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Synthesis and Fluorescence Studies of Spirooxazine-Functionalized Poly(phenylene Vinylene) Prepared via Gilch Polymerization and Click Chemistry

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Synthesis and Fluorescence Studies of Spirooxazine-Functionalized
Poly(phenylene vinylene) Prepared via Gilch Polymerization and Click
Chemistry

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A Thesis presented to the Graduate Faculty
of the College of William and Mary in Candidacy for the Degree of
Master of Science

Department of Chemistry

The College of William and Mary
August, 2011

APPROVAL PAGE

This Thesis is submitted in partial fulfillment of
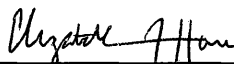the requirements for the degree of
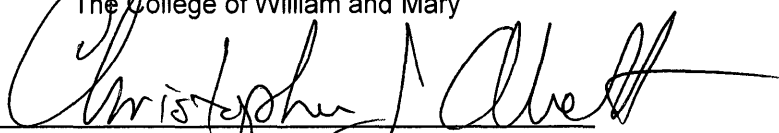
Master of Science

Kathryn Anne Peth

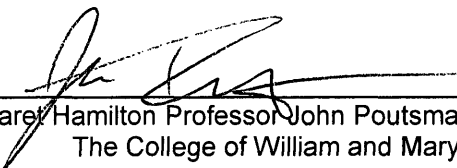Approved by the Committee, July, 2011

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ABSTRACT PAGE

This work describes the synthesis of poly(phenylene vinylene) derivatives and their subsequent functionalization with photochromic spirooxazine. The effects of different reaction conditions for the Gilch polymerization technique are examined, and a general procedure to successfully create poly(phenylene vinylene) polymers with varying amounts of bromine functionalization is proposed. After polymerization, two different reactions were carried out to attach the photochromic compound spirooxazine to the poly(phenylene vinylene) backbone: a SN2 Williamson ether reaction and a click reaction known as the Huisgen 1,3-dipolar cycloaddition. Absorbance and fluorescence studies were conducted on all collected products, and several of the click reaction products showed definite photomodulation. These results, combined with preliminary nanoparticle studies, suggest we may have obtained the ability to selectively quench the fluorescence of the polymer backbone using light signals, and have thus successfully bound the spirooxazine compound to the poly(phenylene vinylene) backbone.

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Acknowledgements

First and foremost I would like to thank Dr. Elizabeth Harbron for guiding and mentoring me for the past two years, always providing support when I needed it. Conducting research in her lab for the past two years has reminded me of why I wanted to do chemistry in the first place (despite reactions not working the way I want them to!) and has inspired me to further my education by starting the PhD program in Chemistry at UT Austin this fall. I would also like to thank Dr. Christopher Abelt and Dr. John Poutsma, two wonderful professors who are willing to indulge me a second time by serving on my Masters committee after having already sat through my boring Honors committee just last year.

I would also like to thank my labmates Brooklynd Saar and Will Czaplyski for building the foundation for a good part of the research shown in this thesis, as well as Beth Childress for helping me with my preliminary nanoparticle studies and reminding me how to make those frustrating graphs in IGOR. I would also like to thank all my lab mates, past and present, for listening to me rant and rave and always lending a sympathetic ear. I would also like to thank all my friends, family, and loved ones without whose support I wouldn't be where I am today.

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Background

Poly (phenylene vinylene) (PPV) is a conjugated polymer that has been a subject of great interest in the study and application of photochemistry. Due to their photo- and electro-luminescent qualities, conjugated polymers such as PPV and its derivatives have many practical uses such as organic LEDS, photovoltaic devices, biomedical imaging, field effects transistors, and electrochromic devices.[1-3] PPV was actually the first conjugated polymer to show electroluminescent properties, and due to its good film-forming properties, it remains one of the most frequently used polymers in LED development today.[1] We are specifically interested in manipulating the fluorescence of PPV using a light signal, which can be done by attaching a photochromic molecule onto the polymer backbone. A photochromic molecule has the ability to undergo photo-induced isomerization resulting in a change in the structure and color of the molecule.[4] This change in structure could also affect the fluorescent qualities of the polymer the photochrome is attached to in ways that will be examined in more detail later. This project focuses on two different goals: 1) perfecting the Gilch polymerization technique to synthesize a PPV derivative and 2) determining a method to attach a photochromic molecule spirooxazine (SO) to the polymer.

PPV derivatives have the same basic backbone, displayed in Figure 1. It consists of phenyl groups that are attached through vinyl bonds, usually para to one another.
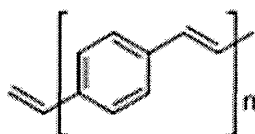
Figure 1 – Backbone of Poly(phenylene vinylene) (PPV)

The extended conjugation of this system leads to a delocalization of the π bonds, causing

PPV to have a high dielectric constant which effectively renders it insoluble in most

organic solvents.[5] Fortunately, the PPV backbone is relatively easy to functionalize with

different side groups that not only make it more soluble in organic solvents but also add

other desirable properties to the polymer.[3] In this work, all PPV polymers were

synthesized with either decyloxy or methoxy sidechains (Figure 2), providing the extra

organic layer needed to make the polymer more soluble in common organic solvents such

as tetrahydrofuran (THF).
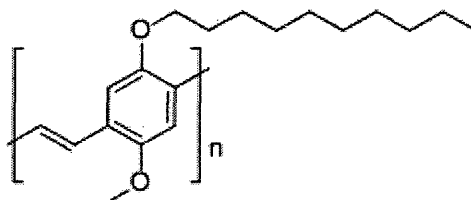
Figure 2 – Structure of Poly((2-decyloxy-5-methoxy)-1,4-phenylene vinylene)

The extended planar conjugation of the PPV backbone combined with its rigid aromatic

structure also causes PPV to be a highly fluorescent molecule. It is this fluorescence that

we will try to selectively quench with the addition of the SO compound.

SO is a photochromic molecule, and thus undergoes a reversible change in structure between the closed "spiro" form and the open, more planar merocyanine (MC) form when irradiated with UV light; these two structures are outlined in Figure 3.
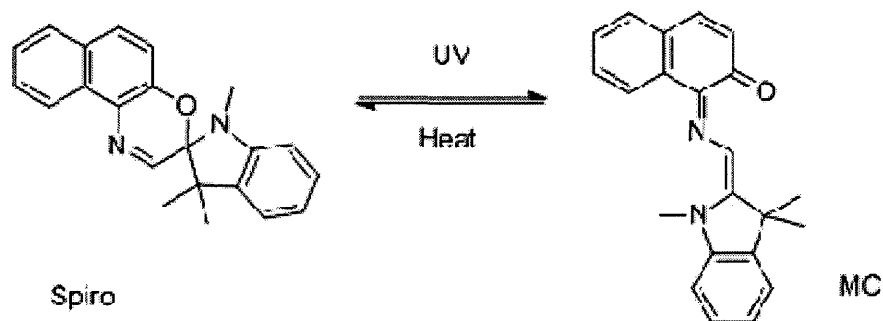
Figure 3 – Spiro and Merocyanine (MC) Structures of SO

The irradiation causes a photochemical cleavage of the spiro C-O bond in the oxazine ring. The hybridization of this bond thus changes from sp^3 to sp^2, extending the π conjugation of the molecule in the MC form and shifting the absorption to the visible region.[6] This structural change also causes a color change, as the spiro form is colorless when dissolved in organic solutions, then changes to the blue MC form when irradiated with UV light.[7] After UV irradiation, the SO molecule rapidly reverts back to its more thermally stable spiro form. We aim to take advantage of this UV-induced structural change by using SO as a reversible quencher for the fluorescence of PPV.

Fluorescence is a form of luminescence and is defined as the emission of a photon during a transition between states with the same quantum spin numbers.[8] When a fluorescent molecule is irradiated with a UV/VIS light source, it will absorb energy from that radiation at specific wavelengths corresponding to its absorbance spectra. The molecule then ascends from a low energy "ground state" (S_0) to an "excited state" of

higher energy (S₁) as shown in the Jablonski diagram on the next page. During

absorption, both the vibrational and electronic modes of the S_1 molecule are excited, and

the photon of light can go from the lowest vibrational mode of S_0 to a non-zero

vibrational level of S_1 upon excitation.
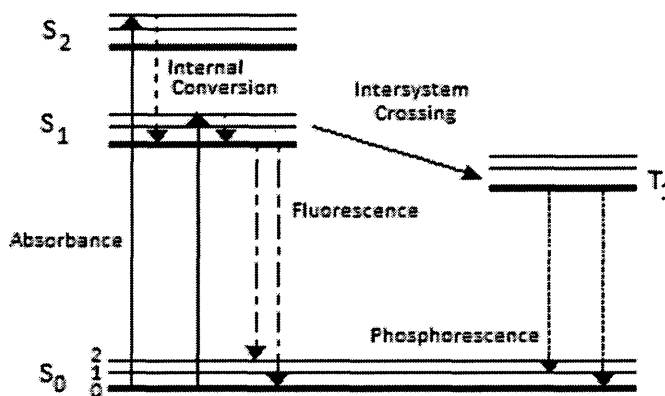
Figure 4 – Jablonski Diagram of Fluorescence. [8]

After absorption, the vibrationally excited molecules usually relax back to the lowest

vibrational level in the excited state through internal conversion. As can be seen in the

Jablonski diagram above, the absorbed energy can be lost through a variety of processes

depending on the nature of the molecule. Molecules with rigid structure such as the

aromatic PPV polymer have a lower probability of losing absorbed energy through some

form of radiationless deactivation due to its decreased degrees of rotational freedom,

leading to its highly fluorescent properties.

The ultimate goal of this project is to control the fluorescence of PPV with a light

signal by reversibly photogenerating a fluorescence quencher. This can occur by

transferring the excited state energy of the fluorophore (PPV) to the light-activated

quencher (SO) via a mechanism called fluorescence energy resonance transfer (FRET).

This name is sort of a misnomer, as the energy exchange does not arise due to a physical transfer of excited photons, but rather occurs due to dipole-dipole interactions between the fluorophore and the quencher.[9] In order for FRET to occur, the fluorophore must emit energy at wavelengths that overlap well with the absorption spectrum of the quencher. The amount of spectral overlap also affects the rate of the energy transfer, as does the orientation and distance between the fluorophore and quencher dipoles. It is for this reason that the SO group was chosen as a potential quencher. Figure 5, taken from previous labmate Christina Davis's ('10) nanoparticle studies, shows the clear spectral overlap between the emission spectrum of MEH-PPV, a PPV derivative, and the absorption spectrum of the open MC form of SO.
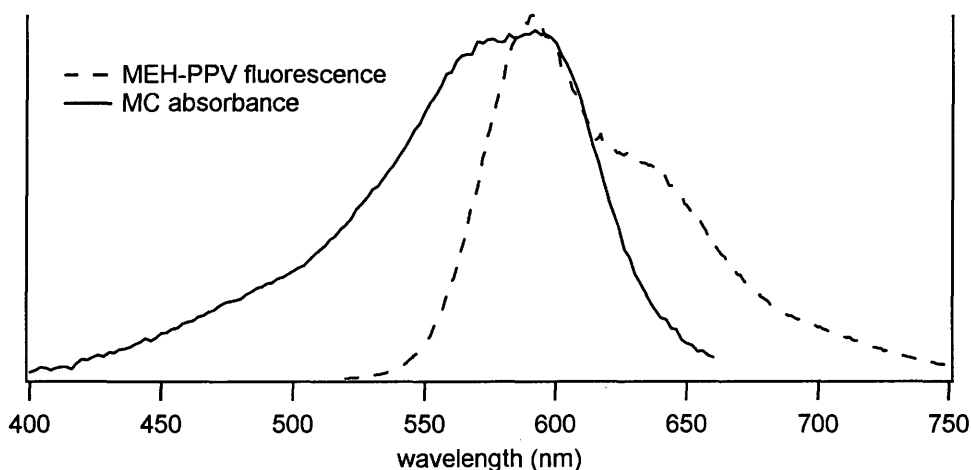
Figure 5- Spectral Overlap of MC-SO and MEH-PPV derivative

In theory, when a SO-functionalized PPV polymer is irradiated, the SO group will change from the spiro form to the MC form, facilitating FRET between the PPV backbone and SO side group and thus effectively decreasing the fluorescence of the entire molecule. More importantly, once UV irradiation stops, the SO group will transform back to the

spiro form and the fluorescence of the polymer will be restored. This sort of reversible

quenching ought to be obtainable with SO, as it is known to be a fatigue resistant

molecule due to the photochemical stability of the oxazine structure both forms.[6,7] Two

different types of SO groups were used in this thesis, both shown in Figure 6.
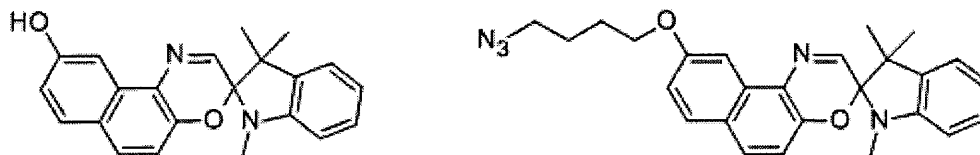
Figure 6 – Hydroxyspirooxazine and Azide-functionalized Spirooxazine

The main difference between the two structures is the functional group that will be used

to attach the SO to a PPV derivative. One merely has a hydroxyl group to be used in a

Williamson ether reaction, while the other is functionalized with an azide group for use in

a new type of chemistry known as "click" chemistry.

Click chemistry is a different approach to organic synthesis that was introduced

by K. Barry Sharpless of the Scripps Research Institute in 2001.[10] While acknowledging

the rich history of natural product synthesis and its successes, Sharpless proclaimed that

focusing organic synthesis on long, complicated, and costly syntheses with extremely low

yields has pervasive effects on the process of drug discovery, development and

manufacture. Another problem he identified is that synthetic routes seem to get bogged

down with long-winded methods to try to form contiguous C-C bonds, which are present

in most bioactive natural products. However, Sharpless stated that these compounds are

not the only useful type of biologically effective molecules, and that there are plenty of

interesting and useful molecules that can be formed through short steps and heteroatom

coupling. He proposed a philosophy of utilizing a more modular, faster style of

chemistry where one should be able to jump easily from one series to another, drawing inspiration from natural synthesis where large oligomers are formed from small building blocks of molecules.[10] In this way an organic chemist would not get stuck on trying to create an overly complicated structure, but rather focus on the functionality of the molecule and its usefulness. In his 2001 review in *Angewandte International Chemie Edition*, Sharpless outlined quite an extensive criterion for a reaction to be considered a click reaction:

> "The reaction must be modular, wide in scope, give very high yields, generate only inoffensive byproducts that can be removed by nonchromatographic methods, and be stereospecific (but not necessarily enantioselective). The required process characteristics include simple reaction conditions ... readily available starting materials and reagents, the use of no solvent or a solvent that is benign or easily removed, and simple product isolation. Purification must be by nonchromatographic methods, such as crystallization or distillation, and the product must be stable under physiological conditions."[10]

He goes on to state that most click reactions that meet these criteria do so because they naturally have a high thermodynamic driving force, so they tend to go rapidly to completion. Most of these reactions also tend to be highly selective to produce a single product. By limiting the scope of chemistry to these types of reactions, Sharpless is confident that advances can be made in the field of drug manufacturing and organic synthesis much more swiftly.[10]

The type of click reaction that will be focused on in this thesis is a variation of the azide-alkyne Huisgen cycloaddition first characterized by Rolf Huisgen in the 1950s, an example of which can be seen in Figure 7. It is a [1,3]-dipolar cycloaddition that takes place between a terminal alkyne and an azide to produce a 1,2,3-triazole with a mixture of 1,4-disubstituted and 1,5-disubstituted regioisomers.
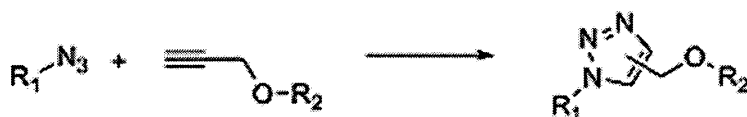
Figure 7 – Example of [1,3]-Huisgen Cycloaddition

This reaction has been praised by Sharpless as "the cream of the crop" in click chemistry, as it unites two kinetically stable reactants and provides an opportunity for the production of a variety of heterocyclic molecules.[10] In this project we follow the version of this reaction that employs a copper catalyst and reducing agent that is supposed to selectively produce the 1,4 regioisomer of the triazole, as it has been shown to be successful in adding functional groups to conjugated polymers.[11-13]

We hypothesized that if we could prepare alkyne-functionalized PPV polymer and azide-functionalized SO, then attachment of the SO to the PPV backbone should proceed with relative ease using a click reaction. The success of this reaction can be measured not only with NMR, but by fluorescence photomodulation studies as well. If the SO compound is successfully attached to the PPV backbone, then the fluorescence spectrum of the polymer will surely decrease upon the UV-induced conversion of the SO to MC form. If the molecule does not undergo any photobleaching in this state, then the fluorescence should be restored after allowing the SO to revert back from its MC form to

its spiro form. Achieving this sort of photomodulation would be tremendous in showing the functional capabilities of SO as a light-activated quencher, as well as supporting the fact that we have successfully bound this quencher to a responding fluorophore.

Results and Discussion

Two different routes for the synthesis of SO functionalized PPV were attempted

and are outlined below in Figure 8. While both schemes feature utilization of the Gilch

polymerization, they differ in how they approach the goal of attaching the SO moiety to

the polymer chain. The first route involves an S_N2 Williamson ether reaction, while the

second features the new click chemistry discussed earlier.
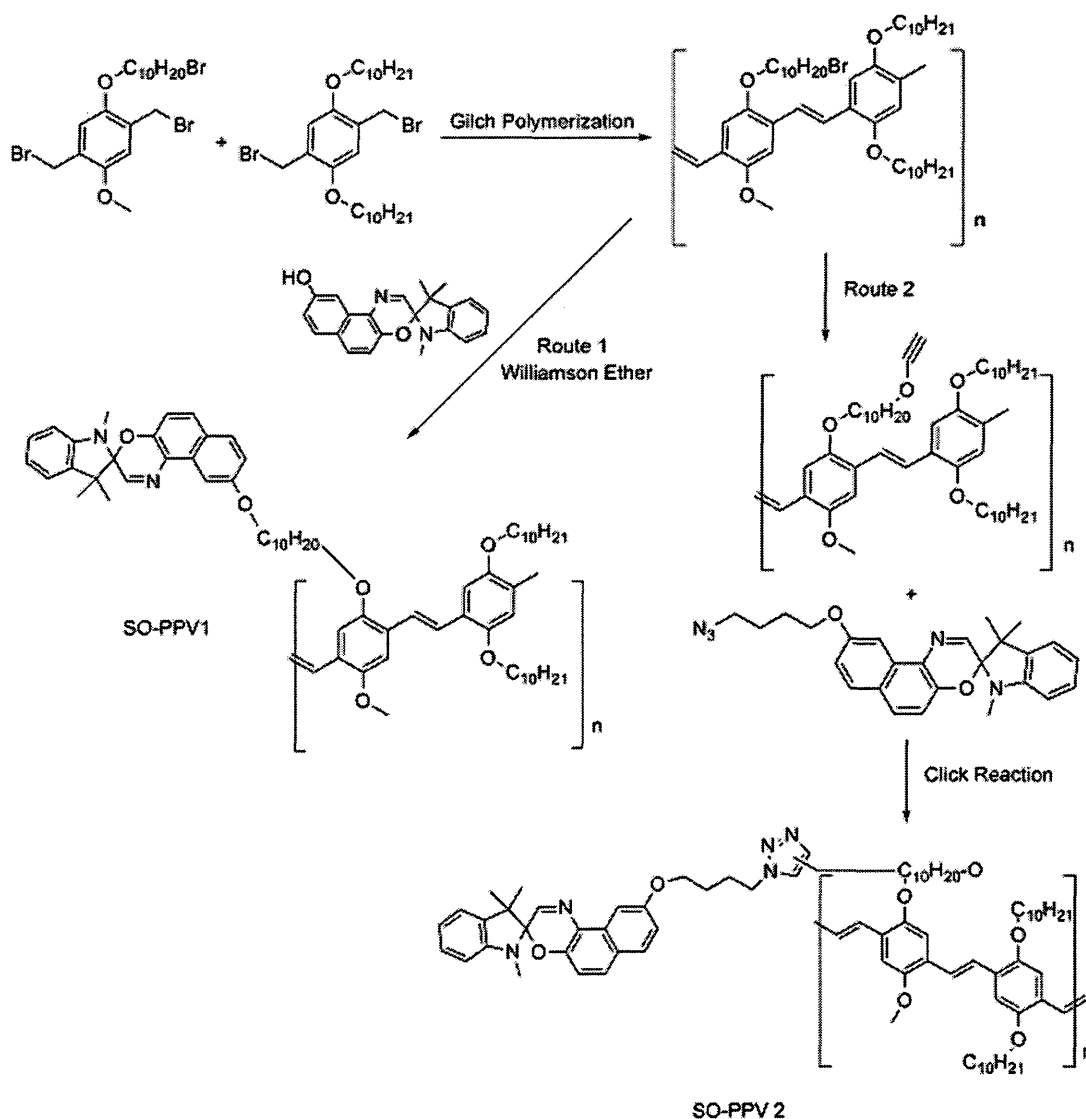
Figure 8 – General Synthetic Routes to SO-PPV1 and SO-PPV2

Monomer Synthesis for the Gilch Polymerization
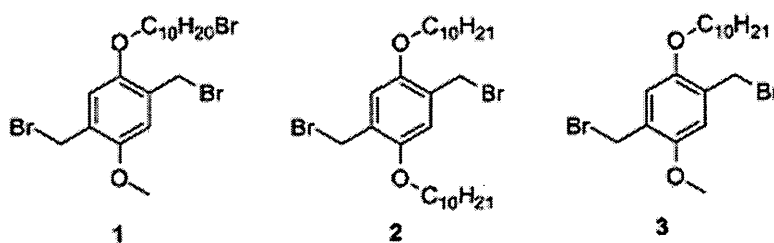
Figure 9 – Monomers used in Gilch Polymerization

The above scheme shows the different monomers that have been synthesized for

use in the Gilch polymerization. The ultimate SO-functionalization of the polymer

comes from monomer **1**, the only monomer with a bromoalkyl chain. Monomers **2** and **3**

were also constructed for use in the Gilch polymerization in order to decrease the

bromine functionality of the polymer to help alleviate later solubility problems. In my

undergraduate thesis I exclusively used monomer **3**; however, for this project the focus

was shifted onto monomer **2**.[14] Monomer **2** has two decyloxy chains para to one another,

as opposed to monomer **3** with only one decyloxy and a methoxy group. It was theorized

that the extra hydrocarbon chain on monomer **2** would further increase the solubility of

the polymer in organic solvents.

The synthesis of monomer **1** involves two separate steps, shown below.
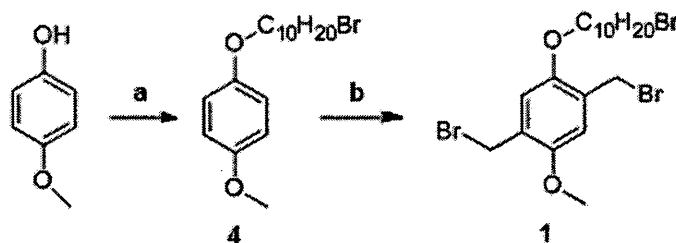
Figure 10 – Overall Synthetic Route for Monomer **1** a) reflux in acetone with K₂CO₃ and
dibromodecane, 24 hours b) reflux in HOAc with HBr and paraformaldehyde, 24 hours

The first step is a Williamson Ether synthesis between commercially available molecules

p-methoxyphenol and dibromodecane using potassium carbonate as a base.
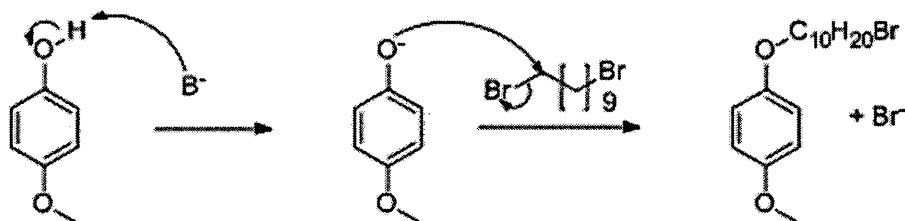
Figure 11 – Williamson Ether Synthesis Mechanism

The hydrogen from the phenol group on the p-methoxyphenol is removed by the base,

effectively forming a nucleophilic phenoxide ion. This ion then reacts with the

dibromodecane via an S_N2 reaction to expel one of the bromines and add the bromoalkyl

chain to the oxygen. The biggest problem with this reaction is that the dibromodecane

must be used in excess, usually up to 7 to 8 molar equivalents. This is necessary to avoid

having the phenoxide ions reacting with newly formed product to create a

difunctionalized byproduct.
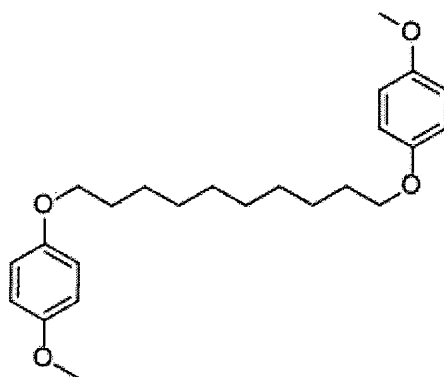
Figure 12 – Difunctionalized Byproduct in Synthesis of **4**

Due to this excess, the final product must undergo multiple recrystallizations in hexanes in order to remove all the unused dibromodecane, leading to low yields. The best yield obtained during this monomer synthesis was 44%, with an average of about 32%.

After purification, a bromomethylation is carried out using paraformaldehyde and 33% (weight) HBr in glacial acetic acid to form the final product monomer **1**. First, the paraformaldehyde is thermally decomposed to formaldehyde, which is then protonated by the HBr to form a carbocation. This carbocation initiates an electrophilic aromatic substitution with the reactant and remaining bromine ions to ultimately form a benzylic alcohol. HBr is again used for protonation, this time protonating the alcohol to form a good leaving group that is then removed by the recently deprotonated bromine ions.
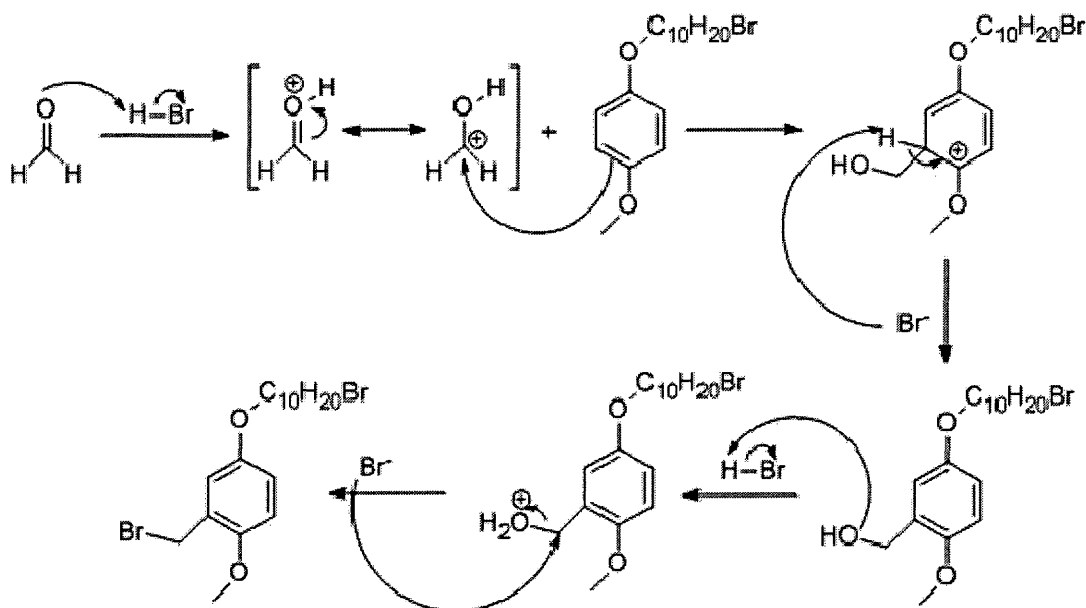
Figure 13 - Methylbromination Mechanism of Monomer **1**

This entire substitution process is then repeated para to the newly substituted bromomethyl group, thus resulting in the dimethyl bromo monomer **1**. This reaction was performed several times with an average 70% yield.

The synthesis for monomer **2** is another straightforward electrophilic aromatic substitution, shown in Figure 14.
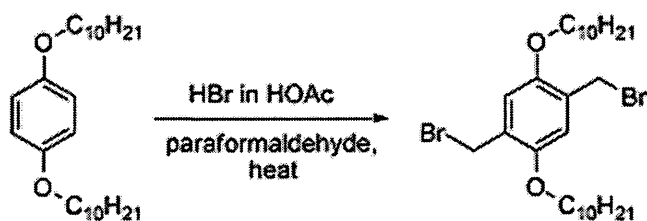
Figure 14 – Synthesis of Monomer **2**

The mechanism and procedure for this transformation is exactly the same as for the earlier dibromomethylation shown in Figure 13. As such it has also been show to work extremely well, with an average yield of 82%. After these monomers are all synthesized, the next step is to polymerize.

Polymerizations

This project utilized anionic Gilch polymerization techniques for creating all the polymers used in the UV/VIS studies. Although there is still a debate on the exact details of the Gilch polymerization mechanism, there is a general consensus that it starts with the base-catalyzed deprotonation of the dimethylbrominated monomer to form an anionic intermediate that then undergoes a [1,6] elimination to form a diquinone intermediate.[15,16] Another anionic intermediate can then initiate the polymerization with the diquinone, effectively joining the two monomers and generating new anions to continue the polymerization. The final vinylic form of the connecting bond between the monomers in the polymer backbone is created using an excess of base to facilitate an E2 reaction, eliminating the remaining bromine atom.
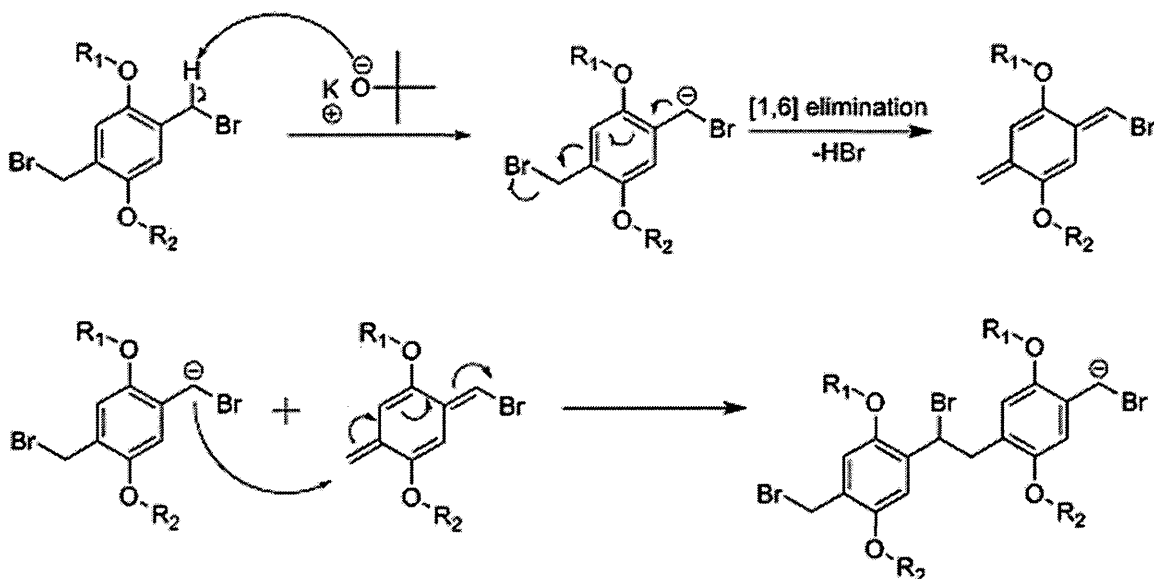
Figure 15 – Gilch Polymerization Mechanism

One of the most common bases used for this polymerization is potassium tert-butoxide (tBuOK). The tBuOK base we have used is drawn from a solution of 1M tBuOK in THF

and then diluted with additional anhydrous THF before it is added to the reaction mixture

avoid complications such as crosslinking.

The functionalization of the polymer can to some extent be controlled by varying

the ratios of the monomers used within the polymerization. If the only monomer used

were monomer **1**, the resulting polymer would be a homopolymer, in which each

benzylic unit of the polymer chain would contain the bromoalkyl side group.
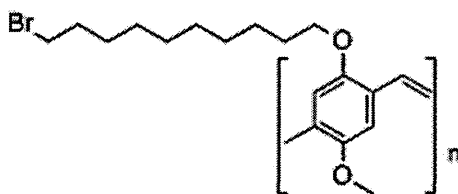
Figure 16 – 100% Br-functionalized PPV (100% PPV-Br)

This polymer would be termed a 100% Br-functionalized poly(phenylene vinylene), or

100% PPV-Br. Trying to create spirooxazine functionalized PPV (SO-PPV) with 100%

PPV-Br, however, proved to be very difficult; any product that was isolated was

essentially insoluble, making UV/VIS and fluorescence studies nearly impossible. To

avoid this frustration, we started making random copolymers by combining monomers

without the bromine functionalized sidechain with monomer **1** in the polymerization

process. For example, if I used monomers **1** and **2** in a 1:3 ratio, as shown on the next

page, I would end up with a polymer that is about 25% Br-functionalized, as roughly 1 in

every 4 backbone units would have the bromoalkyl side chain.
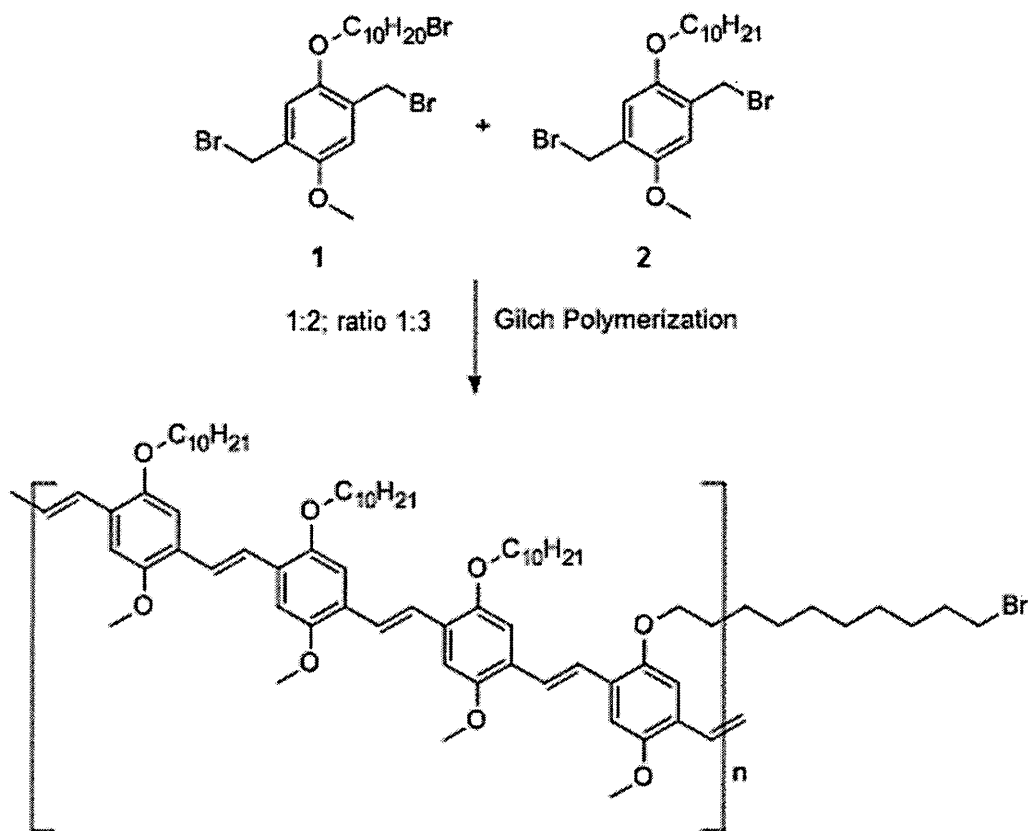
Figure 17 – Synthesis of 25% PPV-BR

The percent functionalization of the polymer can be estimated and verified in NMR

analysis by comparing the integrated values of peaks known to arise due to the bromine

functionalization versus those that appear due to the unfunctionalized monomer.

A variety of polymers were made with varying bromine functionality to be used

for SO-PPV synthesis, as outlined in the table on the next page. One of the main

problems that can be encountered during the Gilch polymerization is crosslinking. If the

tBuOK is added to the reaction mixture too quickly, the amount of bonding and reaction

between the molecules can occur in undesirable locations. The resulting high density of

#	Eq. of 1	Eq. of 2	tBuOK:THF ratio (mL)	Addition time (min)	Use of additive	Use of heat	Stir time (hrs)
1	1	3	1:8	20	No	Yes	2
2	1	3	1:15	30	No	Yes	2
3	1	4	1:16	45	No	Yes	2
4	1	4	1:5	Instant	Yes	No	0
5	1	4	1:5	15	Yes	No	24
6	1	4	1:10	28	Yes	No	24
7	1	10	1:11	26	Yes	No	24
8	1	10	1:12	30	Yes	No	24
9	1	10	1:22	33	Yes	No	19
10	1	4	1:22	51	Yes	No	16
11	1	10	1:22	120	No	Yes	3
12	2	3	1:50	133	Yes	No	2
13	1	1	1:22	36	Yes	Yes	2

Table 1 – Gilch Polymerization Attempts with Reaction Conditions

networking bonds, or crosslinking, forms a globular product that is completely insoluble and unusable. This is what occurred in polymerizations 2, 4 and 5. However, I've discovered that this problem can be circumvented by both diluting the base added with anhydrous THF and adding this diluted solution to the reaction mixture very slowly, dropwise over a long period of time. As can be seen in the table above, I have found the most effective conditions are when the tBuOK:THF ratio is at least 1:20 mL, with an addition time of at least 30 minutes. .

Product isolation was another problem that occurred in polymerizations 1 and 3 after polymer precipitation in methanol. When trying to filter out the polymer flakes, most just went right through the filter paper; what could be recovered was stuck to the filter paper, and had to be dissolved off with THF or chloroform and then evaporated with rotary distillation to get any sort of workable product back. I found that letting the polymer stir in MeOH overnight after precipitation as opposed to just 20 minutes made it more likely to successfully filter out. The inclusion of a 4-(tert butyl) benzyl chloride

additive, also seemed to help circumvent this problem; the polymer would form a thin

layer on the filter paper and then break into a mosaic-like pattern of flakes when air dried,

which were very easy to collect.
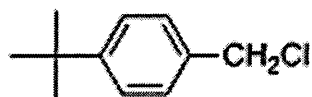
Figure 18 – 4-(tert butyl) benzyl chloride additive

This nonpolymerizable acidic chloride additive first caught our interest because it

was reported to have been useful at eliminating cross linking and facilitating easier

polymer recovery in Gilch polymerizations, via the mechanism below.[17,18]
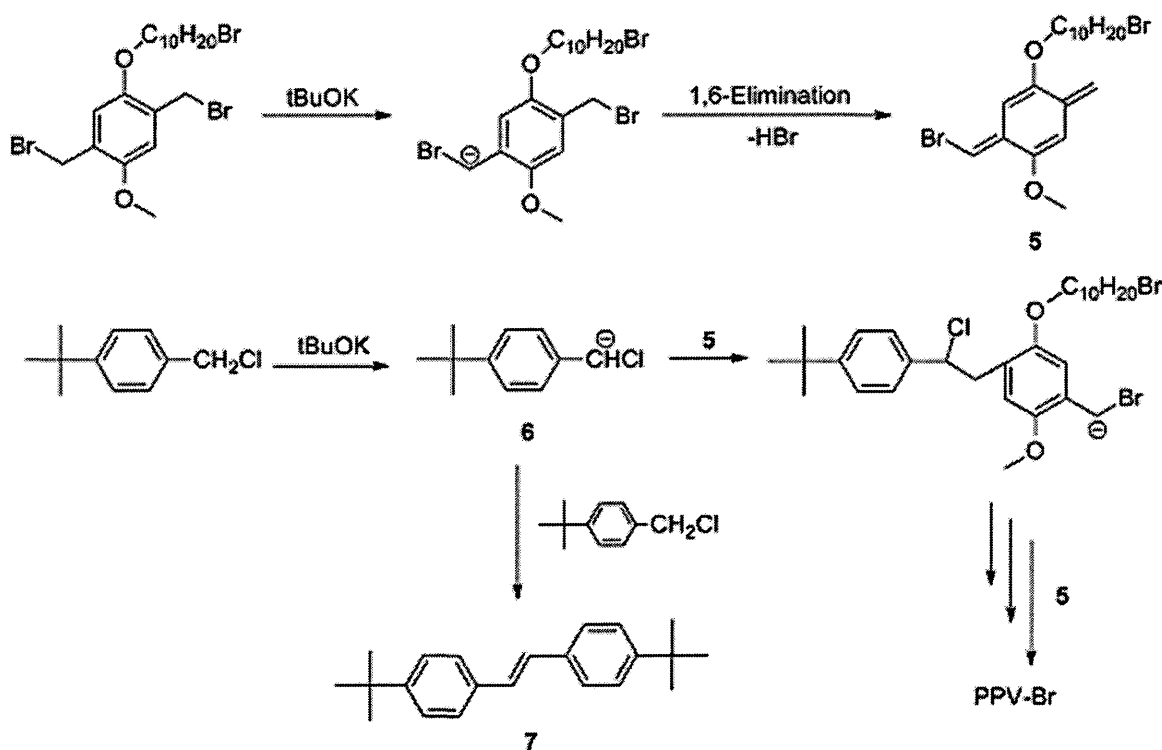
Figure 19 – Modified Gilch Polymerization Mechanism with Chloride Additive.[17]

Much like the procedure discussed earlier, this modified mechanism starts with the protonation of the bromomethyl monomer by the tBuOK base to form an anionic intermediate. According to Hseih et al, this intermediate undergoes a [1,6]-dehydrohalogenation to form the intermediate **5**.[15] Meanwhile, the chlorine additive is also deprotonated by the tBuOK base to form the anionic molecule **6**. Intermediate **5** is then nucleophilically attacked by anion **6**, initiating the anionic polymerization which ultimately results in the formation of the PPV-Br polymer. However, there are other competing reactions, one involving the anion intermediate **6** reacting with other chlorine additive molecules to form the ditertbutylstilbene side product **7**. Another side reaction that could occur is the premature termination of the polymer chain between the anion on the polymer and a second anionic intermediate **6**. Both these competing side reactions can be effectively reduced, however, by keeping the concentration of chloride additive relatively low compared to the amount of monomer present within the reaction.

The additive is to be added to the solution of dissolved monomers in THF before the addition of the tBuOK base. However, the procedure in the paper differed from the procedure I was familiar with in several different ways. For example, no matter how many moles of monomer were present, the same amount of tBuOK was added: 4.4 ml. Also, there was no mention of the tBuOK being diluted with THF when being added to the reaction mixture. Lastly, the reaction was done at room temperature and allowed to stir for 24 hours after addition, whereas I had been running the reaction at about 50°C and letting it stir for 2-4 hours. For the first polymerization with the new additive, I followed the procedure in the paper and added the 4.4 mL of tBuOK all at once with the reaction

running at room temperature. The result was instantaneous crosslinking. For the next polymerization, #5, I intended to add the 4.4 mL of tBuOK much more slowly; I actually added only 3 mLs because I noticed that the solution was starting to take on the sort of consistency I had come to associate with crosslinking polymers. Indeed, after letting it stir for 24 hours, whatever polymer that could be collected refused to dissolve in organic solvents; it would swell, but not dissolve, a common characteristic of cross linked polymers. With the third attempt, I retreated back to familiar territory; after adding the chloride additive, I used 4.02 eq of tBuOK diluted in about 20 ml of THF as in earlier Gilch polymerizations, which was then added to the reaction mixture over 30 minutes. After letting the reaction stir for 24 hours, the polymer was precipitated into methanol and collected via Buchner filtration.

The next step was to experiment with the reaction conditions to find the most optimum procedure for the Gilch polymerization. Variables that could be changed included the amount of tBuOK added, how dilute the tBuOK was during addition, the addition time, use of the chlorine additive, the use of heat, and how long the reaction was allowed to stir before precipitation. I already knew from previous experiments that roughly 4.02 eq of tBuOK (compared to the total moles of monomer present) had to be diluted with at least 20 times the amount of THF and added very slowly to the reaction mixture. I also found that the reaction would not go at all in the absence of both heat and the chloride additive. With the chloride additive at room temperature, the rate of the reaction appeared to be quite slow; additional tBuOK had to be added over a longer period of time in order to obtain the orange-red color indicating that the reaction had

begun. This was exemplified by polymerization #12, where nearly 1.8 mL of additional THF had to be added over 133 minutes in order to achieve the desired color change. In polymerization #13 it was found that putting the reaction under heat drastically reduces the amount of time needed for the addition of tBuOK, while only 3-4 drops of additional tBuOK were needed to make the reaction start. It was eventually found that there was not any noticeable difference between letting the reaction stir for 24 hours versus only 2 hours as long as the reaction was heated.

Based on these experiments, a general procedure for Gilch polymerization has been established. The monomers are to be measured out in the appropriate ratios needed to achieve the desired functionalization percentage. The monomers are then dissolved in anhydrous THF and added to a flame-dried 3 neck round bottom under N_2 atmosphere, equipped with an addition funnel. The chlorine additive is added to the monomer solution, while a mixture of tBuOK and THF is added to the monomer in at least a 1:20 mixture. The amount of tBuOK used should be equal to about 4.2 times the total moles of monomer used in the reaction. After heating the reaction to about 50°C, the tBuOK/THF solution is to be added to the reaction mixture over at least 25 minutes with rapid stirring. Frequent stoppages of the addition may be required, especially when observing color changes, so as to avoid any dangers of crosslinking. If crosslinking has occurred, the stirring of the reaction will be impaired by the formation of soft, gel-like precipitation, accompanied by a very rapid color change to red-orange or bright red. During addition the successful reaction will go from pale yellow to cloudy yellow to orange, and the addition is completed when the mixture reaches an orange-red color with

blue-green fluorescence. If it has not reached this color, a few more drops of tBuOK

should be added, leaving a full minute between each drop, until the desired color change

is achieved. After letting the reaction stir rapidly for 2 hours, remove it from the heat and

pour into at least 500 mLs of methanol to get bright red polymer precipitate. Let stir

overnight and collect via Buchner filtration to obtain darker red, PPV-Br polymer flakes.

This is the procedure that was used for polymerization #13.

Any polymer products that could be dissolved in THF or chloroform underwent

UV/VIS studies, the results of which are displayed in the table below.

#	Absorbance max (nm)	Fluorescence max (nm)	SO-PPV Route
1	492	573	SO-PPV1
3	488	562	SO-PPV1
7	487	544, 583	SO-PPV1
8	501	584	N/A
9	473	535, 584	N/A
10	480	545	SO-PPV1
12	481	543	SO-PPV2
13	486	547	SO-PPV2

Table 2 – Absorbance and Fluorescence Data for Dissolvable PPV-Br Polymers

Past studies have shown that PPV polymer samples in THF typically have an absorbance

maximum around 480 nm and a fluorescence maximum around 545 nm. As can be seen

above, polymers 10 and 12 fit this criterion pretty well. Some of the polymers (7 and 8)

showed evidence of crosslinking, even with the use of the chlorine additive. This is

apparent through the appearance of an additional broad shoulder of fluorescence around

the 580 nm range. Using these UV/VIS results, polymers 1, 3, 7, 10, 12, and 13 were

selected for use in later reactions to form SO-PPV.

SO-PPV1 Synthetic Route and UV/VIS Studies

The first attempted synthetic route to SO-functionalized PPV is an extension of

my undergraduate work, outlined in Figure 20 below.[14]
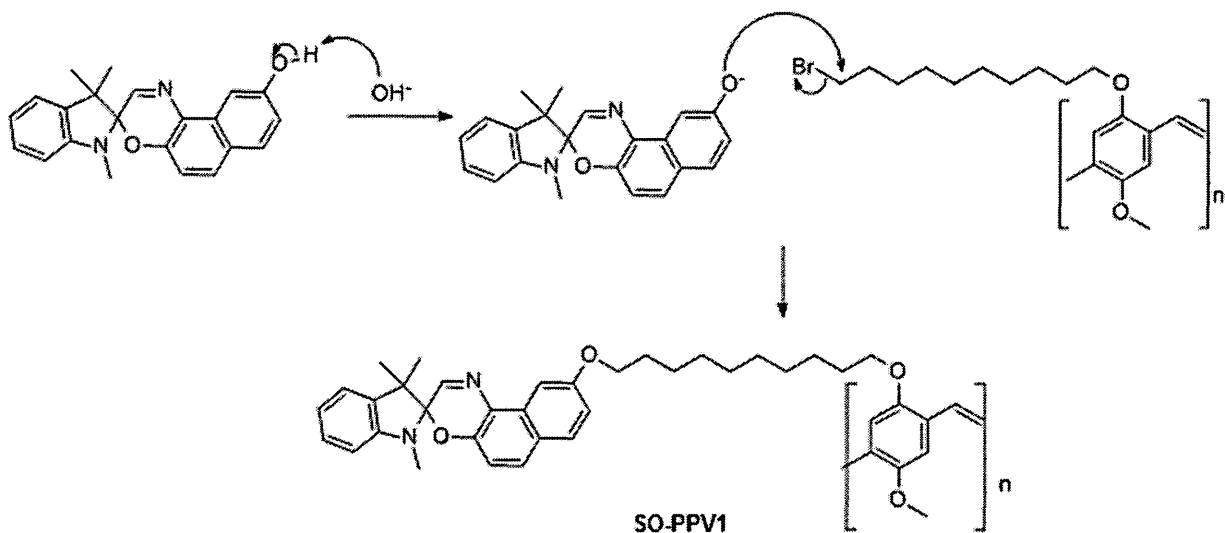
Figure 20 - S_N2 Reaction Mechanism for Synthesis of SO-PPV1

We planned to facilitate an S_N2 reaction between the bromine leaving group of the

polymer and the hydroxyl group of the SO. Only four attempts were carried out in my

undergraduate work, with one product having promising results, so I tried several

reactions with different PPV-Br polymers to see if I could recreate the desired effect.

Most of the SO-PPV products from my undergraduate work did not easily dissolve in

most organic solvents; the process to get them dissolved enough for UV/VIS study

proved to be time-consuming and not always successful. Because of this, polymers with

low percentages of bromine functionalization were synthesized. By reducing the amount

of reaction sites for the SO to attach to the polymer, it was hypothesized that the issue of

solubility could be circumvented. The different SO-PPV1 synthetic attempts are outlined

below in Table 3.

#	Precursor PPV-Br polymer	% Functionalization	Reaction Solvent	UV/VIS Studies?
1	1	25	DMF	No; Reaction solvent evaporated
2	1	25	DMF	No; Solubility issues
3	3	20	THF	Yes
4	3	20	THF	No; Solubility issues
5	7	10	THF	No; Solubility issues
6	10	20	Xylenes	Yes
7	10	20	DMF	No; Solubility issues

Table 3 – Details of SO-PPV1 Synthesis Attempts

Unfortunately, most of the products of these SO-PPV reactions still suffered from

solubility issues. The two products that were dissolved could not be concentrated enough

to produce any analyzable NMR data, and so they underwent UV/VIS studies instead to

determine whether or not the SO group was successfully attached to the PPV polymer.

First, absorption and fluorescence spectra were recorded for each SO-PPV products.

After the initial fluorescence reading, the sample was irradiated for 5-10 seconds using a

365 nm UV source and another fluorescence spectrum was measured immediately after

excitation. If the SO group was attached to the PPV polymer, then upon UV irradiation it

would open to the MC form allowing FRET to occur and thus decreasing the

fluorescence intensity of the overall molecule. About 60 seconds after UV irradiation a

final fluorescence spectrum was recorded. By this time the SO should have reverted back

to its more thermally stable spiro form, thus restoring the polymer's fluorescence back to

its original intensity. If the structure had been irreversibly damaged through

photobleaching or fatigue, then the fluorescence intensity will stay at its decreased state.

The product of the third SO-PPV1 reaction was the first that could actually be

solvated enough for UV/VIS studies. The studies were carried out in THF, and the

absorbance λ_{max} of this compound was 448 nm, while the fluorescence λ_{max} was 547 nm.
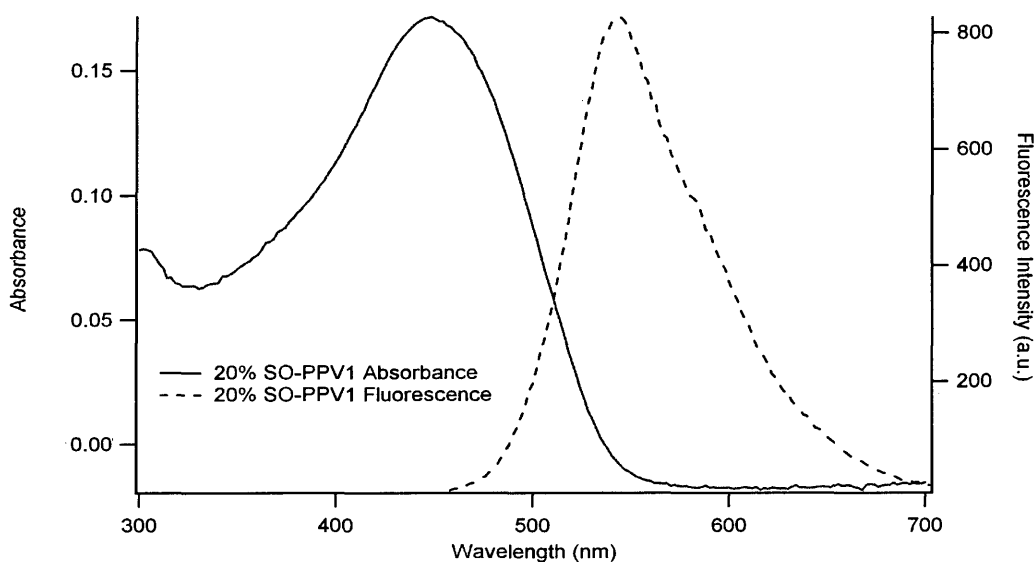
Figure 21 – Absorbance and Fluorescence Spectra for SO-PPV1, Reaction 3

Unfortunately, the compound did not seem to undergo any form of photomodulation.
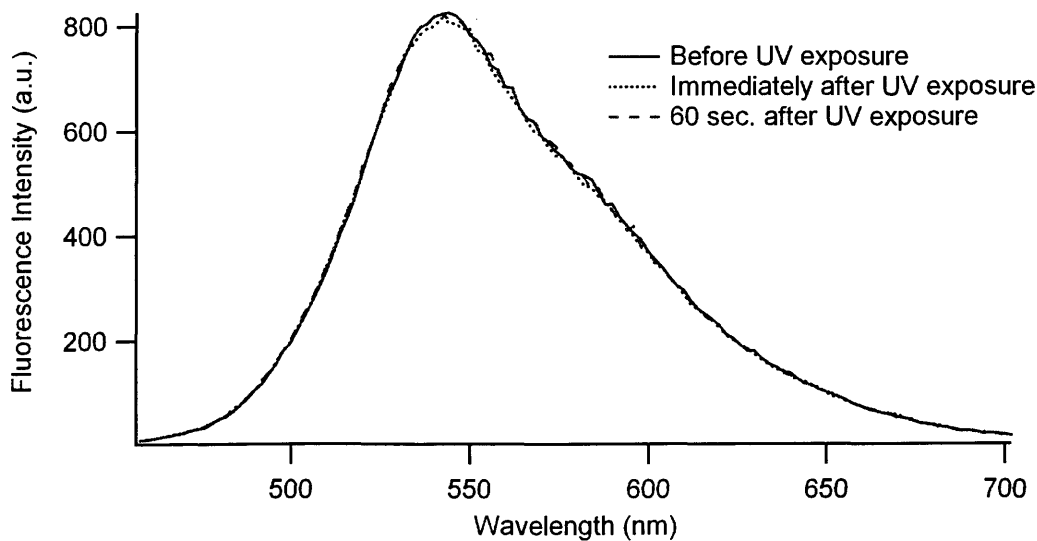
Figure 22 – UV Irradiation Studies of SO-PPV1, Reaction 3

The only other reaction that produced a dissolvable polymer product was reaction

#6. This reaction was unique in that it was carried out in xylenes, which was the same

reaction solvent that produced photomodulated SO-PPV results in my undergraduate

thesis. The absorbance and fluorescence λ_{max} values of this product were 463 and 548

nm, respectively.
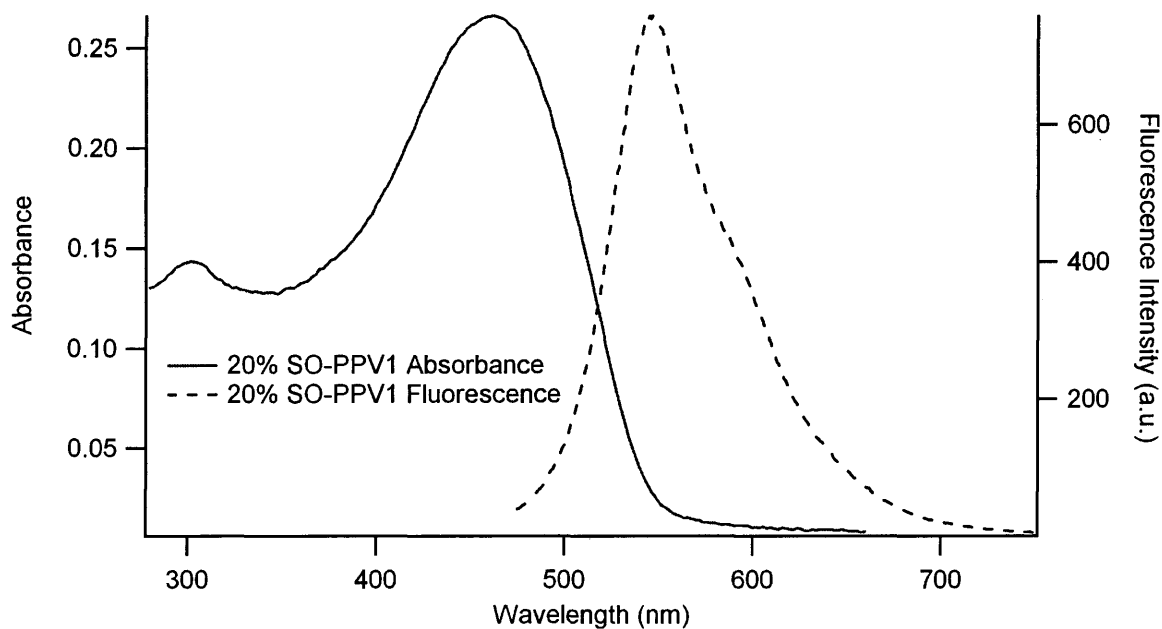
Figure 23 - Absorbance and Fluorescence Spectra for SO-PPV1, Reaction 6

Unfortunately, this molecule also did not seem to undergo any significant

photomodulation, as shown in Figure 24.
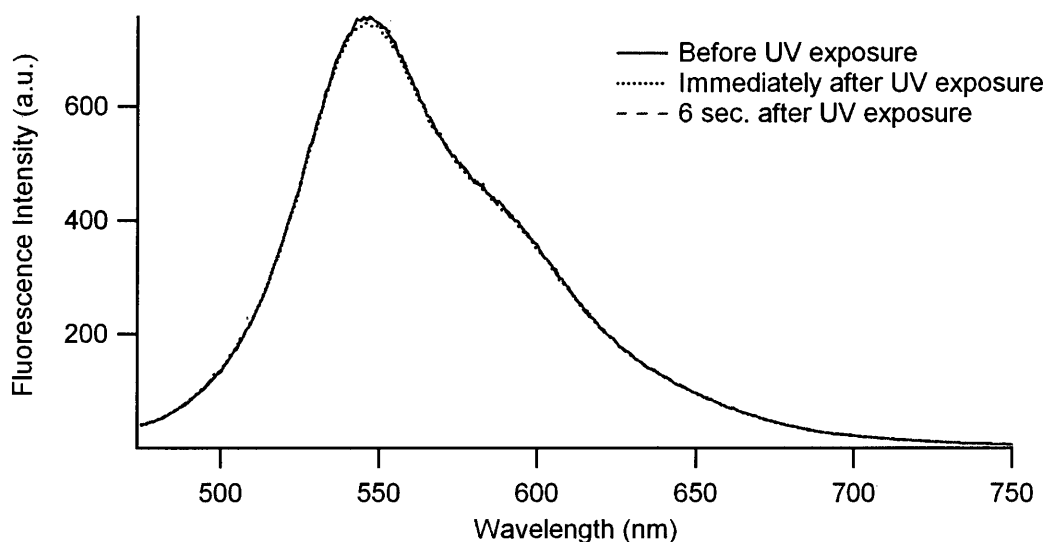
Figure 24 – UV Irradiation Studies of SO-PPV1, Reaction 6

This portion of the project was sadly discouraging. The biggest problem is obviously the solubility issues we encountered with our products. Out of the 6 reactions that were carried out, only two products could actually be dissolved enough to undergo reliable UV/VIS studies. The ones that could be dissolved showed no signs of photomodulation, leading us to the conclusion that the reaction did not actually work the way we wanted. Because of these results, we decided to turn to a different route to making an SO-functionalized PPV polymer: the click chemistry route.

SO-PPV2 Synthetic Route and UV/VIS Studies

The second synthetic route for SO-PPV involves the use of click chemistry

between an alkynized PPV polymer and an azide-functionalized SO group that was

discussed earlier.
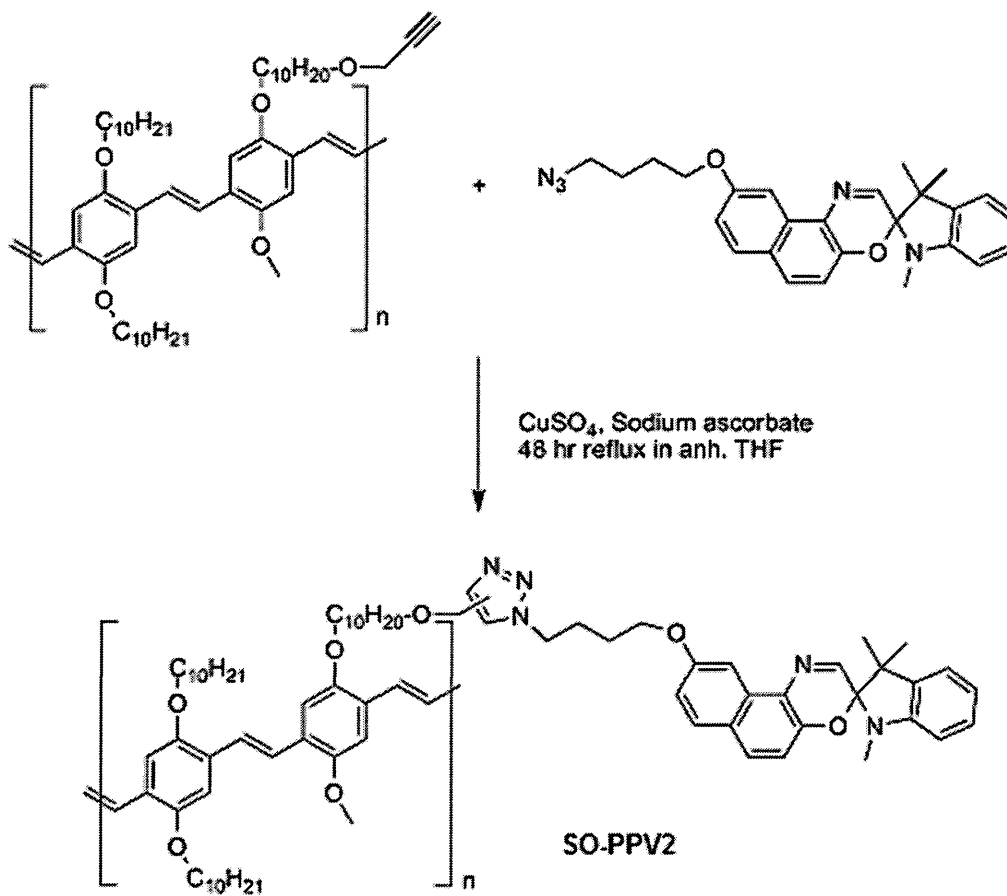
Figure 25 – General Synthesis Route for SO-PPV2

Another labmate, Brooklynd Saar, did most of the preliminary work on this route and

determined that one of the most accessible click reactions we could try was a variation of

the [1,3]-Huisgen cycloaddition between the terminal alkyne and an azide using a copper

catalyst. The mechanism for this reaction will be explored in more detail later.

A series of small trial reactions weas carried out to ensure the feasibility of this

route. First, a sample azide was made using the commercially available materials sodium

azide and bromohexane liquid. This reaction definitely follows the principles of click

chemistry as it is a straightforward reaction conducted at room temperature in DMSO,

with a simple mechanism. The nucleophilic azide ion displaces the bromine atom via

nucleophilic substitution. This reaction was carried out only once, with a yield of 77%.

Figure 26 – Mechanism for the Formation of 1-azidohexane

After making this sample azide, the next step was to conduct a trial click reaction

of the Huisgen cycloaddition between the terminal alkyne on propargyl alcohol and

azidohexane. The negative charge of the azide can react with either sp hybridized carbon

of the alkyne bond to form either a 1,5- or 1,4-disubstituted 1,2,3-triazole product.

1,5- disubstitution   1,4-disubstitution
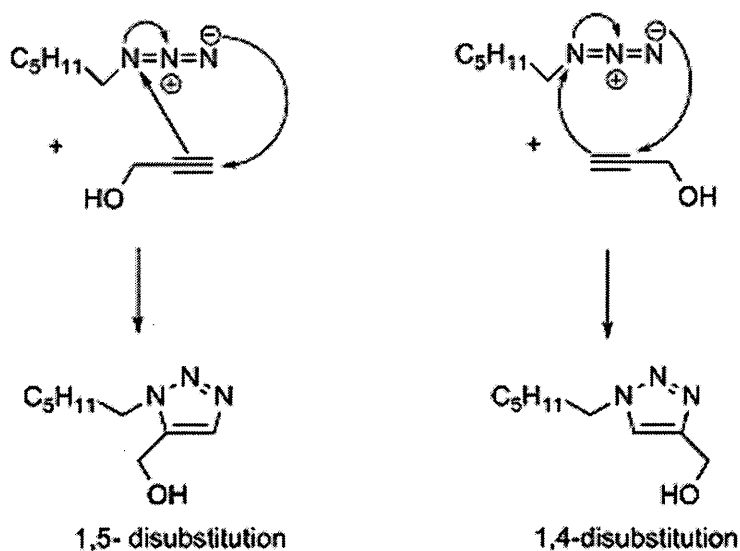
Figure 27 – Mechanism for the [1,3]-Huisgen Dipolar Cycloaddition.

The reaction was carried out in THF with sodium ascorbate and copper sulfate catalyst, the presence of which is supposed to selectively produce just the 1,4 disubstituted triazole.[13] The copper sulfate is reduced to a Cu^+ ion by the ascorbate, which then combines with the terminal alkyne to form a copper acetylide. The binding of the copper increases the differing polarities of the sp carbons as shown in the scheme below and thus facilitates formation of a 1,4-disubstituted product.
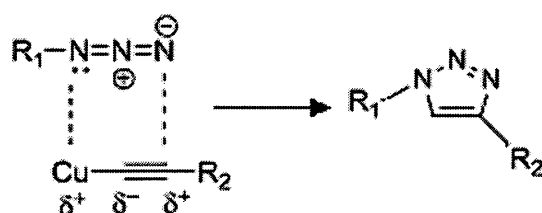
Figure 28 – Copper Acetylide Coordination with Azide [13]

After performing the click trial the success of the reaction was apparent through ^1H NMR analysis with the emergence of triazole product peaks between at around 4.4 and 4.5 ppm, shown in Figures 73-75.

After the success of the trial click reactions, the next step was to functionalize the SO compound with an azide group via the route seen in Figure 30.
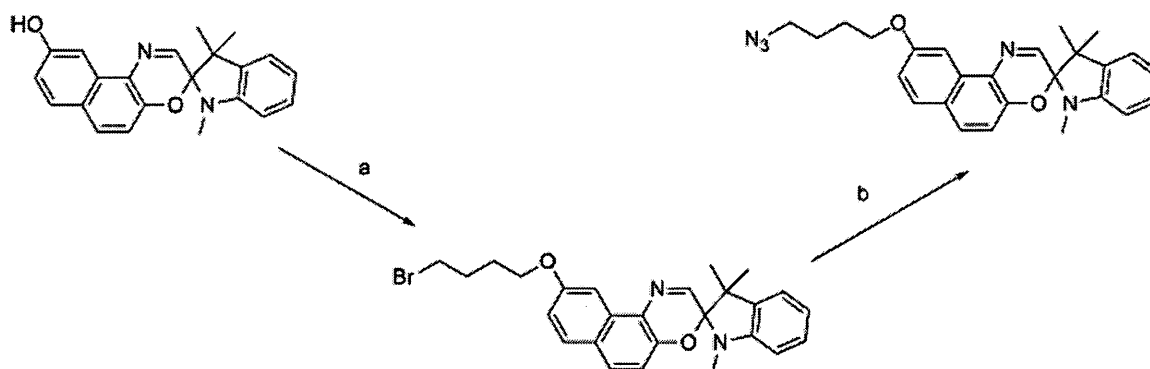
Figure 29 – Overall Synthetic Route for Azide-functionalized SO a) dibromobutane, acetone, K_2CO_3, 24 hour reflux b) DMSO, NaN_3, 24 hours at RT

The first step in synthesizing this new compound involves an S_N2 reaction between

hydroxyspirooxazine and dibromobutane in acetone with potassium carbonate as a base.
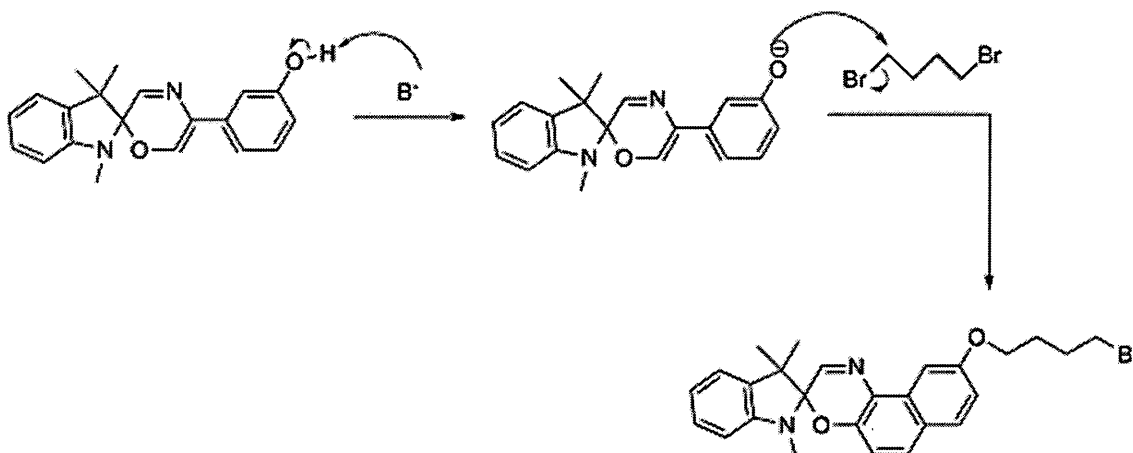
Figure 30 - S_N2 Mechanism to form Br-functionalized SO

This reaction is run with excess dibromobutane, which is easily removed from the

bromine functionalized SO through recrystallizations in hexanes. This reaction was

performed once with a yield of 61%. The final step to form the azide-functionalized SO

involves the same sort of nucleophilic substitution mechanism as the trial reaction to

form azidohexane. This reaction was also performed once with a 72% yield.

After the SO compound was successfully functionalized with the azide, the next

step was to attach a terminal alkyne to the PPV polymer. This occurs through the

familiar S_N2 reaction that has been used throughout this project, shown again in Figure

31.
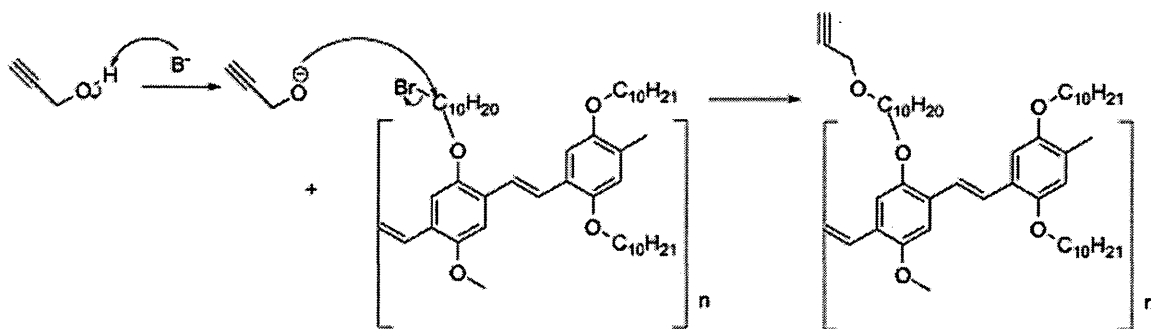
Figure 31 – Mechanism for Alkyne-functionalization of PPV-Br

The reaction was carried out in anhydrous THF at 68°C with tBuOK as a base. After 48-72 hours the excess THF was evaporated off through rotary distillation, and then the remaining reaction mixture was poured into MeOH to precipitate the polymer.

The first alkyne functionalization reaction attempted was carried out on the 40% PPV-Br from polymerization #12. Unfortunately, ^{1}H NMR analysis of the product showed no product peaks around 2.2-2.4 ppm that would indicate the presence of an alkyne, as can be seen in Figure 48 on page 66.

For these sorts of reactions with polymers, a large amount of THF is needed to dissolve a relatively small amount of polymer. For the first reaction we calculated the amount of propargyl alcohol and tBuOK based on the moles of polymer present in the reaction; because of the low amount of polymer used, the amount of propargyl alcohol and tBuOK used was also low. It was hypothesized that these reactants were not available in a high enough concentration to facilitate the desired reaction due to the high volume of THF. By looking at the amounts of propargyl alcohol and tBuOK in successful test alkyne reaction, their concentrations could be calculated using the reaction volume. Then, using these concentration values and the amount of THF needed to

dissolve the PPV-Br, new amounts of propargyl alcohol and tBuOK were calculated for the next reaction attempt, again using 40% PPV-Br. As can be seen in the ^{1}H NMR of this product in Figure 49 on page 67, this attempt showed alkyne product peaks around 2.2 ppm that were missing in the first attempt. Given the success of this reaction, it was repeated with the 50% PPV-Br produced from polymerization #13 in order to increase the amount of alkynes for the SO-PPV2 reactions. 50% alkyne-functionalized PPV was successfully created and confirmed using ^{1}H NMR, displaying an alkyne peak at 2.4 ppm as can be seen in Figure 74 on page 96. Absorbance and fluorescence studies were also carried out to make sure that the alkynization did not drastically alter the λ_{max} values.
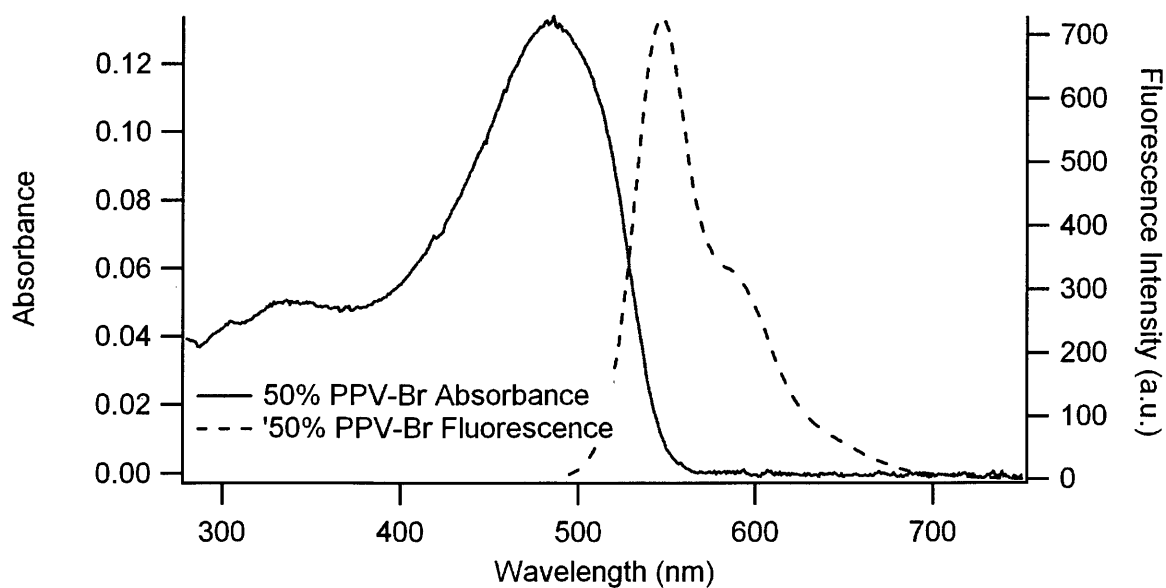
Figure 32 – Absorbance and Fluorescence Spectra of 50% PPV-Br
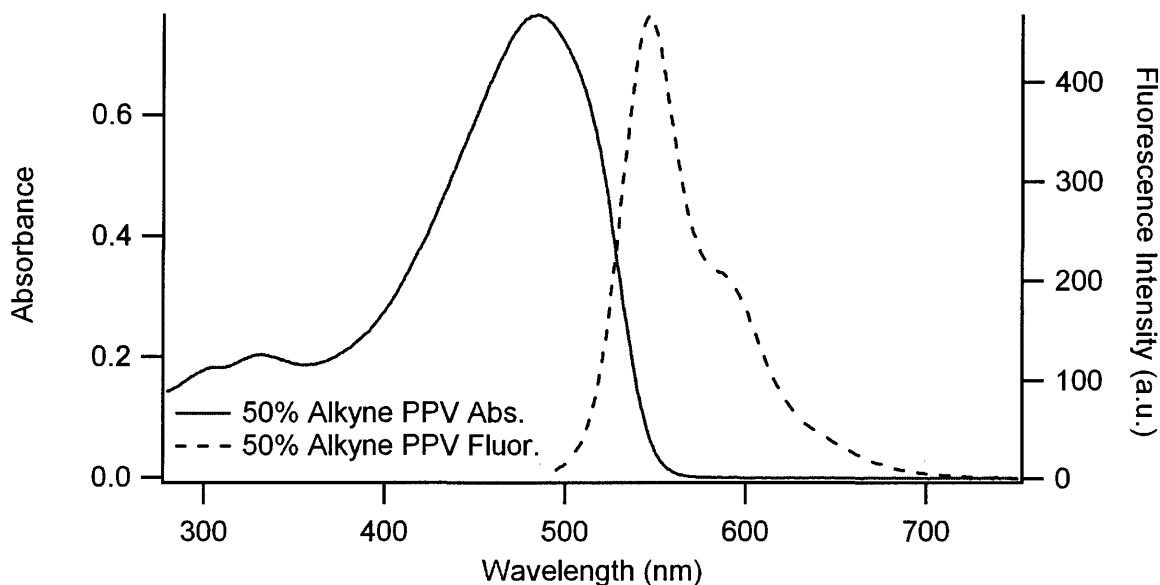
Figure 33 – Absorbance and Fluorescence Spectra of 50% Alkyne-PPV

As can be seen by the earlier two figures, the process of changing the functionalization of

the PPV polymer from bromine to an alkyne does not significantly change the absorbance

and fluorescence of the polymer. The λ_{max} values for both polymers were 485 nm for

absorbance and 546 nm for fluorescence.

The reaction conditions for the SO-PPV2 syntheses were essentially the same as

for the trial click reactions discussed earlier. Three different reactions were carried out in

THF, using copper sulfate, sodium ascorbate, and azidospirooxazine with different

amounts of polymer and differing workups, shown below. The workups will be

explained in more detail later.

#	Amount of Polymer used (g)	Workup
1	0.05	Extractions in Sep. Funnel
2	0.09	Precipitation in MeOH
3	0.05	Half Extractions in Sep. Funnel, Half Precipitation

Table 4 – Different SO-PPV2 Reactions and their Workups

Unfortunately the THF for the first reaction evaporated off at one point during the reaction. When additional THF was added most of the polymer dissolved again, showing that the polymer was not burned. Instead of doing the usual workup for polymers, with this first reaction I followed the same sort of workup that was done for the click trials. This involved evaporating off the THF, then dissolving most of the polymer in dichloromethane (DCM) in a separatory funnel. This organic layer was then washed with first 1 M HCl, then 1 N NH_4OH. At this point there was still a large amountof undissolved polymer that began to block up the separatory funnel. Once all of the polymers were gathered along with the organic layer in an Erlenmeyer flask, the undissolved polymer pieces were filtered out and dried, while the remaining dissolved polymer was dried with magnesium sulfate. The dichloromethane was evaporated by rotary distillation, and we were left with two products: the undissolved polymer flakes, and an oily substance collected after solvent removal. UV/VIS studies were carried out on both substances, the results of which will be discussed in later on.

For the second SO-PPV2 attempt, I returned to the usual workup for polymers: precipitation in MeOH. However, unlike other polymer precipitations hardly any polymer would precipitate out of the MeOH. Instead the MeOH was rotovapped down to collect another oily product for UV/VIS study. For the third and final SO-PPV2

synthesis attempt, both workups were used; half the reaction was precipitated in MeOH,

the other half went through the same workup employed on the first SO-PPV2 reaction,

resulting in 3 more products for UV/VIS study.

The next table provides labels for each type of SO-PPV2 product that was studied.

Each product was dissolved in THF and went through the same UV/VIS procedures as

those for the SO-PPV1 products.

Product Label	SO-PPV2 Reaction #	Appearance	Workup
A	1	Oil	Extractions
B	1	Flakes	Extraction
C	2	Oil	Precipitation
D	3	Oil	Extractions
E	3	Flakes	Extractions
F	3	Oil	Precipiation

Table 5: Labels for the Different SO-PPV2 Products undergoing UV/VIS Studies

All the products showed a major blue shift in absorbance, with many displaying a blue

shift in fluorescence as well; this suggests the presence of lower molecular weight

oligomers with less conjugation than longer polymer chains. Although the products all

vary in their NMR, absorbance and fluorescence spectra, they all appear to have been cut

into shorter polymer chains at some point during the click reaction. Also, the two flaky

products still exhibited poor solubility although nowhere near as severe as the products

from the SO-PPV1 route. It still took at least a couple of hours to dissolve enough

product to achieve the concentration needed for NMR or fluorescence studies.

Nevertheless, they were all subjected to UV/VIS studies in order to determine if there

was any successful binding of the SO molecule to PPV.

Product A showed some strange results. The absorption spectra can be observed

on the next page.
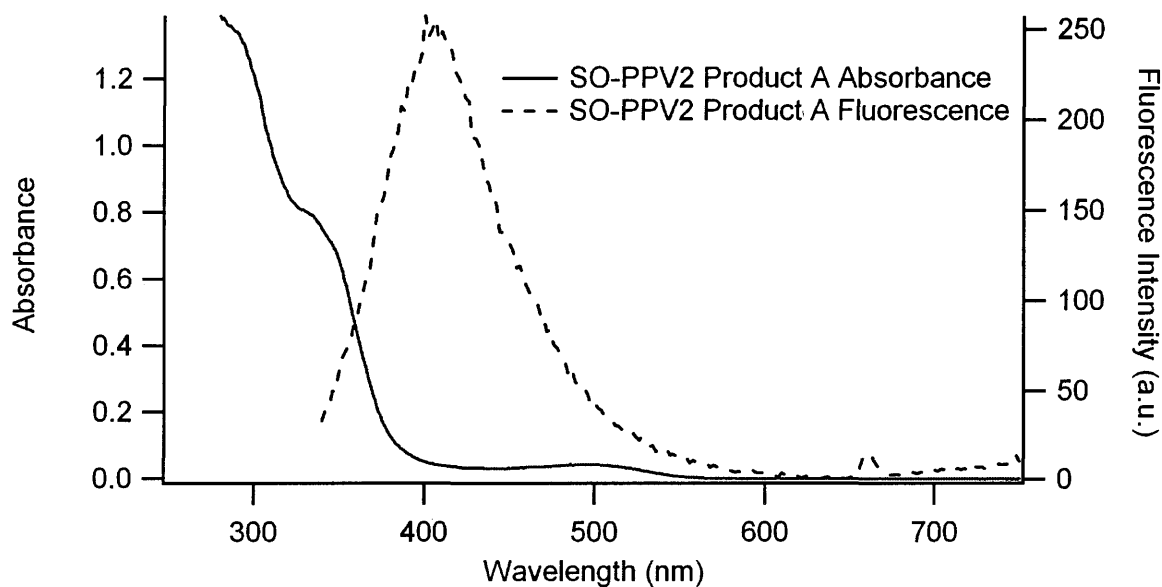
Figure 34 – Absorbance and Fluorescence Spectra of SO-PPV2 Product A

The λ_{max} is down in the 250-350 nm range, with a very slight shoulder around 498 nm.

UV irradiation studies were carried out, exciting the sample at two different wavelengths:

330 and 498 nm. While exciting at 498 nm, virtually no fluorescence signal was

recorded between 508 and 750 nm. When exciting at 330 nm, we obtained a peak with a

λ_{max} at 406 nm as shown above.
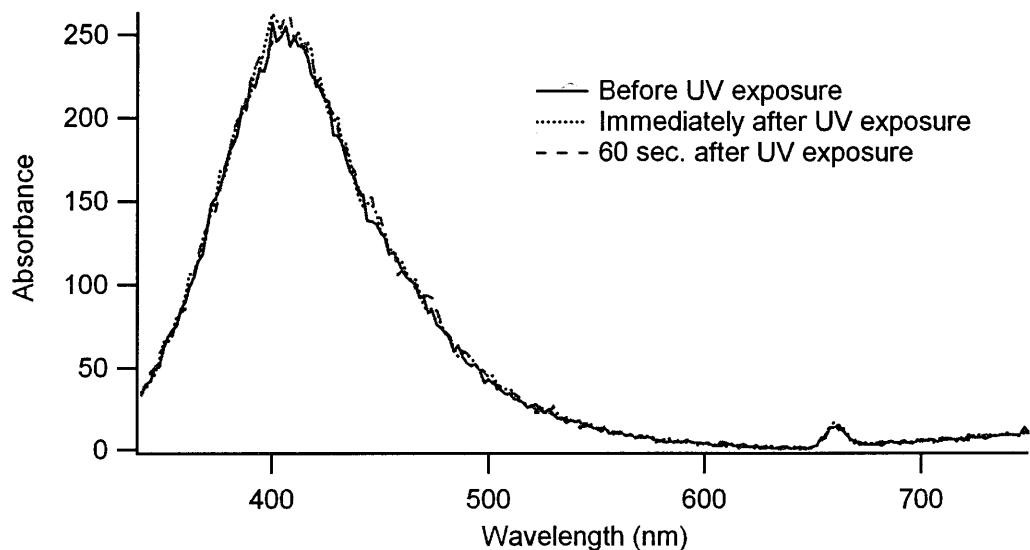
Figure 35 – UV-irradiation Studies of SO-PPV2 Product A

UV-irradiation studies were then carried out on SO-PPV2 product A, but the

sample did not appear to show any signs of photomodulation

SO-PPV2 product C displayed significant blue-shifted absorbance and

fluorescence, with λ_{max} values of 390 and 500 nm respectively, as can be seen below.
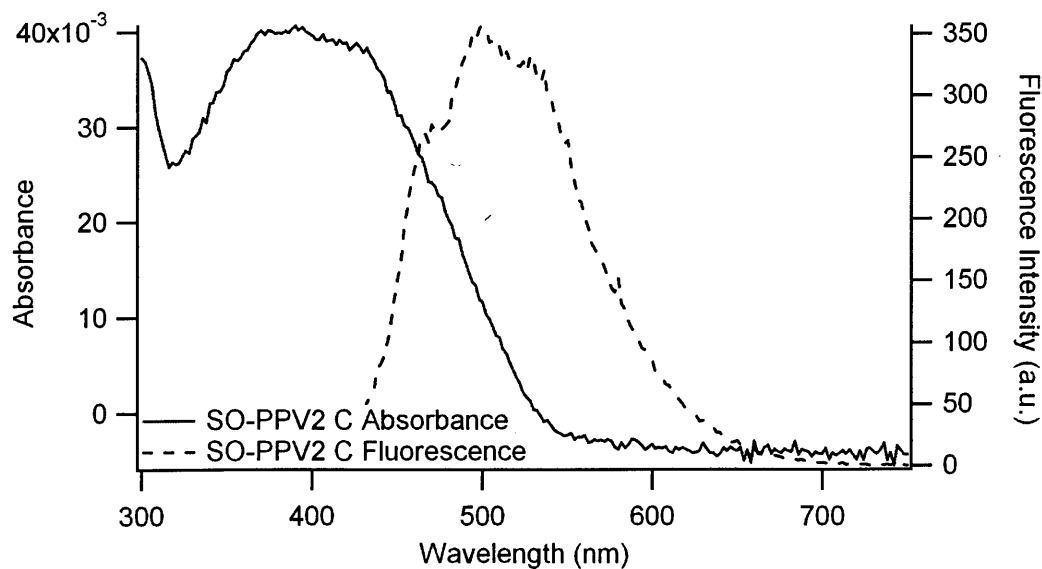
Figure 36 – Absorbance and Fluorescence Spectra of SO-PPV2 Product C

Unfortunately, photomodulation studies showed no activity.
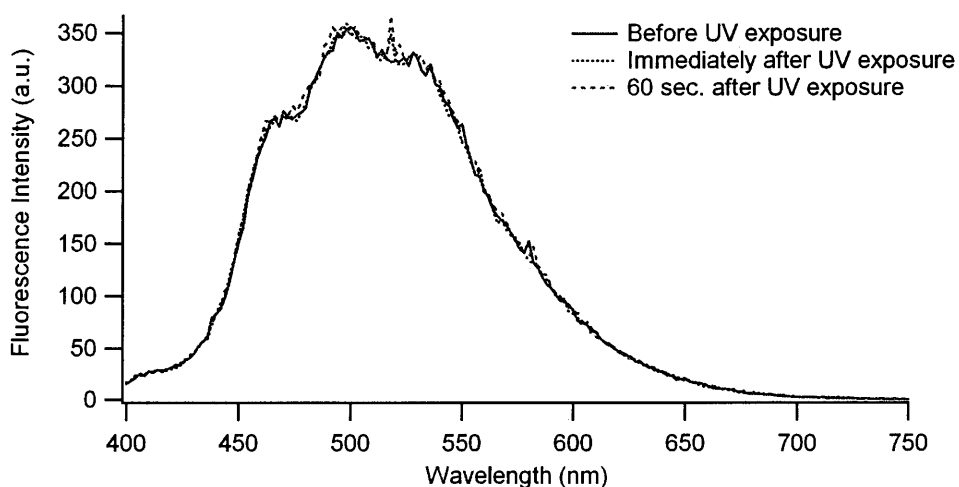
Figure 37 – UV-irradiation Study of SO-PPV2 Product C

UV/VIS studies were also carried out on all three products from the third SO-PPV2 reaction attempt. The absorbance and fluorescence spectra can all be found on the next page. UV-irradiation studies of all these products showed the same bleak conclusion: no photomodulation.
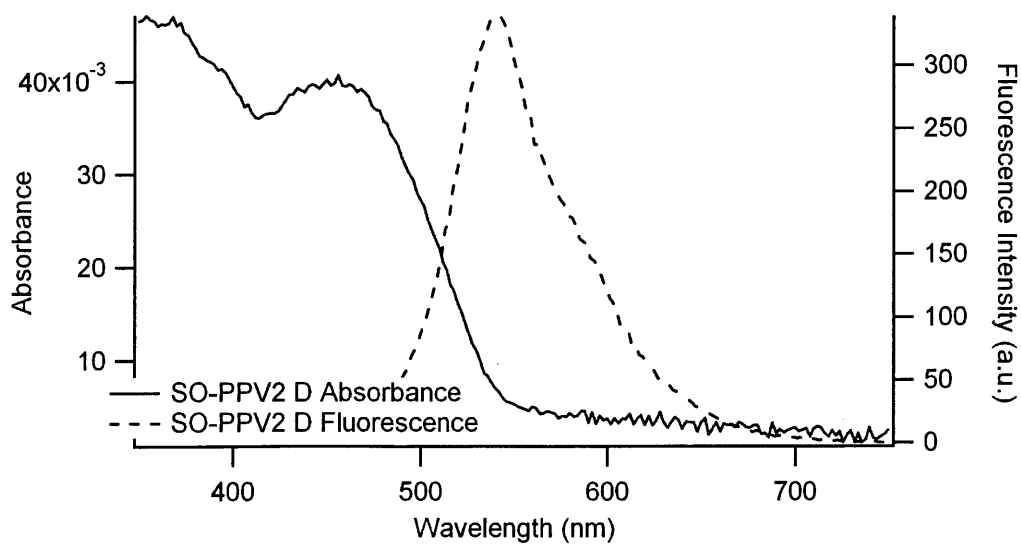
Figure 38 – Absorbance and Fluorescence Spectra of SO-PPV2 Product D
Abs. λ_{max} = 455 nm, Fluor. λ_{max} = 543 nm
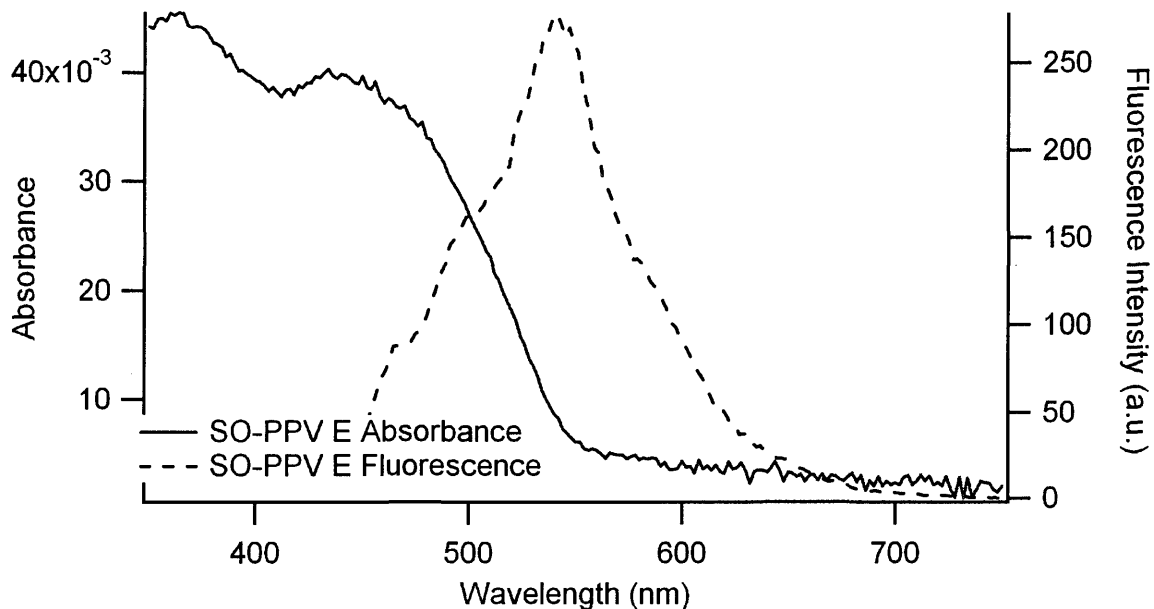
Figure 39 – Absorbance and Fluorescence Spectra of SO-PPV2 Product E
Abs. λ_{max} = 443 nm, Fluor. λ_{max} = 541 nm
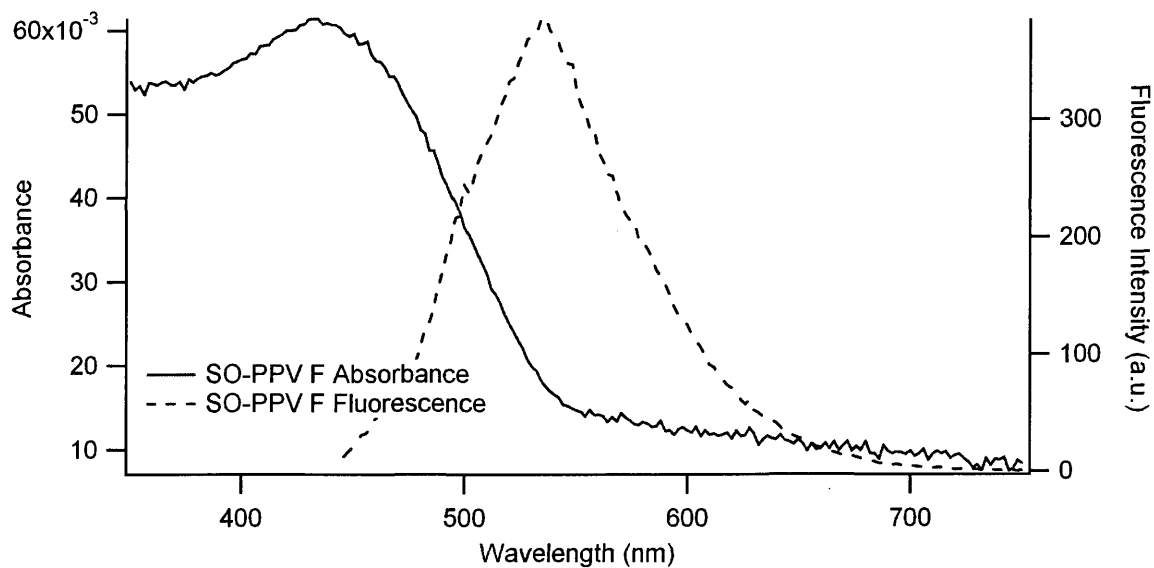
Figure 40 – Absorbance and Fluorescence Spectra of SO-PPV2 Product F
Abs. λ_{max} = 438 nm, Fluor. λ_{max} = 536 nm

However, SO-PPV2 product B showed very promising results. The absorbance

and fluorescence spectra, shown on the next page, were similar to the polymer spectra

prior to the reaction. The absorbance λ_{max} and fluorescence λ_{max} recorded were 451 nm

and 543 nm.
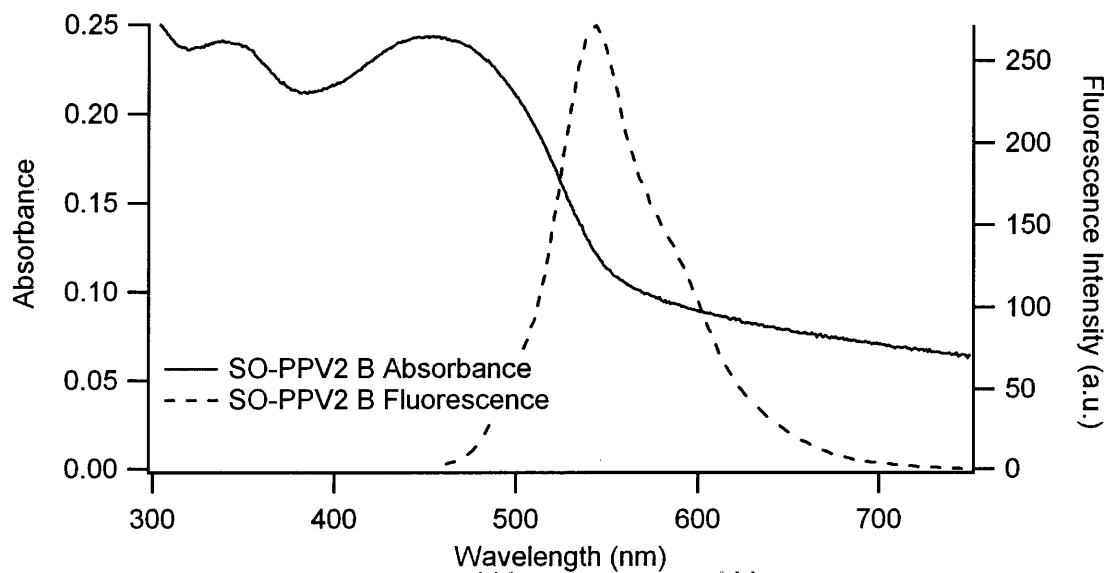
Figure 41 – Absorbance and Fluorescence Spectra of SO-PPV2 Product B

UV irradiation studies showed definite photomodulation, with the peak fluorescence

intensity reduced by 23% upon exposure to 365 nm UV light.
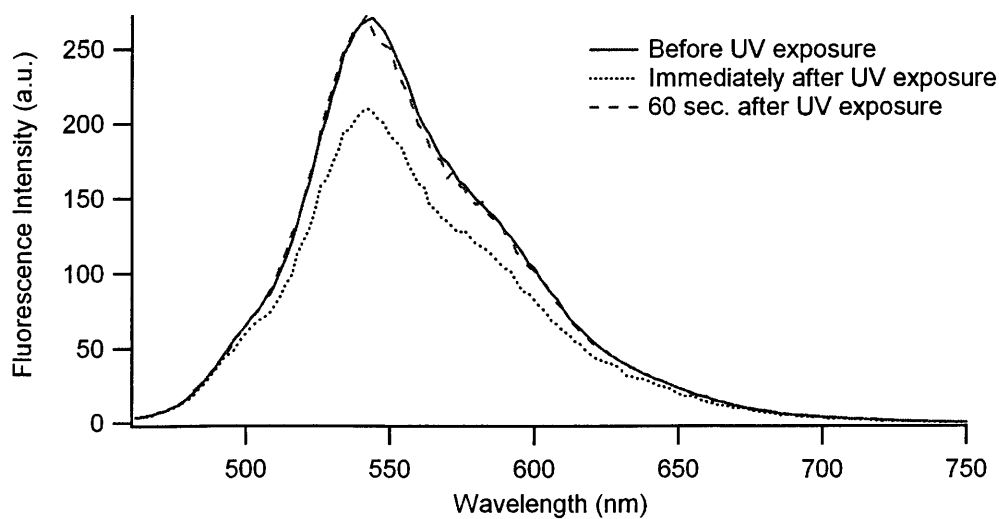
Figure 42 – UV-irradiation Study of SO-PPV2 Product B

A kinetic study was also performed on this SO-PPV2 product to confirm the photomodulation. In this study, the 365 nm UV light was placed next to the sample and switched on and off. The fluorescence intensity of the sample was measure over time while the light was being turned on and off. If the photomodulation occurs as expected, then the amount of fluorescence intensity should decrease when the light is on and then increase when it is turned off. This clearly happens in Figure 50.
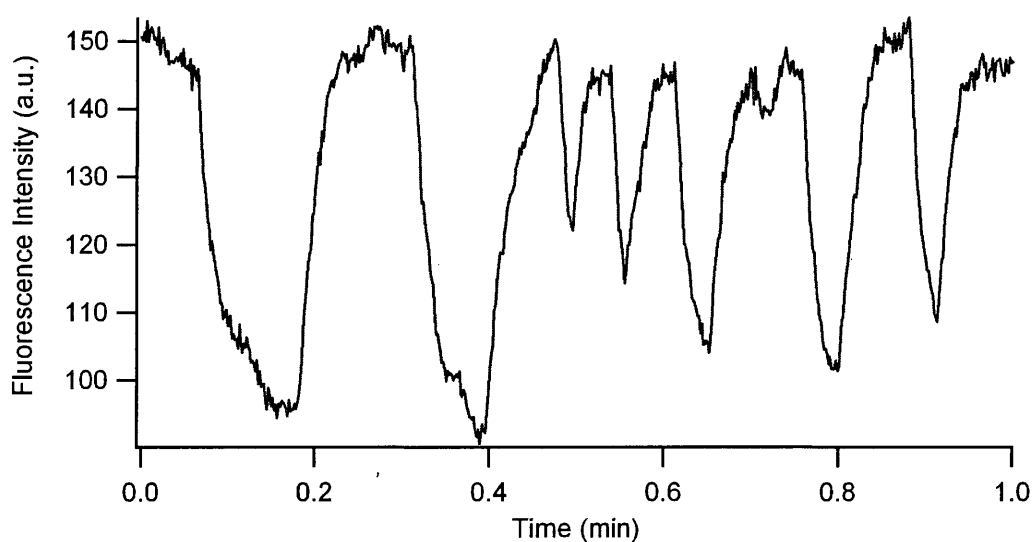
Figure 43 – Kinetic Study of SO-PPV2 Product B

An additional UV-irradiation absorbance study was carried out as well, to see if there was any visual evidence of the MC form of the spirooxazine opening up. The MC form absorbs in the 550 to 650 nm range. Concentrating on this portion of the absorption spectrum, the UV irradiation studies were again carried out on SO-PPV2 Product B. Immediately after UV irradiation there is a very slight increase in absorption in this region, which may have been due to the SO opening to the MC form. However, 60

seconds after UV irradiation the entire absorption spectrum appeared to have been shifted

upwards, rendering the study inconclusive.
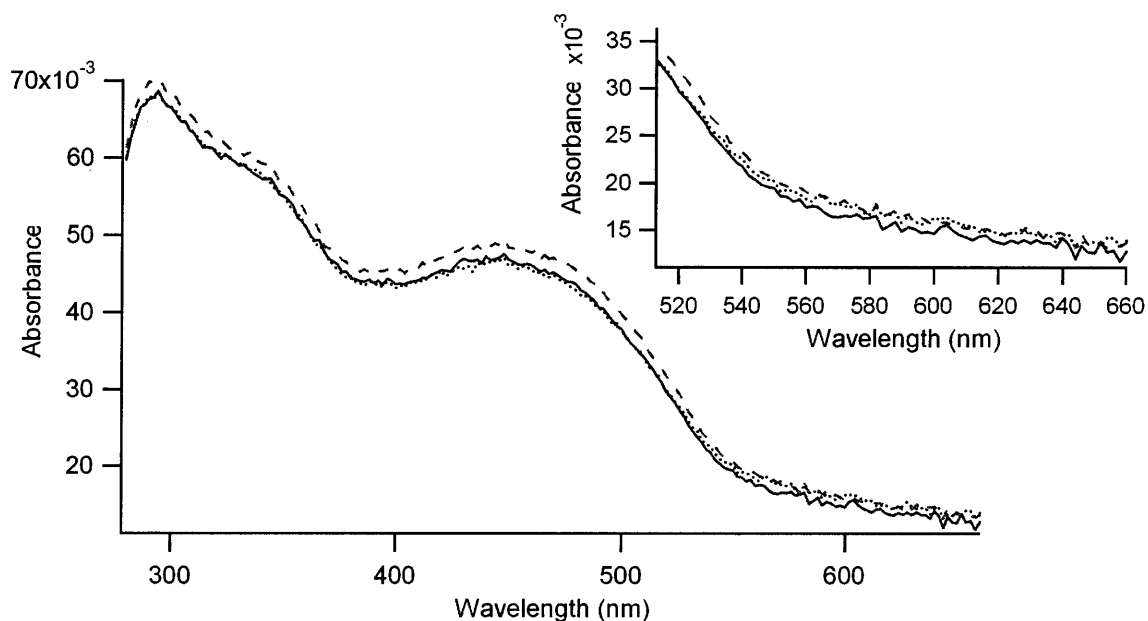
Figure 44- UV-irradiation Absorbance Study of SO-PPV2 Product B: Solid = Before
UV-irradiation, Dotted = Immediately after UV-irradiation, Dashed = 60 sec. after UV-
irradiation

More encouraging results appeared, however in the ^{1}H NMR of the polymer, which

seemed to confirm the formation of the triazole product, with new peaks between 4 and 5

ppm where previously there were none, shown in Figure 76. There are also clear peaks

where one would expect SO peaks, as can be seen when comparing the two figures on

pages 68 and 69. Despite the fact that most of the SO-PPV2 products seemed to display

no photomodulation, I am not discouraged into thinking that the synthesis of a SO-

functionalized PPV polymer using click chemistry is impossible. One of the first SO-

PPV2 products clearly shows photomodulation; this reaction is also the one that

repeatedly suffered from solvent evaporation. Throughout the reaction time, the overall

volume was decreased versus when it was started, resulting in a relative increase in concentration of the reactants. This reminds me very much of when we were trying to get the alkyne functionalization onto the PPV-Br polymer; instead of measuring out the amount of propargyl alcohol and tBuOK base to be used based on molar equivalents with the amount of polymer, we ended up instead measuring the amount of these compounds needed to maintain a similar concentration as a successful trial alkyne reaction. A large amount of THF is needed in order to fully dissolve even a small amount of polymer for the SO-PPV2 reaction, causing the solution to be extremely dilute with regards to the other reactants. Because the most successful results came about from a reaction that experienced a decrease in volume, I believe that future attempts should look at increasing the concentration of copper sulfate, sodium ascorbate, and azidospirooxazine within the reaction mixture. As for workup, I don't really have enough information to make a detailed suggestion.

Nanoparticle Studies

Given the encouraging UV/VIS studies for SOPPV2 product B, we decided to perform some preliminary nanoparticle studies. Nanoparticles are small (5-15 nm) spherical particles that are suspended in water. An SO-functionalized polymer should undergo fluorescence photomodulation of much greater magnitude in nanoparticle form than in organic solution due to the increased proximity of the donor (PPV backbone) and the photogenerated acceptor (MC form of SO). Preparation of the sample followed an already established method for nanoparticle formation.[19] To prepare the sample approximately 2 mg of this product was dissolved in 2 mL of anhydrous THF. After filtration through a 0.7 µm filter to remove any undissolved aggregates, the solution was diluted with additional THF to a concentration of 0.02 mg/mL (20 ppm). Approximately 1 mL of this solution was extracted via a glass syringe and subjected to 20 seconds of UV irradiation to open the SO compounds to their MC forms. We hypothesized that the more polar MC forms would help stabilize the nanoparticle structure. After UV-irradiation the polymer/THF solution was injected into pure water and sonicated for 2 minutes to insure homogeneity of the sample. The sudden injection into water causes the hydrophobic polymer to collapse and form a stable aqueous suspension of nanoparticle polymers, from which the remaining THF was removed via rotary evaporation. It is this remaining mixture that was subjected to UV/VIS studies.

The following pages contain the collected spectra. Figure 45 shows the absorbance and fluorescence of the nanoparticles, with a slight absorbance λ_{max} at 450 nm and a fluorescence λ_{max} at 567 nm. Despite low fluorescence intensities, the UV-

irradiation studies shown in Figure 46 show pronounced photomodulation, with a total

reversible quench of about 78%. We believe that by creating the nanoparticles the SO

groups are forced to come into closer contact with the PPV backbone which causes a

greater amount of FRET to occur, thus the increase in fluorescence quenching. To be

sure that this effect was due to the formation of nanoparticles, the same UV irradiation

studies were performed on the 20 ppm THF/polymer solution.
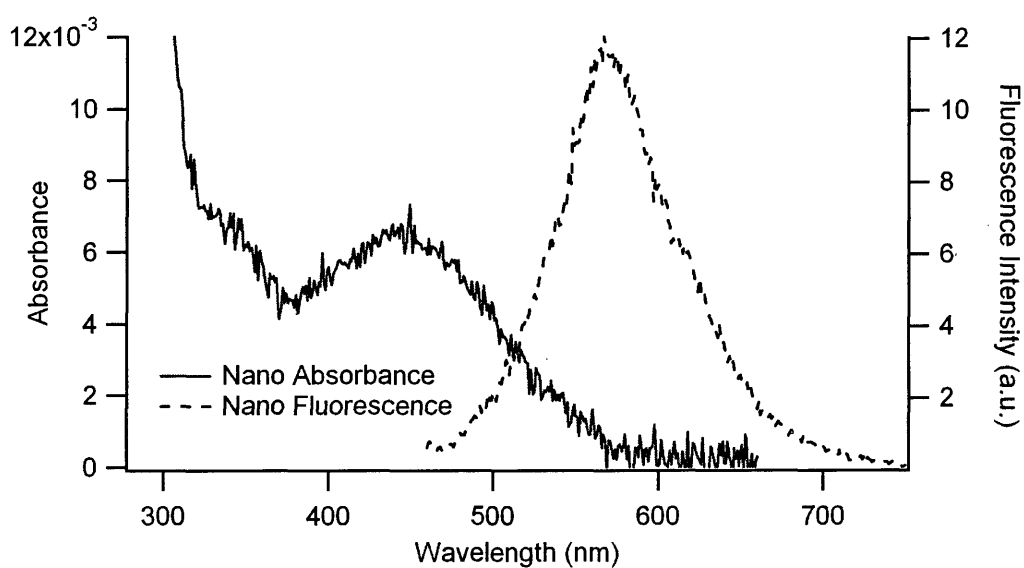
Figure 45 – Absorbance and Fluorescence Spectra of Product B Nanoparticles (20 ppm)
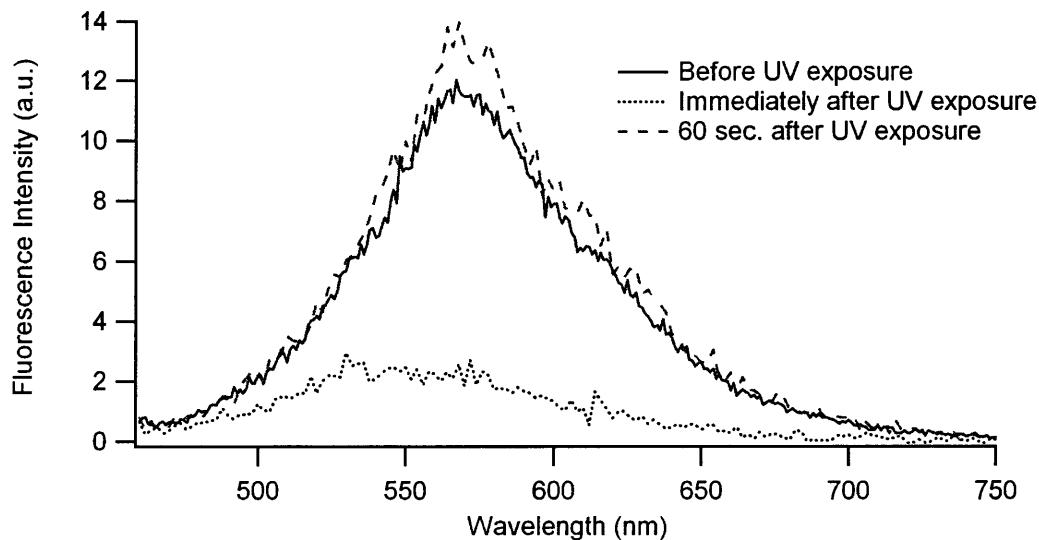
Figure 46 – UV-irradiation Studies of Product B Nanoparticles (20 ppm)
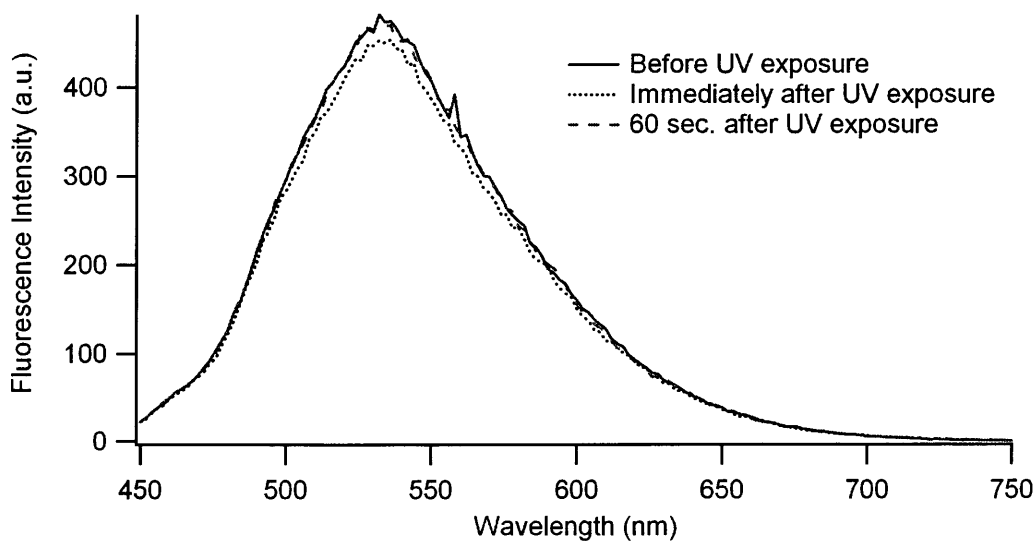
Figure 47 – UV-irradiations Studies of Product B in THF (20 ppm)

Although the above figure does show some photomodulation, it is very slight. This graph

shows only a 6% quench, a far cry from the 78% quench from the nanoparticle studies.

These results are very encouraging for future studies. However, solubility of the

product gets in our way again; much of the polymer ended up filtering out in the form of

aggregates. Although desired nanoparticle studies would be carried out with 40 ppm nanoparticle solutions, we were only able to make a 20 ppm solution. Lower molecular weight polymer chains were able to be dissolved, which is probably the cause of the slight blue shift in absorbance and fluorescence. The fluorescence of the nanoparticles is also very dim, not reaching far beyond only 10 au in intensity. Additional, more systematic UV/VIS studies will have to be carried out, but there is definite evidence to support that SO has been successfully bound to PPV polymer and made to form nanoparticles.

Conclusion

This project sought to successfully synthesize a SO-functionalized PPV polymer that would undergo reversible fluorescence quenching when exposed to UV radiation. Due to the ease of the monomer preparation for this method, a modified Gilch polymerization technique with a chloride additive was used exclusively for the formation of Br-functionalized polymers. An extensive study of 13 different polymerizations was performed to determine the most optimum reaction conditions to create soluble, non-crosslinked polymers that were easy to isolate and collect. Utilizing the findings of the most successful polymerizations, a step-by-step procedure for Gilch polymerizations has been established for future use.

The work done on the synthesis of SOPPV1 via a Williamson ether reaction between the Br-functionalized polymers and hydroxyspirooxazine was a continuation of my undergraduate thesis work. Unfortunately, it seems that the problems that were encountered during that work were also continued here. Most of the SO-PPV1 products could not be dissolved enough for proper UV/VIS studies; the few that could be dissolved showed extremely small or no photomodulation when subjected to UV-irradiation. Because of these discouraging results, we decided to try a new synthetic route to bind SO to PPV using click chemistry.

Click chemistry via a modified [1,3] Huisgen cycloaddition was investigated as an alternate route to SO-PPV synthesis. This route involved imparting different functional groups to the reactants: an alkyne for the PPV polymer, an azide for the SO compound. This reaction creates a 1,2,3-triazole that connects the two reactants together; evidence of

this triazole formation can be found in the 4-5 ppm range on ^{1}H NMR. Three different SO-PPV2 reactions were carried out, with one product showing definite, pronounced photomodulation during UV/VIS studies. However, there is a great deal of additional work that must be done to establish a definite protocol for this reaction. A more reliable method for calculating the amount of reactants needed to push the reaction forward must be established; this work suggests that a concentration method based on the volume of the reaction mixture should be used instead of a molar equivalence method based on the amount of polymer present.

The UV/VIS studies performed on the SO-PPV2 product B were very encouraging, despite the absorbance being blue-shifted. The UV-irradiation study done on this product show a much greater amount of photoquenching then in previous work, and ^{1}H NMR analysis shows definite SO product peaks and triazole formation. Kinetic studies were also carried out on this product to show the reversible quenching over a period of time, and the product seems resistant to fatigue. Preliminary nanoparticle studies show an even greater magnitude of fluorescence quenching, as a result of forcing the SO groups closer to the polymer backbone. However, the fluorescence of these nanoparticles was relatively dim, so future work will need to focus on the increasing the brightness of the nanoparticles and performing more extensive studies. More work is also needed to establish a definite protocol for the click reaction and reproduction of these results.

Experimental

Synthesis of 1-(10-bromodecyloxy)-4-methoxybenzene [4]. 25 g (83.3 mmol, 7

eq) of dibromodecane (DBD) was combined with 1.477 g p-methoxyphenol (11.9 mmol,

1 eq) and 11.826 g of potassium carbonate (85.7 mmol, 7.2 eq) in a 250 mL RB flask

with about 125 mL of dry acetone and a stirbar. The solution was set up with a nitrogen

condenser and oil bath and refluxed at 70°C for 24 hours. After 24 hours, the flask was

removed from heat and Buchner filtered to remove the excess potassium carbonate salt.

The resulting filtrate was rotovapped to get rid of acetone to get a yellow liquid product.

The liquid product was poured into about 250 mL of hexanes and put into a freezer

overnight to recrystallize, and then the white crystals were collected using Buchner

filtration. If there was any resulting DBD byproducts that showed up in the NMR, the

crystals were redissolved in acetone and recrystallized until all the byproducts were

removed. Average percent yield was 32%. ^{1}H NMR (400 MHz, CDCl$_3$) δ 6.83 (s, 4H),

3.90 (t, 2H), 3.77 (s, 3H), 3.41 (t, 2H), 1.85 (quint, 2H), 1.75 (quint, 2H), 1.4-1.5 (br, 4H),

1.3-1.4 (br, 8H). ^{13}C NMR (400 MHz, CDCl$_3$) δ 153.70, 153.33, 115.56, 114.74, 68.88,

56.01, 34.34, 33.15, 29.77, 29.71, 29.68, 29.07, 28.49, 26.38.

Synthesis of 1-(10-bromodecyloxy)-2,5-bis(bromomethyl)-4-methoxybenzene

[1]. 4 g of monomer **4** (11.7 mmol, 1 eq), 1.76 g paraformaldehyde (58.5 mmol,4 eq) and

8.61 ml of HBr in HOAC (35.1 mmol, 3 eq) in a 100 mL RB flask. A mixture of HBr in

HOAC that was 33% HBr in solution was used for this reaction. 30-40 mL of glacial

acetic acid and a stir bar were added to the solution, which was then charged with argon.

The mixture was set up with an argon condenser and oil bath to heat at 70°C for 24 hours.

For this reaction there may be some undissolved salts, and after cooling a cream-colored precipitate appears. Chloroform was added to dissolve most of the organic solids; anything that remained undissolved was assumed to be leftover salts and Buchner filtered out. The chloroform/acetic acid mixture was then poured into a 125 mL separation funnel and washed twice with deionized water, twice with $NaHCO_3$, and once with brine. Color change sometimes occurs with the $NaHCO_3$ wash, from yellow to a creamy white. The organic layer was extracted and dried with magnesium sulfate and the remaining chloroform was evaporated off to obtain a yellow solid product. The product was recrystallized using hexanes to remove impurities, resulting in a white solid product. Average percent yield was 70%. ^1H NMR (400 MHz, $CDCl_3$) δ 6.78 (s, 2H), 4.56 (s, 4H), 4.06 (t, 2H), 3.83 (s, 3H), 3.51 (t, 2H), 1.82 (quint, 2H), 1.76 (quint, 2 H) 1.43 (quint, 2H), 1.29 (br, 10H). ^{13}C NMR (400 MHz, $CDCl_3$) δ 150.5, 148.0, 128.5, 128.0, 114.5, 114.0, 69.0, 56.1, 33.7, 32.6, 29.7 (2C), 29.6 (4C), 28.6, 28.0, 25.9.

Synthesis of 1,4–bis(bromomethyl)-2,5-bisdecyloxy benzene [2]. 4 g of 1.4-bisdecyloxy benzene (10.3 mmol, 1 eq), 1.76 g paraformaldehyde (51.6 mmol, 5 eq) were dissolved in 30-40 mL of glacial acetic acid in a 100 mL 3 neck RB flask. The flask was set up with an argon condenser, stir bar and oil bath set to heat at 70°C. While the reaction mixture was heating, 7.6 ml of HBr (33%) in HOAC (31.0 mmol, 3 eq) was added dropwise to the solution via syringe. The mixture was stirred at reflux temperatures for 24 hours. For this reaction there may be some undissolved salts, which will dissolve if the solution is heated to higher temperatures (85-90°C). After removed from heat, solution precipitates white solid upon cooling. This precipitate was dissolved

with 200 mLs of chloroform; the resulting chloroform/acetic mixture was then poured

into a 500 mL separation funnel and the organic layer washed twice with deionized water,

twice with $NaHCO_3$, and once with brine. During washes the organic layer goes from a

creamy white color to more transparent amber. After drying the organic layer with

magnesium sulfate, the remaining chloroform was evaporated off using rotary distillation

to gain amber solid product. This product was recrystallized in hexanes to remove

impurities and the crystals filtered out using Buchner filtration to give pure, pale yellow

fluffy product. Average percent yield was 82% ^1H NMR (400 MHz, $CDCl_3$) δ 6.78 (s,

2H), 4.56 (s, 4H), 4.06 (t, 4 H), 1.76 (quint, 4 H), 1.43 (quint, 4 H), 1.31 (quint, 4 H),

1.29 (quint, 12 H), 1.26 (quint, 4 H), 0.88 (t, 6 H) ^{13}C NMR (400 MHz, $CDCl_3$) δ 147.3,

128.1, 114.1, 69.0, 31.9, 29.7, 29.6 (8 C), 29.3, 25.9, 22.7, 14.1 (everything 2 C except

for shift 29.6)

Synthesis of 1-azidohexane. 6.92 g NaN3 (96.1 mmol, 1.00 eq) was dissolved

in about 200 mL of DMSO in a 500 mL RB flask equipped with a stir bar. 13.68 mL of

bromohexane (97.0 mmol, 1.01 eq) was added to the reaction with stirring. After stirring

at RT for 4 hours, the reaction mixture was poured into a separation funnel and the

product extracted two times using diethyl ether. The organic layer was dried with

magnesium sulfate and the remaining diethyl ether rotovapped off to give a pale yellow

liquid product. ^1H NMR (400 MHz, $CDCl_3$) δ 1.49 (t, 2H), 1.3 (quint, 2 H), 1.29 (quint,

4H), 1.31 (quint, 2H), 0.88 (t, 3H) ^{13}C NMR (400 MHz, $CDCl_3$) δ 50, 31.5, 30.1, 26.4,

14.1.

Trial click reaction procedure to form(1-hexyl-1H-1,2,3-triazol-4-yl)

methanol. A 100 mL 3-neck RB flask was flame dried twice under inert atmosphere,

then set up with a stir bar on a condenser under N_2. 20 mL of anhydrous THF was added

to the flask via syringe, followed by 0.40 mL of propargyl alcohol (2.1 mmol, 1 eq). In a

separate, flame dried glass vial 1.826 g of azidohexane (4.1 mmol, 2 eq) was dissolved in

20 mL of anhydrous THF. The azidohexane/THF mixture was added slowly to the flask

via syringe. 135 mg of (+) sodium L-ascorbate (0.681 mmol, 0.1 eq) and 18 mg of

copper (II) sulfate (0.113 mmol, 0.02 eq) were then added to the flask. At the end of

addition the reaction mixture was slightly cloudy with the undissolved sodium ascorbate

visible at the bottom of the flask. The reaction was set to reflux at 68°C for 23 hours.

The cloudy white-green solution was removed from heat and the THF evaporated via

rotary distillation, leaving behind a greenish-yellow oil. This oil was diluted with 60-80

mLs of chloroform and poured into a 250 mL separation funnel. About 60 mL of 1 M

HCl was added to the funnel; after shaking with the acid, the organic layer turned a clear

brown color. The organic layer was then washed with 1 N NH4OH, upon which it turned

a peach-brown color while the aqueous layer turned a solid blue-white color. The

organic layer was extracted, washed one time with brine, dried with magnesium sulfate

and the chloroform evaporated to give a brown oil product. ^{1}H NMR (400 MHz, CDCl$_3$)

δ 7.59 (s, 1 H), 4.79 (s, 2 H), 4.46 (t, 2 H), 3.65 (s, 1 H), 1.74 (quint, 2 H), 1.31 (quint, 2

H), 1.29 (quint, 4 H), 0.88 (t, 3 H). ^{13}C NMR (400 MHz, CDCl$_3$) δ 142.3, 128.6, 53.5,

52.4, 31.5, 28.4, 26.8, 22.7, 14.1.

Synthesis of 9'-(4-bromobutyl)-spirooxazine. 1.035 g of hydroxyspirooxazine

(3 mmol, 1 eq) was dissolved in 100 mL of dry acetone in a 3-neck 250 mL RB flask.

2.902 g of K2CO3 (21 mmol, 7 eq) was added to the acetone and the flask set up with a

heat plate and stir bar on a condenser under nitrogen atmosphere. 0.36 mL of

dibromobutane (3 mmol, 1 eq) was added to the reaction mixture dropwise vis syringe.

The reaction was set to reflux at 56°C for 24 hours. After removal from heat the acetone

is evaporated off to leave a slimy green-brown sludge. When trying to dissolve this

product in hexanes, it started to get less slimy and adopted a grey, clay-like subsistency.

The product was recrystallized in 80 mL of hexanes and filtered out via Buchner filtration

to give gray powder. This reaction was carried out once with a 61% yield. ^{1}H NMR (400

MHz, CDCl$_3$) δ 7.78 (d, 2 H), 7.50 (s, 1 H), 7.12 (s, 1 H), 7.07 (t, 1 H). 7.06 (s, 1 H), 6.94

(d, 2 H), 6.71 (d, 1 H), 6.56 (d, 1 H), 4.16 (t, 2 H), 3.51 (t, 2 H), 3.06 (s, 3 H), 1.82 (quint,

2 H), 1.76 (quint, 2 H), 1.40 (s, 6 H). ^{13}C NMR (400 MHz, CDCl$_3$) δ 163.7, 158.6, 151.7,

148.4, 137.1, 129.8, 129.5, 128.0, 127.3, 126.4, 126.5, 125.1, 118.6, 117.8, 116.2, 116.8,

106.9, 105.2, 67.7, 48.2, 35.2, 30.0, 28.9, 28.0, 18.2 (2).

Synthesis of 9'-(4-azidobutoxy)-spirooxazine. 0.13 g of sodium azide was

dissolved in about 5 mL of DMSO in a 50 mL RB flask set up on a stir plate. 0.882 g of

Br spirooxazine (1.8 mmol, 0.92 eq) was added to the flask along with 20-25 additional

mL of DMSO. The reaction was stirred for 4 hours at RT, changing from a grey color to

a greenish-blue. The reaction mixture was poured into a 250 mL separation funnel.

About 80 mL of deionized water was added, turning the solution grey and cloudy. The

addition of water also caused an exothermic reaction, making the solution in the

separation funnel warm. 110 mL of diethyl ether was also added to the funnel. Upon

vigorous shaking the cloudiness disappeared and the organic layer turned a dark grey-

yellow. The product was extracted with diethyl ether two times in 110 mL portions. The

organic layer was dried with magnesium sulfate and the ether rotovapped off to leave

light brown-grey powder product. This reaction was carried out once with 72% yield. ^{1}H

NMR (400 MHz, CDCl$_3$) δ 7.78 (d, 2 H), 7.50 (s, 1 H), 7.12 (s, 1 H), 7.07 (t, 1 H). 7.06 (s,

1 H), 6.94 (d, 2 H), 6.71 (d, 1 H), 6.56 (d, 1 H), 4.16 (t, 2 H), 3.06 (s, 3 H), 1.76 (quint, 2

H), 1.49 (quint, 2 H), 1.40 (s, 6 H), 1.3 (quint, 2H). ^{13}C NMR (400 MHz, CDCl$_3$) δ 163.7,

158.6, 151.7, 148.4, 137.1, 129.8, 129.5, 128.0, 127.3, 126.4, 126.5, 125.1, 118.6, 117.8,

116.2, 116.8, 106.9, 105.2, 68.4, 50, 48.2, 35.2, 26.4, 26.7, 18.2 (2).

Gilch Polymerization of 50% Br-PPV using Monomers [2] and [3]. A

3 neck 100 mL RB flask was set up with the left and right neck fitted with rubber septa.

A needle that was hooked up to an argon tank was inserted into the left septum, along

with a corresponding disposable syringe needle in the right septum to let out excess air.

A 50 mL addition funnel was set up on the middle neck of the RB flask, also fitted with a

rubber septum. The entire system was flame-dried to get rid of excess moisture. 0.300 g

of **1** (0.057 mmol, 1 eq) and 0.328 g of **2** (0.057 mmol, 1 eq) was dissolved in anhydrous

THF and the resulting solution injected into the 3 neck RB flask. 0.220 mL of 4-(tert

butyl) benzyl chloride additive (0.113 mmol, 2 eq) was added to the clear, yellow

reaction mixture vis syringe. This solution was heated to 50°C, with a steady nitrogen

flow. Next, a solution of 2.27 mL of 1M tBuOK in anhydrous THF (0.226 mmol, 4 eq)

and 40 mL of additional anhydrous THF was prepared in the addition funnel. After the

reaction reached 55°C, addition of the tBuOK/THF solution began. After 3.6 minutes the addition was stopped as the reaction turned a brighter yellow. 2.5 minutes later the reaction was started again. 7.5 minutes after the addition was started it was stopped again as the solution started getting cloudy. After 2.3 minutes the addition was started again. A close eye needs to be kept on the stirring, as any problem with the stirring may indicate the formation of crosslinked polymer. The starting and stopping of the addition occurred each time there was a color change from yellow to yellow-orange to orange, until the entire tBuOK/THF solution was added 36 minutes after the addition began. By this point the solution was bright orange, but not quite the right color. A couple more drops of tBuOK was added straight to the reaction mixture, with a full minute between each drop. The total amount of additional tBuOK needed was about 0.5 mL, leading me to think that the mole equivalence of tBuOK should be increased for polymerizations. After letting the reaction stir for 2 hours at It was sometimes necessary to inject several mL of anhydrous THF every couple of minutes, as the reaction solvent kept evaporating. In the last 2-3 minutes of adding the tBuOK:THF solution the mixture changes color from a creamy white to dark orange or red. The solution was stirred for 2 hours at 55°C, and then removed from heat. One of the rubber septa was removed and the red-orange solution was poured into at least 400 mL of vigorously stirring methanol to precipitate the polymer. After letting the mixture stir overnight it was Buchner filtered to collect the red flakes of polymer, while the filtrate came out as a light green color. Before collection the polymer was washed with acetone to remove any remaining monomer or lower molecular weight polymers. Upon drying the polymer broke into easily collected flakes.

Sample SO-PPV1 reaction #6. 0.101 g of 20% PPV-Br polymer (0.050 mmol, 1 eq) was added to a 10 mL RB flask along with 6 mL of xylenes. 0.019 g of hydroxyspirooxazine (0.060 mmol, 1.2 eq), 0.048 g K_2CO_3 (0.348 mmol, 7 eq), and a stir bar were added to the flask, which was then set to heat at 150°C with a condenser under inert atmosphere. The reaction was allowed to run for 7-9 days, at the end of which the reaction changed from orange to dark green-orange. The solution was poured into 250 mL MeOH and allowed to stir overnight. The dark-red precipitate was Buchner filtered to collect bright red polymer flakes.

Alkyne Polymer Reaction for 50% PPV-Br. A 3 neck 250 mL flask set up with a 50 mL addition funnel on one of the side arms was flame-dried twice under argon and then set up on a condenser under inert atmosphere. 0.050 g of 50% PPV-Br was dissolved in 100 mL anhydrous THF through vigorous stirring and sonication, and then added to the reaction flask via syringe. This reaction mixture was then heated to 65°C. 1.42 mL propargyl alcohol (24 mmol, maintaining 0.012 M) and 3.03 mL tBuOK (X mmol, maintaining 0.025 M) along with 5 mL anhydrous THF were added to the addition funnel via syringe. This mixture of THF/tBuPOK/propargyl alcohol was then added dropwise to the reaction mixture, then an additional 5 mL of anhydrous THF was used to wash down the sides of the addition funnel. After complete addition, the reaction was a cloudy orange color. After stirring for 48 hours, the reaction was removed from heat, most of the THF was evaporated off and the remainder was poured into 600 mL MeOH. Bright red polymer flakes were precipitated and allowed to stir overnight, then collected via Buchner filtration.

SO-PPV2 Reaction for Products A & B. A 3-neck 100 mL RB flask with stirbar was flame-dried twice under argon, then set up with a condenser and nitrogen atmosphere. 0.058 g of 50% alkyne-functionalized PPV (0.008 mmol, 1 eq) was dissolved in 15 mL of anhydrous THF and added to the RB flask via syringe. 0.083 g of azidospirooxazine (0.016 mmol, 2 eq) was dissolved in 20 mL THF in a separate vial, then also added to the reaction flask via syringe. 5 mg of (+) sodium L- ascorbate (0.0008 mmol, 0.1 eq) and 1 mg of copper (II) sulfate (0.00016 mmol, 0.02 eq) was then added to the reaction mixture and set to heat at about 65°C. After 3 days the reaction solvent had been evaporated; before the polymer was burned too badly it was able to be mostly dissolved again in THF. After 2 more hours of stirring in THF the reaction was removed from heat and the THF rotovapped off. A majority of the polymer was then dissolved and diluted with 200 mL of DCM and poured into a 500 mL sep funnel; not all of the polymer fully dissolved, however. The organic layer was washed once with 1 M HCl and once with 1 N NH$_4$OH. The organic layer never changed from its orange color, while both aqueous layers took on an orange tint. With both washings frothy light emulsions appeared between the two layers that simply dissipated over time. After these two washings there was still undissolved polymer that was starting to block up the separation funnel. The undissolved polymer was then filtered out and air dried via Buchner filtration, forming product SO-PPV2 product **B.** The remaining filtrand was put back into the separation funnel to wash with brine, then the organic layer was dried with magnesium sulfate and the DCM evaporated via rotary distillation to give an oily dark orange SO-PPV2 product A.

SO-PPV2 Reaction for Product C. A 3-neck 100 mL RB flask with stirbar was flame-dried twice under argon, then set up with a condenser and nitrogen atmosphere. 0.090 g of 50% alkyne-functionalized PPV (0.014 mmol, 1 eq) was dissolved in 15 mL of anhydrous THF and added to the RB flask via syringe. 0.124 g of azidospirooxazine (0.0.028 mmol, 2 eq) was dissolved in 20 mL THF in a separate vial, then also added to the reaction flask via syringe. 5 mg of (+) sodium L- ascorbate (0.0008 mmol, 0.1 eq) and 1 mg of copper (II) sulfate (0.00016 mmol, 0.02 eq) was then added to the reaction mixture and set to heat at about 70°C for 48 hours. Most of the THF was boiled off, and the remaining THF/polymer mixture was poured into 600 mL MeOH to precipitate the polymer. Most polymer precipitation was stuck to the stir bar; while the MeOH was Buchner-filtered, the polymer from the stir bar was also scraped off and air dried to give SO-PPV product C.

SO-PPV2 Reaction for Products D, E, and F. A 3-neck 100 mL RB flask with stirbar was flame-dried twice under argon, then set up with a condenser and nitrogen atmosphere. 0.050 g of 50% alkyne-functionalized PPV (0.008 mmol, 1 eq) was dissolved in 15 mL of anhydrous THF and added to the RB flask via syringe. 0.070 g of azidospirooxazine (0.016 mmol, 2 eq) was dissolved in 20 mL THF in a separate vial, then also added to the reaction flask via syringe. 5 mg of (+) sodium L- ascorbate (0.0008 mmol, 0.1 eq) and 1 mg of copper (II) sulfate (0.00016 mmol, 0.02 eq) was then added to the reaction mixture and set to heat at about 70°C. After 48 hours the reaction was taken off heat. About 10 mLs of the resulting solution was taken out and poured into 400 mL of MeOH to precipitate, while the rest of the solution underwent the same

workup as in SO-PPV2 procedure for products A and B, effectively forming products D and E. For the precipitation reaction, it seemed that nothing precipitated out at all; whatever could be Buchner-filtered remained stuck to the filter paper and had to be dissolved off using DCM and THF. After both these solvents were evaporated off, all that was left was slightly oily product E.

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Appendix

INDEX	FREQUENCY	PPM	HEIGHT
1	3001.253	7.500	10.7
2	2905.129	7.260	151.2
3	2869.961	7.172	12.4
4	1623.469	4.057	17.9
5	1575.016	3.936	14.5
6	1349.944	3.373	10.7
7	744.281	1.860	18.6
8	618.850	1.546	69.5
9	550.860	1.377	37.7
10	502.407	1.255	140.7
11	346.888	0.867	55.7

PPV-BR + Propargyl
Automation directory:
Sample : kp030311b
Pulse Sequence: s2pul
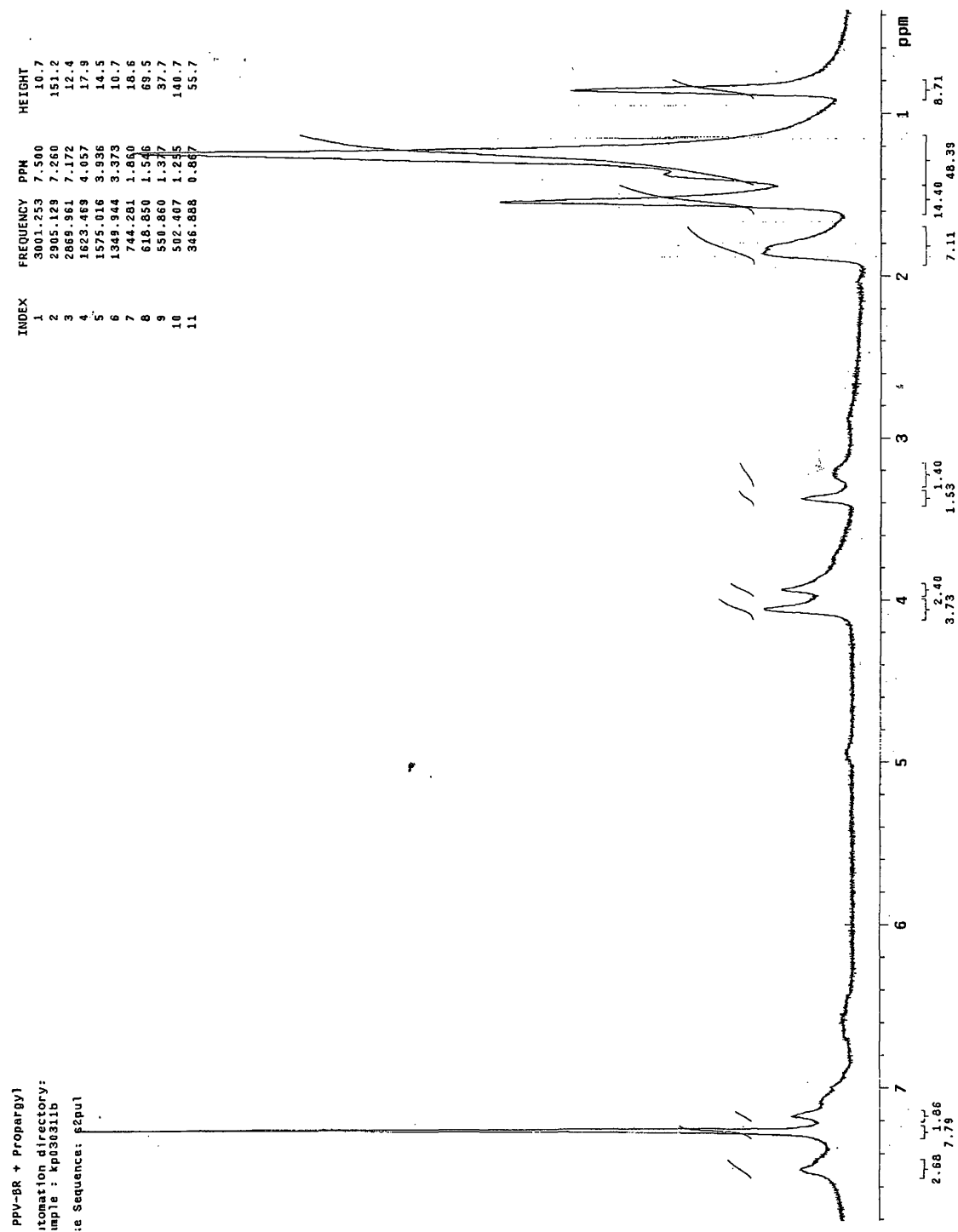
Figure 48 – ^{1}H NMR Spectrum of 40% alkyne-PPV, First Attempt

INDEX	FREQUENCY	PPM	HEIGHT
1	2904.738	7.259	150.0
2	1398.397	3.494	9.0
3	1394.098	3.484	10.3
4	868.540	2.170	889.8
5	847.439	2.118	18.3
6	825.948	2.064	7.1
7	815.007	2.037	6.4
8	804.457	2.010	8.0
9	627.838	1.569	54.0
10	499.281	1.248	31.1
11	346.888	0.867	6.7

40%
alkynized PPV
Automation directory:
Sample : kp032811a
Pulse Sequence: s2pul
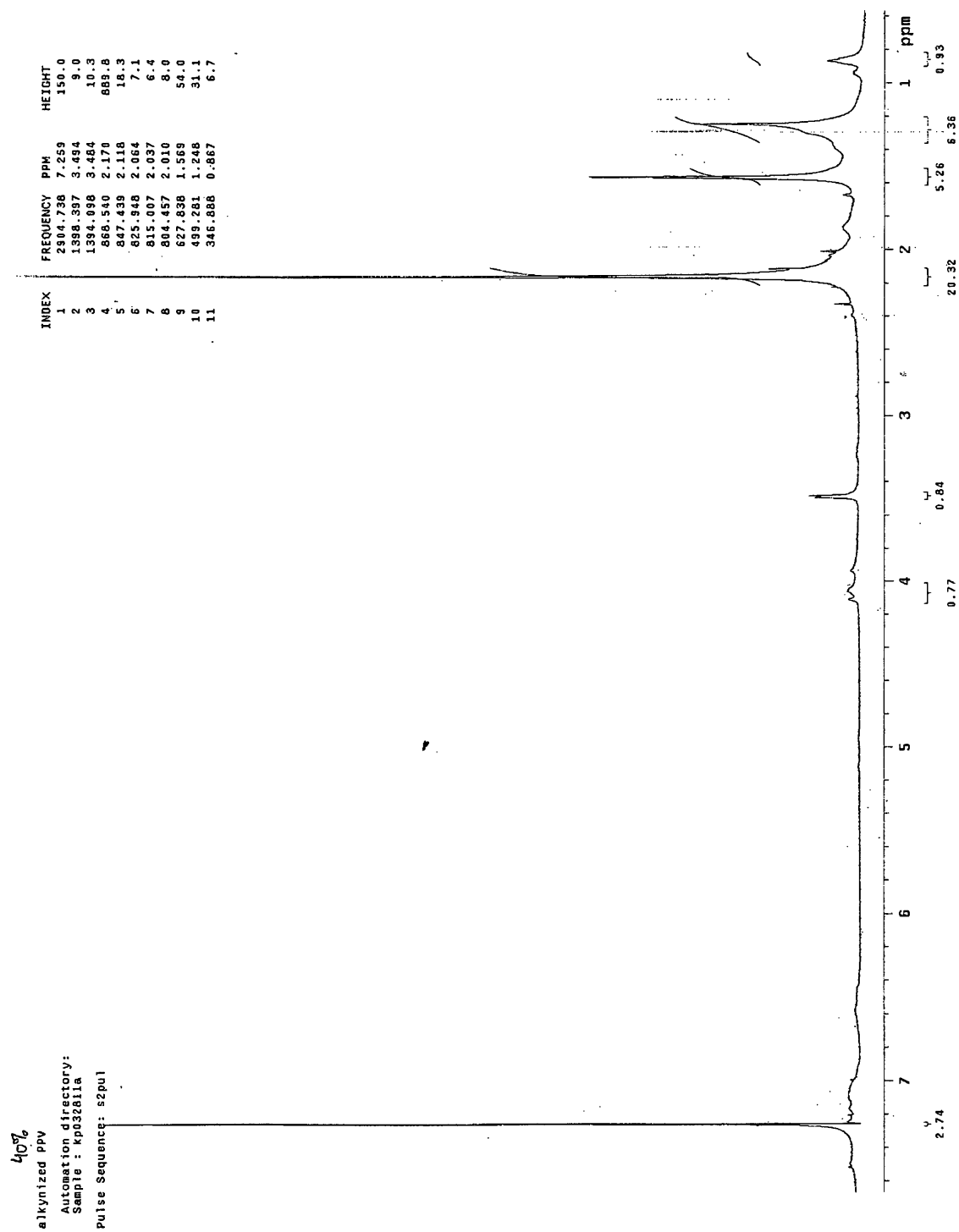
Figure 49 - ^{1}H NMR Spectrum of 40% Alkyne-PPV, Second Attempt
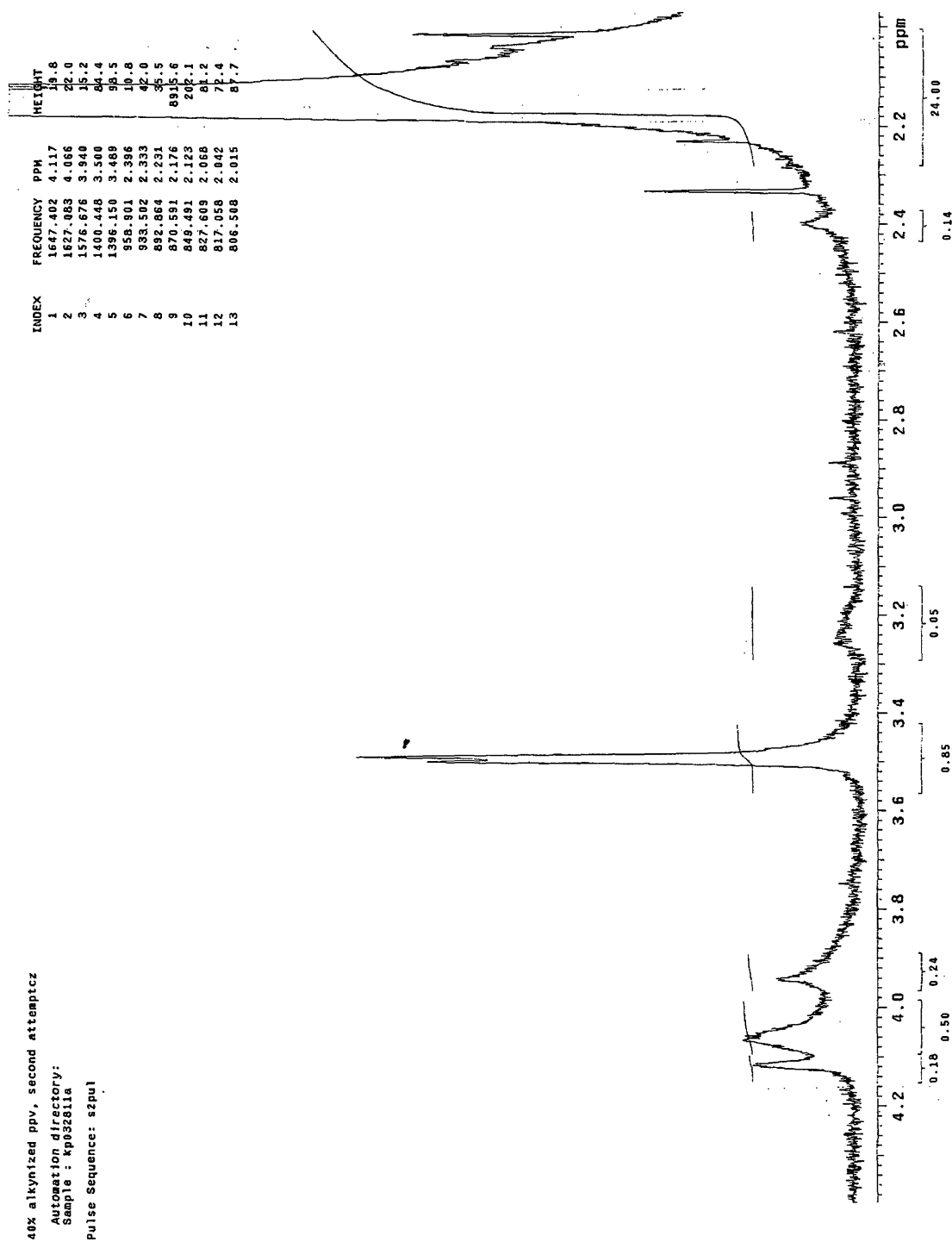
Figure 50 - ^{1}H NMR Spectrum of 40% Alkyne-PPV, Second Attempt, 2.0 – 4.3 ppm
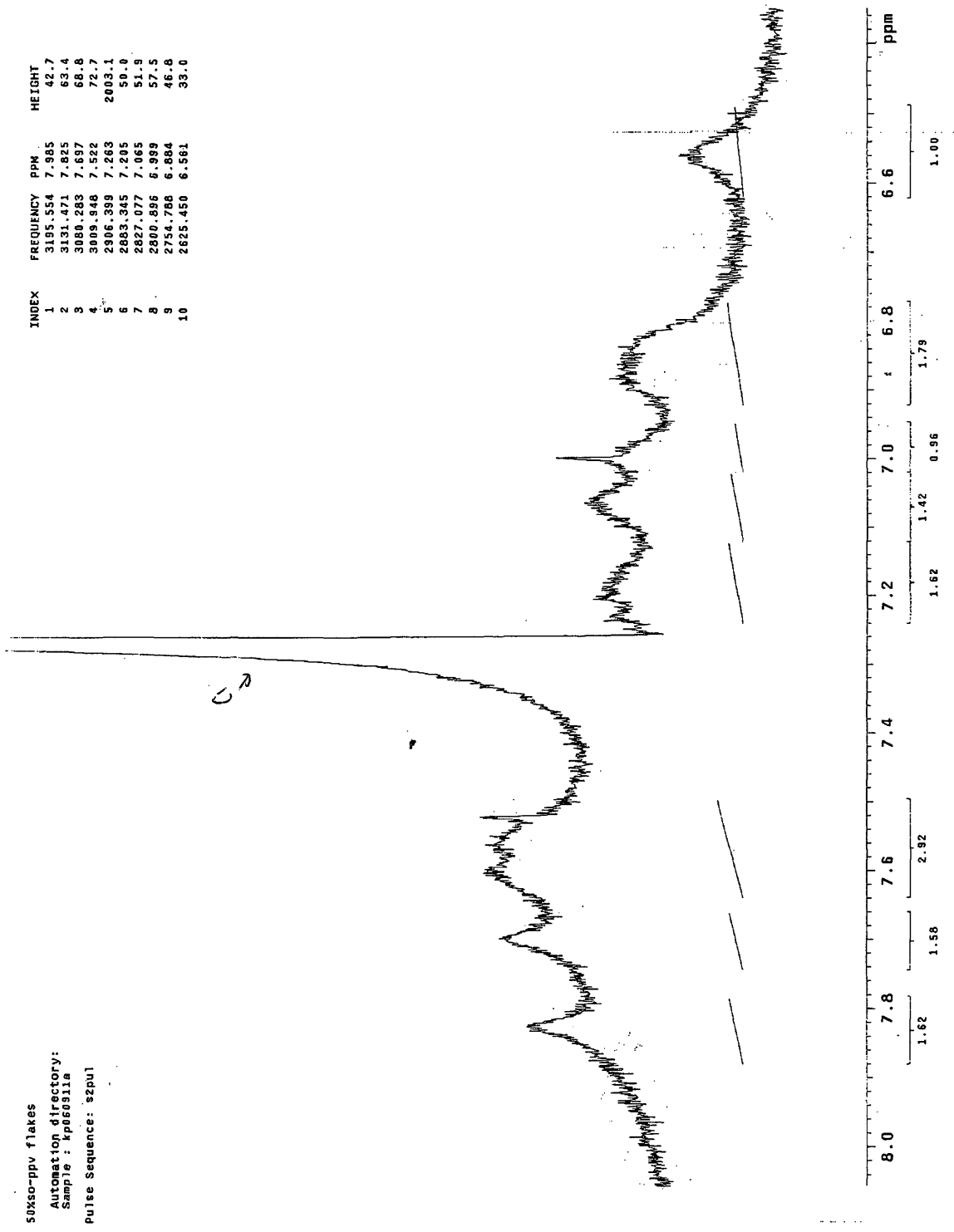
Figure 51 - ^{1}H NMR Spectrum of SO-PPV2 Product B, 6.5-8 ppm
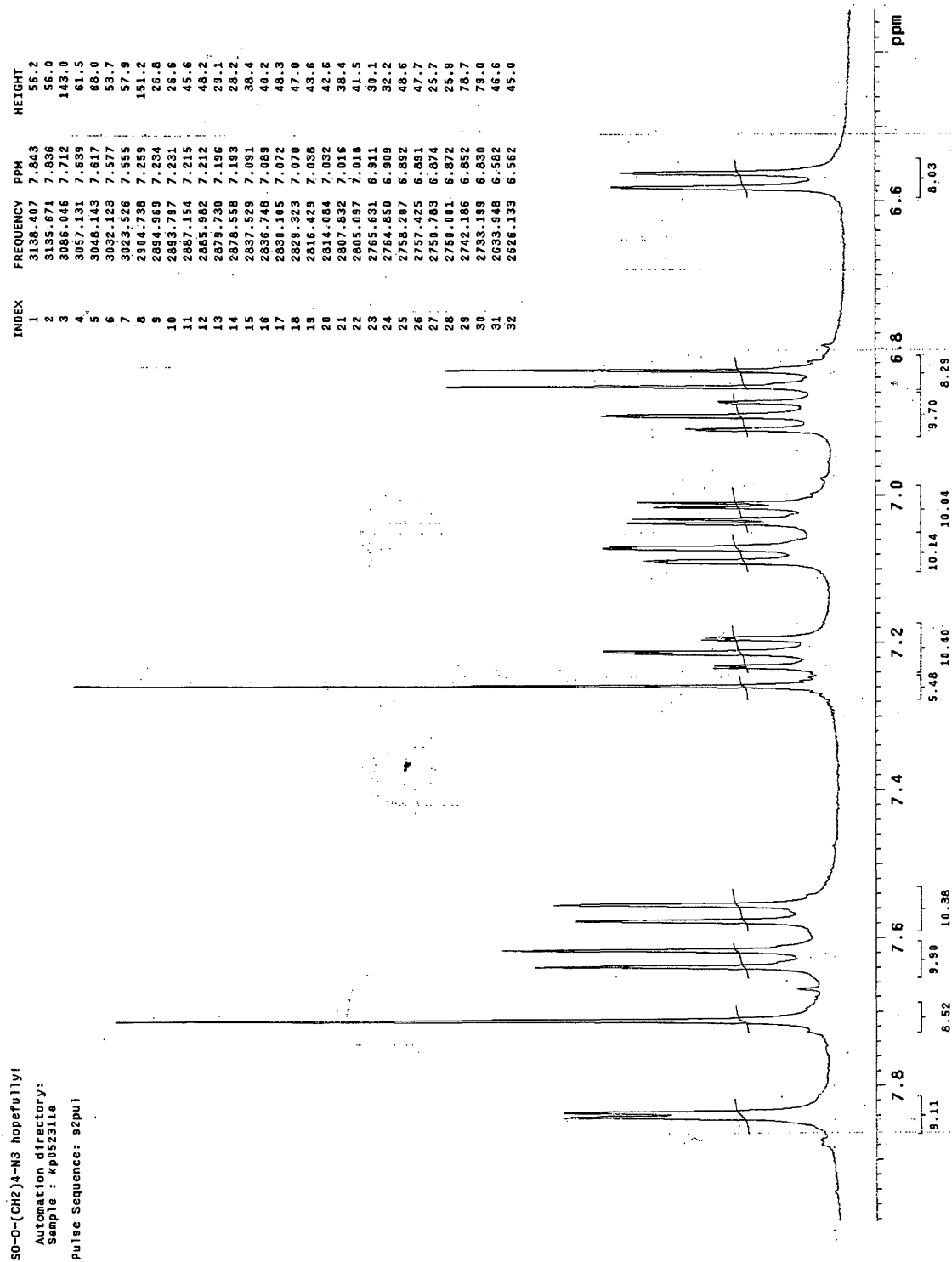
Figure 52 - ^{1}H NMR Spectrum of SO, 6.5-8 ppm
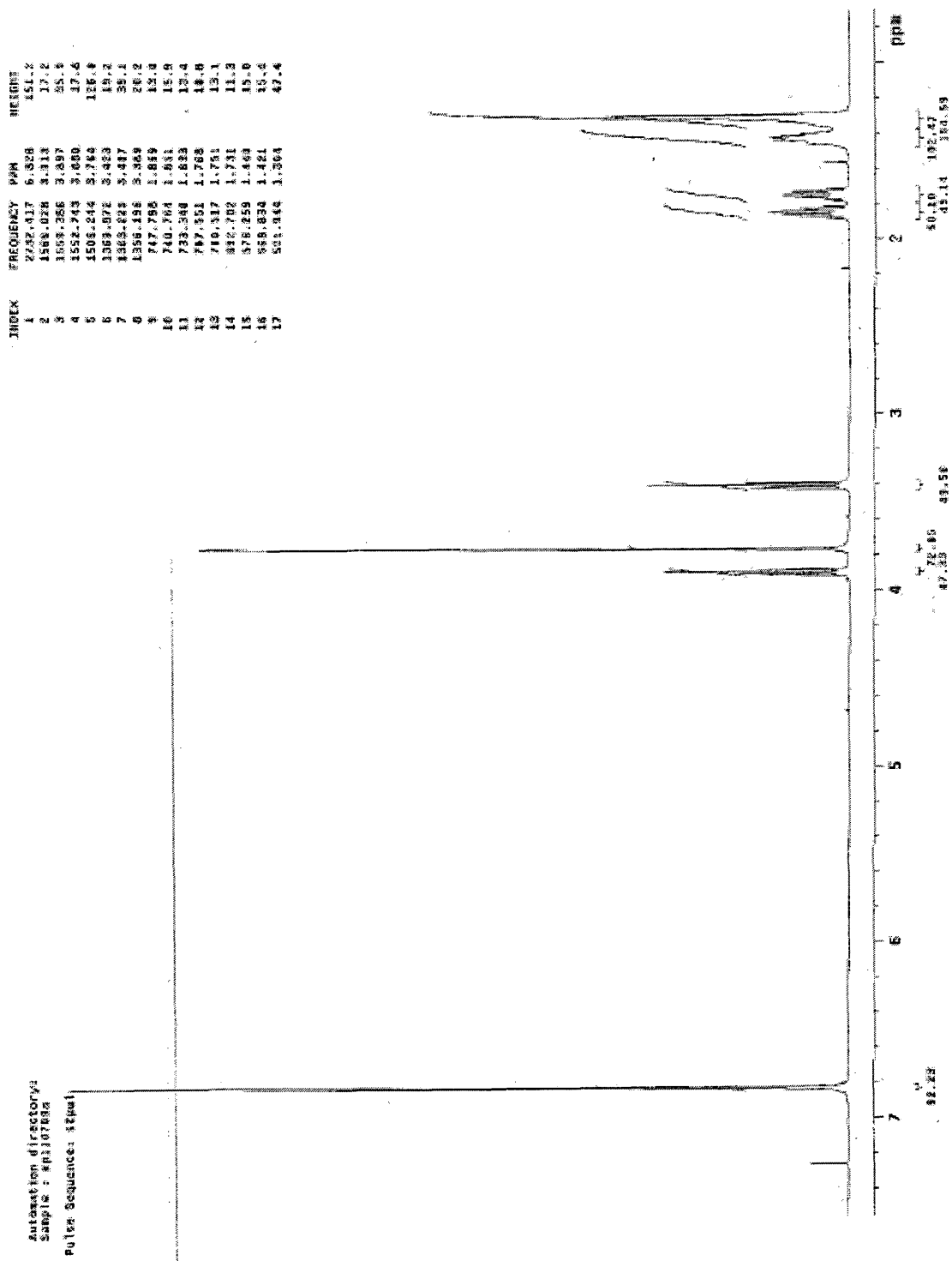
Figure 53 – ¹H NMR Spectrum of 1-(10-bromodecyloxy)-4-methoxybenzene [**4**]

Figure 54 – ^{13}C NMR Spectrum of 1-(10-bromodecyloxy)-4-methoxybenzene [4]
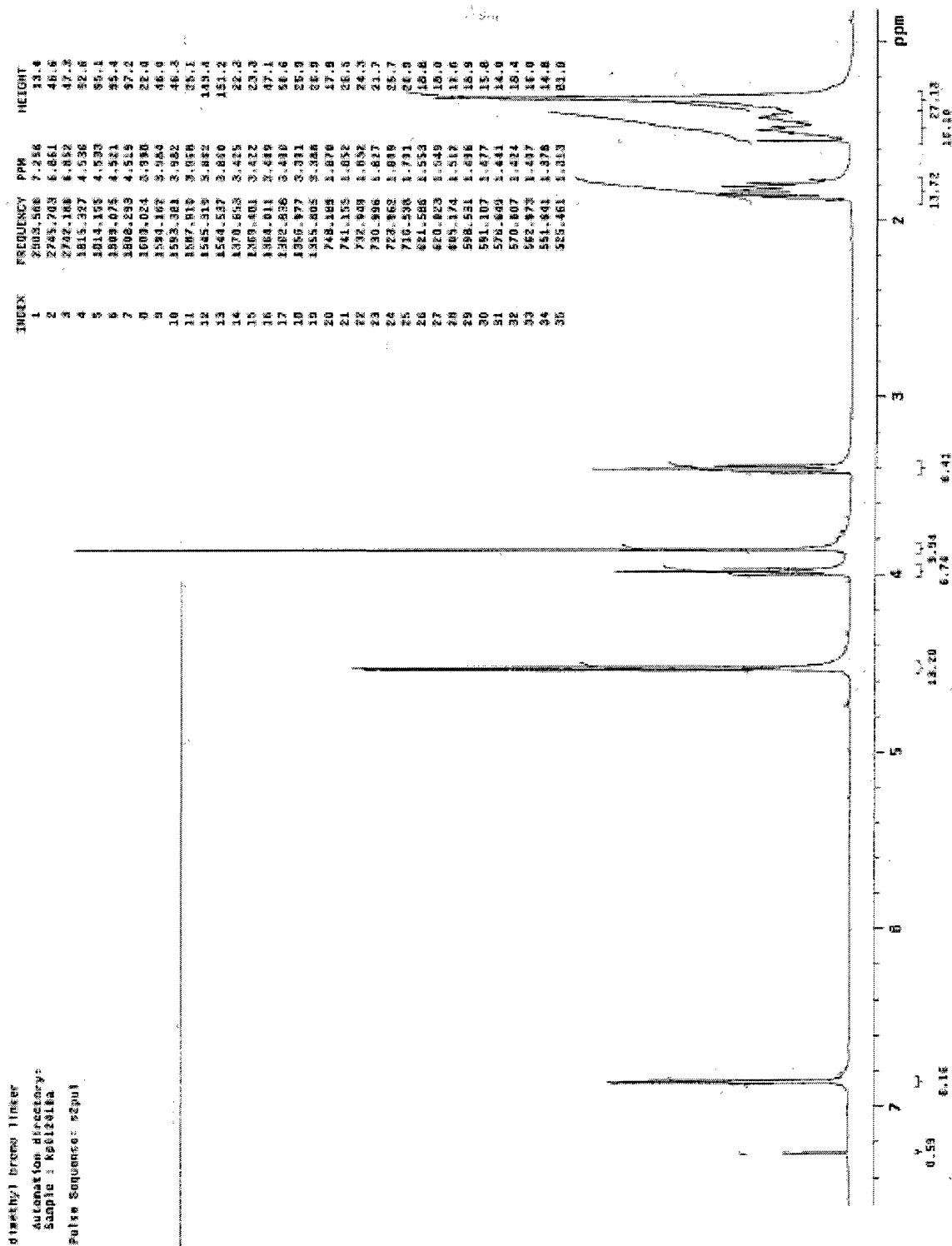
Figure 55 – ^{1}H NMR Spectrum of 1-(10-bromodecyloxy)-2,5-bis(bromomethyl)-4-methoxybenzene [1]

Figure 56 – ^{13}C NMR Spectrum of 1-(10-bromodecyloxy)-2,5-bis(bromomethyl)-4-methoxybenzene [1]

dimethyl bromo linker (bisdecyloxy)

Automation directory:
Sample: kp061610
Pulse Sequence: s2pul

INDEX	FREQUENCY	PPM	HEIGHT
1	2905.129	7.260	13.7
2	2739.842	6.847	81.8
3	1810.638	4.525	151.2
4	1598.461	3.994	35.4
5	1592.209	3.979	77.8
6	1585.957	3.963	40.5
7	736.466	1.840	8.7
8	729.823	1.824	24.4
9	723.181	1.807	30.4
10	714.975	1.787	29.6
11	708.723	1.771	14.2
12	614.943	1.537	21.2
13	610.645	1.526	10.2
14	603.611	1.508	17.5
15	602.048	1.514	17.2
16	596.187	1.490	26.4
17	588.372	1.470	23.2
18	581.338	1.453	14.2
19	540.700	1.351	26.0
20	528.587	1.321	41.8
21	509.831	1.274	119.7
22	359.392	0.858	32.9
23	352.750	0.881	98.7
24	345.716	0.864	44.3

Figure 57 – ^{1}H NMR Spectrum of 1,4–bis(bromomethyl)-2,5-bisdecyloxy benzene [2]

Figure 58 – ^{13}C NMR Spectrum of 1,4–bis(bromomethyl)-2,5-bisdecyloxy benzene [2]

25% PPV-Br Glch+
Automation directory:
Sample : kp050210a
Pulse Sequence: s2pul

INDEX	FREQUENCY	PPM	HEIGHT
1	3008.948	7.522	5.0
2	2908.399	7.263	370.9
3	287.311	7.188	8.5
4	1630.991	4.078	7.0
5	1570.630	3.945	16.7
6	1500.732	3.765	31.7
7	1500.089	3.749	68.3
8	1494.228	3.734	35.4
9	749.068	1.872	37.5
10	748.942	1.864	43.9
11	742.425	1.855	82.3
12	739.299	1.847	46.5
13	736.173	1.840	39.8
14	622.856	1.556	489.1
15	567.726	1.401	19.5
16	502.505	1.256	59.1
17	350.894	0.877	20.1

Figure 59 - ^{1}H NMR Spectrum of Polymer 1 (25% PPV-Br)

20% PPV-Br

Automation directory:
Sample : kp071610c

Pulse Sequence: s2pul

INDEX	FREQUENCY	PPM	HEIGHT
1	2904.738	7.259	41.1
2	2903.957	7.257	-4.5
3	2773.837	6.932	6.0
4	2767.194	6.915	5.0
5	2758.207	6.892	5.4
6	2731.636	6.826	6.5
7	1970.845	4.925	4.4
8	1965.375	4.911	4.8
9	1884.490	4.709	5.2
10	1880.582	4.699	5.3
11	1868.469	4.669	4.9
12	1812.201	4.529	10.2
13	1657.855	4.143	4.7
14	1624.250	4.059	8.2
15	1625.422	4.062	8.2
16	1619.561	4.047	7.7
17	1610.965	4.026	6.7
18	1612.137	4.029	6.8
19	1603.931	4.008	6.8
20	1599.242	3.996	6.4
21	1595.725	3.988	7.0
22	1571.499	3.927	13.6
23	1565.247	3.911	15.2
24	1558.995	3.896	15.0
25	1552.352	3.873	13.5
26	1545.709	3.863	12.4
27	1537.894	3.843	12.1
28	1518.357	3.794	10.5
29	1508.979	3.771	9.7
30	1506.244	3.764	12.5
31	1498.819	3.745	9.0
32	1420.279	3.549	4.9
33	1392.145	3.479	6.3
34	1387.846	3.468	6.8
35	1385.502	3.462	7.8
36	1381.594	3.452	6.4
37	1369.872	3.423	6.1
38	1362.838	3.406	7.9
39	1356.196	3.389	5.8

INDEX	FREQUENCY	PPM	HEIGHT
40	879.871	2.199	4.8
41	868.540	2.170	4.5
42	863.069	2.157	4.4
43	850.565	2.125	4.8
44	813.835	2.034	6.1
45	803.675	2.008	5.4
46	768.508	1.920	6.5
47	747.407	1.868	12.0
48	740.374	1.850	12.3
49	732.559	1.831	11.8
50	725.525	1.813	10.8
51	690.358	1.725	22.0
52	670.039	1.674	15.3
53	638.388	1.595	8.2
54	632.136	1.580	8.0
55	620.023	1.549	9.0
56	612.208	1.530	8.6
57	562.192	1.405	21.6
58	554.767	1.386	20.5
59	503.970	1.259	151.2
60	385.963	0.964	8.2
61	378.539	0.946	9.8
62	374.241	0.935	7.8
63	371.506	0.928	7.9
64	366.817	0.917	7.3
65	349.233	0.873	54.3
66	344.153	0.860	45.9
67	26.083	0.065	50.9
68	-2.051	-0.005	35.7

ppm

Figure 60 - ^{1}H NMR Spectrum of Polymer 3 (20% PPV-Br)

10% PPV-Br

Automation directory:
Sample : kp080610b

Pulse Sequence: s2pul

INDEX	FREQUENCY	PPM	HEIGHT
1	2904.347	7.258	151.2
2	1618.389	4.044	5.0
3	813.835	2.034	5.7
4	743.109	1.857	6.6
5	695.828	1.739	5.8
6	626.275	1.565	114.1
7	499.281	1.248	80.3
8	351.577	0.879	18.7
9	346.107	0.865	20.9

Figure 61 - ^{1}H NMR Spectrum of Polymer 7 (9% PPV-Br)

10% PPV-Br
Automation directory:
Sample : kp080610b
Pulse Sequence: s2pul

INDEX	FREQUENCY	PPM	HEIGHT
1	3009.948	7.522	10.7
2	2998.616	7.493	13.3
3	2906.399	7.263	894.2
4	2869.278	7.170	18.3
5	1620.440	4.049	21.6
6	1576.286	3.939	13.3
7	815.866	2.039	24.3
8	745.160	1.862	27.5
9	697.880	1.744	21.0
10	628.326	1.570	649.1
11	501.332	1.253	471.8
12	353.629	0.884	104.4
13	347.768	0.869	120.8

Figure 62 - ^{1}H NMR Spectrum of Polymer 7 (9% PPV-Br), vs = 2000

Figure 63 - ^{1}H NMR Spectrum of Polymer 12 (40% PPV-Br)

PPV-Br 50% mine

Automation directory:
Sample : kp04131lb

Pulse Sequence: s2pul

INDEX	FREQUENCY	PPM	HEIGHT
1	3007.896	7.516	3.7
2	3000.081	7.497	3.2
3	2904.738	7.259	151.2
4	2869.961	7.172	3.4
5	1626.985	4.066	5.9
6	1576.579	3.940	5.6
7	1351.897	3.378	5.0
8	925.980	2.314	5.5
9	904.879	2.261	4.2
10	745.453	1.863	7.2
11	738.420	1.845	6.8
12	730.996	1.827	6.8
13	723.571	1.808	6.0
14	664.177	1.660	3.8
15	622.367	1.555	139.2
16	557.503	1.393	12.5
17	505.142	1.262	28.8
18	348.842	0.872	13.3
19	342.199	0.855	8.3
20	1.465	0.004	5.7
21	-1.661	-0.004	92.9
22	-5.177	-0.013	5.5

Figure 64 - ^{1}H NMR Spectrum of Polymer 13 (50% PPV-Br)

azidohexane Will's synthesis

Automation directory:
Sample : bs092810a

Pulse Sequence: s2pul

INDEX	FREQUENCY	PPM	HEIGHT
1	1318.000	3.294	3.6
2	1303.542	3.257	43.5
3	1296.509	3.240	79.8
4	1289.475	3.222	42.5
5	1282.051	3.204	2.9
6	1037.051	2.591	14.5
7	1036.269	2.590	15.0
8	668.573	1.671	2.8
9	648.254	1.620	14.9
10	641.221	1.602	35.7
11	634.187	1.585	47.6
12	626.763	1.566	39.7
13	619.730	1.549	17.0
14	612.305	1.530	3.4
15	604.881	1.512	3.4
16	597.457	1.493	3.4
17	590.423	1.475	3.7
18	559.163	1.397	17.1
19	552.130	1.380	30.2
20	550.958	1.377	30.2
21	545.487	1.363	38.4
22	543.143	1.357	37.0
23	536.109	1.340	41.3
24	530.248	1.325	45.9
25	523.996	1.309	63.5
26	521.601	1.304	92.7
27	518.525	1.296	62.5
28	515.059	1.287	42.2
29	509.588	1.273	15.7
30	505.240	1.263	8.5
31	502.405	1.257	7.0
32	501.352	1.253	6.8
33	496.263	1.240	4.1
34	376.883	0.941	8.0
35	362.225	0.905	58.2
36	355.963	0.890	115.8
37	348.929	0.871	52.1

Figure 65 – ^{1}H NMR Spectrum of 1-azidohexane

INDEX	FREQUENCY	PPM	HEIGHT
1	7816.050	77.675	
2	7783.616	77.353	
3	7751.919	77.038	
4	5194.045	51.618	
5	4132.564	41.069	
6	3170.596	31.509	
7	2915.546	28.975	
8	2673.027	26.564	
9	2282.343	22.682	
10	1415.467	14.067	

1-azidohexane
Automation directory:
Sample : kp072111a

Pulse Sequence: s2pul
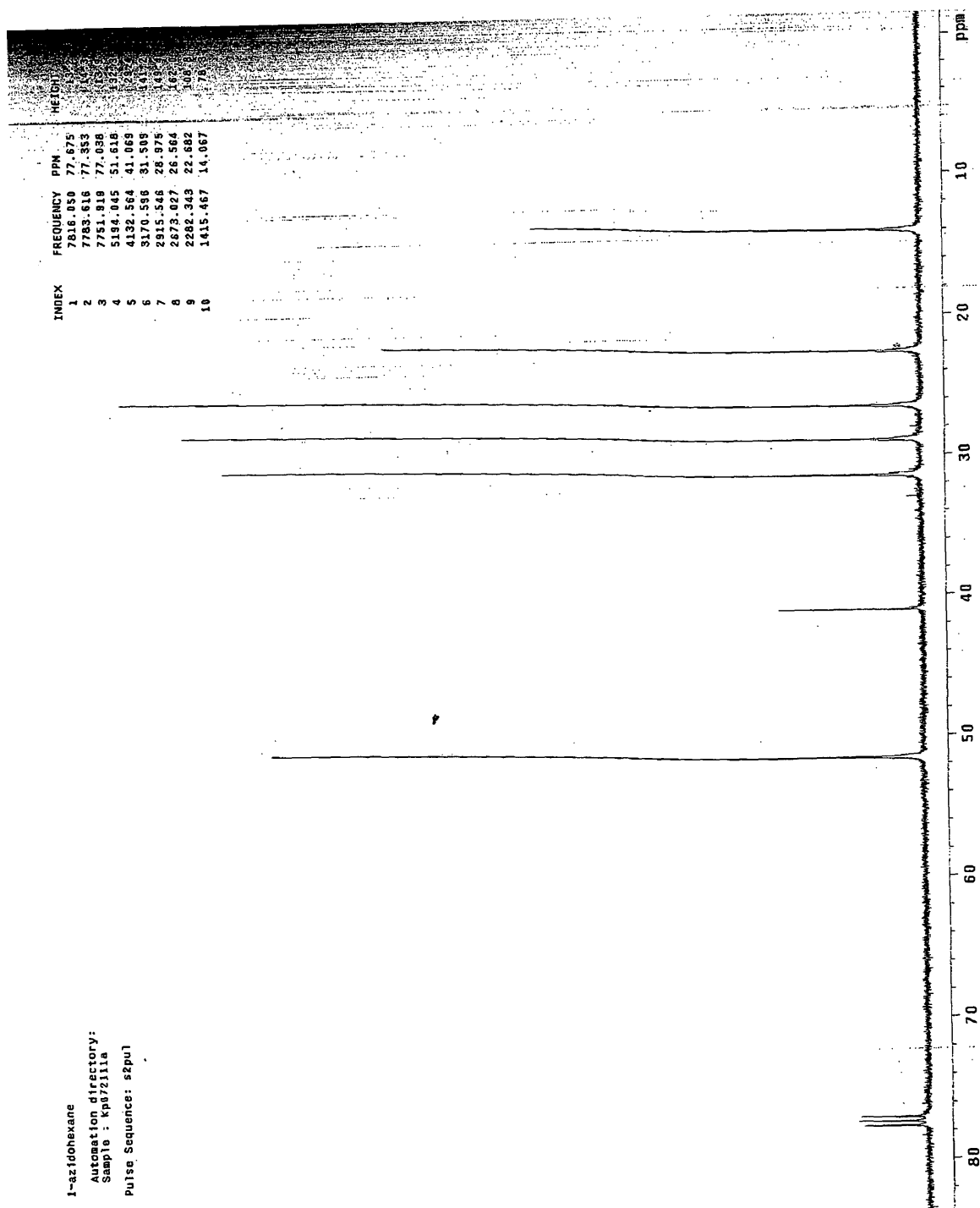
Figure 66 - ^{13}C NMR Spectrum of 1-azidohexane
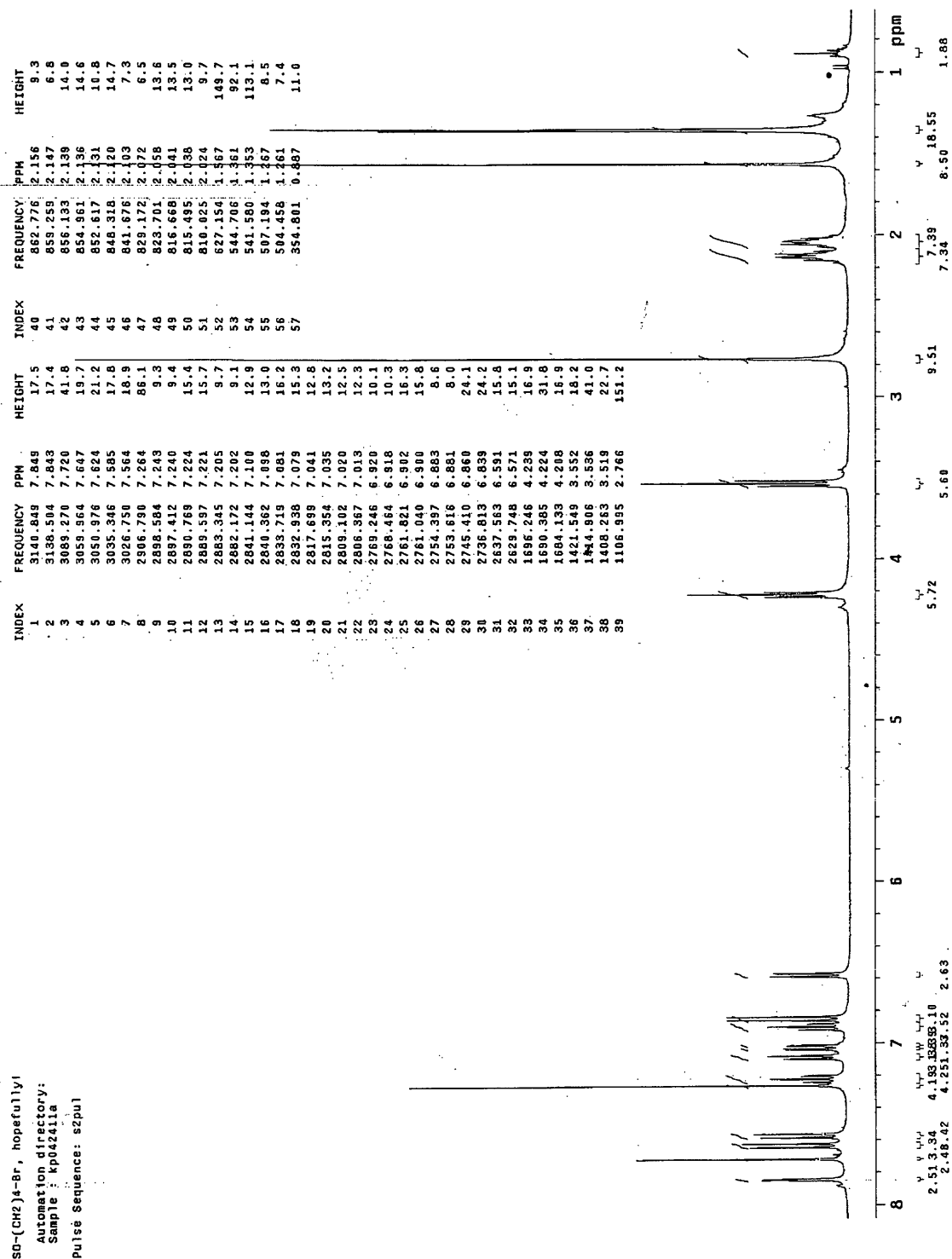
Figure 67 - ^{1}H NMR Spectrum of 9'-(4-bromobutyl)-spirooxazine.

SO-O-(CH2)4-Br (?)
Automation directory:
Sample: kp05i8i1a

Pulse Sequence: s2pul

INDEX	FREQUENCY	PPM	HEIGHT
1	15943.014	158.441	35.6
2	15144.692	150.507	41.4
3	14877.110	147.848	41.3
4	14600.683	145.101	38.8
5	13696.949	136.119	29.6
6	13342.385	132.596	20.8
7	13099.866	130.188	53.4
8	13048.267	129.673	54.7
9	12903.050	128.230	72.0
10	12566.177	124.882	18.9
11	12335.453	122.588	17.0
12	12246.996	121.710	64.7
13	12076.928	120.040	69.5
14	11801.764	117.285	54.8
15	11501.011	114.296	65.1
16	10800.728	107.337	48.5
17	10132.142	100.693	29.8
18	9938.275	98.766	39.8
19	7804.993	77.566	154.4
20	7772.559	77.243	158.6
21	7740.862	76.928	162.0
22	7703.268	76.555	18.9
23	6753.832	67.119	55.1
24	5231.639	51.992	34.5
25	4596.961	45.684	15.6
26	3391.001	33.700	26.5
27	3118.997	30.996	-16.6
28	3004.003	29.854	46.1
29	2999.580	29.810	78.0
30	2830.038	28.125	64.0
31	2583.833	25.678	67.5
32	2116.487	21.034	71.1

Figure 68 - ^{13}C NMR Spectrum of 9'-(4-bromobutyl)-spirooxazine.

azide so

Automation directory:
Sample : kp06301la

Pulse Sequence: s2pul

INDEX	FREQUENCY	PPM	HEIGHT
1	3142.412	7.853	24.0
2	3140.458	7.848	22.3
3	3090.442	7.723	43.0
4	3077.547	7.690	6.5
5	3060.745	7.648	24.2
6	3052.149	7.627	25.0
7	3036.128	7.587	24.0
8	3027.531	7.565	25.0
9	2906.399	7.263	29.9
10	2898.584	7.243	11.4
11	2891.160	7.225	20.0
12	2883.345	7.205	12.5
13	2841.144	7.100	18.4
14	2834.110	7.082	22.4
15	2820.434	7.048	15.1
16	2818.089	7.042	14.1
17	2811.447	7.026	14.5
18	2809.102	7.020	13.7
19	2769.636	6.921	13.4
20	2762.212	6.902	21.1
21	2754.788	6.884	11.6
22	2746.191	6.862	23.6
23	2737.595	6.841	22.0
24	2637.954	6.592	20.5
25	2630.139	6.572	19.9
26	1695.074	4.236	20.8
27	1689.212	4.221	40.2
28	1682.960	4.206	22.9
29	1398.494	3.495	7.1
30	1391.461	3.477	7.6
31	1372.314	3.429	17.9
32	1365.671	3.413	34.7
33	1359.029	3.396	19.8
34	1107.776	2.768	146.0
35	1049.945	2.624	14.4
36	796.349	1.990	13.0
37	790.487	1.975	18.2
38	782.282	1.955	17.9
39	776.420	1.940	9.7

INDEX	FREQUENCY	PPM	HEIGHT
40	759.227	1.897	9.1
41	752.585	1.881	18.3
42	745.551	1.863	19.3
43	738.127	1.845	13.8
44	731.484	1.828	6.2
45	575.184	1.437	9.0
46	545.487	1.363	135.3
47	542.752	1.356	151.2
48	493.517	1.233	9.7
49	486.484	1.216	15.4
50	479.450	1.198	9.2
51	2.345	0.006	34.9

Figure 69 - ^{1}H NMR Spectrum (4-azidobutoxy)-spirooxazine

Std Carbon experiment

Automation directory:
Sample : kp060711V

Pulse sequence: s2pul

INDEX	FREQUENCY	PPM	HEIGHT
1	15942.277	158.433	29.0
2	15143.954	150.500	46.3
3	14876.373	147.840	32.1
4	14617.637	145.269	-17.1
5	14599.945	145.093	35.7
6	13696.212	136.112	26.1
7	13099.866	130.186	47.9
8	13049.004	129.680	54.4
9	12902.313	128.222	56.0
10	12246.259	121.703	53.8
11	12078.928	120.040	54.3
12	11801.764	117.285	60.9
13	11499.536	114.282	68.6
14	10799.991	107.330	53.6
15	10565.581	105.000	-23.6
16	10132.860	100.760	26.2
17	9937.538	98.759	29.0
18	7805.730	77.573	153.9
19	7774.033	77.258	162.0
20	7742.336	76.943	156.9
21	6787.003	67.449	59.4
22	5230.901	51.984	28.6
23	5176.353	51.442	70.2
24	4146.569	41.208	77.2
25	3002.529	29.839	38.8
26	2687.770	26.711	69.6
27	2622.902	26.066	85.7
28	2583.096	25.671	59.4
29	2115.013	21.019	58.1

Figure 70 - ^{13}C NMR Spectrum of (4-azidobutoxy)-spirooxazine

INDEX	FREQUENCY	PPM	HEIGHT
1	3039.156	7.595	16.3
2	3006.333	7.513	21.9
3	2904.738	7.259	95.2
4	1919.266	4.796	27.2
5	1906.762	4.765	15.8
6	1751.635	4.377	18.4
7	1745.383	4.362	25.2
8	1743.820	4.358	18.7
9	1738.349	4.344	33.8
10	1730.925	4.325	22.8
11	1309.306	3.272	35.7
12	1302.272	3.254	67.1
13	1295.239	3.237	39.4
14	765.772	1.914	18.3
15	758.348	1.895	19.3
16	739.983	1.849	17.4
17	645.812	1.614	52.5
18	638.388	1.595	50.1
19	630.573	1.576	43.9
20	623.539	1.558	24.5
21	571.179	1.427	57.2
22	561.410	1.403	20.4
23	554.377	1.385	40.6
24	547.734	1.369	43.5
25	544.608	1.361	43.7
26	537.965	1.344	54.7
27	525.461	1.313	123.0
28	523.117	1.307	151.2
29	520.381	1.300	106.2
30	516.865	1.292	78.5
31	499.672	1.249	58.3
32	486.777	1.216	17.2
33	364.081	0.910	51.5
34	357.439	0.893	126.3
35	350.796	0.877	89.5

test click 40 hrs
Automation directory:
Sample: Kp031811a
Pulse Sequence: s2pul

Figure 71 - ^{1}H NMR Spectrum of Click Trial Product after 48 hrs

test click saturday
Automation directory:
Sample : kp03191la

Pulse Sequence: s2pul

INDEX	FREQUENCY	PPM	HEIGHT
1	3032.513	7.578	8.1
2	3003.989	7.507	10.1
3	2904.738	7.259	17.4
4	2903.957	7.257	18.7
5	2898.877	7.244	8.3
6	2117.767	5.292	8.7
7	1915.750	4.787	16.0
8	1902.855	4.755	10.4
9	1749.681	4.372	8.5
10	1742.647	4.355	13.1
11	1736.005	4.338	15.9
12	1729.362	4.321	11.1
13	1307.352	3.267	32.9
14	1300.709	3.250	74.5
15	1294.457	3.235	61.4
16	1288.205	3.219	21.8
17	866.195	2.165	11.3
18	865.414	2.163	11.9
19	764.209	1.910	9.3
20	757.176	1.892	10.6
21	750.533	1.876	8.4
22	738.811	1.846	7.8
23	657.144	1.642	13.0
24	651.673	1.628	16.8
25	644.640	1.611	34.3
26	637.216	1.592	55.0
27	630.182	1.575	53.2
28	623.539	1.558	30.3
29	616.897	1.542	12.0
30	570.788	1.426	17.9
31	569.616	1.423	18.7
32	564.145	1.410	14.8
33	560.238	1.400	15.7
34	552.814	1.381	35.8
35	546.562	1.366	51.9
36	538.356	1.345	60.1
37	522.726	1.306	151.2
38	519.209	1.297	144.2
39	499.672	1.249	41.2

INDEX	FREQUENCY	PPM	HEIGHT
40	362.909	0.907	50.9
41	357.048	0.892	130.3
42	356.266	0.890	124.6
43	350.405	0.876	118.7
44	344.544	0.861	52.9

Figure 72 - ^{1}H NMR Spectrum of Click Trial Product after 72 hrs

test click sunday

Automation directory:
Sample : kp032011a

Pulse Sequence: s2pul

INDEX	FREQUENCY	PPM	HEIGHT
1	3005.552	7.511	10.1
2	2904.738	7.259	41.4
3	2903.175	7.255	43.3
4	2119.330	5.296	11.2
5	2117.767	5.292	11.3
6	1918.876	4.795	17.6
7	1904.418	4.759	8.8
8	1750.072	4.373	9.0
9	1743.820	4.358	12.8
10	1736.788	4.340	15.2
11	1729.362	4.321	8.8
12	1307.352	3.267	40.9
13	1300.709	3.250	80.7
14	1293.676	3.233	45.0
15	765.382	1.913	8.1
16	758.348	1.895	9.2
17	650.892	1.627	14.6
18	643.858	1.609	41.5
19	637.216	1.592	76.2
20	630.573	1.576	52.9
21	623.539	1.558	22.1
22	571.179	1.427	21.8
23	570.007	1.424	22.2
24	560.238	1.400	17.4
25	552.814	1.381	41.7
26	545.389	1.363	51.2
27	538.356	1.345	56.9
28	523.507	1.308	151.2
29	499.672	1.249	43.7
30	362.909	0.907	62.4
31	357.438	0.893	134.5
32	356.266	0.890	137.9
33	350.405	0.876	91.4

Figure 73 - ^{1}H NMR Spectrum of Click Trial Product after 96 hrs

alkynized PPV, 50%

Automation directory:
Sample : kp04131la

Pulse Sequence: s2pul

INDEX	FREQUENCY	PPM	HEIGHT
1	1644.960	4.111	151.2
2	1625.813	4.063	120.5
3	1575.406	3.937	112.9
4	1401.523	3.502	61.0
5	1394.880	3.486	108.5
6	1388.237	3.469	80.6
7	1284.688	3.210	29.4
8	959.584	2.398	54.7
9	813.835	2.034	33.3
10	745.453	1.863	113.1
11	669.257	1.672	60.6

Figure 74 - ^{1}H NMR Spectrum of 50% Alkyne-functionalized PPV, 1.8-4.2 ppm

50%so-ppv flakes

Automation directory:
Sample: kp060911a

Pulse Sequence: s2pul

INDEX	FREQUENCY	PPM	HEIGHT
1	3079.892	7.696	17.2
2	3009.557	7.521	18.2
3	2906.008	7.262	500.8
4	1681.788	4.203	17.0
5	1506.732	3.765	17.0
6	1500.480	3.750	21.5
7	1096.054	2.739	24.3
8	942.880	2.356	18.4
9	934.283	2.335	17.6
10	870.591	2.176	41.5
11	815.886	2.039	40.6
12	742.425	1.855	45.8
13	671.309	1.678	67.4
14	634.578	1.586	67.2
15	501.723	1.254	145.5
16	352.066	0.880	30.1
17	345.032	0.862	31.2

Figure 75 - ^{1}H NMR Spectrum of SO-PPV2 Product B

Figure 76 - ^{1}H NMR Spectrum of SO-PPV2 Product B, 2.5-5.5 ppm

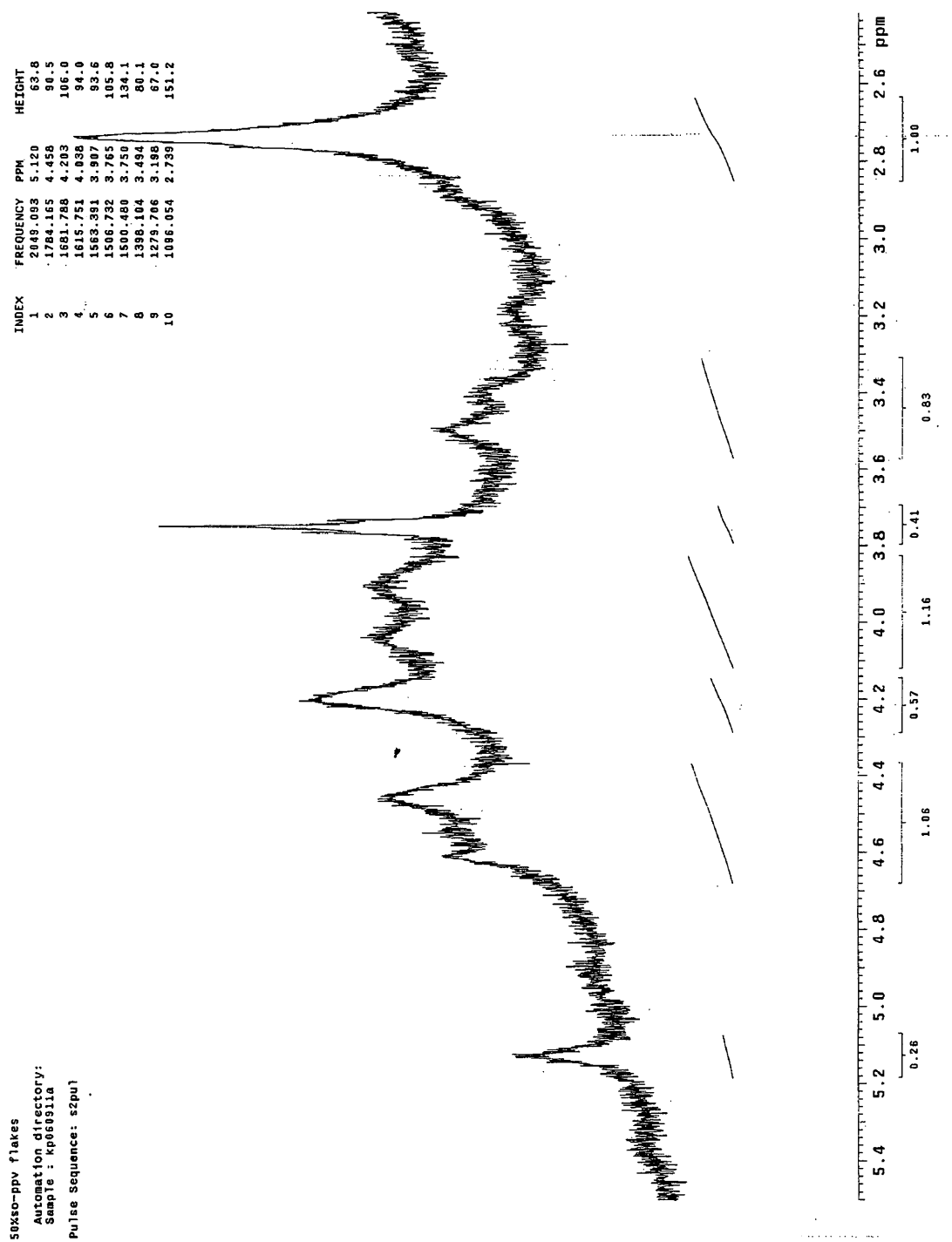| INDEX	FREQUENCY	PPM	HEIGHT
1	2932.579	7.328	16.0
2	2907.180	7.265	18?.5
3	2864.198	7.157	17.5
4	2767.292	6.915	13.3
5	2681.718	6.701	10.4
6	2050.656	5.124	17.8
7	1647.402	4.117	42.2
8	1564.563	3.910	35.5
9	1396.150	3.489	42.2
10	1277.753	3.193	17.4
11	960.464	2.400	11.3
12	816.277	2.040	81.6
13	710.38?	1.775	40.5
14	672.090	1.679	13?.2
15	624.028	1.559	65.3
16	502.11?	1.255	56?.6
17	381.765	0.954	3?.7
18	346.98?	0.867	12?.5
19	125.040	0.312	11.8
20	?8.525	0.071	1?.1
21	0.782	0.002	229.8
22	-58.61?	-0.146	13.0

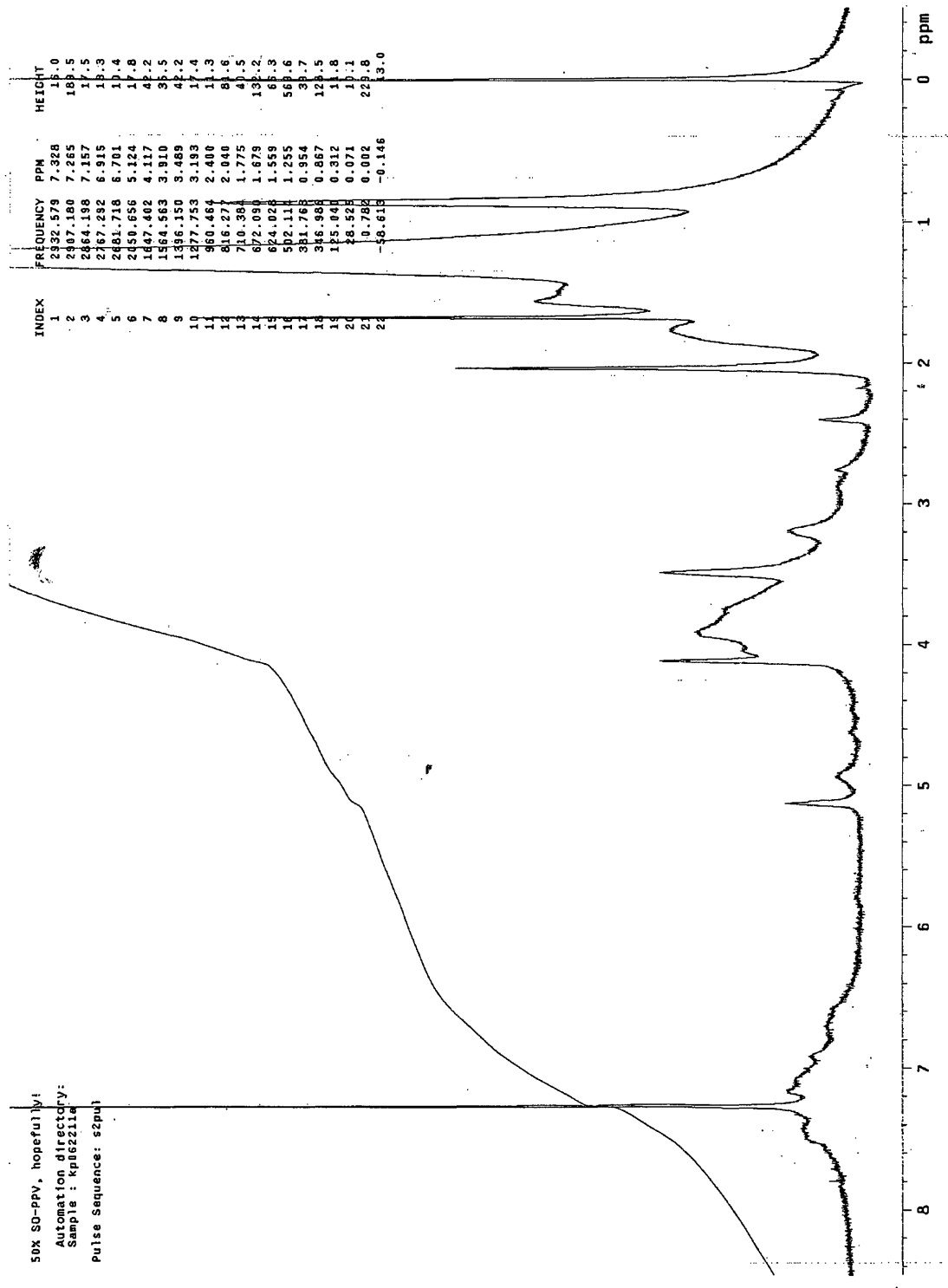50% SO-PPV, hopefully!
Automation directory:
Sample : kp162211e
Pulse Sequence: s2pul

Figure 77 - ^{1}H NMR Spectrum of SO-PPV2 Product C