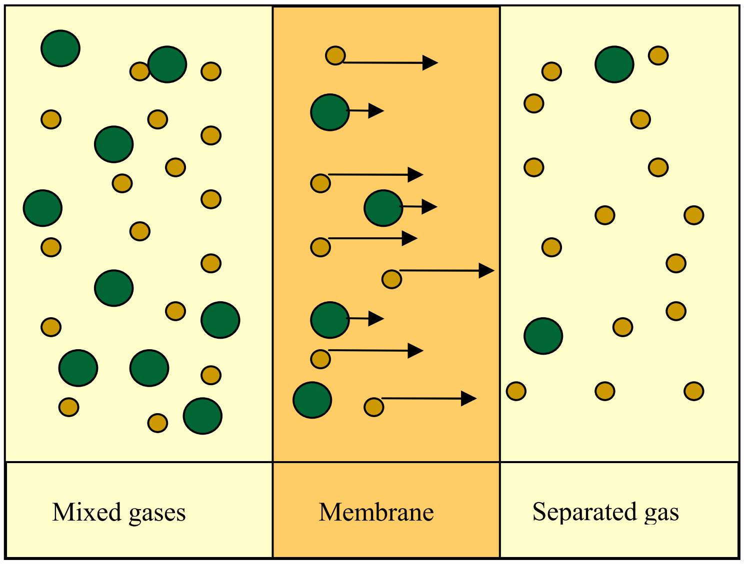


FIGURE 20. Schematic diagram of gas separation membrane

Ideally, a GSM polymer should exhibit high but selective permeability, as well as good chemical, thermal, and mechanical stability (especially with respect to plasticization) for a long service lifetime.[52] An inverse relationship exists between permeability and permeselctivity, so it is difficult to enhance both concurrently. Polymer chain mobility or stiffness and intersegmental distance are two main criteria in determining the transport properties. Chain rigidity provides higher permeselectivity but lower permeability whereas greater interchain distance provides parameters is typically a glassy polymer with bulky side group substitution.

higher permeability but lower selectivity. The category of polymers that optimizes both

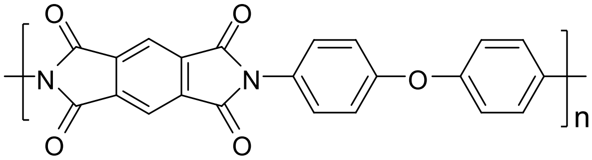


FIGURE 21. Polyimide, the most commonly used polymer for gas separation membranes

Polyimides (Figure 21.) are the “standard” polymers used for gas separation membrane in recent years. In addition to high selectivity, polyimides can have high glass transition temperatures ($T_g > 200$ °C) and relatively high hydrophobicity. On the other hand, the high melting points and strong hydrogen bonding of polyimides make solubility low and film processing difficult. Moreover polyimides typically have low gas permeabilities. Consequently there is a search for alternative GSMs.[55, 56]

Poly(phenylene oxide) (PPO) (Figure 22.) and its derivatives are also interesting as gas separation membranes. They have high T_g (> 220 °C) and superior mechanical strength. The chain kinks arising from ether linkages suppress close packing. Therefore this polymer has a high free volume and good permeability. On the down side, the permeselectivity of PPO is low compared to other glassy polymers. Introduction of polar groups in the polymer backbone can increase the intermolecular attractional force. As a result the interchain spacing will be decreased and the polymer will achieve permeselctivity. Excellent results are obtained by introducing bromine, sulfone, methyl, esters, and carboxyl etc polar groups on the polymer backbone.[53]

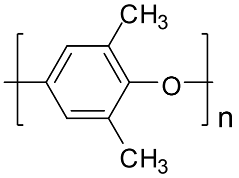


FIGURE 22. Polyphenylene oxide

Other polymers that show similar structure-activity relationships in GSM performance include poly(arylsulfone)s and poly(aryl ketone)s.

Fujimoto and coworker have reported Diels-Alder polyphenylenes (Figure 23.) that show both permeability and permeselctivity simultaneously. The steric hindrance created by the bulky side group substitutions tends to orient the backbone phenyl rings orthogonal to each other. The chain segmental motion is restricted.[57] Therefore the polymer becomes very rigid having a high glass transition temperature and increases the selectivity towards gas separation. On the other hand the bulky side groups also increase the polymer free volume which directly increases the gas permeability. High solubility in many common organic solvents, easy film forming behavior, along with high selectivity and permeability make DAPPs a promising choice for gas separation membranes.

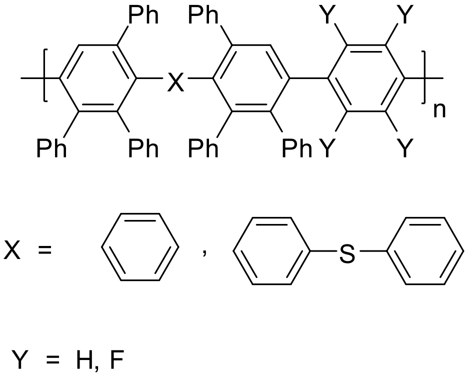


FIGURE 23. Polyphenylene gas separation membrane

1.3. Expected Properties of Highly Fluorinated DAPPs. In this section we will speculate on some of the unique properties and applications that we are anticipating from our highly fluorinated DAPPs. Essentially, we think our polymers will be similar to the non-fluorinated DAPPs studied originally by Stille[2] and later by the Dow team of Godschalx, Martin, and Smith, and by the Sandia team of Fujimoto,[49, 57] Cornelius, and coworkers.

1.3.1. Expected Structure-Property Relationships of the Polymer. (Figure 24.) shows a three-dimensional structure of one repeating unit of the proposed polymer. We proposed the following microscopic and macroscopic properties will be obtained from this polymer based on its structure. The following paragraphs describe some ways in which high fluorine content will modulate physical properties.[58, 59]

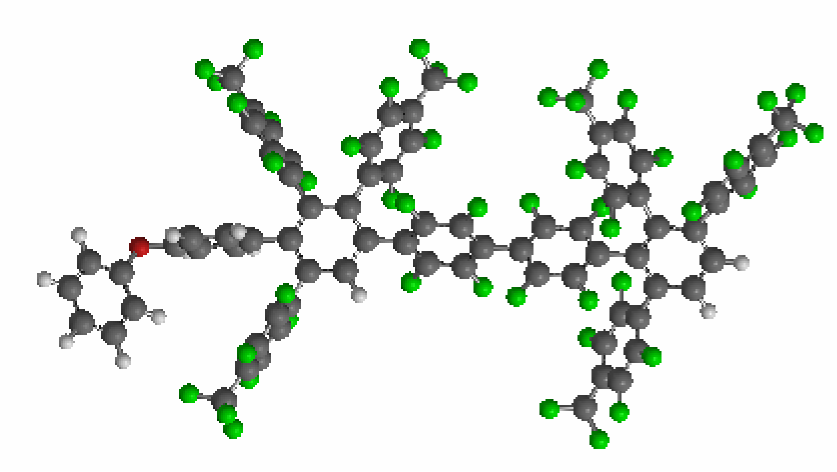


FIGURE 24. One repeat unit of proposed polymer

Microscopic Properties.

Chain Rigidity. The bulky aromatic side group substitutions will restrict the free chain rotation and segmental motion of the polymer chain. The Vander Waals radius of fluorine is somewhat larger than that of hydrogen, so we anticipate less rotational flexibility along the backbones of our fluorinated DAPPs because of increased steric crowding. Therefore it is logical to suppose that the glass transition temperatures will remain high.

Superior Free Volume. Steric hindrance introduced by the CF_3 groups of the C_7F_7 substituents will prevent close packing of chains. Consequently the polymer will have a significantly high free volume. Here we want to mention that in discussions with Prof. Benny Freeman (UT – Austin), our group learned that our highly fluorinated polyphenylenes might be promising candidates for gas separation membranes. This is an area that we would need to explore more thoroughly before discussing in detail – but it does sound exciting. The high chain rigidity, high glass transition temperature and high free volume of the polymer are anticipated to provide the rare combination of high permeselectivity and permeability. The high thermal and chemical stability of the polymer will offer high temperature performance. Obviously, though, we would have to study the permeselectivity/permeability trade-offs very closely. If the CF_3 groups were replaced by longer perfluoroalkyl chains, however, it might be possible to envision them either "crystallizing" among themselves, or lowering the T_g by internal plasticization. My colleague, Charles Carfagna, is studying the effects of substituent perfluoroalkyl chain length in a related fluorinated DAPP system.

Macroscopic Properties

Proton Conductivity. Looking toward PEM applications, proton conductivity could be achieved by introducing sulfonate groups in the *para* positions of either phenyl or pentafluorophenyl lateral substituents. To be candid, we are not sure how we will accomplish this task synthetically. Considering the synthetic challenges we have faced in our bis-CPD monomer syntheses, the best option appears to be to incorporate the sulfonate functionality into the dialkyne monomer or to sulfonate after copolymerization with a non-fluorinated bis-CPD monomer.

The second option is shown in (Figure 25.). Depending upon the reactivity ratio we will get the random ($r_1 = r_2 = 1$) or block copolymers ($r_1 > 1$ and $r_2 > 1$ and depending upon the concentration of monomers). To get the optimal properties in our polymer, random polymers will be preferred over the block copolymers because closely situated hydrophilic sulfonated groups form cylindrical channels for the transportation of the ions and these must not phase separate into domains but rather they have to be distributed evenly throughout the membrane. And to make the polymer proton exchangeable we have to sulfonate the pendant aromatic moieties.

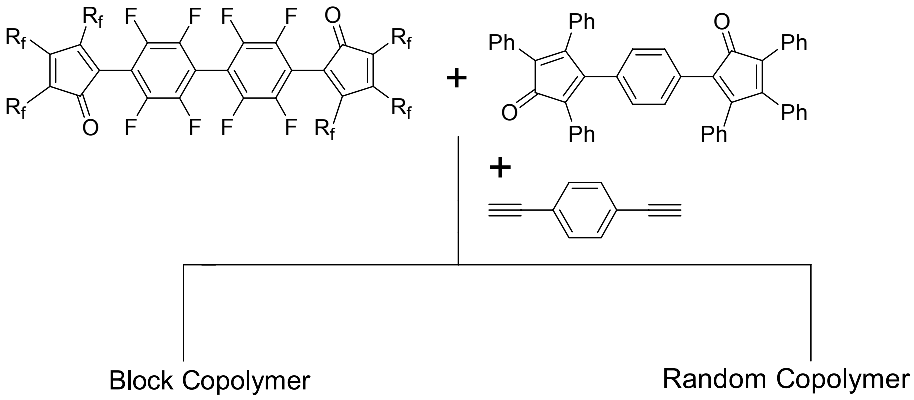


FIGURE 25. Different types of copolymer

Electron Conductivity and Dielectric Behavior. Fluorination usually improves dielectric performance. We anticipate that our fluorinated DAPPs will be poor electron conductors and excellent dielectric materials.

Thermal, Chemical, and Water Stability. Since the polymer chain will be sheathed by fluorine atoms, the polymer will be highly stable towards acids, bases, oxidants and other chemicals. The polymer will repel water (hydrophobic) and hydrocarbons (oleophobic) also. The aromatic backbone along with strong C-F bonds will effect good thermal stability.

Other Properties. There are some important properties that we really cannot estimate well. These include solubility and mechanical behavior. As we work toward prototype systems synthetically we hope to learn about these properties soon, so that we can start designing them to be better.

Chapter 2. Design and Synthesis of a Perfluorinated Bis-Cyclopentadienone (Bis-CPD) Monomer for Diels-Alder Polymerization.

This chapter describes the synthesis of a first-generation fluorinated CPD monomer for use in Stille-type Diels-Alder polymerizations with dialkynes. Section (2.1) summarizes our motivation for undertaking the synthesis of highly fluorinated polyphenylenes. Section 2.2 shows how our CPD monomer design evolved by recognizing that a highly fluorinated version of Stille's phenyl-substituted CPD monomer could be achieved using synthetic methods already developed in our research group for other purposes. Section 2.3 describes the monomer synthesis in full detail.

2.1 Motivation. Fluoropolymers exhibit several useful physical properties, such as low dielectric constant, high thermal stability, resistance toward acids and oxidants, low refractive index, resistance to abrasion, and so on. Many of these "advantages" are based on the properties of polymers obtained by free-radical chain polymerization of a relatively limited monomer repertoire (tetrafluoroethylene or TFE and its derivatives). The special properties are believed to arise because $(CF_2O)_n$, $[CF(CF_3)CF_2O]_n$, and especially $(CF_2)_n$, chains are protected from attack not only by the electronic properties of fluorine but also because the carbon atoms are sterically saturated. The same reasons also account for the highly crystalline nature of $(CF_2)_n$ containing polymers like PTFE, compared to corresponding hydrocarbon derivatives (e.g., polyethylene). Of course, all of the properties of aliphatic fluoropolymers will not necessarily carry over into the aromatic polymer area. But on the other hand aromatic CF bonds are very strong, so we hope that many of the advantages of fluorination will apply to our polymers. In addition, Diels-Alder polyphenylenes (DAPPs) are attractive because the all-aromatic carbon skeleton is intrinsically stable, and the enchainment reaction is not reversible. All these facts motivated us to synthesize highly fluorinated DAPPs. A summary of the properties that we anticipate from highly fluorinated DAPPs was provided already in Section 1.3.

2.2 Evolution of the Monomer Design. A quick glance at Stille's CPD monomer reveals a key skeletal feature: Aryl-substituted cyclopentadienes (Figure 26.).[30] From 1995 onward, the Deck research group focused much of its efforts on the synthesis of arylated cyclopentadienes, however the aromatic groups are perfluorinated. This section identifies a few of those synthetic findings and shows how they led us to the design of specific first-generation monomer targets.

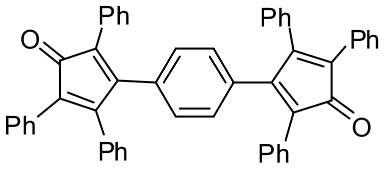
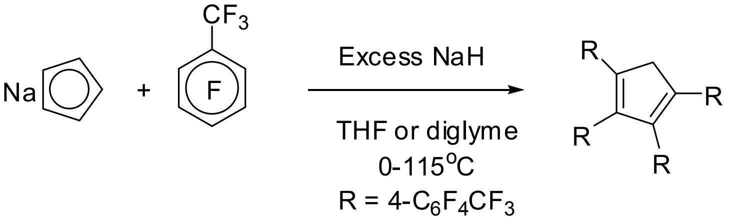


FIGURE 26. Stille's monomer

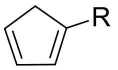
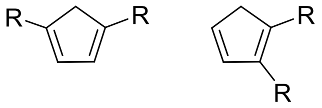
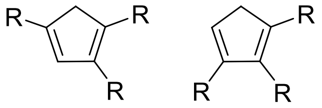
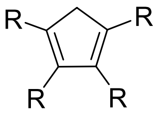
2.2.1 Perfluoroaryl-Substituted Cyclopentadiene Synthesis. The approach taken by Prof. Deck and co-workers combines a cyclopentadienyl (Cp) anion with a perfluoroarene in a classic nucleophilic substitution (S_NAr) reaction (Scheme 2). The Cp anion may bear other substituents.

SCHEME 2



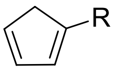
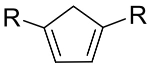
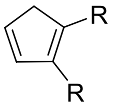
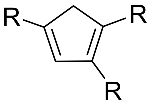
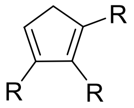
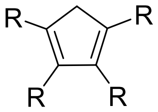
The perfluoroarene may be hexafluorobenzene, octafluorotoluene, or pentafluoropyridine (among others). Multiple arylations may be carried out in one-pot procedures with excess base (usually sodium hydride) and excess perfluoroarene. The number of aryl groups attached in one pot can be controlled by varying reaction conditions (Tables 1 and 2).[60-63] One important feature of the results shown in Tables 1 and 2 is that 1,2,3,4-tetraarylated products are formed selectively an in high yields under forcing conditions; pentaarylated products are not observed. Also, *gem*-diarylated products are not formed, because the Cp carbons already bearing perfluoroaryl groups are less nucleophilic. This reaction therefore affords cyclopentadienes bearing four perfluoroaryl (e.g., C_6F_5 or $C_6F_4CF_3$) substituents in an efficient manner.

Table 2. Reactions of NaCp with Octafluorotoluene (R = 4-$C_6F_4CF_3$).

Product	RF : NaCp	Solvent	Temperature	Time	Yield
	1 : 1.25	THF	-10 to 25 ^{o}C	16 h	75%
	2.2 : 1	THF	25 ^{o}C	24 h	64% [a]
	4.2 : 1	THF	60 ^{o}C	2 d	70% [b]
	6 : 1	diglyme	115 ^{o}C	2 d	55%

[a] Total yield for inseparable mixture of skeletal regioisomers.
[b] Total yield for 1:1 mixture of regioisomers separated by silica gel chromatography.

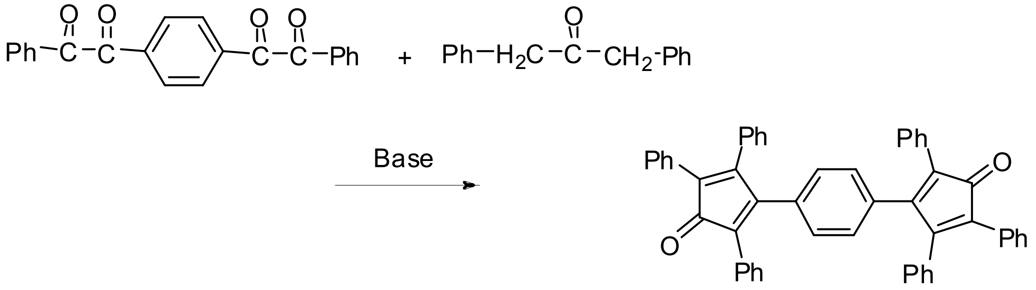
Table 3. Reactions of NaCp with Hexafluorobenzene (R = C_6F_5).

Product	RF : NaCp	Solvent	Temperature	Time	Yield
	1 : 1.2	THF	0 to 25 °C	18 h	80%
 	3 : 1	THF	65 °C	3 d	54% [a]
 	5 : 1	diglyme	110 °C	15 h	60% [b]
	6 : 1	HMPA	140 °C	2 d	70%

[a] The 1,2-diarylcyclopentadiene isomer is obtained in small amounts and not reliably.
[b] Total yield for ca. 1:1 mixture of regioisomers separated by silica gel chromatography.

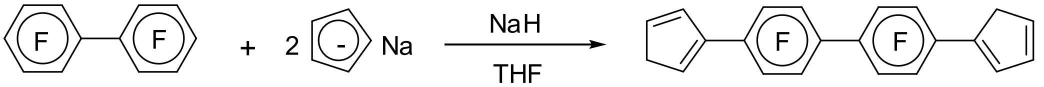
2.2.2. Perfluoroarylene-Linked Bis-Cyclopentadienes. The other key skeletal feature of Stille's monomer (Figure 26.) is the presence of two CPD units linked by a single phenylene group. This linkage was achieved by preparing a difunctional derivative of benzil (Scheme 3)[30] and reacting it with 2 equiv of dibenzyl ketone in an Aldol condensation. However, Prof. Deck and co-workers subsequently demonstrated that two cyclopentadienyl groups can be linked by a

SCHEME 3



perfluoroarylene group in a one-pot, double nucleophilic aromatic substitution reaction (Scheme 4).[64] More recently, Prof. Deck and Evans extended this technique to the more nucleophilic (*tert*-butyl)cyclopentadiene, *en route* to an analogous CPD monomer system.

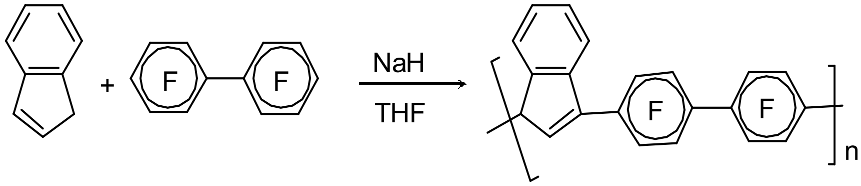
SCHEME 4



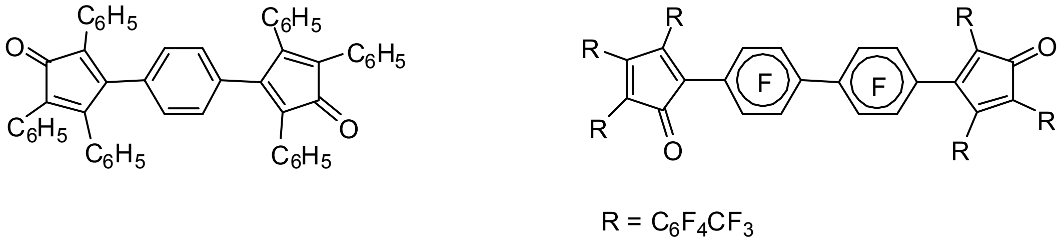
(1)

Prof. Deck and co-workers also demonstrated the analogous deliberate polymerization using indene (Scheme 5). Unlike cyclopentadiene, indene can only react twice, so it is strictly a difunctional nucleophile and gives a linear polymer. *All of these systems show that decafluorobiphenyl is a versatile synthon for connecting two cyclopentadienyl moieties* using a well-defined perfluoroarylene linkage.[65]

SCHEME 5



2.2.3. Emergence of Our Monomer Design. Sections 2.1.1 and 2.2.2 show that *both of the key skeletal features* of the Stille CPD monomer – arylene linkage and lateral aryl substituents – can be achieved using the fluoroarylated cyclopentadiene chemistry developed by Prof. Deck and co-workers. (Figure 27.) shows the structure of our proposed CPD monomer alongside Stille's monomer. Four comments are appropriate here. First, we had to extend the arylene linkage to take advantage of the tendency for decafluorobiphenyl to undergo two neucleophilic substitutions regioselectively. Hexafluorobenzene only reacts once with cyclopentadienyl anion,



Stille's Monomer

Our Monomer

FIGURE 27. Structural comparison between Stille's monomer and our proposed monomer

even under severe conditions. Even if two substitutions could be "forced," it is not clear, from established literature, that the second substitution would be regioselective.[66] Second, the arylation chemistry established by Deck and co-workers (Tables 1 and 2) attaches a maximum of four perfluoroaryl groups to a cyclopentadiene. This finding is fortuitous for the proposed CPD monomer because it leaves one cyclopentadiene carbon unsubstituted, which in principle can be converted to the corresponding C=O. Third, the chemistry summarized in Tables 1 and 2 gives cyclopentadienes, not cyclopentadienones. Thus the problem of oxidizing CH_2 to C=O presents a potentially significant synthetic challenge. Fourth, there is no obvious way to control the regiochemistry of the cyclopentadienone substituents in the proposed monomer. However, the latter two issues were considered secondary to the attraction of assembling the needed carbon skeleton in a few simple steps.

2.3 Synthesis of the Monomer. This section describes how we assembled the CPD monomer proposed in the previous sections. Section 2.3.1 essentially follows the published chemistry shown in (Scheme 4) but emphasizes the issue of purity, which takes on a higher significance in step-growth polymerization applications than it does in organometallic chemistry, where it is generally expected that products can be recrystallized. Section 2.3.2 shows how the lateral perfluoroaryl groups are attached, and section 2.3.3 describes the oxidation of the CH_2 group.

2.3.1 Establishing the Arylene Linker. The published reaction shown in (Scheme 4)(was given above) was followed. Excess NaCp and excess NaH were combined with decafluorobiphenyl in THF at reflux. The excess NaCp ensures that both *para* fluorines of decafluorobiphenyl react completely. The ^{19}F NMR spectrum of the product shows the absence of *para* signals (ca. −149 ppm, Figure 28.). The excess NaH traps the cyclopentadiene moieties of the product as their conjugate bases, preventing them from undergoing Diels-Alder self-dimerization during the reaction. The absence of signals in the range 2.0 – 3.0 ppm in the ^{1}H NMR spectrum of the product confirms that Diels-Alder self-dimerization was completely suppressed. Another side-reaction that can occur is the reaction of one cyclopentadienyl group with two perfluoroarenes. Even though the second arylation is retarded by the electron-withdrawing effects of the first perfluoroaryl substituent, care must still be taken because the “over-arylation” by-products could be difficult to remove. This process is minimized by starting the reaction at room temperature and then warming to reflux (70 °C). The absence of signals in the range 3.9 – 4.2 ppm in the ^{1}H NMR spectrum of the product confirms that no over-arylation occurred. The NMR spectra of the product **(1)** are complicated because **(1)** is obtained as a mixture of regioisomers. The reaction workup involves a cold acidic hydrolysis. Unfortunately the product **(1)** is not soluble in hexane, so silica gel chromatography is not a scalable method of purification. Recrystallization from warm solvent is not possible because the compound would dimerize upon heating. So, the bis-diene is simply triturated with cold pentane.

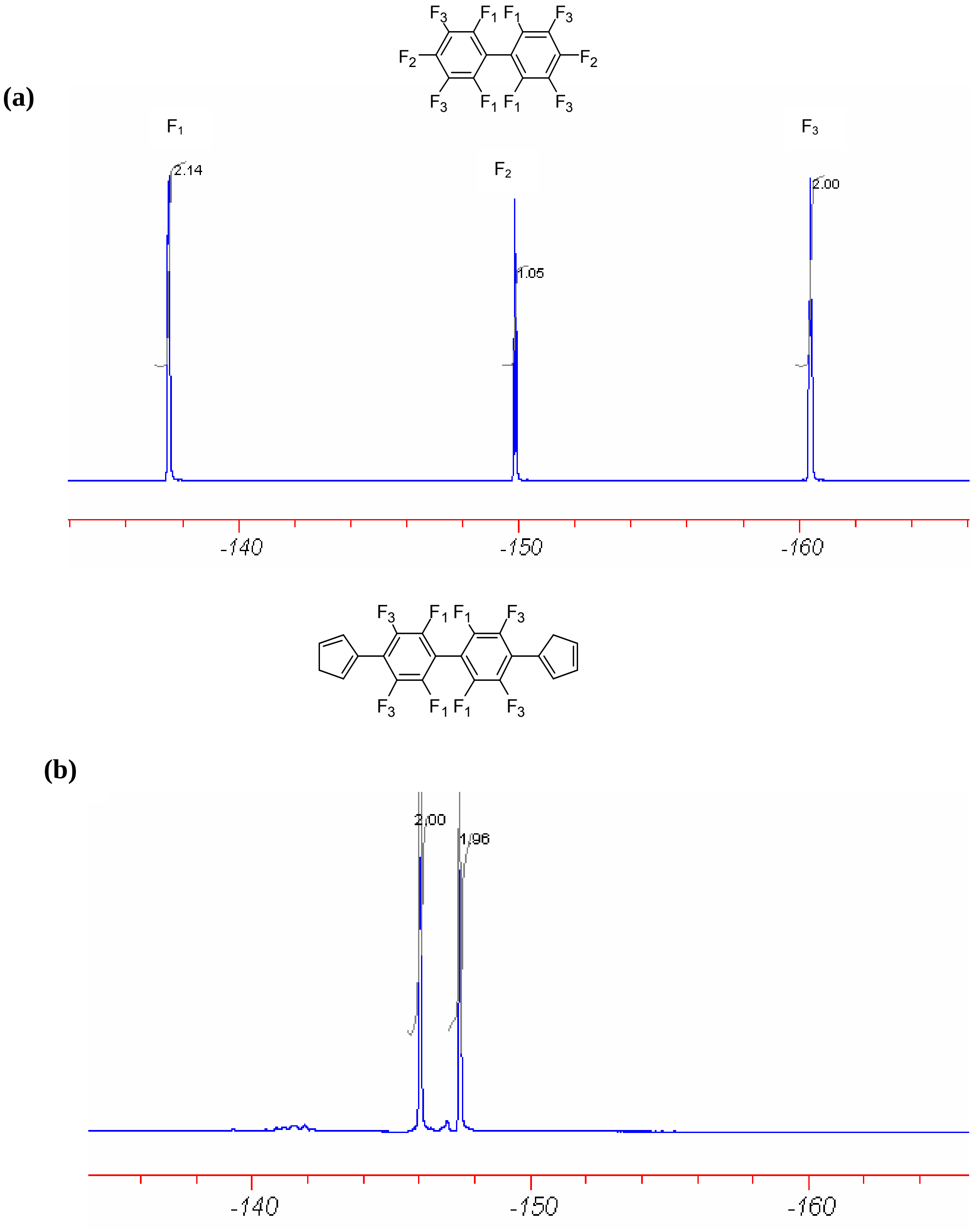
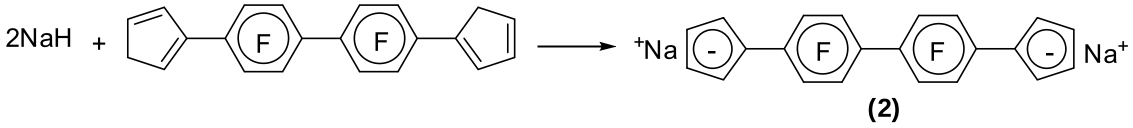


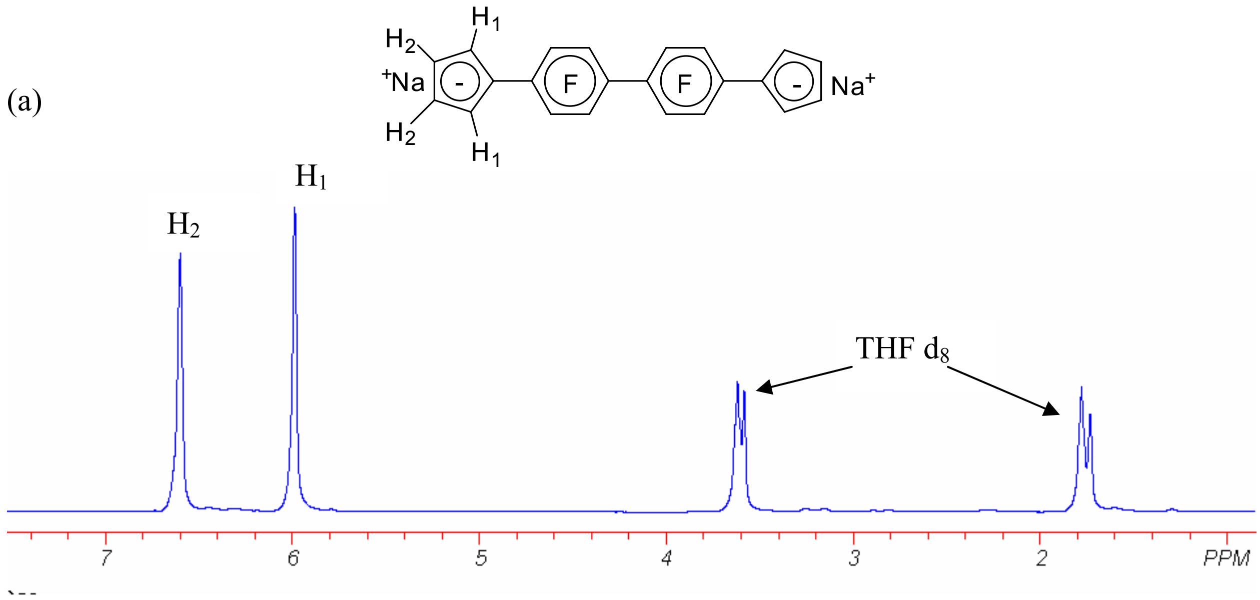
FIGURE 28. (a) ^{19}F NMR spectrum of decafluoro biphenyl
(b) ^{19}F NMR spectrum after addition of cyclopentadiene groups

Because **(1)** can undergo Diels Alder self-dimerization even at room temperature, it is converted immediately to the corresponding disodium salt (**2**) by treatment with NaH (Scheme 6), and the air-sensitive disodium salt is stored in a nitrogen glove box.[64]

SCHEME 6



One final point here is that the disodium salt is a symmetrical compound and exhibits only two signals in the ^{1}H NMR spectrum and two signals in the ^{19}F NMR spectrum (both in duetoriated THF).[64] The simplicity of these spectra (Figure 29..) allows purity to be scrutinized carefully at this stage.



(b)

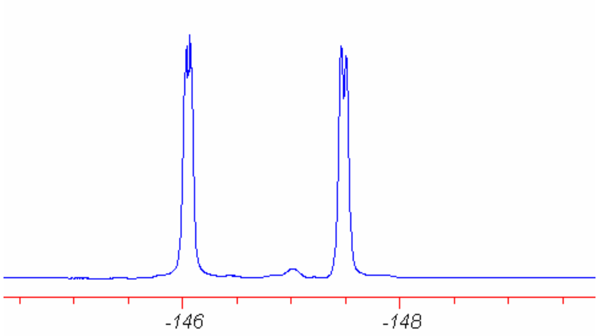
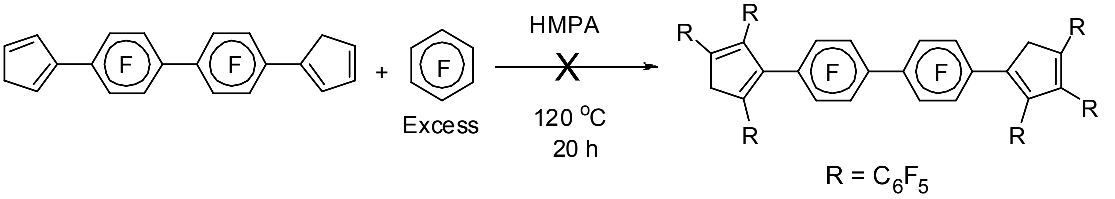


FIGURE 29. (a) ^{1}H NMR spectrum of disodium salt
(b) ^{19}F NMR spectrum of disodium salt

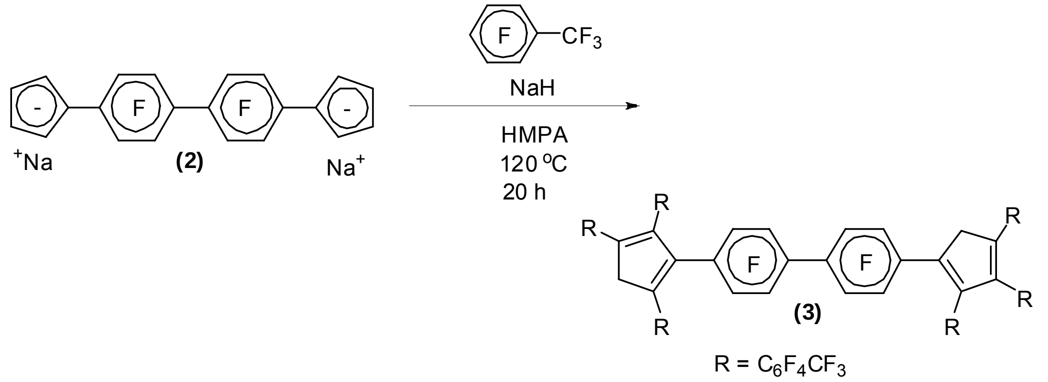
2.3.2 Six-Fold Arylation with Hexafluorobenzene. We tried initially to arylate the cyclopentadiene moieties of **(2)** with hexafluorobenzene under the usual basic conditions (NaH, diglyme, 80 – 140 °C). However, despite many attempts, we were not able to affect three arylations on each side. Thus the desired product was never isolated. One of the main frustrations was not being able to get the analytical data that we needed to really understand what went wrong in these reactions.

SCHEME 7



2.3.3 Six-Fold Arylation with Octafluorotoluene. We hypothesized that we could facilitate the aromatic substitution reactions by replacing one fluorine of C_6F_6 with a CF_3 group. The CF_3 group makes octafluorotoluene more electron deficient and therefore more reactive toward nucleophilic substitution. The data tabulated in Section 2.2.1 shows that arylations with octafluorotoluene occur at lower temperatures than arylations with hexafluorobenzene, and that the substitution reactions gave exclusively *para* regioisomers.[62]

SCHEME 8



2.3.3.1 Issues with the Solvent. Our initial experiments with octafluorotoluene were promising. We used the "typical" conditions used previously in our group for attaching four perfluoroaryl groups to cyclopentadienyl anion: Excess sodium hydride, excess perfluoroarene, and diglyme as the solvent. The first problem that we encountered was the inability of these reactions to connect all three aryl groups to each "side" of the bis-(cyclopentadienyl)octafluorobiphenyl structure under the same conditions that tetraarylated cyclopentadiene cleanly. This observation came as a surprise, because we had imagined that the dianionic character of **(2)** would have made it more nucleophilic than corresponding monoanionic cyclopentadienyl anions.

Then, when we tried to increase the temperature to force triarylation on both Cp moieties, we encountered some minor side-reactions that our group had never observed in ten years of doing S_NAr chemistry. NMR spectroscopic analysis of the crude product mixture showed signals in the region 3.0 – 4.5 ppm (Figure 30.) that we tentatively assigned to glycolated solvent fragments that had reacted nucleophilically with aromatic CF bonds. Under certain forcing conditions, fluoroaromatic substituents such as C_6F_5 can undergo further CF substitution reactions with strong nucleophiles. Even $C_6F_4CF_3$ can be susceptible to further attack despite the fact that the *para* position is blocked.[67]

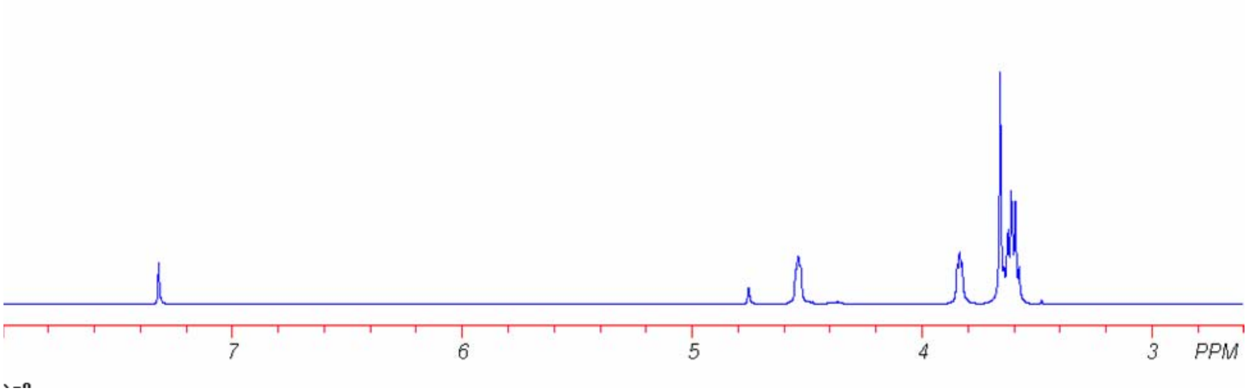
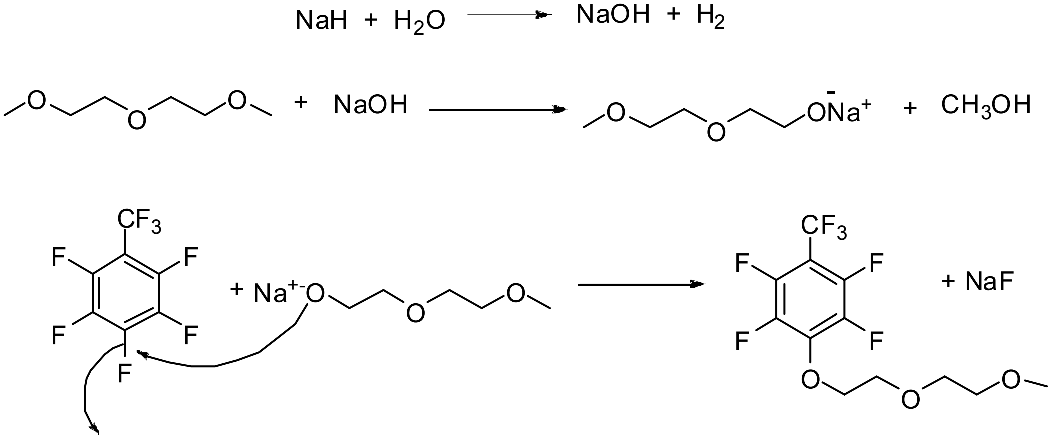


FIGURE 30. ^{1}H NMR spectrum of arylation in Diglyme

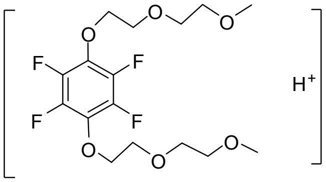
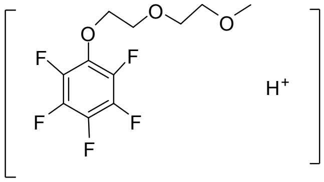
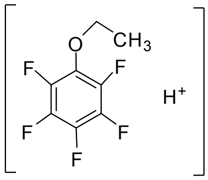
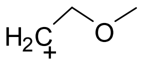
In a control study, we reacted hexafluorobenzene with sodium hydride, diglyme, and potassium fluoride (to model the fluoride leaving group present in our substitution reactions). The idea here was that under forcing conditions traces of NaOH resulting from the reaction of NaH with adventitious moisture or even the mildly nucleophilic fluoride anion could open the ether bonds of diglyme to form glycolate anions (Scheme 9). Normally ethers are supposed to be inert to bases, but we are trying to rationalize minor by-products observed under harsh conditions. As shown in Table 4, MS analysis showed signals that could be assigned to mono- and di-substitution products. Although we are still unclear about the mechanism of formation of

SCHEME 9



these by-products in our reaction mixtures, the need for high purity in our CPD monomer drove us to search for a less reactive solvent.

Table 4. Mass spectrum of by-products of six-fold arylation in Diglyme.

Mass (m/z)	Structure	Rel. Intensity
387		100% (base)
287		15%
211		17.5%
59		24.5%

The choice of solvent is subject to severe restrictions. First of all, a high boiling point is needed; otherwise we would have to conduct the reactions in an autoclave to achieve conversion at a reasonable rate. The solvent must not be nucleophilic because it would then attack the perfluoroarene. Acidic solvents would react with NaH. Electrophilic or oxidizing solvents would react with the strong carbanionic nucleophiles present. Finally the solvent must be polar enough to dissolve the charged intermediates and to promote nucleophilic aromatic substitution, which proceeds through charged transition states. Many typical “polar aprotic” solvents like acetonitrile, dimethyl sulfoxide, dimethyl formamide, and sulfolane do not meet these tight restrictions.

As shown in Table 5, we searched through a variety of aliphatic ethers without success. A striking example of the frustrating nature of these experiments is the very rapid formation of intractable substances using 2-methyltetrahydrofuran: Within an hour at reflux, the reaction is a sticky black mess from which no cyclopentadiene derivatives can be isolated. We don't know why 2-methyl-THF causes such rapid decomposition. However, it is possible that the aromatic substitution reaction involves radical-anionic intermediates. The more substituted 2-hydrogen of 2-methyl THF (compared to THF itself) could be more reactive toward radical species.

Table 5. Solvent screening for aromatic substitution reactions.

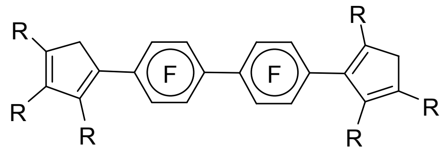
Solvent used	**Problem faced**
Diglyme	Minor side-products formed
Tetraglyme	Minor side-products formed, same as digylme
THF	Bp too low; reaction was incomplete
TMEDA	Reaction did not proceed
2-methyl-THF	Black intractable tars, even under mild conditions
THF + Tetraglyme	Black intractable tars
HMPA	Reaction worked

Finally we tried HMPA in desperation. Luckily, HMPA worked very well, under relatively mild conditions (120 °C). A 95% conversion to crude product and an isolated yield of 76% was realized for all six arylations in one pot. The ease of removing HMPA by aqueous extraction is also a useful property of this solvent. Another solvent that has been suggested by a professor at another institution (Daren Timmons of VMI) is N,N-dimethyl-1,3-propyleneurea (DMPU), also a polar aprotic solvent but less toxic than HMPA. We will try this solvent in the near future.

2.3.3.2.Isomers and Other Characterization Issues. One of the problems associated with the 6-fold arylation of cyclopentadiene moiety is the formation of regioisomers depending on the arylating position. Essentially, the linking ocatfluorobiphenylene group may be in either the 1- or the 2-position with respect to each of the two cyclopentadienes, giving rise to two symmetrical isomers and one unsymmetrical isomer (Figure 31.). The statistical ratio of these isomers would be 1:1:2, respectively, and there is at present no means of imparting any selectivity.

1,1 type regioisomer

2,2 type regioisomer



1,2 type regioisomer

FIGURE 31. Regioisomers formed during arylation

Unfortunately we are also not able to separate these isomers using flash chromatography or TLC, nor could we quantify their relative abundance by NMR spectroscopy. As a consequence we need to rely on the *absence* of other signals in the NMR spectrum to verify complete conversion. For example, a cyclopentadiene with only three aryl substituents would still have a vinylic CH group, which can be detected (notably no vinylic CH groups in the range 6.5 to 7.5 ppm, Figure 32.).

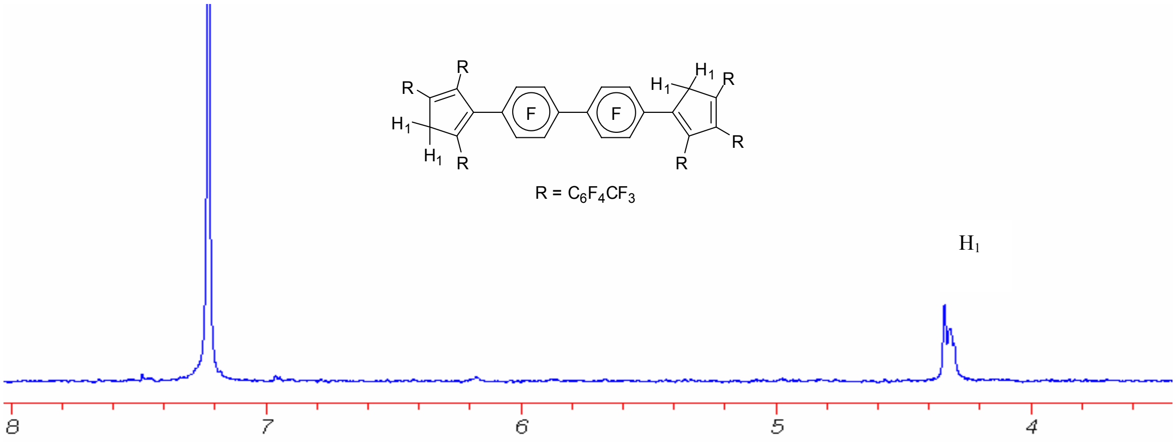
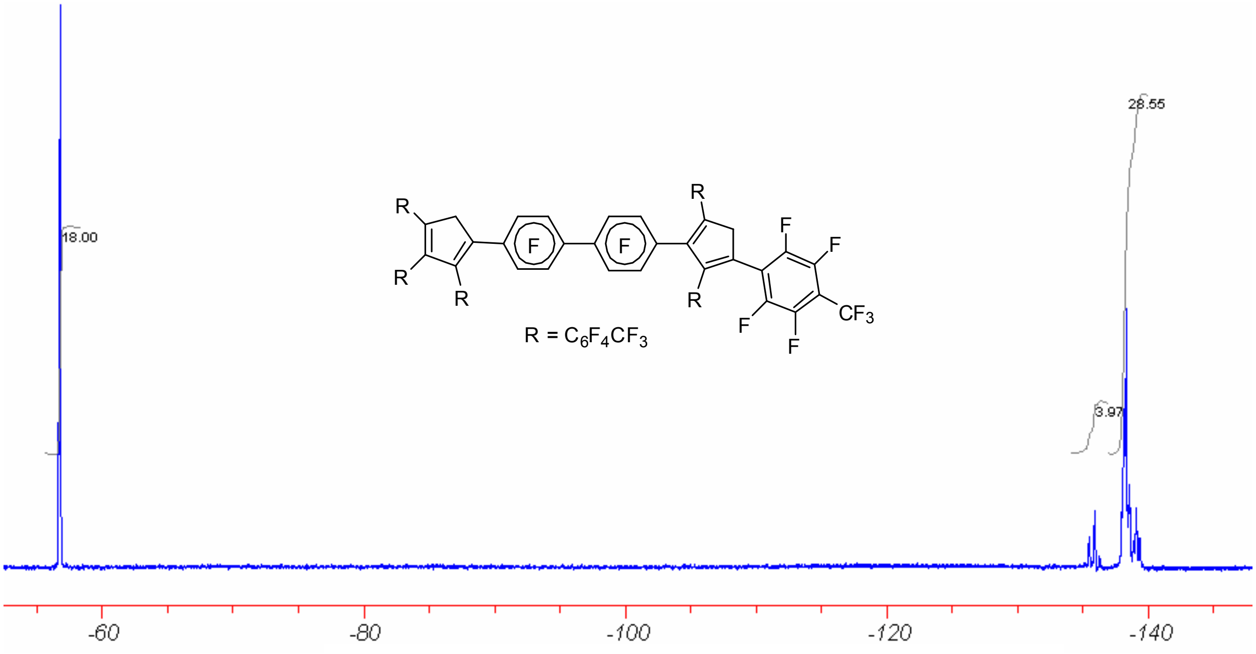
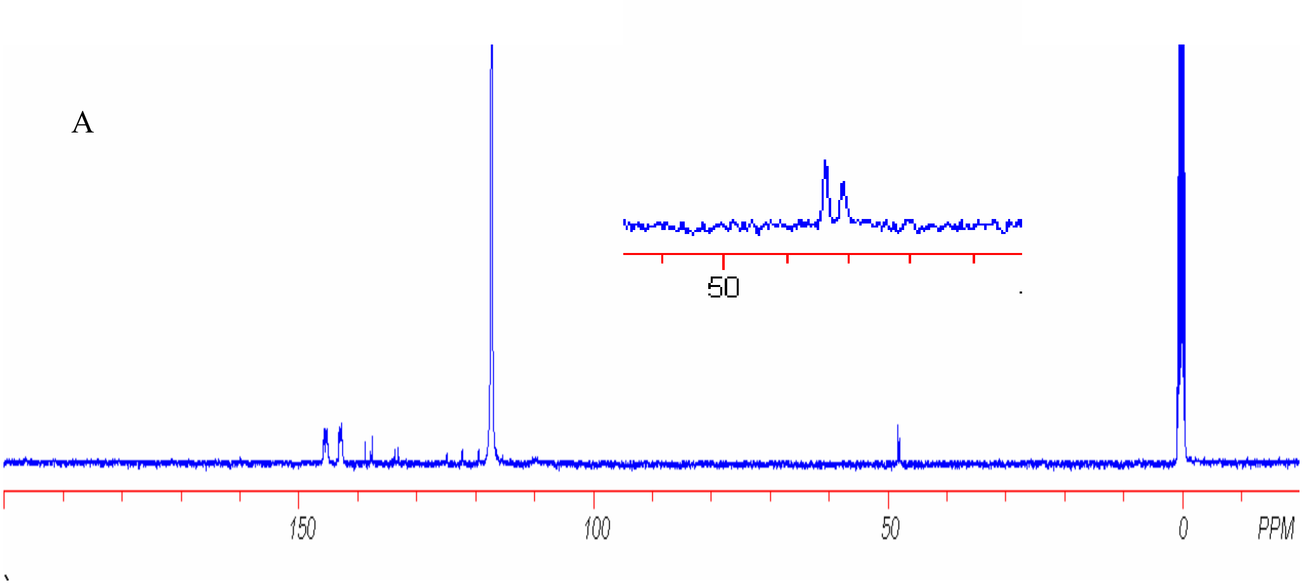


FIGURE 32. ^{1}H NMR spectrum after six-fold arylation



FIGUR 33. ^{19}F NMR spectrum after six fold arylation

To confirm the generation of more than one isomer during the 6-fold arylation, ^{13}C NMR spectra were recorded for both the bis-cyclopentadiene **(2)** and the corresponding diketone **(6)**. The ^{13}C NMR of **(2)** shows two adjacent peaks at 48.1 ppm and 48.4 ppm (Figure 34(A)). These two peaks correspond to two different CH_2 environments which are either adjacent (or not) to the perfluorinated linker (Figure 31.). Because of the close chemical shifts we cannot really assign either isomeric form conclusively, but the spectrum does confirm that both are present and in roughly equal concentrations. Moreover we infer that all statistical combinations of the two isomeric forms of the cyclopentadienes must be present, giving a total of three isomers (1,1 type, 1,2 type, and 2,2 type). The chemical shifts of two different CH_2 groups of 1,2 type isomers are coincident with the same of 1,1 type and 2,2 type isomers respectively, because the differences in the long-range substituent effects are just too small.[68-70]



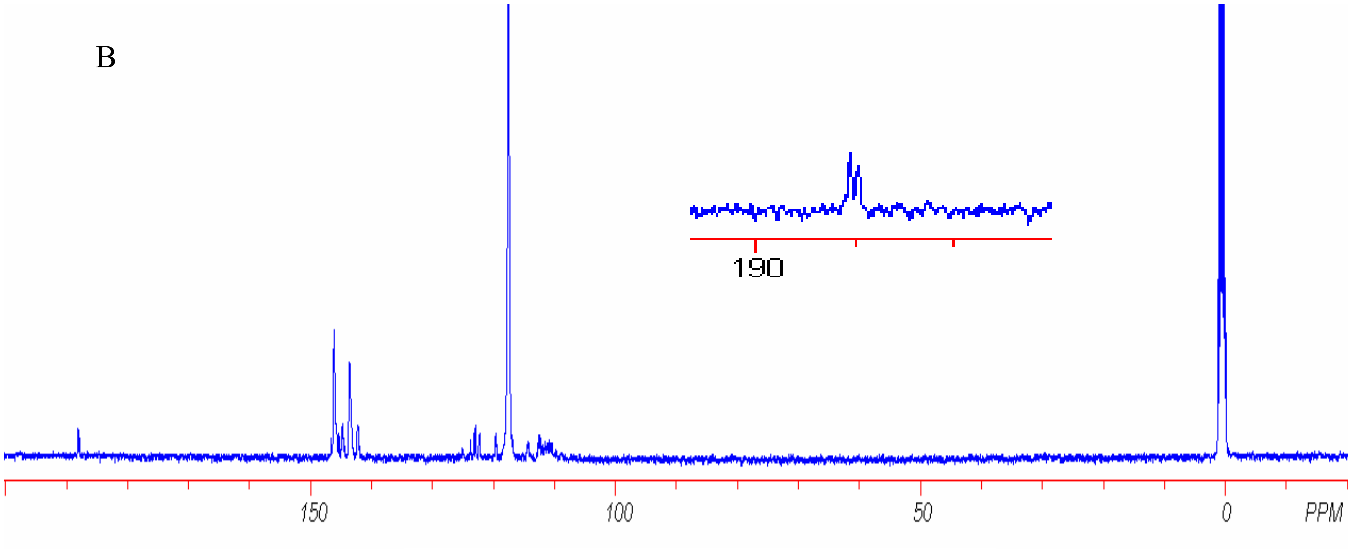


FIGURE 34. ^{13}C NMR spectra
A> Biscyclopentadiene
B> Bisketone

The ^{13}C NMR of the corresponding diketone shows no signals near 48 ppm (all CH_2 groups are absent), while two new signals appear at 187.9 ppm and 188.1 ppm, which we assign to the carbonyl carbons (Figure 34(B)). The above discussion about different chemical shifts of two different CH_2 groups is also applicable for the two C=O groups of the diketone.[70]

There are other peaks present in the ^{13}C NMR of both bis-cyclopentadiene and the bis ketones in the aromatic region and for the CF_3 groups but we cannot assign them specifically.

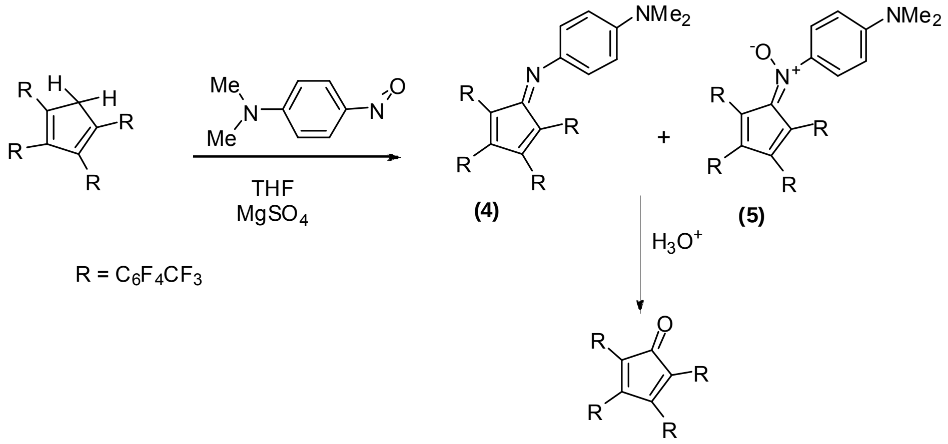
2.3.3.3 Purification of the Bis-Diene. Another issue related to the arylation is purification of the compound. The crude product showed small NMR signals that are not assigned to the product. For example, there were traces of HMPA which were not removed by the work up. Column chromatography with 10% dichloromethane in hexane removed all extraneous NMR signals, except for a signal at 6.1 ppm in the ^{1}H NMR spectrum, which we have not yet assigned. One important task for the near future is to check for the presence of pentaarylated cyclopentadienes using mass spectrometry. We found that reprecipitation from 25% aqueous methanol followed by recrystalization from 10% dichloromethane in toluene removed the impurity and afforded a product that nearly eliminated the unassigned NMR signal at 6.1 ppm (Figure 32.).

2.3.3.4 Best Method for the Bis-Diene. Summarizing the above information, we found that treatment of **(2)** with 15 equiv of perfluorotoluene in HMPA for 28 h at 120 °C followed by aqueous workup, filtration through a short column of silica gel, reprecipitation, and recrystallization reliably afforded the desired bis-cyclopentadiene. Although the workup and purification seems lengthy, all of the steps are easily scalable.

The ^{1}H NMR spectrum of the bis-cyclopentadiene product shows only one broad signal at 4.3 ppm for the methylenes (CH_2) of the three possible isomers. The ^{19}F NMR spectrum shows a complex pattern (several overlapping triplets) at −56.76 ppm for the 4-CF_3 groups (coupled to the CF groups in the 3- and 5-positions of the rings, $^4J = 64$ Hz), and a complex set of signals at −135.40 to −139.40 ppm corresponding to the aromatic CF groups. The integration of CF_3 to CF was found to give a 18.0:32.5 ratio, which compares well with the calculated 18.0:32.0 ratio. Elemental analysis value is given here, Calculated for $C_{64}H_4F_{50}$: C, 44.62; H, 0.23. Found C, 43.90; H, 0.69.

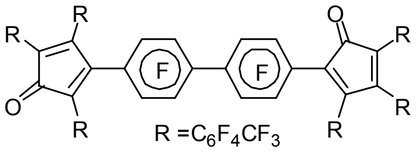
2.3.4 Oxidation. With the bis(cyclopentadiene) intermediate in hand, the next challenge was to oxidize it to the diketone needed for the DA polymerization reactions. Our group has developed several methods for this oxidation, none of them particularly general. The first is based on chemistry described by Ogliaruso in the 1960s.[71] As shown in (Scheme 10), a cyclopentadiene is first treated with *N*,*N*-dimethyl-4-nitrosoaniline to give a mixture of an imine **(4)** and a nitrone **(5)**. The imine/nitrone mixture is hydrolyzed under acidic conditions to give the ketone. We have found this reaction to work extremely well for tetrakis(pentafluorophenyl)cyclopentadiene (95% overall yield of the corresponding ketone). The first conversion (to imine/nitrone mixtures)

SCHEME 10



seems to work well for **(3)**, but the hydrolysis was extremely slow and gave a lot of byproducts that we could not characterize. The reasons for this lack of generality are not clear.

Returning to the literature, we found that activated ring methylene carbons can be oxidized with selenium dioxide (SeO_2),[72] typically in acidified 1,4-dioxane, to the corresponding ketone. We applied this method first to a model compound $C_5(C_6F_5)_4H_2$ and achieved a quantitative conversion to crude product and a 95% isolated yield. Work-up seems trivial (filtration through silica gel to remove the colloidal selenium by-product), although I will return to this point below.Then we applied the same method to our monomer precursor **(3)**. With some optimization, we found that heating at 70 ^{o}C the reaction mixture for 6 h in dioxane gave the desired diketone, again in quantitative conversion and in about 95% isolated crude yield. The diketone is a bright orange, glassy solid. (Figure 35.) shows the synthesized diketone.

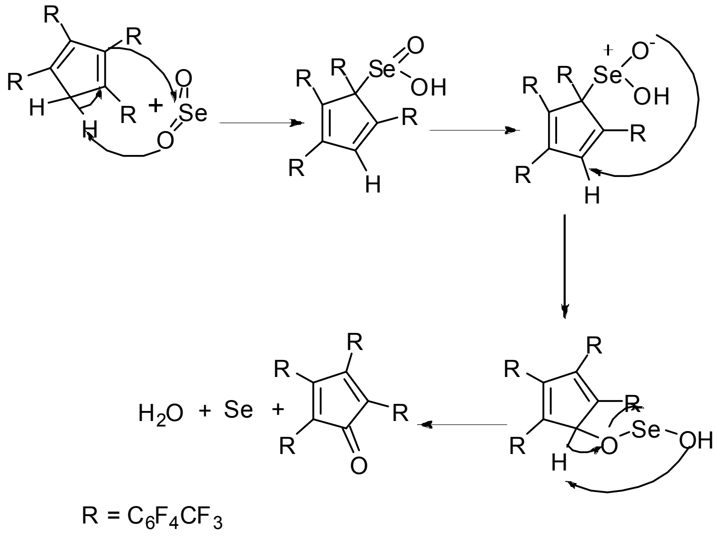


(6)

FIGURE 35. Diketone

The exact mechanism of this reaction is not known, but one possible pathway suggested in the literature is in (Scheme 11).[73-76]

SCHEME 11



An alternative method developed recently by a co-worker (Brian Hickory) uses oxygen as the oxidant and a ligated copper(I) catalyst system (typically CuI, CuBr and CuCl pyridine or bipyridine as the ligand, and acetonitrile as the solvent). This reaction is analogous to the well-known Gif Oxidation. Unfortunately we have found that this reaction does not work well for our most acidic cyclopentadienes, which means it is also not promising for our monomer precursor. Another system Brian Hickory has been working on uses nitrous acid as the oxidant, but this was not found to be promising for my oxidation.

2.3.5 Purification of the Diketone. The NMR spectra of the crude product suggested that the product was already fairly pure. No signals were observed in the ^1H NMR spectrum other than traces of water and solvents. Special care must be taken to remove the excess selenium dioxide and the reduced red amorphous selenium, both of which are toxic, by filtering a dichloromethane solution of the product through silica gel. A second chromatographic purification on silica gel, eluting with 10% dichloromethane in hexane, followed by recrystallization from 10% dichloromethane in toluene gave samples that were pure by NMR spectroscopy. The IR spectrum shows a broad peak at 1741 cm^{-1} for the ketones.

We had not intended to explore other oxidation methods because the SeO_2 oxidation seemed to be working well. Unfortunately, elemental analysis of the diketone showed much lower than calculated percentages of carbon, suggesting that the compound is still impure. The impurity does contain neither hydrogen nor fluorine, otherwise we would expect to see additional signals in the NMR spectra. One possibility, then, is that the compound is somehow encapsulating the by-product colloidal selenium from the oxidation step. Colloidal Se is also either orange or red, so we cannot inspect our samples for this impurity visually. Although it seems unlikely that selenium would survive all of the purification steps described above, other authors have reported difficulty in removing selenium-containing byproducts.[76] We plan to search for different oxidation methods while sending our samples back to the microanalytical laboratory to check for selenium.

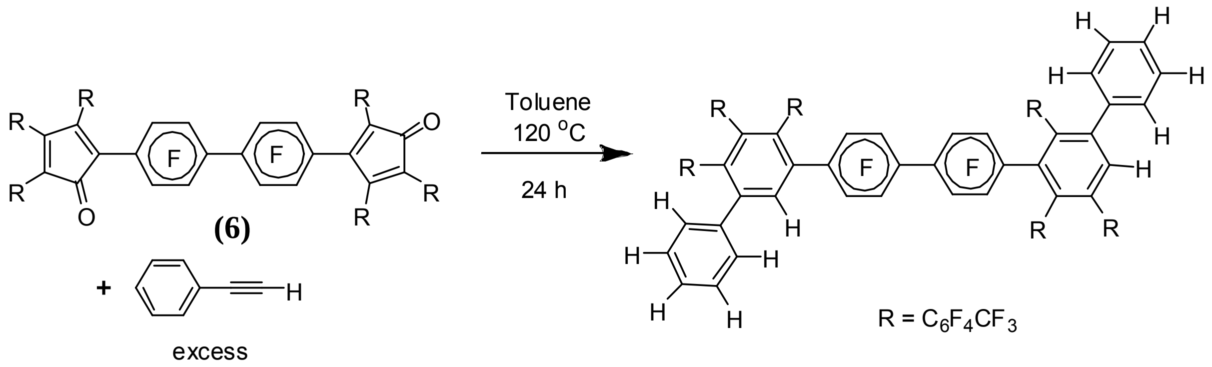
.2.5. Concluding Remarks. From the above discussion and NMR spectroscopy studies it can be concluded that Bis-cyclopentadiene and the corresponding diketone were synthesized and characterized successfully and are pure enough to proceed with initial polymerization experiments, although the poor microanalysis on the diketone is cause for some concern.

Chapter 3. Studies Toward Highly Fluorinated Diels-Alder Polyphenylenes

Introduction. This chapter describes our initial efforts to use the monomer described in Chapter 2 in the synthesis of Diels-Alder polymers. Section 3.1 describes a model reactivity study with phenylacetylene. Section 3.2 then describes our attempts to copolymerize **(6)** with 1,4-diethynylbenzene. These reactions did not work as well as we had expected, so we changed to a a different dialkyne monomer that has been used previously in successful DAPP syntheses. Section 3.3 describes the synthesis of this monomer, bis(4-ethynylphenyl)ether. Section 3.4 describes our attempts to copolymerize this monomer with the bis-CPD compound **(6)**.

3.1. Model Reactions of the Fluorinated Bis-CPD Monomer with Phenylacetylene. Before proceeding to the actual polymerization we tried to do a model DA reaction with the diketone **(6)** and the monofunctional "capping" reagent, phenylacetylene (Scheme 12). We hoped this reaction would help us understand the reactivity of **(6)** toward aromatic alkynes in general. A mixture of the diketone (**6**) and phenylacetylene in toluene was maintained at 140 ^{o}C for 24 h. The ^{1}H NMR spectrum (Figure 36.) of the end product showed new peaks between 7.75 to 7.85. These new peaks in the aromatic region are due tothe newly generated benzene ring. The other peaks found in the aromatic region are due to the phenylacetylene monomer.

SCHEME 12



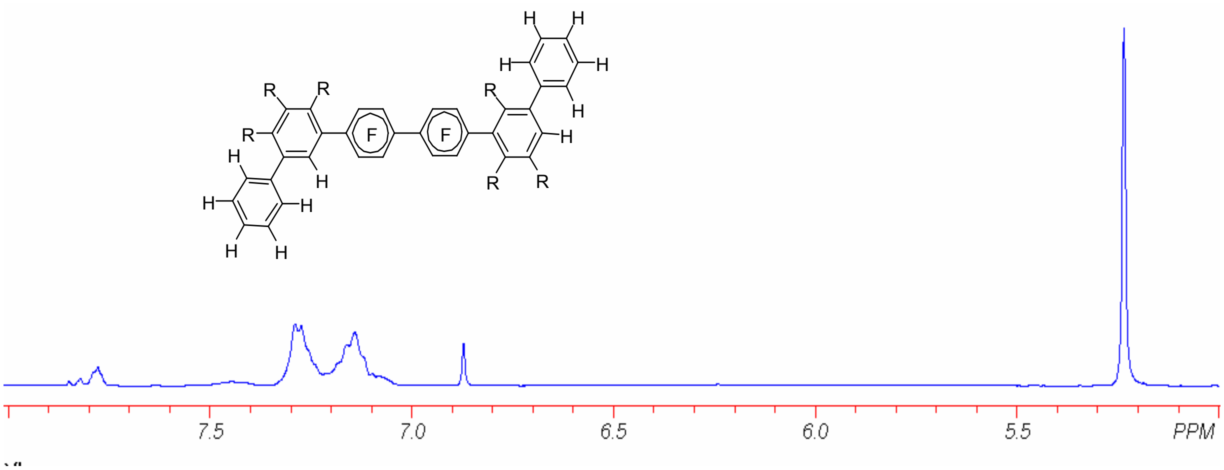


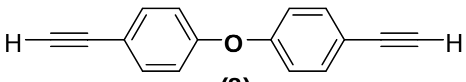
FIGURE 36. ^{1}H NMR spectrum of the model reaction with phenyl acetylene

Although these results show that the diketone reacts with phenylacetylene, it was troubling to us that a temperature of 140 °C was needed for complete conversion in 24 h, because the "capping" reagent was present in large excess, whereas during a polymerization the reactive alkynyl end groups will be dilute.

3.2. Attempted Copolymerization Reactions of (6) With Diethynylbenzene. We proceeded to attempt a polymerization of **(6)** and 1,4-diethynylbenzene, however the initial reactions were not successful. We believe that relatively short oligomeric products were precipitating, preventing propagation to higher molecular weight. A dichloromethane-soluble fraction was reprecipitated in methanol. The ^{1}H NMR spectrum of the product showed a newly formed aromatic hydrogen, which indicated that a Diels-Alder reaction did proceed. Also evident in the spectrum are large signals assignable to alkynyl end groups.

3.3. Search for a More Reactive Dialkyne Comonomer. The poor result obtained in the polymerization with p-diethynylbenzene suggested that we needed to select an alternative dialkyne. To attain a high molecular weight, we needed to improve the solubility of the growing polymer in the reaction medium. Ideally, the dialkyne would be more flexible than the rigid p-diethynylbenzene, imparting additional torsional degrees of freedom to the polymer and improving solubility. We also speculated that the rather electron withdrawing character of the ethynyl group could make the first reaction of p-diethynylbenzene relatively slow. Our DA reactions follow “Inverse Electron Demand” substituent effects, so we need to pair our electron-deficient fluorinated CPD with a more electron-rich dialkyne. We also wanted a monomer that we could either buy or make cheaply and cleanly, but we had to stay with very stable functional groups.

Considering the factors described above, we selected bis(4-ethynylphenyl) ether (Figure 37.) as the alternative dialkyne. Rotational flexibility and electron-donation are both afforded by the central oxygen atom. Diphenyl ether is also a stable compound, and its derivatives are synthetically accessible, albeit not commercially available. Finally, the use of bis(4-ethynylphenyl) ether in DAPP synthesis is already described in Dow Chemical Company patents.



(8)

FIGURE 37. Proposed flexible dialkyne

3.3.1 Synthesis of Bis(4-ethynylphenyl) Ether. The most challenging step of this reaction turned out to be the aromatic halogenations. Several methods are described in the literature, but very few are cleanly selective for 4,4’-dihalogenation. We could not afford to have mixtures that we would need to separate. Direct treatment with Br_2, for example, gives significant amounts of ortho-brominated products.[77, 78] Br_2 that is generated *in situ* by reacting HBr with oxygen using a sodium nitrite redox catalyst (eq 1-3) was reported to be regioselective, but we found this reaction difficult to scale up. It was hard to bubble in enough oxygen without volatizing excessive amounts of HBr.[79]

$$\text{Initiation: } 4\,HBr + 2\,NaNO_2 = 2\,NO + 2\,H_2O + 2\,NaBr + Br_2 \quad (1)$$

$$O_2 + 2\,NO = 2\,NO_2 \quad (2)$$

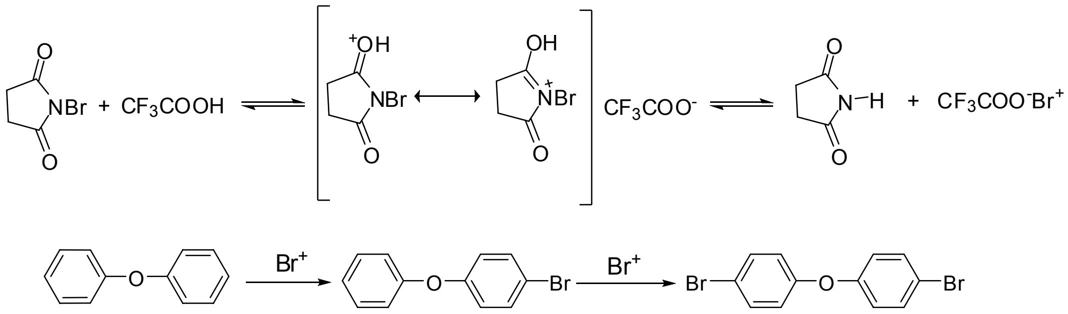
$$2\,NO_2 + 4\,HBr = 2\,H_2O + 2\,Br_2 + 2\,NO \quad (3)$$

Generation of bromine from hydrogen peroxide and HBr (eq 4) gave some conversion, but we decided ultimately that scaling up a reaction in which electron-rich organic compounds are mixed with hydrogen peroxide could be dangerous.

$$H_2O_2 + 2\,HBr = Br_2 + 2\,H_2O \quad (4)$$

We next considered iodination with N-iodosuccinimide (NIS) with catalytic trifluoroacetic acid (TFA) but this reagent is quite expensive and also seemed unstable.[80-82] However the corresponding bromination with N-bromosuccinimide (NBS) worked very well (Scheme 13).[83-86]

SCHEME 13



Diphenylether was refluxed with NBS in the presence of a catalytic amount of trifluoroacetic acid in acetonitrile for 6 hours. Completion of the reaction was confirmed by ^1H NMR spectroscopy (Figure 38.). A 98% yield of the product was obtained.

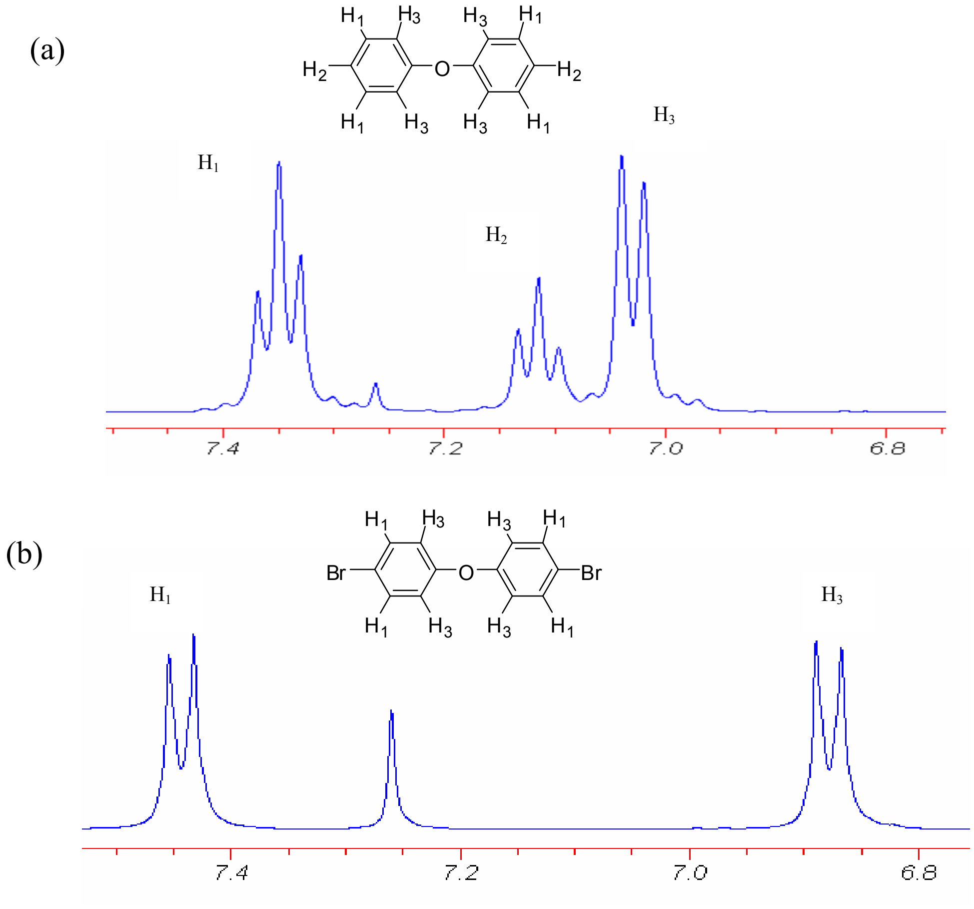


FIGURE 38. ^{1}H NMR spectra (a) before and (b) after bromination

The next step was the coupling of the alkyne groups with the aryl moiety at two para positions. For this step we would employ the Sonogashira–Hagihara coupling reaction with (trimethylsilyl)acetylene.[87, 88] The exact mechanism of copper co-catalyzed Sonogashira reaction is still unknown. However, it seems likely that Pd(0) oxidatively adds the aromatic C-Br bond. Meanwhile the Cu(I) activates the acetylenic CH bond and forms a copper(I) acetylide that transfers the acetylenic unit to the Pd(II) center. Finally reductive elimination from Pd(II) affords the new CC bond. Terminal alkynyl moieties are revealed by cleaving the trimethylsilyl groups with tetra-*n*-butylammonium fluoride (TBAF).

The product dialkyne was purified by silica gel chromatography followed by recrystalization from methanol. A ^{1}H NMR spectrum (Figure 39.) shows only the desired alkynyl protons along with the two expected doublets in the aromatic region.

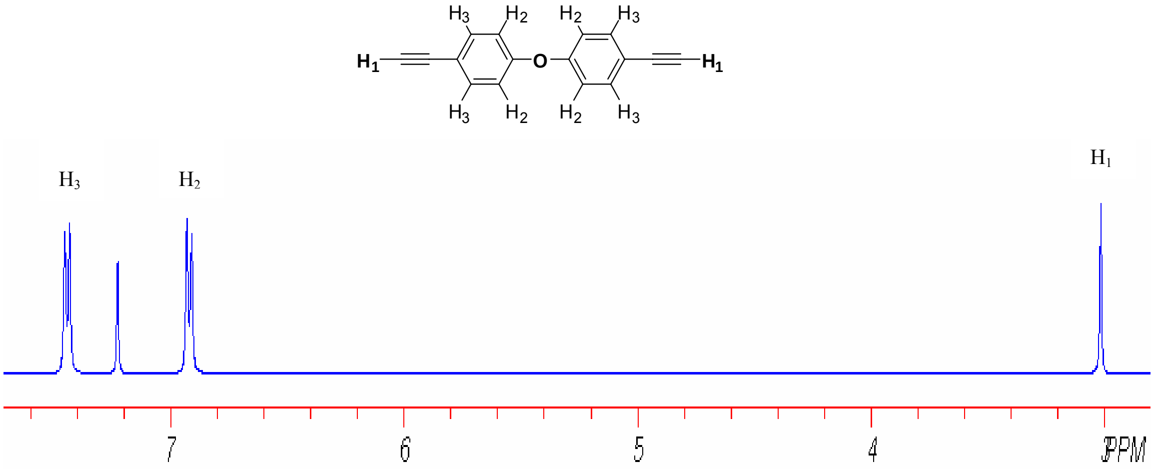
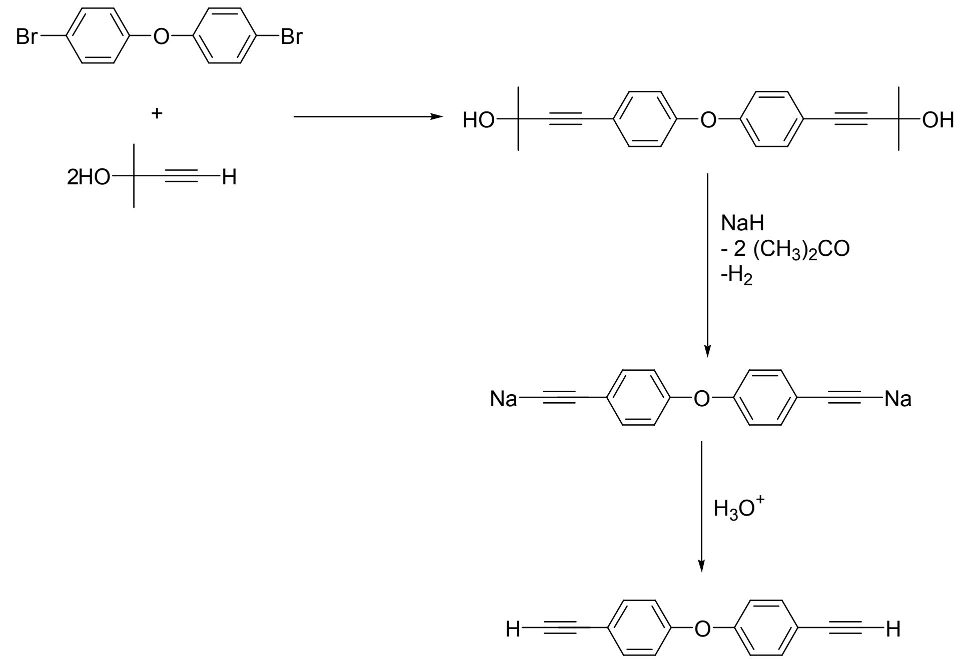


FIGURE 39. ^{1}H NMR spectrum of the dialkyne

Note that the Dow team used a different strategy to arrive at the same compound (Scheme 14). They reacted the dibromide with 2-methyl-3-butyne-2-ol ($HOC(CH_3)_2C{\equiv}CH$) using a palladium catalyst; the resulting tertiary carbinols are treated with sodium hydride, formally liberating acetone.[89] Probably this method is easier to scale and does not involve fluorides, which pose problems with reactor corrosion and especially with hazardous waste disposal.

SCHEME14



3.4. Polymerization Reactions of Bis(4-ethynylphenyl) Ether with (6). A concentrated solution of the diketone (**6**) and dialkyne (**7**) in o-dichlorobenzene (1:1 reactant ratio) was maintained at 165 °C for 24 hrs. An undetectable (with dichloromethane and acetone) black residue was obtained along with a reaction medium soluble part. After workup of the solvated part, it was characterized by ^{1}H and ^{19}F NMR. The ^{1}H NMR spectrum shows four broad peaks at the aromatic region along with a singlet in the alkyne region (Figure 40.). End group analysis shows that in an average there are 2 repeating units in each polymer chain giving approximate molecular weight 6000 gm/mol, which is rather disappointingly low for this type of polymerization, considering the high molecular weight of each end group. Our prediction is again the lack of solubility of the polymer in the reaction medium limiting from obtaining a higher molecular weight. Same polymerization reaction has been conducted with various solvents like toluene, 1,2-diclorobenzene, 1,2,4-tricholrobenzene, diphenylether, DMAC. In all cases black undetectable residue is obtained.

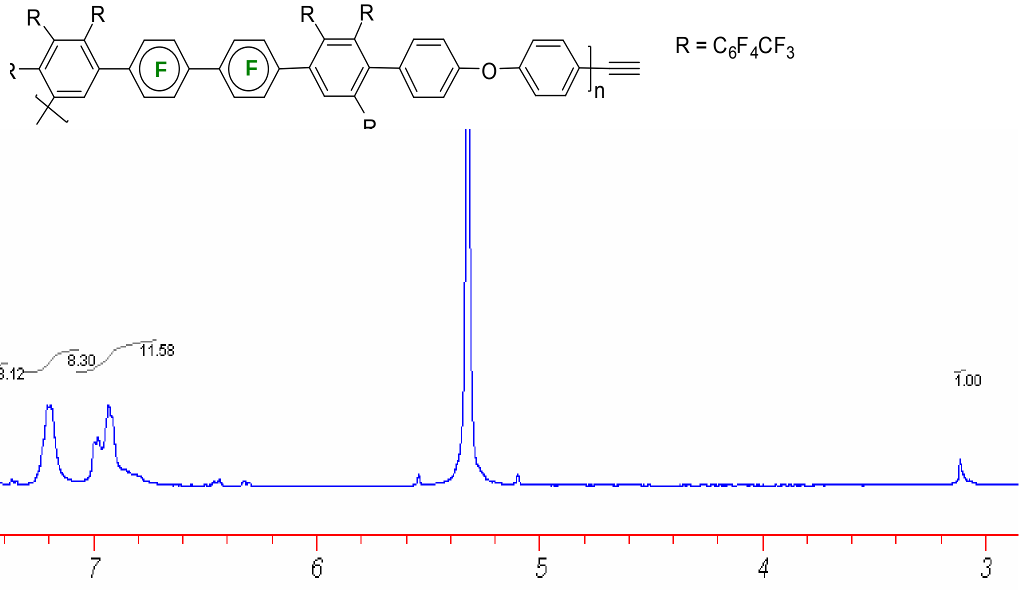


FIGURE 40. ^{1}H NMR spectrum of initial polymerization

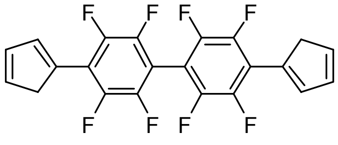
Currently we are in search of an appropriate solvent system to conduct the polymerization reaction. Once we found out the appropriate solvent for polymerization we will go back to the more rigid 1,4-diethynylbenzene system and will try to synthesis some polymers.

Chapter 4. Experimental

4.1 Instrumentation: NMR spectra were obtained using Varian Unity 400 or Varian Inova 400 instruments. ^{13}C NMR spectra were referenced to the solvent. ^{1}H NMR spectra were referenced to residual solvent isotopomers, and ^{19}F NMR spectra were referenced to external C_6F_6 in $CDCl_3$ (−163.0 ppm). Mass spectra were obtained using a JEOL HX-110 operating in FAB mode using 3-nitrobenzoic acid as the ionization matrix. IR spectra were obtained on a Nicolet 6700.

4.2 Materials. Hexafluorobenzene, octafluorotoluene, and decafluorobiphenyl were used as received from Oakwood Products, Matrix Scientific, or Apollo Chemicals. Fluororaromatics obtained from these three suppliers are comparable in quality. Diphenyl ether (Aldrich), diglyme (Alfa), tetraglyme (Aldrich), 2-methyltetrahydrofuran (Aldrich), 1,4-dioxane (Aldrich), TMEDA (Aldrich), and HMPA (Aldrich) were distilled from calcium hydride (under reduced pressure as needed to maintain boiling points in the range 60-100 °C). NBS (Aldrich), trifluoroacetic acid (Alfa), (trimethylsilyl)acetylene (GFS), copper(I) iodide (Alfa), acetonitrile (Fisher HPLC), and triethylamine (Fisher) were used as received. Triphenylphosphine (Columbia) was recrystallized from hexanes. THF (VWR, inhibitor-free HPLC grade) was purified by passage through a column of 4 Å molecular sieves in a method analogous to that published by Grubbs.[90]

4.3. Literature Preparations. 4,4'-Bis(cyclopentadien-1-yl)octafluorobiphenyl **(1)** and disodium [4,4′-bis(cyclopentadienyl)octafluorobiphenyl]diyl **(2)** were prepared according to a published procedure.[64] The identities and purities of these compounds were confirmed by comparing the ^{1}H and ^{19}F NMR data ($CDCl_3$, 400 MHz instrument) to the literature data.



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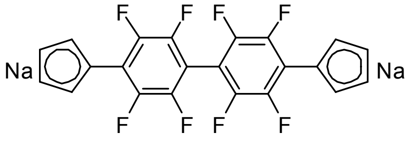

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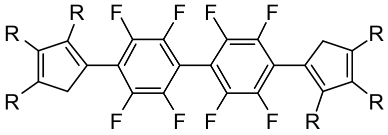
4.4 New Preparations.

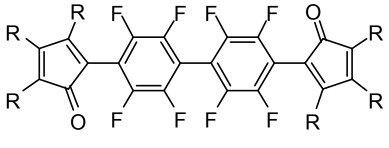
Preparation of Bis-Cyclopentadiene (3).



3 (1,1-isomer, R = $C_6F_4CF_3$)

A mixture of disodium salt **(2)** (0.468 g, 1.0 mmol), sodium hydride (0.480 g, 20.0 mmol), octafluorotoluene (4.60 g, 19.5 mmol), and HMPA (15 mL) was stirred under a nitrogen atmosphere at 120 ^{o}C for 28 h. Reaction progress was monitored by examining the ^{1}H NMR spectrum of a hydrolyzed aliquot. After the complete disappearance of the vinyl proton peaks (7.0-7.6 ppm), the reaction mixture was cooled and diluted with ether. Excess sodium hydride was quenched by addition of water. The compound obtained in the organic phase was separated, washed with a least 15 portions of water (to remove HMPA), dried over $MgSO_4$, filtered, and concentrated under vacuum. A pale yellow solid was obtained in 76% crude yield. Purification required first silica gel chromatography (1:9 dichloromethane/hexane), then reprecipitation from 25% aqueous methanol, and finally recrystallization from hot toluene to obtain a white solid (yield 60%). ^{1}H NMR ($CDCl_3$): δ 4.32 (m). ^{19}F NMR ($CDCl_3$): δ −56.75 (m, 18F), between −135.00 to −140.00 (br m, 32 F).

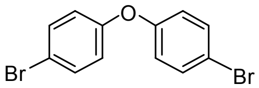
Preparation of Diketone (6).



6 (2,2-isomer, R = $C_6F_4CF_3$)

A solution of bis-diene **(3)** (0.50 g, 0.30 mmol) and selenium dioxide (0.20 g, 1.80 mmol) in 1,4-dioxane (10 mL) was stirred at 70 °C for 6 h. The progress was followed by working up small aliquots and analyzing the crude product using ^{1}H NMR spectroscopy, and the reaction was continued until the spectrum was silent. The solvent was evaporated, and the residue was extracted with dichloromethane, filtered through silica gel to remove red amorphous selenium, and evaporated to afford the crude product as an orange solid in 97% yield. Purification by silica gel chromatography, eluting with 10% dichloromethane in hexane, followed by recrystalization from hot toluene gave the final, analytically pure product in (Yield 92%). ^{1}H NMR ($CDCl_3$): no signals. ^{19}F NMR ($CDCl_3$): δ −56.58 (m, 18F), −132.94 to −138.81 (br m, 30F) (aromatic fluorines); IR ($CDCl_3$): $\nu_{C=O} = 1741\ cm^{-1}$.

4,4'-Dibromodiphenyl Ether (8).



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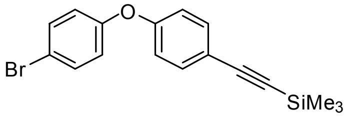
A solution of diphenyl ether (0.50 g, 3.00 mmol), NBS (1.04 g, 9.00 mmol), and TFA (5 drops), in acetonitrile (10 mL) was stirred at 80 °C for 6 h. Progress was monitored using ^{1}H NMR spectroscopic analysis of small aliquots. When the *para* CH signals were absent, the solvent was evaporated and the residue was dissolved in 10 mL chloroform. The solution was washed with water (3 x 25 mL), saturated sodium bicarbonate solution (25 mL), and again water (25 mL). The pale yellow solid crude product was obtained in 98% yield. Pure samples were obtained using silica gel chromatography, eluting with hexanes, followed by recrystalization from methanol. A white solid product was obtained (yield 88%). The NMR spectra confirmed the identity and purity of the product. ^{1}H NMR ($CDCl_3$): δ 7.44 (d, *J*=8.8Hz, 2H), δ 6.88 (d, *J*=8.8 Hz, 2H). ^{13}C NMR: δ 116.76 (C-Br), 121.00 (CH), 132.97 (CH), 156.66 (C-O).

4,4’-Bis(trimethylsilylethynyl)diphenyl Ether (9). A mixture of dibromide **(8)** (0.328 g, 1.00 mmol), $Pd(PPh_3)_2Cl_2$ (0.071 g, 0.10 mmol), PPh_3 (0.052 g, 0.20 mmol), CuI (0.038 g, 0.20 mmol), and triethylamine (20 mL) was stirred at 50 ^{o}C.[87] (Trimethylsilyl)acetylene (0.215 g, 2.20 mmol) was added using a syringe. After 0.5 h, the temperature was raised to 80 ^{o}C. TLC analysis of the reaction mixture showed three spots at R_f = 0.83 (**8**), 0.72 (**10**), and 0.51 (**9**). Additional portions (0.10 g, 1.0 mmol) of volatile $Me_3SiC{\equiv}CH$ (bp = 53 ^{o}C) and additional catalyst $Pd(PPh_3)_2Cl_2$ (0.05 mmol) were added after 24 h. After 4 d, TLC analysis showed the reaction was nearly complete but making no additional progress. After cooling, aqueous HCl (2 M, 10 mL) and water (20 mL) were added, and the mixture was extracted with dichloromethane (1X 10 mL). The organic layer was washed with 20% aqueous ammonium chloride to remove copper salts (these are detected by the characteristic blue color in the aqueous layer), dried over $MgSO_4$, filtered, and evaporated to give a black crude residue in approximately 100%. The crude product is black because of the presence of traces of colloidal palladium. The crude product was purified by silica gel chromatography, eluting with hexanes. The initial band contained the



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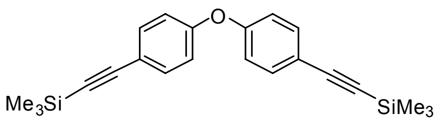

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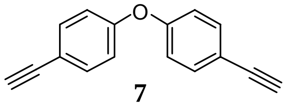
intermediate **(10)** and triphenylphosphine. The second band contained mainly the desired product **(9)**, along with some Ph_3P, which streaks on the column. The product was then recrystalized from hot methanol to remove the trace amount of triphenylphosphine. The final yield was 54%. ^{1}H NMR. ^{1}H NMR ($CDCl_3$): δ 0.14 (s, 18H), 6.89 (d, *J*=8.4 Hz, 4H), 7.44 (d, *J*=8.4 Hz, 4H). This data matched literature values.[91] Melting point of the product is in the range 101-103 °C (literature value 103-106 °C).[91]

4,4'-Diethynyldiphenyl Ether (7).



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A solution of the disilylated derivative **(9)** (0.25 g, 0.69 mmol) in THF (18 mL) was treated with tetrabutylammonium fluoride (2 mL, 1.0 M in THF, 2.0 mmol) using a syringe. When the starting material was no longer observed by TLC (after 45 min), the reaction was quenched with water (50 mL) and extracted with several portions of dichloromethane. The organic layer was dried over $MgSO_4$, filtered, and evaporated. The crude product was purified by silica gel chromatography. The product was eluted with hexane and evaporated to afford a white solid. The final yield was 50%. ^{1}H NMR ($CDCl_3$): δ 3.02 (s, 2H), 6.92 (d, *J*=8.4 Hz, 4H), 7.44 (d, *J*=8.4 Hz, 4H). This spectrum is comparable with spectra available in the literature.[91, 92] Melting point obtained is 77-79 °C (literature value 74.5-75 °C).[91, 92]

Model Polymerization Reaction of Bis-CPD Monomer (D) with Phenylacetylene. A resealable Carius tube was charged with a mixture of the diketone **(6)** (0.10 g, 0.057 mmol) and phenylacetylene (0.030 g, 0.30 mmole) in toluene (1 mL). The vessel was degassed by a series of three freeze-pump-thaw cycles, sealed, and heated at 140 °C for 24 hours. The orange solution turned brown in color. After cooling, the reaction was extracted with dichloromethane and reprecipitated using methanol. The tan colored product was filtered and dried in the vacuum oven at 80 °C (0.1 mmHg). Final yield is about 53%. ^{1}H NMR (CD_2Cl_2): δ 7.17 (m, 4H), 7.29 (m, 4H), 7.78 (m, 1H). ^{19}F NMR (CD_2Cl_2): δ -56.94 (m, 18F), -134.64-140.46 (m, 30F).

Reactions of Monomer (6) with 4,4'-Diethynyldiphenyl Ether. This section describes a general procedure that applies to skewed oligomerizations and attempted polymerization reactions. A resealable Carius tube was charge with the bis-CPD monomer **(6)**, (131.25 mg, 0.075 mmol), the dialkyne **(7)**, (16.35 mg, 0.075 mmol), and 1 mL of 1,2-dichlorobenzene. The vessel was degassed using three freeze-pump-thaw cycles and then heated at 165 ^{o}C in a sand bath for 24 h. After cooling, the reaction mixture was extracted with dichloromethane and reprecipitated using methanol. The straw colored product obtained was collected on a fritted funnel, washed well with hexane and dried in the vacuum oven. Characterization of these products by NMR spectroscopy is described in Chapter 3 (Figure 40.).

Chapter5. Future research Plans.

At this point our main problem is achieving high molecular weight in our polymerization reactions. Unless we can achieve a molecular weight of at least 100,000, we believe we will not be able to form films from our polymeric materials. We are well below that target now. The key steps that we will take in solving this problem are outlined in the following paragraphs.

Stoichiometry. Step-growth polymerization requires an exact 1:1 stoichiometric ratio to achieve high molecular weight. We can weigh our samples accurately. However, with the bis-CPD monomer the issue of purity has called into question the monomer assay. Also, especially diethynylbenzenes are quite volatile and tend to sublime from the reaction. This problem we can hopefully solve by enveloping the entire reaction chamber in a sand or oil bath. We have already addressed purity and heating techniques fairly well, so we believe stoichiometry is not the "weakest link" for us any more.

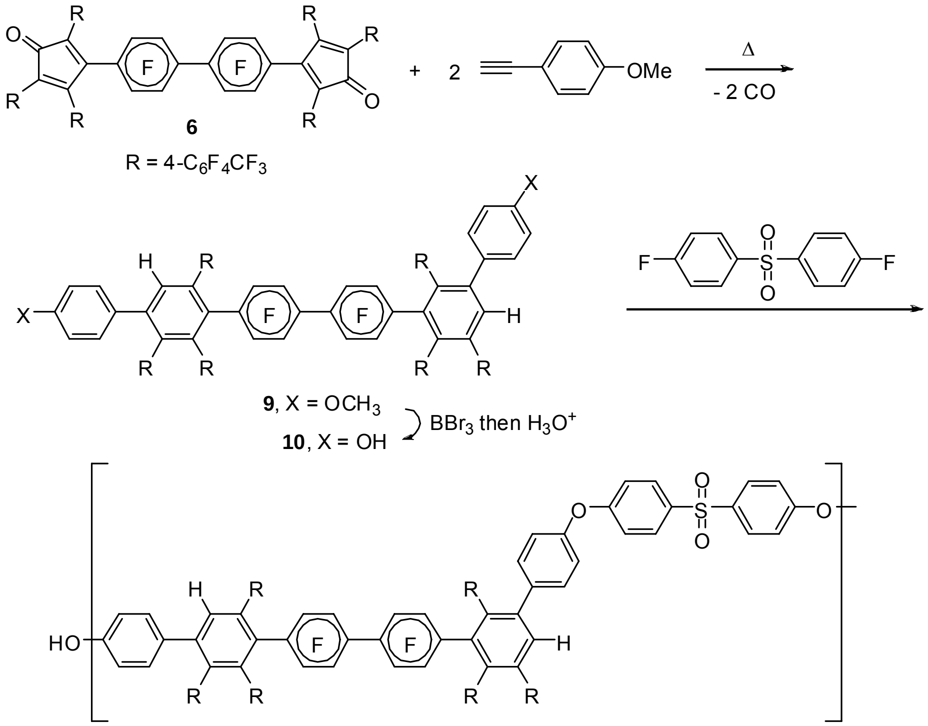
Solubility and Solvent Selection. Diels-Alder reactions are known to be catalyzed Lewis acids, including hydrogen bond donors. Therefore, we would prefer to conduct our polymerizations in a polar, protic solvent. J.P. Evans and Charles Carfagna in our group have obtained good results on related Diels-Alder polymerizations using *m*-cresol as the solvent of polymerization. They believe that hydrogen bond donation by the cresol OH group makes the CPD functional group more electron deficient, allowing the reaction to proceed more quicky and under milder conditions.

Unfortunately my diketone **(6)** is not soluble in *m*-cresol even at higher temperatures. In fact, one problem that I have had with all of my polymerizations is precipitation of the product before it reaches a high molecular weight. We are in a process of searching for an ideal solvent or solvent mixture that will dissolve the monomers and also impart the required catalytic activity in DA polymerization.

One way to tackle the solubility issue could be through adjustment in the structure of the dialkyne. We initially thought that changing from 1,4-diethynylbenzene to 4,4'-diethynyl-diphenyl ether would afford more hydrocarbon character and chain flexibility to improve the solubility of oligomers and keep the reaction in solution to achieve high molecular weight. But this structural change is apparently not enough.

Another approach would be to use supercritical carbon dioxide ($scCO_2$). $scCO_2$ is an environmental friendly, nontoxic, nonflammable, and economical choice, but for us, the high affinity of fluorinated compounds for $scCO_2$ offers the opportunity to overcome our present limitations. We plan to collaborate with Prof. E. Kiran at Virginia Tech on these studies.

Polymerization through building blocks. We propose to use our DA polymerization



methods to add fluorine content to other polymeric systems through a building block approach. First, the DA reaction of our diketone **(6)** and commercially available (methoxyphenyl)acetylene should give the corresponding arylene dimethyl ether **(9)**. Either the *para* or *meta* isomer may be used. Second, the alkoxy groups are easily demethylated with boron tribromide according to published methods.[93, 94] Finally, the resulting bis(phenol) can be reacted with a suitable electrophilic monomer like 4,4'-difluorodiphenylsulfone (DFDPS) or decafluorobiphenyl. The latter reaction is a relatively simple polycondensation for which there is ample precedent. Of course, the solubility of the polymer during polymerization is still an issue, but the additional diaryl ether linkage should improve flexibility. The polymer produced in this method will contain a highly fluorinated component along with the aromatic component. Functionality like sulfonic acids groups can be introduced in the aromatic part to gat a polymer suitable for use as a proton exchange membrane, and it is likely that we would strongly consider collaboration with Prof. J. E. McGrath on that type of project.

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