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The Synthesis and Subsequent Fluorescence Studies of Spirooxazine-Functionalized Poly(phenylene vinylene) Using the Gilch Polymerization Technique

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The Synthesis and Subsequent Fluorescence Studies of Spirooxazine-Functionalized Poly(phenylene vinylene) Using the Gilch Polymerization Technique.

A thesis submitted in partial fulfillment of the requirement
for the degree of Bachelors of Arts / Science in **Chemistry** from
The College of William and Mary

by

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Accepted for _____
(Honors, High Honors, Highest Honors)

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Williamsburg, VA
May 6th, 2010

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Abstract

A synthetic route for and fluorescence study of spirooxazine-functionalized poly(phenylene vinylene) is presented. Attempts using the Heck polymerization have proven to be difficult; this fact combined with the lengthy synthetic route needed to simply make the monomers needed for polymerization along with discouraging fluorescence studies led to a search for a new synthetic route. This study shows the results of using the Gilch polymerization, which have proven to be successful for the creation of the poly(phenylene vinylene) backbone of the polymer. The monomers used for the polymerization were synthesized using a Williamson ether synthesis and electrophilic aromatic substitution. Addition of the spirooxazine to the poly(phenylene vinylene) to form a spirooxazine-functionalized polymer (SO-PPV) via a S_N2 reaction have also proven to be difficult, but a 100% and 25% functionalized SO-PPV product may have been obtained. Fluorescence and absorbance studies have been conducted on these products, and one particular study shows small but definite photomodulation that show a success in binding the SO group to the PPV polymer and thus obtaining the ability to selectively quench the fluorescence of the polymer.

Acknowledgements

First, I would like to thank Dr. Elizabeth Harbron for being one of the best advisors ever. When I first expressed interest in joining her lab, I was honestly afraid that she would remember my less-than-stellar grade in her Organic Chemistry II class and be less inclined to let me work in her lab. But of course, she didn't hold that against me, and I thank her for that because the time I've spent in her lab has made me realize how much I like to do research (even when it's at its most frustrating) and why I decided to study chemistry in the first place. Dr. Harbron has allowed me to grow as a researcher in the past year, and I look forward to working with her again for my Masters work.

Next, I would like to thank my defense committee members, Dr. Christopher Abelt, Dr. John C. Poutsma and Robert Horvath. You've all been great professors during my time here at the college, and I thank you so much for taking the time to read my thesis and take part in my defense, and for remaining patient with me throughout all of my scheduling issues. I especially thank Robert Horvath for agreeing to be on my committee at the last minute. I would also like to thank the labs of Dr. Abelt, Dr. Hinkle and Dr. Scheerer for allowing me to borrow several different miscellaneous chemicals and solvents during my research time.

And last but not least, I would like to thank my research group and my family. First, I'd like to thank Jordan Walk, my former labmate who was my mentor in the Harbron lab and left me this project. I especially thank Christina Davis, who helped me so much in learning how to conduct fluorescence studies and work the IGOR system; I wouldn't have known what to do without her. I would also like to thank the rest of my labmates – Becca Allred, Beth Childress, Brooklynd Saar, Meg Schmierer, and Will Czaplyski- for listening to me vent and keeping me laughing throughout the year. And of course, I'd like to thank my

parents, Joni and Scott Peth, my brother Ian Peth and my boyfriend Ryan Logue for supporting me and always listening to me when I would talk about my research, even if they had no clue what I was talking about. I don't know what I would've done without all this support, and I thank everyone from the bottom of my heart.

Background

Conjugated polymers have been a subject of great interest to the Harbron lab, especially the fluorescence of these polymers.^{1,2} This fluorescence makes conjugated polymers useful for organic LEDs, photovoltaics, transistors, batteries, molecular electronic devices, and biomedical imaging.^{3,4,5} Conjugated polymers are also easy to functionalize with a variety of different side groups to improve solubility in organic solvents and/or impart different functionalities to the polymer.³ Originally the lab was more focused on attaching azobenzene groups to the backbone of a particular conjugated polymer, poly(phenylene vinylene) (PPV).² Once attached, these azobenzenes could be used to quench the fluorescence of the PPV. Azobenzenes are photochromic molecules, which are molecules that can reversibly isomerize with the absorption of UV-irradiation. Spirooxazine (SO) is another photochromic molecule from a different family. My predecessor Jordan Walk '09, a former Masters student in the Harbron lab, worked on trying to attach SO to PPV, with the aim of gaining the ability to selectively quench the fluorescence of the polymer. His work attempted a synthesis of the SO-PPV polymer through Stille Coupling and the Heck polymerization. This thesis slightly extends the Heck polymerization route, but mainly focuses on a new synthetic approach, the Gilch polymerization. The absorbance and fluorescence properties of the SO-PPV products will also be presented.

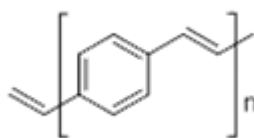


Figure 1 – Backbone of Poly(phenylene vinylene) (PPV)

As displayed in Figure 1, the backbone of PPV consists of phenyl groups that are attached to each other with vinyl groups. These vinyl groups are usually *para* to each other, but can be located at any location on the phenyl groups. PPV is not only a conjugated polymer, but also a conducting polymer, which combines electrical and optical properties of semiconductors with the managing of polymers.⁶ The delocalization of π bonds in conducting polymers such as PPV cause them to have high dielectric constants, and thus renders them insoluble in solvents that have small dielectric constants; namely, most organic solvents.⁶ This insolubility can be reduced, however, by adding side chains to the polymer backbone; these chains provide an extra organic layer around the polymer, reducing its melting point and making it more soluble in organic solvents.⁶ It has also been found that the bulkier the side groups, the stiffer the polymer chain, which in turn reduces coiling and improves the electronic order of the molecule.⁶ For these reasons, most PPV work in Harbron lab involved attaching one or two alkoxy groups to the PPV backbone to improve solubility in chloroform and tetrahydrofuran (THF). For this work, one decyloxy group was attached to the backbone with a methoxy group attached *para* to the decyloxy group, as can be seen in Figure 2.

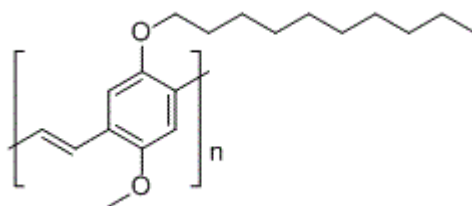


Figure 2 – Structure of Poly((2-decyloxy-5-methoxy)-1,4-phenylene vinylene)

PPV is also a highly fluorescent molecule due to its rigid aromatic character in combination with its planar conjugated systems.⁷ It has been demonstrated that substitution on the

phenylene ring not only affects the solubility of the polymer, but its electrical and optical properties as well.⁴ It is this fluorescent property of the polymer that we are trying to selectively quench.

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 Basically, if one irradiates a fluorescent molecule with a specific-wavelength UV/VIS light source, that molecule will absorb a certain amount of energy from the light. This absorption excites the molecule from its ground electronic state, S_0 , to an excited singlet state, S_1 . After removal of the light the molecule then emits the energy it collected from that photon, causing it to “shine” (fluoresce) a certain color until it loses all that energy. The lifetime of fluorescence is very short, meaning that the population of the excited state decays at a very high rate.⁸ Fluorescence is lower in energy than the initial absorption and has a longer wavelength.

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. As seen in the Jablonski Diagram shown in Figure 3, after absorption the vibrationally excited molecules usually relax back to the lowest vibrational level in S_1 through internal conversion before emitting back to the ground state S_0 ; then, the emitted photon can go to any vibrational level of S_0 . The emitted photon usually goes to the same vibrational level in S_0 that it went to in S_1 , causing the absorption and emission spectra to become mirror images of one another if the vibrational spacings are roughly equivalent.⁸ Molecules with rigid structure like the aromatic PPV polymer have decreased degrees of freedom and cannot lose absorbed energy through radiationless deactivation; instead, they emit the energy through fluorescence.

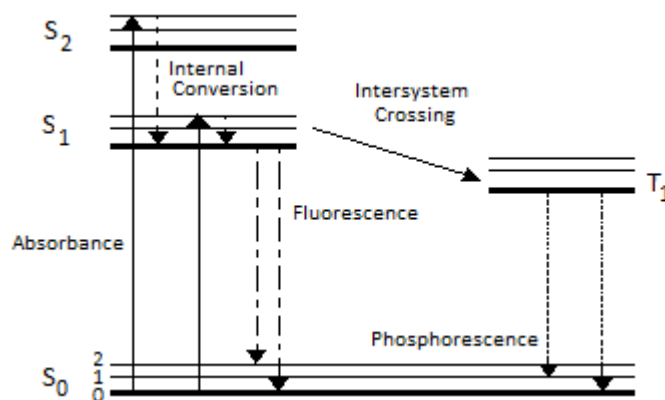


Figure 3 – Jablonski Diagram of Fluorescence.⁸

What we are trying to do with the fluorescence of PPV is control it through quenching with the SO group; essentially, decreasing its intensity in response to a specific stimulus. Usually this is achieved through collisional encounters between a fluorophore and a quencher that cause either collisional or dynamic quenching.⁷ The quenching mechanism we are focusing on is called fluorescence resonance energy transfer (FRET). This involves a transfer of excited state energy from the donor (fluorophore) to an acceptor (quencher).⁷ This energy transfer actually does not include an exchange of photons, but occurs due to dipole-dipole interactions between the fluorophore and the quencher.⁷ In this experiment the fluorophore is the modified PPV polymer group and the quencher is the SO functional group. In FRET, the donor molecules typically emit at short wavelengths that overlap well with the absorption spectrum of the acceptor.⁷ This spectral overlap must occur in order to successfully quench the fluorophore. The amount of spectral overlap affects the rate of this energy transfer, as do the orientation of the donor and acceptor dipoles and the distance between the two molecules.⁷

As mentioned before, past work in the Harbron lab involved attaching azobenzenes to PPV polymers. For this work we are attempting to covalently bond the photochromic

compound SO to PPV instead because it has a greater spectral overlap with PPV than azobenzene, and thus should act as a better quencher. The spectral overlap of an SO derivative and a PPV derivative can be seen in Figure 4, courtesy of lab mate Christina Davis.

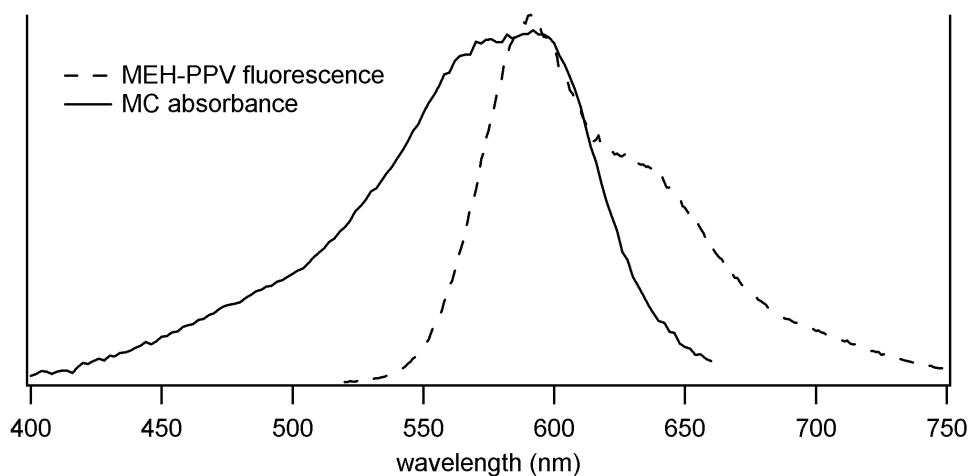


Figure 4- Spectral Overlap of SO and PPV derivatives

Photochromism in SO involves the reversible color change between the closed “spiro” structure and the open planar merocyanine (MC) structure, as shown in Figure 5.⁹

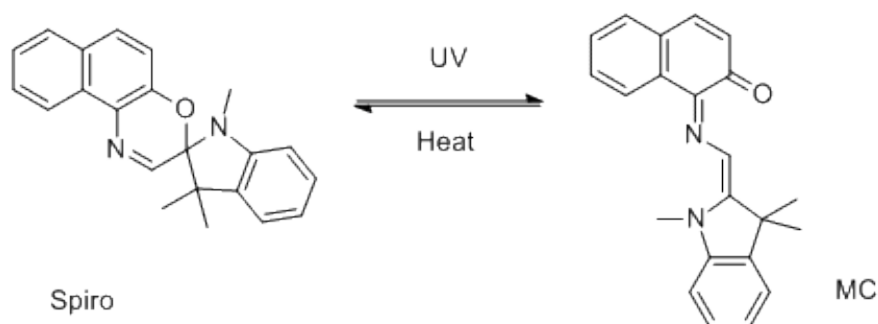


Figure 5– Spiro and Merocyanine (MC) Structures of SO

The dissociation of the spiro C-O bond in the oxazine ring from sp^3 hybridization to sp^2 hybridization is UV-induced.¹⁰ This dissociation causes the originally colorless SO form to physically change to the more conjugated MC form, which absorbs visible light around 600-610 nm.⁹ In theory, if the SO-PPV product is UV-irradiated, the SO group should

change from the spiro form to the MC form, which encourages an energy transfer to occur between the PPV group and the SO group. This transfer of energy is what decreases the fluorescence of the polymer. After UV irradiation stops, the MC form then thermally reverts back to the spiro form and the fluorescence of the PPV should revert back to its original value. This type of reversible quenching is desired so that we can control the intensity and amount of fluorescence. One problem with working with photochromic compounds is the possibility of photobleaching. Photobleaching occurs when the UV irradiation photochemically destroys the fluorophore; in this case, the PPV polymer. Another problem is fatigue of the quencher, which is when the UV-irradiation causes a non-reversible reaction that essentially disrupts the photochromaticity of the molecule. These are both problems that need to be avoided, and thus SO is an attractive option for the quencher as it is more resistant to cyclic fatigue and photobleaching than other photochromic molecules.¹⁰ The SO that is used in the following experiments is functionalized with a hydroxyl group to facilitate a later connection of the SO group to our PPV polymer via an S_N2 reaction.

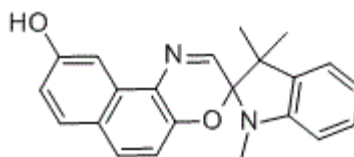


Figure 6– Structure of Hydroxyspirooxazine

All SO used has been synthesized by Jordan Walk '09 and purified by recrystallizations in ethanol.

Results and Discussion

Two synthetic routes using different polymerization techniques were explored for this project. Both routes involved first polymerizing monomers to create a polymer containing bromine leaving groups, and then reacting these polymers with SO to produce SO-PPV.

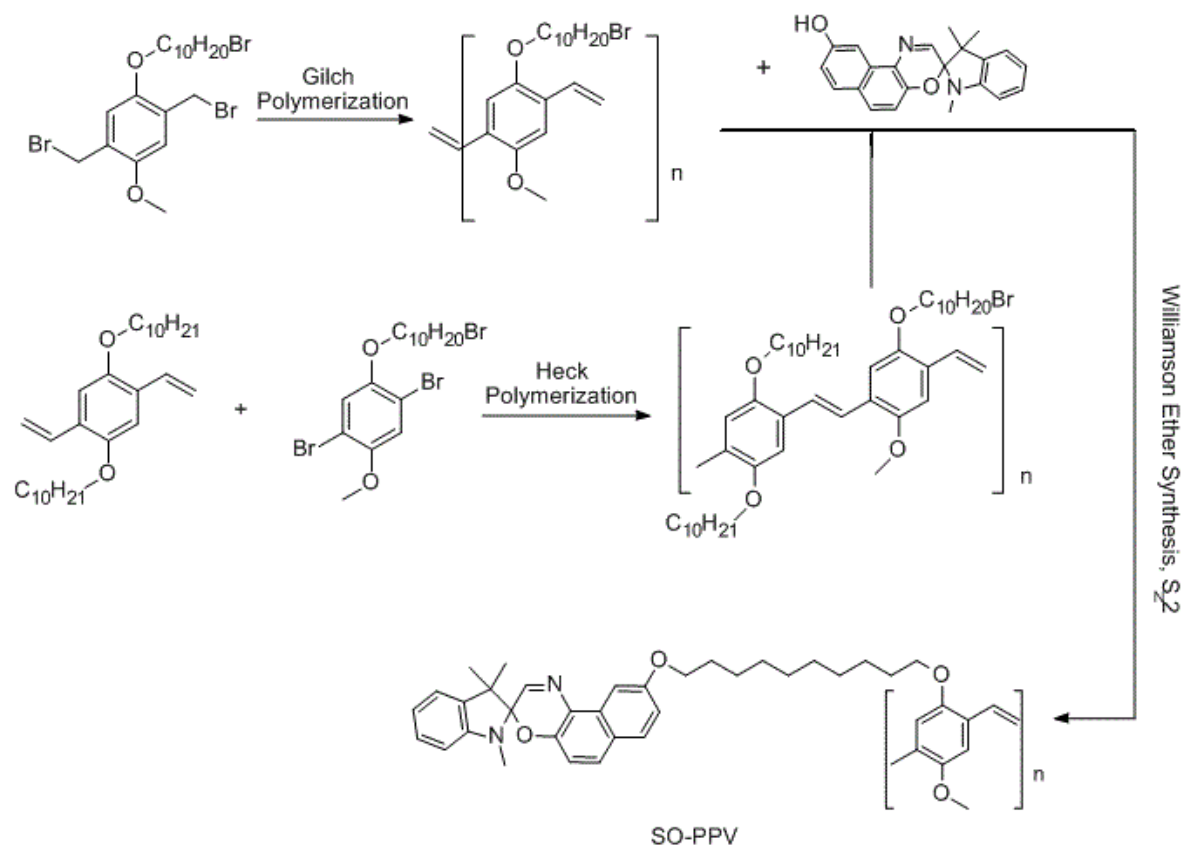


Figure 7– Overall General Synthetic Routes for SO-PPV with Gilch and Heck Polymerizations

Monomer Synthesis for the Gilch Polymerization

Before utilizing the Gilch polymerization to synthesize the polymer of interest, first monomer **2** had to be synthesized.

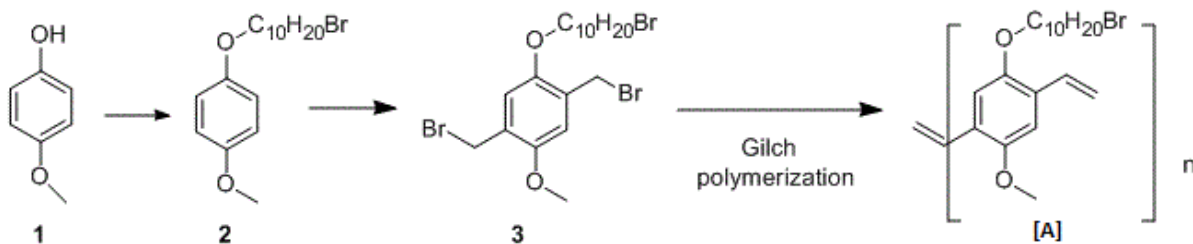


Figure 8-Synthesis of 100% Br-Functionalized PPV through Gilch Polymerization [A]

The process to form monomer **2** is a two step synthesis that begins with the Williamson ether synthesis of p-methoxyphenol (**1**) with dibromodecane, both commercially available chemicals to create **2**.

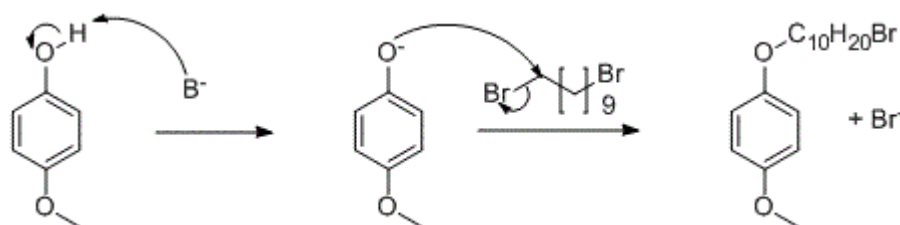


Figure 9 – Williamson Ether Synthesis Mechanism

First, potassium carbonate base is used to remove the hydrogen from the phenol group on p-methoxyphenol, creating a negative charge on the oxygen. This nucleophilic phenoxide ion then reacts with the alkyl halide dibromodecane via a S_N2 reaction to remove one of the bromines and attach the alkyl group to the oxygen of the methoxyphenol molecule. This is a synthesis that has been performed in Dr. Harbron's lab for many years, and the dibromodecane is always used in excess to minimize the amount of difunctionalized byproduct shown in Figure 10 in which the phenyl rings are linked together by the long carbon chains.

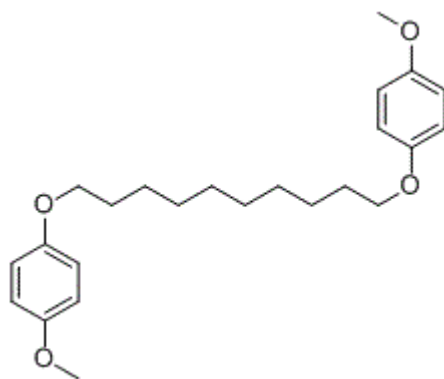


Figure 10 – Difunctionalized Byproduct in Synthesis of **2**

As a result, this synthesis has had notoriously low yields due to multiple recrystallizations having to be carried out to remove excess dibromodecane and purify the product. The best yield obtained during this monomer synthesis is 40%, with an average of about 32%.

After synthesis of **2**, it is bromomethylated to form monomer **3** needed for polymerization using paraformaldehyde and 33% HBr in glacial acetic acid.

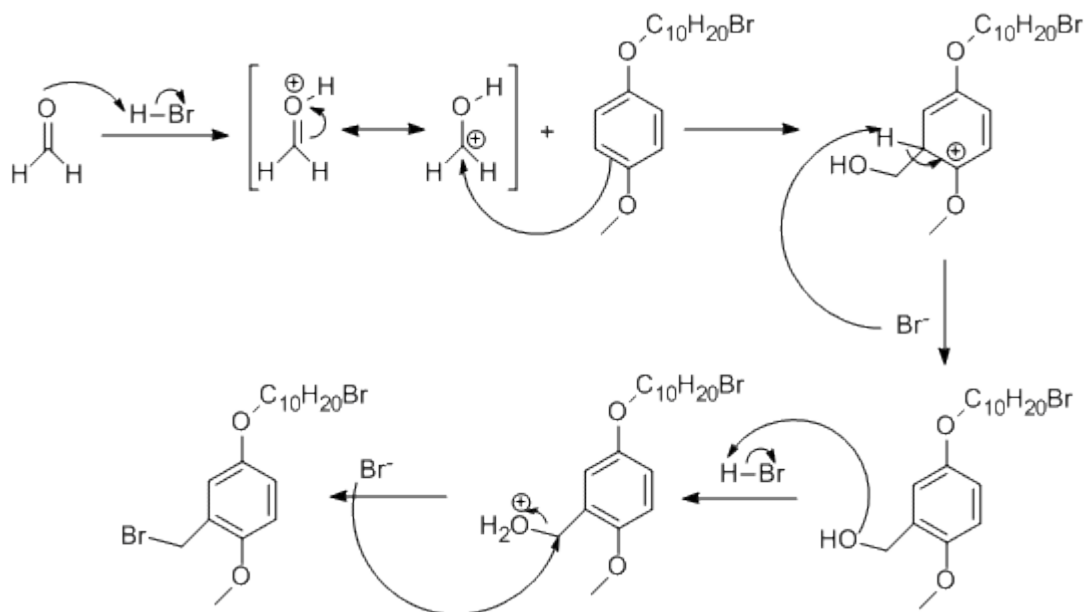


Figure 11 - Methylbromination Mechanism of Monomer **3**

Upon addition of heat, the paraformaldehyde is decomposed to formaldehyde, which is protonated to form a carbocation. Then an electrophilic aromatic substitution takes place

between monomer **2** and the carbocation to form a benzylic alcohol. The benzylic alcohol is converted to a better leaving group through protonation, and then reacts with the remaining bromide ions through substitution to form the final product, monomer **3**. This synthesis was only performed twice with an average yield of 67%

Polymerizations

The first attempted polymerization technique was the Heck polymerization, shown in Figure 12. The general mechanism for this polymerization involves the substitution of an alkene in the place of an aryl or vinyl halide.¹¹ This substitution is driven by the presence of palladium (II) acetate, tri-*o*-tolyl phosphine, and triethylamine.

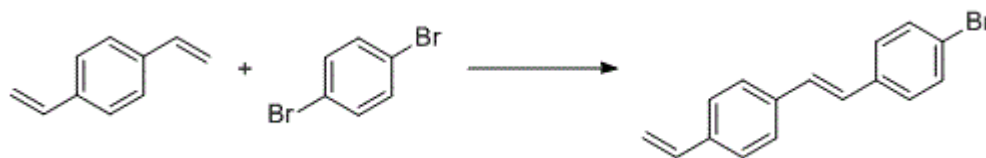


Figure 12- General Heck Polymerization

The phosphine ligands of tri-*o*-tolyl phosphine replace the acetate groups on palladium (II) acetate in the presence of triethylamine, a Lewis base. This reduces the palladium (II) acetate, and then the palladium atom reaches an oxidation state of +2 after the addition of an aryl halide. This causes the palladium atom to form a π -complex with the alkene bond in monomer 3. β -hydride elimination then causes a double bond to form in our product, removing it from the palladium complex. The leftover palladium is reduced by excess base, and then it starts the whole cycle over again. The detailed mechanism can be found in Figure 13.

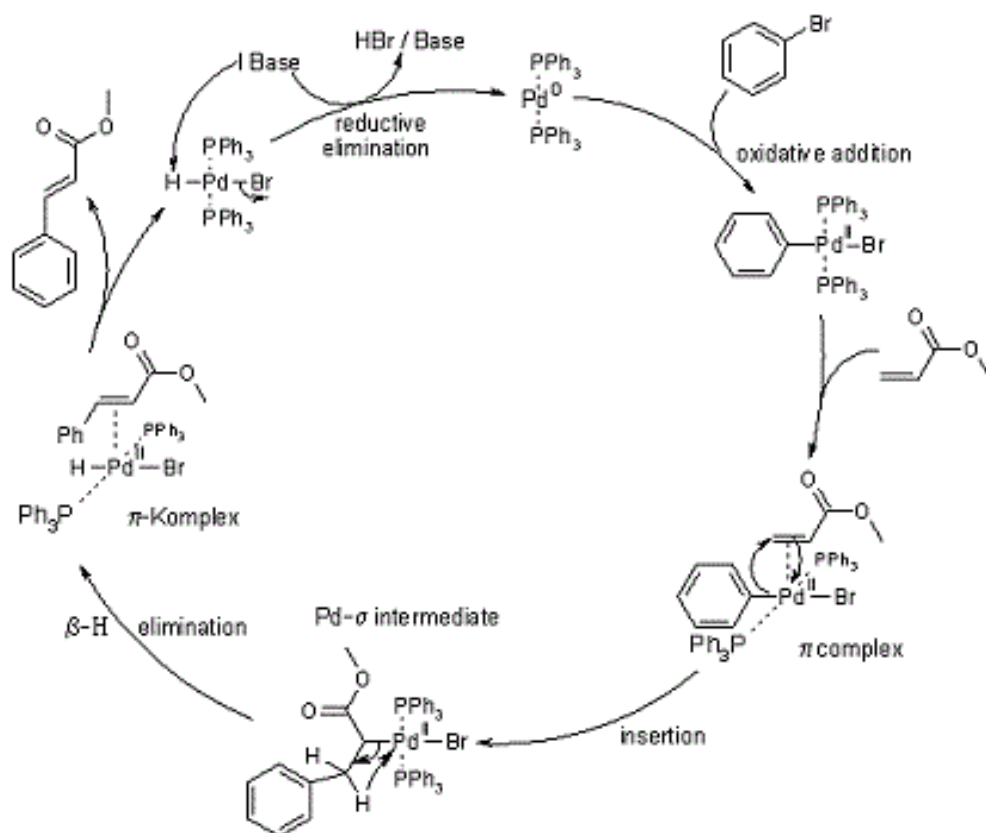


Figure 13 – Detailed Heck Polymerization ¹²

Previous attempts at synthesizing SO-PPV through the Heck polymerization involved polymerizing monomers that already had the SO group attached, as displayed in Figure 14.

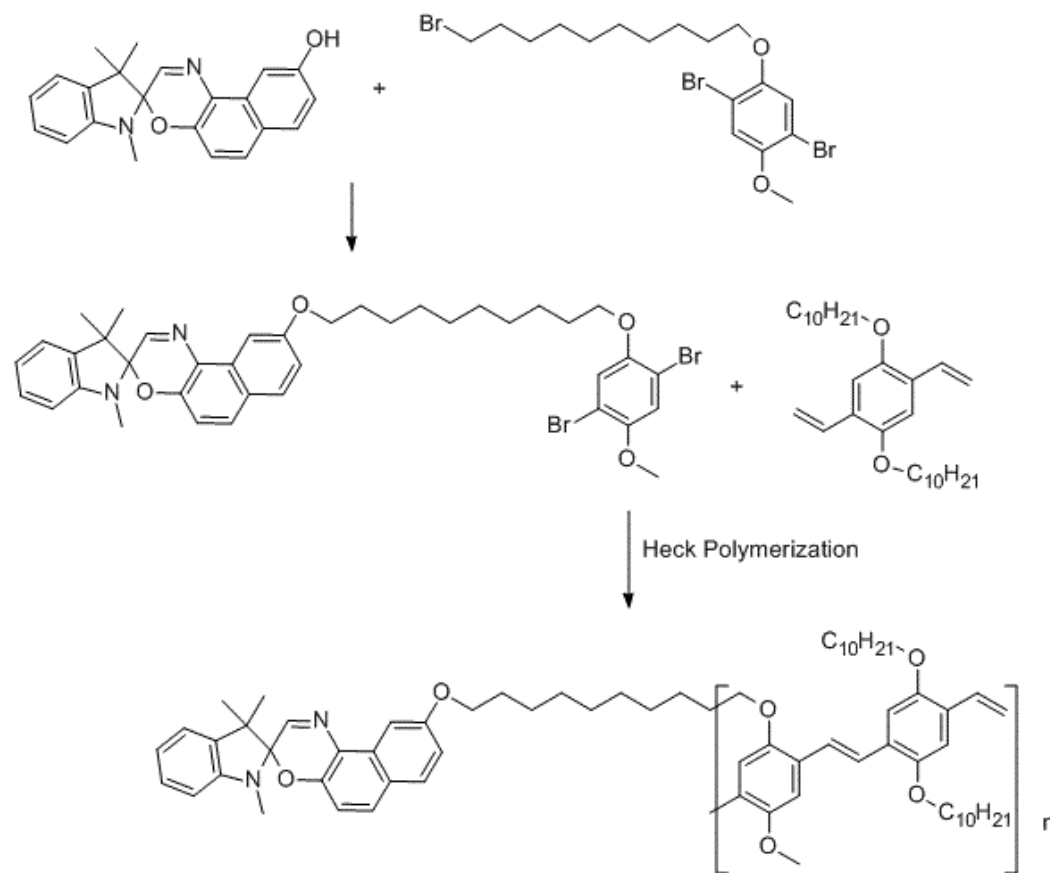


Figure 14 – Previous Synthetic Route using Heck Polymerization

This work shows a different approach, in which the monomers are first polymerized, and then we attempt to add the SO group to the polymer via a S_N2 reaction. The general synthetic route for this is shown in Figure 15. The first polymerization that was carried out using the Heck mechanism created a control polymer, 25% Br-functionalized PPV [**B**], that was used for fluorescence studies of the PPV polymer. Polymer **B** was also used as the main reactant in the later SO-PPV synthesis attempt.

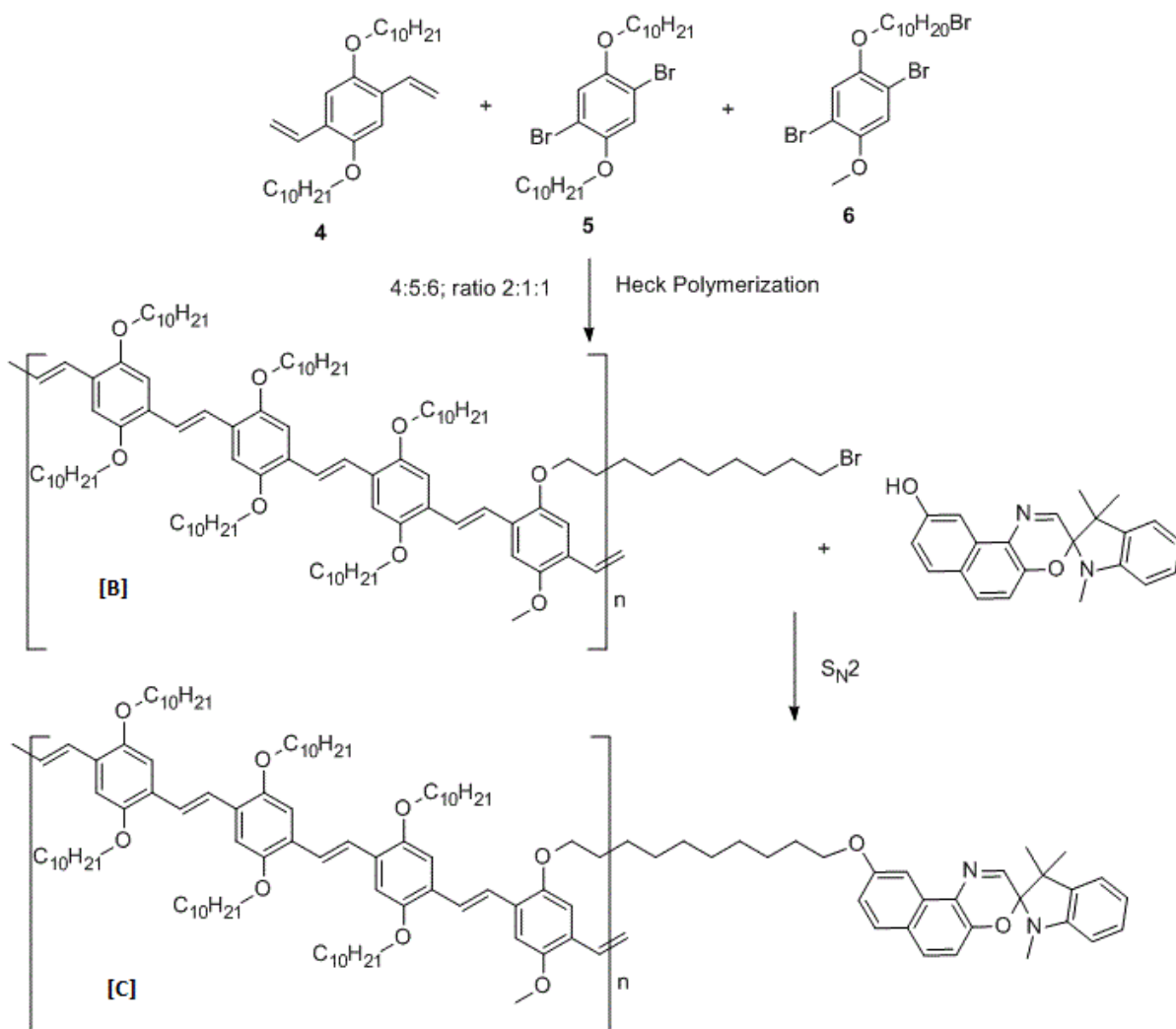


Figure 15 – New Synthetic Route for Heck Polymerization of 25% SO-functionalized PPV [C]

The monomers used for the control polymerization were used in ratios that should give a decyloxybromine chain on one out of every four backbone units. Previous work with synthesizing SO-PPV via the Heck mechanism have shown the product to be nearly insoluble in organic solvent, so the functionalization of the SO-PPV was decreased to 25% in this experiment to help improve solubility.

To create the Polymer **B**, three monomers were required for polymerization.

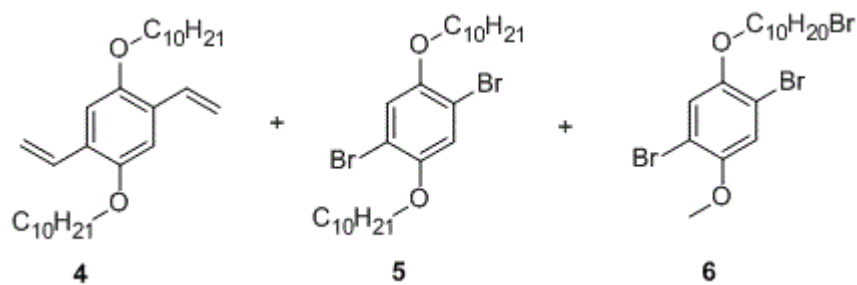


Figure 16 – Monomers used for the Heck Polymerization

Monomers **4** and **5** had already been synthesized for Jordan Walk's Masters work. Monomer **6** was created by brominating monomer **2** from Figure 8.

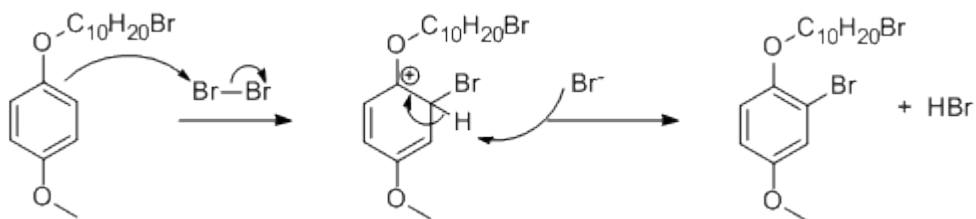


Figure 17 – Bromination Mechanism of **6**

The bromine atoms replace the hydrogen on the benzene ring via an electrophilic aromatic substitution mechanism, creating a carbocation intermediate and eventually creating a byproduct of HBr. The product was recrystallized with acetone to remove impurities and byproducts. This synthesis was performed once with a 69% yield.

Monomers **4**, **5** and **6** were used with the ratio 2:1:1, respectively, in combination with tri-*o*-tolyl phosphine, palladium(II)acetate, and triethylamine and heated in dimethylformamide (DMF) with a condenser under argon atmosphere for 48 hours. Purification of the product through precipitation failed, and so purification was carried out using Soxhlet extraction with acetone, methanol and hexanes solvents. By the end there was just some black crud leftover in the Soxhlet thimble; it seemed as though most of the polymer

had dissolved into the hexanes solvent. The hexanes solvent was evaporated off to collect product, on which fluorescence studies was carried out. Those studies will be discussed in detail later.

The next step was to try and replace the bromine groups on the control polymer with SO as shown in Figure 17. This reaction was done with THF instead of DMF, because our lab had run out of DMF at the time. Reflecting back on this now with what I know from the Gilch polymerizations, this might be one of the main reasons why this synthesis attempt did not work out as well as hoped. THF is relatively non-polar compared to DMF, and this decrease in polarity affects the likelihood of the occurrence of the desired S_N2 reaction. The Polymer **B** and SO were combined in THF, with potassium carbonate acting as a base to initiate the desired S_N2 reaction to product 25% SO-functionalized PPV [**C**].

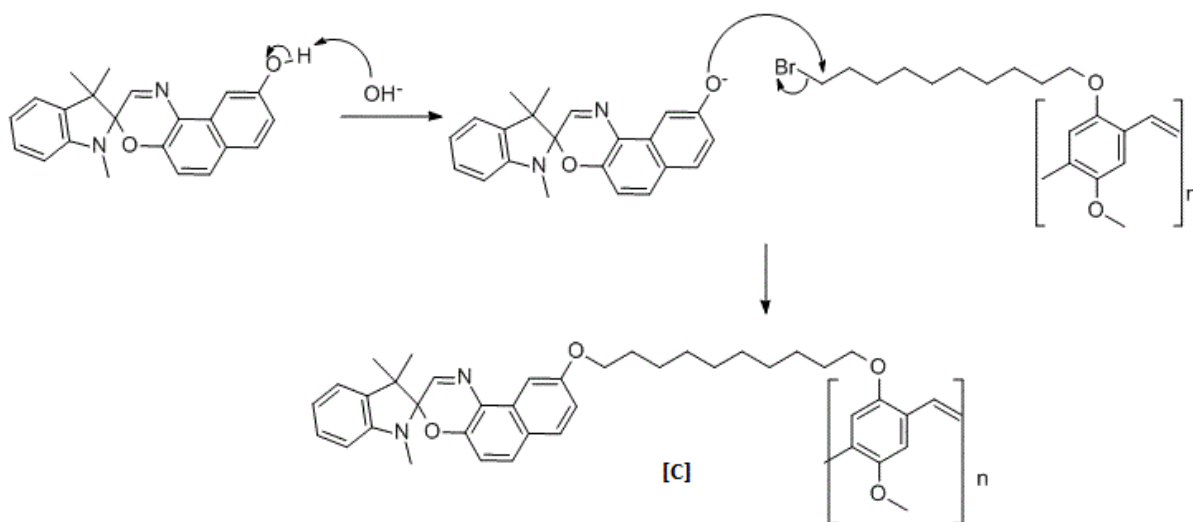


Figure 18 – Desired S_N2 Reaction Mechanism for Polymer **C**

After several days of heating, the product was collected and then purified through precipitation. There was too little product to obtain NMR spectra, but there was enough for fluorescence studies, which are also discussed later. The results of the fluorescence studies weren't particularly encouraging. Also, the syntheses involved in creating monomer **4** for

the control polymer is long and time consuming, involving a six step synthesis with relatively dangerous chemicals. Combining this with the findings of the fluorescence study, we decided to try a different route; namely, the Gilch polymerization route shown in Figure 7.

The rest of the polymerizations were carried out using the Gilch mechanism for polymerization displayed in Figure 19.

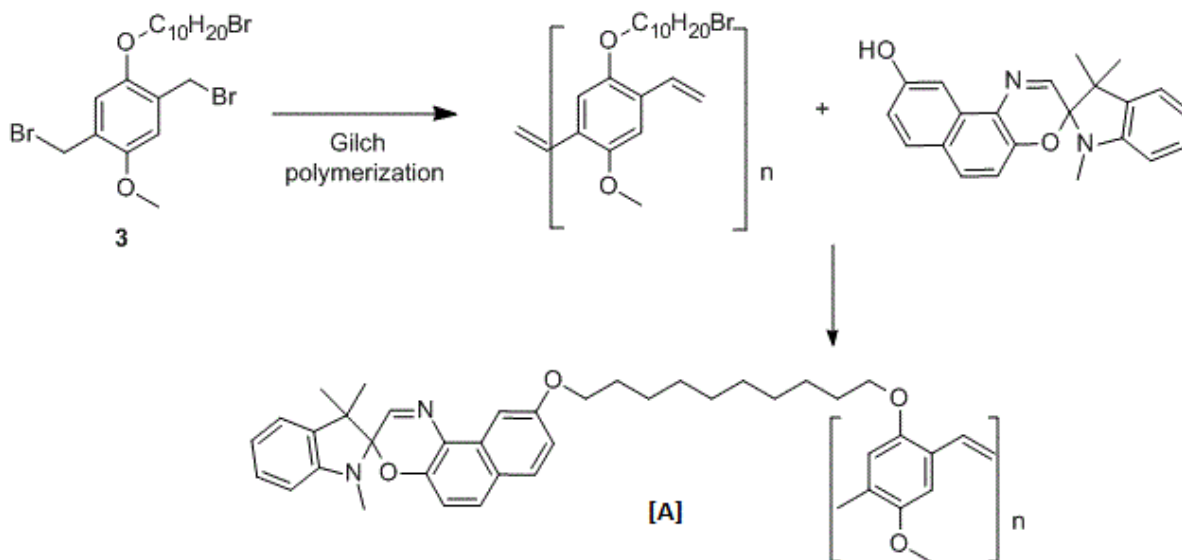


Figure 19 – General Synthesis Route using Gilch Polymerization

The details of the Gilch polymerization mechanism can be seen in Figure 20. The first step of this mechanism involves the deprotonation of the most acidic hydrogen by the basic oxygen of the tert-butoxide (tBuOK). This creates a resonance-stabilized carbanion that then attacks the benzylic hydrogens of other monomer molecules in a $\text{S}_{\text{N}}2$ reaction, causing the bromine to leave and thus connecting the two molecules. The presence of more base then causes an E2 reaction to occur, forming the vinyl bonds present within the polymer backbone.

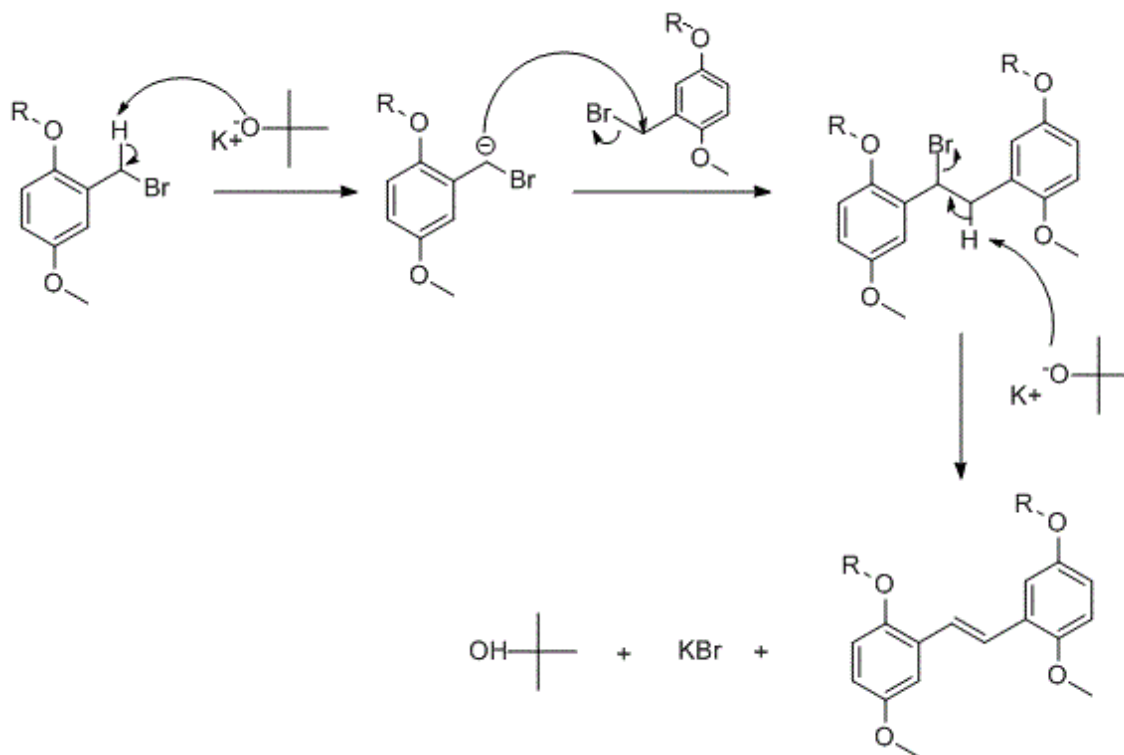


Figure 20 – Gilch Polymerization Mechanism

These polymerizations require about two hours to form the crude form of the polymer, which was then redissolved in a minimal amount of THF and precipitated into methanol to purify and give the product.

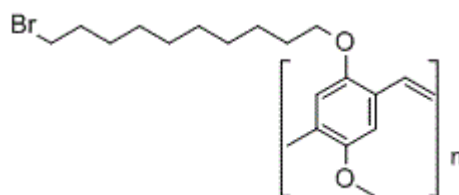


Figure 21 – 100% Br-functionalized PPV Product [A]

100% and 25% Br-functionalized PPV polymers were synthesized through Gilch polymerizations using a variety of monomer combinations, $\text{tBuOK}:\text{THF}$ ratios, and addition times, as shown in the following table.

Gilch Attempt #	Eq. of 3	Eq. of 7	tBuOK:THF ratio (mL)	Addition time (min)	Success?
1	1	0	1:5	10	N
2	1	0	1:10	18	Y
3	1	0	1:10	15	Too little to tell
4	1	0	1:10	17	N
5	1	0	1:15	30	Y
6	1	3	1:15	27	Y

Table 1: Chart of Gilch Attempts with the Amount of Monomers used, tBuOK:THF Ratio, and Addition Time.

The results of these different reaction conditions will be discussed next.

Most of the polymerizations were designed to yield homopolymer products in which each unit of the backbone of the polymer would have bromine attached at the end of the decyloxy group, theoretically making the polymer 100% Br-functionalized. For the first polymerization attempt about 1.2 mL of tBuOK was diluted with only 5 mL of anhydrous THF before it was added to the reaction. This diluted mixture was added dropwise with a 10 mL syringe over 10 minutes. Unfortunately, it seems that the tBuOK was either not diluted enough or added too quickly, for the reaction occurred too quickly and the polymer ended up reacting with itself to give a highly cross-linked polymer. This gave a single solid mass when the solution was precipitated in methanol, which is essentially useless for analysis as opposed to the desired fine red flakes. From this result it was determined that the tBuOK had to be diluted more, and possibly added over a longer period of time so as to not overwhelm the reaction and cause the polymer to bind to itself while it is being formed.

Keeping this in mind, the next polymerization (attempt #2) was carried out again with a few alterations. The tBuOK:THF ratio was raised from 1:5 to 1:10 and added over a course of about 18 minutes. Upon full addition of the tBuOK:THF mixture, the color of the reaction changed from pale yellow to dark orange. After precipitating and washing with acetone to dissolve any remaining monomer, the red polymer flakes were collected for NMR.

The NMR showed tell-tale polymer and aromatic peaks around 8 ppm, as well as bromomethylene peaks from the decyloxy chain around 3.5 ppm.

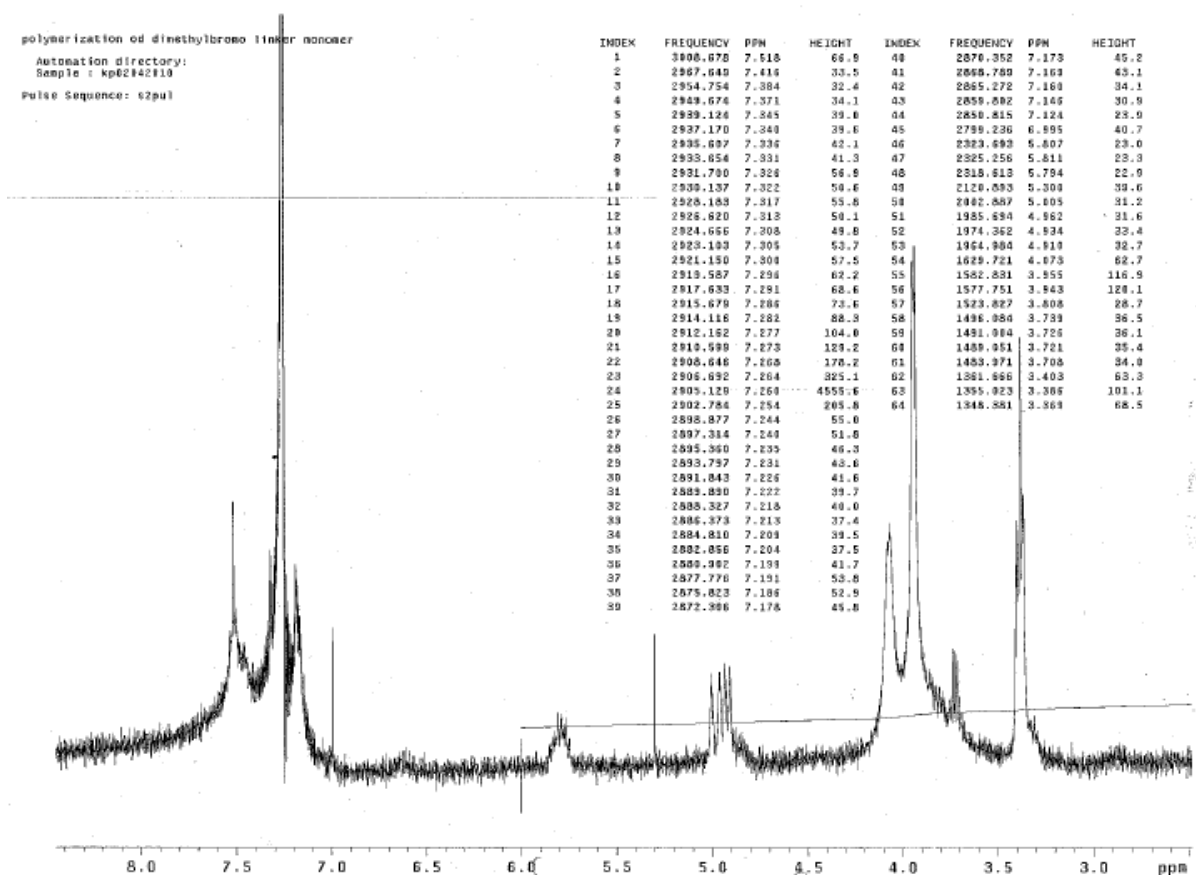


Figure 22 - ^1H NMR of Gilch Polymerization Product Polymer A with Elimination Byproducts

The NMR also showed some vinyl peaks between 5 and 6 ppm that indicate that in some parts of the polymer, the bromine also reacted with the tBuOK in an elimination reaction to create a carbon-carbon double bond at the end of the decyloxy chain, giving an unwanted byproduct in the reaction that is shown in Figure 22. These byproduct vinyl peaks are distinct from the polymer chain vinyl peaks, which can be found around 7.22 ppm.

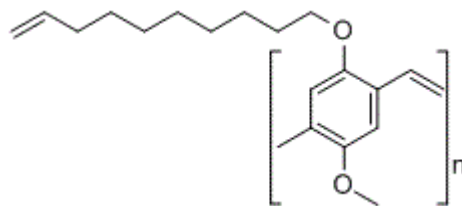


Figure 23 – Elimination Byproduct of Gilch Polymerization

Although the amount of elimination byproduct was small, it could still complicate the S_N2 reaction of adding the SO to the polymer, so it had to be purified. The polymer seemed reluctant to dissolve in THF, so chloroform was used instead; the polymer seemed a little more soluble in the more polar solvent, but not by much. The dissolved polymer was precipitated in methanol again and Buchner filtered. Unfortunately there was too little polymer to take an NMR, so it was instead used to “test out” the SO S_N2 reaction, which will be explored in detail later.

Later polymerizations (attempt #3 and #4) using the 1:10 tBuOK:THF ratio proved to produce very little polymer that stuck to the filter paper, prompting the use of chloroform to dissolve the polymer off of the filter paper, and then evaporating the filtrate to collect the polymer. Even then, the amount of the polymer collected seemed to be too little to do many effective studies. One polymerization even resulted in the creation of the cross-linked polymer again. Because of this, for the next polymerization (attempt #5) the tBuOK was diluted even more so that the ratio was 1:15 tBuOK:THF, and the dropwise addition time was spread out to almost half an hour. For both polymerizations the expected color change from pale yellow to dark orange did not take place at the end of the addition of the tBuOK:THF solution as it had for the earlier polymerizations. Several more drops of tBuOK were then added to the reaction until color change occurred, with at least a full 2 minutes between each drop. It seemed that if the tBuOK solution was to be diluted that much, the equivalencies of

the tBuOK in relation to the amount of monomer present needs to be increased in order for the desired reaction to take place. This method of polymerization proved to be the best course, for the NMR of the precipitated polymer showed no peaks to suggest that the E2 elimination reaction with the bromine occurred, which removed the need for purification. This NMR can be found in the Appendix, Figure 50.

The second polymerization using the 1:15 tBuOK:THF ratio (attempt #6) differed from the earlier polymerizations in that instead of creating a homopolymer product in which each backbone unit contained the bromine leaving group, only about one in four did; a random copolymer was made instead.

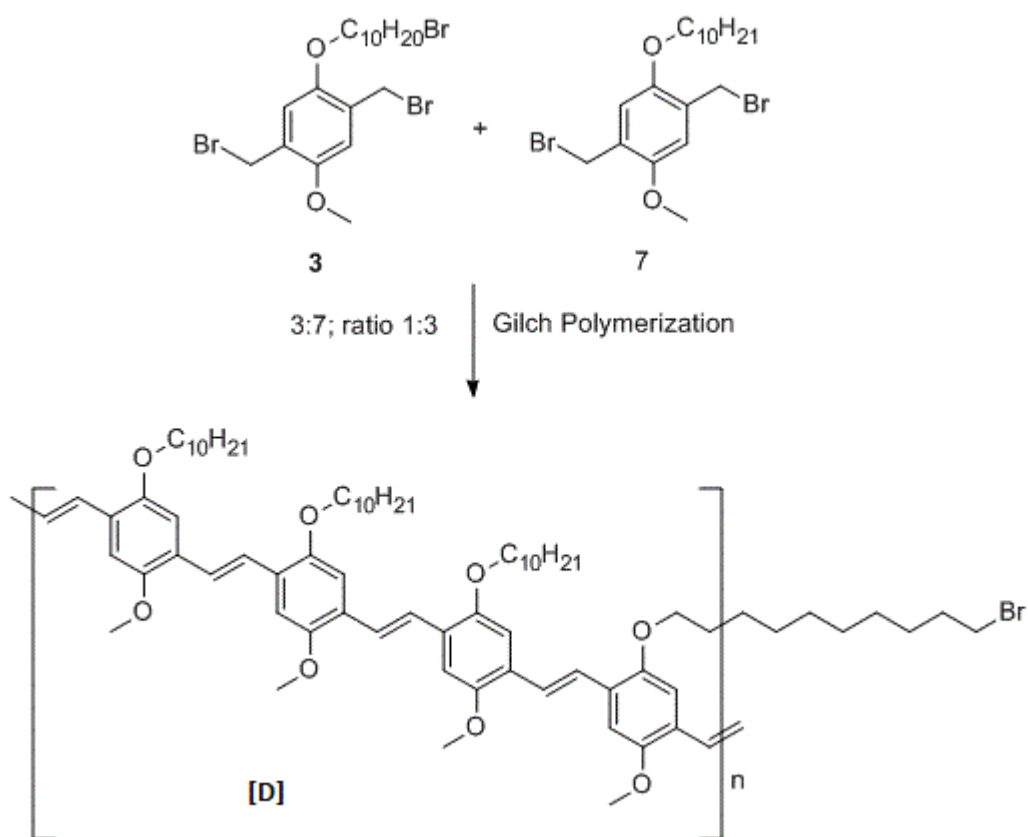


Figure 24 – Gilch Polymerization of 25% Br-functionalized PPV [D]

The monomer **7** used for this polymerization was originally synthesized and purified by former research student Chris Lee '08. This different procedure was used so that when the SO group is added to the polymer, it will only attach at certain key locations along the backbone instead of every point, hopefully improving the solubility of the SO-PPV product.

Synthesis attempts of SO-PPV

Many different attempts have been made to synthesize SO-functionalized PPV through an S_N2 reaction (shown in Figure 13) between the hydroxyl group on the SO and the bromine leaving group on the PPV. Each attempt used a variety of solvents and bases to help determine which reaction conditions were most likely to facilitate the desired product. These different reaction conditions are discussed next.

Reaction #	Polymer Used	Reaction Solvent	Polymer Created	Reaction Temp. ($^{\circ}\text{C}$)	Base	Color Change?
1	A	THF	100% SO-PPV (E)	65	K_2CO_3	N
2	A	Xylenes	100% SO-PPV (F)	150	K_2CO_3	N
3	A	DMF	100% SO-PPV (G)	160	Ce_2CO_3	Y
4	D	DMF	25% SO-PPV (H)	160	Ce_2CO_3	Y

Table 2 – Chart of SO-PPV Synthesis Attempts and their Reaction Conditions

The first reaction attempt took place using THF as the solvent and potassium carbonate as the base to create SO-PPV. Although the reaction was set up using a condenser in a nitrogen atmosphere, there were many problems with the THF evaporating and a couple of milliliters of THF had to be added every couple of hours. Also, the temperature had to be turned down at night so as to avoid the solvent being completely boiled off. There was no color change in the reaction; it stayed a reddish-orange during all the days it was running, and fluorescence studies of the product showed no measurable SO functionalization on the product.

Next we tried a higher boiling solvent to raise the heat of the reaction, which would hopefully make the S_N2 reaction more likely to occur. Xylenes was used for the reaction; the color appeared to be a slightly darker red-orange than the reaction with THF, but there was

no drastic color change. Preliminary fluorescence studies also showed little to no SO functionalization of the product; however, fluorescence and absorbance studies showed that the polymer survived the high temperature of the reaction very well, with little to no shifting in the absorbance and fluorescence peaks of the polymer before and after the reaction. This proved that the polymer did not degrade into smaller pieces during the reaction, which was a concern. Later fluorescence studies showed much more interesting results, which will be discussed later.

For the third attempt the solvent DMF was used because of its high boiling temperature and its increased polarity over xylenes, which should help enhance the S_N2 reaction. The base was also changed from potassium carbonate to cesium carbonate, which is stronger and thus also increases the likelihood of the S_N2 reaction taking place. Unlike the first two attempts of this reaction, this attempt showed an immediate color change near the beginning of the reaction, to a dark color that had a slight green tint to it. After the reaction was finished, most of the solvent was boiled off and the remaining solution was poured into methanol. The methanol turned a light green color where it had turned red for the earlier synthesis attempts, and there were several dark flakes of precipitated product that was Buchner filtered and collected. Unfortunately the product was insoluble in both THF and chloroform, and only partly soluble in dimethyl sulfoxide (DMSO). After days of sonicating the product, there were still some very fine, brown flakes that refused to dissolve, rendering NMR useless. Fluorescence studies were carried out that showed a shift in absorbance and fluorescence, but no sign of the reversible photo quenching associated with the SO group. It has been surmised that the brown flakes are the parts of the polymer that contain the SO

functionalization, and the fact that they cannot be completely dissolved has affected the fluorescence studies.

For all the SO-PPV synthesis attempts described thus far, Polymer A was used in the S_N2 reaction. It was theorized that if each bromine group of that 100% Br-functionalized polymer was indeed replaced with a SO group in the last attempt, that may have been the main reason why the SO-PPV product seems so reluctant to dissolve. Following this theory, a random copolymer in which about one of four backbone benzyl groups had a bromine group attached to the decyloxy branch was used in the last SO-PPV synthesis attempt. It was theorized that if there were fewer places for the SO to attach to the polymer, then it would follow that there would be less total SO in the product and thus help improve solubility. DMF and cesium carbonate were used for this experiment as well. The same color change as the last attempt was observed at the start of the reaction, with a slightly more reddish tint to it. After about a week, the reaction was taken off of heat and poured into methanol to precipitate. The methanol again turned a green-yellow color with dark flakes of product, which were Buchner filtered and collected. Only a couple of milligrams of product was collected, which is too small for an effective NMR. However, there was enough to carry out a few fluorescence studies, which are discussed in the next section.

Fluorescence Studies

The main goal of this project was to be able to successfully functionalize PPV with SO to the point where we can selectively and reversibly quench the fluorescence of the polymer.

Several fluorescence studies were done on both SO-PPV products and control polymers.

Polymer Label	Compound (Polymerization Method)	Precursor Polymer	S_N2 Reaction Solvent
B	25% Br-PPV (Heck)	N/A	N/A
C	25% SO-PPV (Heck)	B	THF
A	100% Br-PPV (Gilch)	N/A	N/A
E	100% SO-PPV (Gilch)	A	THF
F	100% SO-PPV (Gilch)	A	Xylenes
G	100% SO-PPV (Gilch)	A	DMF
D	25% Br-PPV (Gilch)	N/A	N/A
H	25% SO-PPV (Gilch)	D	DMF
Polymer Label	Absorbance λ_{\max} (nm)	Fluorescence λ_{\max} (nm)	Photomodulation?
B	463	542	N/A
C	376	505	No
A	480	543	N/A
E	492	547	No
F	475	545	Yes
G	450	555	No
D	480	545	N/A
H	465	547	No

Table 3 – Chart of Compounds Used for Fluorescence Studies and their Results.

While only one obtained product appears to show definite photomodulation, all of the fluorescence studies carried out will be discussed.

The first fluorescence study shown in Figure 25 was carried out on the control polymer **B** synthesized using the Heck reaction.

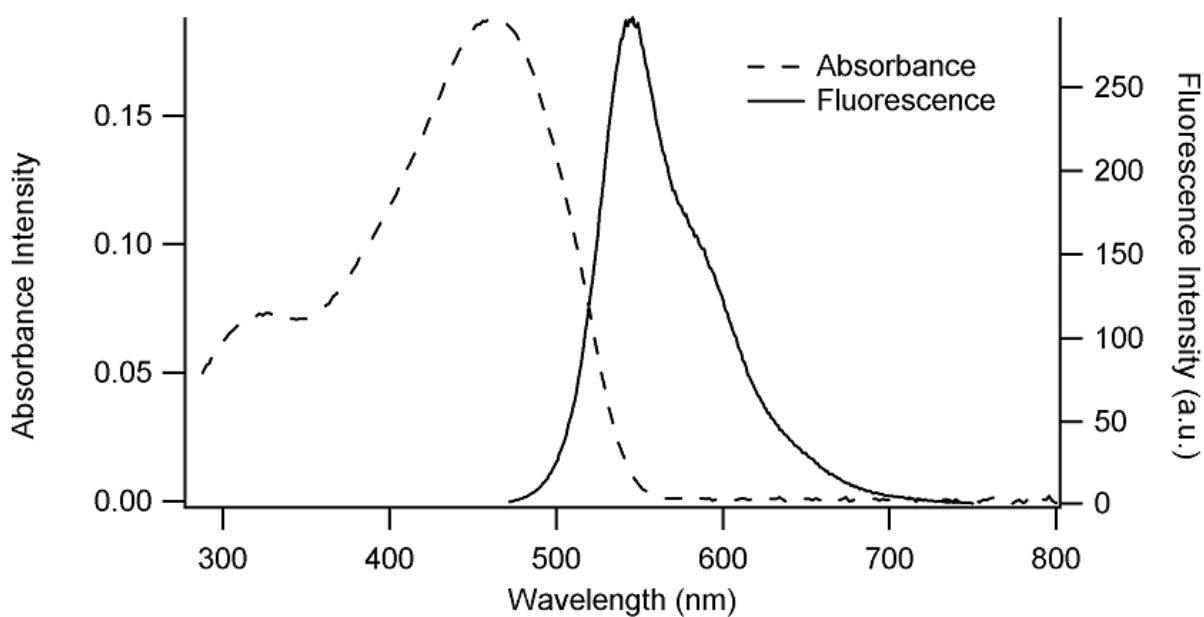


Figure 25 – Absorbance and Fluorescence Spectra for Polymer **B**

The absorption and fluorescence spectra showed that Polymer **B** had a λ_{max} of 463 and 542 nm, respectively. These numbers correspond well with those found by Jordan Walk '09.

Fluorescence studies of the Polymer **C** synthesized with the Heck polymerized Polymer **B** were carried out next.

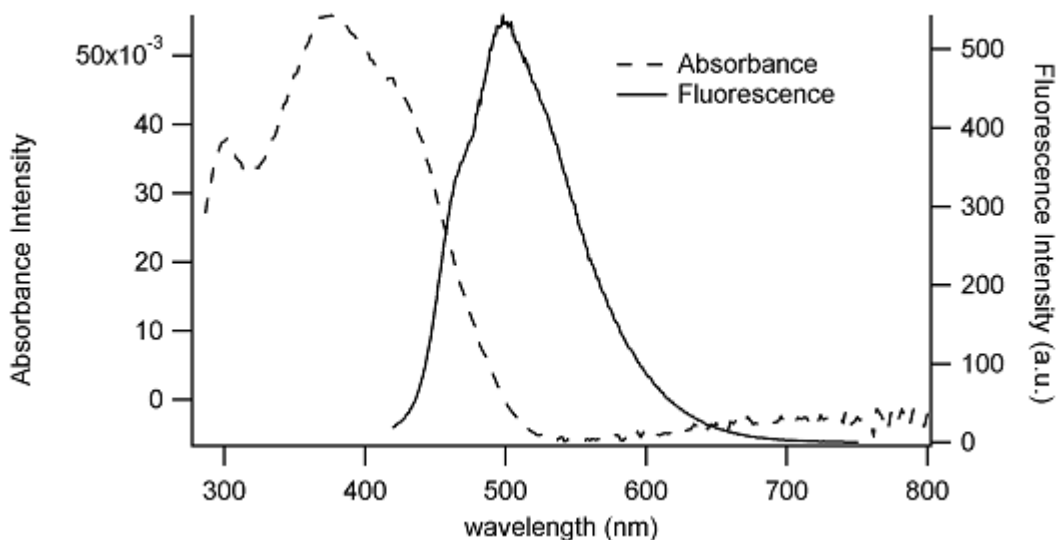


Figure 26 – Absorbance and Fluorescence Spectra for Polymer **C**

The absorbance and fluorescence spectra are drastically different from the control polymer, with a λ_{max} at 376 nm, a blue shift of almost 100 nm. This blue shift is most likely caused by the presence of shorter polymer chains in the polymer **C** product as opposed to the control polymer **B**. The decreased amount of conjugation would increase the amount of energy needed for absorption, thus resulting in a shorter wavelength of absorption. The fluorescence spectrum shows a λ_{max} at 505 nm, which is also blue shifted but not quite as much as the absorbance. Next, polymer **C** was UV-irradiated for 10 seconds. Fluorescence spectra of the polymer were measured before UV-irradiation, immediately after UV-irradiation, and then 60 seconds after UV-irradiation. Immediately after UV-irradiation, the spiro form of the SO group should be opened to the MC form. After UV-irradiation is stopped, the MC form will thermally revert back to the spiro form, a process that occurs with a half-life of 4 seconds.¹² If photomodulation is achieved, then we should see a decrease or quenching of the fluorescence immediately after UV-irradiation, and then a reacquisition of full fluorescence 60 seconds after UV-irradiation, since by 60 seconds any opening of the MC

form of the SO should be fully reverted back to the spiro form. The spectra from these irradiations are presented in Figure 27.

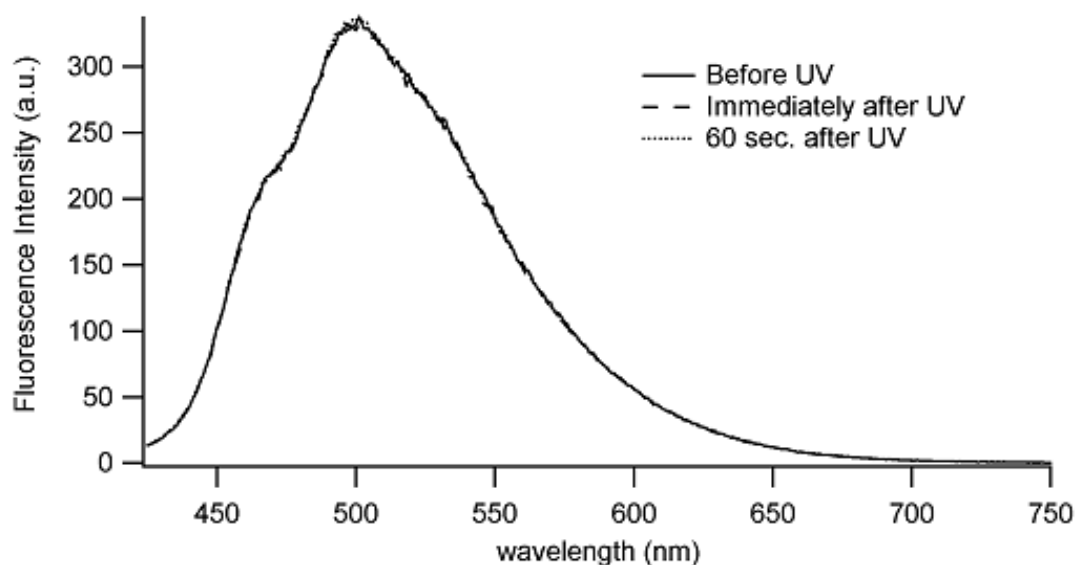


Figure 27 – UV-irradiation Studies of Polymer C

Unfortunately, there seems to be no photo reactivity in the molecule. The spectrum in Figure 27 does not show any sort of photomodulation between the different states of UV-irradiation. These findings match those of Jordan Walk '09, in which soluble SO-PPV products show no photoreactivity and relatively insoluble SO-PPV products show some reactivity. The high amount of synthetic steps needed for the Heck polymerization combined with the discouraging fluorescence studies prompted the use of the new synthetic route utilizing the Gilch polymerization.

Two control polymers were created using the Gilch polymerization, one that was 100% Br-functionalized PPV [**A**] and one that was 25% Br-functionalized PPV [**D**]. Polymer **A** showed an absorption and fluorescence λ_{max} at 480 and 543 nm respectively, while polymer **D** showed an absorption and fluorescence λ_{max} at 480 and 545 nm respectively.

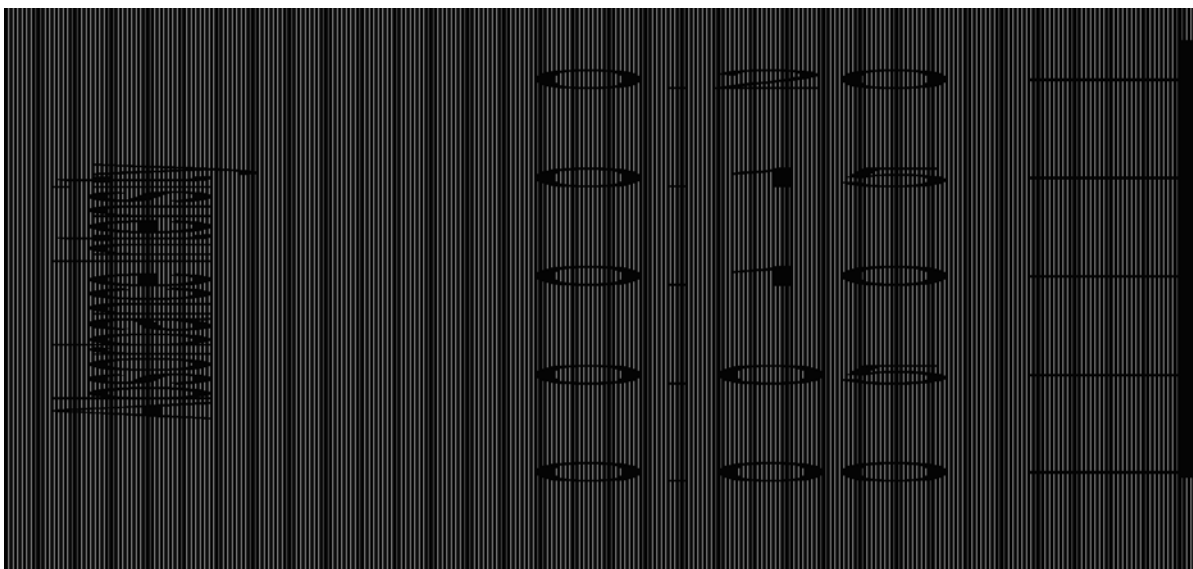


Figure 28 – Absorbance and Fluorescence Spectra of Polymer **A**

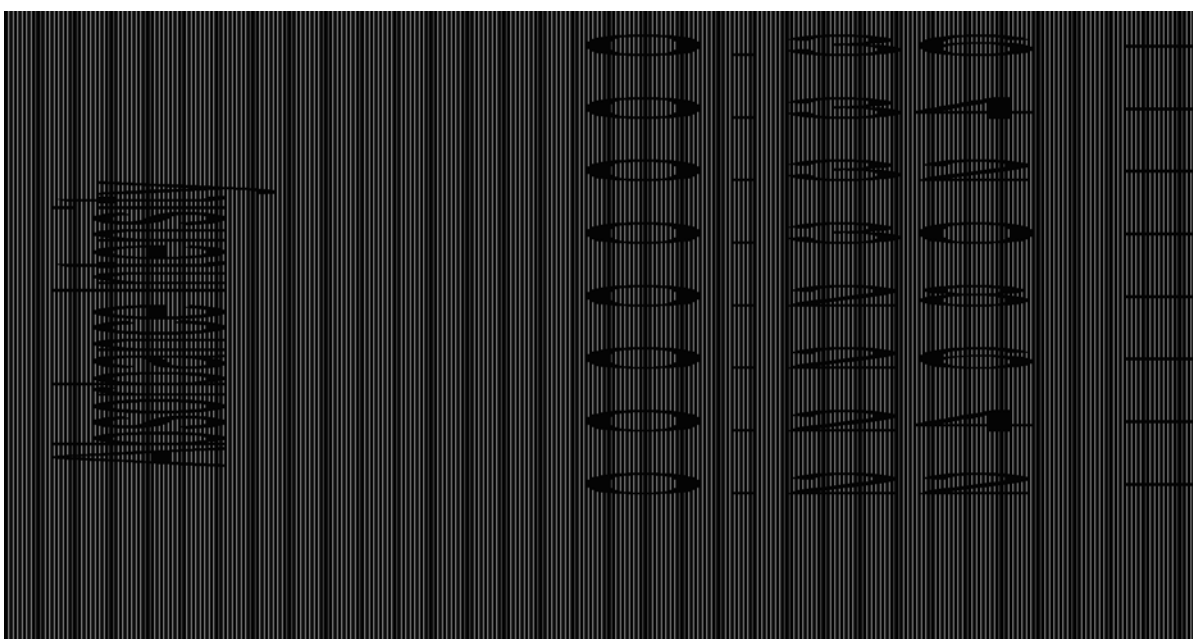


Figure 29 – Absorbance and Fluorescence Spectra of Polymer **D**

The 100% SO-functionalized PPV product that was synthesized using THF as the reaction solvent [**E**] was studied next. The absorption and fluorescence spectra had a λ_{max} at 472 and 547 nm respectively, which do not differ significantly from those of the polymer **A**. These spectra are displayed in Figure 29.

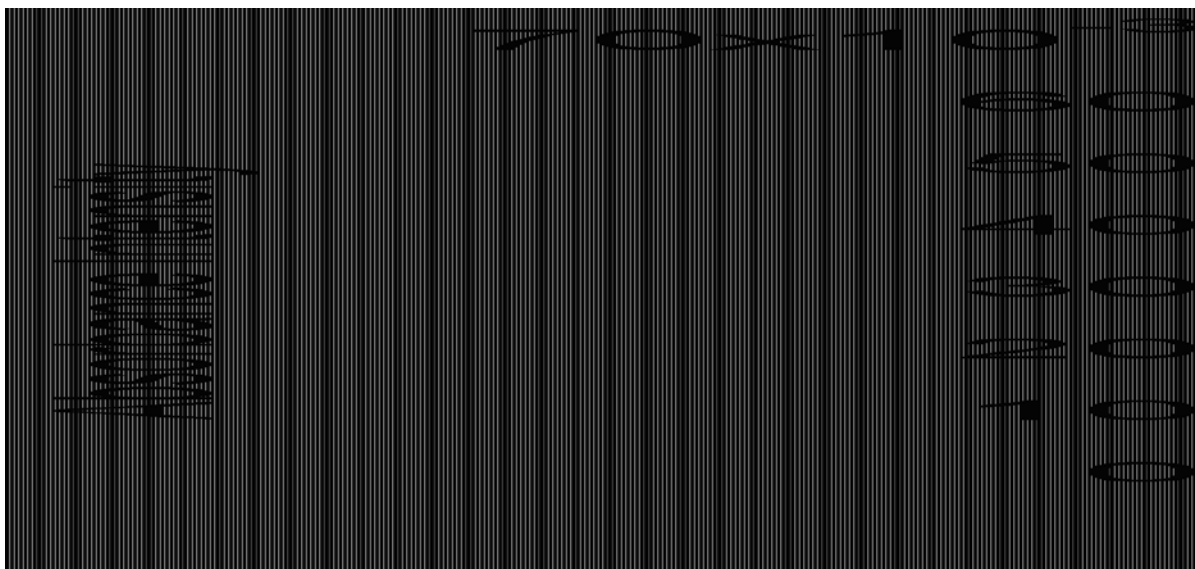


Figure 30 – Absorbance and Fluorescence Spectra for Polymer **E**

UV-irradiation studies (Figure 30) of the polymer product show that the polymer unfortunately undergoes photobleaching during irradiation, as evidenced by the lack of any increase in fluorescence 60 seconds after UV-irradiation.

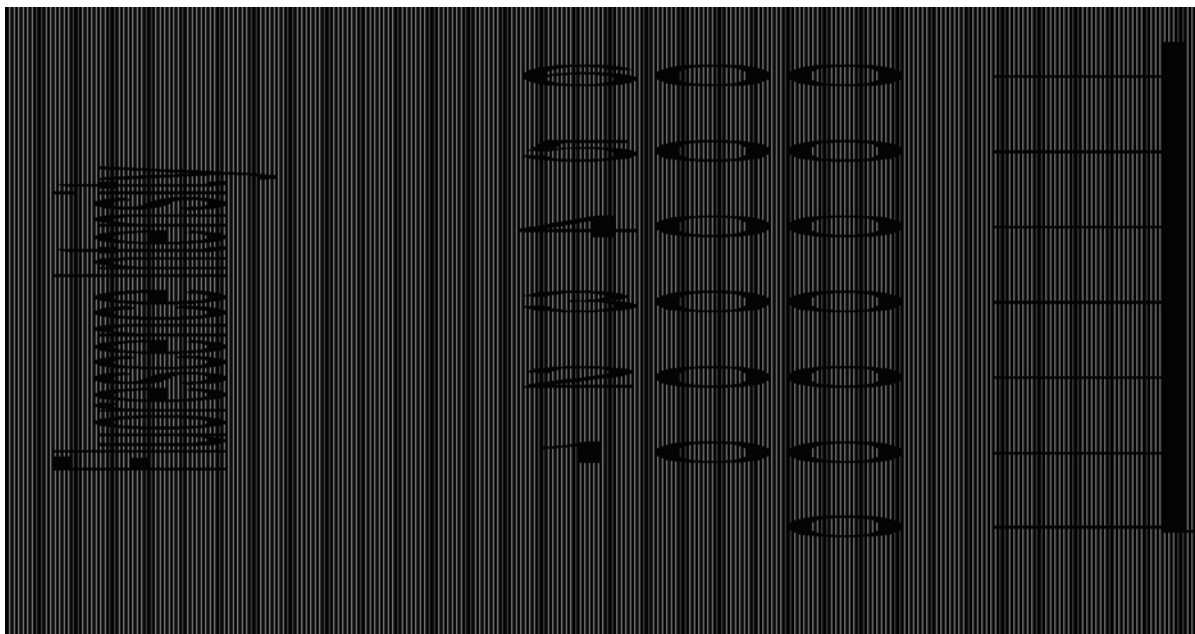


Figure 31 – UV-irradiation Studies of Polymer **E**

This study shows that there is some sort of photo reactivity in the product, but unfortunately the UV light seems to irreversibly alter the polymer structure instead of allowing us to achieve reversible fluorescence quenching.

The next sample to be discussed is the 100% SO-functionalized PPV synthesized using DMF as the reaction solvent [G]. This sample proved to be extremely hard to solvate, refusing to dissolve in the usual organic solvents used for fluorescence studies. The best solvent to use was DMSO, and even then it seemed that only small molecular weight polymer chains were actually dissolved; a good amount of the product stayed suspended in DMSO in the form of very fine, brown flakes. Nevertheless fluorescent studies were still carried out, and the absorption and fluorescence spectra had a λ_{max} at 450 and 555 nm respectively.

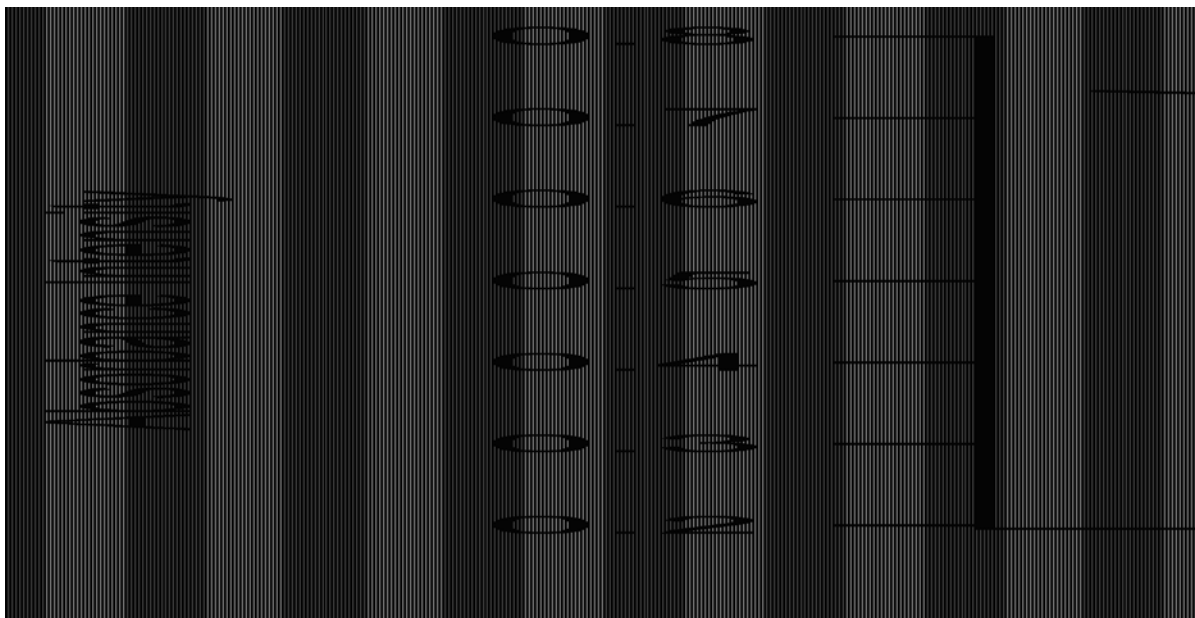


Figure 32 – Absorbance and Fluorescence Spectra of Polymer G

UV-irradiation studies showed no photo reactivity.

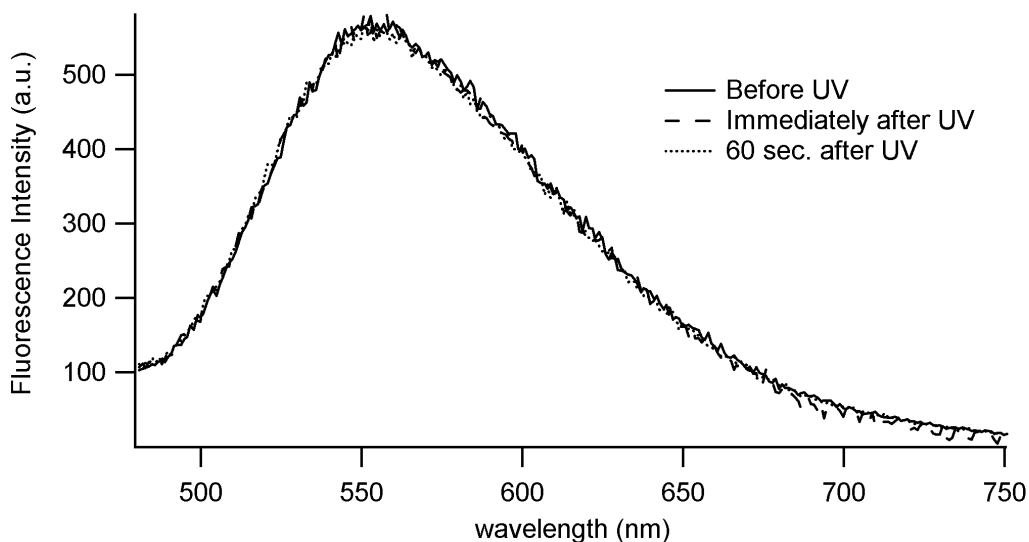


Figure 33- UV-irradiation Studies of Polymer **G**

It has been theorized that despite these discouraging findings, they might simply be due to the poor solubility of the product. It is very possible that the SO group did succeed in binding to the PPV polymer, but that the high amount of SO-functionalization caused the poor solubility and that the SO groups are present in the undissolved brown flakes. If the SO-functionalization of the product could be decreased, that might increase the solubility and thus allow fluorescent studies to be carried out on the actual SO-PPV.

Therefore, a study was carried out on the 25% SO-functionalized PPV product that was also synthesized with DMF as the reaction solvent [**H**]. Unfortunately, solubility did not

seem to be much improved.

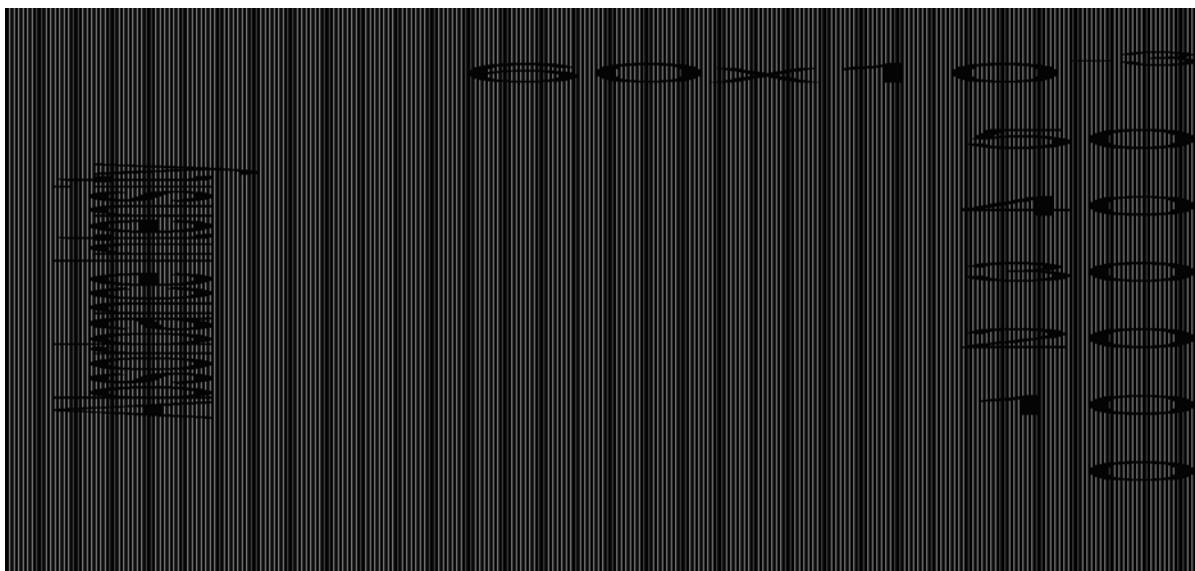


Figure 34 – Absorbance and Fluorescence Spectra of Polymer **H**

The absorption and fluorescence spectra showed a λ_{max} at 465 and 547 nm respectively. The UV studies showed no photoreactivity, as was expected from the lack of solubility.

Despite these disappointing studies, there was one product that showed promise in our goal of achieving selective fluorescence quenching by attaching an SO group to a PPV polymer. Preliminary studies performed on the 100% SO-functionalized PPV synthesized with the xylenes reaction solvent [**F**] seemed to mimic that of polymer **E**. However, when the studies were repeated to produce printable graphs for this writing, they turned out to be much different. First, the absorption and fluorescence spectra presented in Figure 34 give a λ_{max} at 475 and 545 nm respectively.

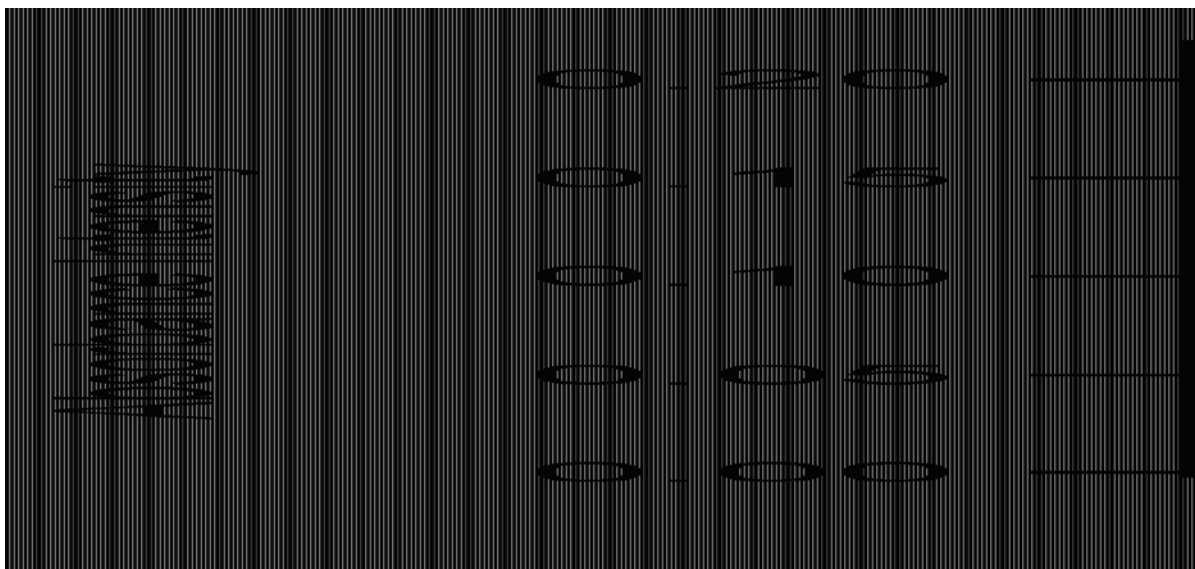


Figure 35 – Absorbance and Fluorescence Spectra of Polymer **F**

After carrying out the UV-irradiation studies, it appeared that we may have achieved selective quenching as seen in Figure 36.

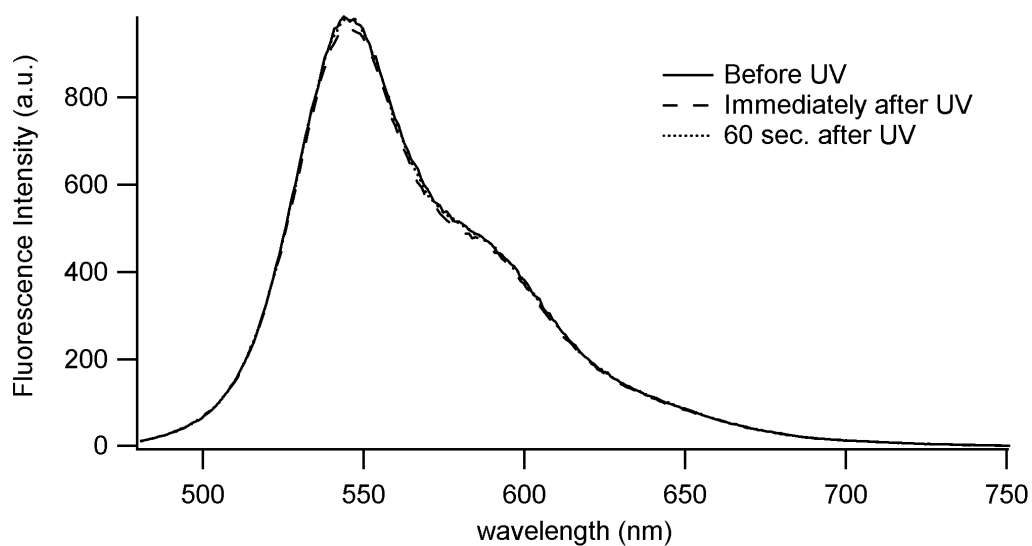


Figure 36 – UV-Irradiation Studies of Polymer **F**

A closer look at the region from 530 to 630 nm shows that the products fluorescence indeed decreases with UV-irradiation, and successfully returns to its original fluorescence after 60 seconds.

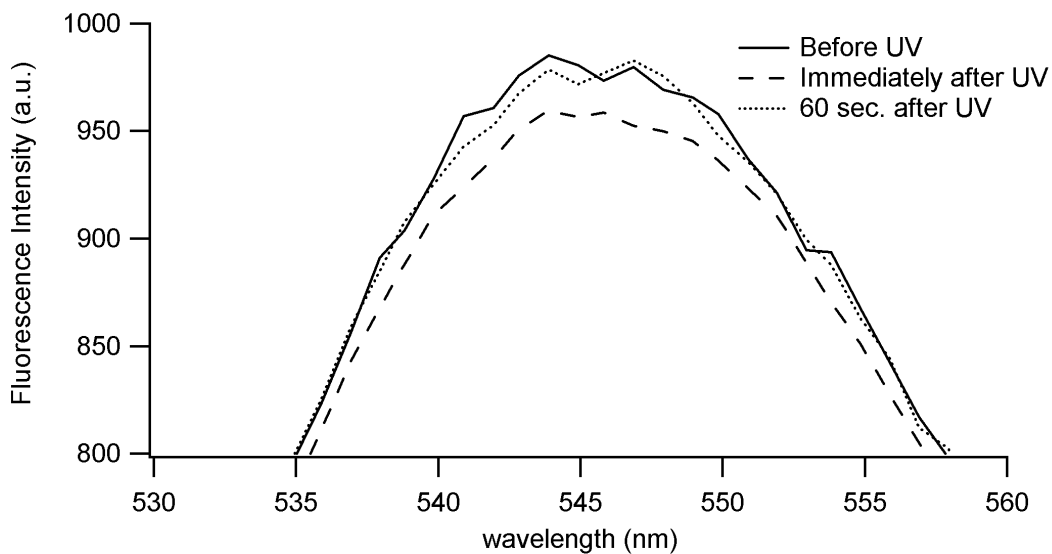


Figure 37 – UV-Irradiation Studies of Polymer **F**: 530-560 nm

Another UV-irradiation study (Figure 38) was carried out, this time measuring the absorbance immediately after UV-irradiation.

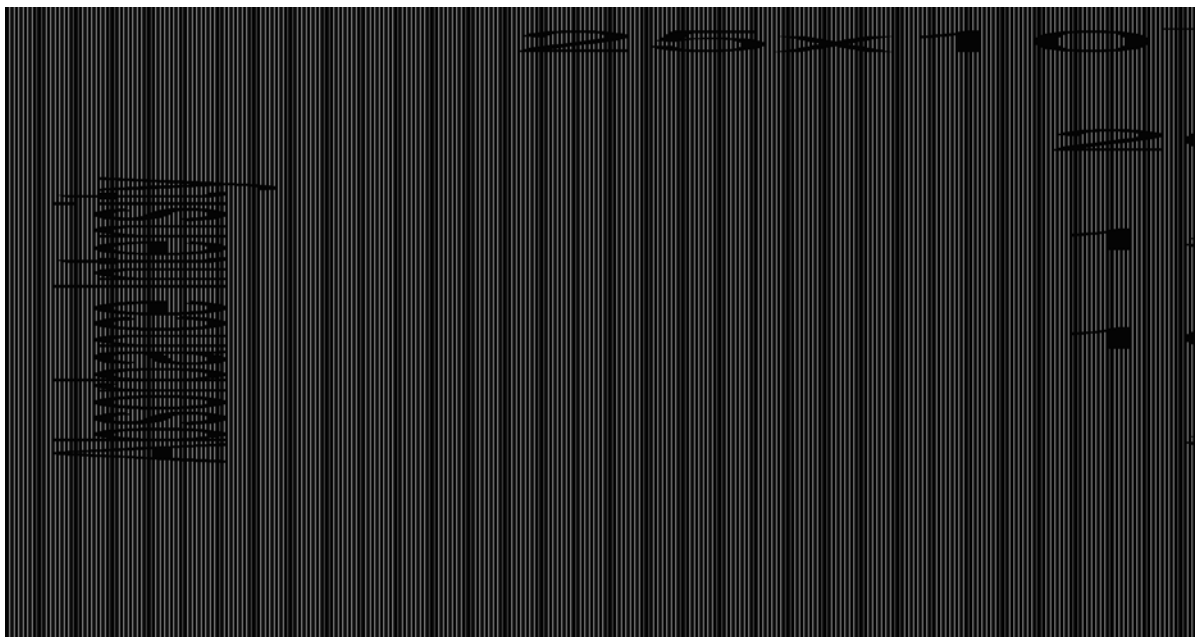


Figure 38 – UV-irradiation Absorbance Studies of Polymer **F**

The difference in absorbance from about 550 to 630 nm is shown in Figure 37. From previous experience in the lab, we know that this shows that the SO group in the product is

indeed changing from the closed SO form to the open MC form upon UV irradiation as expected.¹³

A small kinetic study shown in Figure 39 was also performed on the polymer, and was carried out while exciting the SO-PPV at maximum fluorescence (545 nm).

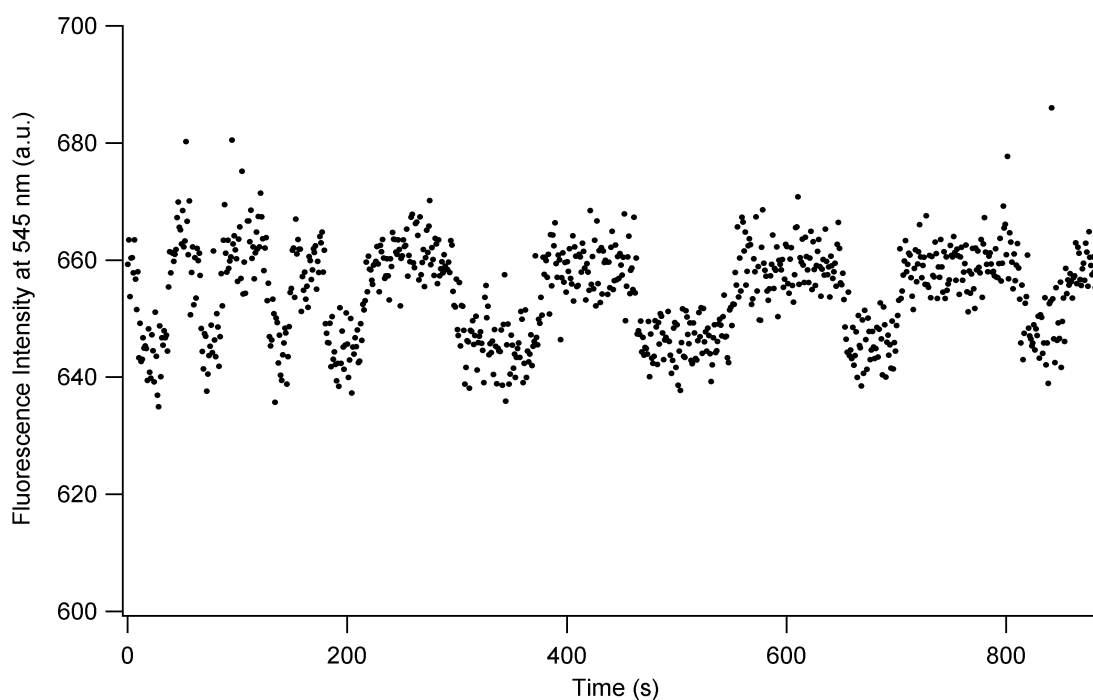


Figure 39 – Kinetic Study of Polymer **F**: Excited at 545 nm.

The points of lower intensity are all points where the product is being UV-irradiated, while at the points of higher intensity it is not being UV-irradiated. This study shows that the quenching achieved in Figures 35 and 36 is selective and reproducible, and that the SO-PPV is resistant to fatigue as it carried out with no signs of degradation for almost 14 minutes. The quenching of the fluorescence is very small, but it is there, and shows promise for future work.

Conclusion

This project proposed the Gilch polymerization as an alternate synthetic route to produce SO-PPV as opposed to previous work that utilized the Heck polymerization. The route that involved the Heck polymerization was very arduous, as it required a six step synthesis to make just one of the monomers needed for polymerization. This new synthetic route has proven to be much less time-consuming, requiring only three major synthetic steps and simple purification techniques to produce SO-PPV. The shortened route utilizing the Gilch polymerization has allowed better yields because of its decrease in synthetic steps, thus providing more product for fluorescence studies.

Many of the fluorescence studies carried out for this project showed little or no photomodulation. The discouraging results of at least two of these studies, the 100% and 25% SO-functionalized PPV products synthesized using DMF as the reaction solvent for the S_N2 reaction, are most likely due to solubility issues. It has been theorized that the parts of the polymer in which the SO has successfully been bound are the same parts that seem to be insoluble. Future work can be carried out on trying to either a) find organic solvents that the SO-PPV product is soluble in or b) improve solubility of the SO-PPV product through synthetic means by attaching longer carbon chains to the polymer backbone.

One of the products, 100% SO-functionalized PPV synthesized using xylenes as the reaction solvent during the S_N2 reaction, showed photomodulation. Though the difference is very small, fluorescence studies have proven that we have achieved selective quenching of the PPV polymer for this product. Kinetic studies show that this reversible quenching is reproducible, and that the product seems resistant to both fatigue and photobleaching. Future

work can be carried out to improve the amount of this quenching, and it may be very possible to create nanoparticles out of this polymer.

Experimental

Synthesis of 1-(10-bromodecyloxy)-4-methoxybenzene [2]. 25 g (83.3 mmol, 7 eq) of dibromodecane (DBD) was used 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. ¹H NMR (400 MHz, CDCl₃) 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). ¹³C NMR (400 MHz, CDCl₃) 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 [3]. 4 g of dibromo linker (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 was 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 NaHCO₃, and once with brine. Color change sometimes occurs with the NaHCO₃ 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. ¹H NMR (400 MHz, CDCl₃) 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, 2H), 1.43 (quint, 2H), 1.29 (br, 10H). ¹³C NMR (400 MHz, CDCl₃) 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-dibromo-2-(10-bromodecyloxy)-5-methoxybenzene [6]. 5.586 g of **2** (16.3 mmol, 1 eq), 45 mg of Iron powder (0.814 mmol, 0.05 eq), and 250 mL of chloroform was added to a 500 mL RB flask, along with a stirbar. Using an ice bath, the temperature of the mixture was cooled down to 0°C. In a separate flask, 1.76 mL of Br₂ (34.2 mmol, 2.1 eq) was diluted with about 20 mL of chloroform and added dropwise to the cooled mixture. The solution turned slightly orange when first adding the bromine, then grew steadily darker to red, then a cranberry red, and then finally a dark wine red upon complete addition. The solution was then warmed to room temperature and stirred for 6 hours. The solution was poured into a 500 mL separation flask and washed four times with water. The organic layer was dried with magnesium sulfate, and the red chloroform was evaporated off to give an orange liquid product which solidified at room temperature. This product was then recrystallized with acetone to remove impurities. ¹H NMR (400 MHz, CDCl₃) δ 7.09 (s, 2H), 3.94 (t, 2H), 3.84 (s, 3H), 3.40 (t, 2H), 1.75-1.90 (m, 4H), 1.4-1.5 (m,

4H), 1.25-1.40 (br, 8H). ^{13}C NMR (400 MHz, CDCl_3) δ 150.60, 150.26, 118.83, 117.23, 111.46, 110.61, 70.62, 57.32, 34.35, 33.20, 29.76, 29.70, 29.58, 29.48, 29.10, 28.54, 26.29.

Gilch Polymerization of 1,4-bis(bromomethyl)-2-methoxy-5-bromodecyloxy benzene [3] to make Polymer A. A 3 neck 50 mL RB flask was set up with each neck fitted with a rubber septum. A needle that was hooked up to an argon tank was inserted into the middle septum, along with a corresponding disposable syringe needle to let out excess air. The entire system was flame-dried to get rid of excess moisture. 0.1575 g of **3** (0.298 mmol, 1 eq) was dissolved in anhydrous THF and the resulting solution injected into the 3 neck RB flask. This solution was heated to 50°C, with a steady nitrogen flow. Next, a solution of 1 mL tBuOK (1.25 mmol, 4.2 eq) and 10-15 mL of anhydrous THF was prepared, and then injected into the monomer-THF mixture dropwise over 15-20 minutes. 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 50°C, and then taken off of the heat. One of the rubber septums was removed and the red-orange solution was poured into about 175 mL of vigorously stirring methanol to precipitate the polymer. After 10 minutes of stirring the mixture 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. If the polymer appeared to be so fine that it is essentially stuck to the filter paper, it was dissolved with chloroform into a Buchner filter and the chloroform evaporated to collect product.

Gilch Polymerization of 1,4-bis(bromomethyl)-2-methoxy-5-bromodecyloxy benzene [3] and 1,4-bis(bromomethyl)-2-(decyloxy)-5-methoxybenzene [7] to make Polymer D. A 25 mL 3-neck RB flask was set up with a stir bar and rubber septums on all three necks. A needle connected to an argon tank and corresponding degassing needles were injected into the middle septum to provide a steady flow of argon while the set up was flame dried. After establishing an inert environment, 75 mg of **3** (0.142 mmol, 1 eq), and 190 mg of **7** (0.426 mmol, 3 eq) were dissolved in about 15 mL of anhydrous THF and injected into the flask. This solution was then heated to 50°C. A solution of 2.4 mL tBuOK (2.39 mmol, 4.2 eq of whole monomer count) and 15 mL of anhydrous THF was prepared and added dropwise to the heated flask over 27 minutes. Color change from yellow to dark orange failed to occur, so about 0.5 mL of extra tBuOK was added to the solution over 10 minutes to achieve color change. After color changed to dark orange the solution was allowed to stir at 50°C for two hours, then taken off heat. The reaction was then poured into stirring methanol, at which time the methanol turned a reddish-orange with dark red precipitate. This precipitate was collected using Buchner filtration, and then washed with acetone to get rid of residual monomer. Most of the product stuck to the filter paper, so chloroform was used to dissolve the product and then evaporated using rotary distillation to obtain final product of red film.

Heck Polymerization of Control Polymer B. 0.50 g of Divinyl (1.13 mmol, 2 eq), 0.310 g of Dibromo benzene (0.565 mmol, 1 eq), and 0.283 g of Dibromo linker (0.565 mmol, 1 eq) were added to a 50 mL RB flask, as well as 21 mg of palladium(II) acetate (0.0904 mmol, 0.04 eq), 165 mg of tri-tolyl-phosphine (0.542 mmol, 0.24 eq), 16 mL of DMF and 7 mL of triethylamine. The flask was charged with argon and then set up on an

argon condenser. The solution was stirred at 90°C for 24 hours, then the temperature was increased to 110°C and the solution was stirred for another 24 hours. The resulting solution was then poured into about 60 mL of methanol, precipitated, and Buchner filtered to collect the resulting red precipitate product. A soxhlet purification technique was used to purify the product using acetone, methanol, and hexanes. The product seemed to dissolve in the hexanes solvent, so that flask was evaporated to collect fine red flakes of product.

Attempted Synthesis of Polymer C from Precursor Polymer B. 89.5 mg of Control polymer (0.0139 mmol Br, 1 eq) was added to a 25 mL RB flask along with 6 mg of SO (0.0167 mmol, 1.2 eq) and 14 mg of potassium carbonate (0.0973 mmol, 7 eq). About 12 mL of THF was added to this mixture, which was then set up to a nitrogen condenser and refluxed between 75°C and 85°C for several days. After taking it off heat, the mixture was evaporated to leave a dark brown-orange product, which was dissolved in a minimal amount of THF and then poured into a flask of vigorously stirring methanol. The methanol turned yellow, with green-brown flecks of precipitate. After several minutes of stirring the solution was Buchner-filtered to collect the sticky polymer product.

Attempted Synthesis of Polymer H from Precursor Polymer A. 15 mg of polymer A (0.0400 mmol, 1 eq), 16 mg of spirooxazine (0.0480 mmol, 1.2 eq), and 39 mg of potassium carbonate (0.280 mmol, 7 eq) were added to a 10 mL RB flask along with a stir bar. About 7 mL of xylenes was then added to the flask and the reaction was set up to reflux at 160°C under a nitrogen condenser. After around 5-7 days, the solvent of the reaction was boiled down to a minimum. The reaction was then taken off of heat and poured into about 150 mL of vigorously stirring methanol. The methanol turned a yellow-green color with some dark brown precipitate specks, which were collected through Buchner filtration.

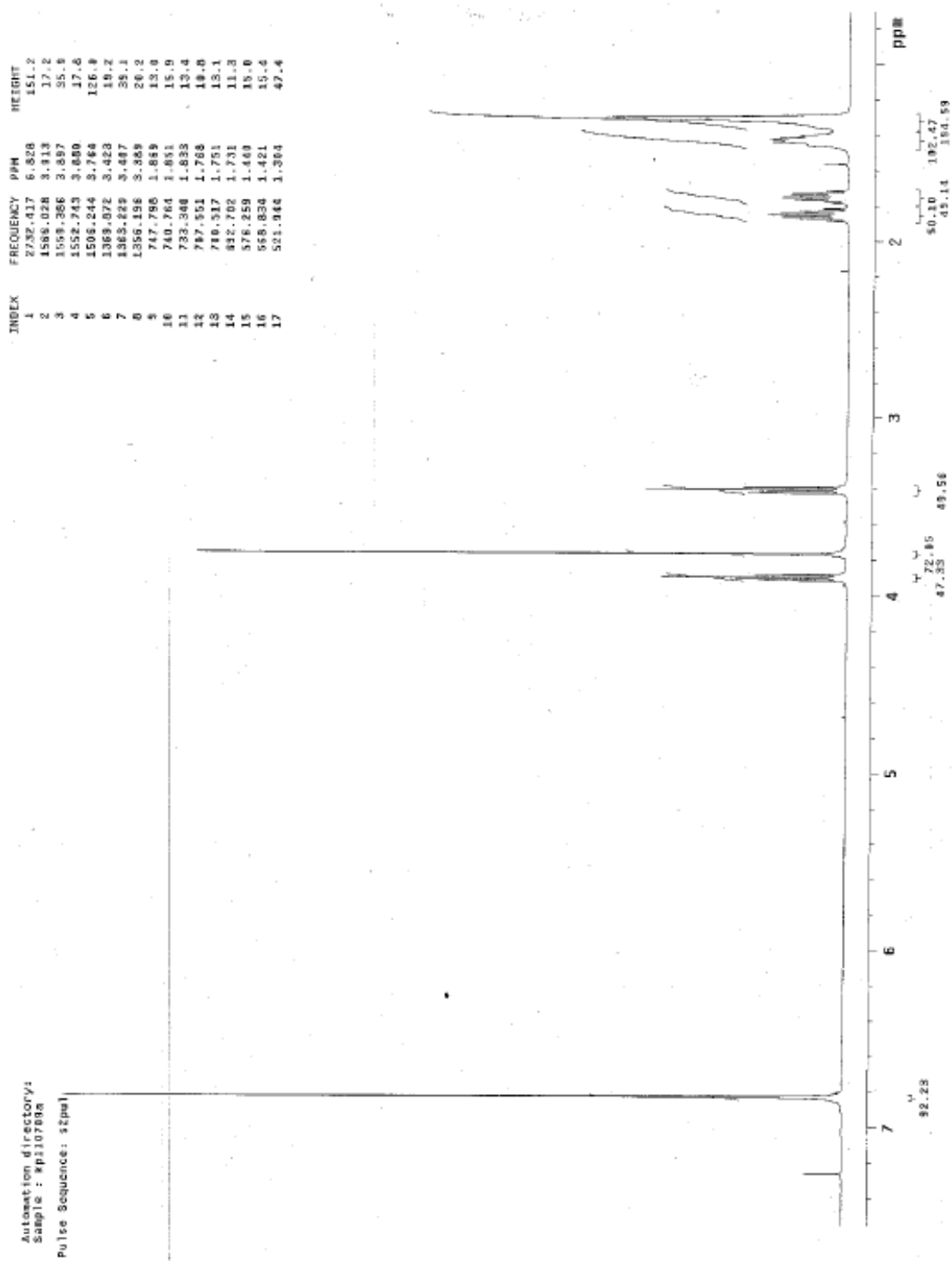
Polymer **E** and Polymer **G** were synthesized using the same procedure with THF/potassium carbonate and DMF/cesium carbonate respectively.

Attempted Synthesis of Polymer H from Polymer D. 8.5 mg of PPV-BR (0.0227 mmol, 1 eq), 9.1 mg of spirooxazine (0.0272 mmol, 1.2 eq), and 52 mg of cesium carbonate (0.159 mmol, 7 eq) were added to a 10 mL RB flask along with a stir bar. About 7 mL of DMF was then added to the flask and the reaction was set up to reflux at 160°C under a nitrogen condenser. After around 5-7 days, the solvent of the reaction was boiled down to a minimum. The reaction was then taken off of heat and poured into about 150 mL of vigorously stirring methanol. The methanol turned a yellow-green color with some dark brown precipitate specks, which were collected through Buchner filtration.

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Appendix

Figure 40 – ^1H NMR Spectrum of 1-(10-bromodecyloxy)-4-methoxybenzene [2]

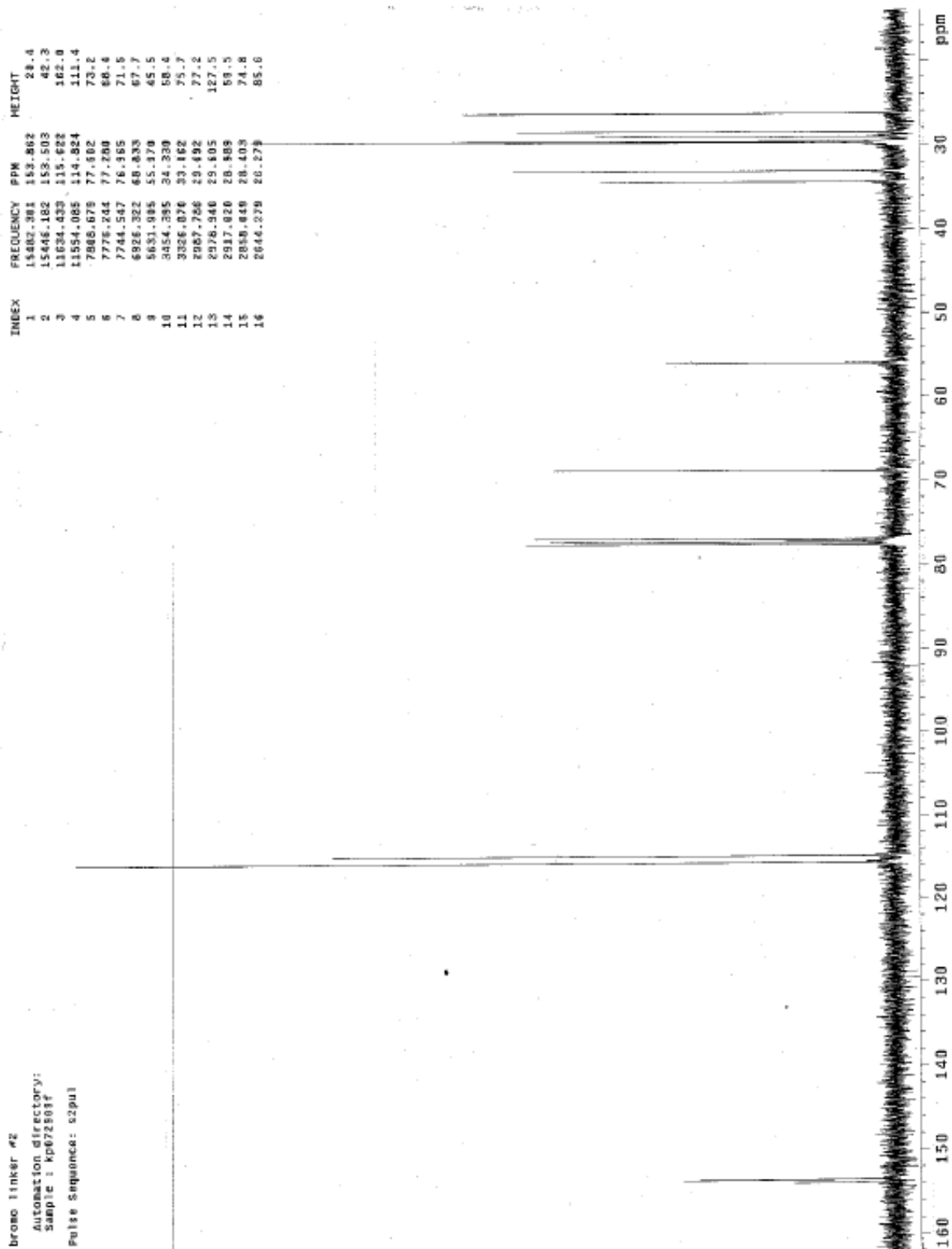


Figure 41 – ^{13}C NMR Spectrum of 1-(10-bromodecyloxy)-4-methoxybenzene [2]

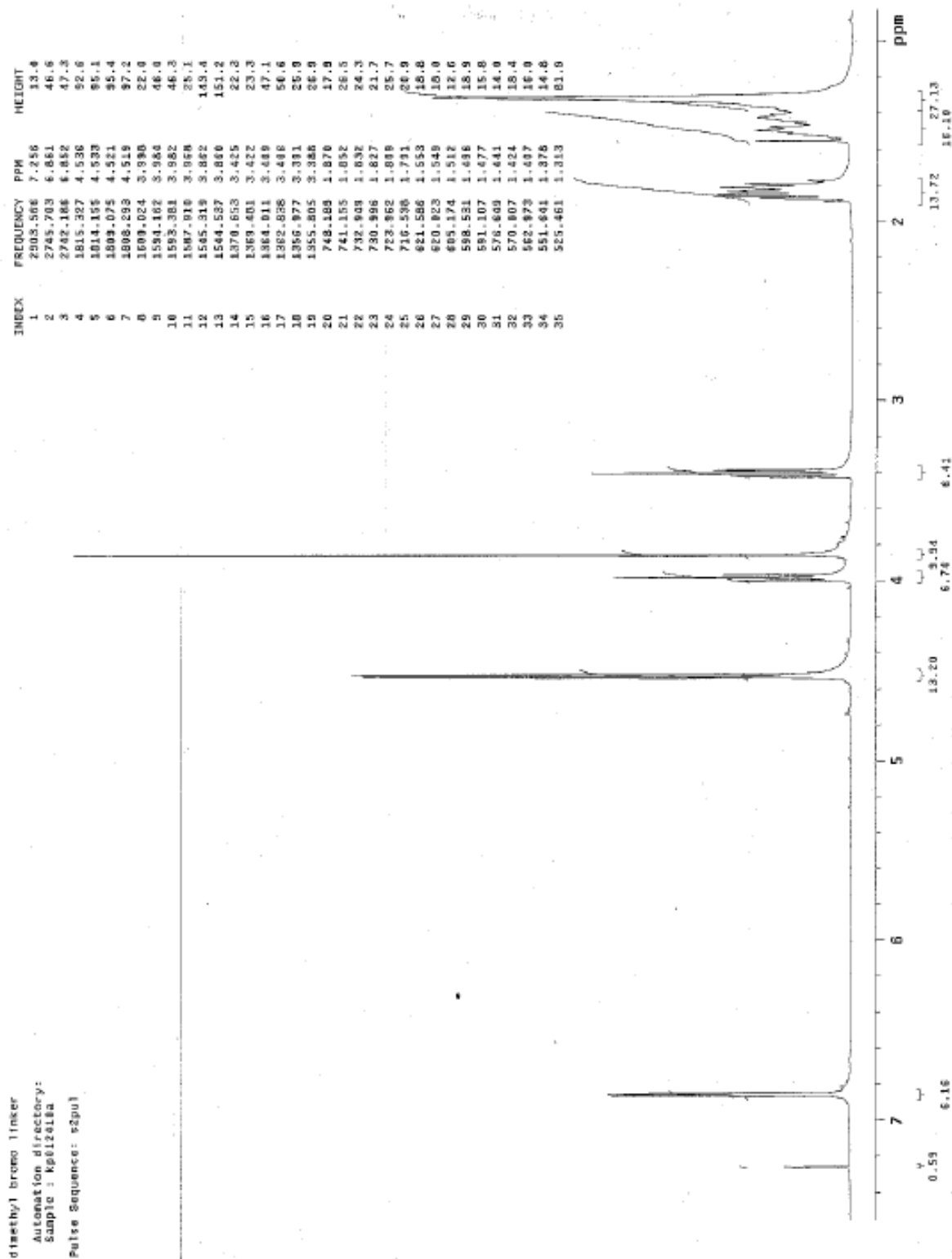


Figure 42 – ^1H NMR Spectrum of 1-(10-bromodecyloxy)-2,5-bis(bromomethyl)-4-methoxybenzene [3]

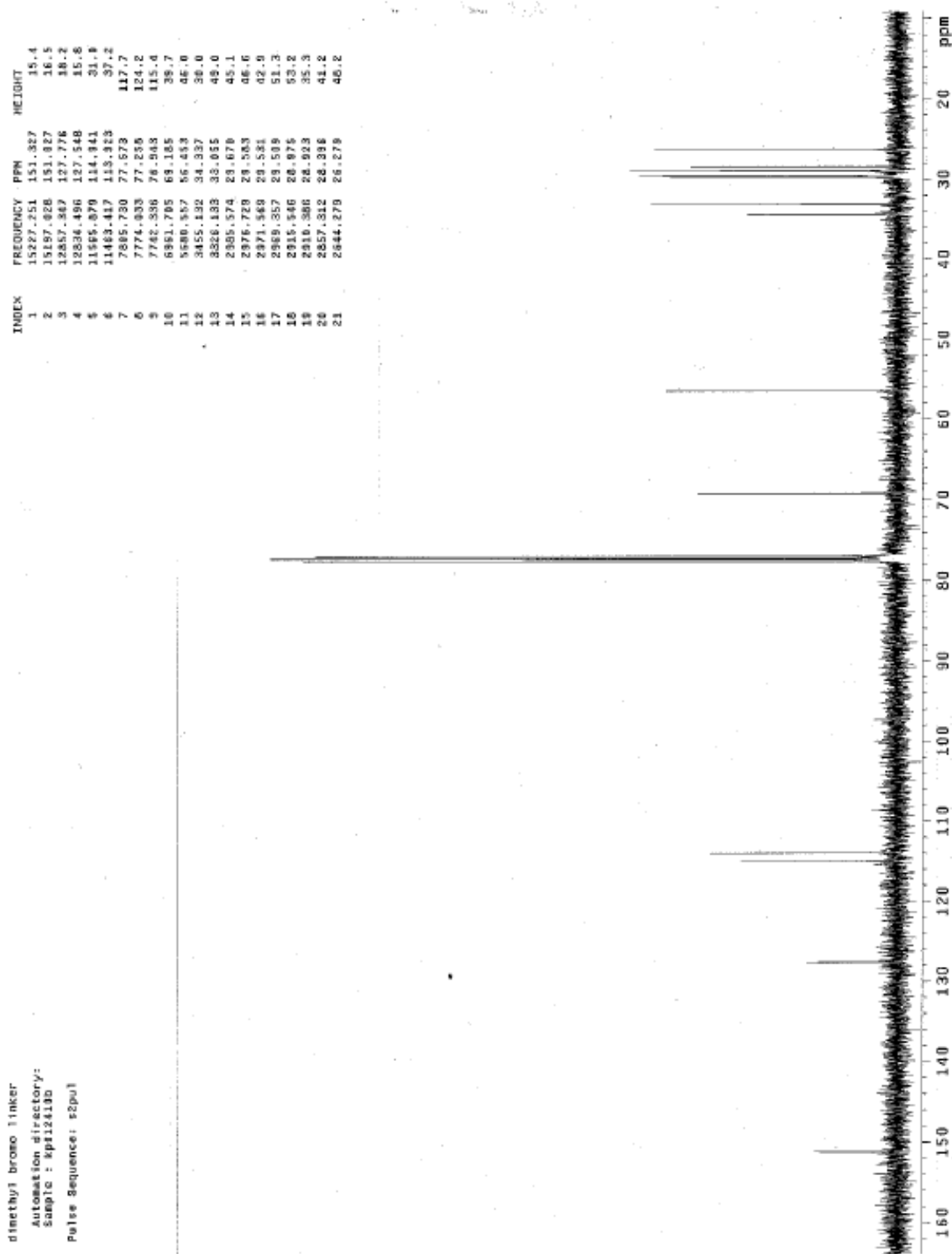


Figure 43 – ^{13}C NMR Spectrum of 1-(10-bromodecyloxy)-2,5-bis(bromomethyl)-4-methoxybenzene [3]

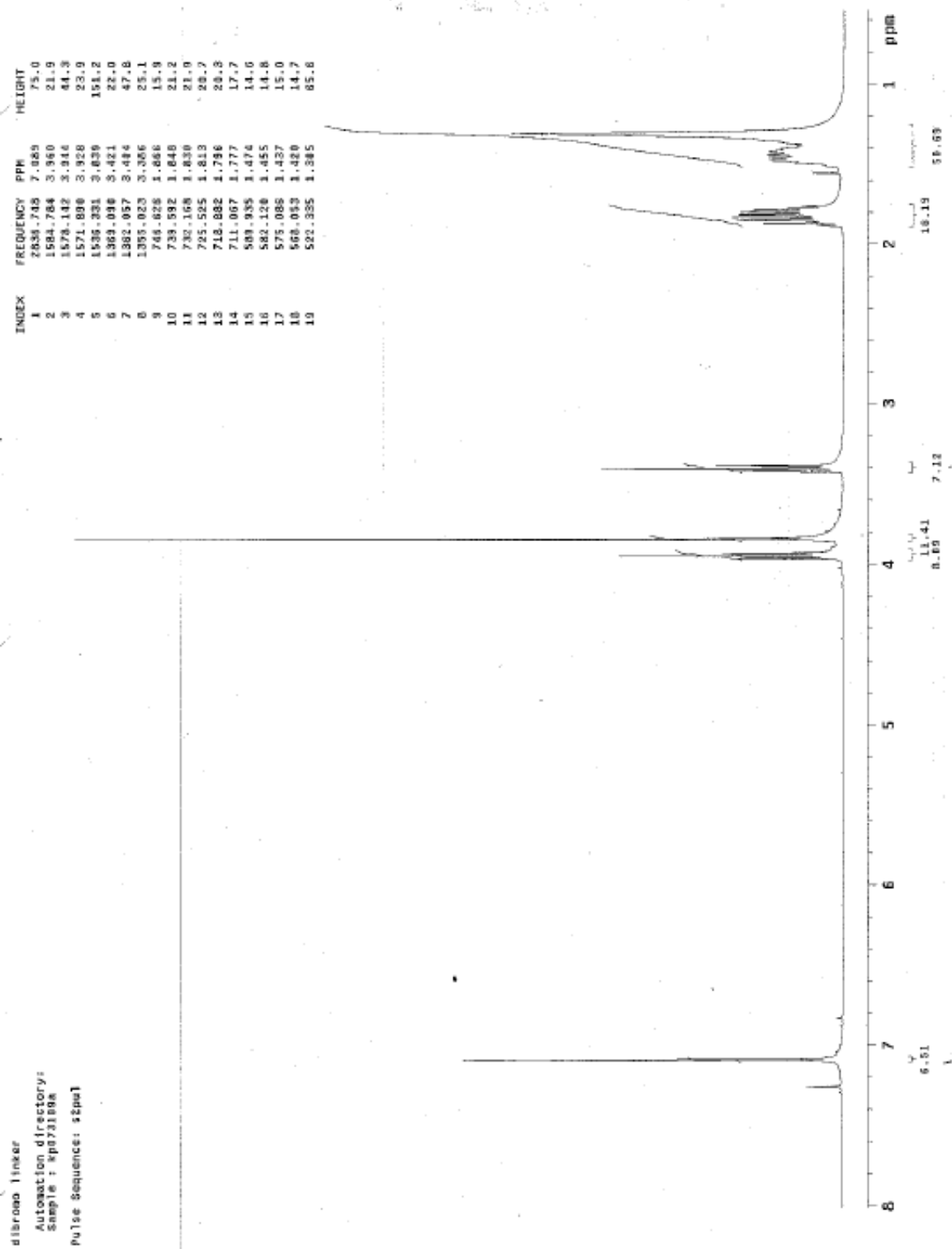


Figure 44 – ^1H NMR Spectrum of 1,4-dibromo-2-(10-bromodecyloxy)-5-methoxybenzene [6]

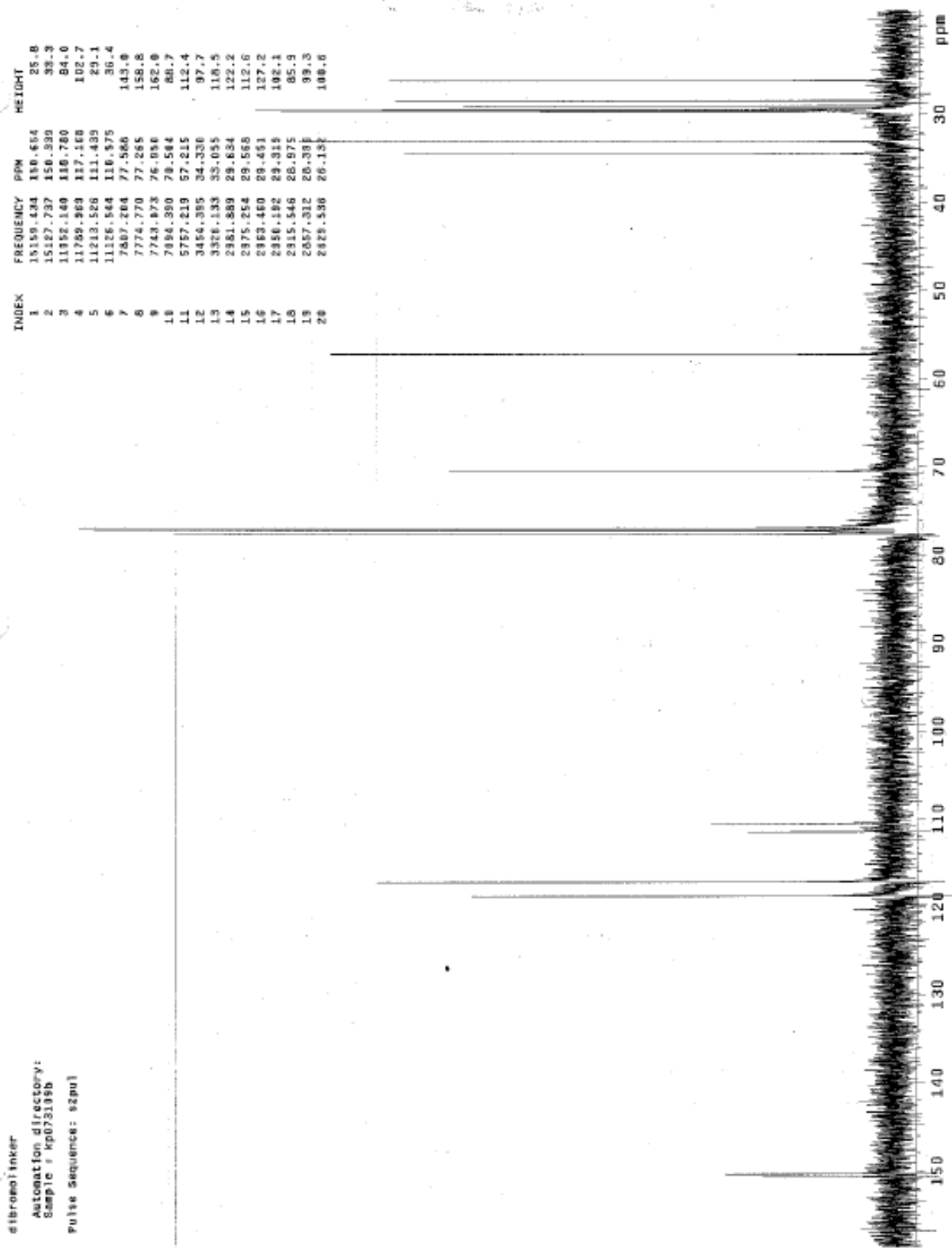
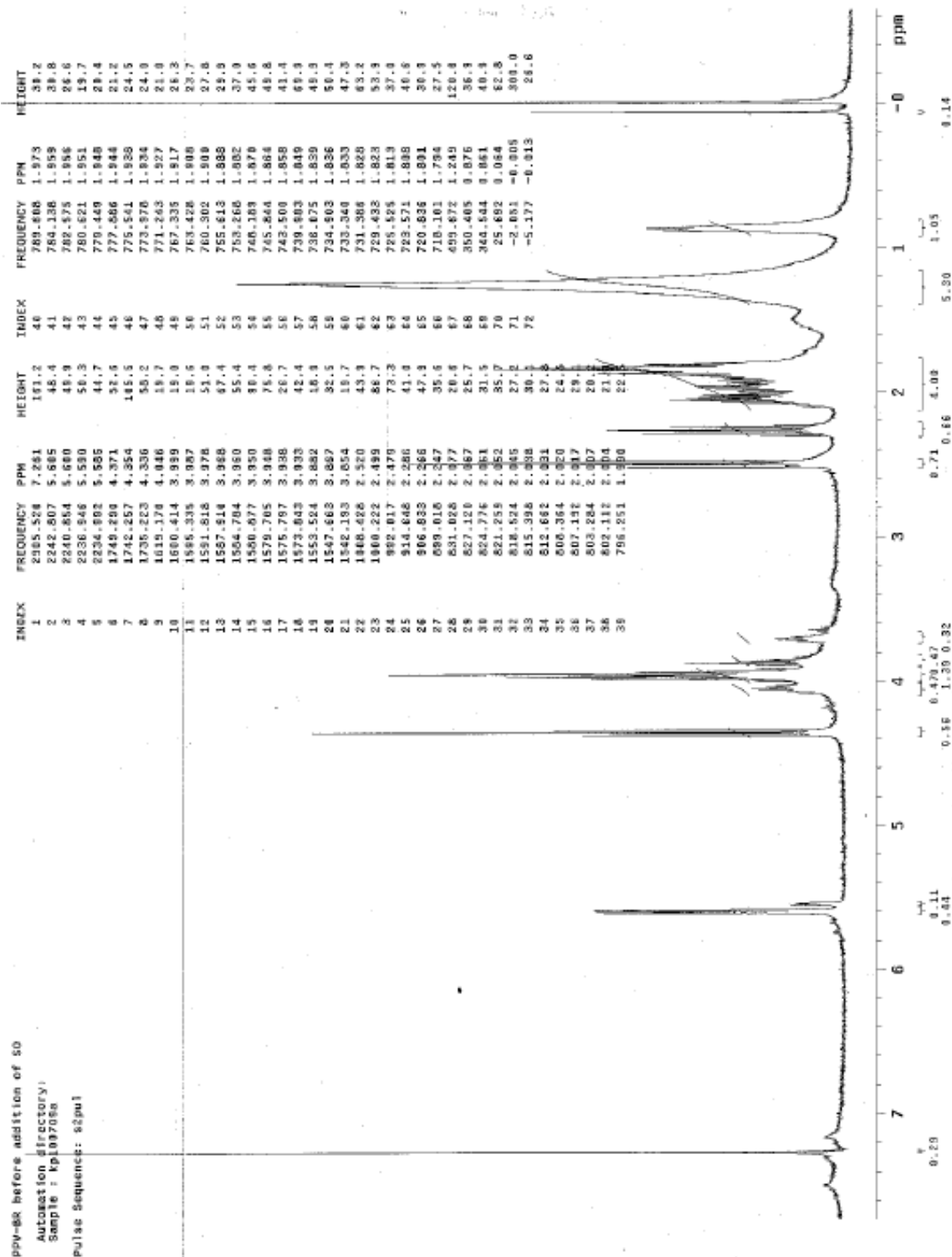


Figure 45 – ^{13}C NMR Spectrum of 1,4-dibromo-2-(10-bromodecyloxy)-5-methoxybenzene [6]

Figure 46 – ^1H NMR Spectrum of Polymer B

25K 80-PPV
 Automation directory:
 Sample : kp102909a
 Pulse Sequence: szpu1

INDEX	FREQUENCY PPM	HEIGHT
1	2984.738	7.259
2	689.618	1.873
3	499.281	1.248
4	441.450	1.193
5	344.544	0.851
6	29.539	0.874
7	28.053	0.855
8	27.388	0.856
9	1.485	0.804
10	-1.551	-0.804
11	-4.787	-0.812

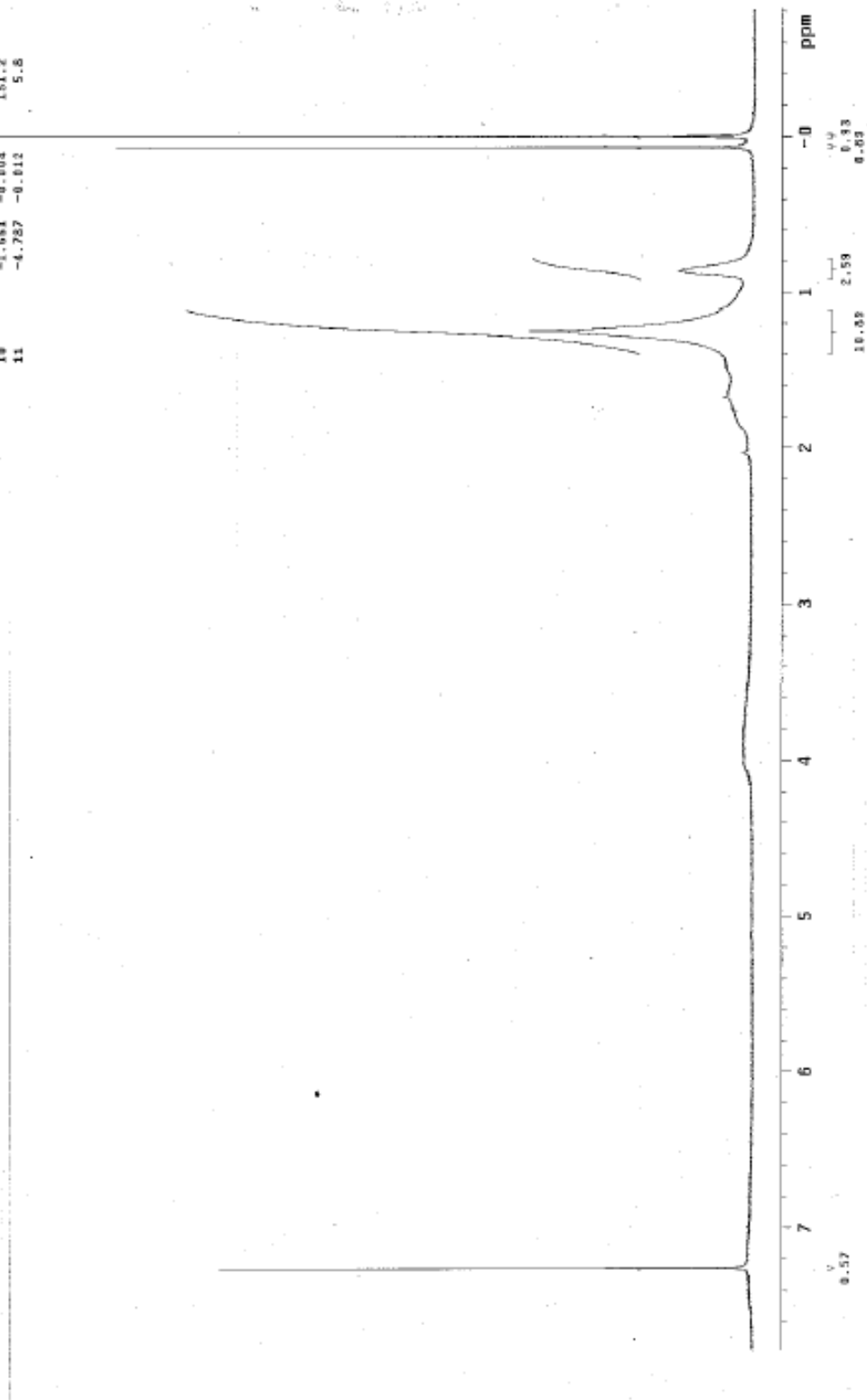
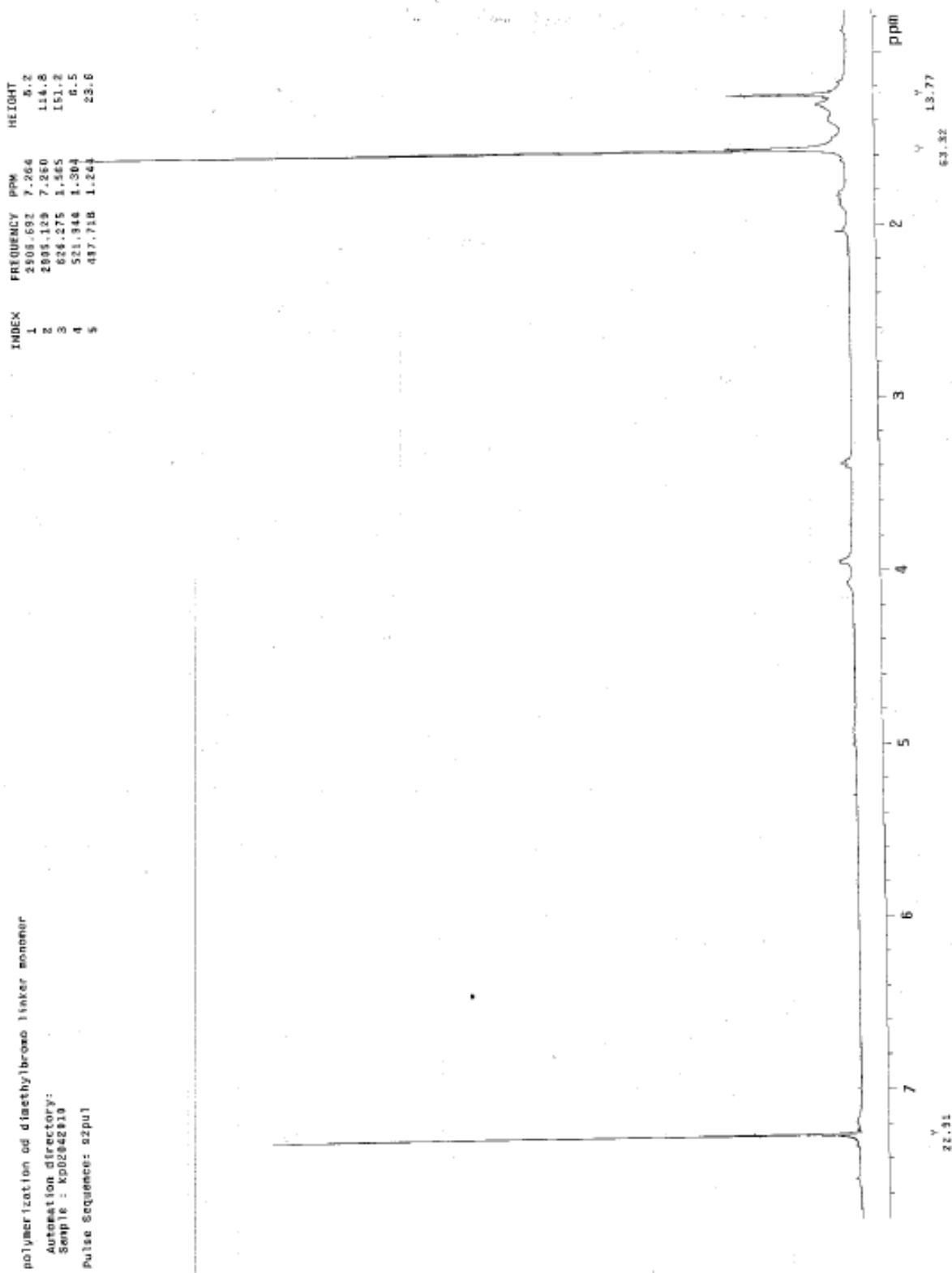
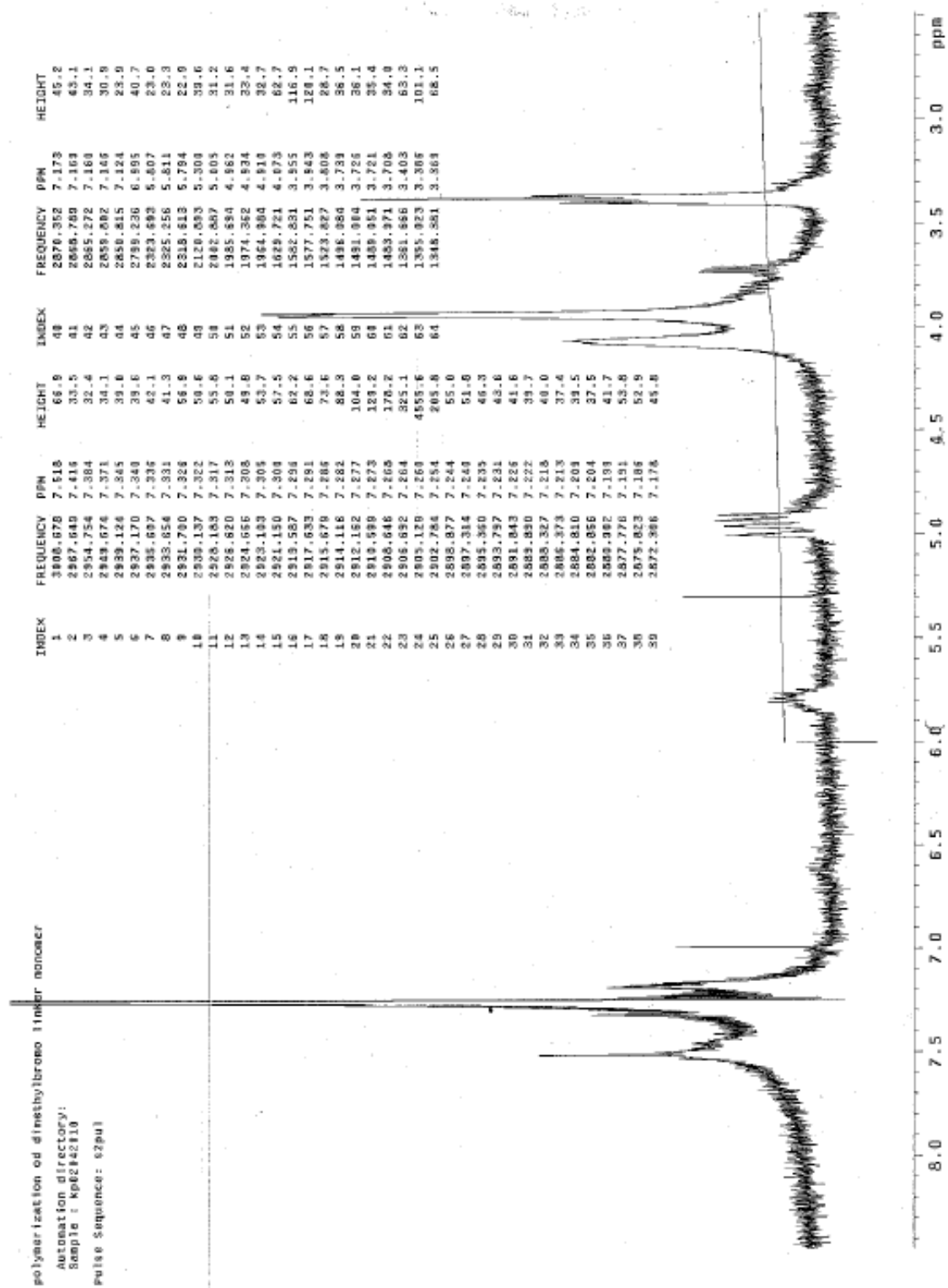
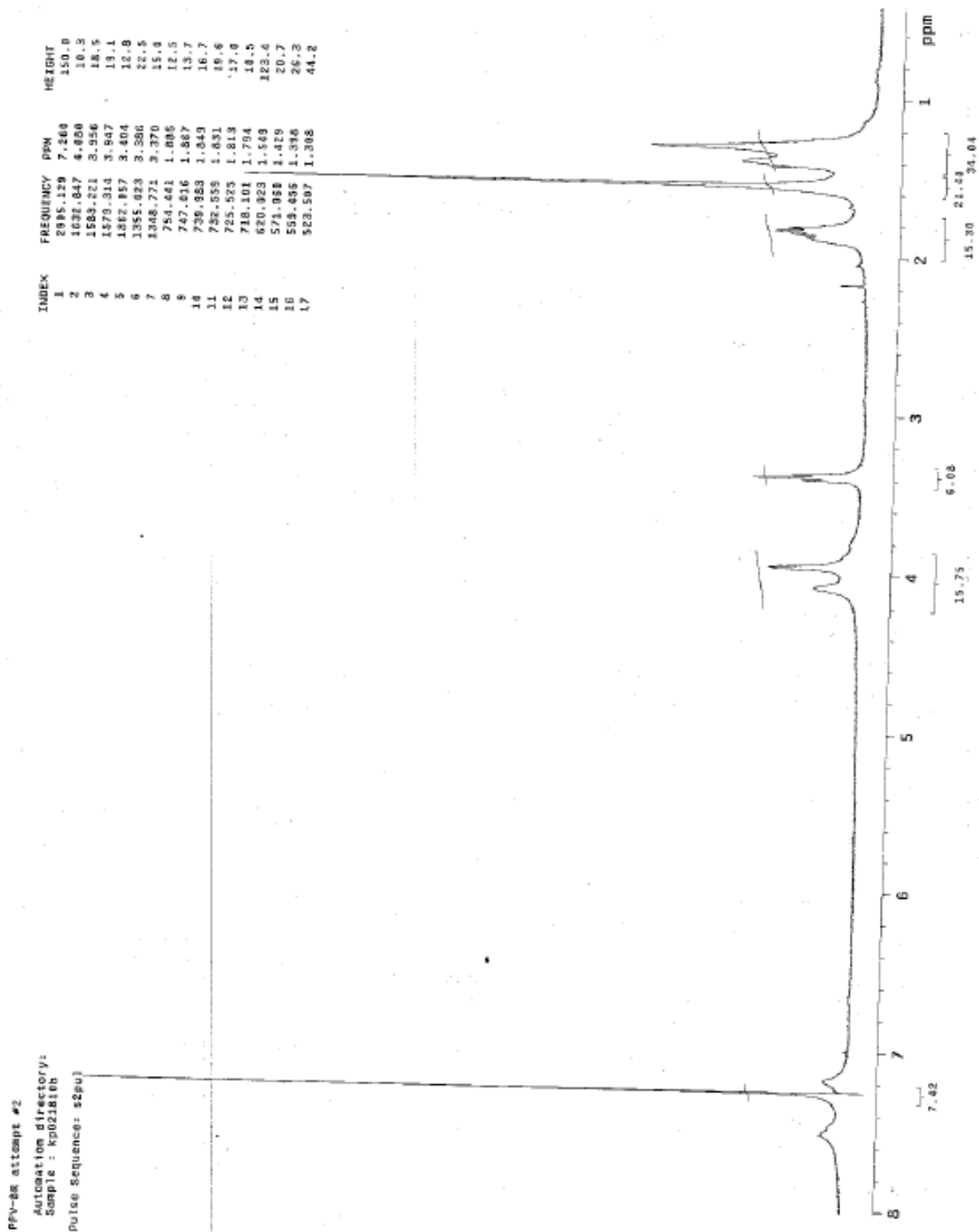
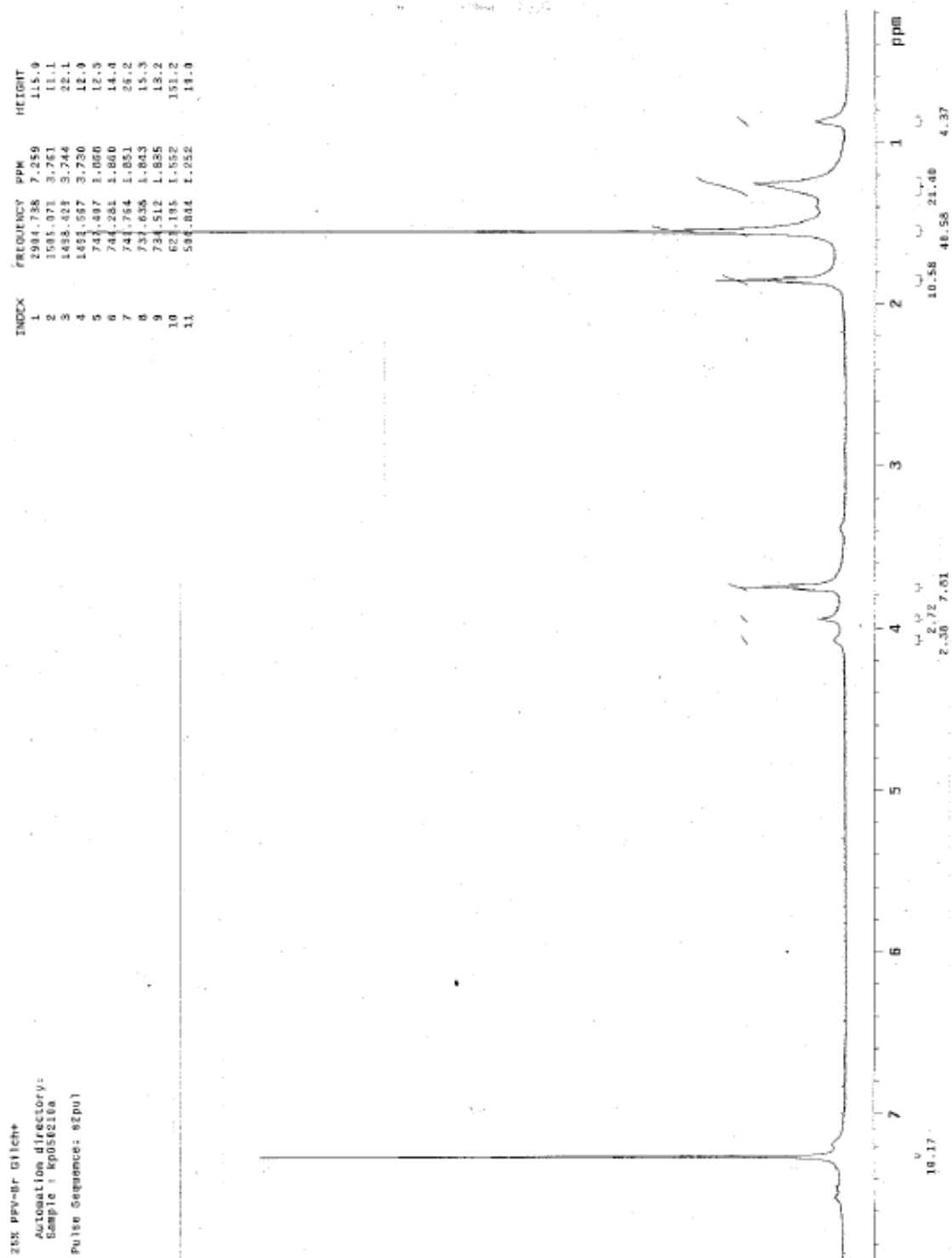


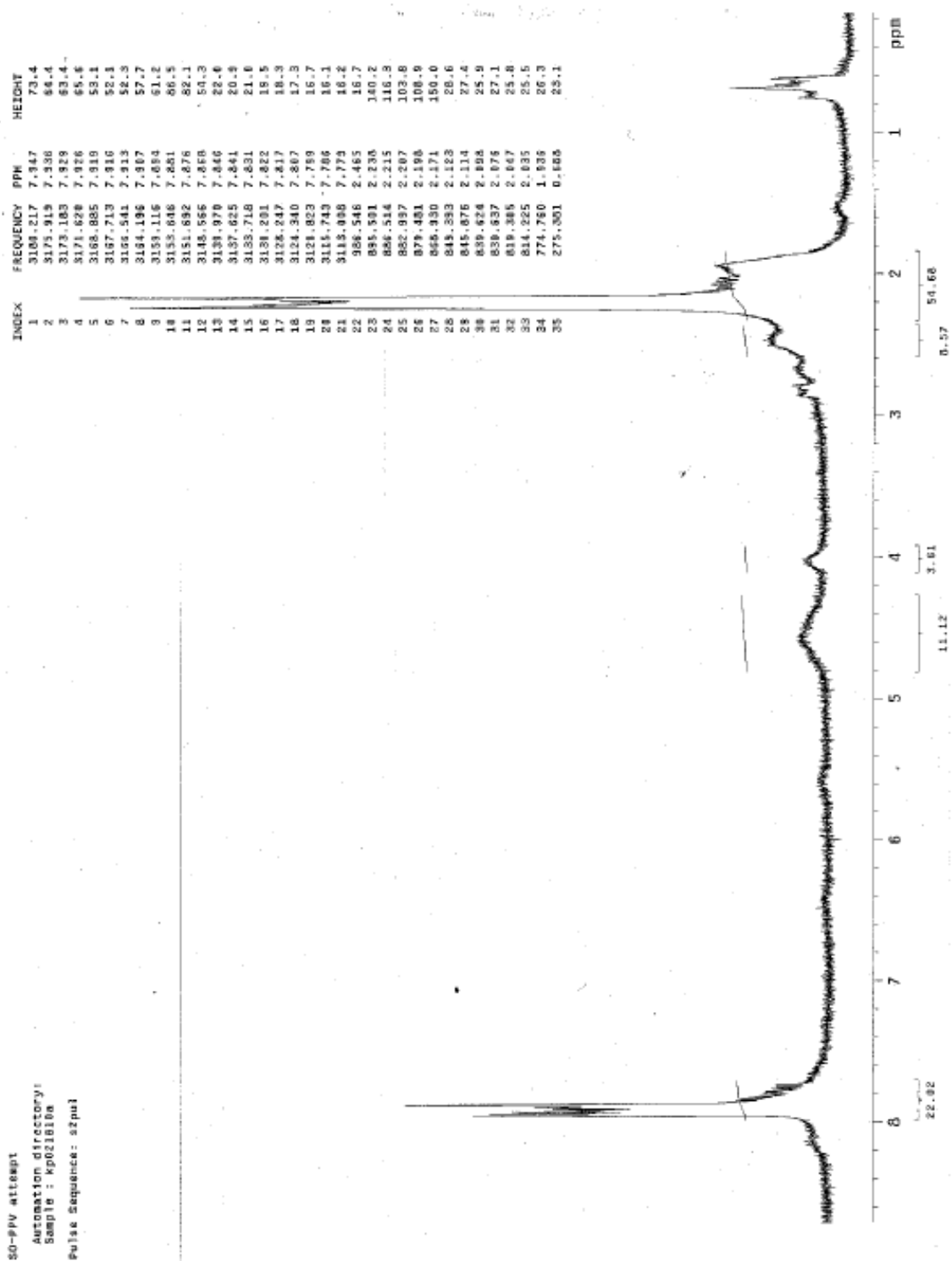
Figure 47 – ¹H NMR Spectrum of Polymer C

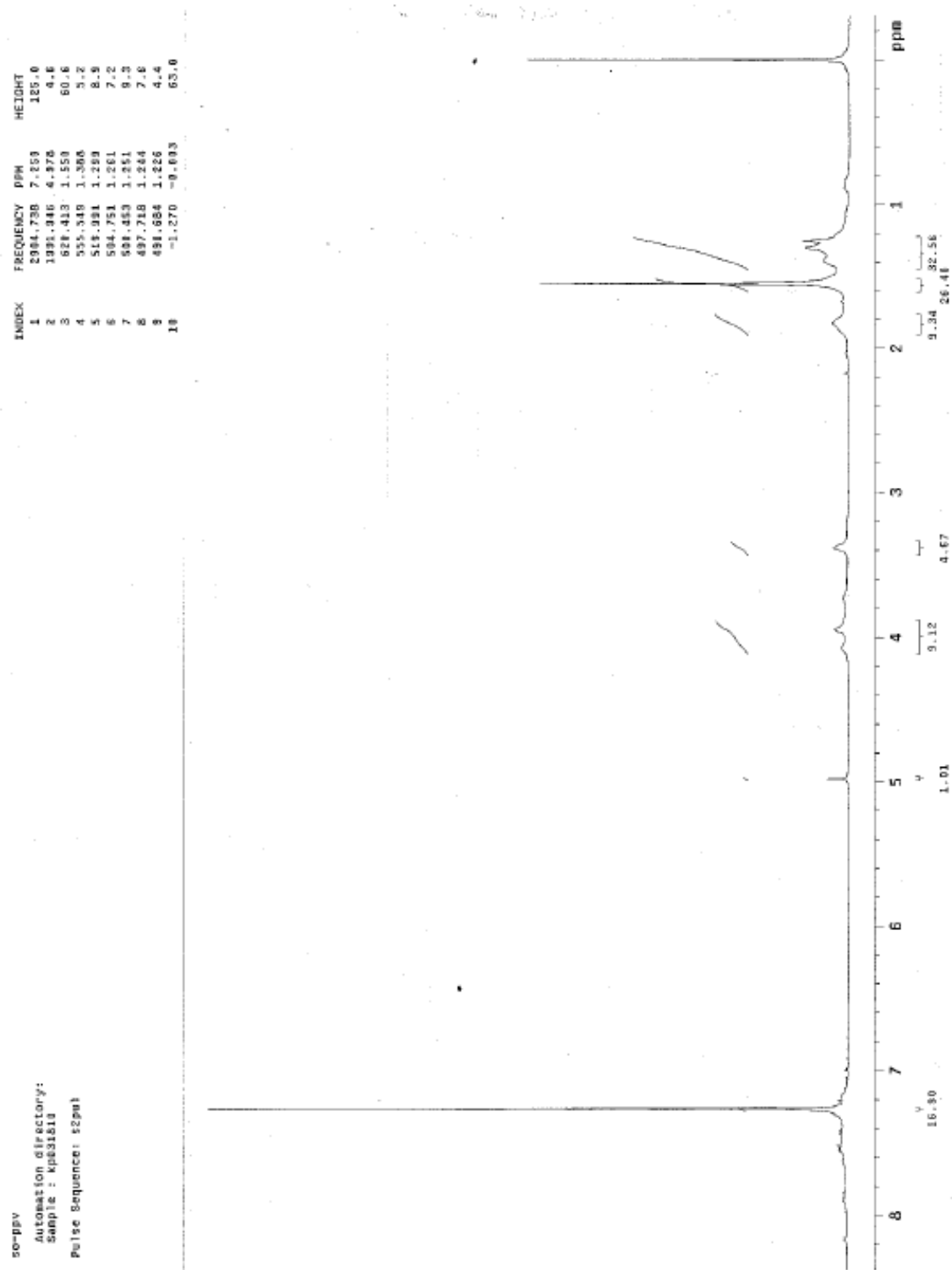
Figure 48 – ^1H NMR Spectrum of Polymer A with Elimination Byproduct

Figure 49 – ^1H NMR Spectrum of Polymer A with Elimination Byproduct: 3.0 – 8.0 ppm

Figure 50 – ^1H NMR Spectrum of Polymer A

Figure 51 – ^1H NMR Spectrum of Polymer D

Figure 52 – ^1H NMR Spectrum of Polymer E

Figure 53 – ^1H NMR Spectrum of Polymer F

INDEX	FREQUENCY	PPM	HEIGHT
1	1691.946	4.878	189.4
2	1624.711	4.873	41.3
3	1578.532	3.845	75.6
4	1693.693	3.730	32.8
5	1691.094	3.726	33.1
6	1353.488	3.282	80.5

50-ppv
Automation directory:
Sample : kp03b10
Pulse Sequence: s2pul

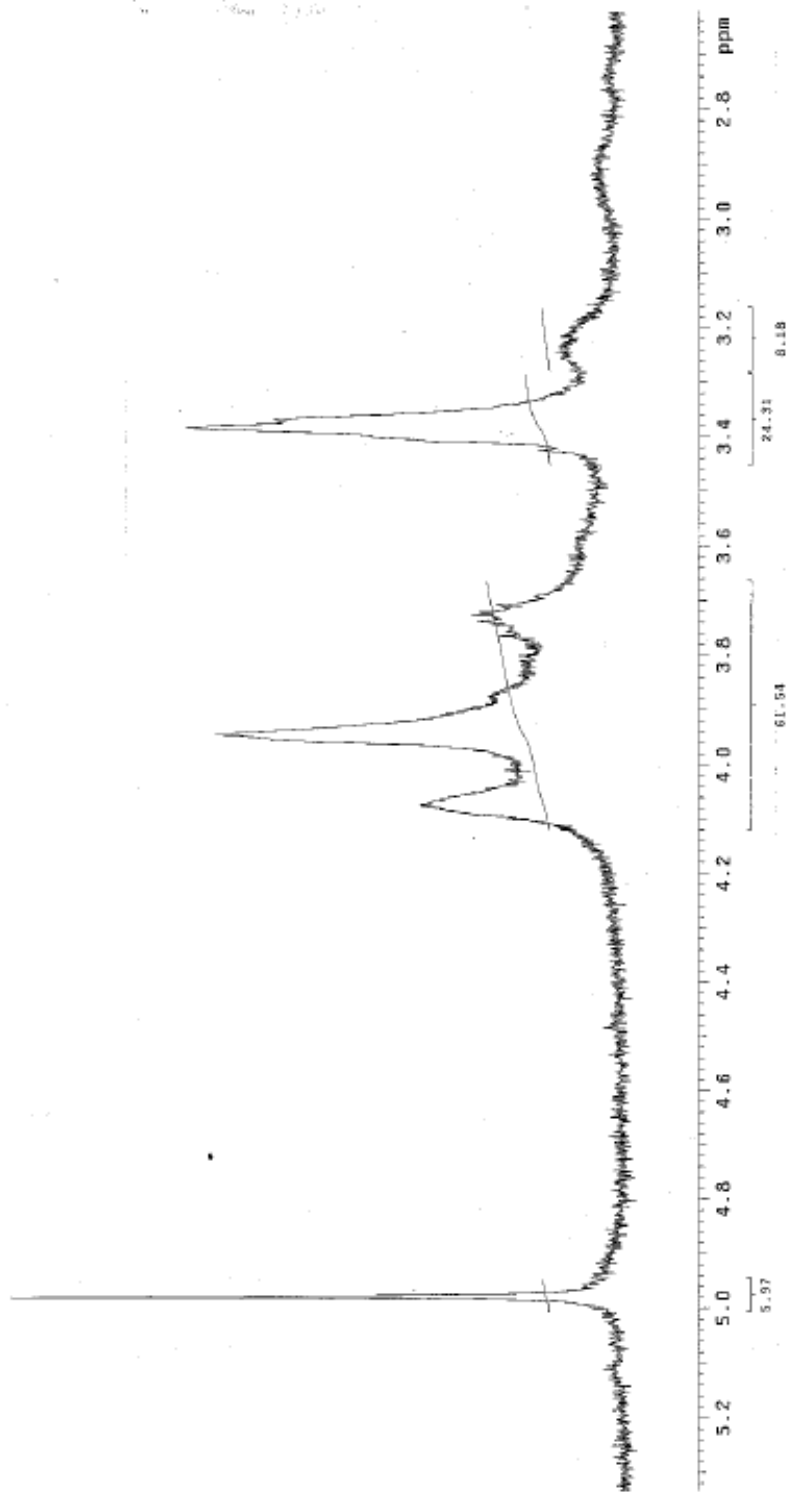
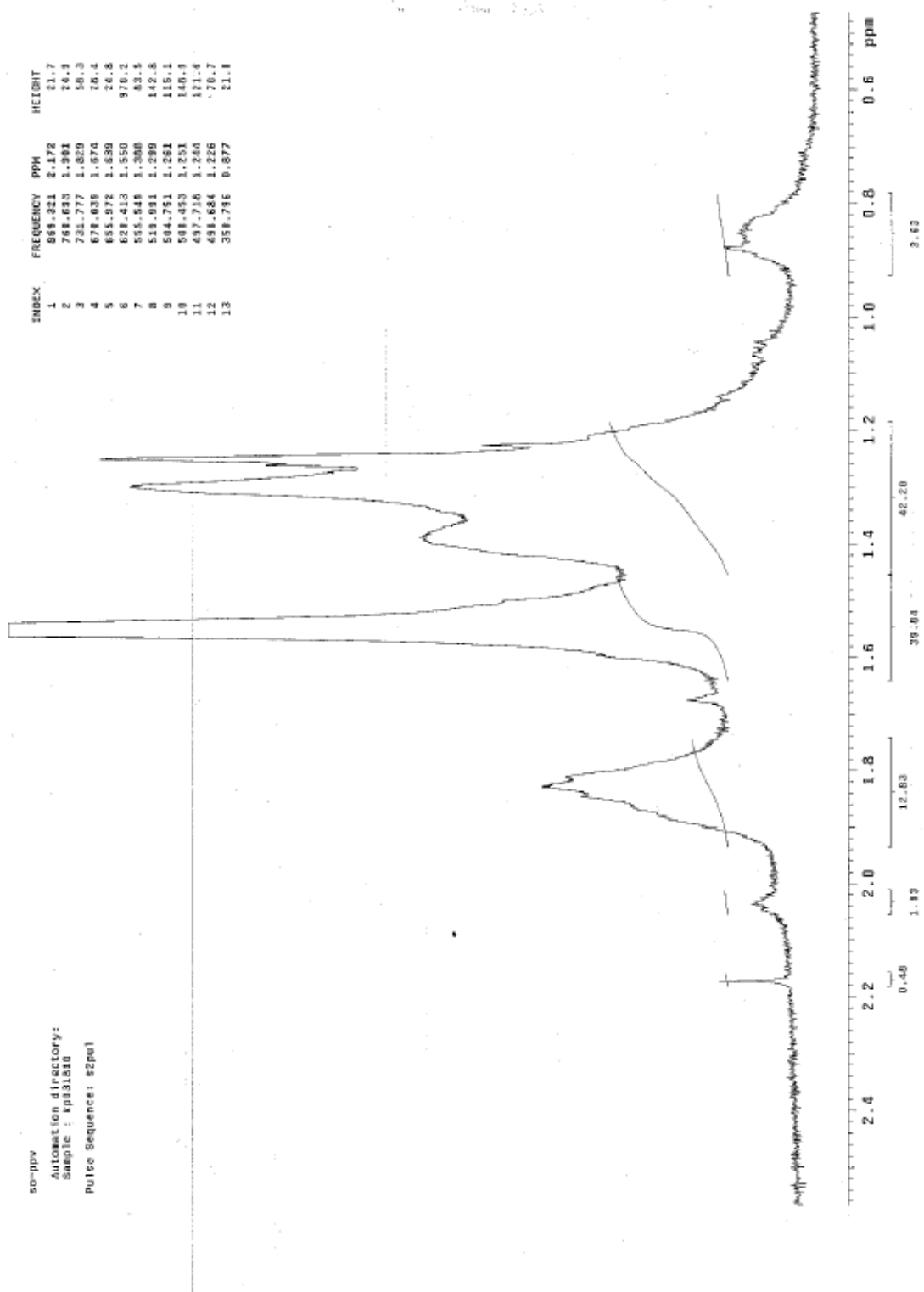


Figure 54 - ^1H NMR Spectrum of Polymer **F**: 2.8 – 5.2 ppm

Figure 55 - ^1H NMR Spectrum of Polymer **F**: 0.6 – 2.4 ppm

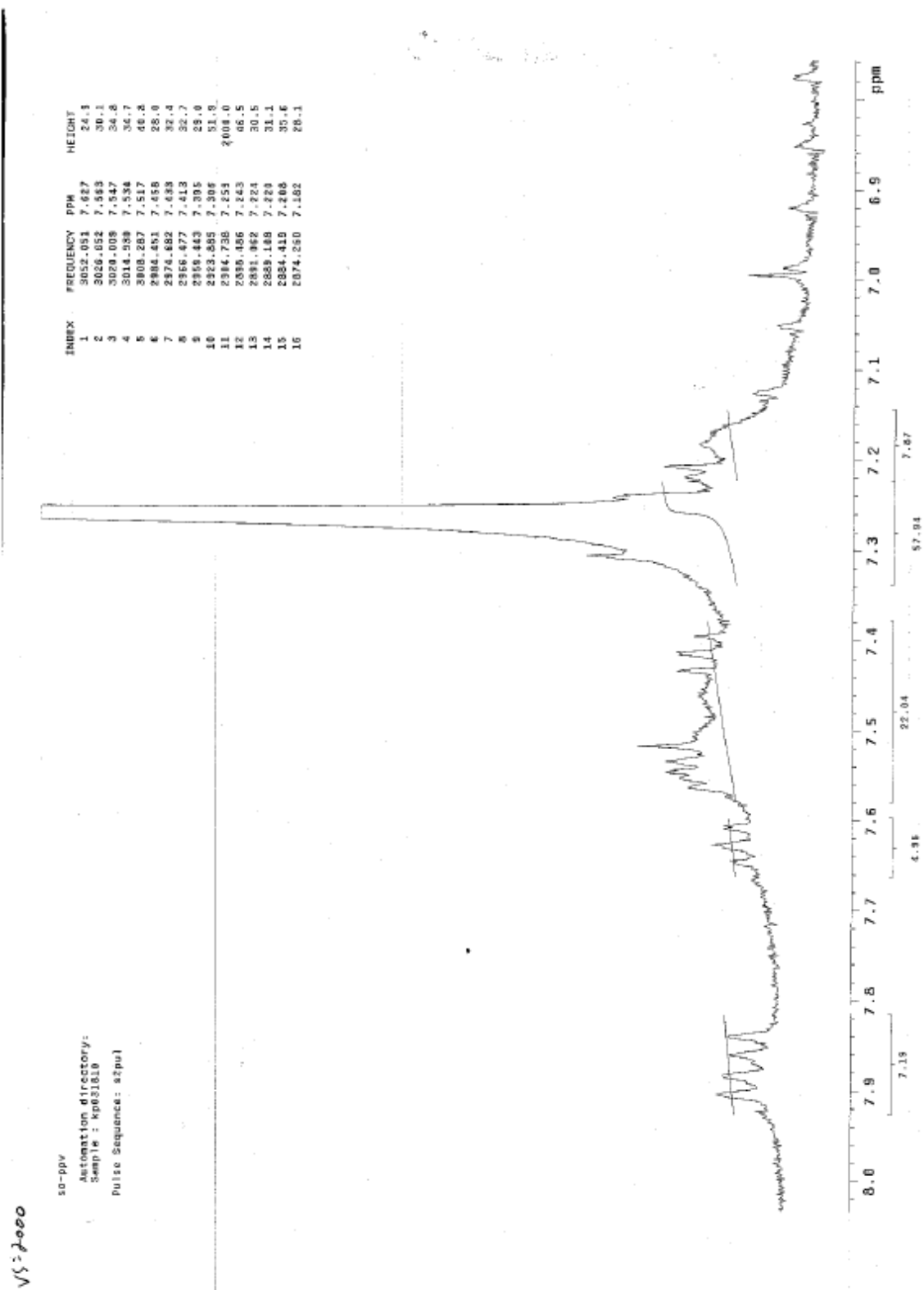


Figure 56 - ^1H NMR Spectrum of Polymer F: 6.8 – 8.0 ppm