Perfluoroarylated Cyclopentadienones: Synthesis, Characterization and Polymerization

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Abstract

The first chapter of this dissertation reports the synthesis of highly fluorinated Diels-Alder polyphenylenes. The first section of this chapter describes the three-pot synthesis of a perfluoroarylated bis(cyclopentadienone) monomer. The synthesis begins with the previously reported substitution reaction of decafluorobiphenyl and sodium cyclopentadienide. To the resulting 4,4'-octafluorobiphenylene-linked bis(cyclopentadiene), six perfluoro-4-tolyl groups (three on each of the two cyclopentadienyl moieties) are attached by nucleophilic aromatic substitution (S_NAr) reactions. The remaining ring methylenes are subjected to a selenium dioxide-catalyzed oxidation to obtain the desired bis(cyclopentadienone) monomer. The next part of this chapter describes the polymerization of the perfluoroarylated bis-(cyclopentadienone) monomer and bis(4-ethynylphenyl) ether. The reaction affords an oligomer (M_n ~ 14,000 g/mol according to size-exclusion chromatographic analysis) that is soluble in several solvents and that decomposes above about 300 °C according to thermogravimetric analysis.

The second chapter of this dissertation describes a novel method to oxidize per-fluoroarylated cyclopentadiene compounds to the corresponding ketones using catalytic selenium dioxide and stoichiometric hydrogen peroxide. The first part of this chapter shows the synthesis of some perfluoroarylated cyclopentadiene substrates, while the second part of the chapter explores the oxidation of these compounds along with other perfluoroarylated cyclopentadienes already available within our research group. This chapter also explains how the reactivity of the perfluoroarylated cyclopentadienes under the oxidation conditions depends on their structure.

Generally more electron-deficient cyclopentadienes react more readily, while sterically crowded cyclopentadienes react more reluctantly.

This third chapter of this dissertation describes the synthesis and characterization of a reversible Diels-Alder polymer from an octafluorobiphenylene-linked bis(cyclopentadiene). In the first section, the synthesis of a reversible homopolymer of the bis(cyclopentadiene) monomer is described. The polymer reaches an optimized molecular weight of 11,000 g/mol (degree of polymerization is 20) under the reaction conditions because there is an equilibrium between polymerization and depolymerization even at the mild polymerization temperature (65 °C). The TGA trace of the polymer shows that chain degradation takes place beyond 300 ^{o}C. The thermal reversibility of the polymer was examined by bulk thermolysis, and flash-vacuum thermolysis. The second section describes the synthesis of a methylated bis(cyclopentadiene) that does not undergo self-polymerization at comparatively lower temperature but instead reacts with a second bis(maleimide) monomer. The resulting polymer typically shows a number-average molecular weight of 15,400 g/mol. This polymerization also is limited by the attainment of steady-state end group concentrations. The reversibility of the polymerization is demonstrated by solution thermolysis experiments in which unmasked cyclopentadiene groups are trapped by a monofunctional maleimide.

This dissertation is dedicated in memory of my grandmother Anjali Sen.

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Chapter 1.

Synthesis of Highly Fluorinated Aromatic Polymers by the Diels-Alder Reaction

1.1. Introduction. Polymers formed by the catenation of benzene rings are known as *polyphenylenes* (Fig. 1.1). As these polymers are made from benzene rings they are chemically and thermal stable. Polyphenylenes also have interesting properties because of their aromatic

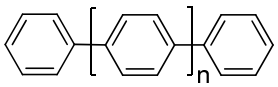


Figure 1.1. Poly(para-phenylene) (PPP)

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.[5-7] I reviewed these synthetic approaches in my Master's Thesis in considerable detail. Herein I will only give a brief overview of Diels-Alder polyphenylenes and their applications, and then summarize the additional results obtained in this project following the conclusion of my Master's degree program.

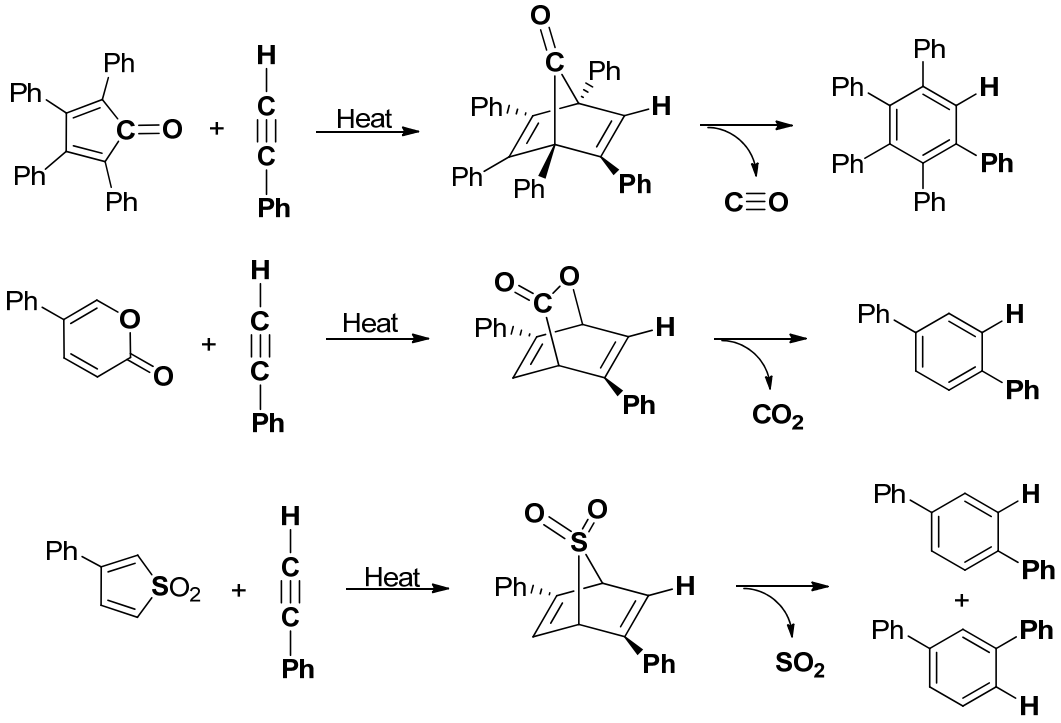
1.1.1. Overview of Fluoropolymers. Fluoropolymers exhibit interesting and useful properties that are commonly attributed to the low polarizability, strong electronegativity, and small size of

the fluorine atom, along with the high carbon-fluorine bond-dissociation energy. Characteristic features of fluoropolymers include low dielectric constant, thermal stability, high chemical resistance (particularly toward acids and oxidants), low refractive index, and resistance to abrasion.[8-14] Applications of fluoropolymers range from biomedical appliances,[15-18] marine antifouling coatings,[19-21] and aerospace engineering materials[22, 23] to fuel cell PEMs,[24-27] gas separation membranes,[28, 29] reverse osmosis membranes,[30, 31] coatings,[32, 33] and optical devices.[34-36]

While there are many synthetic approaches to fluorinated macromolecules, the most general methods seems to be free radical addition polymerization of tetrafluoroethylene (TFE) and its derivatives,[14, 27, 37-41] and polycondensations involving decafluorobiphenyl and other fluoroarenes.[42-45] Another viable approach is post-modification of a readily-made polymer with a fluorinated reagent such as a perfluoroalkylmethanol.[14, 28, 29, 46] In my Master's Thesis, and again in this chapter, I will demonstrate the use of Diels-Alder polycondensation to prepare highly fluorinated, linear aromatic polymers. My synthetic approach is based on a technique initially developed fifty years ago, when Stille devised an interesting class of polymers by reacting bis(cyclopentadienone)s (CPDOs) with dialkynes.[47-49]

1.1.2. 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.

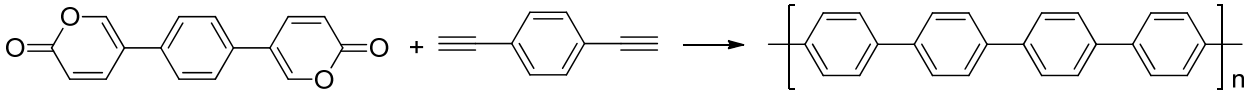
1.1.3. Stille's Irreversible DA Polymerization Systems. Stille chose to base his irreversible Diels-Alder polymerizations on cycloadditions of cyclopentadienones (CPDOs), alpha-pyrones, and thiophene oxides, which proceed with extrusion of a small molecule (CO, CO_2, or SO_2, respectively) (Scheme 1.1).[2, 47, 48] These model reactions, especially the CPDO and pyrone reactions, were extended to polymerizations by constructing phenylene-linked bis(CPDO) and



Scheme 1.1. Irreversible Diels-Alder reactions

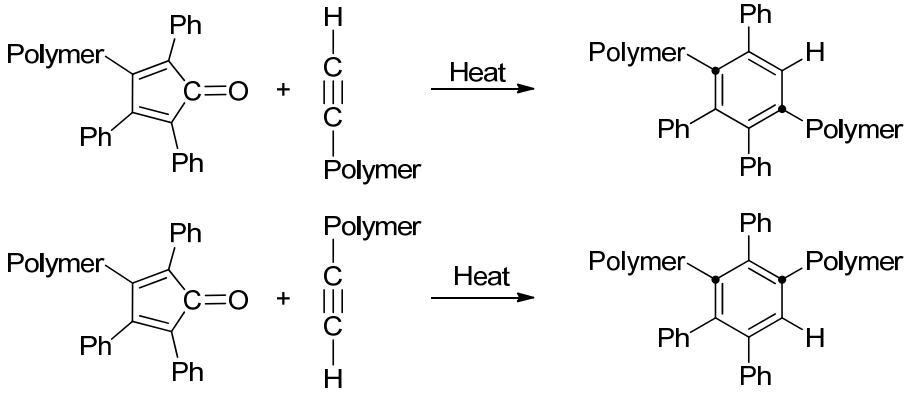
bis-pyrone monomers and reacting them with dialkynylbenzenes. A schematic of the bis-pyrone system is shown in Scheme 1.2. The polymerization temperatures were high – often as high as 250 ^{o}C – in solvents like diphenyl ether, 1,2,4-trichlorobenzene, or 1-methylnaphthalene. This particular reaction 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.



Scheme 1.2. Poly-phenylene from bis(pyrone) and dialkyne

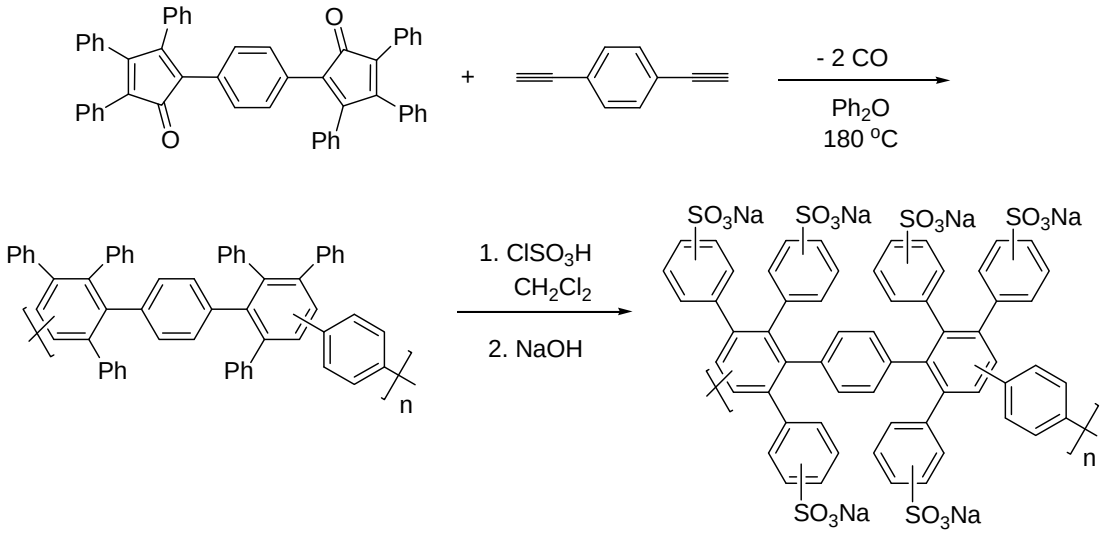
The CPDO systems readily accessible to Stille were only stable with three or preferably four aromatic substituents. Less fully substituted CPDOs can undergo Diels-Alder reactions with themselves, which would lead to defects in the resulting polymers due to stoichiometric disturbance. So, the *CPDO polymerizations 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 pale in color. Solubility is brought about by the lateral phenyl groups, which prevents interchain arene stacking and decreases the crystalline property of the polymer. Unlike the pyrone system, the regioselectivity of alkyne addition in the CPDO system is poor. Both *para* and *meta* linkages can be formed during the formation of the bicyclic intermediate (dots in Scheme 1.3).



Scheme 1.3. Para and meta catenation in Stille's Diels-Alder polyphenylene

1.1.4. Applications of Diels-Alder Polyphenylenes. Dow commercialized the Stille-type polyphenylenes as low-k spin-on dielectric coatings under the trade-name SiLK™. Leading microchip manufacturers used Dow SiLK to make integrated circuits for 10-12 years. The product is "b-staged," which means it is partially polymerized to reach the desired viscosity for a spin-coat resin. The low molecular weight (M_n < 10,000) and the low concentration (5-20%) of the polymer allow the viscosity to be low enough to 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. 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.[50]

Fujimoto and coworkers (Sandia National Laboratories) reported the synthesis of a Stille-type phenylated polyphenylenes (Scheme 1.4) that showed promise as PEM materials. The



Scheme 1.4. Poly-phenylene ionomer synthesized by Fujimoto

Sandia innovation was post-sulfonation of the lateral phenyl groups (selectivity is thought to be steric in origin) using chlorosulfonic acid in dichloromethane solution.[51, 52] Again the remarkable solubility of the polymer come from the lateral phenyl group substitution along with of *meta* and *para* linkages.

Fujimoto and coworker have also reported Diels-Alder polyphenylenes (Fig. 1.2) that show both permeability and selectivity simultaneously. The steric hindrance created by the

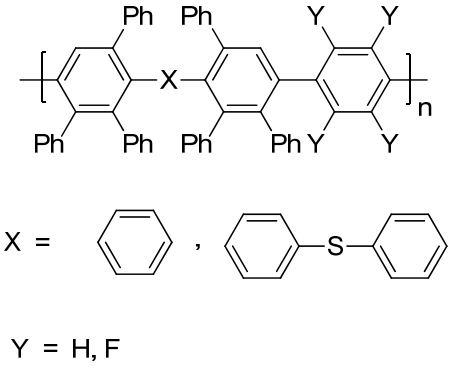


Figure 1.2. Polyphenylenes used for gas separation membranes

lateral aryl groups tends to orient the backbone phenyl rings orthogonal to each other. The chain segmental motion is restricted.[53] 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.

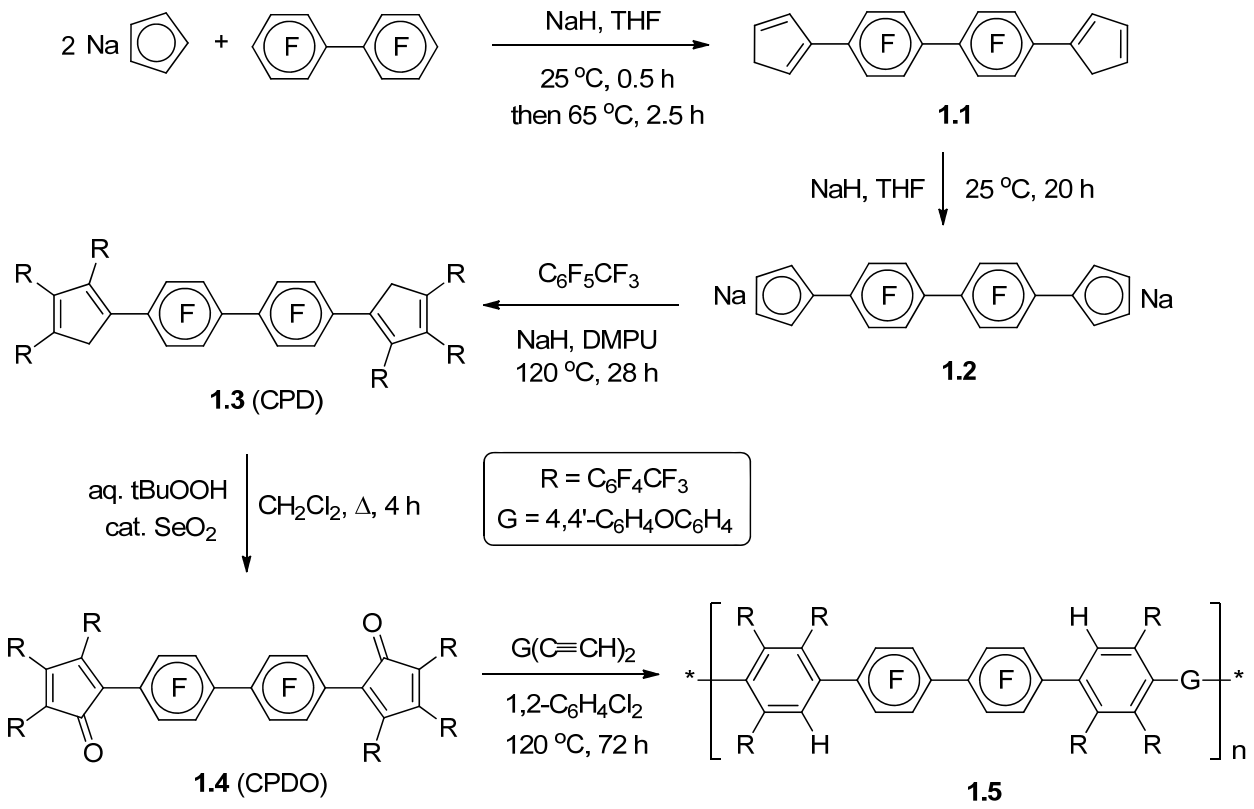
Müllen and coworkers have used analogous Diels-Alder chemistry to construct a range of nanosized polyphenylene dendrimers,[5, 54, 55] including an example in which pentafluorophenyl substituents were attached to the exterior of the dendrimer by reactions of terminal aromatic

alkynes with tetrakis(pentafluorophenyl)cyclopentadienone.[54, 56] Other examples of fluorination in the Stille-type polyphenylene systems are relatively sparse.[57]

1.2. Results and Discussion. I have already discussed the monomer design in great detail in my Master's Thesis, so not repeating that, I will directly concentrate on the improvements made to the CPDO monomer synthesis. The first three subsections below describe the synthetic measures I applied to synthesize the perfluoroarylated bis(cyclopentadienone) monomer, and the latter two describe the polymer synthesis and characterization.

1.2.1. Monomer Syntheses. As shown in Scheme 1.5 our CPDO monomer design is based on the use of octafluorobiphenylene as the linker and subsequent cyclopentadiene arylations to connect the "lateral" aryl substituents. Our group showed previously that two cyclopentadienyl groups can be linked by the 4,4'-octafluorobiphenylene moiety as shown in Scheme 1.5.[58] Bisdiene **1.1** was found to be stable for several hours to a couple of days at –20 °C. I have additionally explored the homopolymerization of **1.1** and those results are reported in Chapter 3 of this Dissertation. Fortunately bisdiene **1.1** can be stored indefinitely as its disodium salt, **1.2**.[58]

1.2.2. Sixfold Arylation with Octafluorotoluene. Our group also showed previously that multiple perfluoroaryl groups can be attached to cyclopentadiene in one-pot procedures based on classical nucleophilic aromatic substitution (S_NAr) reactions.[59-61] Analogous conversion of the bis(cyclopentadienide) **1.2** into the intermediate CPD **1.3** was ultimately successful, but some of my early failures are worth mentioning here. Initial attempts to use hexafluorobenzene as the arylating agent gave an inseparable mixture of fluorinated species, including compounds in which two of the fluorines of C_6F_6 had been substituted (a prominent signal at ca. –140 ppm in the ^{19}F NMR spectrum indicated formation of 1,4-tetrafluorophenylene moieties). Such "double substitution," which our group had not observed in related studies using hexafluorobenzene, was averted by switching to octafluorotoluene as the arylating agent;[62] the "second" substitution was blocked by the CF_3 group. Using diglyme as the solvent (which our group had trusted in



Scheme 1.5. Monomer synthesis and polymerization

analogous chemistry for over ten years) resulted in a product that showed signals in the region 3.0 – 4.5 ppm, which I tentatively assigned to glycolates (diglyme solvent molecule fragments) that had reacted nucleophilically with aromatic CF bonds. Even $C_6F_5CF_3$ can undergo multiple substitutions despite the fact that the *para* position is blocked,[63] and the conditions needed to achieve the formation of all six new C–C bonds are indeed forcing. The absolute requirement of high purity in a step-growth monomer drove us to search for a more "innocent" solvent that would still have the needed high boiling point to promote complete arylation, sufficient polarity to solubilize the ionic intermediates, low nucleophilicity to avoid direct attacks on the perfluoroarenes, low acidity to avoid direct reaction with NaH, and low electrophilicity and non-oxidizing character to avoid reactions with the organosodium intermediates. Many typical "polar aprotic" solvents like acetonitrile,

dimethyl sulfoxide, dimethyl formamide, and sulfolane do not meet these tight restrictions in our experience. However HMPA worked well in small-scale trials. Due to the health and safety issues of HMPA I switched to a comparatively less hazardous solvent, *N*,*N*'-dimethyl-1,3-propyleneurea (DMPU). I found that in aqueous workups using ether or dichloromethane as the organic phase, HMPA or DMPU can be removed rigorously with five aqueous washes. Also, the reactions using HMPA or DMPU as the solvent could be run at lower temperature (120 °C) compared to the 140-150 °C needed with diglyme.

Using DMPU as the solvent, the desired fluoroarylation proceeded in 76% purified yield using excess NaH and excess octafluorotoluene at 120 °C. A broad signal (4.31 ppm), as well as a lack of signals in the vinyl CH region (5.5 to 7.5 ppm) (Fig 1.3), in ^{1}H NMR spectrum of the

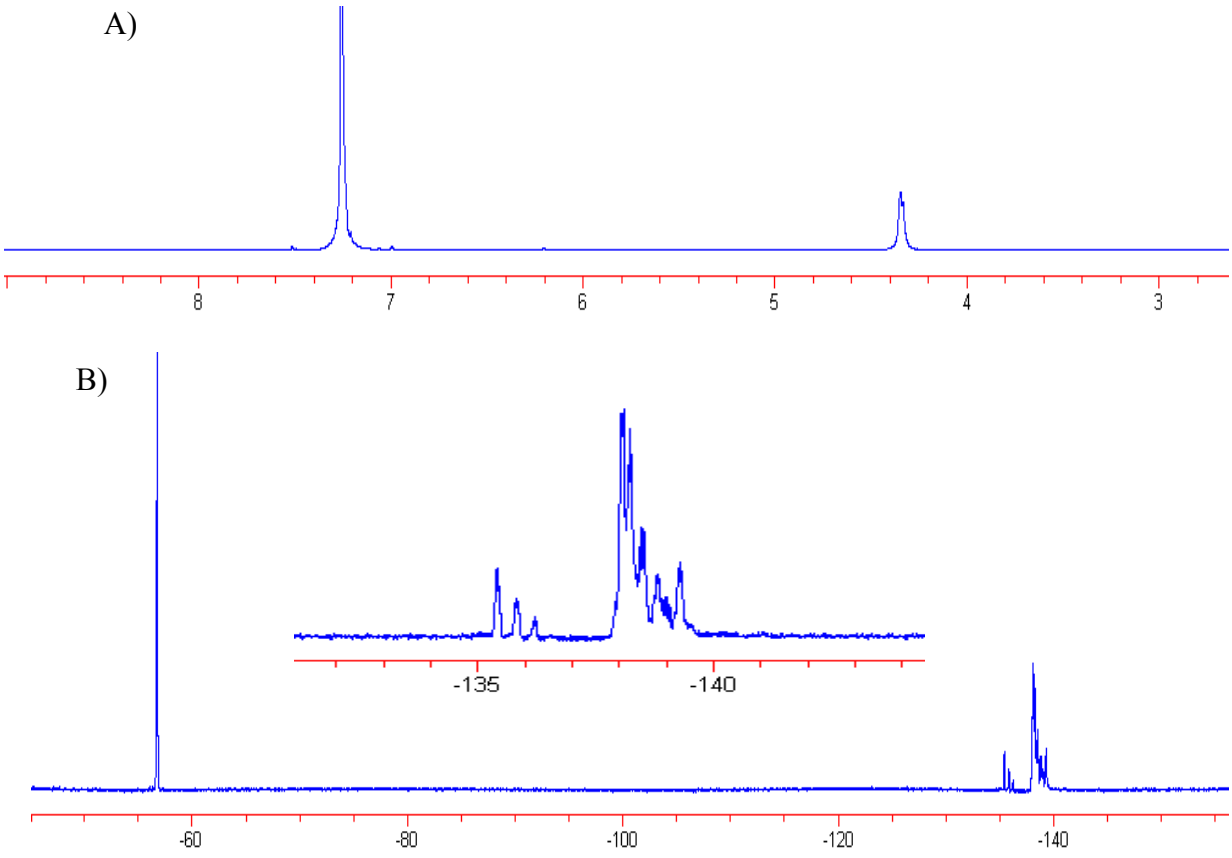


Figure 1.3. A) ^{1}H NMR spectrum of **1.3** in $CDCl_3$ B) ^{19}F spectrum NMR of **1.3** (Inset: aromatic region)

product verified selective attachment of three $C_6F_4CF_3$ groups to each cyclopentadiene moiety. This result was consistent with our previous experience that pentaarylated cyclopentadienes are not formed in these kinds of reactions.[59, 62] That selectivity is critical here because I need to oxidize the remaining CH_2 groups of the CPD **1.3** to the C=O groups of the CPDO **1.4**.

1.2.3. Oxidation of Monomer Precursor 1.3. The final synthetic step was oxidation of the methylene carbon. 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.[64] A cyclopentadiene is first treated with *N*,*N*-dimethyl-4-nitrosoaniline to give a mixture of an imine and a nitrone. The imine/nitrone mixture is hydrolyzed under acidic conditions to give the ketone. This reaction works well for tetrakis(pentafluorophenyl)cyclopentadiene (95% overall yield of the corresponding ketone). The first conversion (to imine/nitrone mixtures) seemed to work well too for (**1.3**), but the hydrolysis was extremely slow and gave a lot of byproducts that I could not characterize. The reasons for this lack of generality are not clear.

Returning to the literature, I found that activated ring methylene carbons can be oxidized with selenium dioxide (SeO_2).[65, 66] Depending on that idea I developed a modified oxidation for my monomer precursor. Here the terminal oxidant is *tert*-butyl hydroperoxide, the active-catalytic oxidant is selenium dioxide (5 mol% SeO_2), and the solvent is a biphasic mixture of dichloromethane and water.[65] The water is present because we purchase and handle ^{t}BuOOH as an aqueous solution. Conversion is immediately visible because the CPDO **1.4** (and, presumably, the mono-oxidized intermediate) is orange. A happy coincidence for us is the observation that the color of monomer **1.4** is close to the "burnt orange" that is one of Virginia Tech's school colors. Complete conversion is confirmed by disappearance of the broad peak in the aliphatic

region (4.31 ppm) (Fig 1. 4) of the ^{1}H NMR spectrum. Workup and purification afforded 90% of CPDO **1.4**.

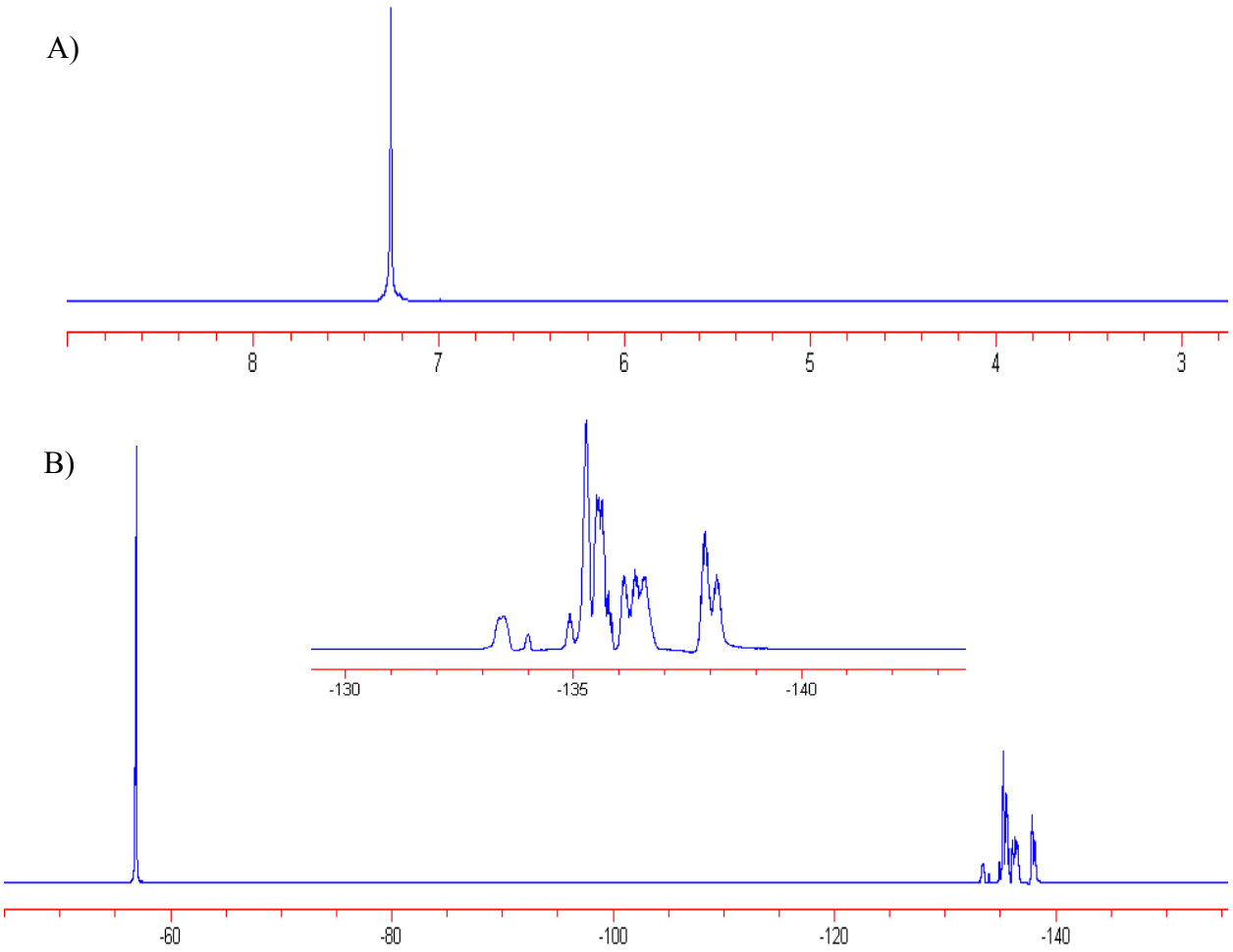


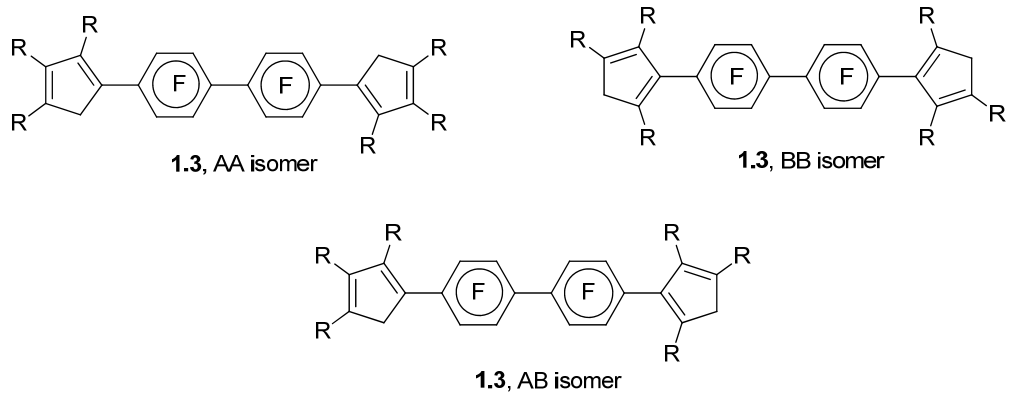
Figure 1.4. A) ^{1}H NMR spectrumof **1.4** in $CDCl_3$ B) ^{19}F NMR spectrum of **1.4** (Inset: Aromatic region)

I subsequently found this catalytic selenium dioxide oxidation method is quite versatile. I applied the same system on a selection of perfluoroarylated cyclopentadienes already available in our group, and synthesized additional novel cyclopentadienes to address key issues of scope and mechanism. Those results will be discussed in details in Chapter 2 of this Dissertation.

An alternative method developed recently by my co-worker (Brian Hickory) uses oxygen as the oxidant and a ligated copper catalyst system (typically CuI, CuBr, $CuBr_2$ or $Cu(OAc)_2$ as the metal ion source, pyridine or bipyridine as the ligand, and acetonitrile or ethyl acetate as the solvent). Unfortunately I have found that this reaction does not work well for the most acidic cyclopentadienes, which means it is also not promising for my monomer precursor.

1.2.4. Monomer Regioisomerism. The sixfold arylation step in the monomer synthesis (Scheme 1.5) afforded CPD **1.3** as a mixture of three regioisomers (Chart 1.1). Essentially, the linking octafluorobiphenylene group may be in either the 1- or the 2-position with respect to each of the

Chart1.1 Different regioisomers formed during the monomer synthesis

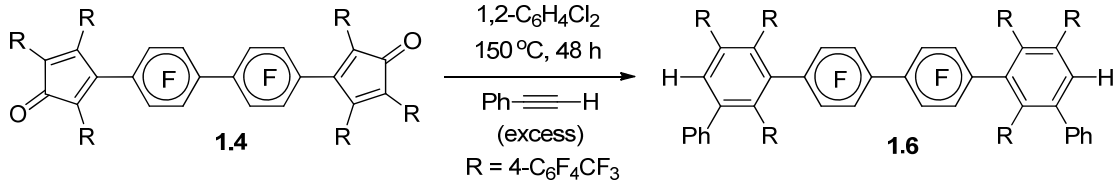


two cyclopentadiene moieties, giving rise to two symmetrical isomers (AA type and BB type) and one unsymmetrical (AB type) isomer. The methylene signals of CPD **1.3** were not resolved, but the isomerism of **1.3** did rationalize the observation of a broadened ^{1}H NMR signal. The ^{13}C NMR spectra of both **1.3** and **1,4** showed sufficient dispersion to confirm the presence of more than one isomer. Two signals in the ^{13}C spectrum of **1.3** (48.38 ppm and 48.10 ppm) and in the spectrum of **1.4** (188.10 ppm and 187.90 ppm) were attributed to the two canonical isomeric forms (A and B) of each cyclopentadiene moiety. We could not assign the two isomeric forms, but the spectrum did confirm that both were present and in roughly equal (i.e., statistical)

concentrations.[67] The ^{19}F spectra were too complex to assign anything except general spectral regions (e.g., CF_3 vs C_6F_4).

1.2.5. Model Studies. In our ongoing work on fluoroarylated polymer synthesis we have found that model chemistry helps "pre-optimize" certain reaction conditions and provides NMR spectral data that aids the subsequent characterization of the target polymers. In the present case the two obvious studies are (a) combination of CPDO **1.4** with an excess of a "capping" aromatic alkyne such as phenylacetylene (ethynylbenzene), and (b) combination of the intended dialkyne monomer, 4,4'-diethynyldiphenyl ether (**1.7**) with a mononuclear or "capping" CPDO, in this case tetrakis(perfluoro-4-tolyl)cyclopentadienone (**1.8**).

1.2.5.1. Model Study (a). As shown in Scheme 1.6, treatment of CPDO monomer **1.4** with a fivefold excess of phenylacetylene in 1,2-dichlorobenzene required 30 h at 120 °C to reach full conversion of **1.4** as determined by ^1H NMR spectroscopic analysis. The product arene **1.6** was recovered easily by precipitation from hexane. The ^1H NMR spectrum of arene **1.6** (Fig. 1.5)



Scheme 1.6. Model study (a)

showed signals expected for the unsubstituted phenyl groups, plus a new downfield signal (7.8 to 8.0 ppm) assigned to the hydrogens of the aromatic rings newly-formed from the Diels-Alder cycloaddition and CO extrusion processes. The presence of multiple signals was consistent with the formation of regioisomers (Scheme 1.7), arising from isomerism in the reactant **1.4** and from different cycloaddition orientations. While I could not assign the different isomers, this observation is important because the same types of isomers should be also present in the

backbone of target polymer, because the "linker" (Z) and Ph groups in Scheme 1.7 correspond to backbone connections. This result differed from the Stille and Müllen systems, which afforded

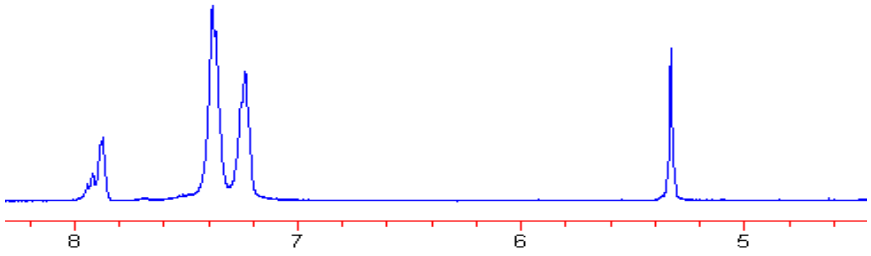
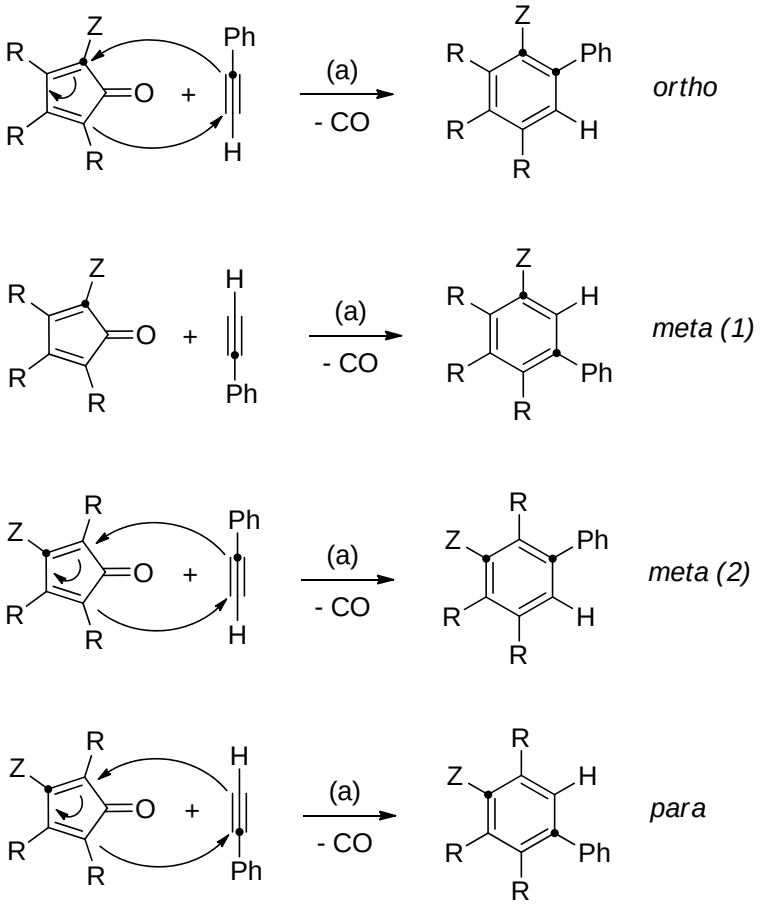


Figure 1.5. ^{1}H NMR spectrum (CD_2Cl_2) from model study (a)



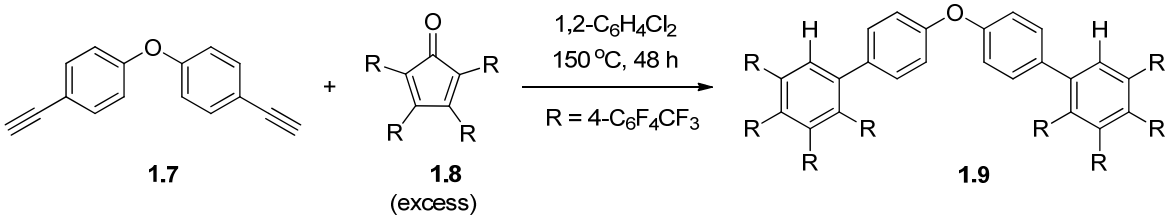
(a) 1,2-$C_6H_4Cl_2$, 150 ^{o}C, 48 h
R = 4-$C_6F_4CF_3$; Z = $C_6F_4C_6F_4$ linker

Scheme 1.7. Different regioisomers formed during model study (a)

only *meta(2)* and *para* connections because their CPDO monomers are region pure. Catenation regiochemistries other than *para* imparted flexibility (torsional degrees of freedom) and should help the polymers retain solubility at higher molecular weights.

1.2.5.2. Model Study (b). In a preliminary polymerization experiment, I combined CPDO **1.4** with 1,4-diethynylbenzene, attempting to prepare a true polyphenylene that would be directly analogous to the Stille system. Unfortunately we found that oligomers of very low molecular weight (e.g., DP = 2) precipitated from the reaction medium. The choice of 4,4'-diethynyldiphenyl ether (**1.7**) for the studies reported here reflects my attempt to increase the torsional flexibility (and therefore the solubility of the product polymer). I also reasoned that after one ethynyl group of 1,4-diethynylbenzene reacted, the other might engage in a slower Diels-Alder reaction because of electronic substituent effects transmitted through the single phenylene moiety, whereas the diphenyl ether moiety of **1.7** should insulate the two ethynyl groups from one another.

My second model reaction is shown in Scheme 1.8. This reaction required the preparation of a new ketone (**1.8**), which was prepared by tBuOOH/SeO_2 oxidation of the previously reported tetra arylated cyclopentadiene.[62] The Diels-Alder reaction was monitored by NMR spectroscopy and continued until the peaks for alkyne proton disappeared. The ^{1}H NMR spectrum of isolated diphenyl ether derivative **1.9** showed the "new" aromatic hydrogens (7.80 ppm) (Fig 1.6), and



Scheme 1.8. Model reaction study (b)

crystals suitable for single-crystal X-ray diffraction were obtained from a hexane / dichloromethane solution. The molecular structure of ether **1.9** (Fig. 1.7) did not show any unexpected features but did reveal the highly non-planar relationship of the newly formed aromatic ring and both the diphenyl ether linker (the two torsion angles are 44°C and 64°) and

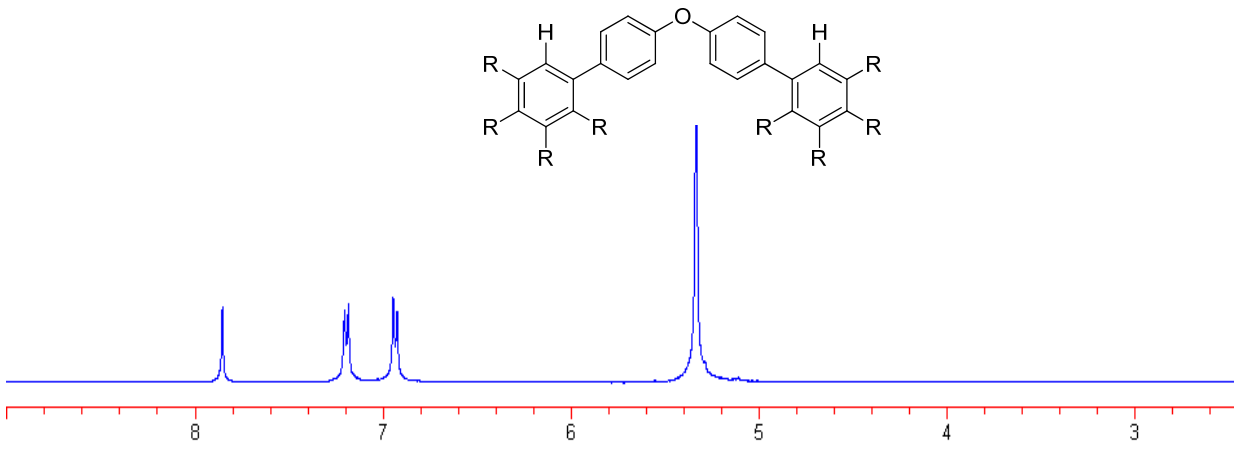


Figure 1.6. ^{1}H NMR spectrum (CD_2Cl_2) from model study (b)

the terminal $C_6F_4CF_3$ groups (torsional angles are in the range 60-75°). I expect these structural relationships to persist in polymers formed from dialkyne **1.7** and CPDO **1.4**.

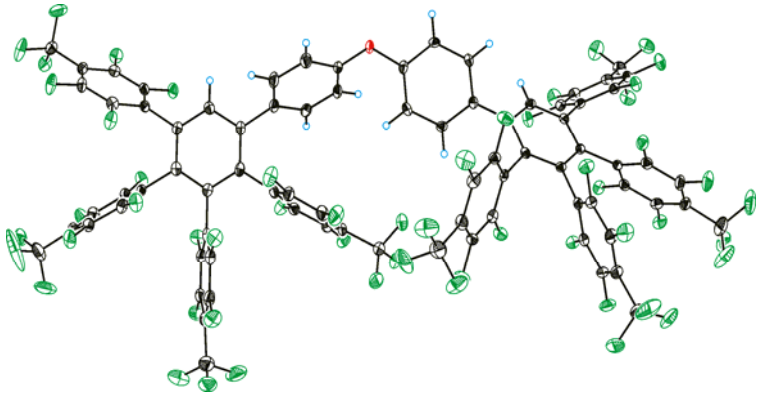


Figure 1.7. Thermal ellipsoid plot (50% probability) of the molecular structure of crystalline **1.9**.

1.2.6. Polymerization Reactions. In the optimized procedure, a rigorously degassed mixture of dialkyne **1.7** and CPDO **1.4** in freshly distilled 1,2-dichlorobenzene is heated in a sealed reaction tube for 72 h (Scheme 1.5). A color change is observed from dark orange to pale yellow, tan, or brown, and invariably a small amount of black residue also collects on the inner walls of the reaction vessel. The black residue is intractable and can be excluded from the workup by decanting the soluble portion away. Polymer **1.5** was isolated as a pale-tan glassy solid in 83% yield.

1.2.7. Polymer Characterization. Polymer **1.5** was readily soluble in polar solvents like dichloromethane, chloroform, THF, DMAc, and DMF. In the ^{1}H NMR spectrum (Fig. 1.8), the

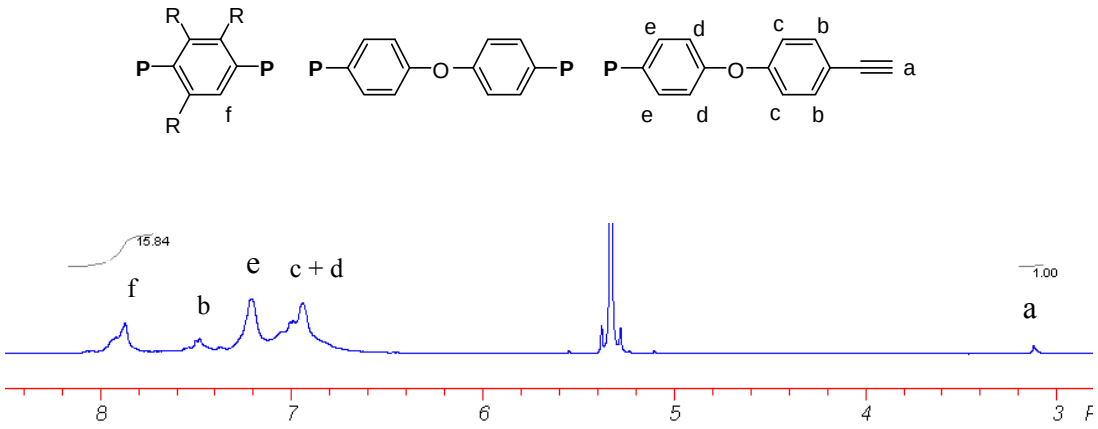


Figure 1.8. ^{1}H NMR spectrum of polymer **1.5**

"new" aromatic hydrogens were assigned to the downfield-most signal in the aromatic region (7.8-8.0 ppm) in analogy to the model compound spectrum (Fig. 1.6). The small signal at 3.10 ppm was assigned to alkyne end groups. End group analysis obtained by integrating the newly generated aromatic proton peak with respect to the alkyne end group, and assuming that each chain has, on average, one alkyne end group and one CPDO end group, gave a molecular weight (M_n) of 15,100 g/mol (DP ~ 7). The ^{19}F NMR spectrum was consistent with the assigned

polymer structure but otherwise rather uninformative. Size exclusion chromatography (SEC) found M_n = 14,000 g/mol, M_w = 17,000 g/mol., and PDI = 1.2.

1.2.8. Thermal Stability of the Polymer. TGA analysis in a nitrogen atmosphere (Fig. 1.9) showed a small weight loss near 180 ^oC, which is assigned to residual solvent loss. Such losses can often signal passage through the glass transition temperature, however no glass transition was observed up to 200 ^oC in the essentially featureless DSC trace of the polymer. Irreversible degradation of the polymer chain began in earnest above about 300 ^oC.

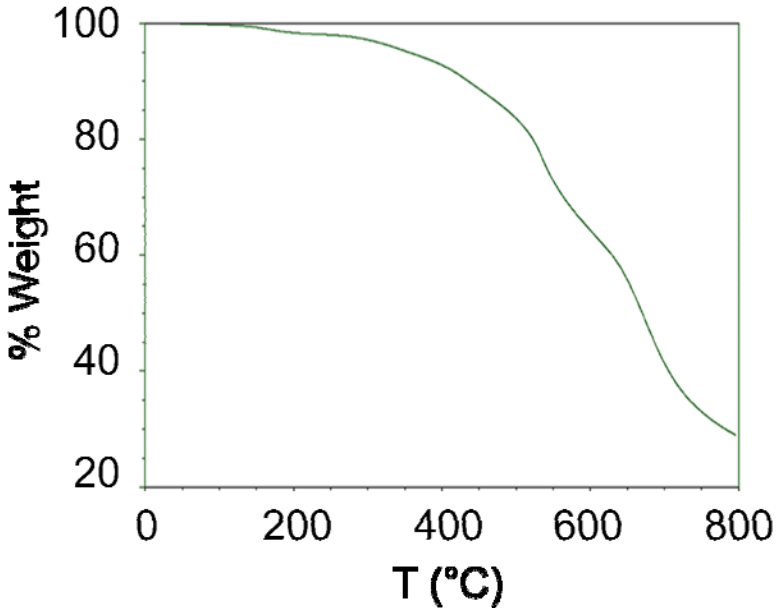


Figure 1.9. Thermogravimetric analysis (TGA) of polymer **1.5**.

The relatively low degree of polymerization observed molecular weight is attributed to an as-yet unidentified side-reaction which could disturb the stoichiometric relationship needed for continued propagation. This side-reaction might also lead to the formation of the intractable black residue observed in the reaction vessel. In some of my less successful polymerization experiments, new signals appeared in the 3-4 ppm reaction of the ^1H NMR spectrum. I have not

been able to assign these signals. The low PDI could reflect some fractionation of the polymer upon workup. The supernatant was analyzed and lower molecular weight oligomers were found.

1.2.9. Discussion of the Polymerization Reaction. While the reactions proceed at temperatures that are substantially lower than those required in Stille-type polymerizations of non-fluorinated CPDOs, they are still slower than we would prefer. Unfortunately at higher temperature (135 °C) I observed an increased quantity of the intractable black material without an increase in the molecular weight of the dichlorobenzene-soluble product fraction. Also the molecular weight of polymer **1.5** was not increased if the reaction time at 120 °C was increased to 100 h. Moreover, control studies showed that neither the diyne **1.7** nor the CPDO monomer **1.4** undergo self-reactions that we can detect by NMR spectroscopy when heated by themselves in 1,2-dichlorobenzene solution at 120 °C. I expect the end groups of growing polymer chains to be as stable, but I cannot rule out side reactions taking place at the stage of the bicyclic intermediates. In an attempt to explore the origins of the black intractable residue, I also tried oligomerization of CPDO **1.4** and diyne **1.7** at stoichiometric ratios of 1.5 to 1.0 and 1.0 to 1.5, respectively. The number average DP of these samples was lower as expected (ca. 3-4 based on end-group analysis), but the amount of black residue formed seemed unchanged.

Currently we are working to increase the degree of polymerization using different solvent systems. So far we know that *m*-cresol is unsuccessful because the CPDO monomer **1.4** is only sparingly soluble in that solvent, while mixtures of dichlorobenzene and *m*-cresol show significant decomposition. Toluene, despite having a boiling point (111 °C) near our optimized reaction temperature of 120 °C, gives a cleaner but unacceptably slow reaction. Essentially we need to find a solvent system in which our monomers and the polymer will be soluble, and we can increase the temperature to bring about a faster propagation toward the end of the reaction

when end groups are dilute, while suppressing the as-yet-unidentified decomposition pathway. Another alterative will be chain-extension of segments bearing functional end groups.

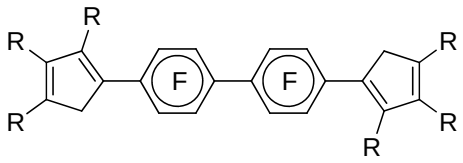
1.3. Experimental

1.3.1. Materials and Methods. Hexafluorobenzene, octafluorotoluene, and decafluorobiphenyl were used as received from Oakwood Products, Matrix Scientific, or Apollo Chemicals. DMPU (Alfa Aesar) was distilled from calcium hydride (under reduced pressure as needed to maintain boiling points in the range 60-100 °C, typically 0.1 mmHg). THF and dichloromethane (VWR, inhibitor-free HPLC grades) were purified by passage through a column of 4 Å molecular sieves or alumina, respectively, using a method adapted from Pangborn, et al.[68] Selenium dioxide and *tert*-butyl hydroperoxide were used as received from Aldrich. Methods for silica gel chromatography were adapted from Still et al.[69] NMR spectra were obtained using Varian Unity 400 or Varian Inova 400 instruments. ^{19}F NMR spectra were referenced to external C_6F_6 in $CDCl_3$ (−163.0 ppm). GPC experiments were performed on Waters Alliance 2690 using Styragel HR columns with chloroform as the eluent (30 °C, 1.0 mL/min) and a Viscotek dual detector system. The experiment was conducted under a nitrogen atmosphere. TGA measurements used a TA Instrument Q-500 with a heating rate of 10 ^{o}C/min.

1.3.2. Synthesis

Synthesis of Previously Reported Compounds. Biphenyl derivatives **1** and **2**,[58] diphenyl ether derivative **7**,[70, 71] were prepared by published methods. The purity was checked comparing the NMR spectra.

Synthesis of CPD 1.3.

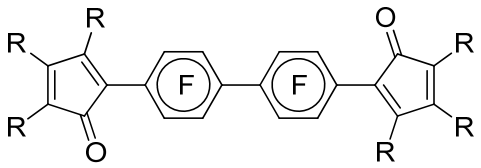


R = $C_6F_4CF_3$

A mixture of organoosodium **1.2** (0.47 g, 1.00 mmol), sodium hydride (0.360 g, 15.0 mmol), octafluorotoluene (2.60 g, 12.0 mmol), and DMPU (15 mL) was stirred under a nitrogen

atmosphere at 120 °C for 28 h. Reaction progress was monitored by examining the ^{1}H NMR spectra of a hydrolyzed aliquots. After the complete disappearance of the vinyl proton peaks (7.0-7.6 ppm), the reaction mixture was cooled and diluted with diethyl ether. Excess sodium hydride was quenched by cautious addition of water. The compound obtained in the organic phase was separated, washed with 10 small portions of water (to remove DMPU), dried over $MgSO_4$, filtered, and concentrated under vacuum. Purification required first silica gel chromatography (1:9 dichloromethane/hexane) and then recrystallization from hot toluene to obtain a white solid (yield 1.31 g, 0.76 mmol, 76%). ^{1}H NMR ($CDCl_3$): δ 4.32 (m). ^{19}F NMR ($CDCl_3$): δ −56.8 (m, 18 F, CF_3 groups), −135.0 to −140.0 (br m, 32 F, C_6F_4 groups). HRMS calculated for $C_{64}F_{50}H_4$ $(M^*)^-$ 1721.9526, found 1721.9515.

Synthesis of CPDO 1.4.

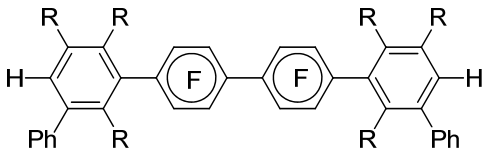


R = $C_6F_4CF_3$

A mixture of CPD **1.3** (0.50 g, 0.30 mmol), selenium dioxide (0.006 g, 0.06 mmol), *tert*-butyl hydroperoxide (1.08 g, 1.2 mmol, 70% solution in water) and dichloromethane (8 mL) was stirred under reflux for 4 h. Reaction progress was followed by working up small aliquots and analyzing the product mixture using ^{1}H NMR spectroscopy; the reaction was continued until the spectrum was silent. The solvent was evaporated under vacuum, and the residue was extracted with dichloromethane, washed with water to remove unreacted *tert*-butyl hydroperoxide and any remaining potentially toxic selenium species. Silica gel chromatography, eluting with 10% dichloromethane in hexane, followed by recrystalization from hot toluene, afforded 0.473 g (27 mol, 90%) of a glassy orange solid. ^{1}H NMR ($CDCl_3$): no signals. ^{19}F NMR ($CDCl_3$): δ −56.58

(m, 18 F, CF_3 groups), −132.94 to −138.81 (br m, 32 F, C_6F_4 groups); IR ($CDCl_3$): $\nu_{C=O}$ = 1741 cm^{-1}. HRMS calculated for $C_{64}F_{50}O_2$ $(M^*)^-$ 1749. 9098, found 1749.9101.

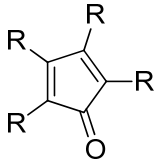
Synthesis of Arene 1.6.



R = $C_6F_4CF_3$

A Carius tube was charged with CPDO **1.4**, (150 mg, 0.086 mmol), phenylacetylene (88 mg, 0.86 mmol), and 4.0 mL of 1,2-dichlorobenzene. After degassing three times (freeze-pump-thaw), the tube was slowly heated to 120 ^oC and held at that temperature for 30 h. The dark orange color changed to light yellow-brown. After cooling to room temperature, the product (153 mg, 0.08 mmol, 94%) was recovered by precipitation in hexane followed by overnight drying in the vacuum oven at 80 ^oC. ^1H NMR (CD_2Cl_2): δ 7.23 (s, 2H), 7.38 (s, 3H), 7.88 (m, 1H). ^{19}F NMR (CD_2Cl_2): δ 56.9 (m, 18 F), between −134.8 to −140.0 (br m, 32 F) HRMS calculated for $C_{78}F_{50}H_{12}$ $(M^*)^-$ 1898.0070, found 1898.0141.

Synthesis of 1,2,3,4-Tetrakis(perfluoro-4-tolyl)cyclopentadienone model compound (1.8).

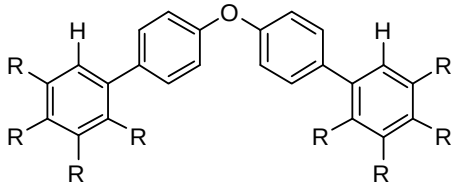


R = $C_6F_4CF_3$

A mixture of 1,2,3,4-tetrakis(perfluoro-4-tolyl)cyclopentadiene (400 mg, 0.42 mmol), selenium dioxide (5 mg, 0.045 mmol), *tert*-butyl hydroperoxide (108 mg, 0.84 mmol), and dichloromethane (5 mL) was stirred at room temperature for 10 h. The progress was followed by working up small aliquots and analyzing the crude product using ^1H NMR spectroscopy, and the reaction was continued until the spectrum was silent. The reaction mixture was filtered through silica gel to remove selenium dioxide. Then solvent was vacuum dried to obtain a bright orange

colored product solid in 95% yield. The crude product was purified by silica gel chromatography, eluting with hexane. ^{1}H NMR ($CDCl_3$): No signals. ^{19}F NMR ($CDCl_3$):δ −56.79 (m, 12F), −135.28 (q, 4F), −135.59 (q, 4F), −136.08 (m, 4F), −137.80 (m, 4F). IR (CH_2Cl_2): $\nu_{C=O}$ = 1742 cm^{-1}. HRMS calculated for $C_{33}F_{28}O$ $(M^*)^-$ 943.9502, found 943.9524.

Synthesis of Model Compound 1.9.



R = $C_6F_4CF_3$

A solution of ketone **1.8** (0.24 g, 0.25 mmol) and 4,4'-diethynyldiphenyl ether **1.7** (0.022 g, 0.10 mmol) in 1,2-dichlorobenzene (5 mL) was stirred at 120 ^{o}C for 60 h. The solvent was evaporated under reduced pressure. Excess ketone **1.8** was removed by silica gel chromatography, eluting with 9:1 hexane:dichloromethane. The desired ether **1.9** was recrystallized from hot hexane to afford 198 mg (0.097 mmol, 97%) of a white solid. ^{1}H NMR ($CDCl_3$): 6.92 (d, 2H), 7.16 (d, 2H), 7.80 (s, 1H). ^{19}F NMR ($CDCl_3$): δ −56.91 (m, 12F), −136.01 (m, 2F), −136.78 (m, 2F), −138.32 (m, 10F), −139.19 (m, 2F). HRMS calculated for $C_{80}F_{56}H_{10}O$ $(M^*)^-$ 2049.9657, found 2049.9837.

Polymer Synthesis (1.5). A Carius tube was charged with CPDO **1.4**, (150.0 mg, 0.0860 mmol), 4,4'-diethynyldiphenyl ether **1.7** (18.8 mg, 0.0860 mmol), and 5. mL of 1,2-dichlorobenzene. After degassing three times, the tube was slowly heated to 120 ^{o}C and held there for 72 h. The color changed from dark orange to a pale yellow/brown. After cooling the reaction solution was decanted away from a small amount of black residue lining the inner walls of the reaction tube. Precipitation into hexane afforded a pale solid, which was vacuum-dried at 80 ^{o}C to afford 138 mg (83%) of **1.5**. ^{1}H NMR (CD_2Cl_2): δ 3.11 (s, 1H, CCH end group), 6.96 (br s, 36H), 7.23 (br s,

30H), 7.50 (br s, 3H), 7.89 (br s, 19H). ^{19}F NMR ($CDCl_3$): –57.39 (br s, 18 F), −135.00 to −143.10 (br m, 32 F). SEC results give a number average molecular weight of 14,000 g/mol and a weight average molecular weight of 17,000 g/mol.

Crystallographic Studies. A colorless prism (0.04 x 0.14 x 0.25 mm^3) grown by cooling / partial evaporation of a hexane / dichloromethane solution was centered on the goniometer of an Oxford Diffraction SuperNova diffractometer operating with MoKα radiation. The data collection routine, unit cell refinement, and data processing were carried out with the program CrysAlisPro.[72] The Laue symmetry was consistent with the triclinic space groups P1 and P-1. The centric space group P-1 was chosen based on the E-statistics ($|E^2 - 1| = 0.985$) and the preferred $Z' = 1$ value. The structure was solved using SHELXS-97[73] and refined using SHELXL-97[73] via the Olex2 interface.[74] The preliminary anisotropic displacement parameters suggested dynamic and/or positional disorder in many of the $–CF_3$ groups. For the two most severely disordered $–CF_3$ groups, a 2-position disorder model was used with relative occupancies that refined to 0.912(3) and 0.088(3) for F59A, F59B, F59C and F59D, F59E, F59F, respectively and to 0.713(9) and 0.287(9) for F66A, F66B, F66C and F66D, F66E, F66F, respectively. The final refinement model involved anisotropic displacement parameters for all non-hydrogen atoms except F59D, F59E, and F59F of a disordered $–CF_3$ group. A riding model was used for all hydrogen atoms.

1.4.1. Conclusions

This chapter demonstrates first that fluorinated bis(cyclopentadienone) (CPDO) monomers analogous to Stille's CPDO monomer are efficiently prepared from inexpensive fluoroaromatic compounds and cyclopentadiene, and second that despite wholesale changes in electronic substituent effects, the fluorinated CPDO undergoes Diels-Alder polymerization with a dialkyne under conditions that are milder than those used for the non-fluorinated CPDOs. The product oligomers are soluble in polar solvents and thermally stable. While we have not yet achieved high enough molecular weights for applications (e.g., membranes) that would require robust films, work toward that end is underway in our laboratories.

1.5. Future Work. At this point our main problem is achieving high molecular weight in our polymerization reactions. The key steps that we will take in solving this problem are outlined in the following paragraphs.

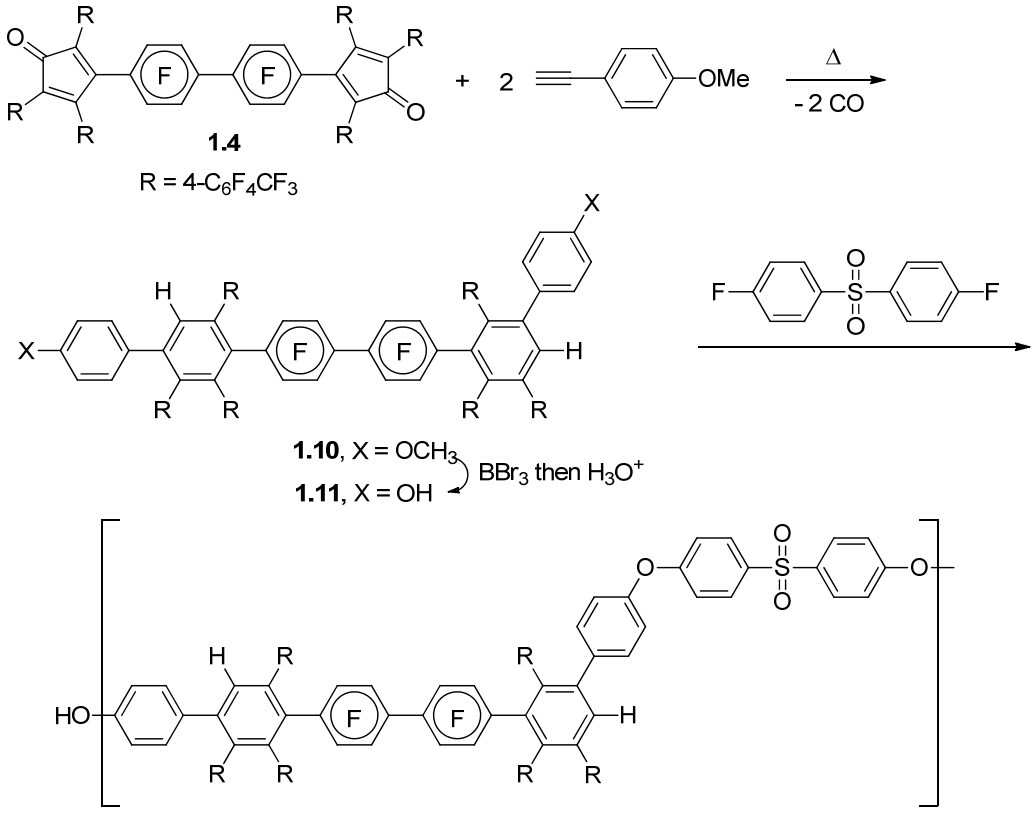
1.5.1. Solubility and Solvent Selection. Diels-Alder reactions are known to be catalyzed Lewis acids, including hydrogen bond donors. Therefore, we would prefer to conduct our polymerizations in a polar, protic solvent. Dr. Jessica P. Evans and Mr. Charles S. Carfagna in our group have obtained good 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 fluorinated CPDO (**1.4**) 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. Additionally $scCO_2$ can be "modified" by adding alcohols, possibly including trifluoroethanol, which would enable us to include hydrogen-bond-donor properties in the reaction medium.

1.5.2. Polymerization through Building Blocks. I 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 my bis(cyclopentadienone) (**1.4**) and commercially available (methoxyphenyl)acetylene should give the corresponding arylene dimethyl ether (**1.10**). Either the *para* or *meta* isomer may be used. Second, the alkoxy groups are easily demethylated with boron tribromide according to published methods.[75, 76] The rest of the molecule will withstand the harsh Lewis acid easily. Finally, the resulting bis(phenol) can be reacted with a suitable electrophilic monomer like 4,4'-difluorodiphenylsulfone (DFDPS). If DFDPS is not reactive enough to prevent self-reactions of the diol monomer with its own aromatic CF groups, then we could switch to decafluorobiphenyl as the electrophile as it is much more reactive. 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.



1.5.3. Microwave Heating. Microwave heating is a combination of well known thermal effects and controversial nonthermal effects and together it is known as microwave effect.[77-79] Therefore microwave heating is considered to be more proficient than the conventional oil bath heating. My lab mate Dr. Jessica P. Evans got encouraging results using microwave heating to effect some related polymerizations.[80] However actually the gains in reaction efficiency were relatively modest and most importantly she did not find any increase in the molecular weight of the polymer.

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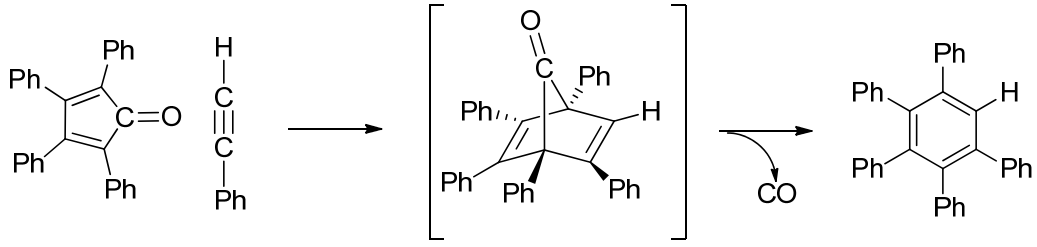
Chapter 2

Oxidation of Perfluoroarylated Cyclopentadienes to Cyclopentadienones Using Selenium Dioxide and Hydrogen Peroxide

2.1. Introduction.

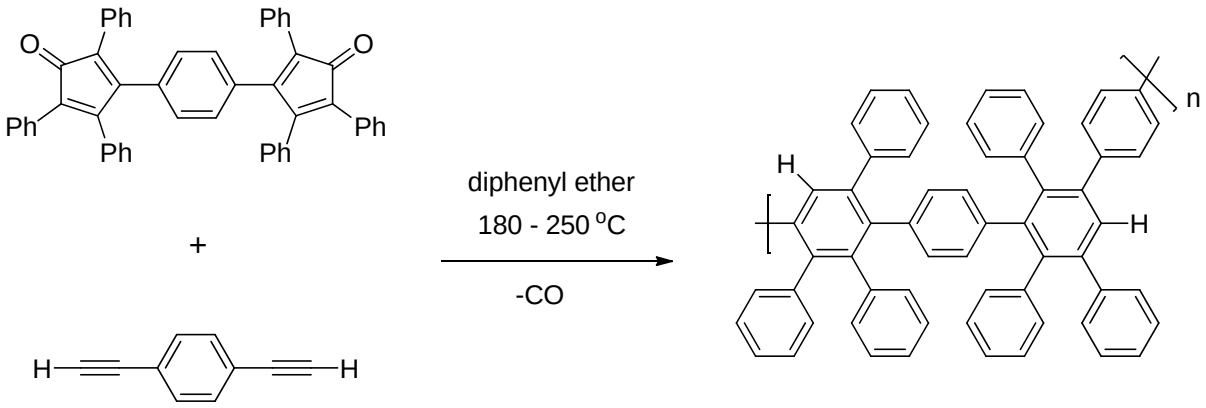
Cyclopentadienones. Cyclopentadienones (CPDOs) represent a well known class of compounds with an "antiaromatic" nature.[1, 2] Due to their locked s-cis configuration, CPDOs molecules are excellent dienes for the Diels-Alder reaction.[3] Unsubstituted, monosubstituted, and disubstituted CPDOs are so reactive that they are difficult to prepare and isolate. For example, the parent cyclopentadienone dimerizes immediately even at low temperature, but it can be trapped *in situ*.[4]

2.1.1. Uses of Cyclopentadienones. Because much of this dissertation (and my MS Thesis) concerns polymer synthesis, I am chiefly interested in reactions of CPDOs with alkyne dienophiles, because these reactions have served as the basis for the synthesis of aromatic polymers. Tetraphenylcyclopentadienone (tetracyclone) and its aryl-substituted derivatives react with alkyne dienophiles to form highly substituted benzenes (Scheme 2.1).[5, 6] A bicyclic Diels-Alder adduct forms, but this intermediate is unstable and extrudes carbon monoxide to form the new benzene ring.



Scheme 2.1. Reaction of tetracyclone and phenylacetylene to afford pentaphenylbenzene

Stille and co-workers used this reaction to synthesize aromatic polymers as shown in Scheme 2.2.[7, 8] A bis-cyclopentadieneone reacts with a dialkyne to propagate the polymer chain in a step-growth fashion. The specific polymerization shown in Scheme 2.2 gives a *phenylated polyphenylene* because the bis-CPDO linking group and the dialkyne linking group are both phenylenes, while all of the remaining CPDO substituents are phenyl groups. The polyphenylenes that Stille synthesized were found to be soluble in organic solvents and, as expected, they have excellent thermal stability. Kumar and co workers found that the polymer



Scheme 2.2. Polymer synthesis from bis(cyclopentadienone)

chain degradation took place above 400 °C.[7, 9] Stille-type polyphenylenes have found application as low-k dielectric resins (insulating layers within microelectronic devices).[10]

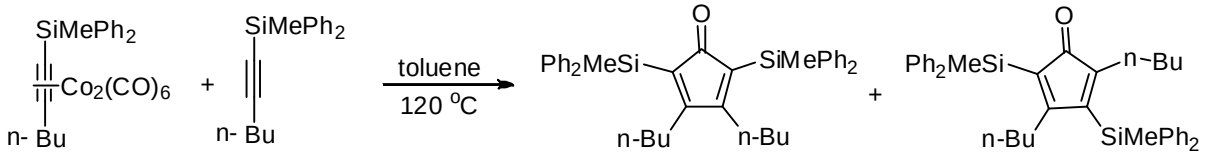
Numerous variants on Stille's theme have also been reported in which the linking groups are not arylenes but instead are arylene ethers, chains of methylene groups, and so on. In addition, one can modify the "lateral" phenyl groups after polymerization. The best example of this approach was reported by Cornelius and Fujimoto.[11-13] They used chlorosulfonic acid to sulfonate the lateral phenyl groups selectively, which gave rise to an ionomer that they proposed

for use as a proton exchange membrane for a hydrogen fuel cell, and as a gas-separation membrane. These applications highlight the tendency of the rigid Stille-type polyphenylenes to behave as amorphous glasses with significant internal void volume. Müllen and coworkers have developed related methods to construct dendrimeric polyphenylenes using Stille-type Diels-Alder chemistry. Diverse applications of polyphenylene dendrimers include materials for light-emitting diodes (LEDs).[14-16]

There are applications for cyclopentadienones besides polymer synthesis. Because of their predictable chemistry and functional-group-rich structures, they have been used as synthetic precursors to natural products and other interesting organic compounds. [17, 18] Finally, the formal addition of two electrons to cyclopentadienone (C_5H_4=O) gives the oxycyclopentadienyl anion, (C_5H_4–O), and various coordination complexes of both have been prepared, and some are useful in catalysis.[19-21]

2.1.2. Synthetic Routes to Cyclopentadienones. Many selective and efficient methods of synthesizing cyclopentadienones have been reported.[6] These include metal mediated carbonylative alkyne-alkyne [2+2+1] coupling reactions,[22, 23] [3 + 2] cycloaddition of cyclopropenones and alkynes using organometallic catalysts,[24, 25] base-catalyzed condensation of benzils with dibenzyl ketones,[6-9, 11, 12] and direct oxidation of cyclopentadienes.[6]

2.1.2.1. Carbonylative Alkyne-alkyne Coupling. In 1998 Shibata et al. reported the synthesis of cyclopentadienones by inter- or intramolecular carbonylative alkyne-alkyne coupling using octacarbonyldicobalt, $Co_2(CO)_8$ at atmospheric pressure of carbon monoxide (Scheme 2.3).[22, 23]



Scheme 2.3. Cyclopentadienones obtained by Shibata's [2+1+1] coupling

(The more famous variant is the Pauson-Khand Reaction, which involves the coupling of one alkene and one alkyne with CO to produce a cyclopentenone.[26])

Formally the reaction is a [2+2+1] cycloaddition but it is not mechanistically concerted. Previously Pearson and co-workers had reported similar carbonylative alkyne-alkyne coupling reaction in presence of an iron carbonyl complex. The products were (cyclopentadienone)iron complexes, which they demetalated to get the cyclopentadienones.[27-29] The advantage of Shibata's cobalt-mediated method was the direct synthesis of the cyclopentadienones without requiring an oxidative demetalation. Shibata later demonstrated carbonylative intramolecular [2+2+1] cycloaddition of 1,6-diynes, this time using an iridium(I) phosphine complex, under one atmosphere or less of CO.[30, 31] The proposed mechanism is shown in Fig. 2.1. First the diyne

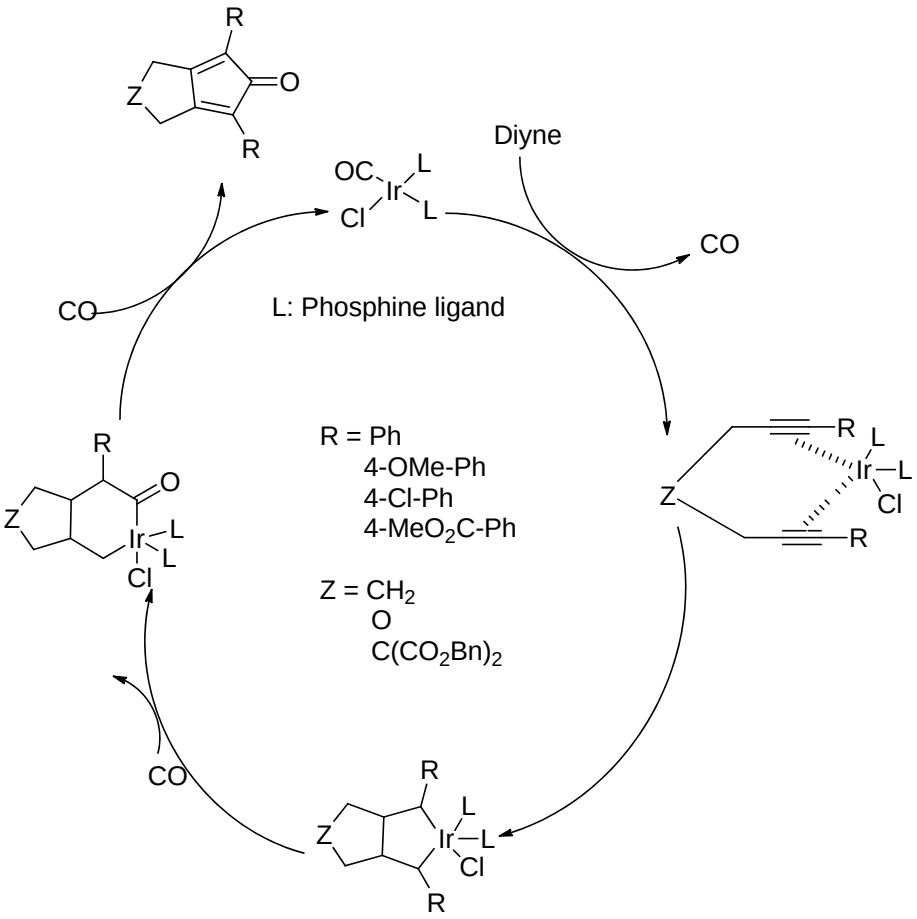
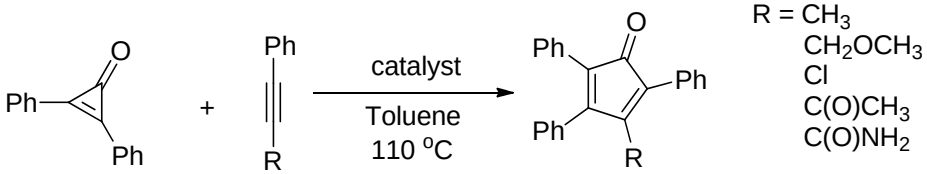


Figure 2.1. Shibata's iridium-catalyzed CPDO synthesis

forms a π-complex, followed by insertion of carbon monoxide in the complex. Reductive elimination affords the product while regenerating the catalyst.[31] Shibata and co workers showed only silyl substituted and aryl substituted internal diynes undergo this catalytic cycloaddition. Diynes with aliphatic substitution did not respond at all. Shibata and group obtained the best result when an electron donating group was attached to the *para* position of the aryl moiety.[23] One serious disadvantage of alkyne coupling reactions is that other processes often compete, such as the cyclotrimerization of the alkyne to produce a substituted benzene.[32] Avoiding this side-reaction often requires larger pressures of CO or stoichiometric quantities of cobalt. On the other hand the insertion of two CO molecules can give a quinone.[33] These problems have limited the synthetic utility of alkyne-alkyne-CO couplings.

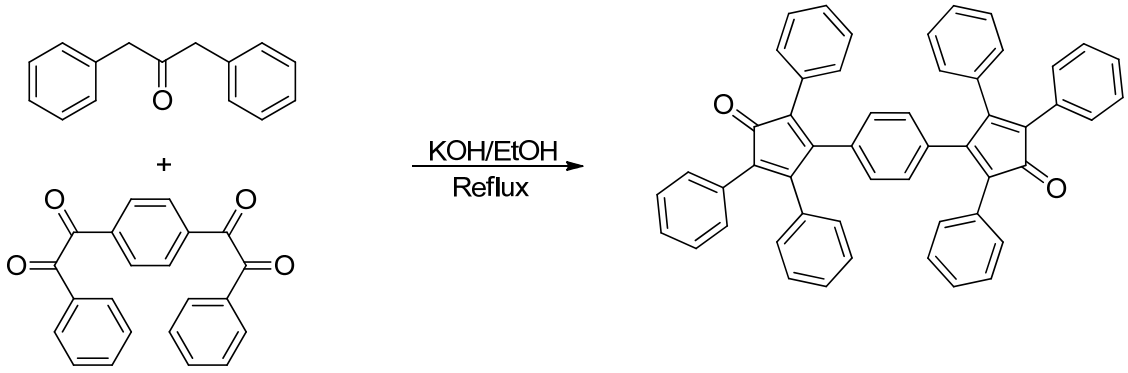
2.1.2.2. [3+2] Cycloaddition. Combining a cyclopropenone and an alkyne (Scheme 2.4) is formally analogous to alkyne-alkyne-CO coupling, except that now "crossed" couplings are facilitated. Usually a rhodium(I) catalyst, $[RhCl(CO)_2]_2$ is used. Wender and co-workers showed that aromatic and aliphatic alkynes containing a variety of functional groups (methoxymethyl, ketone, chloride) and cyclopropenones with either alkyl and aryl substitutents can form the corresponding cyclopentadienones.[24] They also showed that the aromatic internal alkynes with *para* trifluoromethyl substitution or *ortho* fluoro substitution can also undergo this reaction. Isobe et al. later showed that cyclopropenone acetals also cyclize with an electron



Scheme 2.4. Cyclopentadienones synthesized by [3+2] cycloaddition

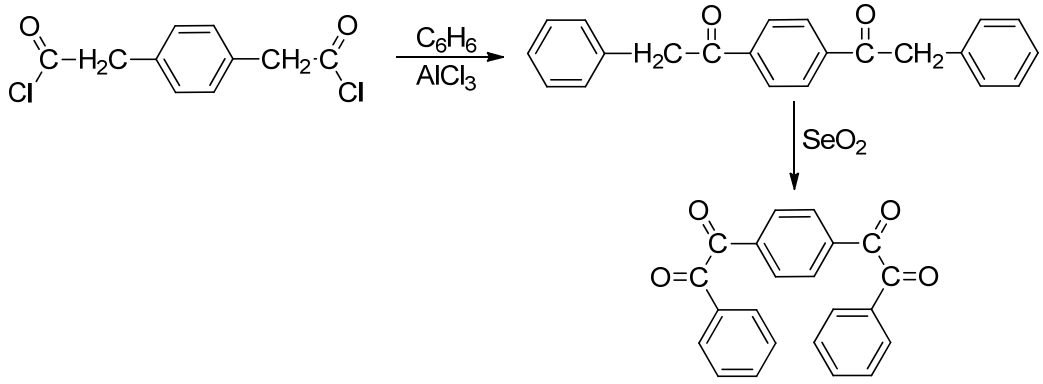
deficient alkyne in presence of palladium catalyst.[25] CPDOs were obtained after hydrolysis of the resulting cyclopentadienone acetals.

2.1.2.3. Base Catalyzed Aldol Condensation. One of the oldest and most important synthetic routes especially to aryl-substituted cyclopentadienones is the base catalyzed condensation of benzils with benzyl ketones (Scheme 2.5).[6] This method is the best-developed for CPDOs and is used almost exclusively for the CPDO-based monomers used to make Stille-type aromatic polymers.[34]



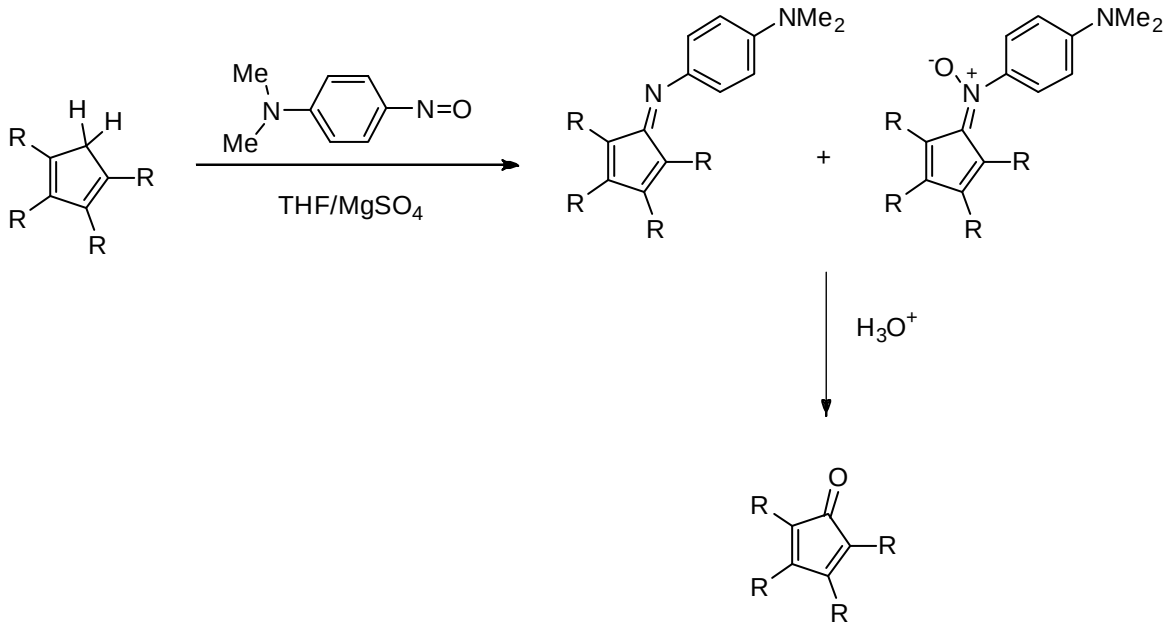
Scheme 2.5. Base catalyzed condensation of dibenzils with benzyl ketones

Unsubstituted benzil and dibenzyl ketone give tetraphenylcyclopentadienone or "tetracyclone."[6] However, the reaction tolerates any alkali-stable functional groups such as aryl halides and ethers on either the benzil or the dibenzyl ketone, and yields are often nearly quantitative.[6-9, 14, 16, 34, 35] However for base catalyzed condensation, the synthetic challenge then becomes making the starting materials (Scheme 2.6), which often require hazardous chemicals and difficult purification processes.[7, 8]



Scheme 2.6. Synthesis of starting material for base catalyzed condensation

2.1.2.4. Direct Oxidation of Cyclopentadienes. *N*,*N*-Dimethyl-4-nitrosoaniline is the most common oxidant used to convert cyclopentadienes directly to cyclopentadienones.[6] Here a cyclopentadiene is first treated with *N*,*N*-dimethyl-4-nitrosoaniline to give a mixture of an imine and

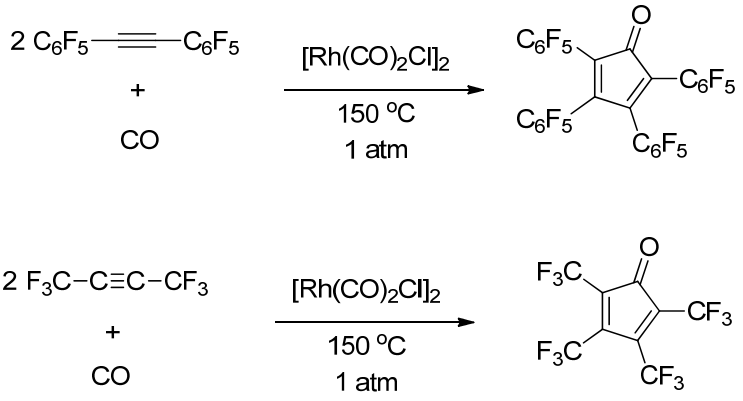


Scheme 2.7. Oxidation by *N*,*N*-dimethyl-4-nitrosoaniline

a nitrone (Scheme 2.7). The imine/nitrone mixture is then hydrolyzed under acidic conditions to give the ketone. My lab mate Mr. Brian S. Hickory found tetrakis(pentafluorophenyl)cyclopentadiene can be oxidized to corresponding ketone using *N*,*N*-dimethyl-4-nitrosoaniline followed by acid hydrolysis. He obtained 97% yield of pure product.[36]

2.1.3. Approaches to Fluorinated CPDOs. While the methods discussed above are useful and generally broad in scope, product lists curiously do not include CPDOs that have fluoro, trifluoromethyl, pentafluorophenyl, or other perfluoroaryl substituents. In the case of carbonylative alkyne-alkyne couplings, while there have been a few successful examples (see below), problems include the synthesis of the starting tolane and the tendency for some electron-rich late-transition metal complexes to undergo rapid oxidative addition of activated aromatic CF bonds.[37-42] Base-catalyzed aldol condensation is ruled out immediately because activated vinylic and especially aromatic CF bonds are subject to substitution under the alkaline reaction conditions.

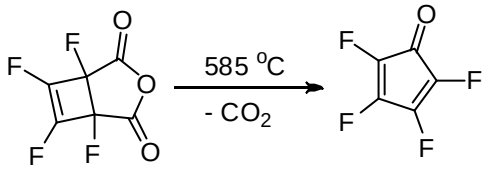
As just mentioned, alkyne-CO couplings have been successful in a couple of cases to synthesize fluorinated cyclopentadienones. Analogous processes gave tetrakis(pentafluorophenyl)cyclopentadienone and tetrakis(trifluoromethyl)cyclopentadienone (Scheme 2.8).[43]



Scheme 2.8. Synthesis of fluorinated cyclopentadienones by alkyne-CO coupling

Ren (and a few other groups before him) made tetrakis(pentafluoro)cyclopentadienone by refluxing decafluorotolane with $Co_2(CO)_8$ in xylene (Scheme 2.9).[44-47]

There have been other creative and useful syntheses of fluorinated CPDOs. Grayston synthesized tetrafluorocyclopentadienone from tetrafluorocyclobutenedicarboxylic anhydride by vacuum cracking at 585 ^{o}C (Scheme 2.9) with elimination of CO_2.[48] Lemal and co-workers reported the synthesis of same compound by flash vacuum pyrolysis of tetrafluoro-o-benzoquinone.[49] However in both cases synthesis of the starting materials was difficult.

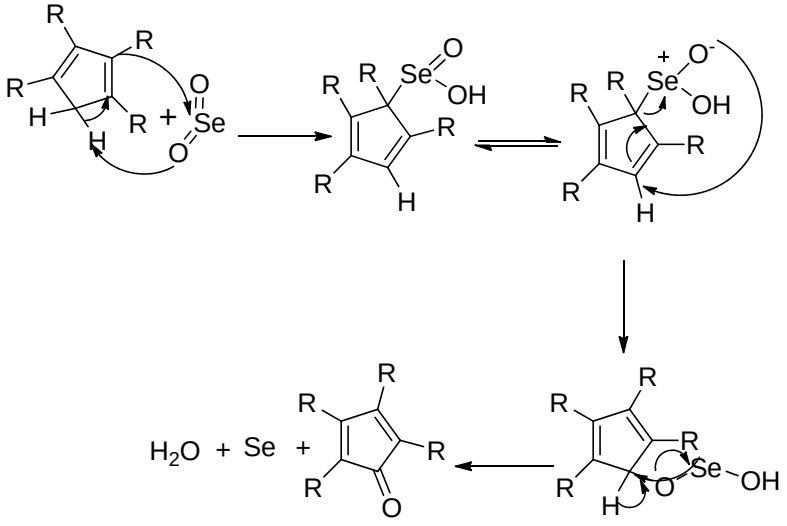


Scheme 2.9. Thermolysis of tetrafluorocyclobutenedicarboxylic anhydride

The remaining method is direct oxidation of cyclopentadienes. This opportunity presented itself uniquely to the Deck Group at Virginia Tech because our group has developed, over the past fifteen years, general synthetic methods for the synthesis of perfluoroaryl-substituted cyclopentadienes.[50] Recently our group has been exploring a variety of methods of oxidizing these compounds because of their relevance to the development of highly fluorinated Stille-type aromatic polymers. Brian Hickory in our group has explored DMNA-based oxidations as well as a new copper-catalyzed air-oxidation that he discovered, and the details of these will be described in his doctoral dissertation. My work involves the use of selenium dioxide as the chemical oxidant, so before presenting my findings I need to review the use of selenium dioxide in oxidations generally to establish a rich context for my findings.

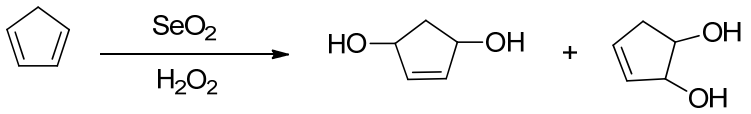
2.1.4. Selenium Dioxide as an Oxidant. Selenium dioxide (SeO_2) is a well known oxidant in synthetic organic chemistry, especially for the conversion of allylic methylene groups to the corresponding alcohols or, more typically, carbonyl compounds. SeO_2 is also used for the synthesis of α-dicarbonyl compounds.[7, 51-53] A plausible mechanism of this oxidation process is

shown in Scheme 2.10.[53] The applications of this method in synthesis are well documented in most advanced organic chemistry textbooks.



Scheme 2.10. A plausible mechanism of SeO_2 oxidation

A particularly useful variant of the SeO_2 oxidation uses catalytic selenium with stoichiometric hydrogen peroxide or tert-butyl hydroperoxide.[54, 55] The peroxide reoxidizes the selenium to Se(IV), minimizing the amount of toxic selenium needed and preventing the formation of red colloidal selenium, which is difficult to remove during workup procedures. Hydrogen peroxide especially is a "green" oxidant as its byproduct is water. Interestingly SeO_2 / H_2O_2 and other peroxide-type oxidations have been applied to cyclopentadienes, but the products are not cyclopentadienones. Stoll treated cyclopentadiene with SeO_2 / H_2O_2 and obtained a mixture of isomeric diols (Scheme 2.11).[56]



Scheme 2.11. Diol produced during the reaction of cyclopentadiene with selenium dioxide and hydrogen peroxide

Other substrates have resulted in ring-openings to afford functionalized stilbenes.[57] Tetracyclone reacts with hydrogen peroxide, albeit under much harsher conditions (acetic acid at reflux, which means the oxidant is probably peracetic acid), to afford tetraphenyl-2-pyrone.[58]

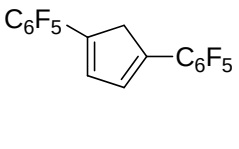
2.2. Result and Discussion

This chapter describes the use of the SeO_2 / H_2O_2 oxidant system to convert fluoroaryl-substituted cyclopentadienes to the corresponding cyclopentadienones. My main motivation was to develop a general oxidation method that we could also put to use in the synthesis of bis-CPDO monomers for the synthesis of fluorinated Stille-type aromatic polymers. We discovered, not surprisingly, that aside from the practical objective, the oxidation chemistry turned out to be interesting and exciting in its own right.

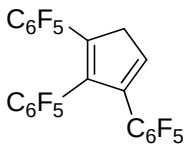
As mentioned above, our group already has a good collection of cyclopentadiene substrates (or, at least, the methods to prepare them). However in some cases, in order to examine trends in reactivity and selectivity, I have needed to synthesize additional novel cyclopentadienes. The first section below will discuss their synthesis, while the second section will describe our oxidation findings.

2.2.1. Synthesis of Fluoroaryl-Substituted Cyclopentadienes. Fluoroaryl groups are attached to cyclopentadienes in a nucleophilic aromatic substitution process involving treatment with a perfluoroaromatic compound in the presence of a strong, non-nucleophilic base, usually sodium

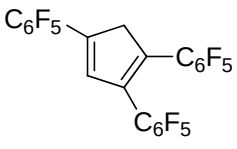
Chart 2.1. Compounds already available in Deck lab



2.1



2.2



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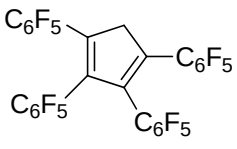

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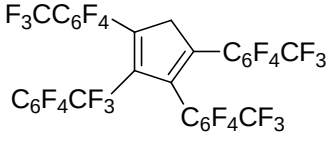

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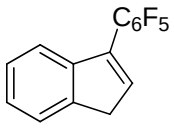

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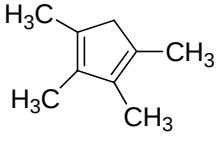
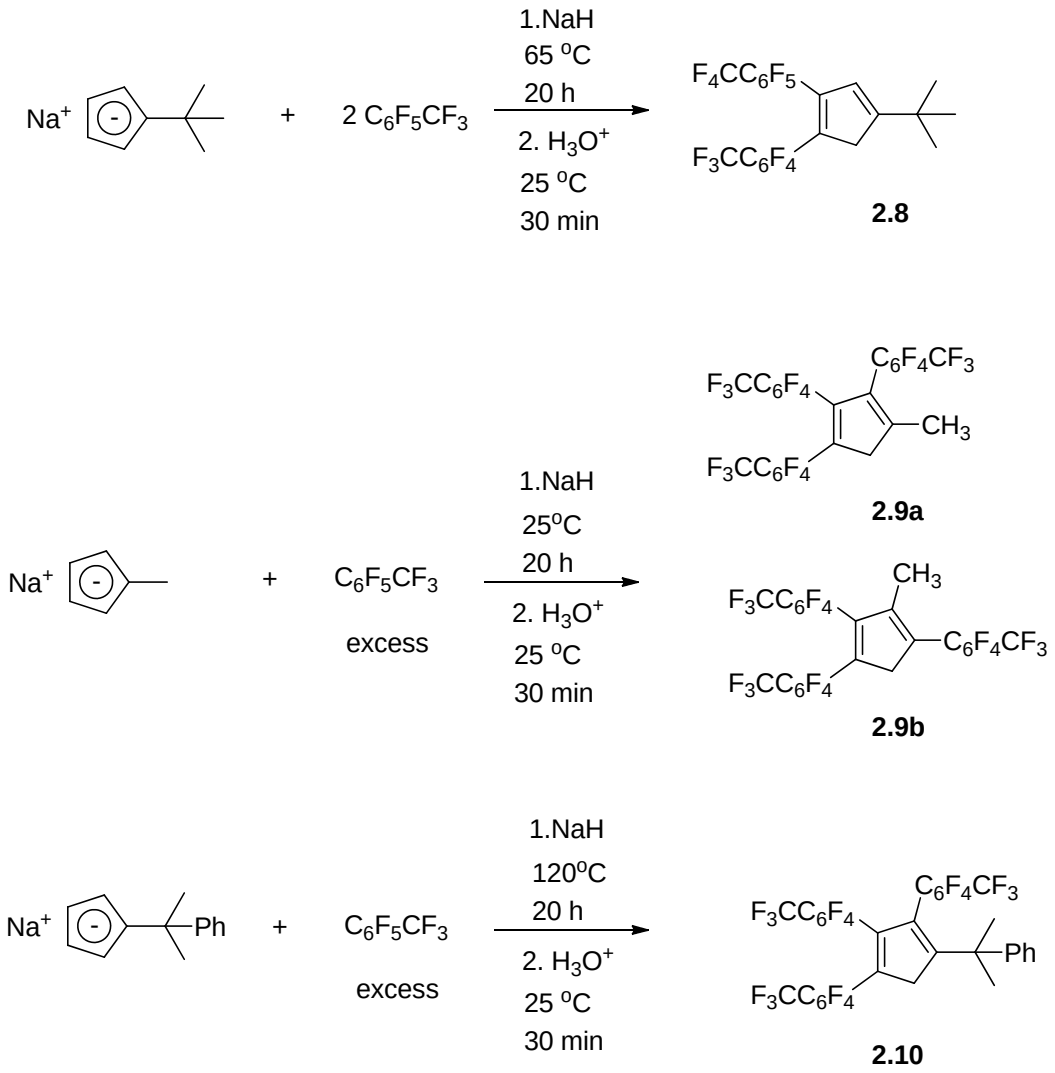


2.7

hydride.[50]

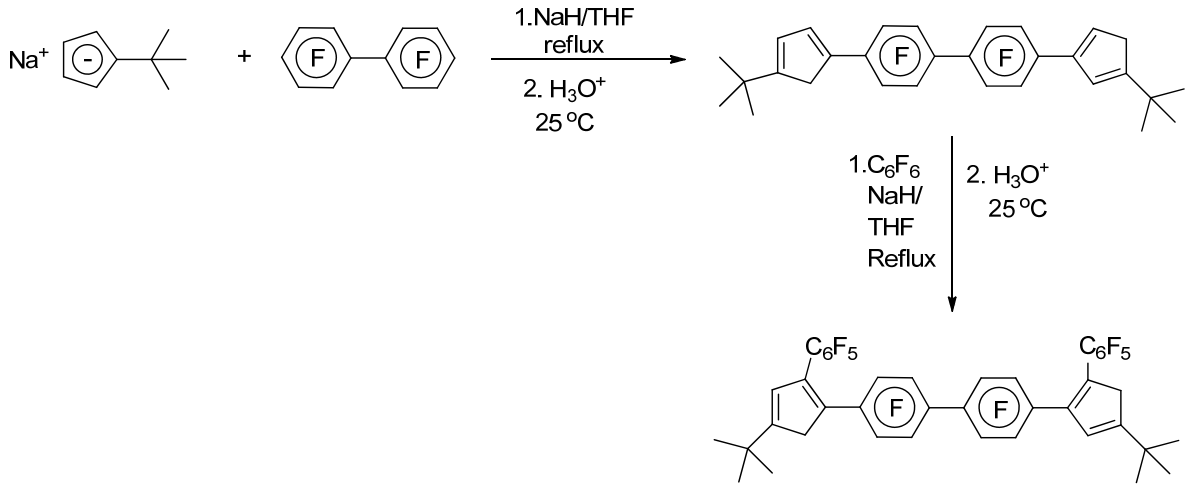
Because the conversion of cyclopentadiene to cyclopentadienone is an allylic oxidation, we also wanted to test the selectivity of the reaction with substrates bearing potentially reactive alkyl groups, including methyl groups. Moreover, some of our target bis-CPDO monomers have alkyl groups attached to the five-membered rings, so we wanted to establish good conditions on monocyclic model compounds first. Compound **2.7** was commercially available but we also wanted to test a few compounds that contained both alkyl and perfluoroaryl substituents, as these are more relevant to our work in macromolecular synthesis. We therefore synthesized dienes **2.8**, **2.9**, and **2.10** by reactions of the corresponding alkylcyclopentadienes with excess octafluorotoluene ($C_6F_5CF_3$) under carefully optimized conditions (Scheme 2.12). Octafluorotoluene is a convenient arylating agent because it is somewhat more reactive than hexafluorobenzene, but with cyclopentadienyl anions it always reacts selectively at the 4-position.[20] The disadvantage of octafluorotoluene is that the perfluoro-4-tolyl substituent does not present nearly as useful NMR spectroscopic handles for characterization; the pentafluorophenyl group shows exceptional dispersion, especially of the *para* fluorine triplet signals.[59, 60]

We previously[61] found that arylation of tert-butylcyclopentadiene is selective for the distal positions on the five-membered ring because of steric effects. Thus under mild conditions, two aryl groups are attached to afford diene **2.8** as a single isomer. The product **2.8** is a white solid. The ^{1}H NMR spectrum shows a single vinylic hydrogen in the expected region (ca. 6 ppm), while the cyclopentadiene methylene hydrogens appear at ca. 4.0 ppm. In the ^{19}F spectrum the two chemically inequivalent $C_6F_5CF_3$ groups can be resolved (two distinct CF_3 signals downfield).



Scheme 2.12. Synthesis of perfluoroarylated cyclopentadienes

The regiocontrolling property of t*ert*-butyl-substituted cyclopentadienes is the basis of one of our bis-CPDO monomer syntheses (Scheme 2.13) as described in the doctoral dissertation of Jessica Evans.[62] After connection of two tert-butylcyclopentadienyl groups to decafluorobiphenyl, a second aryl group is attached selectively to each. Oxidation affords the target monomer. Dr. Evans achieved an overall yield of 50% in this procedure, which involves the formation of four CC bonds and oxidation of two cyclopentadiene methylenes.



Scheme 2.13. Monomer precursor synthesized by Evans

In contrast, the smaller methyl group allows proximal arylation even at room temperature to afford diene **2.9** as a mixture of isomers (Scheme 2.12). This reactivity – attaching three aryl groups at room temperature – was somewhat surprising to us, because in previous work we found that triarylation of the unsubstituted cyclopentadienyl anion with three $C_6F_4CF_3$ groups required heating the corresponding reaction at 60 °C for 2 d.[20] These observations obviously attest to the significantly increased nucleophilicity of the methylcyclopentadienyl anion toward S_NAr reactions compared to unsubstituted cyclopentadienyl anion.

^{1}H NMR spectroscopic analysis of the methylated diene **2.9** in $CDCl_3$ solution showed two methylene signals at 4.01 and 3.84 ppm (Fig. 2.2) The downfield signal was assigned to the 3-

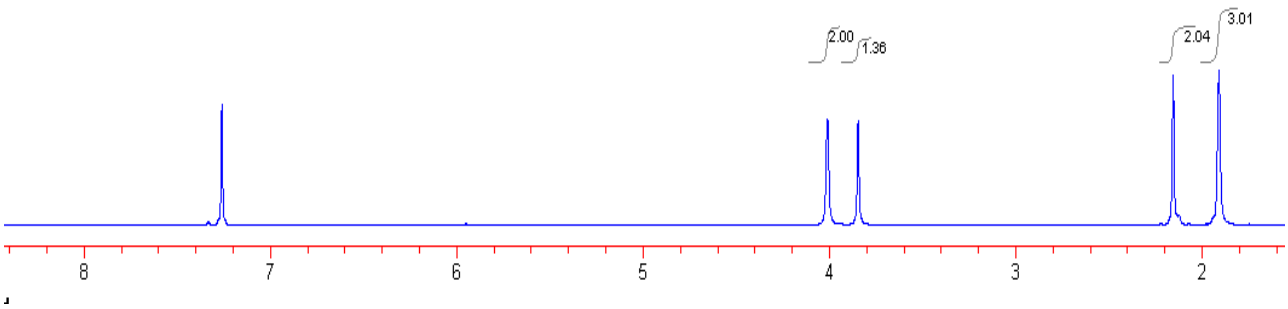
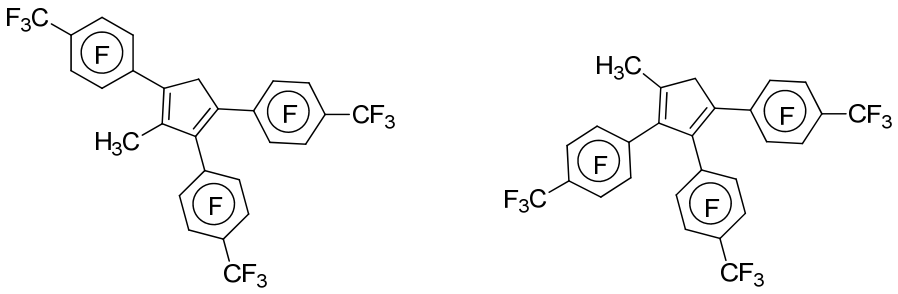


Figure 2.2. ^{1}H NMR spectrum of ketone **2.9** (mixture of isomers)

methyl isomer, which has two electron-withdrawing $C_6F_4CF_3$ substituents vicinal to the methylene carbon, whereas the upfield signal corresponds to the 4-methyl isomer, which has only one $C_6F_4CF_3$ group vicinal to the methylene (Fig 2.3). Likewise dienes **2.2** and **2.3** show methylene chemical shifts of 3.82 and 4.14, respectively,[60] while the corresponding 1,2,3- and 1,2,4-tris(perfluoro-4-tolyl)cyclopentadienes show methylene chemical shifts of 3.93 and 4.26 ppm, respectively.[20] A small sample of the major (3-methyl) isomer was isolated by fractional crystallization from methanol but we were unable to obtain crystals suitable for X-ray diffraction analysis. However the purified single isomer turned out to be useful in assigning the spectra of the isomeric mixture of corresponding CPDOs (Fig 2.4).



2.9a **2.9b**

Figure 2.3. Tris(perfluoro-4-tolyl)methylcyclopentadiene isomers **2.9a** and **2.9b**

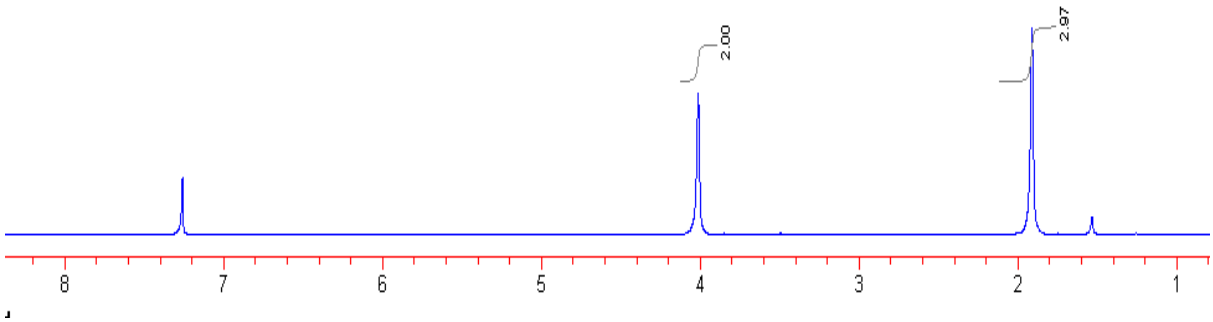


Figure 2.4. ^{1}H NMR spectrum of the **2.9a** tris(perfluoro-4-tolyl)methylcyclopentadiene

In the case of the cumyl-substituted derivative **2.10**, the steric effect of the cumyl group is evident in both the decreased reactivity (triarylation with $C_6F_5CF_3$ required 120 °C in DMPU solvent) and selectivity (only one isomer is obtained). In order to confirm conversion to the triarylated derivative, the reaction was checked by NMR spectroscopy and continued until all of the vinylic hydrogen signals vanished (Fig 2.5). While we expected the product to be the 4-

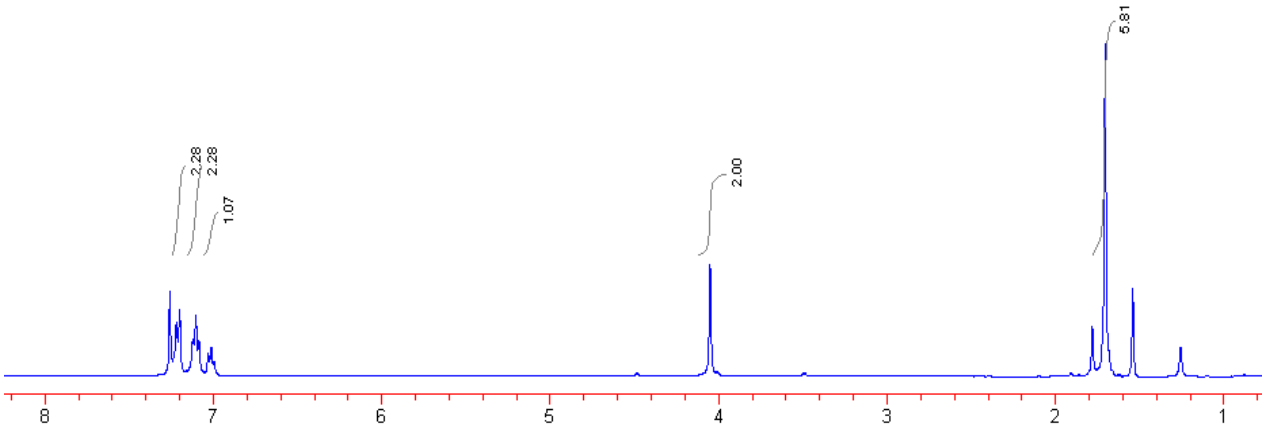


Figure 2.5. ^{1}H NMR spectrumof 1,2,3-tris(perfluoro-4-tolyl)-4-cumylcylopentadiene **2.10**

cumyl isomer, the ^{1}H NMR spectrum showed a chemical shift of ca. 4.0 ppm for the methylene CH_2 group, which was close to the value observed for the 3-methyl isomer of **2.9**. Fortunately we were able to confirm the structure of **2.10** by single-crystal X-ray diffraction. The molecular structure is shown in Fig. 2.6.

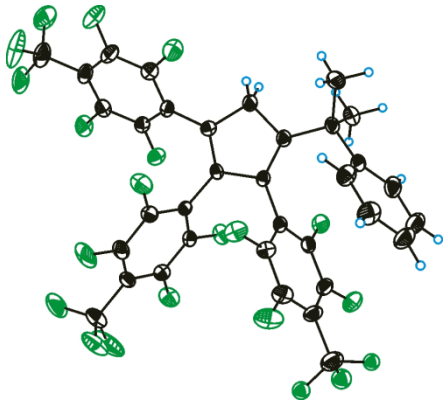
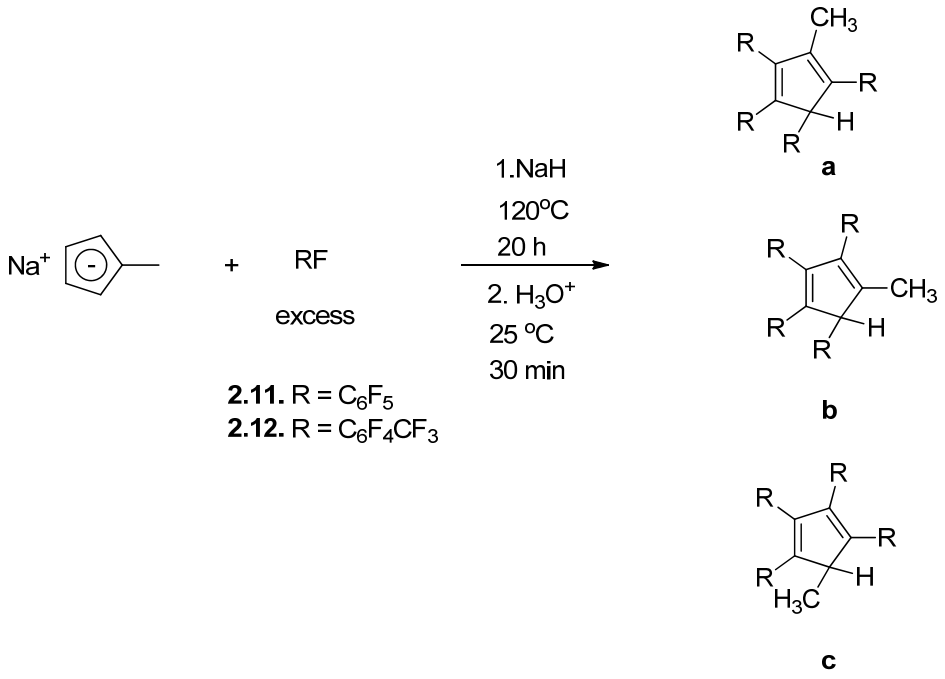


Figure 2.6 Thermal ellipsoid plot (50% probability) of the molecular structure of crystalline **2.10**

While we expected that cyclopentadienes having an unsubstituted CH_2 group would undergo conversion directly to the corresponding ketones, I also was curious to learn whether pentasubstituted cyclopentadienes would undergo smooth conversion to tertiary carbinols. I therefore prepared dienes **11** and **12** by reactions of methylcyclopentadienyl anion with the appropriate perfluoroarenes (Scheme 2.14). Based on the reactivity of the methylcyclopentadienyl anion described above, I expected to achieve tetraarylation readily, but



Scheme 2.14. Synthesis of **2.11** and **2.12**

perhaps at a somewhat temperature because of the combination of increased steric crowding and decreasing nucleophilicity with increasing fluoroaryl substitution. The reaction required 120 °C for 20 h in in DMPU as the solvent to achieve tetraarylation.

An interesting feature of these syntheses is the isolation of a single, pure isomer in the case of **2.11** and a 2:1 mixture of isomers **2.12a** (3-methyl) and 2.**12b** (4-methyl). I can find no rationale for selectivity in these reactions, so we tentatively conclude that **2.11** was obtained as a single isomer only because it was isolated by crystallization. Because I know C_6F_5 groups are slightly

less electron-withdrawing than $C_6F_4CF_3$ groups,[20] I expected that the methine hydrogen of **2.11** would be slightly upfield of a corresponding signal in **2.12**.[20] On that basis I assign the single observed isomer of **2.11** to the 3-methyl structure (analogous to **2.12a**). I speculate that an alternative method of isolation (e.g., silica gel chromatography) would reveal that **2.11** is actually formed as an isomeric mixture too. The other possible isomer (**2.11c** / **2.12c**) is not observed in the NMR spectra of either **2.11** or **2.12**. The location of an aryl group on the methine (sp^3) carbon is reflected in the downfield shift of the methine hydrogen (5.5 to 6.1 ppm, Figs. 2.7 and 2.8).

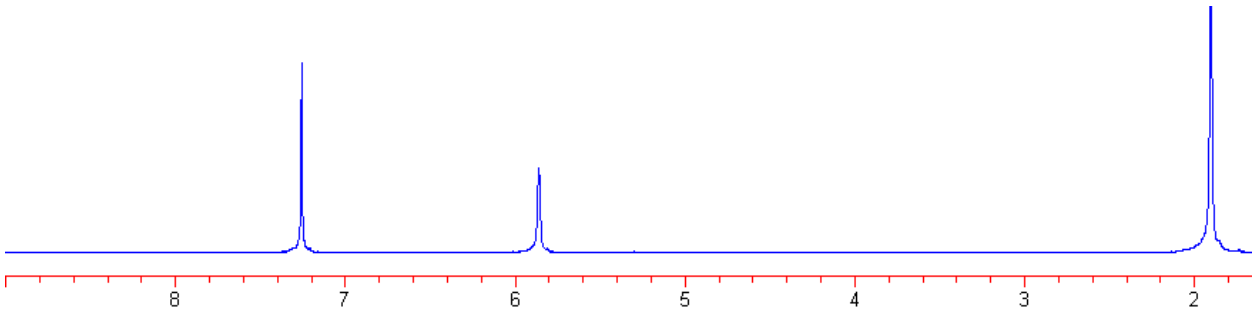


Figure 2.7. ^{1}H NMR spectrum of 1,2,3,4-tetrakis(pentafluorophenyl)-5 -methylcyclopentadiene **2.11**

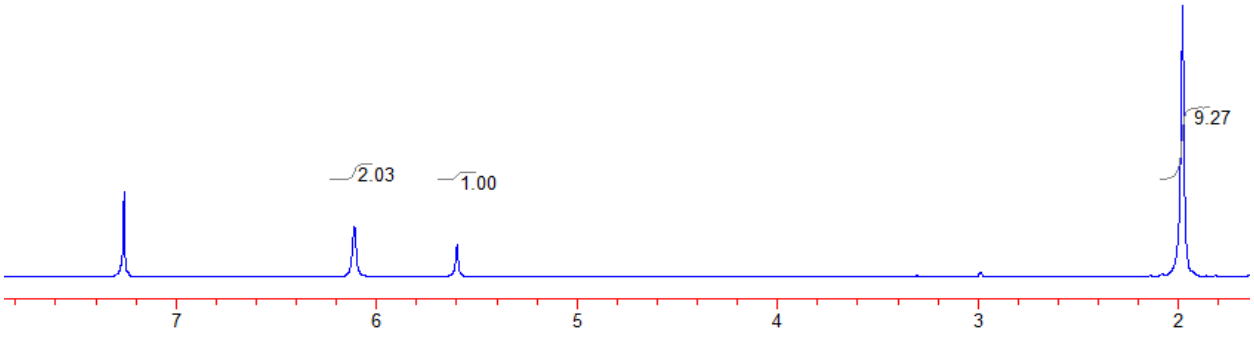
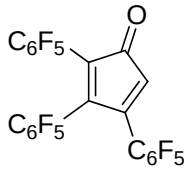


Figure 2.8. ^{1}H NMR spectrum of 1,2,3,4-tetrakis(perfluoro-4-tolyl) -5-methylcyclopentadiene **2.12** (mixture of isomers)

2.2.2. Oxidations. Reaction conditions and isolated product yields are provided in Table 1. Ketone product structures are shown below. Oxidations were carried out using selenium dioxide as the primary oxidant. Using hydrogen peroxide as the secondary, stoichiometric oxidant, requires only catalytic SeO_2 and prevents the formation of troublesome colloidal selenium.[54] THF was used as the solvent for all the oxidation reactions because it is miscible with water, which allowed us to use commercial aqueous hydrogen peroxide, while preventing the catalytic selenium species from separating into a different phase from the substrate. Attempts to use dichloromethane as the solvent gave significantly inferior results. Ketone products are easily detected in these reactions because they are orange. Complete reactant conversion was confirmed by the disappearance of the ring methylene hydrogens (3.5 to 4.2 ppm) from the ^{1}H NMR spectrum of the reaction mixture. Control experiments carried out on substrates **2.2**, **2.3**,**2. 4**, and **2.5**, in which only the selenium dioxide was omitted, showed no conversion to ketone products and occasionally (but not reproducibly) small conversions (5-10%) to other unidentified products.

Chart 2.2. Isolated products of selenium dioxide/hydrogen peroxide oxidations



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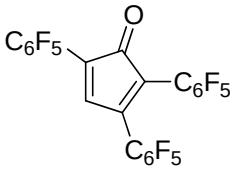

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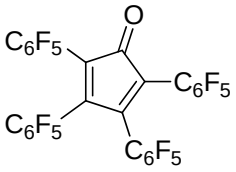

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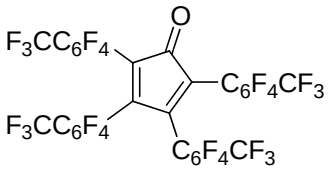

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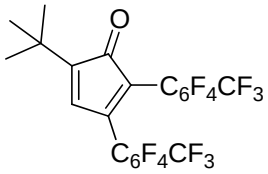

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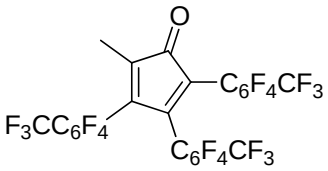

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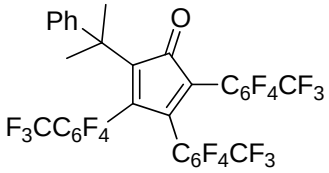

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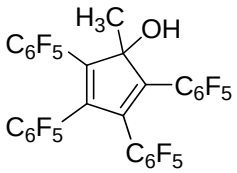

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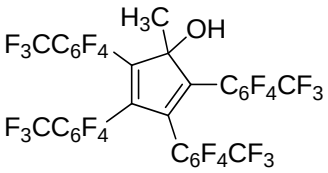


2.21

The data in Table 1 show that more highly arylated cyclopentadienes (e.g., **2.4** and **2.5**) oxidize more readily than their less substituted counterparts (e.g., **2.1**, **2.2**, and **2.3**). I surmise that increased acidity of the methylene C–H bond with increasing fluoroaryl substitution contributes accelerates the initial polar "ene" mechanistic step in which the reactive hydrogen is transferred to an oxygen atom of SeO_2.[55] Acidity measurements on the Streitwieser "lithium indicator" scale in THF solution have determined pK values for **2.1** (6.3), **2.2** (3.5), **2.3** (2.9), **2.4** (–0.34), and **2.6** (13.7). For comparison cyclopentadiene is about 15 on the same scale, so all of these dienes (except indene **2.6**) are substantially more acidic than cyclopentadiene. And in fact, neither cyclopentadiene **2.1** nor indene **2.6** was reactive at all under our conditions, and they are

the least acidic of the group. However the inert behavior of **2.1** contrasts with the ready oxidation of the unsubstituted parent cyclopentadiene to a mixture of cyclopentenediol isomers under even milder conditions,[56] so factors other than the methylene acidity must be in play.

An important feature of our oxidations is that the product fluoroarylated cyclopentadienones do not undergo further oxidation to aryl-subsituted 2-pyrones.[63] It is also noteworthy that there is no evidence for dimerization in the NMR spectrum of either of the triarylated cyclopentadienones **2.13** and **2.14**, because the analogous non-fluorinated (triphenyl) derivatives were reported to exist as mixtures of monomer and dimer in solution,[64, 65] however it should be noted that those reports precede the widespread use of NMR spectrometry for solution structural characterization of organic compounds!

All of the oxidations (Table 1) were optimized at 5 mol% of SeO_2 and 3 equiv of H_2O_2 at room temperature, except for the sterically encumbered dienes **2.8** and **2.10**, which were optimized at higher temperature, longer reaction time, and using three times as much SeO_2 (15 mol%). Neither diene had reacted at 25 °C (24 h). A steric effect could also account for the lower reactivity of the 1,2,4-triarylated diene **2.3** relative to the 1,2,3-triarylated diene **2.2**. We expect the latter two dienes to have nearly the same CH acidities. Notably diene **2.8** has only two fluoroaryl substituents and might be expected to have reactivity similar to diene **2.1**, however we are aware that $C_6F_4CF_3$ substituents are significantly more electron-withdrawing than C_6F_5 groups. In addition, it is possible that the two aryl groups increase the methylene acidity somewhat, while the electrophilic selenium atom could be attacking the electron rich alkyl-substituted double bond. As expected the tertiary substituents in **2.8** and **2.10** are not degraded in these reactions, as the mechanism is not appreciably carbocationic. Despite the variations in electronic substituent effects in ketones **2.13** – **2.19**, IR spectra of the ketones

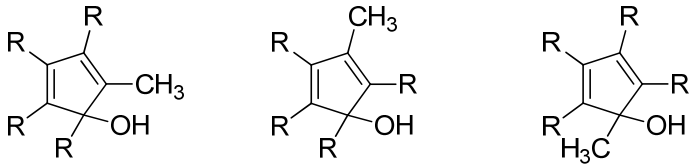
showed little change. The carbonyl stretch is always in the same narrow range of 1720cm^{-1} – 1752 cm^{-1}.

Next I wanted to examine oxidations of ring-methylated cyclopentadienes to ensure that only the methylene CH bonds would react. While I was able to find conditions to oxidize **2.9** to the corresponding ketone, the yield of this reaction is somewhat lower because of the formation of a second product that we were not able to identify. Using 3 equiv of H_2O_2 resulted in lower yield of the desired ketone and higher conversion to the unidentified blue side product, and therefore the reaction was optimized using 2 equiv of H_2O_2. Tetramethylcyclopentadiene **2.7** reacted reluctantly and afforded only an intractable mixture of products.

Oxidation of the pentasubstituted dienes **2.11** and **2.12** gave the corresponding tertiary alcohols as the major products under mild oxidizing conditions. The intermediacy of secondary alcohols is likewise presumed in the reactions leading to cyclopentadienones. The reactions of both **2.11** and **2.12** are somewhat complicated by the fact that various isomers are present. Product separation proved difficult, but the major product by far, in both cases, turns out to arise from the oxidation of the *trace* (i.e., not observed) isomer of the diene (Scheme 2.15). We surmise that under the reaction conditions, the diene tautomerizes by proton exchange processes, and that the isomers **2.11c** and **2.12c** reaction much faster than the others to afford the corresponding tertiary alcohols. The result is fortuitous in the sense that the NMR spectra of **2.20c** and **2.21c** are greatly simplified by the mirror planes of symmetry in those molecules. Thus, in **2.20c** only two *para* ^{19}F NMR signals (Fig. 2.9) are observed due to symmetry-enforced chemical equivalence. There should be four each of the *ortho* and *meta* signals; the spectrum is consistent with this prediction, however some of the signals overlap. Likewise for **2.21c** there are only two CF_3 signals and a simple aromatic CF region with three signals resulting from

coincidental chemical shift overlaps (Fig. 2.10). These results suggest that oxidation to an alcohol, under our reaction conditions, is still a valid mechanistic step *en route* to the ketone products in the other examples.

Chart 2.3. Possible tertiary alcohols formed during oxidation of **2.11** and **2.12**



a **b** **c**

2.20. R = C_6F_5
2.21. R = $C_6F_4CF_3$

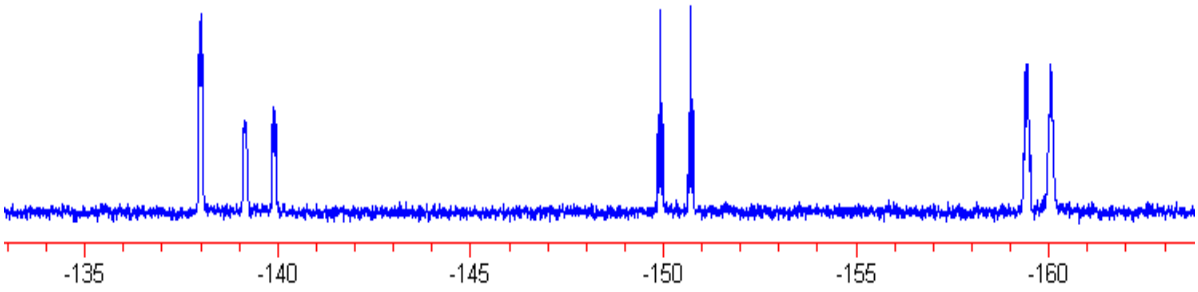


Figure 2.9. ^{19}F NMR spectrum of **2.20c**

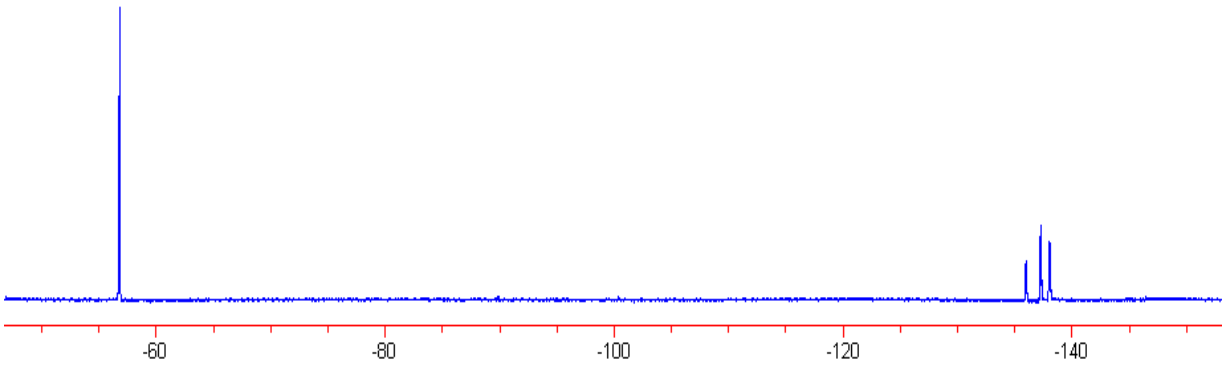


Figure 2.10. ^{19}F NMR spectrum of **2.21c**

Table 1. Reaction conditions and yields of cyclopentadiene oxidations.

Substrate	SeO_2 (mol %)	H_2O_2 (equiv)	t (h)	T (°C)	Conversion of substrate (%)	Product	Yield (%)
1	20	3	50	65	0		0
2	5	3	40	25	100	**13**	84
3	10	3	20	65	100	**14**	78
4	5	3	5	25	100	**15**	91
5	5	3	3	25	100	**16**	93
6	25	3	48	65	0		0
7	20	3	24	65	100	[a]	0
8	15	3	30	65	100	**17**	70
9	5	2	25	25	100	**18**	55
10	15	3	30	65	100	**19**	78
11	5	3	38	25	100	**20**	84
12	5	3	40	25	100	**21**	82

[a] A complex mixture of unidentified products was obtained.

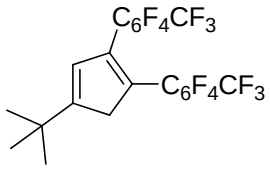
2.3. Experimental

2.3.1. Materials and Methods. Hexafluorobenzene and octafluorotoluene were used as received from Matrix Scientific or Oakwood Products. DMPU was distilled from calcium hydride (ca. 70 °C at 0.2 mmHg). Inhibitor-free, nitrogen-sparged THF was purified by passing through a column of 4 Å molecular sieves. Selenium dioxide and hydrogen peroxide obtained from Aldrich were used as received. Sodium methylcyclopentadienide was prepared by reacting freshly distilled methylcyclopentadiene with sodium hydride in THF tert-butylcyclopentadiene and cumylcyclopentadiene were synthesized as reported earlier.[61, 66] Dienes **2.1**,[19] **2.2** and **2.3**,[60] **2.4**,[59] **2.5**,[20] and **2.6**[67] were prepared by published methods. Diene **2.7** was purchased from Boulder Scientific.

Instrumentation: NMR spectra were obtained using Varian Unity 400 or Varian Inova 400 instruments. ^{19}F NMR spectra were referenced to external C_6F_6 in $CDCl_3$ (−163.0 ppm). IR spectra were obtained on a Nicolet 6700 in dichloromethane medium. Mass spectra were collected on an Agilent 6220 LC-ESI-TOF instrument.

2.3.2. Synthesis

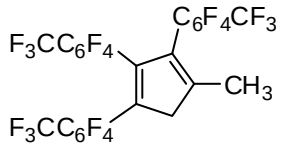
Synthesis of 3,4-Bis(perfluoro-4-tolyl)-1-*tert*-butylcyclopentadiene (2.8).

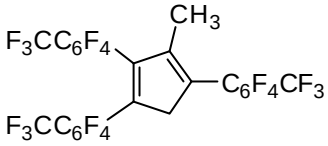


To a stirred, ice-cold mixture of sodium hydride (1.00 g, 0.025 mol), sodium *tert*-butylcyclopentadiene (3.2 g, 0.020 mol) and THF (50 mL) was added octafluorotoluene (5.9 g, 0.025 mol) in small portions over 15 min. The reaction turned dark orange and brown in color. The reaction stirred for 15 min at 0 °C and for 1 h at room temperature. TLC showed that starting material remained after 1 h, but not after 24 h. We expected the reaction, at this point,

to contain a mixture of monoarylated and diarylated cyclopentadienes and were therefore surprised when NMR spectroscopic analysis of a worked-up aliquot showed only the diarylated compound **2.8**. The THF was evaporated from the black, viscous solution to a cold trap. The residue was dissolved in hexane (50 mL), and then water (50 mL) was cautiously added. The organic layer was extracted, dried over $MgSO_4$, filtered, and evaporated. The product was purified using silica gel chromatography (10 cm x 2.5 cm, hexanes). The hexane was evaporated to yield a pale yellow solid (4.2 g, 62%). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 6.35 (s, 1H), 3.64 (s, 2H), 1.28 (s, 9H). 19F NMR (376 MHz, $CDCl_3$) δ (ppm): –56.6 (m, 6F), –138.6 (m, 2F), –139.4 (m, 2F), –140.2 (m, 2F), –140.6 (m, 2F). HRMS calcd for $C_{23}H_{12}F14$ (M*) 554.0690, found 554.0715.

Synthesis of Tris(perfluoro-4-tolyl)methylcyclopentadiene, mixture of isomers (2.9).

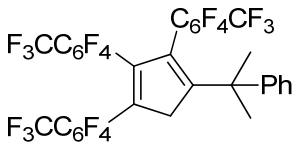




To a stirred mixture of sodium methylcyclopentadienide (500 mg, 5.0 mmol), sodium hydride (530 mg, 21 mmol), and THF (20 mL), maintained at 25 °C under a nitrogen atmosphere, was added octafluorotoluene (5.3 g, 22 mmol) over about 5 min. Stirring was continued for 18 h. The reaction was monitored by ^{1}H NMR spectroscopy and continued until all the peaks for vinylic hydrogens disappeared. The solvent and unreacted octafluorotoluene were removed using a vacuum pump, and then ether (15 mL), water (10 mL), and 2 M aqueous hydrochloric acid (7 mL) were cautiously added. The biphasic mixture was stirred for 30 min under nitrogen medium to ensure complete hydrolysis of the unreacted sodium hydride. The organic layer was

separated, washed with water, dried over anhydrous magnesium sulfate, and evaporated to afford a white solid. The product was purified by silica gel column chromatography (hexane) to afford a white solid (2.84 g, 80%). NMR analysis showed that the product is a mixture of two isomers. TLC analysis showed that separation of the two isomeric products by silica gel chromatography would not be possible (only one spot was observed with hexanes as the eluent). However a small quantity of the major isomer was isolated by fractional crystallization from methanol. The minor isomer remained in the mother liquor along with trace of the major isomer. Comparing the NMR spectra of the two samples enabled us to determine which signals should be assigned to each isomer. 1,2,4-Tris(perfluoro-4-tolyl)-3-methylcyclopentadiene (60% of the product): ^{1}H NMR ($CDCl_3$): δ 4.01 (s, 2 H), 1.91 (s, 3 H), ^{19}F NMR ($CDCl_3$): δ –56.30 (m, 9 F, 3 CF_3), –137.00 (m, 2 F), –137.22 (m, 2 F). –138.20 (m, 2 F), –138.54 (m, 2 F), –138.934 (m, 2 F), –140.02 (m, 2 F). 1,2,3-Tris(perfluoro-4-tolyl)-4-methylcyclopentadiene (40% of the product): ^{1}H NMR ($CDCl_3$): δ 3.84 (s, 2 H), 2.16 (s, 3 H), ^{19}F NMR ($CDCl_3$): –56.30 (m, 9 F, 3 CF_3), –137.58 (m, 2 F), –138.34 to –138.72 (m, 4 F), –138.83 to –139.40 (m, 2 F). HRMS calcd for $C_{27}H_5F_{21}$ $(M-H)^-$ 726.9983, found 727.0008.

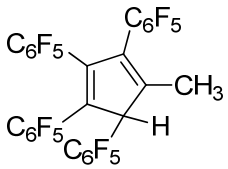
Synthesis of 1,2,3-Tris(perfluoro-4-tolyl)-4-cumylcylopentadiene (2.10).



A mixture of sodium cumylcyclopentadienide (400 mg, 2.00 mmol), sodium hydride (250 mg, 10.4 mmol), octafluorotoluene (2.40 g, 10.0 mmol), and DMPU (15 mL) was stirred at 120 ^{o}C for 20 h under a nitrogen atmosphere. The reaction was monitored by ^{1}H NMR and continued until all the peaks for vinylic hydrogens disappeared. After diethyl ether (50 mL) followed by 2

M hydrochloric acid (10 mL) was added to the reaction vessel, and the mixture was stirred for 30 min under nitrogen atmosphere to ensure complete hydrolysis of the unreacted sodium hydride. The organic layer was separated, extracted 10-15 times with 5 mL of water to remove DMPU, dried over anhydrous magnesium sulfate, and evaporated. The crude product was purified by silica gel column chromatography using hexane as the eluent. Evaporation of the solvent afforded 1.20 g (76%) of a white solid. ^{1}H NMR ($CDCl_3$): δ 7.20 (d, 2 H), 7.11 (t, 2 H), 7.01 (t, 1H), 4.05 (s, 2 H), 1.71 (s, 6 H); ^{19}F NMR ($CDCl_3$): δ −56.37 (m, 6 F, 2 CF_3), −56.81 (m, 3 F, CF_3), −134.65 (m, 2 F), −137.75 (m, 2 F), −138.15 (m, 2 F), −138.47 (m, 2 F), −139.11 (m, 2 F), −140.72 (m, 2 F). HRMS calcd for $C_{35}H_{13}F_{21}$ $(M^*)^-$ 832.0745, found 832.0682.

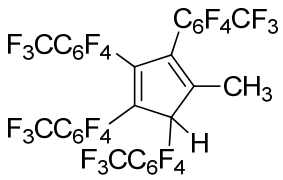
Synthesis of 1,2,3,4-Tetrakis(pentafluorophenyl)-5-methylcyclopentadiene (2.11).



A mixture of sodium methylcyclopentadienide (300 mg, 3.0 mmol), sodium hydride (430 mg, 18.0 mmol), pentafluorophenyl (3.16 g, 17.0 mmol), and DMPU (15 mL) was stirred at 120 ^{o}C for 20 h under a nitrogen atmosphere. The reaction was monitored by ^{1}H NMR and continued until the signals for vinylic protons disappeared. The reaction was quenched by cautious addition of water. Diethyl ether (15 mL) and 15% hydrochloric acid (10 mL) were added, and the mixture was stirred for 0.5 h to ensure complete hydrolysis. The organic layer was separated and washed several times with water to remove traces of DMPU, dried over anhydrous $MgSO_4$, filtered, and evaporated. The resulting residue was purified by silica gel column chromatography using hexane as the eluent to afford a white solid (2.05 g, 91%). ^{1}H NMR ($CDCl_3$): δ 5.86 (s,

1H), 1.89 (s, 3H), ^{19}F NMR ($CDCl_3$): δ –137.50 (d, 1F), –140 (br s, 2 F), –140.55 (d, 2F), –141.08 (d, 1F), –142.83 (d, 1F), –143.19 (d, 1F), –151.21 (t, 1F), –151.42 (t, 1F), –152.66 (t, 1F), –152.85 (t, 1F), –159.5 to −161.0 (m, 8F). HRMS calcd for $C_{30}F_{20}H_3O$ $(M^*)^-$ 742.9966, found 742.9915.

Synthesis of Tetrakis(perfluoro-4-tolyl)methylcyclopentadiene isomers (2.12).

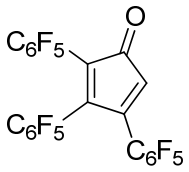


A mixture of sodium methylcyclopentadienide (300 mg, 3.0 mmol), sodium hydride (430 mg, 18.0 mmol), octafluorotoluene (4.25 g, 18.0 mmol), and DMPU (15 mL) was stirred at 120 ^{o}C for 20 h under nitrogen. The reaction was monitored by ^{1}H NMR and continued until all the peaks for vinylic protons disappeared. The workup was carried out in the same manner as for compound **2.12** to afford a white solid (2.43 g, 85%). ^{1}H NMR spectrometric analysis revealed the presence of two isomers, assigned tentatively as follows. **2.12a** (3-methyl, ca. 67% of mixture): ^{1}H NMR ($CDCl_3$): δ 6.10 (s, 1H), 1.98 (s, 3H). **2.12b** (4-methyl, ca. 33% of mixture) ^{1}H NMR ($CDCl_3$): δ 5.59 (s, 1H), 1.98 (s, 3H). The ^{19}F NMR spectra of the two isomers were not resolved and could not be individually assigned: ^{19}F NMR ($CDCl_3$): δ –56.4 (m, 12F), –137.9 (m, 16F). HRMS calcd for $C_{34}F_{28}H_3$ $(M^*)^-$ 942.9788, found 942.9821.

General Oxidation Procedure. A mixture of the substrate cyclopentadiene, selenium dioxide, 30% aqueous hydrogen peroxide (120 mg of commercial 30% solution corresponds to 1 mmol of H_2O_2) and THF (ca. 10 mL) was stirred for several hours. See Table 1 for reaction scales and reagent proportions. Generally the product formation was apparent within a few minutes, as the

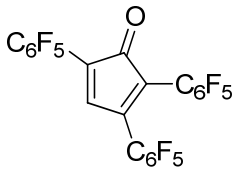
ketones are orange. The reaction temperature was ordinarily left at room temperature (ca. 25 °C), but when ^{1}H NMR spectroscopic analysis of the first aliquot revealed that the substrate was reacting slowly, a reflux condenser was fitted and the reaction temperature was raised to 65 °C (reflux). The reaction was continued until the signal for the methylene hydrogens disappeared from the ^{1}H NMR spectrum. Reaction temperatures and times are recorded in Table 1. The solvent was then evaporated under reduced pressure and the residue was dissolved in diethyl ether (20 mL), washed with water (5 mL), dried over anhydrous magnesium sulfate, filtered, and evaporated. The crude product was purified by silica gel chromatography, eluting with hexanes, as to afford the desired ketone upon evaporation of the solvent. Yields after silica gel chromatography are shown in Table 1.

Data for 1,2,3-Tris(pentafluorophenyl)cyclopentadienone (2.13).



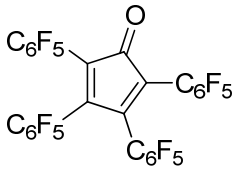
^{1}H NMR ($CDCl_3$): δ 6.23 (s, 1H). ^{19}F NMR ($CDCl_3$): δ −137.86 (m, 4F), −138.23 (m, 2F), −148.26 (m, 1F), −149.17 (m, 1F), −150.34 (m, 1F), −158.88 (m, 2F), −159.57 (m, 2F), −160.45 (m, 2F). HRMS calcd for $C_{23}F_{21}HO$ $(M^*)^-$ 577.9814, found 577.9788**.**

Data for 1,2,4-Tris(pentafluorophenyl)cyclopentadienone (2.14).



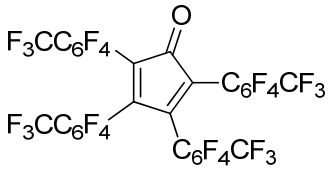
^{1}H NMR ($CDCl_3$): δ 7.58 (s, 1H). ^{19}F NMR ($CDCl_3$): δ −135.82 (d, 2F), −137.46 (dd, 2F), −138.04 (dd, 2F), −148.04 (t, 1F), −150.53 (t, 1F), −151.54 (t, 1F), −159.14 (m, 2F), −160.53 (m, 2F), −161.18 (m, 2F). HRMS calcd for $C_{23}F_{21}HO$ $(M^*)^-$ 577.9812, found 577.9788.

Data for 1,2,3,4-Tetrakis(pentafluorophenyl)cyclopentadienone (2.15).



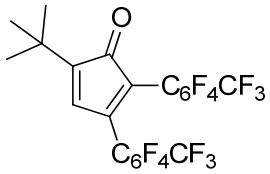
^{1}H NMR ($CDCl_3$) δ No signals. ^{19}F NMR ($CDCl_3$) δ −139.57 (d, 2F), −139.84 (d, 2F), −150.54 (t, 1F), −151.46 (t, 1F), −159.65 (m, 2F), −160.11 (m, 2F). IR (CH_2Cl_2): $\nu_{C=O}$ = 1739 cm^{-1}. HRMS calcd for $C_{29}F_{20}O$ $(M^*)^-$ 743.9629, found 743.9654.

Data for 1,2,3,4-Tetrakis(perfluoro-4-tolyl)cyclopentadienone (2.16).



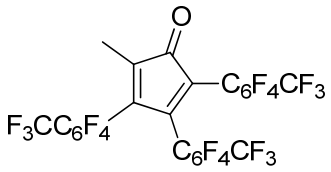
^{1}H NMR ($CDCl_3$) No signals. ^{19}F NMR ($CDCl_3$) −56.81 (m, 12 F) , −135.96 (m, 4 F), −135.57 (m, 4 F), −136.01 (m, 4 F), −137.75 (m, 4 F). IR (CH_2Cl_2): $\nu_{C=O}$ = 1742 cm^{-1}. HRMS calculated for $C_{33}F_{28}O$ $(M^*)^-$ 943.9502, found 943.9524.

Data for 1,2-bis(perfluoro-4-tolyl)-4-tert-butylcyclopentadienone (2.17).



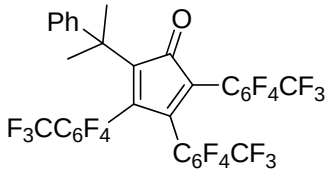
^{1}H NMR ($CDCl_3$): δ 1.27 (s, 9 H), 6.72 (s, 1 H); ^{19}F NMR ($CDCl_3$) δ −56.43 (m, 6 F), −134.27 (m, 2 F), −135.96 (m, 2 F), −138.02 (m, 2 F), −139.42 (m, 2 F). IR (CH_2Cl_2): $\nu_{C=O}$ = 1722 cm^{-1}. HRMS calculated for $C_{23}F_{14}H_{10}O$ $(M^*)^-$ 568.0514, found 568.0535.

Data for Tris(perfluoro-4-tolyl)methylcyclopentadienone, mixture of isomers (2.18).



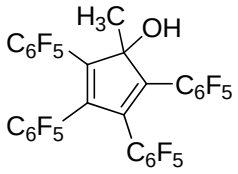
^{1}H NMR ($CDCl_3$). 1,2,4-Tris(perfluoro-4-tolyl)-3-methylcyclopentadienone (60% of the product): ^{1}H NMR ($CDCl_3$): δ 1.22 (s, 3 H). 1,2,3-Tris(perfluoro-4-tolyl)-4-methylcyclopentadiene (40% of the product): ^{1}H NMR ($CDCl_3$): δ 1.98 (s, 3 H). The ^{19}F NMR spectrum was not sufficiently resolved to assign signals to individual isomers. Integrals are approximate. ^{19}F NMR ($CDCl_3$): δ −56.47 (m, 13 F), −135.04 (m, 1F), −135.26 (m, 2 F), −135.68 (m, 5 F), −136.74 (m, 2 F), −137.64 (m, 2 F), −138.41 (m, 3 F). IR (CH_2Cl_2): $\nu_{C=O}$ = 1734 cm^{-1}. HRMS calcd for $C_{27}H_3F_{21}O$ $(M-H)^-$ 741.9863, found 741.9849.

Data for 1,2,3-tris(perfluoro-4-tolyl)-4-cumylcyclopentadienone (2.19).



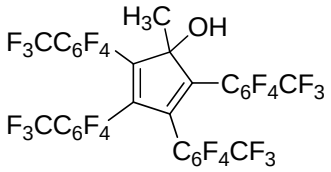
^{1}H NMR ($CDCl_3$) δ 7.25 (d, 2 H), 7.11 (d, 2 H), 7.00 (d, 1 H), 1.78 (s, 6 H), ^{19}F NMR ($CDCl_3$): δ −56.43 (m, 6 F), −56.91 (t, 3 F), −133.56 (m, 2 F), −135.33 (m, 4 F), −136.75 (m, 2 F), −138.42 (m, 2 F), −139.32 (m, 2 F). IR (CH_2Cl_2): $\nu_{C=O}$ = 1730 cm^{-1}. HRMS calcd for $C_{35}H_5F_{21}$ $(M^*)^-$ 846.0475 , found 846.0483**.**

Data for 1,2,3,4-Tetrakis(pentafluorophenyl)-5-methylcyclopentadiene-5-ol (2.20).



^{1}H NMR ($CDCl_3$): δ 2.98 (br, 1H), 2.19 (s, 3H), 1.95 (s, 3H), ^{19}F NMR ($CDCl_3$): δ −138.00 (d, 2F), −139.18 (d, 1F), −139.90 (d, 1F), −149.94 (t, 1F), −150.72 (t, 1F), −159.46 (m, 2F), −160.07 (m, 2F). HRMS calcd for $C_{30}F_{20}H_4O$ $(M^*)^-$ 759.9943, found 759.9953.

Data for 1,2,3,4-Tetrakis(perfluoro-4-tolyl)-5-methylcyclopentadiene-5-ol (2.21).



^{1}H NMR ($CDCl_3$): δ 2.36 (br, 2H), 2.04 (s, 1H), 2.00 (s, 1H), ^{19}F NMR ($CDCl_3$): −56.81 (m, 12F), −135.96 (br, 4F), −137.24 (m, 6F), −137.98 (m, 6F). HRMS calcd for $C_{34}F_{28}H_4O$ $(M^*)^-$ 959.9815, found 959.9844.

2.4.1. Conclusion

Some novel perfluorarylated cyclopentadienes were synthesized by nucleophilic aromatic substitution (S_NAr) reaction. It has been found degree of arylation is dependent on the parent cyclopentadiene structure and reaction conditions. Next the perfluoroaryl-substituted cyclopentadienes were oxidized successfully to corresponding carbonyl or alcohol compounds depending on the starting materials. All the oxidation reactions used selenium dioxide as the primary (and catalytic) oxidant and hydrogen peroxide as the secondary oxidant. The reaction essentially does not proceed in the absence of selenium dioxide. The rate of the reaction strongly depends on the electronic and steric environment of the cyclopentadiene rings. More electron deficient rings oxidize faster while sterically hindered rings need higher temperatures, longer times and larger amounts of catalyst to reach full conversion.

2.5.1. Future work. Of course this method can be expanded in scope to encompass other cyclopentadienes as they arise. We believe our findings, especially including the many negative results that we have carefully documented, will enable researchers in the future to decided quickly whether SeO_2 / H_2O_2 is suitable for their particular cyclopentadiene oxidations. The study is perhaps best considered concluded and we do not envision specific further work.

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Chapter 3

Fluorine-Containing Reversible Diels-Alder Polymerization

3.1. Introduction

Reversible polymers are polymers that can revert to either the monomeric, oligomeric or non-crosslinked state by the application of an external stimulus.[1] Reversible polymers are broadly classified as either non-covalent or covalently bonded.[1] In a non-covalent system, the polymer has been propagated or cross-linked by supramolecular interactions such as hydrogen bonds, labile metal-ligand coordination, ion-pairing, and host-guest binding (which might encompass one or more of the preceding effects). In a covalently bonded system, the reversibility requires the rupture and re-formation of covalent bonds.

Some covalent systems revert to isolable monomers or fragments (true reversibility), while others revert to quasi-stable intermediates long enough to allow thermal reorganization of the macromolecular structure (dynamic covalent polymers). Common synthetic approaches include Diels-Alder (DA) reactions,[2-9] thiol/disulfide interconversions (2 RSH = RSSR + H_2),[10, 11] alkoxyamine homolysis ($BnONR_2$ = Bn• + •ONR_2),[12-14] and photochemical cycloadditions (coumarin [2+2] or anthracene [4+4] dimerizations).[15-17]

This dissertation chapter describes some of the most important methods of preparing reversible polymers specifically using the Diels-Alder reaction and the key relationships among synthetic methods, polymer structure, properties, and applications.

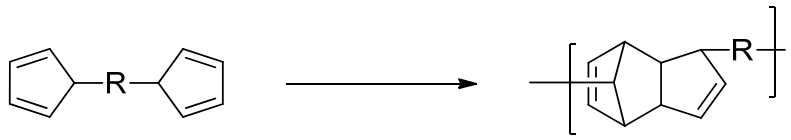
3.1.1. The Diels-Alder Reaction

The Diels-Alder (DA) reaction is a thermal cycloaddition of a diene (4π) and an alkene or alkyne (dienophile, 2π). The attractive features of the DA reaction include its concerted mechanism, which preserves certain regio and stereochemical features of the reactants, and its

exothermicity (two pi bonds are replaced with new sigma bonds).[18-20] Because the s-cis configuration of the diene is required, compounds already locked into the s-cis configuration such as furan and cyclopentadiene are especially suitable reactants.

DA adducts can often undergo cycloreversion or *retro* Diels-Alder (rDA) reactions to afford again the corresponding dienes and dienophiles. The process often requires a high temperature to overcome a substantial activation barrier,[21] which is interesting because the fragmentation selectively breaks just two sigma bonds. While most of that selectivity undoubtedly arises from the so-called "aromatic transition state" common to DA and retro-DA, bicyclic adducts derived from s-cis-constrained dienophiles such as furan or cyclopentadiene also benefit from the release of strain. Thermal cracking of dicyclopentadiene demonstrates these principles.[22]

The reversibility of the DA reaction has played a role in the development of DA polymers since its beginnings fifty years ago. In 1961 Stille et al. reported the synthesis of monomers in which two cyclopentadiene moieties were connected through aliphatic linkers (Scheme 3.1) and polymerized them thermally in aromatic solvents with varying boiling points. The intrinsic viscosities of the resulting polymer solutions decreased with increasing reaction temperature, clearly the result of rDA depolymerization.[23]



R = $(CH_2)_6$, $(CH_2)_9$, $CH_2(C_6H_4)CH_2$

Scheme 3.1. Stille's reversible polymerization of bis(cyclopentadienes)

More recently rDA reactions have been exploited to synthesize "smart materials" like self healing polymers, removable coatings etc. In some cases the rDA reaction disrupts the polymer main chain, while in other cases it releases a pendant group or breaks a crosslink. The next few sections describe some of the more important developments in these areas.

3.1.1.1. Self-Healing DA Polymers

A self healing polymer has the ability to "remend" a crack or deformity in the bulk that has been caused by an itself external force.[9, 24] Healing can be initiated by applying a mechanical stimulus (via hollow glass fibers, microcapsules, microvascular network, or a supramolecular network),[25-28] a thermal stimulus[2, 29, 30] (using rDA reactions or embedded structures that can release repair chemicals when a crack propagates),[31] an electrical stimulus (applicable to carbon fiber composites, shape memory alloys, or coordination polymers),[32-34] a ballistic stimulus (primarily affecting ionomers),[35-38] or a photostimulus (retro 2+2).[15, 39-41]

The scope of this review is limited to thermal healing by DA/rDA processes. Conceptually, DA/rDA has the advantage that it eliminates the need for additional ingredients like healing agents or catalysts. It has been shown that the cracks generally propagate via rDA reactions.[9] One then can envision healing the polymer by re-forming new DA adducts from the exposed end groups in the vicinity of the crack. While healing can be initiated at a relatively low temperature, the thermal glass transition (T_g) of the bulk polymer poses an additional constraint: Complete curing can only take place at temperatures above the T_g, at which chain segments and chain ends become mobile.[2, 9]

In 2002 Wudl et al. reported a self-healing furan-maleimide DA polymer (Fig. 3.1).[29] Polymerization was effected in the bulk at 120 ^{o}C and monitored by solid-state ^{13}C NMR

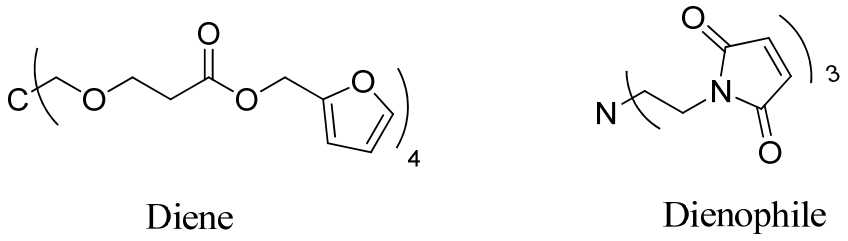


Figure 3.1 Wudl's furan-maleimide hyperbranched system

spectrometry. Signals at 111 and 150 ppm corresponding to the free furan rings disappeared upon polymerization and then reappeared upon heating at 145 ^{o}C due to rDA reactions. The remending property of the polymer was examined again by making a pre-crack on a specimen with a sharp blade. A load was applied perpendicular to the crack to fracture the material. The fractured material was clamped together and placed in an oven (120 to 150 ^{o}C, 2 h) to afford a fully repolymerized material. SEM analysis of the fracture region showed a nearly homogeneous material with a few scars where the tiny gaps between the fractured pieces had formed due to physical mismatching of the fracture surfaces.[29] The authors determined that the first self-healing efficiency of the polymer was 81% while the second healing efficiency was only slightly lower (78%). This result showed that the material could be healed several times over.

In a more recent work, Wudl and co-workers described a thermally remendable polymer prepared by DA reactions of cyclopentadienes.[3] First a "premonomer" was prepared that contained a dicyclopentadiene moiety (Fig. 3.2) as a single-component healing unit.[8] Bulk

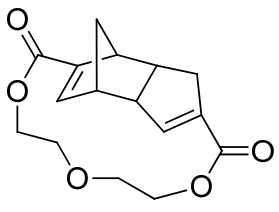


Figure 3.2. Dicyclopentadiene premonomer

thermolysis of the premonomer at 120 ^{o}C afforded two reactive cyclopentadiene groups. These cyclopentadiene moieties can again recombine to give the Diels-Alder adduct. However each DA adduct unit contains two double bonds, which can further act as a dienophile and can form three-dimensional crosslinked structures.

The authors examined the self healing property of the polymer both by making a scratch on the polymer with a razor blade and by inducing a micro crack in a three-point bending test. The damaged specimen was heated at 150 ^{o}C for 2 h and examined with a microscope. The crack disappeared in case of the three point bending test. The razor scratches also healed but left scars.

Syrett and coworkers synthesized poly(methyl methacrylate) using a furan-maleimide DA adduct as initiator (Fig 3.3). Living radical polymerization of the MMA was carried out at 50 ^{o}C to protect the Diels-Alder adduct.[42] The authors then examined the self healing property of the

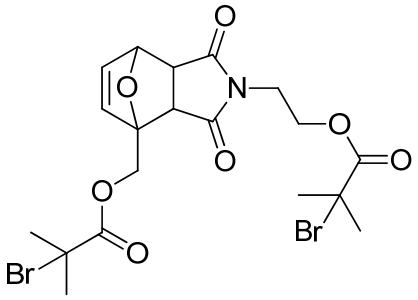
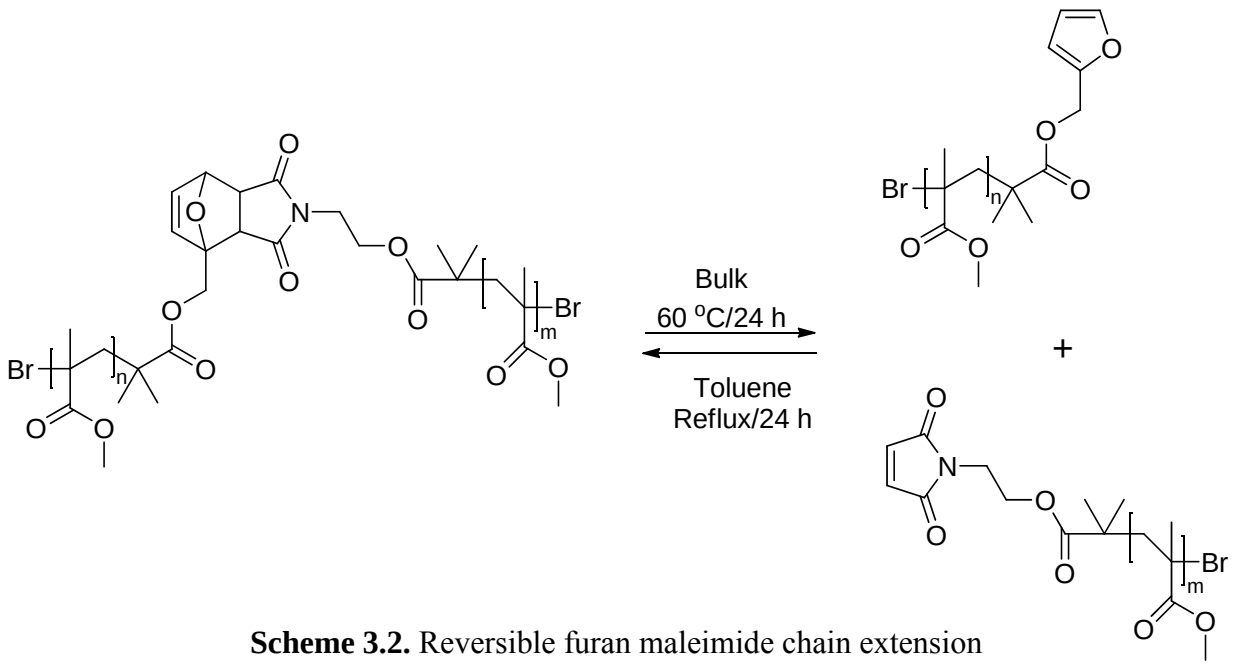


Figure 3.3. Diels-Alder adduct used as an initiator

polymer. After heating for 24 h in refluxing toluene solution and quenching the reaction rapidly, ^{1}H NMR analysis showed signals at 6.89 ppm (maleimide vinyl CH) and at 6.36 and 6.39 ppm (furan CH). Reheating the fragmented polymer again at 60 ^{o}C for 24 h in bulk resulted in repair of about 50% of the cleaved DA adducts (Scheme 3.2).

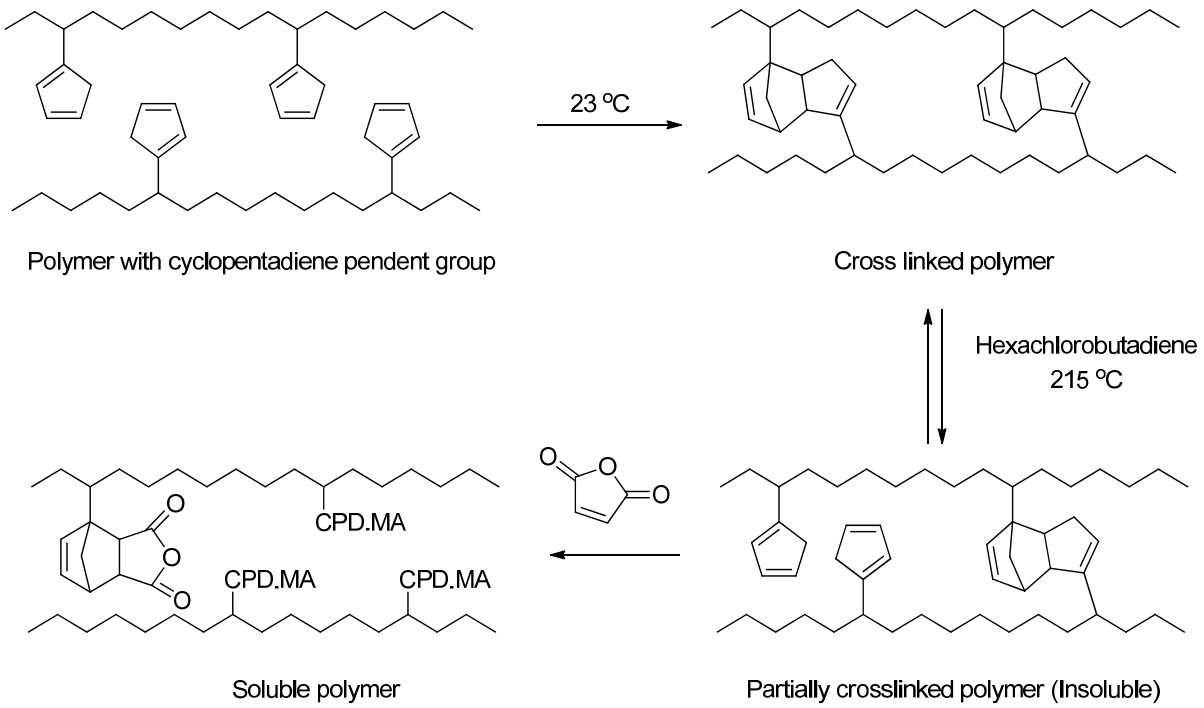


Scheme 3.2. Reversible furan maleimide chain extension

3.1.1.2. Diels-Alder Reactions in Reversible Crosslinking.

Reversible crosslinking can be established using DA reactions, so long as the corresponding rDA reactions occur at a lower temperature than main-chain degradation reactions. Reversible crosslinks have potential applications in controlled drug delivery,[16] biologically active material release purposes, and waste prevention.[43]

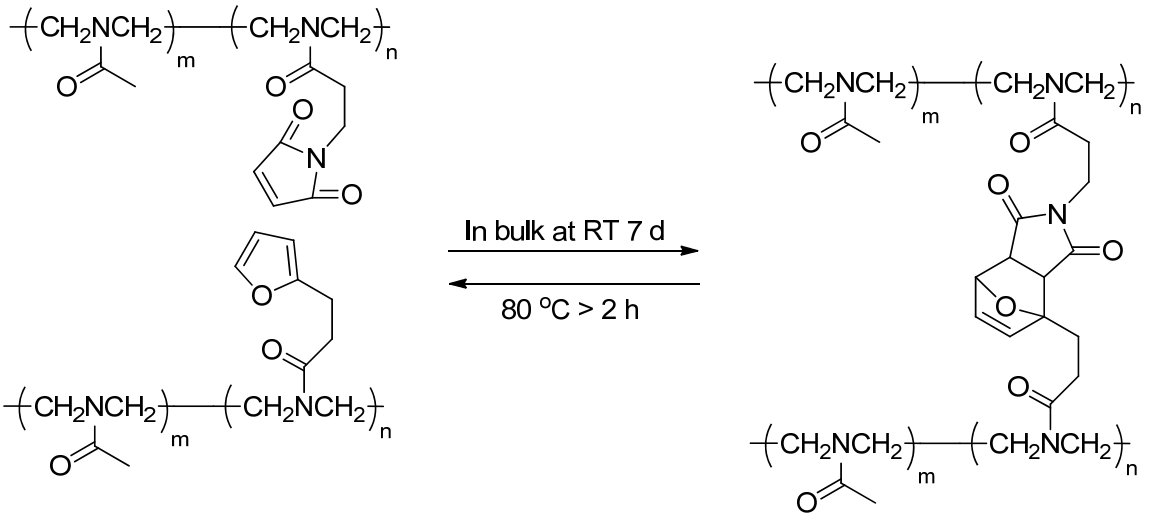
Kennedy and Castner crosslinked butyl rubber and ethylene-propylene rubber using cyclopentadiene pendant groups (Scheme 3.3).[7] The polymer formed an insoluble gel when stored at 23 °C for 72 h as the cyclopentadiene groups formed DA adducts. A sample of the gelled polymer with added maleic anhydride (MA) dissolved in hexachlorobutadiene at 215 °C; unmasked cyclopentadiene groups were trapped by MA. Without the added maleic anhydride the sample swelled but did not dissolve, because the DA/rDA equilibrium retained enough crosslinks to prevent the polymer from becoming soluble.



Scheme 3.3. Reversible crosslinking using cyclopentadiene

Salamone and coworkers reported a similar study of poly[bis(trifluoroethoxy)phosphazene]s with pendant cyclopentadienylethoxy substituents.[44] The resulting cross linked polymer was insoluble in DMF at room temperature but dissolved when heated in presence of maleic anhydride at 85 °C. DSC of the polymer also showed a broad endothermic peak between −30 °C and 170 °C, which the authors assigned to reversible DA crosslinking.

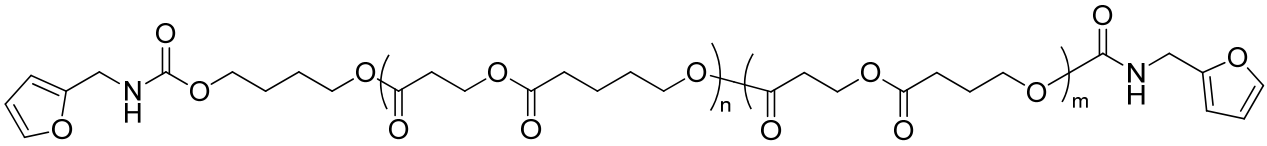
Chujo et al. have explored reversible DA hydrogels.[15] A hydrogel is a three dimensional polymer network that is insoluble in water but can absorb a large quantity of water. Applications include tissue engineering, contact lenses, disposable diapers etc.[45, 46] Reversible hydrogels are used for controlled drug delivery and other controlled-release purposes. Chujo and coworkers synthesized poly(N-acetylethylenimine)s (PAEI) and (polyoxazoline)s with maleimide and furan pendent groups respectively (Scheme 3.4). A 1:1 solution of the modified polymers was stored at room temperature for one week to effect the desired DA coupling and crosslinking.



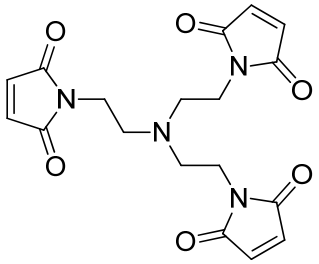
Scheme 3.4. Reversible hydrogel synthesized by Chujo

The degree of crosslinking in the three dimensional network structure varied with the varying degree of maleimide and furan substitutions in the parent polymer chain. The synthesized cross linked polymer was insoluble in water, methanol, and nitromethane at room temperature but dissolved in 2 h at 80 °C, evidence that rDA reactions were releasing soluble linear polymers. ^{1}H NMR of the soluble polymer confirmed the presence of free maleimide and furan moieties. The soluble polymers reverted to the insoluble network structures when stored again at room temperature. Thus the hydrogel formation was thermally reversible.

Ishida et al. applied an A2 + B3 approach to crosslink a bis-furanic poly(1,4-butylene succinate*co*-1,3-propylene succinate) telomers using a tris-maleimide coupling group (Fig. 3.4).[5] The crosslinking was carried out at 70 °C in the bulk. The product was insoluble in chloroform suggesting the formation of a 3D network. Heating at 140 °C for 20 min effected the rDA reaction solubilizing the product in chloroform. The reversibility of the polymer chain was established by applying multiple cycles of heating and cooling respectively.



Furan-terminated segment



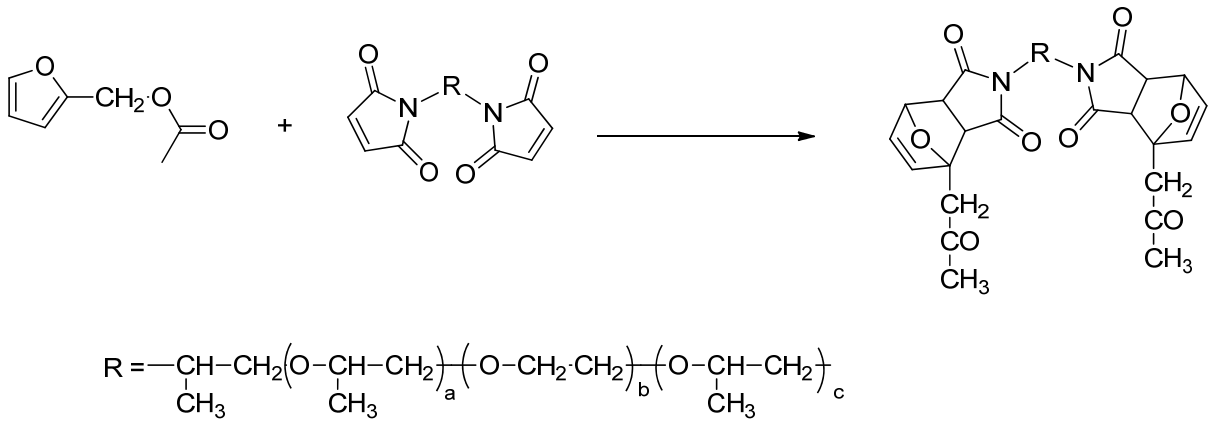
Tris-maleimide linker

Figure 3.4. Reversible DA 2A + 3B hyperbranched system

Goussè and co-workers reported styrene copolymers bearing pendent furans.[47] Upon treating these polymers with bis(maleimide) cross-linking agents in dichloromethane at 40 °C, the reaction medium gelled after 3 h. Subsequently heating the gelled material for 48 h at 130 °C in presence of large excess of 2-methylfuran to trap the dienophile, caused the polymer to revert to the starting furan-functionalized form. The rDA reaction was confirmed by the FTIR analysis of the products obtained from the unzipping reaction.

Crosslinked elastomers used as tires, pipes, hose, etc. are often wasted after use, but DA crosslinking could enable these materials to be thermally recycled to their corresponding thermoplastic precursors. One of the main concerns is keeping the glass transition temperature (T_g) low. Gheneim et al. investigated thermally reversible DA-crosslinked elastomers (Scheme 3.5).[43] Their polymeric diene, poly(hexyl acrylate-*co*-furfuryl methacrylate)s, showed a T_g varying from –78 °C to –30 °C depending on proportion of hexyl acrylate, which drives T_g lower due to its long-chain aliphatic structure. Their polymer dienophile was α,ω-(poly(ethylene

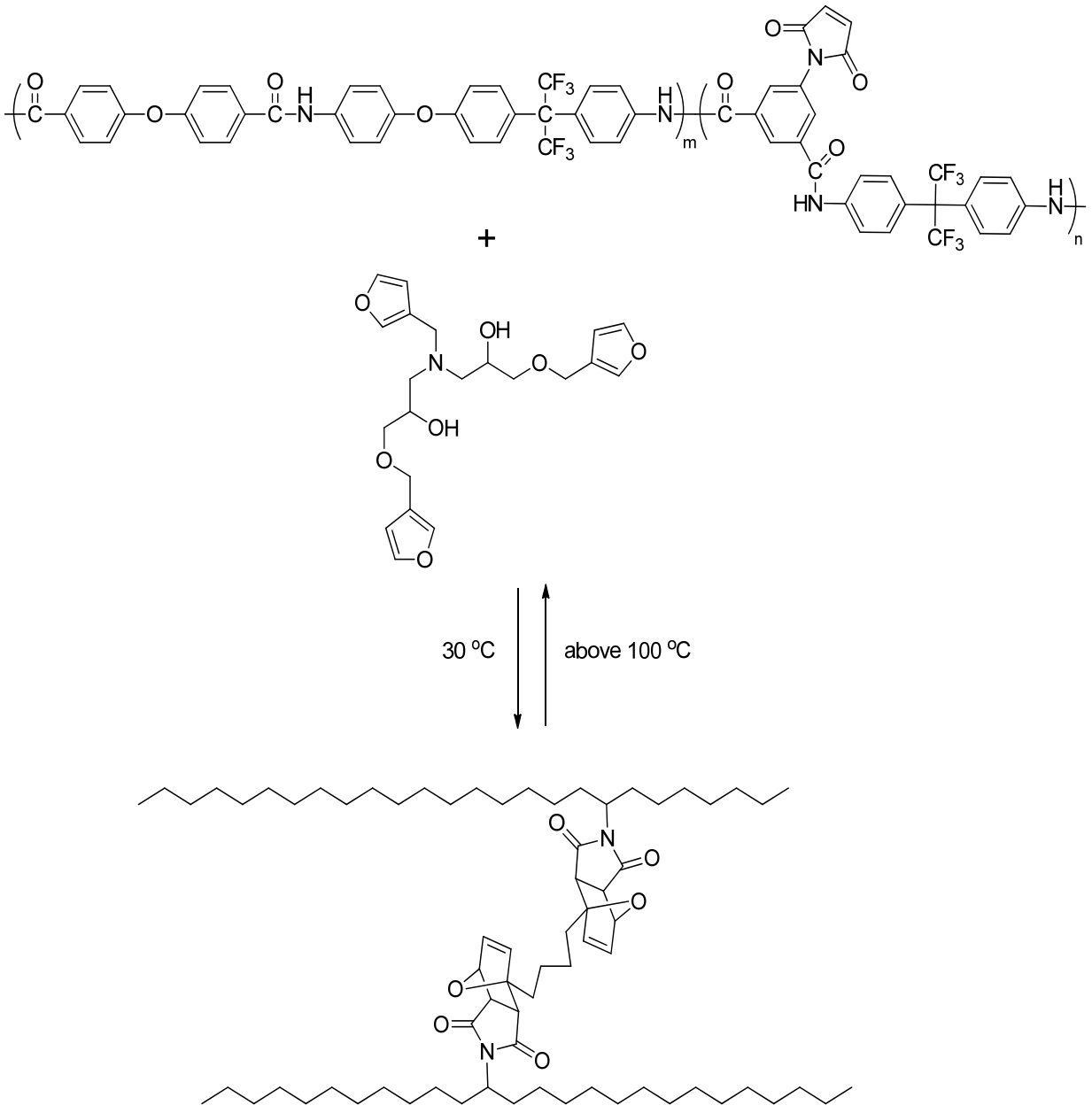
oxide)bis(2-propylmaleamide), which had a T_g of –43 °C. After crosslinking (in dichloromethane at 25 °C for 3 d), the T_g was still very low (–63 °C).



Scheme 3.5. Reversible elastomer synthesized by Gheneim

The reverse reaction was effected by heating the network polymer at 80 ^{o}C in chlorobenzene for 12 h. The products were quenched at a low temperature and characterized by FTIR, ^{1}H NMR, and GPC. FTIR and ^{1}H NMR showed identical spectra with the starting material, while a GPC trace showed the same (original) molecular weights for the polymeric diene and dienophile.

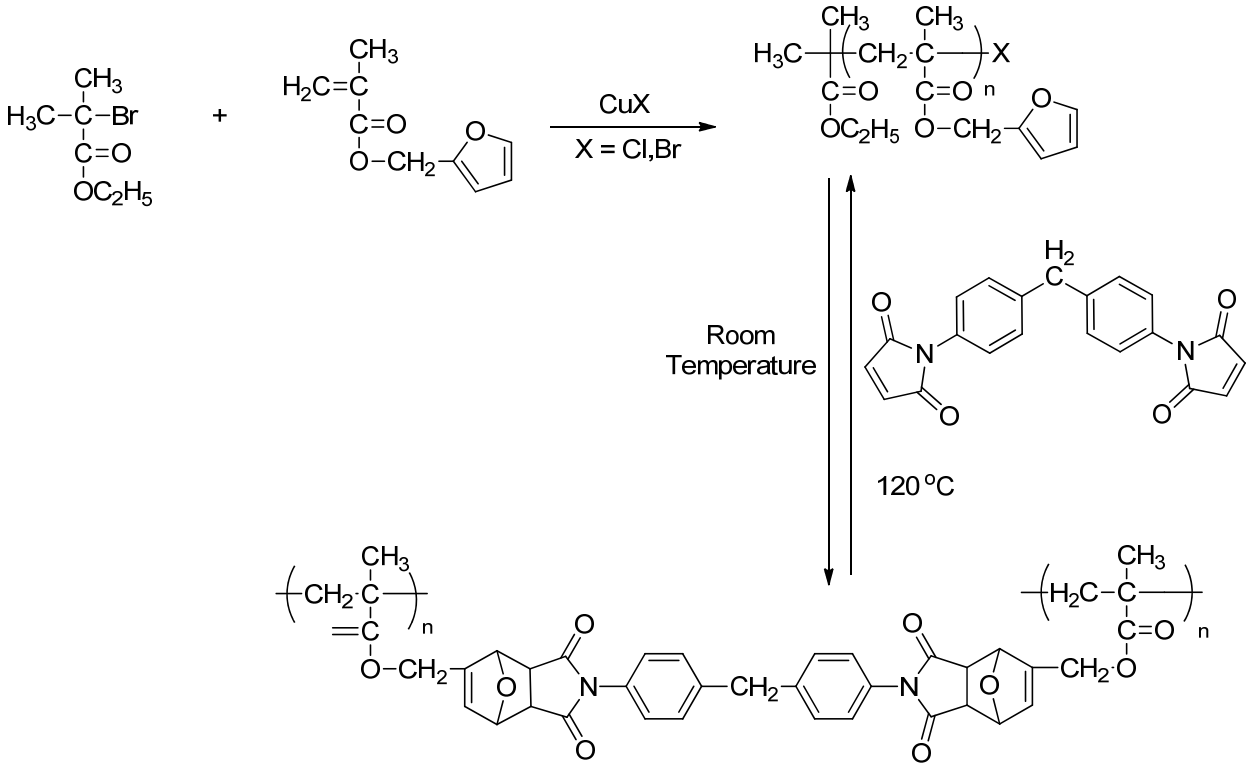
Liu and coworkers synthesized a polyamide with pendent maleimide groups and crosslinked it with a trifunctional furans at 30 °C in *N*,*N*-dimethylacetamide (DMAC) to form a gel (Scheme 3.6).[48] The degree of geletion increased with the increase of maleimide substitution. The gelled sample dissolved in DMAC above 100 °C, as rDA reactions broke down the network. Polymers with higher crosslink densities needed higher temperatures for decoupling. Both swelling ratio and T_g also increased with increasing crosslink densities.



Scheme 3.6. Reversible DA crosslinking using furan and maleimide groups

Kavitha et al. likewise prepared a series of acrylic polymers with pendant furans using atom-transfer radical polymerization (ATRP) and crosslinked them with a bis(maleimide) (Scheme 3.7).[6] In the IR spectrum the peaks at 1501 cm^{-1} and 1012 cm^{-1} (furan) disappeared upon DA crosslinking reaction but reappeared when the crosslinked polymer was heated at 120 °C (rDA).

The first heating cycle of the DSC trace of the crosslinked polymer showed an enodotherm at 121 °C (rDA). Similarly the first cooling cycle showed an exotherm at the same temperature corresponding to the repolymerization. In the second heating cycle a broad endothermic peak at 96 °C was assigned to overlap of depolymerization and the glass transition.



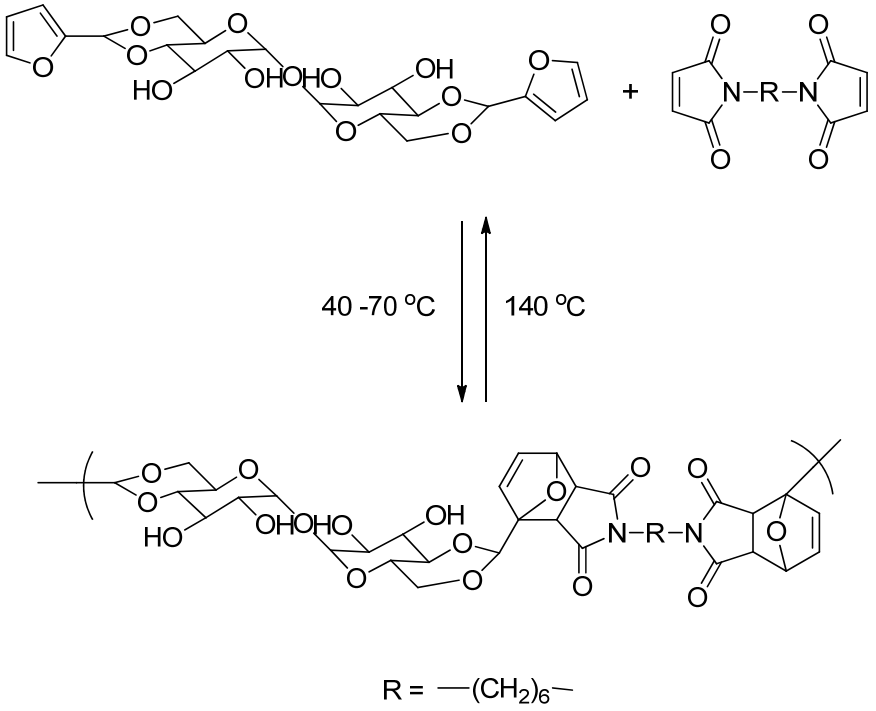
Scheme 3.7. Monomer Synthesized by ATRP method followed by reversible DA polymerization

3.1.1.3. Reversible Diels-Alder Approaches to Recyclable Polymers

Reusable and recyclable polymers may help conserve fossil fuel resources while protecting the environment from pollution and waste. The DA reaction is especially promising because it is completely "atom-economical" (no by-products and usually no catalysts) and its reversibility can be highly selective, which would allow recycling of polymers back to monomer.

Teramoto reported the use of difurfurylidene trehalose (DFTreh) as the monomer precursor and bismaleimide as the linker.[49] Tetrahalose, a non-reducing sugar formed by joining two

glucose units with a 1-1 α bond, can be obtained directly from plants. Tetrahalose is relatively stable at higher temperatures even under acidic conditions, allowing acetalization of furfural to give DFTreh. Polymerization (1:1 of DFTreh and bismaleimide) was carried out in DMF



Scheme 3.8. Recyclable polymer using tetrahalose

Polymerization temperatures varied from 25 °C to 70 °C (Scheme 3.8), but molecular weight was highest using a polymerization temperature of 55 °C, because even at these low temperatures the DA and rDA processes become competitive. DA is a second-order reaction that becomes quite slow at high conversion as end groups become scarce, while rDA is a first-order process that is fastest at high molecular weight when the concentration of adducts is highest. The TGA trace of the polymer showed the degradation temperature was 300 °C. The broad endotherm between 158 °C and 170 °C observed in the DSC was also ascribed to rDA. Samples heated in DMF at temperatures ranging from 70 °C to 140 °C were found by GPC to have molecular weights that decreased with increasing T. Pure monomer was obtained at 140 °C.

Watanabe and Yoshie combined furan-terminated poly(ethylene adipate), PEA2F, as the macromonomer and trismaleimide as the linker,[4] in a bulk polymerization at 60 °C (equal moles of furan and maleimide units) (Fig 3.5). As the reaction proceeded the molecular weight increased and hyperbranched rendered the polymer insoluble in chloroform. However the polymer became soluble in chloroform again when heated at 140 °C for 20 min. The depolymerized product was characterized by both ^{1}H NMR and GPC. The authors showed this polymer system can withstand eight consecutive cycles of depolymerization and repolymerization. The first DSC heating cycle of the polymer showed a broad endotherm at 130 °C, assigned to rDA depolymerization. However neither exothermic nor endothermic peaks were found in subsequent respective cooling and heating cycles. Repolymerization was slow on the time-scale of the DSC cooling cycle. The tensile modulus of the polymer decreased a little with the repetition of heating and cooling cycles but the tensile strength and the elongation at break remained the same.

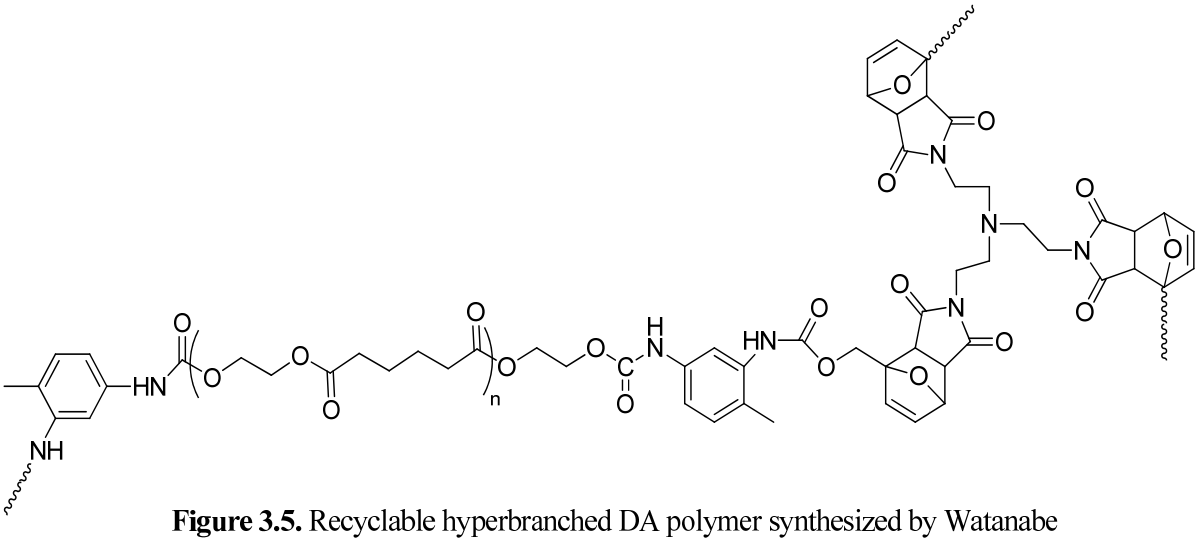


Figure 3.5. Recyclable hyperbranched DA polymer synthesized by Watanabe

Inoue and coworkers reported the synthesis of a recyclable shape-memory DA polymer.[50] Shape memory polymers are "smart materials" that can return to their original shape (permanent)

from a deformed one (temporary) by the application of an external stimulant like heat. Shape memory polymers require a three dimensional crosslinked structure to determine their permanent shape. Therefore thermosets are good for this application. However thermosets cannot be recycled or remolded by application of heat. On the other hand thermoplastics can be remolded in different shape by melting but their shape memory performance is rather poor due to creep.[51] Polymers with thermoreversible crosslinking possess properties of both thermosets (the network structure) and thermoplastic (remolding ability). This combination would be a good choice for shape memory polymers.

In this investigation the authors synthesized four-armed, furan-terminated poly(lactic) acids as the diene along with hexamethylene bismaleimide as linkers. Cross linking was achieved in the bulk by mixing 1:1 mole ratio of furfuryl and maleimidyl moieties in a mold at 100 ^{o}C. The products obtained were insoluble in chloroform and exhibited a T_g of 65 °C. The authors found that the polymer could easily change its shape to a temporary form when heated between 65 °C to 100 °C, but it reverted to its original shape when cooled down below 60 °C for 10 seconds. They also found that heating the polymer above 160 °C disconnected all the intermolecular DA crosslinks and erased the shape memory of the polymer. DSC also showed an exothermic peak at 100 °C and an endothermic peak at 160 °C corresponding to the forward and backward Diels-Alder reactions. Therefore the polymer could be remolded by heating above 160 °C followed by cooling down to room temperature. It would become pliable but retain its shape memory in the new molded structure when heated between 65 ^{o}C to 100 ^{o}C. The DMA trace and the XRD analysis of the polymer showed a lack of crystallinity in the network structure. Crosslinking restricted the molecular motion and formation of crystals. This in turn helped the shape memory

behavior of the polymer. Analogous polymers formed from dodecamethylene-linked bis(maleimide) showed similar properties.[50, 51]

3.1.1.4. Reversible Diels-Alder Approaches to Removable Coatings

Coatings act as barriers against chemicals, moisture, fungus, dust, and other environmental threats. The higher surface area of a coating increases these threats, and therefore polymers used for coating applications need to be especially stable. Removable coatings for electronic goods allow users to service, repair, and upgrade electronic assemblies without causing damage to the circuit boards or their components.[52-54]

In 2002 McElhanon and co-workers introduced thermally reversible epoxy-based polymers.[54] The authors first synthesized the bis-maleimide precursors by attaching 4-hydroxyphenylmaleimide at both ends of dichlorosiloxane tethers. This bis(dienophile) reacted with a furfuryl glycidyl ether at 60 °C in bulk (Fig 3.6). A curing agent was added just prior to molding and heated at 65 °C, whereupon the epoxy units cross-linked the system.

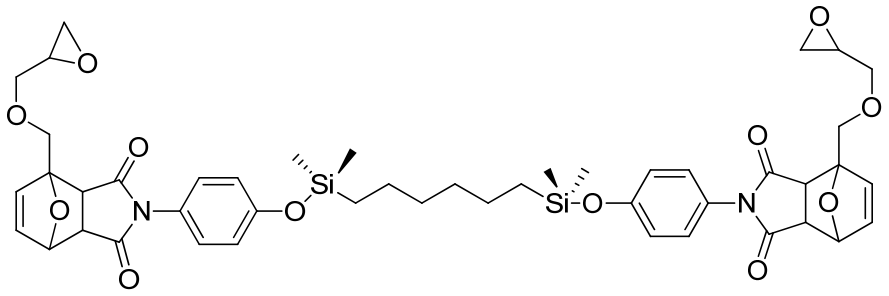


Figure 3.6. Thermally reversible Diels-Alder epoxy resin synthesized by McElhanon

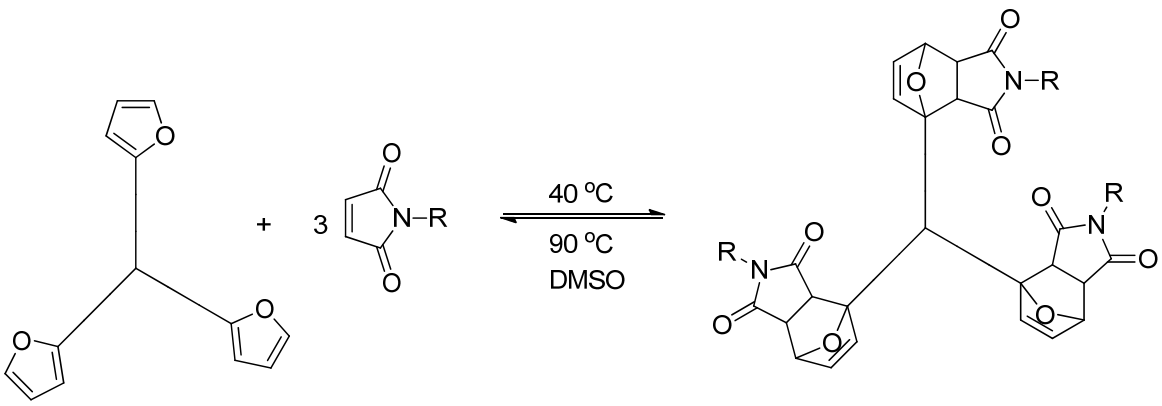
The authors showed the chemical reversibility of the polymer by measuring its shear storage modulus by DMA over a temperature ramp. At about 100 °C almost 95% of the Diels-Alder adducts opened up, and the modulus decreased dramatically. The polymer recovered its modulus when cooled to room temperature again. This process could be repeated several times. The use

of the polymer as removable coating was demonstrated by heating it at 90 °C in presence of a mild solvent (1-butanol). The rDA-depolymerized product slowly dissolved and could be removed from the electronic device. The authors also showed that removal of the reversible coating by application of heat and solvent did not damage the device.[55]

Budy et al. reported the synthesis of a thermally reversible crosslinked polyurethane system for a self-healing coating application.[52, 53] They first synthesized a terpolymer from 5-(hydroxymethyl)furfuryl alcohol, poly(propylene)glycol, and a diisocyanate. DA crosslinking used a bis-maleimide at 65 ^{o}C for 3 h in THF. The reversibility of the cross link was shown from by ATR-FTIR spectra. The distinct peaks of the crosslinked adduct (1409 cm^{-1} and 1042 cm^{-1}) disappeared when heated at 150 ^{o}C for 1 h. To further illustrate the self healing nature of the polymer coating a glass substrate was spray painted with PU-DA polymer solution and a scratch was made on that with a knife. The authors showed that this scar can be healed by heating the system at 130 ^{o}C for 8 h.

3.1.1.5. Removable Star Arms by Diels-Alder Reaction

The Diels-Alder reaction can be used to manipulate polymer architectures and topologies thermally (Scheme 3.9.). Aumsuwan and Urban synthesized a star core with furan end groups and star arms with maleimide functional groups.[56, 57] The star arms were attached (DA) at 40 ^{o}C in DMSO but could be removed again at 90 ^{o}C and reattached again at 40 ^{o}C. The ATR-FTIR spectra after heating at 90 ^{o}C showed bands at 1662 cm^{-1} (characteristic of the maleimide C=C double bond) and 1530 cm^{-1} (characteristic of the furan C=C double bond). ^{1}H NMR showed peaks at 5.2 ppm corresponding to the bridge head C-H proton in the Diels-Alder adduct. This peak disappeared after heating at 90 ^{o}C due to the breaking down of the Diels-Alder adduct.



Sceheme 3.9. Removable star arms by DA reaction

3.2. Results and Discussion

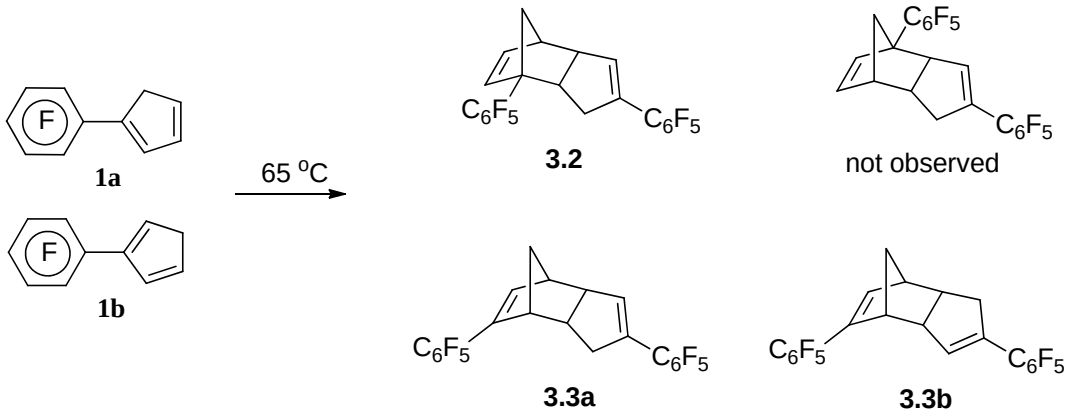
Fluoropolymers exhibit low dielectric constants, high thermal stability, chemical resistance, especially towards acids and oxidants, low refractive index, and resistance to abrasion.[58-62] These properties are ascribed to the low polarizability, high electronegativity, and small size of the fluorine atom, along with high C–F bond energies. Fluoropolymers are used in a wide variety of applications; among these we are interested primarily in coating applications and membranes. However, the preceding discussion of DA/rDA-based reversible polymers was notable for the lack of appreciably fluorinated examples.

This chapter describes the synthesis of two related prototype systems for fluorine-containing reversible DA polymers. Section 3.2.2 presents the synthesis of a reversible homopolymer using a perfluoroarylene-linked bis(cyclopentadiene) as the monomer, while Section 3.2.1.2 presents a polymerization based on a perfluoroarylene-linked bis(cyclopentadiene) and a bis(maleimide).

3.2.1. DA homopolymer from a Perfluoroarylene-linked Bis-cyclopentadiene. This section describes how a compound in which two cyclopentadiene moieties are connected via a perfluorobiphenylene linker can undergo DA homopolymerization. Model reactions and experiments to test the reversibility of the polymer are presented also.

3.2.1.1. Model Chemistry. The polymerizations described in this section are based on DA reactions of perfluoroaryl-substituted cyclopentadienes. In order to gain a better understanding of the polymerization, reactions of model cyclopentadiene compounds were studied in some detail. (Pentafluorophenyl)cyclopentadiene (**3.1**) was synthesized according to the procedure of Deck and co-workers,[63] in which sodium cyclopentadienide (NaCp) and hexafluorobenzene are reacted in presence of a base (excess NaH).

Deck and co-workers reported earlier that diene **3.1** exists as a mixture of two slowly interconverting isomers (3.1a and 3.1b), but that thermal



Scheme 3.10. Dimerization of the model compound **3.1**

dimerization of that isomeric mixture gives primarily compound **3.2** in which a C_6F_5 group occupies a bridgehead position of the bicyclo[2.2.1]heptene core.[63] This result implies that isomer **3.1a** is more reactive both as the diene and as dienophile. However in preparation for the present study I revisited the dimerization of **3.1** as a model for the polymerization of **4**. When heated in benzene solution for several days the isomeric dimer **3.3a**, in which a C_6F_5 group occupies a vinylic ring position of the bicyclo[2.2.1]heptene core (Scheme 3.10), slowly emerges as the major (thermodynamic) product. Using PC Spartan, I calculated the heats of formation of **2** and **3a** using a Hartree Fock method with a 6-31G* basis set, which showed that **3a** is energetically favored by 6 kcal/mol. The calculation of the energy difference should be robust because the two compounds are isomers. Different computational methods might give slightly different results, but the point is that the calculation supports **3.3a** as the thermodynamic product. That is not a surprise because in **3.2** one can imagine steric crowding at the bridgehead, while in **3.3a** the C_6F_5 group has moved into conjugation with the C=C double bond. The molecular structures of **3**.**3a** (Fig. 3.7) was confirmed by single-crystal X-ray diffraction and compared with

the previously published structure of **3.2**.[63] An additional, minor component tentatively assigned to **3.3b** was also detected (^{1}H NMR). **3.3a** was separated from the isomeric

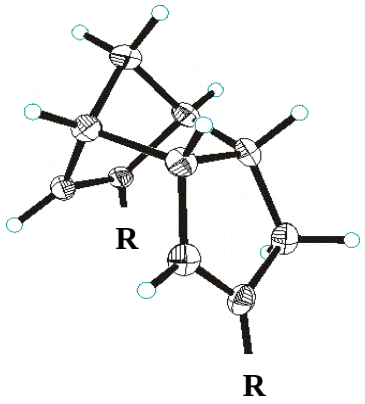


Figure 3.7. Thermal ellipsoid plot of the molecular structure of crystalline **3.3a**; R = C_6F_5

mixture by fractional crystallization. The ^{1}H NMR spectrum of pure **3.3a** is given in Fig 3.8. Importantly the spectrum shows two vinylic CH signals whereas the spectrum of 3.2 shows three

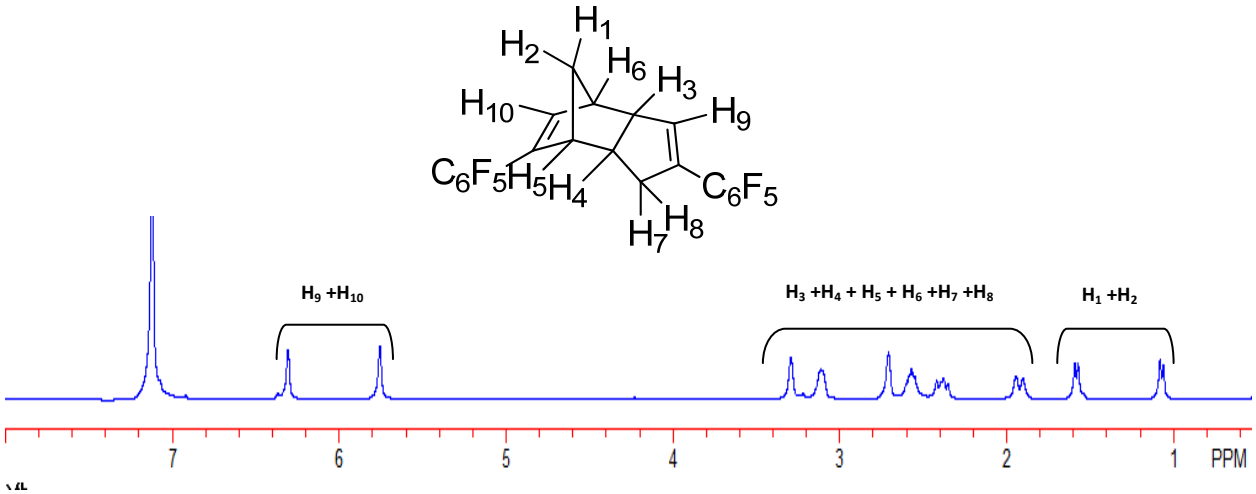


Figure 3.8. ^{1}H NMR spectrum of dicyclopentadiene **3.3a**

signals in that region. These results suggest that homopolymerizations of ditopic analogues might give rise to different regioisomeric backbone microstructures if polymerization is carried

out at different temperatures. Moreover, the chemical shifts and relative signal intensities of the model compounds will help determine which structure(s) is (are) present in the polymer.

As shown in Diagram 1, the seemingly small change in DA regiochemistry can have a profound effect on the progress of the retro-DA reaction. From *ab initio* calculations as described above, we have estimated that adduct **3.3a** is about 6 kcal/mol more stable than adduct **3.2**. Also adduct **3.2** arises from the combination of two molecules of **3.1a**, while **3.3a** arises from one molecule of **3.1a** and one molecule of **3.1b**. From the doctoral dissertation of Matthew P. Thornberry, we know that **3.1b** is more acidic than **3.1a** by approximately 0.57 pK units. He determined this acidity difference by ^{19}F NMR spectroscopic measurements in THF / C_6D_6. Therefore the two interconverting tautomers **3.1a** and **3.1b** are related by an equilibrium constant of 0.27, favoring the fully conjugated tautomer **3.1a**. (Note that the less stable of two tautomers must be the more acidic). This equilibrium constant translates to a roughly 1 kcal/mol difference between **3.1a** and **3.1b** if one attributes the entire free energy difference to the enthalpic contribution. These differences are traced out, not exactly to scale, in Diagram 1. The consequence is apparent when comparing the relative enthalpies of activation for the *reverse* reactions (rDA). At minimum, the activation enthalpy for rDA of **3.3a** must be 7 kcal/mol higher than the activation enthalpy for rDA of **3.2**. Finding a way to control this regiochemistry, at some point in the future, could help design more exact parameters for DA and rDA in cyclopentadiene-based reversible polymer systems.

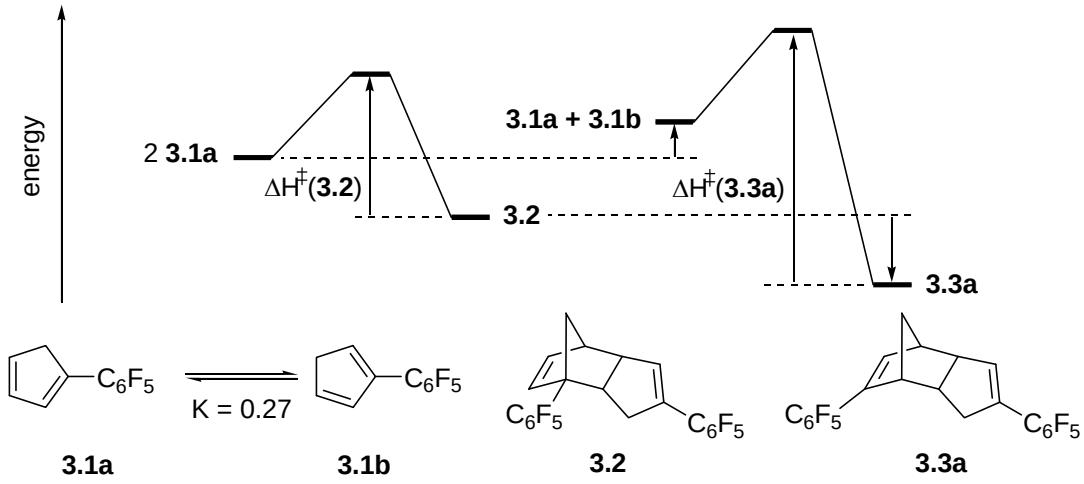
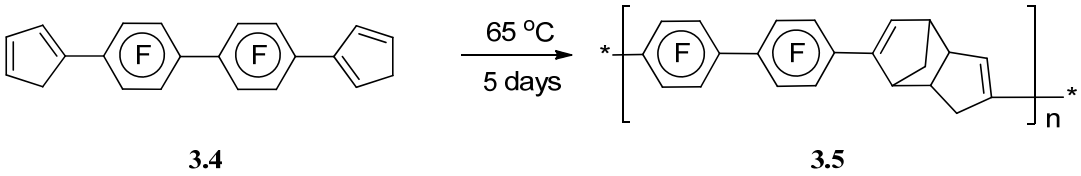


Diagram 1. Energy diagram for adduct formation in (pentafluorophenyl)cyclopentadiene.

3.2.1.2. Homopolymerization of Bis(cyclopentadienes). Bis(cyclopentadienes) are known to undergo thermal self-polymerization as described in the introductory paragraphs of this chapter.[23] Accordingly, monomer **3.4** undergoes smooth polymerization in benzene solution when heated at 65 °C (Scheme 3.11). The reaction is monitored by ^{1}H NMR spectroscopy and



Scheme 3.11. Homopolymerization of bis(cyclopentadiene) **3.4**

continued until the characteristic vinylic signals of **3.4** are absent from the spectrum. New aliphatic signals similar to those observed in model dimer **3.3** (Fig. 3.9) are also observed.

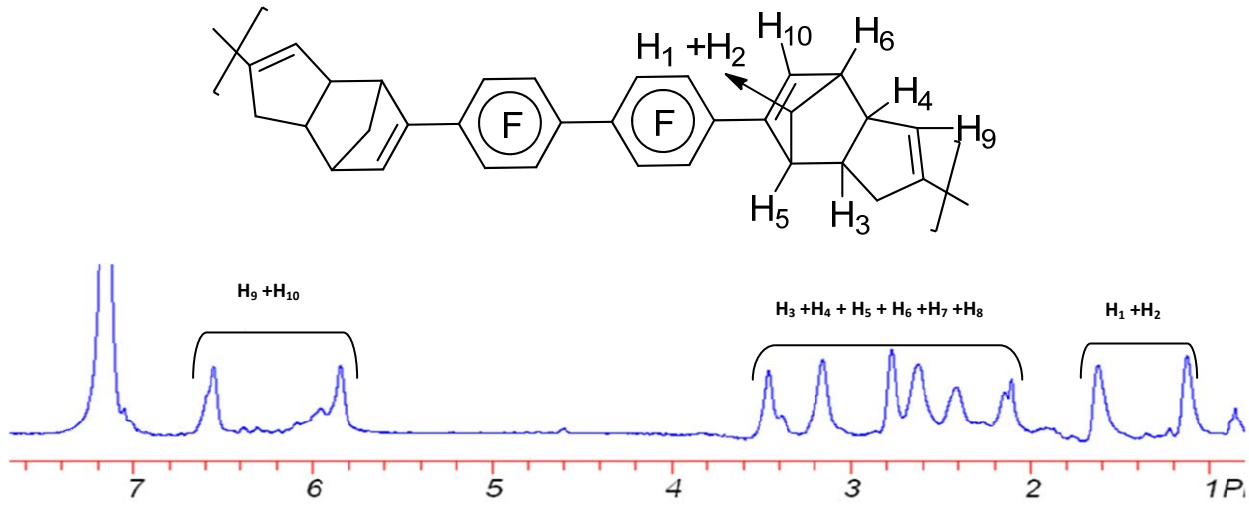


Figure 3.9. ^{1}H NMR spectrum of the polymer **3.5** taken in C_6D_6.

The resulting tan colored polymer **3.5** is soluble in organic solvents like benzene, chloroform, methanol etc. ^{1}H NMR (Fig 3.9) of the polymer showed two new vinylic signals were generated. Because the polymerization was effected by an extended interval of heating, I expected to see a polymeric structure comparable to the model dimer compound **3.3**, where the C_6F_5 group occupied a vinylic position of the bicyclic core. Two equally integrating broad peaks in the vinylic region of the ^{1}H NMR (5.85 and 6.45 ppm) of the polymer also supported this idea.

3.2.2. Polymer Characterization. SEC analysis of the polymer **3.5** in chloroform gave M_n = 11,000 g/mol (DP ~ 20) and PDI = 1.7. The PDI is consistent with a step-growth mechanism. The theoretical PDI for a purely step-growth polymerization is 2.0, but with low-molecular weight polymers some fractionation upon reprecipitation is always possible, removing some low-molecular weight fraction and giving an artificially low PDI value (and perhaps a slightly elevated M_n). The value of 11,000 g/mol seems to be a kind of limit for this polymerization. Increasing the reaction time did not increase them molecular weight. On the contrary, increasing the reaction temperature to 80 °C resulted in an NMR spectrum with *increased* intensity for end-

group signals. In other words, at the higher temperature one observes depolymerization beginning to occur, and an equilibrium is reached. Of course higher temperature favors depolymerization because the entropy of depolymerization is positive.

3.2.3. Thermal Characterization (TGA). We initially attempted bulk depolymerization of polymer **3.5** in a Dailey sublimer at 150 °C but recovered less than 10% of monomer **3.4** on the coldfinger; moreover the unsublimed residue was intractable. In order to understand what might have gone wrong, we switched to TGA analysis to obtain more quantitative results on a smaller scale. Fig 3.10 shows the weight change in a sample of polymer **3.5** over the temperature range 25 °C to 800 °C at 10 °C/min in a nitrogen atmosphere The first weight loss was found between 170 °C to 280 ^{o}C (4%). When the heating rate was increased, the weight loss in this temperature regime increased. This feature is therefore assigned to depolymerization and formation of

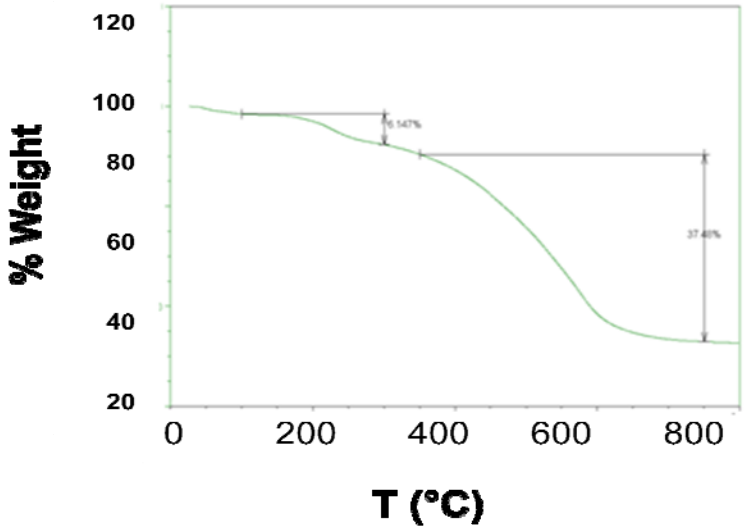


Figure 3.10. TGA trace of the polymer **3.5** taken under N_2 medium at 10 ^{o}C/min heating rate

monomer or perhaps dimeric fragments. The temperature range is a little higher than the temperature that Deck and coworkers found necessary to crack the model dimer **3.1**,[63] but they used flash-vacuum thermolysis which requires monomer molecules to escape only a thin film of

material while decreasing the possibility of unwanted bimolecular processes. Finally there is a broad weight loss feature between 375 °C and 750 °C showing complete polymer degradation.

To investigate whether complete depolymerization was possible during heating in the TGA instrument, an isothermal TGA experiment was performed at 260 ^{o}C. Only 12.5% weight loss was observed after 2 h. The residue of the TGA experiment was insoluble in chloroform and acetone, suggesting that some three dimensional cross linked structures had formed. We speculate that during the initial phase of the isothermal TGA experiment, some depolymerization occurred, unmasking diene end groups, including some small fragments that were lost to the gas phase. However it is known that unmasked dienes can also react with the remaining double bonds in the norbornene structures within the polymer, and that these unwanted cross-linking DA reactions are typically not easily reversible. These findings and the mechanistic conclusions drawn from them are fully consistent with other published work.[2]

3.2.4. FVT Depolymerization of 3.5. Disappointed with the failure of the bulk thermolyses (despite the fact that nobody else can really get that to work either),[9] but recalling that Deck and co-workers were able to effect the cracking of dimer **3.2** under flash vacuum thermolytic (FVT) conditions, we decided to try the same approach (indeed the same apparatus) as shown in Fig 3.11.

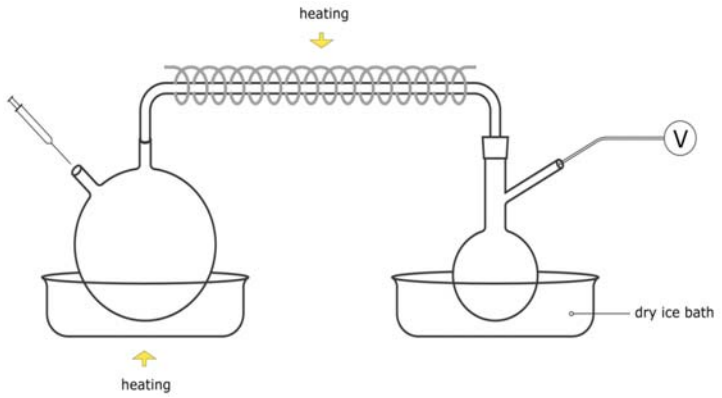


Figure 3.11. Experimental set up for Flash Vacuum Thermolysis (FVT)

The FVT experiment was followed by ^{1}H NMR spectrometry (Fig. 3.12). For clarity only the vinylic region of the ^{1}H NMR has been shown here. Two peaks at 6.34 and 6.26 ppm characteristic of the monomer (Fig 3.12.A) disappeared and two new peaks at 5.81 and 6.53 ppm were generated upon Diels-Alder reaction to afford the polymer **3.5** (Fig 3.12 B). To confirm the assignments I consulted the ^{1}H NMR spectra of the model dimerized compounds (**3.2**, **3.3a** and **3.3b**, see above). Broadening of the corresponding signals in Fig 3.13 B was taken as evidence of polymerization. Flash vacuum thermolysis produced the depolymerized material having the ^{1}H NMR spectrum shown in Fig 3.12 C. Peaks at 6.36 and 6.26 ppm were visible again in this spectrum indicating the presence of free cyclopentadiene moieties (both from the monomers and the end groups of low molecular weight oligomers). Two small broad peaks at

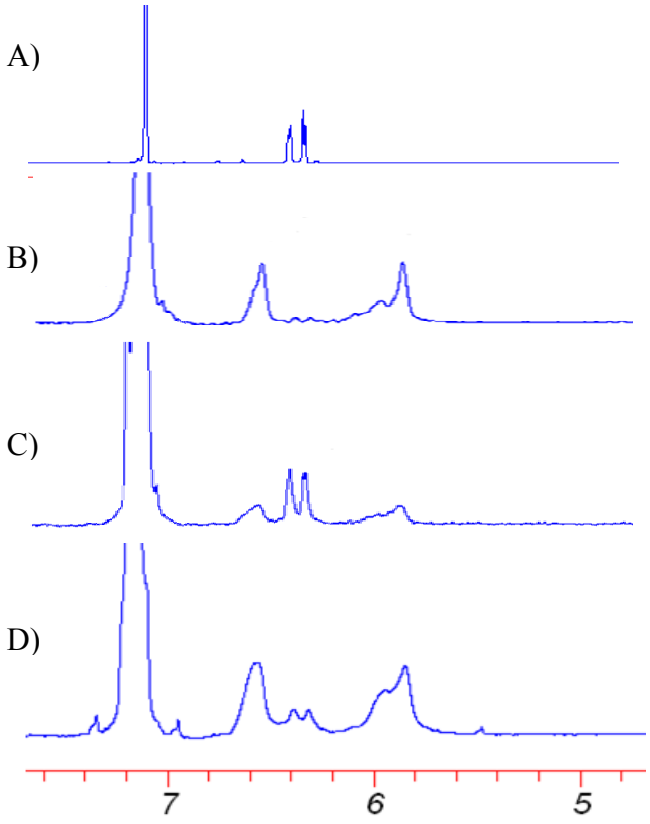


Figure 3.12. ^{1}H NMR spectra study from FVT and following repolymerization taken in C_6D_6. A) monomer B) polymer C) product of FVT D) repolymerized compound

5.85 and 6.45 ppm were also visible indicating some dimers or low molecular weight oligomers were also present. our FVT setup is a simple design and some of these species could have been sent over in an aerosol due to the violent spattering of the solvent in the reaction side of the apparatus. The resultant mixture was then heated at 65 °C for 24 h to effect repolymerization (Fig 3.13 D), confirmed by reappearance of the peaks at to 5.85 and 6.45 ppm. However the vinylic peaks were not lost completely, and we conclude that FVT is not only depolymerizing but also partly degrading the polymer. These results are not too surprising considering the fact that monosubstituted cyclopentadienes undergo a variety of other reactions under such harsh conditions.

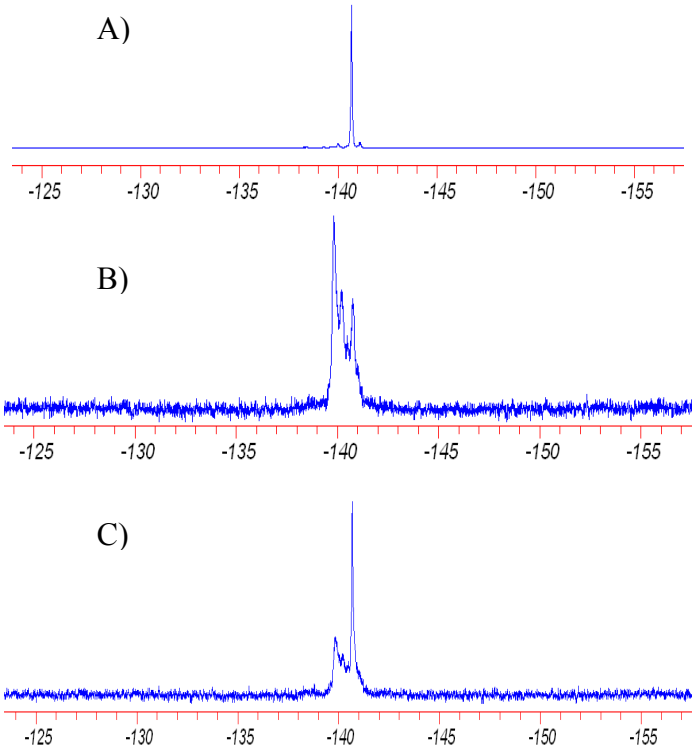


Figure 3.13. ^{19}F NMR spectra study from FVT taken in C_6D_6. A) monomer B) polymer C) product of FVT

The proton NMR spectrum obtained after FVT showed the presence of free cyclopentadiene rings but cannot tell us how much free monomer was obtained. Therefore I took the ^{19}F NMR spectrum before and after FVT experiment (Fig. 3.13). The sharp peak at -141 ppm (Fig 3.13C)

represented the free bis-cyclopentadiene monomer obtained during the depolymerization reaction, while the broadening between -139 to -140.5 ppm depicted the presence of some oligomerized product. Calculating the relative areas I found the sharp peak region (monomers) is almost 1.7 times as the broadened region (oligomers). This result concluded about 62% of the polymer reverted to the monomeric form while rest 38% remained in the oligomeric form.

3.2.5. Synthesis of Reversible Diels-Alder Two Component Polymer

The polymerization described in the preceding section is unfortunately rather limited in scope. There is no clear way to control the molecular weight, not much hope of modifying the structure, and the depolymerization temperature is so high that other kinds decompositions and cross-linking processes inevitably compete. This section describes our effort to lower the depolymerization temperature by switching to a polymerization involving a perfluoroarylene-linked bis-diene and a bis-maleimide dienophile. Such a polymerization is not properly termed a "co-polymerization," but the monomer system is two-component rather than single-component. We already knew that monomer **3.4** would not be suitable for a two-component polymerization because it undergoes relatively rapid single-polymerization even`nevitably compete` at room temperature, as describe in the preceding section. Thus this section begins with a synthesis of a modified bis-diene monomer **3.6** (Fig. 3.14) and proceeds to the selection and synthesis of the bis-maleimide monomer, model chemistry to understand the progress and outcome of the DA reactions involved the polymerization experiments, the characterization of the resulting polymers, and finally the depolymerization experiments.

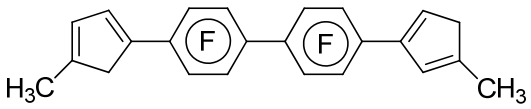
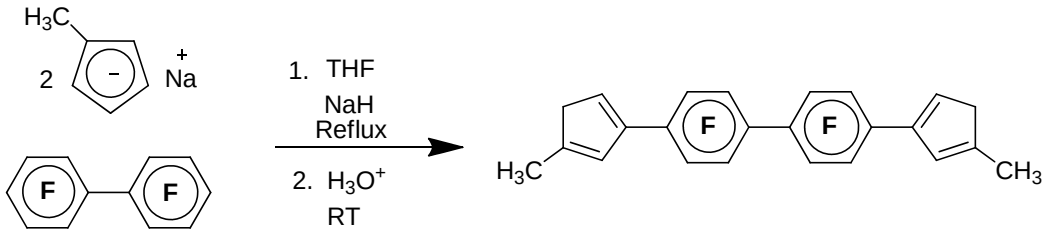


Figure 3.14. Modified bis(cyclopentadiene) **3.6**

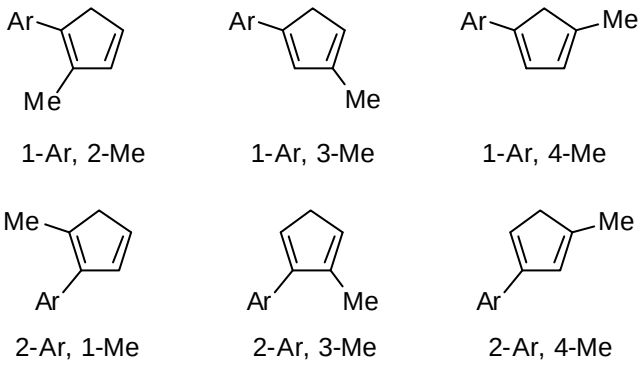
3.2.5.1. Synthesis of Modified Bis-diene. The simplest approach to modifying monomer **3.4** is to replace the cyclopentadienyl anion in its synthesis (Scheme 3.12) with a substituted cyclopentadienyl anion. Nucleophilic substitution of sodium methylcyclopentadienide on decafluorobiphenyl afforded monomer **3.6** as a complex mixture of skeletal regioisomers (CH_3



Scheme 3.12. Synthesis of modified bis-diene **3.6**

can be proximal/vicinal or distal to the biphenylene), complicated by the fact that cyclopentadienes also tautomerize (e.g.,**3.1a** vs **3.1b**). Clean 4,4'-disubstitution of decafluorobiphenyl was verified by ^{19}F NMR analysis. The mixture **3.6** affords a single band on a silica gel column, and attempts to obtain a single regioisomers by crystallization were unsuccessful, so we were forced to continue with **3.6** as the isomeric / tautomeric mixture.

Chart 3.1. Different isomeric / tautomeric forms of **3.6**



A critical NMR-scale experiment showed that **3.6** does not homopolymerize up to 120 °C (Fig. 3.15). Evidently the presence of an additional methyl group on each cyclopentadiene moiety, *regardless of its regiochemical relationship to the linker*, has made the molecule sufficiently sterically hindered (compared to **3.4**) to frustrate self polymerization in the temperature range (under 120 °C) that we anticipated would be adequate to effect reaction with a bis-maleimide monomer. Assigning all of the credit for this finding to steric effects is obviously questionable, but we note that both cyclopentadiene and methylcyclopentadiene freely form dimers at room temperature.

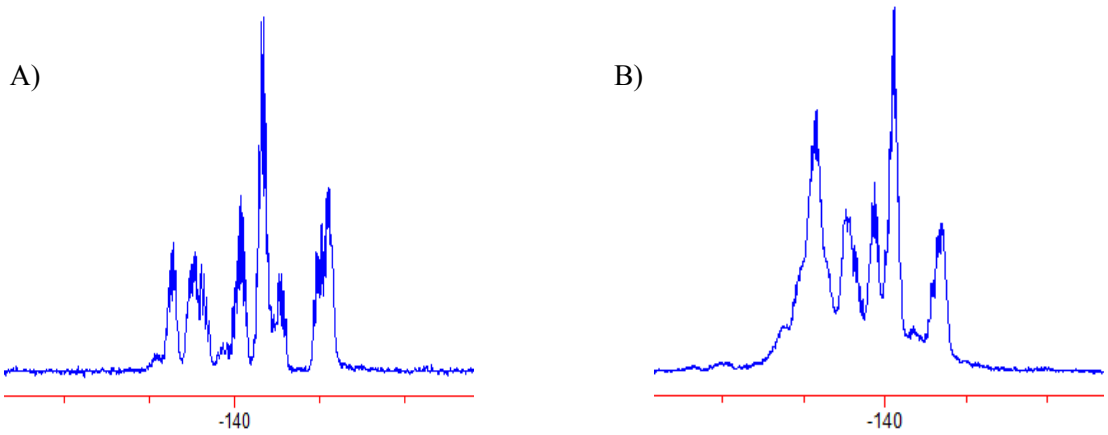


Figure 3.15. A) ^{19}F NMR spectrum of **3.6** B) ^{19}F NMR spectrum of **3.6** after heating at 125 °C for 24 h (showing signs of oligomerization)

3.2.5.2. Bis-maleimide Monomer Synthesis. While the octafluorobiphenylene linker is certainly electron-withdrawing,[64, 65] we still expect the monomer **3.6** to be a "normal" DA diene in terms of its electron demand. In other words, we think the best DA reactivity will be achieved with an electron-deficient dienophiles, rather than an electron-rich one. But because the perfluorinated linker is somewhat electron-withdrawing, we know we will need a very electron-poor dienophile. Moreover in the literature of reversible DA polymerizations the most commonly-used dienophile monomers are based on maleimides. We therefore proposed to use a

simple linked maleimide as the dienophiles monomer. The specific compound we chose **3.7** (Fig 3.16) was based simply on knowing that the starting 4,4'-diaminodiphenyl ether was commercially available and inexpensive, the reaction of the diamine with maleic anhydride was trivial,[66] and the resulting bis-maleimide was expected to be quite stable and easy to work with.

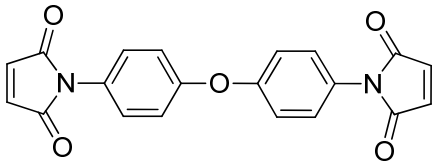
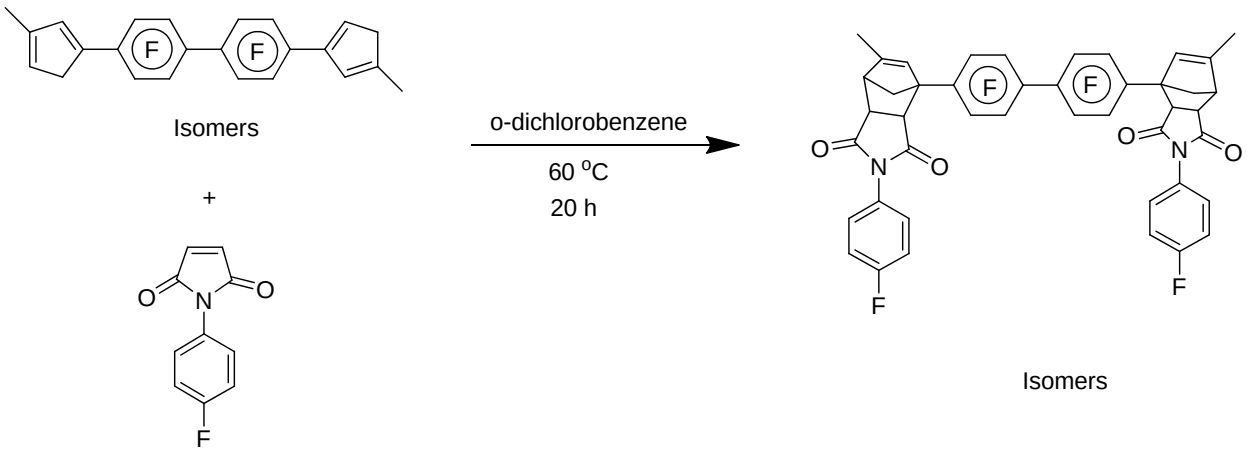


Figure 3.16. Bis-maleimide used for polymerization **3.7**

Rather than leaving questions of electronic effects to chance, however, it is possible to estimate the relative propensity of **3.6** to self-polymerize and to undergo a DA reaction with the maleimide based solely on orbital energies (which ignores steric effects entirely). Because the cyclopentadiene and maleimide are potentially competing as dienophiles, the LUMO energy levels of both bis(cyclopentadiene) and bis(maleimide) were calculated using PC Spartan software (Hartree-Fock, basis set = 6-31G*). I found the LUMO energy of the bis(maleimide) (1.06 eV) is lower than the LUMO energy of bis(cyclopentadiene) (1.20 eV). Therefore The HOMO-LUMO energy gap is smaller in case of the bis(maleimide) dienophile than the bis(cyclopentadiene) by approximately 0.14 eV (3.2 kcal/mol).

3.2.5.3. Model Chemistry. Because the bis-diene monomer is a mixture of isomers / tautomers, we wanted to explore a simplified model system first so that we could understand the progress of the DA reactions and have a better chance of assigning some of the inevitably complex NMR spectra. The model reaction (Scheme 3.13) was executed reacting monomer **3.6** with a slight excess (2.2 equiv) of a monofunctional "capping" dienophile *N*-(4-fluorophenyl)maleimide (**3.8**). A slow reaction of **3.7** and **3.8** was evident within 15 minutes at room temperature in C_6D_6, but

in order to reach complete conversion in a reasonable time the reaction temperature was raised to 50 ^{o}C for 20 h.



Scheme 3.13. Diels-Alder reaction of monomer **3.6** and model maleimide **3.8**

The product mixture was analyzed by NMR spectrometry. The 4-fluorophenyl substituent provides a useful handle for ^{19}F NMR measurements. The 4-fluorine chemical shift (−114.1 ppm) in the starting dienophile is shifted slightly downfield (−112.8 ppm) in the adduct (Fig. 3.17). The spectrum shows that the slight excess, unreacted dienophile is well-resolved from the

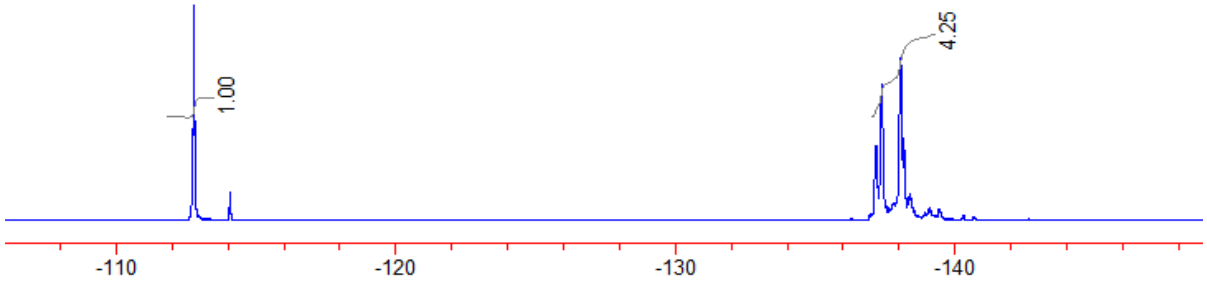


Figure 3.17. ^{19}F NMR spectrum of the DA adduct **3.9** formed reacting bis(cyclopentadiene) monomer **3.6** and model maleimide **3.8**

product signal even though the latter is relatively broad.

The ^{1}H NMR spectrum of the model bis-adduct is still quite complicated by the fact that the starting diene is an inseparable isomeric mixture. Thus the product also is a complex mixture of isomers, but the signals in the ^{1}H NMR spectrum do occur in the correct regions and in the correct approximate ratio to be consistent with the assigned bis-adduct. Separation of the mixture by silica gel chromatography afforded one of the products cleanly (**3.9a**, Fig. 3.18), whereas the second main band obtained from the column was still a complex mixture. It has been found **3.9a**

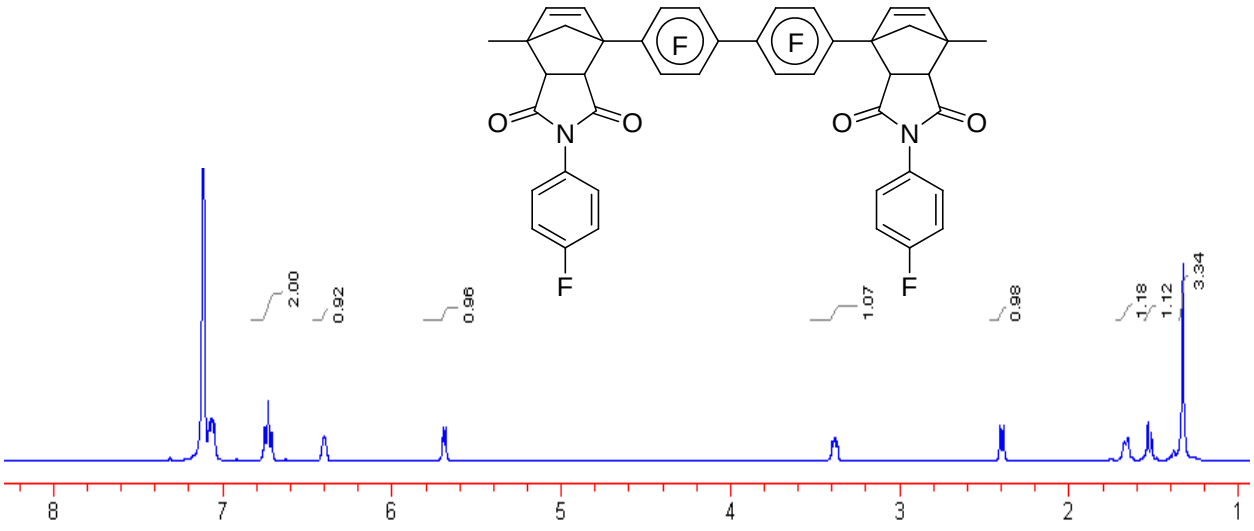
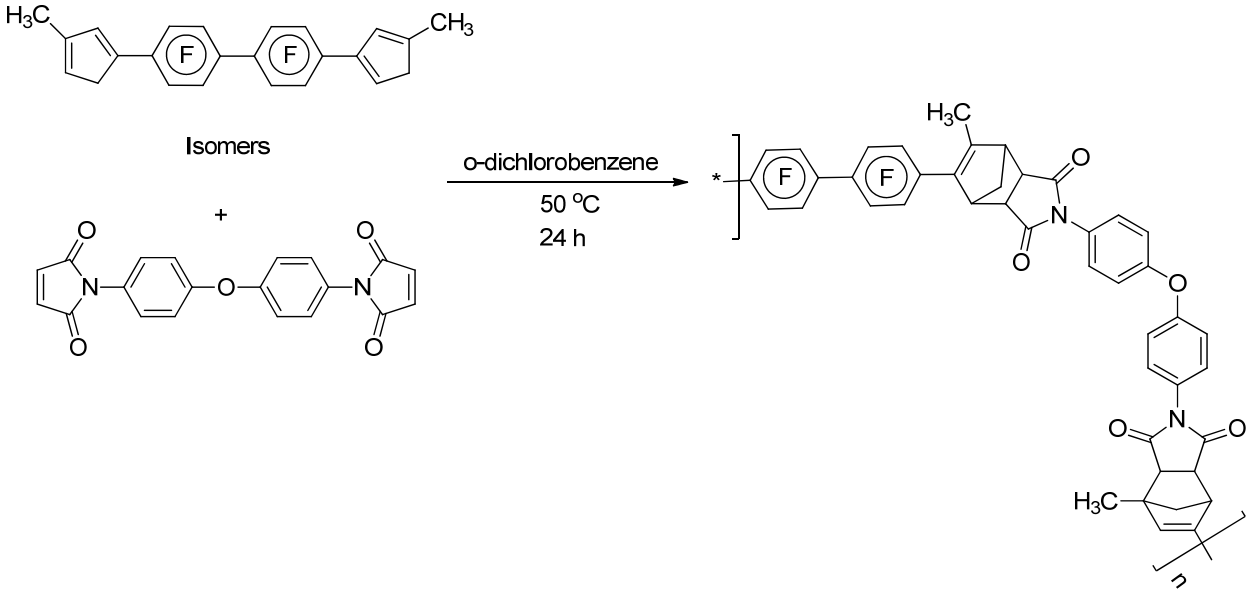


Figure 3.18. ^{1}H NMR spectrum of the DA adduct **3.9a** formed reacting bis(cyclopentadiene) monomer **3.6** and model maleimide **3.8**

is the symmetrical isomer. In other words, both cyclopentadiene moieties of **3.6** reacted in the same way. (The corresponding ^{19}F NMR spectrum likewise confirms the molecular symmetry as there are only three signals, one for the 4-fluorophenyl group and two for the octafluorobiphenylene linker). The ^{1}H NMR spectrum shows two aryl CH signals (one partly occluded by the solvent residual isotopomer $CHCl_3$), two vinylic signals (ruling out the attachment of the methyl group at a vinyl position) and then two signals for the CH groups *alpha* to the carbonyl groups, two signals arising from the mutually coupling (chemically inequivalent) *gem*-CH_2 hydrogens at the 7-position of the norbornene system, and a single methyl signals. We

further speculate that this isomer was eluted first because both of the maleimide carbonyl groups are slightly sterically "protected" from interacting with the stationary phase by adjacent substituents at the bridgehead positions.

3.2.5.4. Polymerization Experiments. The polymerization reaction shown in Scheme 3.14 was monitored by ^{1}H NMR spectrometry (Figure 3.19) and continued until the signal at 6.85 ppm (assigned to unreacted maleimide end groups) reached a constant intensity relative to the other signals in the spectrum. The product was recovered by precipitating from hexane followed by filtration and drying in air. A polymer with 94% yield was obtained.



Scheme 3.14. Polymerization between bis(cyclopentadiene) **3.6** and bis(maleimide) **3.7**

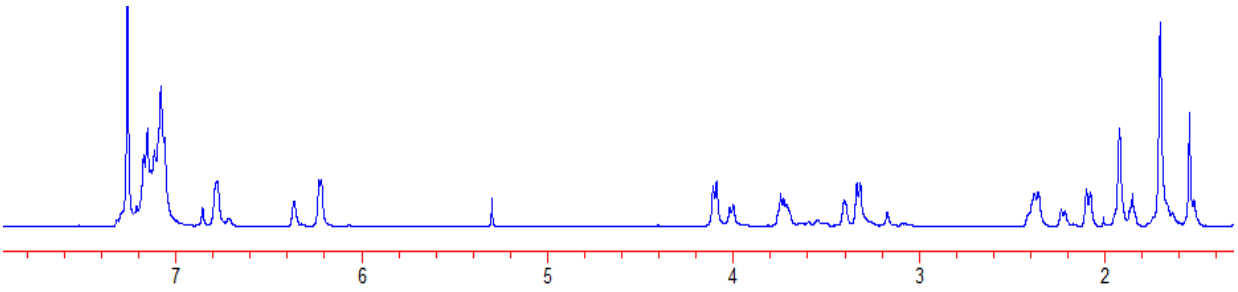


Figure 3.19. ^{1}H NMR spectrum of the polymer **3.10**

3.2.5.5. Polymer Characterization. The resulting polymer **3.10** is white in color and soluble in polar organic solvents like chloroform, ethyl acetate, acetone, dichloromethane, etc. SEC analysis in chloroform gave M_n = 15,400 g/mol (DP ~ 20) and M_w = 40,800 g/mol (PDI = 2.6). I don't have a good explanation for the broadening of the distribution relative to the theoretical value for a step growth polymerization. The PDI value was obtained reproducibly (two samples). One speculative possibility is that the kinked nature of the DA adduct allows some cyclic structures to form. A longer reaction time did not increase the molecular weight of the product polymer. The monomers were repurified very carefully and purification was confirmed by the NMR spectrometry. Polymerization was carried out with the repurified monomer with accurately 1:1 mol ratio. No improvement of the molecular weight was found. From the comparatively lower molecular weight of the polymer we came to the conclusion that the reaction has reached equilibrium. By the time we were analyzing our SEC data, preliminary depolymerization experiments (see below) had already showed that increasing the reaction temperature (even just to 80 °C) facilitates the rDA reaction. A better result may be obtained by continuing the reaction at a lower temperature for longer time, but in the long run the other obvious alternative (modifying the bis-diene structure) will probably be more effective. Ultimately the goal will be to find a combination of monomers that polymerizes and depolymerizes both under relatively mild conditions, but with a sufficient temperature difference between the onset of DA and of rDA to give us complete control over the equilibrium from one extreme (pure monomers) to the other (high molecular weight polymers).

3.2.5.6. Thermal Stability of the Polymer. The polymer **3.10** was also analyzed by thermogravimetric analysis (TGA, Fig 3.20) from 25 ^{o}C to 600 ^{o}C at 10 ^{o}C/min in a nitrogen atmosphere. There was a 10% weight loss at 290 ^{o}C, which we were not able to assign

unambiguously. The temperature seems too high to result from rDA depolymerization but seems closer to the temperatures that one might expect for other covalent bond-fragmentations. Again it must be pointed out that liberation of monomer into the gas phase requires rDA of two adjacent adducts and diffusion of

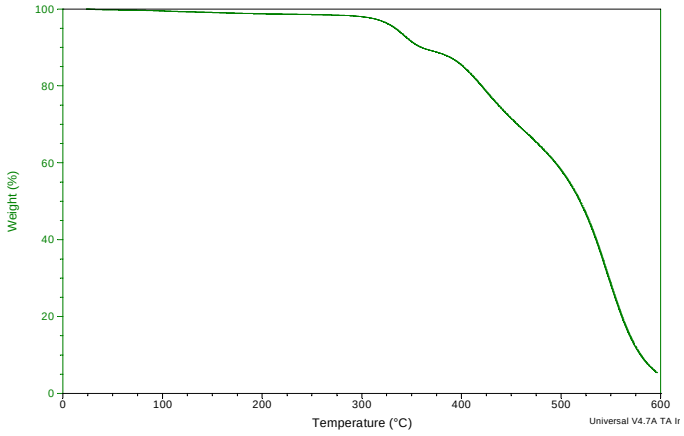
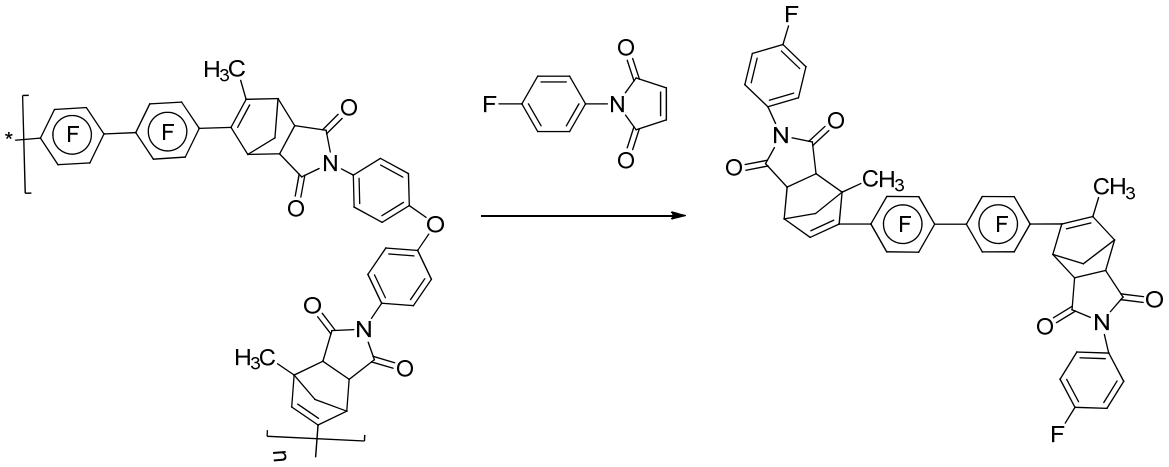


Figure 3.20. TGA trace of the polymer **3.10** taken under N_2 medium at 10 ^{o}C/min heating rate

the monomer through the bulk to the gas-solid interface. In another experiment, the polymer **3.10** was heated at 350 °C for 1 h. The resulting substance was completely insoluble in chloroform and could not be analyzed by solution NMR spectrometry, suggesting extensive degradation and cross-linking at this temperature.

3.2.5.7. Depolymerization of the Two Component Polymer 3.10. We reasoned that one way to study the depolymerization more rationally in solution was to introduce a trap for latent diene moieties unmasked by rDA processes (Scheme 3.15). The maleimide **3.8** provides a convenient way to monitor the progress of rDA/trapping by ^{19}F NMR spectrometry (Fig. 3.21). The 4-fluorophenyl group showed a downfield shift upon reaction as shown in the preceding section. A sample of



Scheme 3.15 Depolymerization in the presence of trapping agent **3.8**

polymer **3.10** combined with fifteen times excess of the maleimide trap **3.8** was slowly warmed in o-dichlorobenzene solvent. Large excess of **3.8** was required for higher conversion (LeChatelier's Principle). At 80 °C slow conversion of the trap was evident in the NMR spectrum. Upon increasing the temperature to 90 ^{o}C the depolymerization was complete in 12 h. A similar result was obtained when the model chemistry experiment was executed at 90 °C.

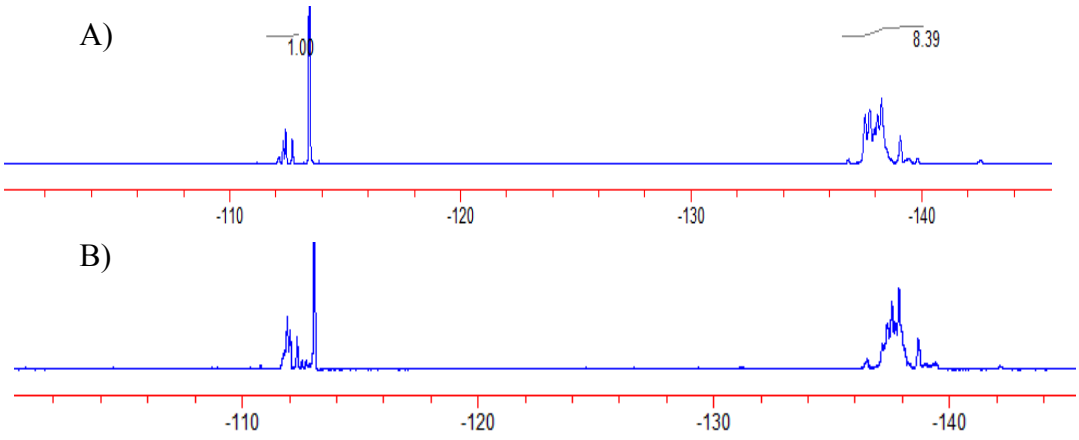


Figure 3. 21. A) ^{19}F NMR spectrum after the depolymerization B) ^{19}F NMR spectrum of the model compound synthesized by heating at 90 ^{o}C for 12 h

^{19}F NMR spectrum (Fig 3.21 A) of the depolymerized trapped compound showed the integration between the peak for 4-fluorophenyl group (-112 to -112.5 ppm) to the aromatic fluorines (-137 to -140 ppm) as 1:8. This result suggested mostly dimmers are formed during this depolymerization reaction.

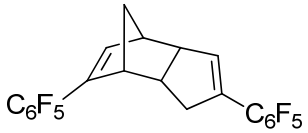
3.3. Experimental.

3.3.1. Materials and Methods. Decafluorobiphenyl and hexafluorobenzene were used as received from Matrix Scientific. THF (VWR, inhibitor-free HPLC grade) was purified by passage through a column of 4 Å molecular sieves. o-Dichlorobenzene was purified by distilling from calcium hydride under reduced pressure. Benzene and ethyl acetate were used as obtained from Fisher Scientific. Sodium cyclopentadienide and sodium methylcyclopentadienide were synthesized by published methods.[67, 68] 4,4-Diaminodiphenyl ether, 4-fluoroaniline, and maleic anhydride were obtained commercially (Aldrich) and used as received. Penta(fluorophenyl)cyclopentadienide (**3.1**) and monomer (**3.4**) were prepared according to a published procedure.[63, 64] The identities and purity of the compounds were confirmed by comparing the ^{1}H and ^{19}F NMR data ($CDCl_3$, 400 MHz instrument) to the literature value. The bis(maleimide) monomer (**3.7**) was synthesized as reported earlier.[66] N-(4-fluorophenyl)maleimide (**3.8**) was prepared by Michael E. Russell, an undergraduate co-worker, according to a published method.[69]

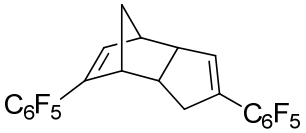
Instrumentation. Size exclusion chromatography (SEC) in chloroform was carried out with an Alliance Waters 2690 Separations Module equipped with a Viscotek T60A dual viscosity detector and laser refractometer and a Waters HR 0.5 + HR 2 + HR 3 + HR 4 styragel column set at 30 °C. Polystyrene standards were used to construct a universal calibration curve to obtain absolute molecular weights. NMR spectra were recorded on Varian Unity-400 or Inova-400 instruments. Mass spectra (HRMS) were obtained using an Agilent 6220 (ESI-TOF). TGA studies used a TA Instruments Q–500 under a nitrogen atmosphere with a heating rate of 10 ^{o}C/min.

3.3.2. Synthesis

Synthesis of Cyclopentadiene Dimer 3.3.



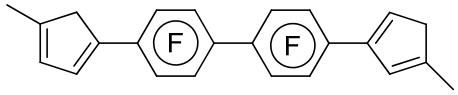
3.3a



3.3b

(Pentafluorophenyl)cyclopentadiene (**3.1**, 400 mg, 1.76 mmol) was dissolved in benzene (10 mL) and heated at 65 ^{o}C for 72 h. Reaction progress was monitored by examining the ^{1}H NMR spectrum and continued until all the original vinylic peaks at 6.94, 6.64, 6.48, 6.34 and 6.23 ppm disappeared. The solvent was evaporated under reduced pressure, and the product was purified by silica gel chromatography (hexane) to afford a white solid (382 mg, 95%). ^{19}F NMR spectroscopic analysis showed that the product is a mixture of two isomers, which were separated by fractional crystallization from methanol. Major isomer (70% of the product): ^{1}H NMR (C_6D_6): δ 6.31 (s, 1H), 5.76 (s, 1H), 3.29 (s, 1H), 3.11 (s, 1H), 2.71 (s, 1H), 2.56 (s, 1H), 2.39 (m, 1H), 1.92 (d, J = 16 Hz, 1H), 1.58 (d, J = 8 Hz, 1H), 1.07 (d, J = 8 Hz, 1H). ^{19}F NMR (C_6D_6): δ −141.30 (d, 1F), −141.74 (d, 1F), −157.43 (m, 1F), −163.62 (m, 2F). Minor isomer (30% of the product) ^{1}H NMR (C_6D_6): δ 6.36 (s, 1H), 5.76 (s, 1H) 3.22 (s, 1H), 3.12 (s, 1H), 2.71 (s, 1H), 2.56 (s, 2H), 1.92 (d, J = 8 Hz, 1H), 1.57 (d, J = 8 Hz, 1H), 1.07 (d, J = 8 Hz, 1H), ^{19}F NMR(C_6D_6): −141.30 (d, 2F), −141.94 (d, 2F), −157.34 (t, 1F), −157.91 (t, 1F), −163.62 (t, 2F), −164.65 (t, 2F).

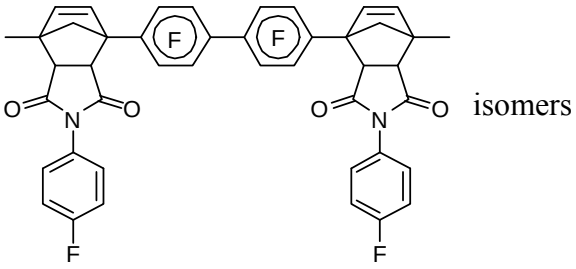
Synthesis of bis(cyclopentadiene) 3.6.



Isomers

A mixture of sodium methylcyclopentadiene (2 g, 20 mmol), sodium hydride (400 mg, 17 mmol), decafluorobiphenyl (1.0 g, 3.0 mmol), and THF (25 mL) was heated at reflux for 2.5 h. The reaction may be followed by ^{19}F NMR spectrometric analysis of worked-up aliquots and continued until the spectrum of the crude product shows the absence of *para* signals (ca. −149 ppm). After an acidic aqueous workup, the crude product was purified (silica gel chromatography, hexane) to afford a white solid (330 mg, 75%). The following NMR spectra represent mixtures; relative integral values are not normalized. ^{1}H NMR ($CDCl_3$): δ 7.22 (s, 2H), 6.65 (s, 1H), 6.53 (s, 2H), 6.39 (s, 2H), 6.33 (s, 4H), 6.29 (s, 2H), 3.56 (s, 4H), 3.50 (s, 8H), 3.42 (s, 2H), 3.18 (s, 4H), 2.18 (s, 12H), 2.09 (m, 10H), 2.02 (s, 3H). ^{19}F NMR ($CDCl_3$): δ -137.25 (m, 2F), -139.56 (m, 3F), -140.07 (m, 3F), -140.34 (m, 4F), -140.55 (m, 2F), -141.04 (m, 4F).

Model DA reaction.



isomers

A solution of bis(cyclopentadiene) **3.6** (252 mg, 0.54 mmol) and N-(4-fluorophenyl)maleimide (**3.8**, 218 mg, 1.14 mmol) in benzene (8 mL) was heated at 60 ^{o}C for 20 h. The reaction medium was then cooled and added to rapidly stirred hexane to precipitate the product. The resulting white solid was collected on a filter and air-dried. Chromatographic separation of the mixture

was made difficult by the tendency of the maleimides to undergo some slow irreversible binding reaction with the stationary phase (silica gel). Nevertheless three fractions were obtained. The first fraction, eluted with 1:2 ethyl acetate:hexane, afforded unreacted **8**. The second fraction, eluted with 1:1 ethyl acetate:hexane, afforded 264 mg (60%) of the major product isomer. ^{1}H NMR (C_6D_6): δ 7.07 (m, 2H), 6.73 (t, 2H), 6.40 (br, 1H), 5.69 (d, *J = 8*, 1H), 3.38 (m, 1H), 2.39 (d, *J = 8*, 1H), 1.66 (m, 1H), 1.52 (d, J = 8, 1H) 1.33 (s, 3H). ^{19}F NMR ($CDCl_3$): δ -112.75 (s, 1F), -137.36 (m, 2F), -138.05 (m, 2F). The third fraction, also eluted with 1:1 ethyl acetate:hexane, gave 105 mg (14%) of product that was still a mixture of isomers. ^{1}H NMR ($CDCl_3$): δ 7.06, 6.73, 6.40, 6.04, 5.70, 3.40, 3.26, 2.73, 2.40, 1.66, 1.33, ^{19}F NMR ($CDCl_3$): δ −112.78 (s, 1F), −137.17 (m, 2F), −137.40 (m, 2F), −138.06 (m, 4F). HRMS (sample to be submitted shortly).

Homopolymerization Reaction. A solution of bis(cyclopentadiene) monomer **3.4** (500 mg, 1.2 mmol) in benzene (10 mL) was heated at 65 ^{o}C for 5 d. The reaction was monitored by ^{1}H NMR spectroscopy and continued until the vinylic signals for **3.4** at 6.34 and 6.26 ppm disappeared. The polymer was recovered by precipitation from hexane, filtration, and air-drying. A yield of 94% was obtained. ^{1}H NMR (C_6D_6): δ 6.53 (s, 1H), 5.81 (s, 1H), 3.41 (s, 1H), 3.13 (s, 1H), 2.74 (s, 1H), 2.60 (s, 1H), 2.38 (s, 2H), 2.09, 1.20 (s, 1H), 1.10 (s, 1H). ^{19}F NMR ($CDCl_3$): δ −139.86 to −140.98 (br, m). SEC analysis gave M_n = 11,000 g/mol and PDI = 1.7.

Two-Component DA Polymerization. A mixture of methylated bis(cyclopentadiene) **6** (150 mg, 0.33 mmol), bis(maleimide) **7** (119 mg, 0.33 mmol), and 1,2-dichlorobenzene (6 mL) was heated at 50 ^{o}C for 24 h. The reaction was monitored by ^{1}H NMR spectroscopy and continued until the peak at 7.32 ppm (corresponding to the bis-maleimide) almost disappeared. The reaction mixture was cooled and precipitated in hexane to afford 242 mg (94%) of a white solid.

^{1}H NMR ($CDCl_3$): δ 7.13, 6.86, 6.78, 6.72, 6.37, 6.22, 4.10, 4.01, 3.74, 3.58, 3.40, 3.33, 3.17, 2.37, 2.33, 2.09. These signals are only partly resolved in most cases; the assignment of integrals and multiplicities is not practical. ^{19}F NMR ($CDCl_3$): −137.82 to −138.86. SEC gave M_n = 15,400 g/mol and M_w = 40,800 g/mol (PDI = 2.6).

Depolymerization of 5 by FVT. Fig 1. showed our simple FVT apparatus. The two-necked flask and transfer bridge were heated at ca. 170 ^{o}C, while the receiving side-arm flask was cooled using dry ice. After applying a vacuum (0.1 mmHg), a solution of the polymer **3.5** in C_6D_6 was injected in small portions through a rubber septum into the heated two-neck flask with a syringe. Volatiles collected in the cooled flask and were recovered as a C_6D_6 solution for ^{1}H and ^{19}F NMR spectroscopic analysis. NMR spectra were presented in Fig. 3.12.

Depolymerization and Trapping Experiment with Polymer 3.10. The depolymerization reaction was followed by heating the polymer 7 mg of **3.10** in presence of excess (20.0 mg) capping reagent **3.8** in *o*-dichlorobenzene as the solvent at 90 ^{o}C for 12 h. The reaction was monitored by ^{19}F NMR, as trapping of latent cyclopentadiene groups by the fluorinated maleimide reagent is detected by a downfield shift of the *N*-4-fluorophenyl group.

3.4.1. Conclusion

Conclusion. This chapter demonstrates the synthesis and initial characterizations of fluorine-containing reversible polymers. First a homopolymer was successfully synthesized from an octafluorobiphenylene-linked bis(cyclopentadiene). The thermal reversibility was shown by flash vacuum thermolysis, however the reversion to monomer is not efficient and is accompanied by extensive decomposition. In response to those findings, we developed a modified polymerization method in which a related bis(cyclopentadiene) reacted with a bis(maleimide) monomer in a Diels-Alder step growth process. The reversibility of this polymer is more readily investigated because it is not nearly so troubled by unwanted side-reactions. The reversion to monomer was demonstrated by heating the polymer in the presence of a compound known to trap the diene moieties as they are released from the polymer.

3.5. Future Work.

3.5.1. Determination of the Polymer Structure. Though I have synthesized the polymer successfully and shown its reversibility, its structure is not known completely. In the model reaction I have shown that more than one isomer is forming depending on the structure of the starting bis(cyclopentadiene). I managed to separate one isomer from the mixture and characterize it. However at present we still can only assume that the Diels-Alder adducts in the polymer are in the *endo* configuration. Attempts to isolate different species using simple silica gel chromatography were unsuccessful. Other chromatographic methods such as preparative reverse-phase HPLC might be better but we do not have this capability in our laboratory. Ultimately we probably need to switch to a monomer system in which there are fewer isomers to start with, to ease both product separations and characterizations of mixtures.

3.5.2. Other Monomer Systems. During the synthesis of thermally reversible polymers I did not get a degree of polymerization more than 20. One reason behind it might be the reversibility of the reaction at polymerization temperature. The temperature window should be large enough to stop depolymerization during polymerization. An undergraduate student in the Deck Group, Michael E. Russell, is working on an analogous system based on *tert*-butylcyclopentadiene. His system has the advantage of regiocontrol in the attachment of the octafluorobiphenylene linker: Substitution vicinal to the *tert*-butyl group is avoided. Mr. Russell's monomer has the additional advantage that its synthesis was already fully described in the doctoral dissertation of Jessica P. Evans. However Mr. Russell has also found that the temperature required to polymerize *tert*-butylcyclopentadiene with **3.7**is relatively high (above 140 °C). Another undergraduate student, Rachele C. Piemonte, is attempting to balance the advantages and disadvantages of a bulky alkyl substituent by switching to isopropylcyclopentadiene. Her work is just underway however and we don't know yet whether that adjustment will retain the regioselectivity of arylation while increasing monomer reactivity. I believe these are the right directions to be taking this project at the present time.

3.6. References

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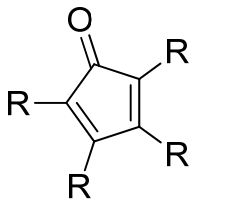
Appendix

NMR Spectra

1.8



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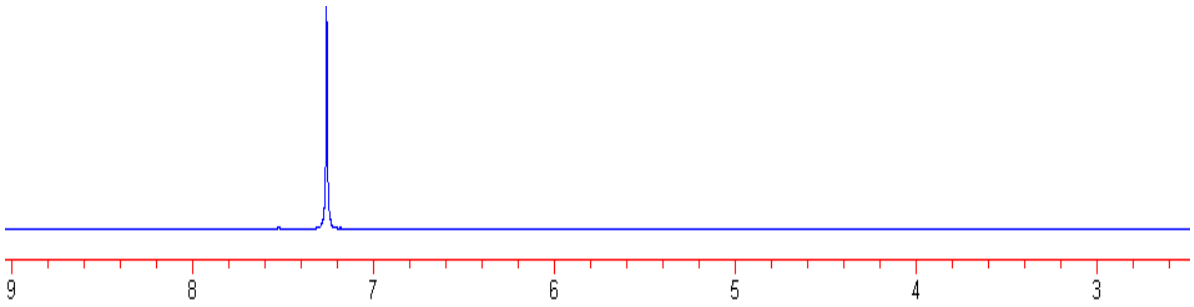
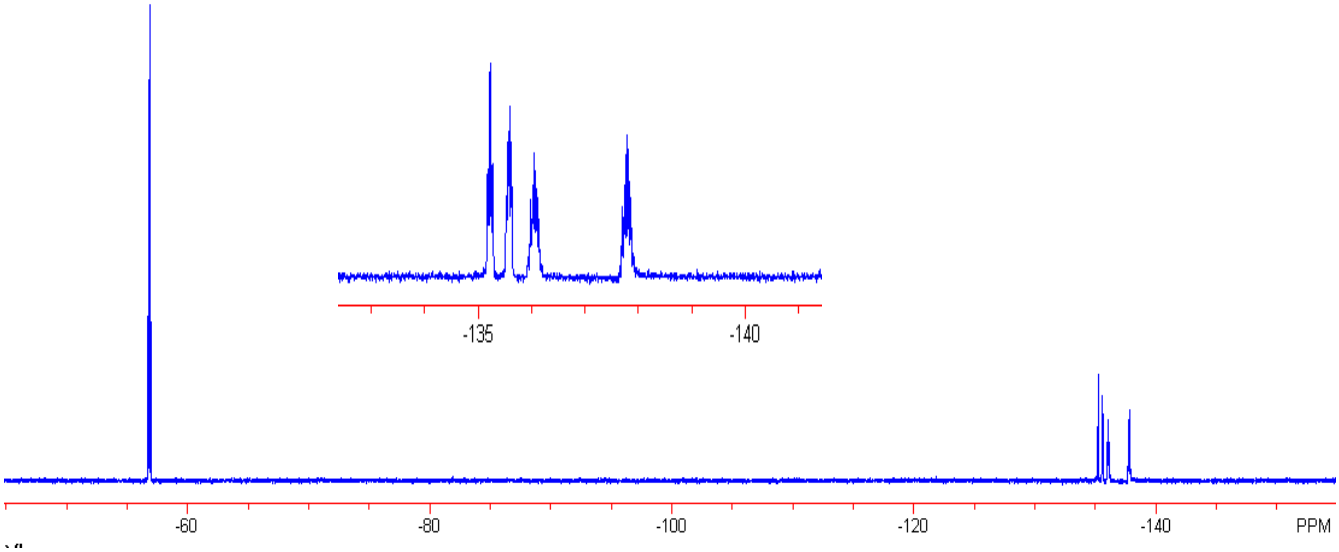
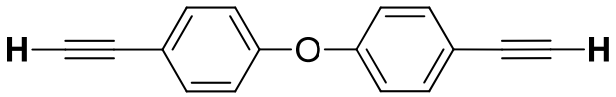


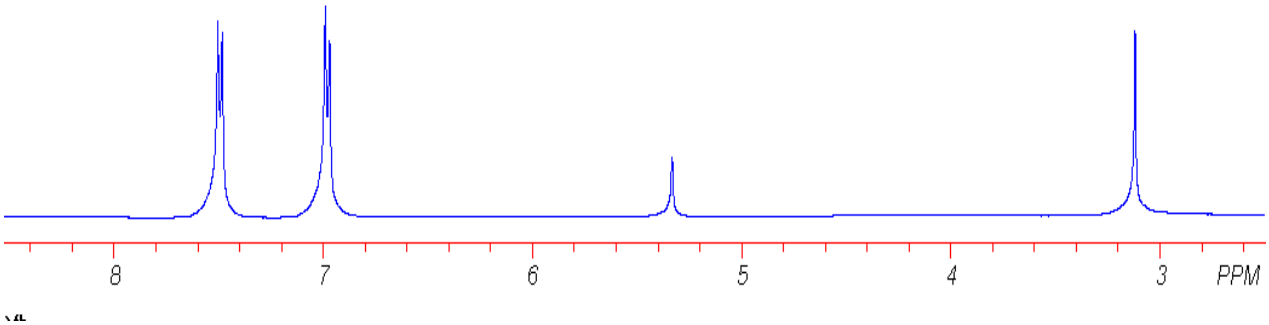
^{1}H NMR



^{19}F NMR

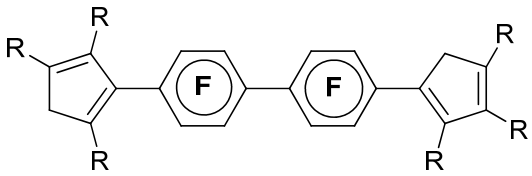
1.7

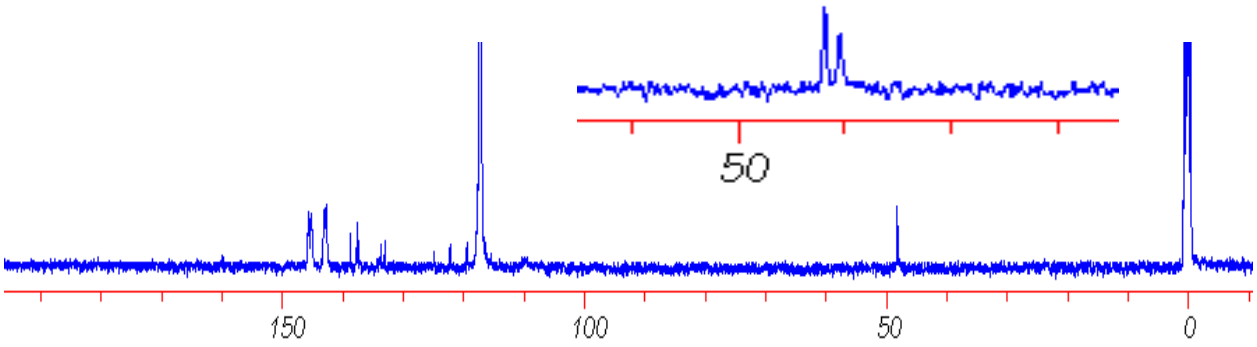




^{1}H NMR

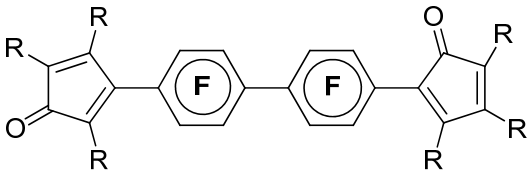
1.3

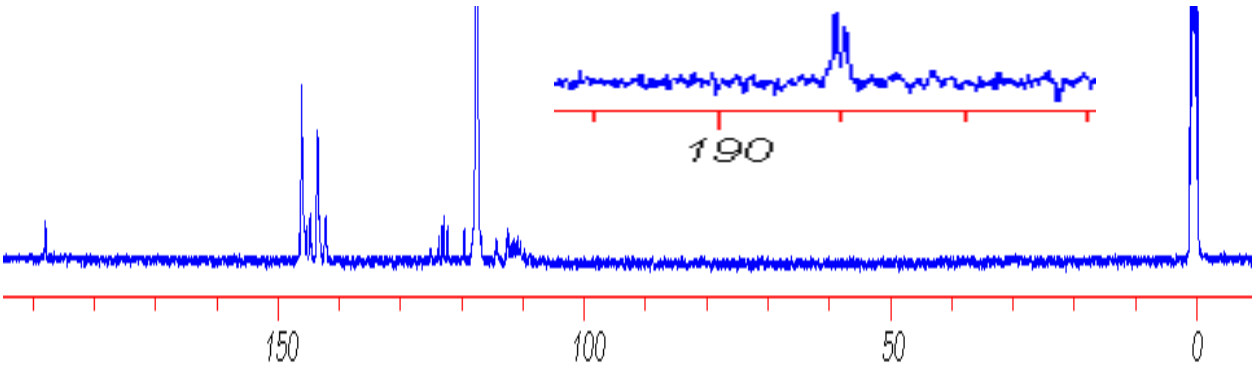




^{13}C NMR

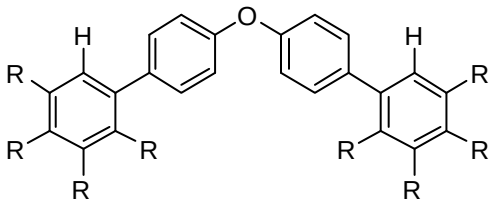
1.4

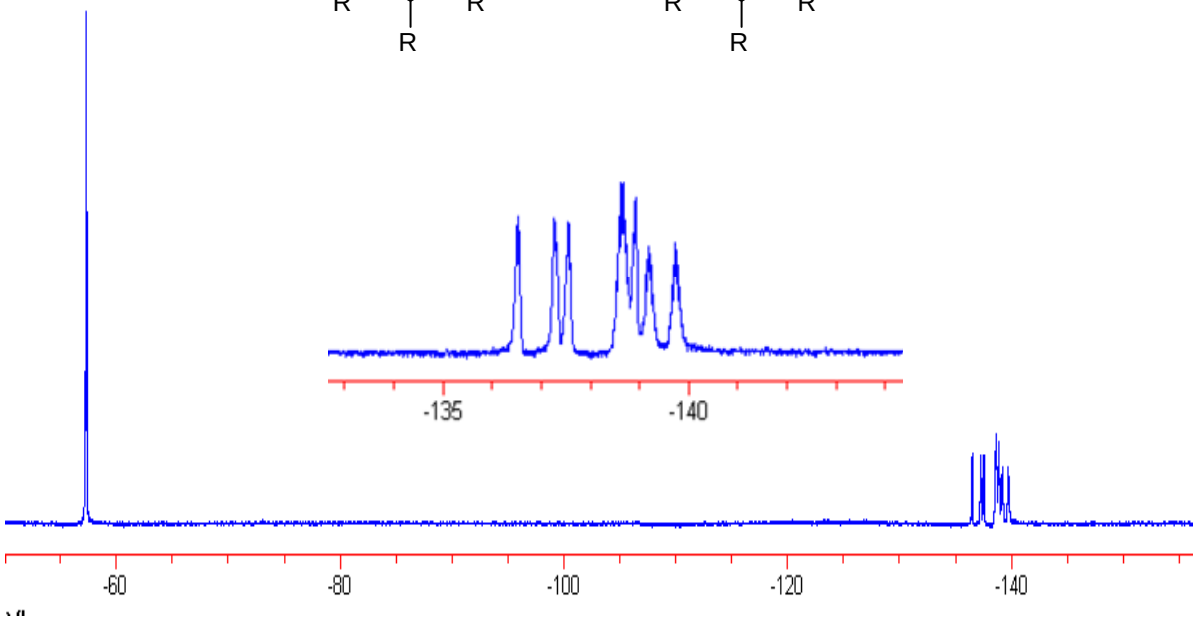




^{13}C NMR

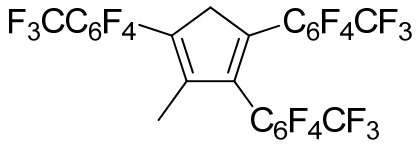
1.9



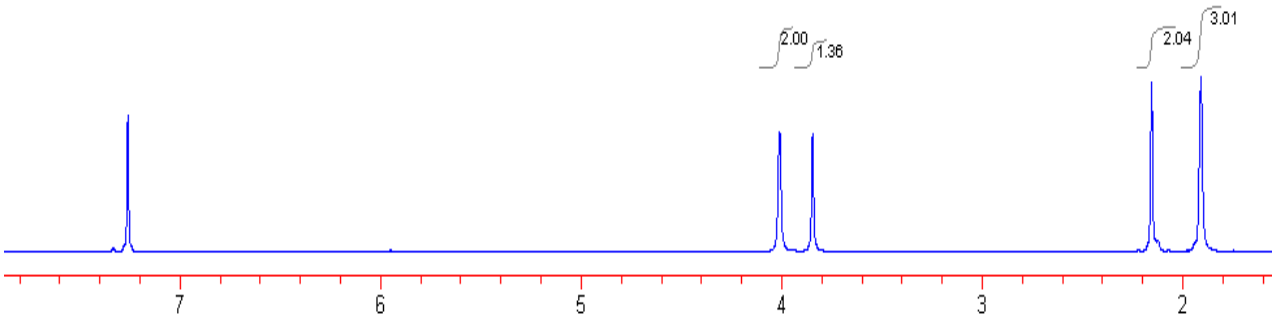


^{19}F NMR

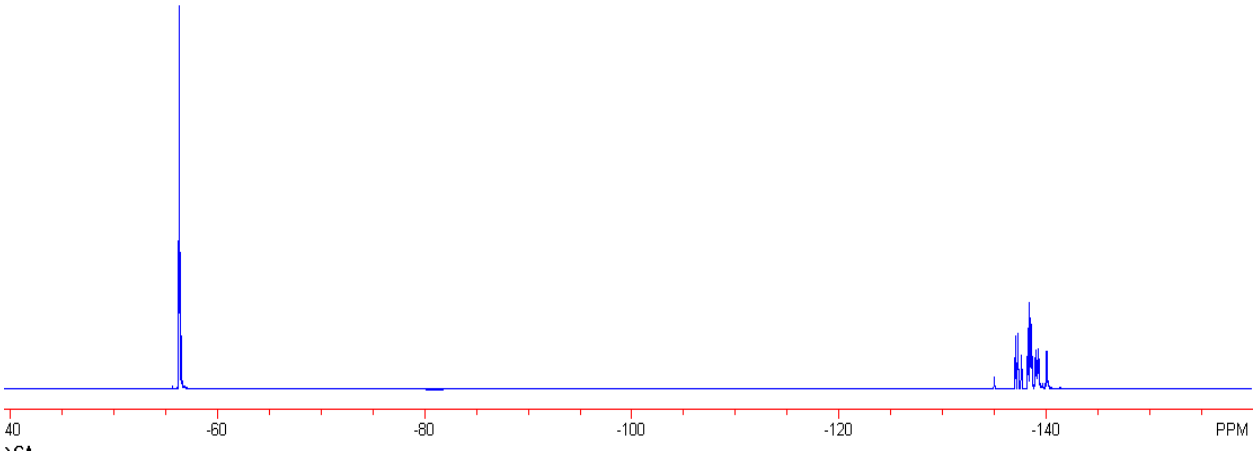
2.9



isomers

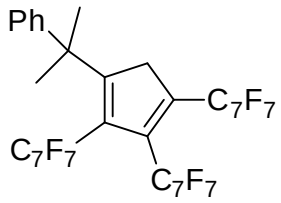


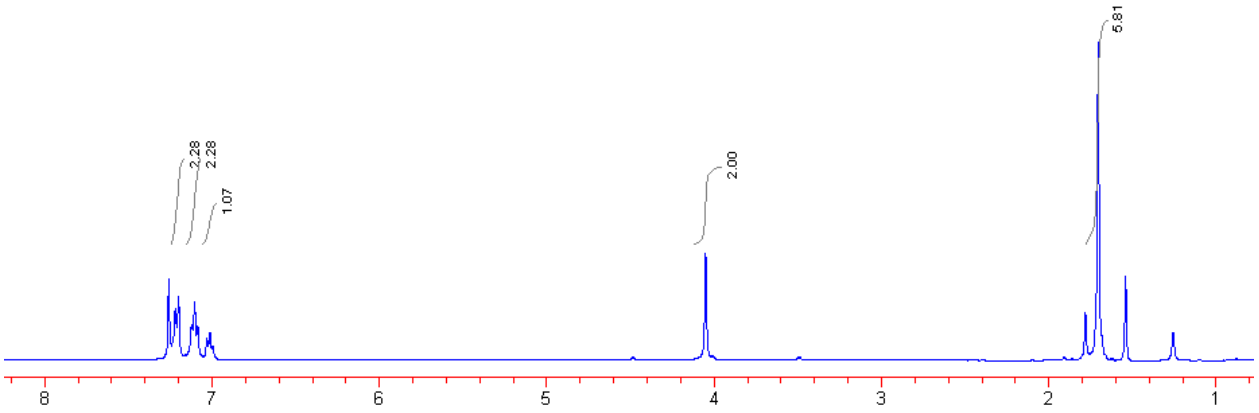
^{1}H NMR



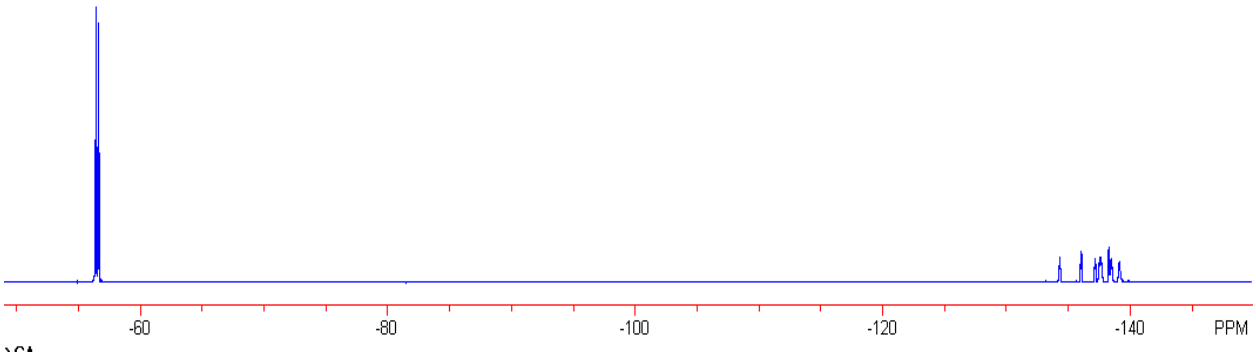
^{19}F NMR

2.10


Ph
C7F7
C7F7
C7F7


2.28
2.28
1.07
2.00
5.81
8
7
6
5
4
3
2
1

^{1}H NMR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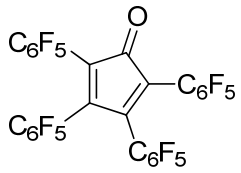
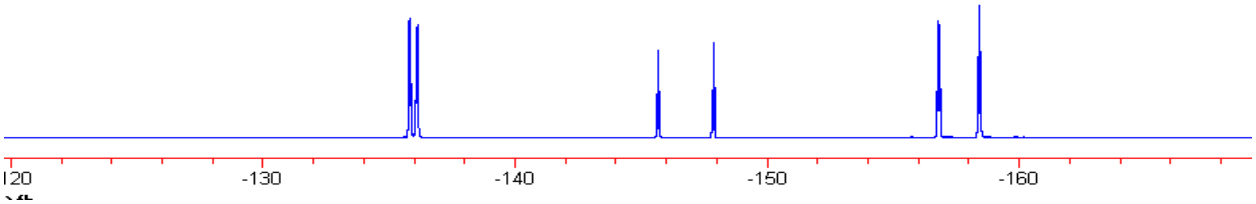
-80
-100
-120
-140
PPM

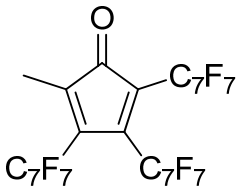
2.15



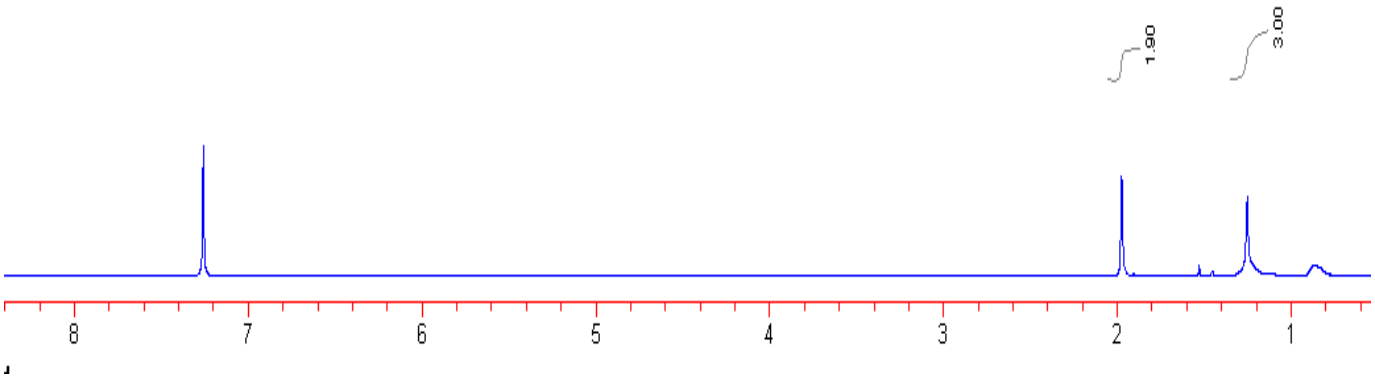


^{19}F NMR

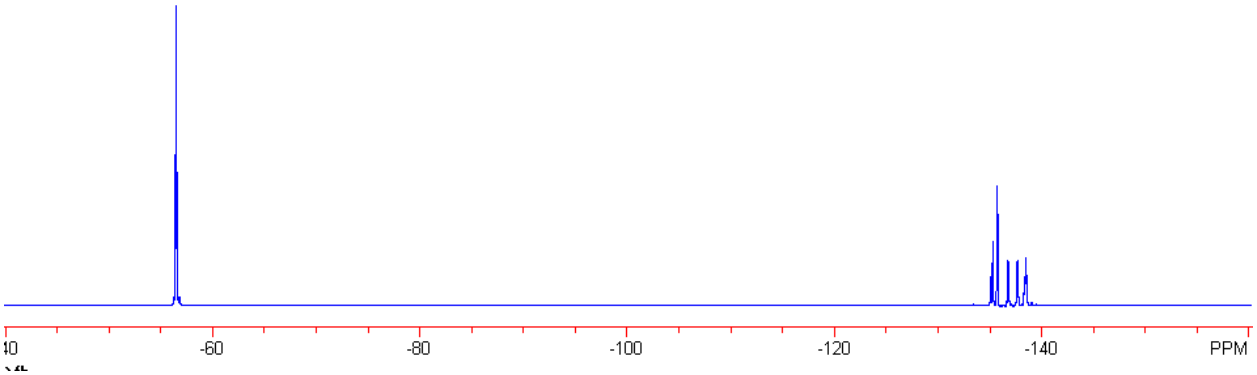
2.18



Isomers

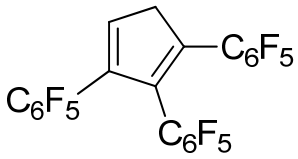


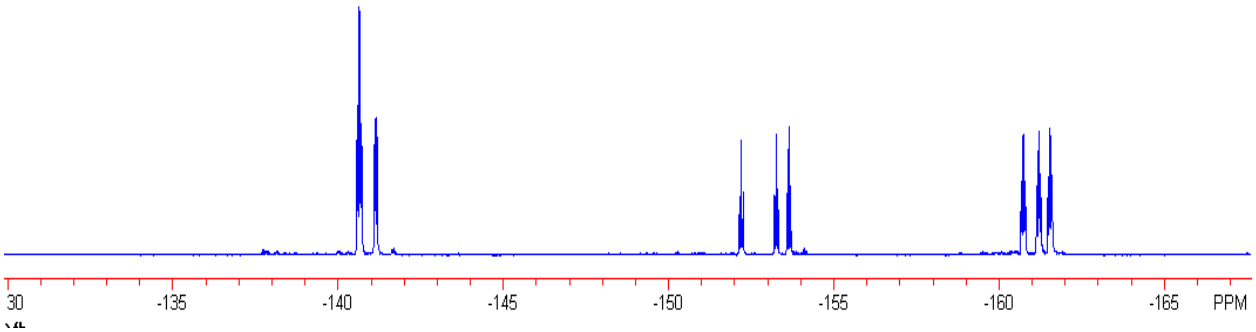
^{1}H NMR



^{19}F NMR

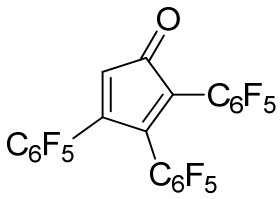
2.2

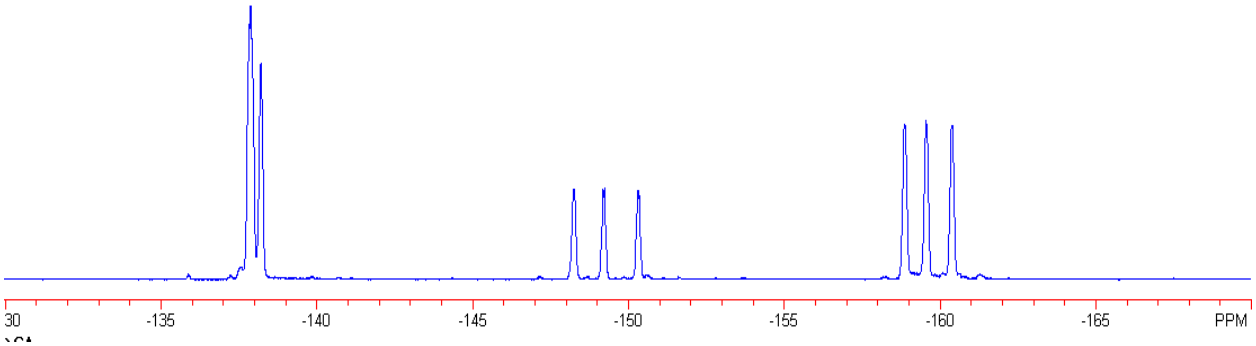




^{19}F NMR

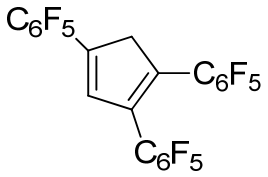
2.13

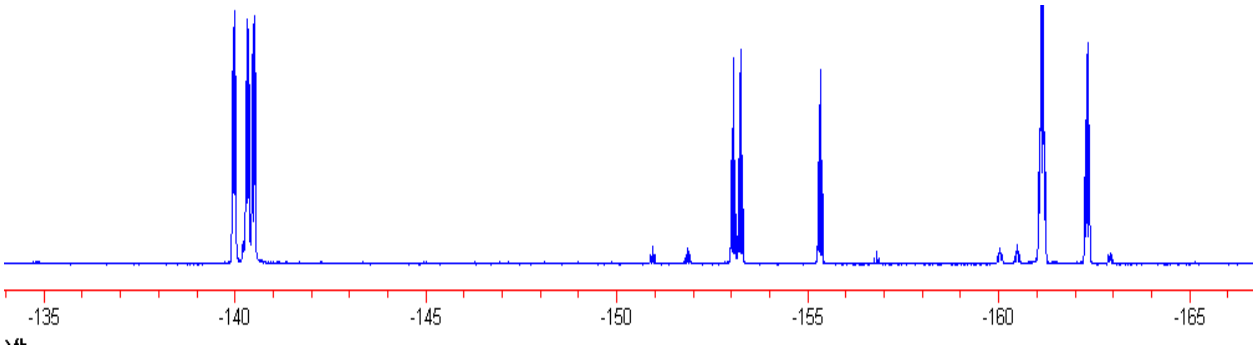




^{19}F NMR

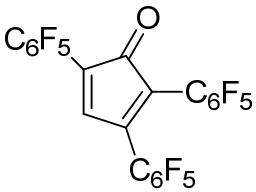
2.3

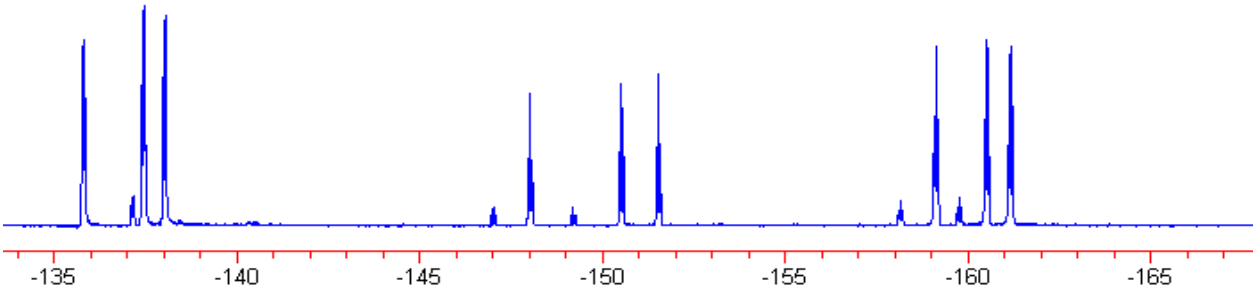




^{19}F NMR

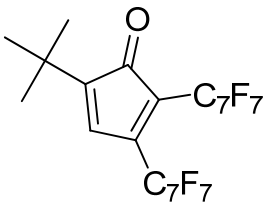
2.14

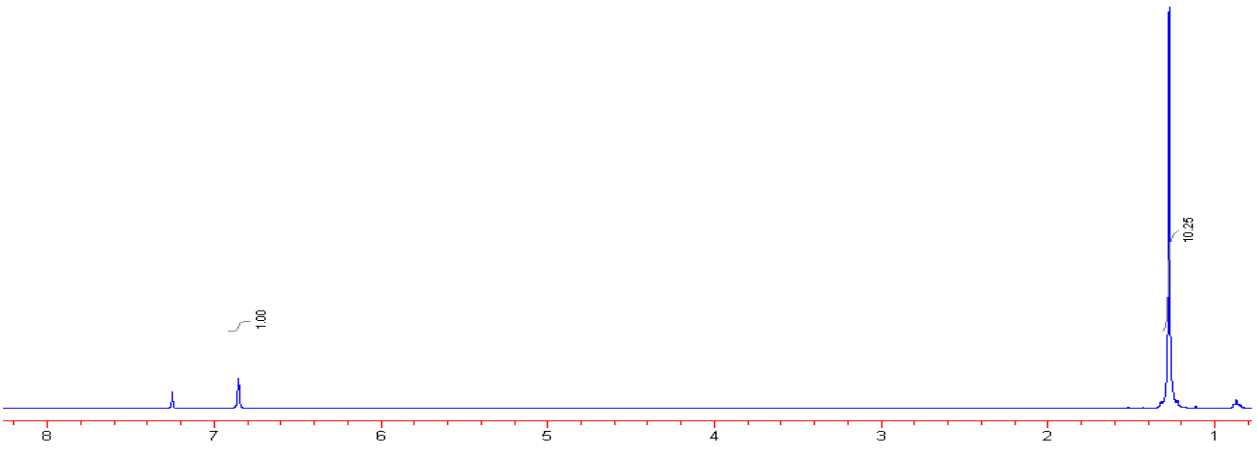




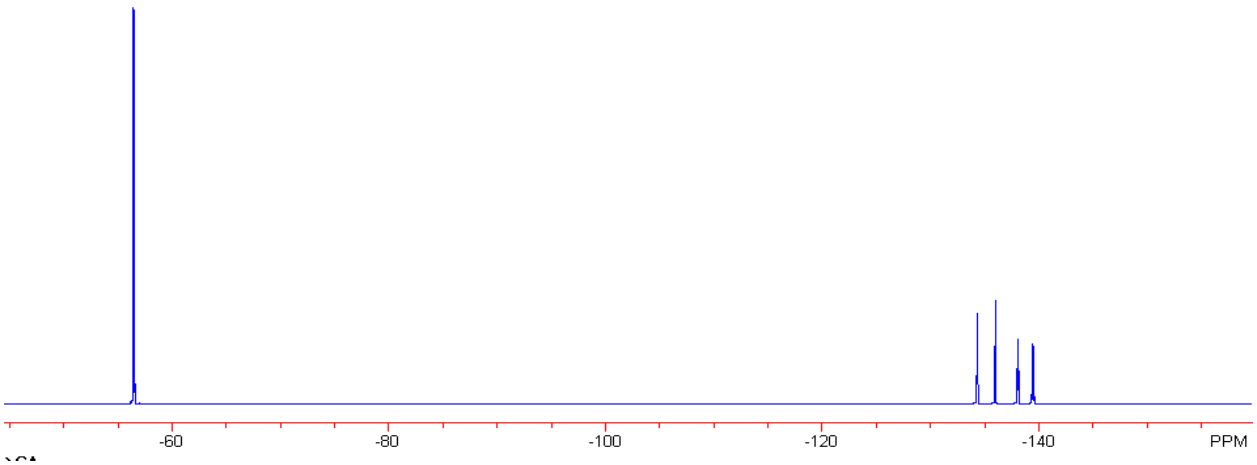
^{19}F NMR

2.17



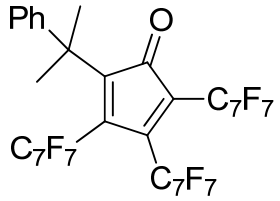


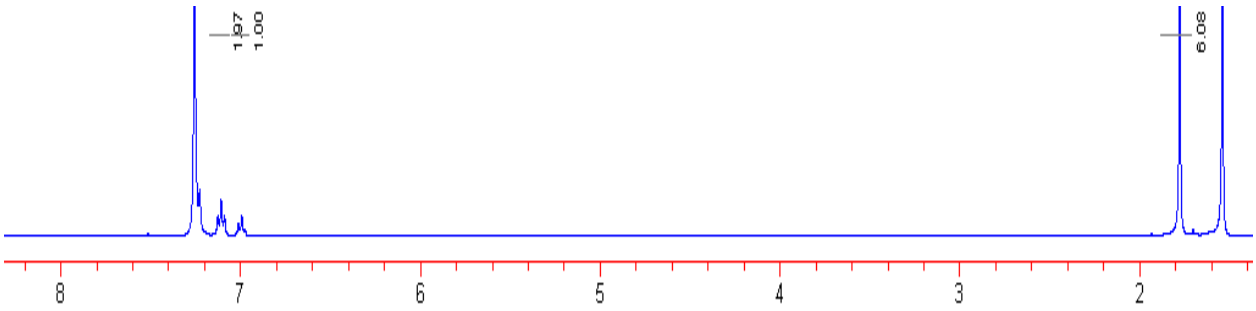
^{1}H NMR



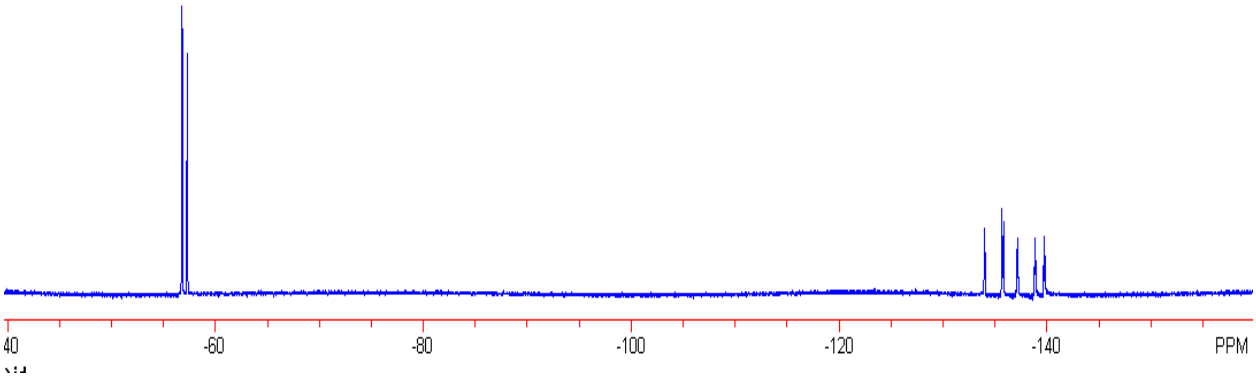
^{19}F NMR

2.19



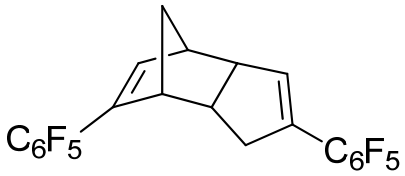


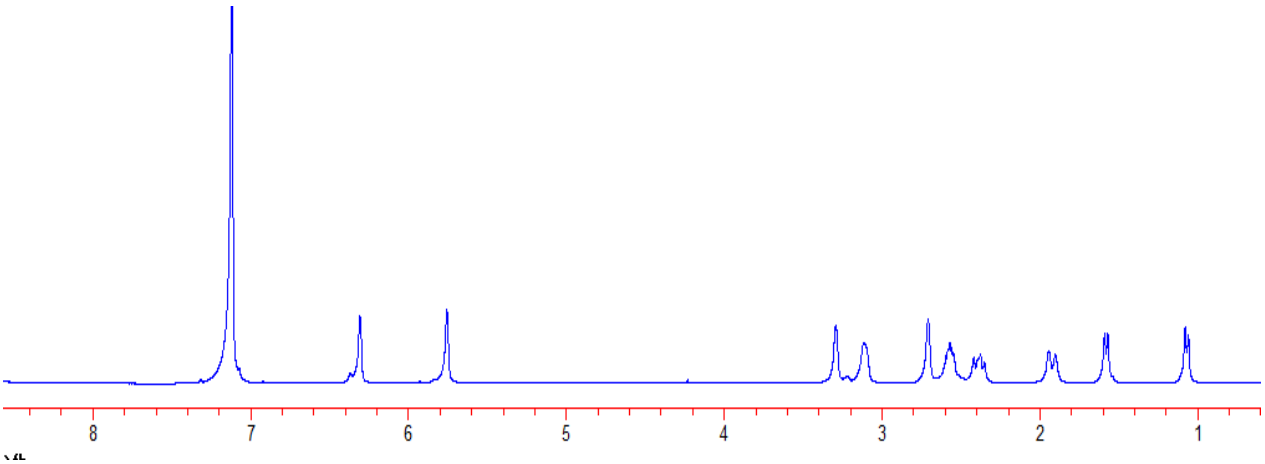
^{1}H NMR



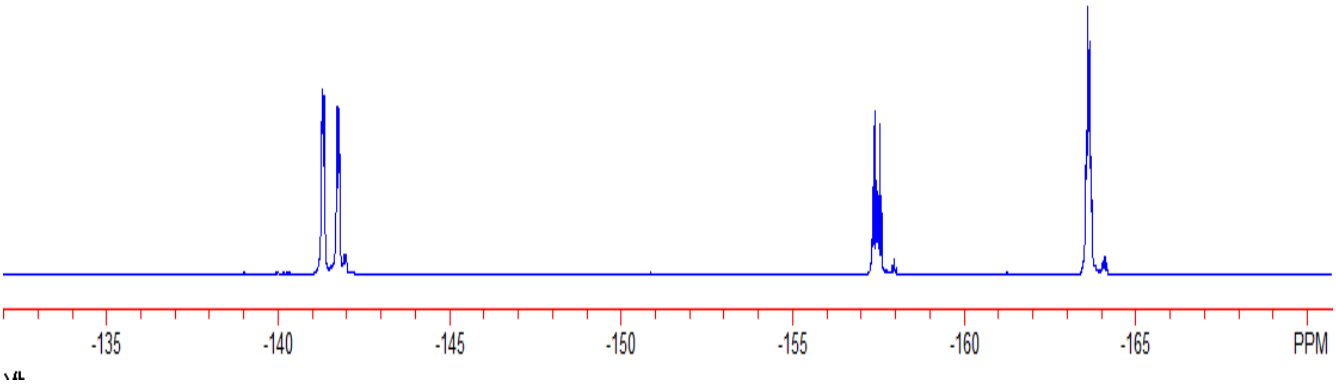
^{19}F NMR

3.3a



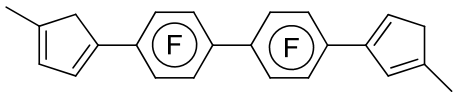


^{1}H NMR

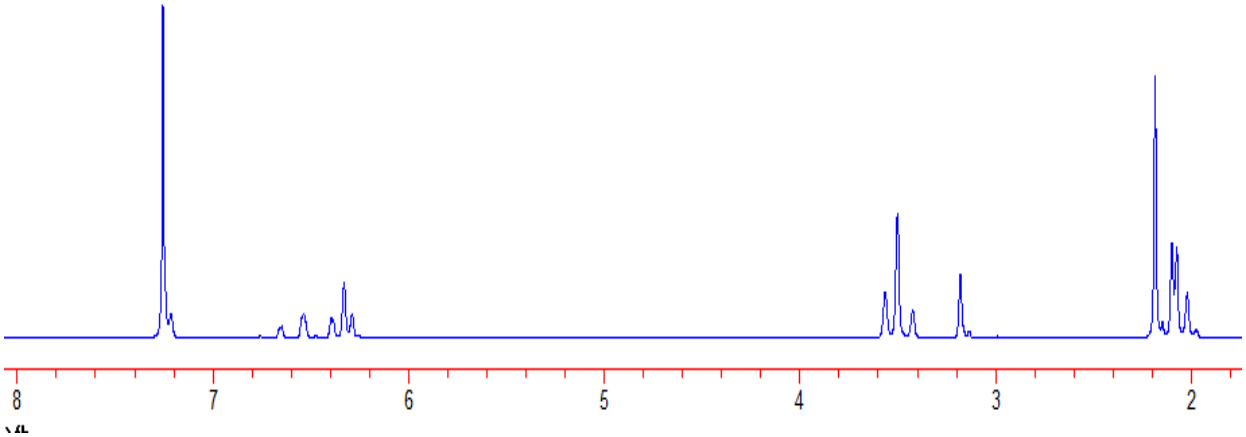


^{19}F NMR

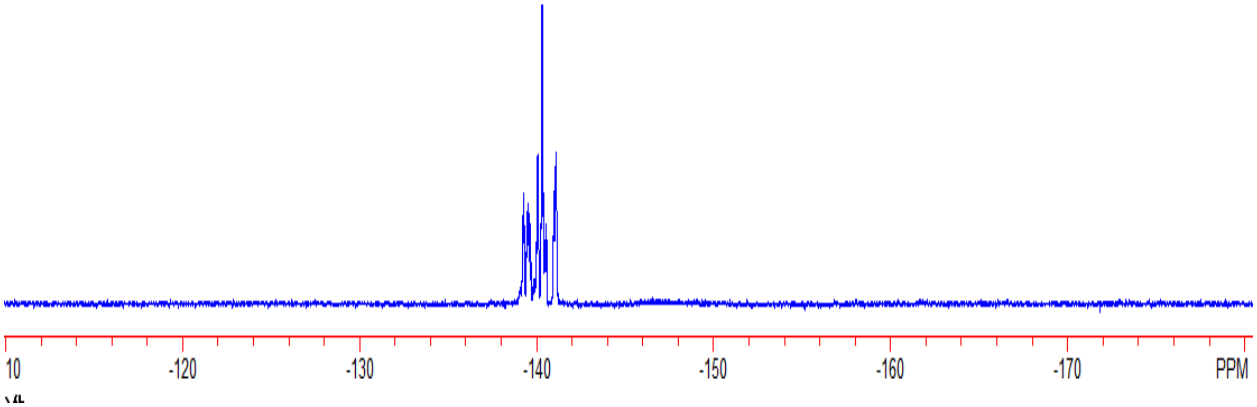
3.6



Isomers

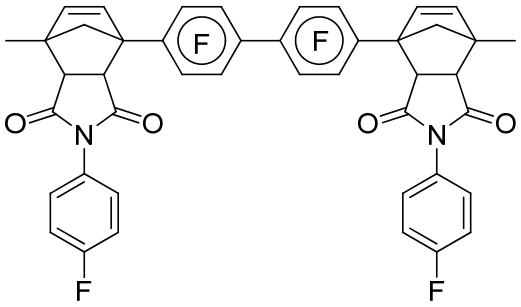


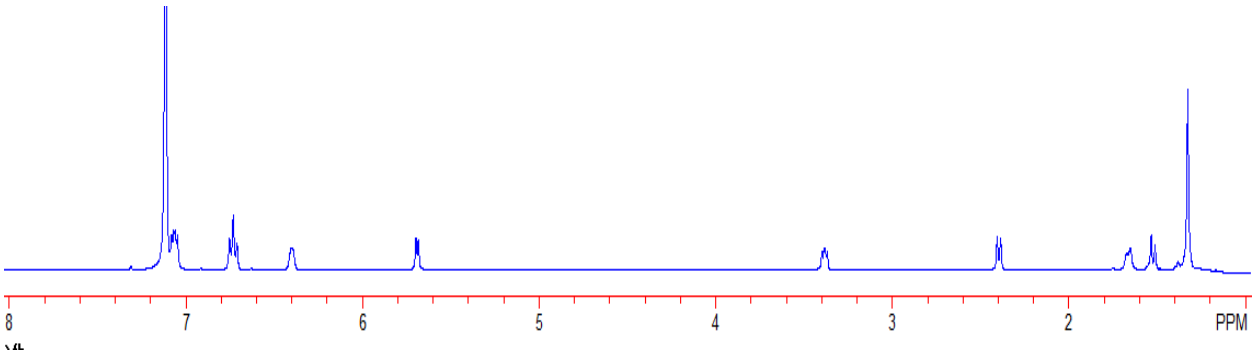
^{1}H NMR



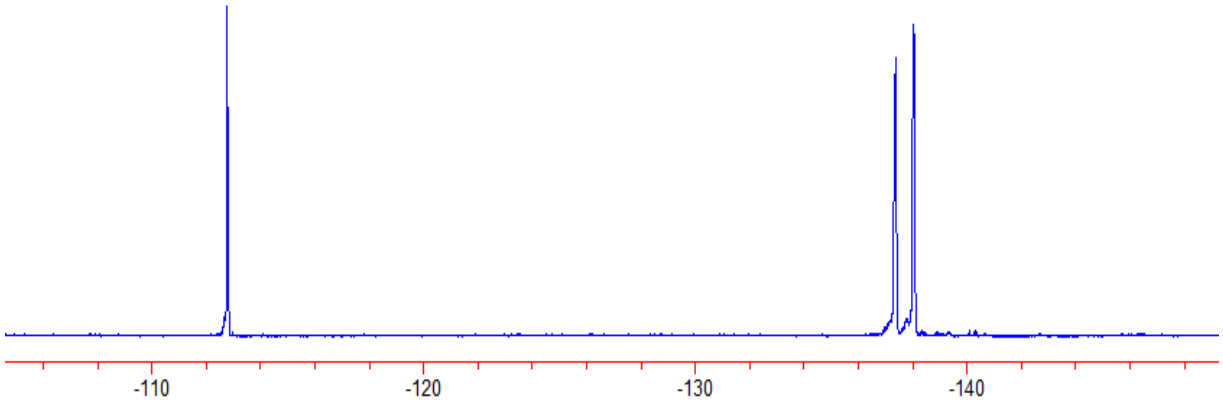
^{19}F NMR

3.9a



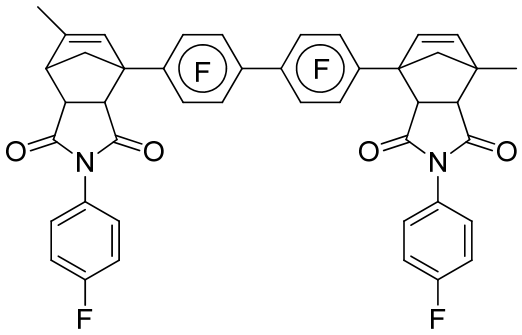


^{1}H NMR

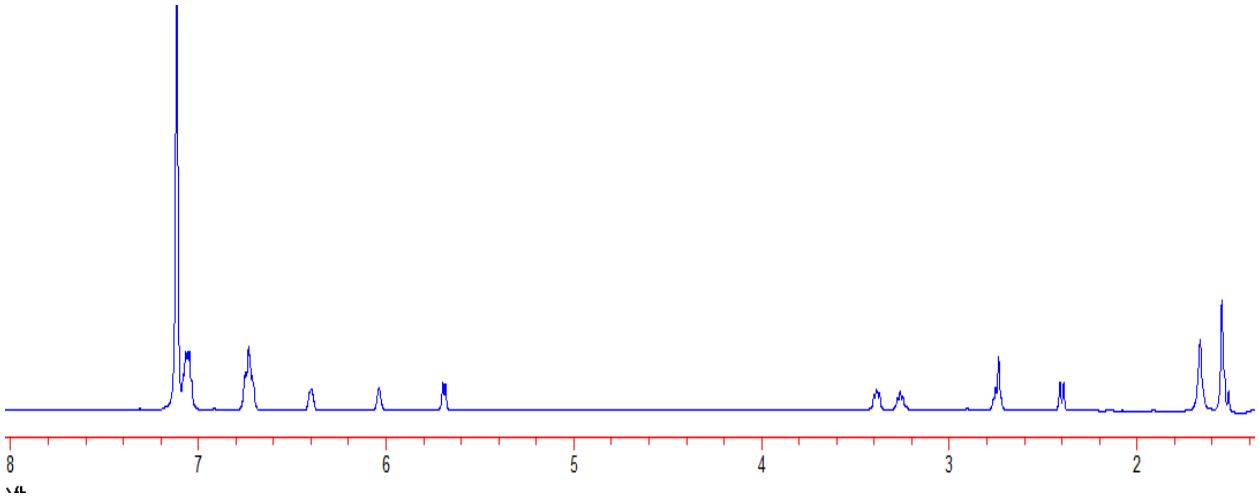


^{19}F NMR

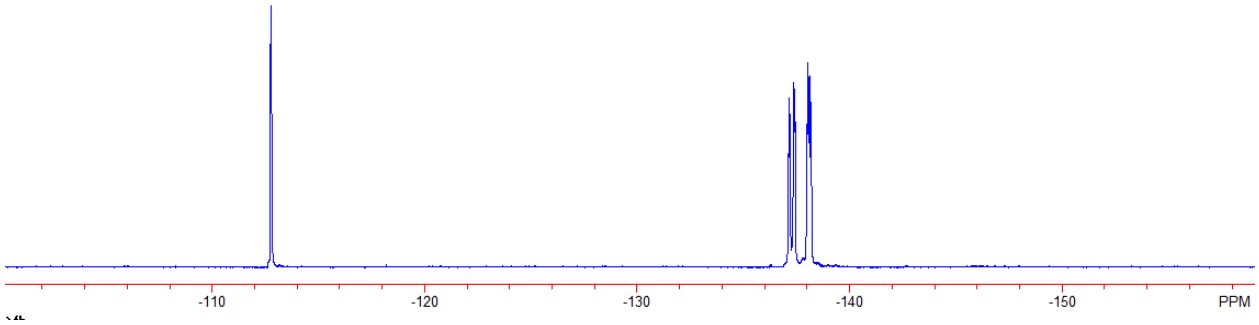
3.9



Isomeric mixture

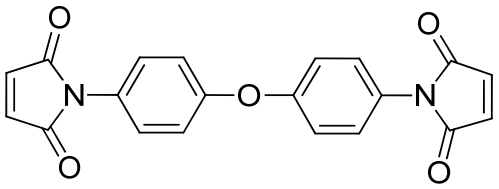


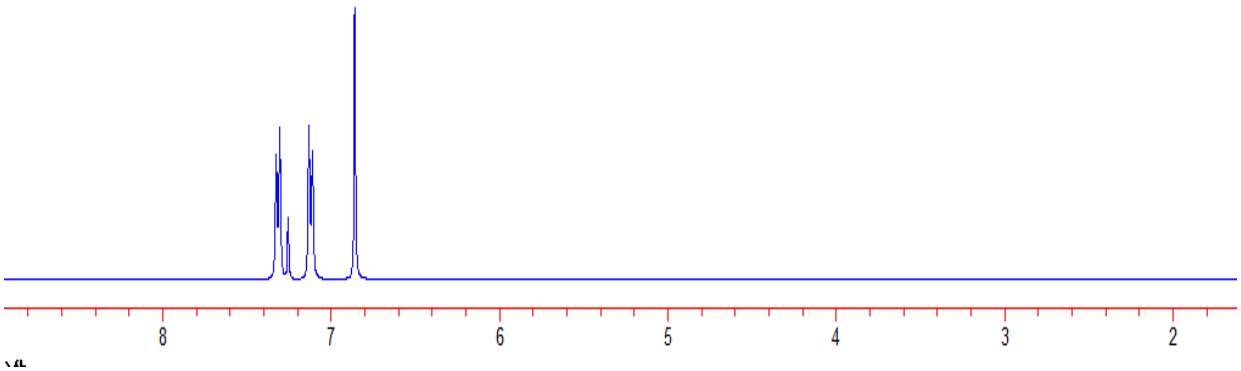
^{1}H NMR



^{19}F NMR

3.7





^{1}H NMR