Appendix for

"Summary of Research"

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Principle Investigator: Sam Sun, Ph.D.

Associate Professor of Chemistry

Center for Materials Research and Chemistry Department

Norfolk State University

700 Park Avenue

Norfolk, Virginia 23504

Tel: 757-823-2993; Fax: 757-823-9054

Email: ssun@nsu.edu

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1. SYNTHESIS AND CHARACTERIZATION OF SF-PPV-I

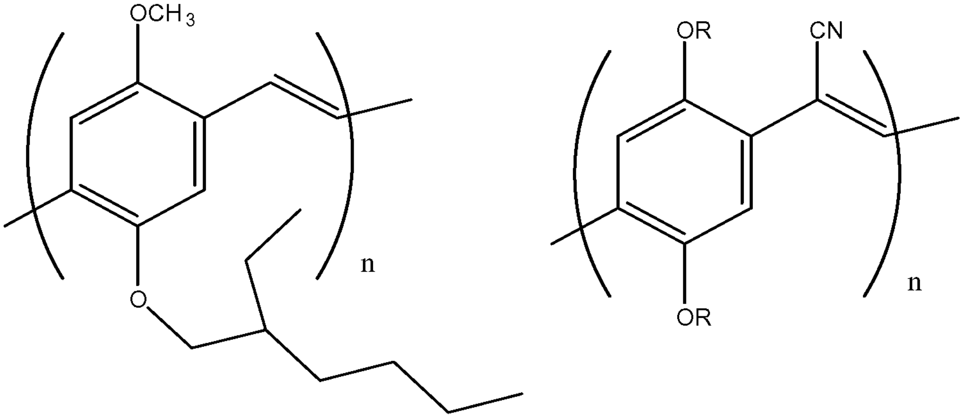
1.1 Introduction

1.1.1 PPV and its derivatives [1]

There are many different kinds of conjugated polymers that may be useful in photovoltaic devices. So far, the most popular and successful conjugated polymers used in photovoltaic devices include poly(1,4-)phenylenevinylenes (PPV), C60 and their derivatives. The discovery of electro-luminescence in PPV has stimulated a great deal of interest in developing "plastic" solid-state semiconductor devices.

The overall synthetic methodology for the preparation of PPV can be divided into three main categories: (1) side chain derivatization, (2) precursor approach, and (3) in-situ polymerization. In this project, the first method was adopted [2-7].

As discussed in project proposal and literatures, the overall efficiency of photovoltaic devices containing conjugated polymers is determined by the materials ability to generate excitons from incoming radiation, and then to separate the charges at donor/acceptor interfaces, and then to transport charges to respective electrodes. Given that effective exciton diffusion range are typical less then 30 nm [1], unique morphological structures are needed. This need led to several research groups to the idea that interpenetrating or bi-continuous networks of donor (electron donating) and acceptor (electron withdrawing) polymers should give better results. One approach involved the use of functionalized PPV. The attachment of electron withdrawing cyano groups to a PPV forms the CN–PPV (Figure 1.1), making it a strong electron acceptor. Underivatized PPV is a generally considered a hole-transporting material. Using blends of MEH–PPV, a soluble donor PPV derivative, as a hole transporter and CN–PPV as an electron transporter, a quantum efficiencies of up to 6% was achieved [8].



MEH-PPV

CN-PPV

Figure 1.1. MEH-PPV and CN-PPV

More recently [8], higher quantum efficiencies (up to 29%) with overall power conversion of ~2% (using a simulated solar spectrum) were obtained using a modified soluble polythiophene as the donor and a CN-PPV as electron acceptor. Perylene is another electron acceptor that increases the quantum efficiency to 6% [9]. An alternative approach uses C_{60} as the electron acceptor [10], giving a quantum efficiency of ~29% and an energy conversion efficiency of 2.9%. However, in a blend D/A system, the charge separation and mobility is limited by poor phase morphology. A block copolymer system containing both donor and acceptor blocks are expected to solve the poor morphology problems as described in the project proposal.

There are a variety of synthetic methods to build the –DBA- type of block copolymer, where D is the conjugated donor block, B is a short non-conjugated bridge, A is the conjugated acceptor block bearing electron withdrawing groups. Several choices of different conjugated polymers could be used for building such a copolymer. In this research project, the donor will adopt a structure similar to MEH-PPV and acceptor will have a sulfone group, which is a well-known electron-withdrawing group.

1.1.2 Existing Conjugated Acceptor Systems

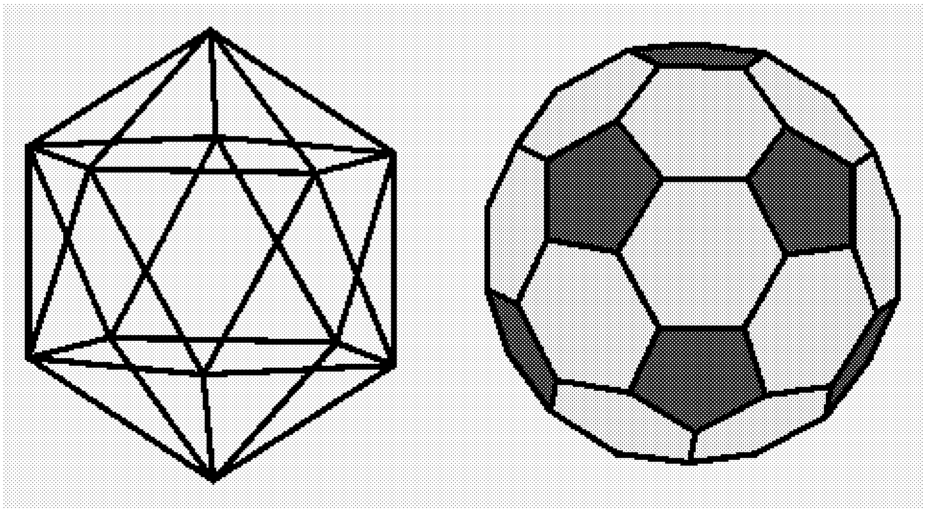


Figure 1.2 C_{60} buckyball

CN-PPV and fullerenes C_{60} are two commonly used conjugated acceptor polymers. In 1996, the Nobel Prize in Chemistry was awarded to the co-discoverers of C_{60}, Richard Smalley, Robert Curl and Harry Kroto (Figure 1.2)[11]. C_{60} potentially could be used as superconductor, HIV protease inhibitor, carbon nanotubes or nanowire as well as an acceptor in the photovoltaic application. The chemical stability, electron transfer ability of fullerenes are better than most existing organic acceptors, but it is also very expensive due to the difficult synthesis and purification process. By using the apparatus shown in Figure 1.3, a mixture of C_{60} and C_{70} are obtained. Chromatographic separation has to be used to purify the C_{60}.

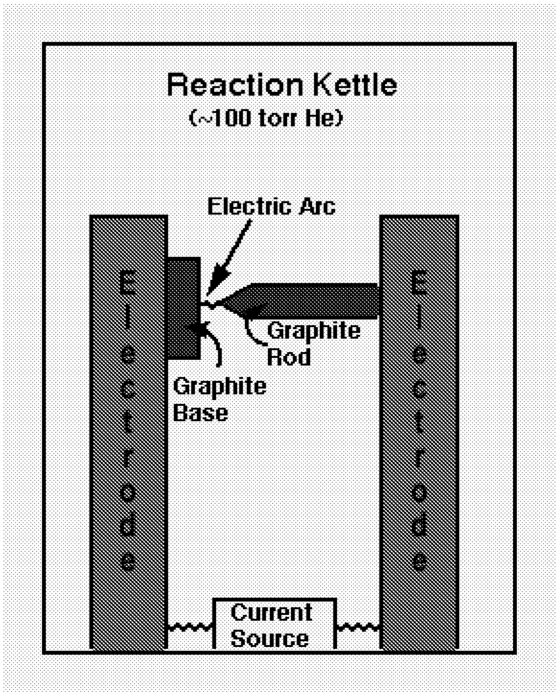
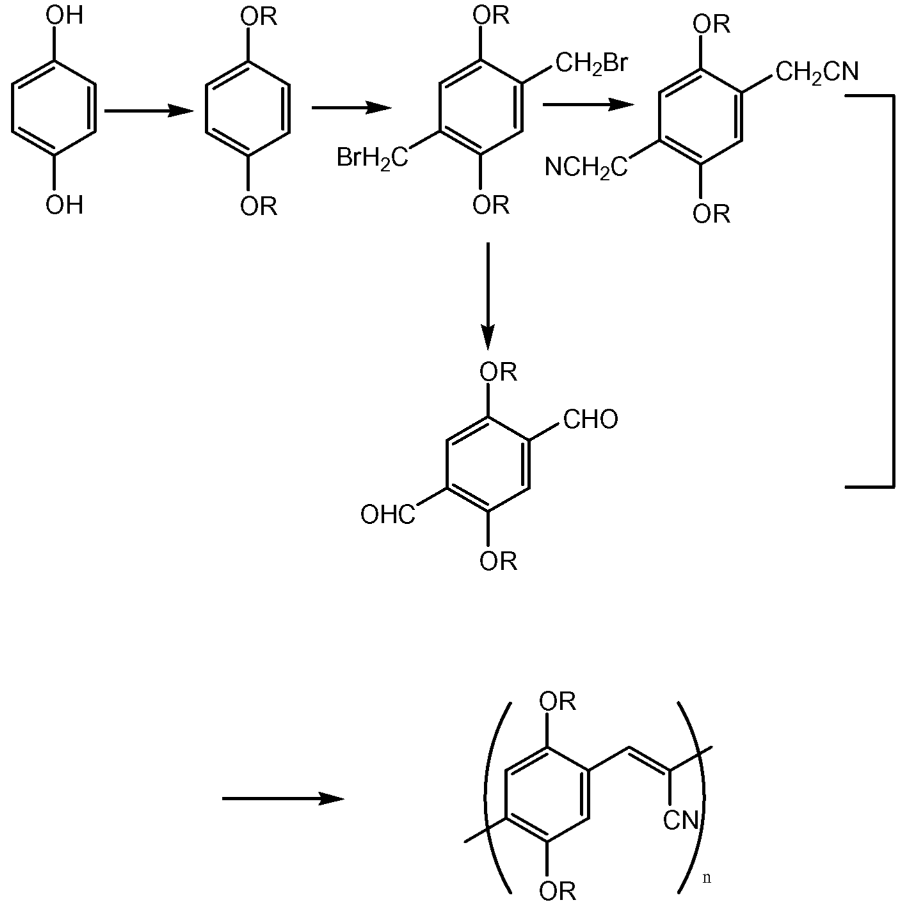


Figure 1.3 Apparatus used to generate C_{60}

In the last decade, many C60-based donor-acceptor dyads have been synthesized and characterized [12-14]. However, only a few examples have been reported in which conjugated oligomers or polymers are covalently attached to C_{60} due to the synthetic difficulties [15-20].

Another commonly used organic conjugated polymer acceptor is CN-PPV (Figure 1.1). The cyano group is an electron-withdrawing group, when it is introduced to the PPV conjugated structure; the resulting polymer becomes an electron-acceptor or n-type. CN-PPV can be synthesized [21-23] by the following scheme:

Scheme 1.1 Synthetic scheme of CN-PPV

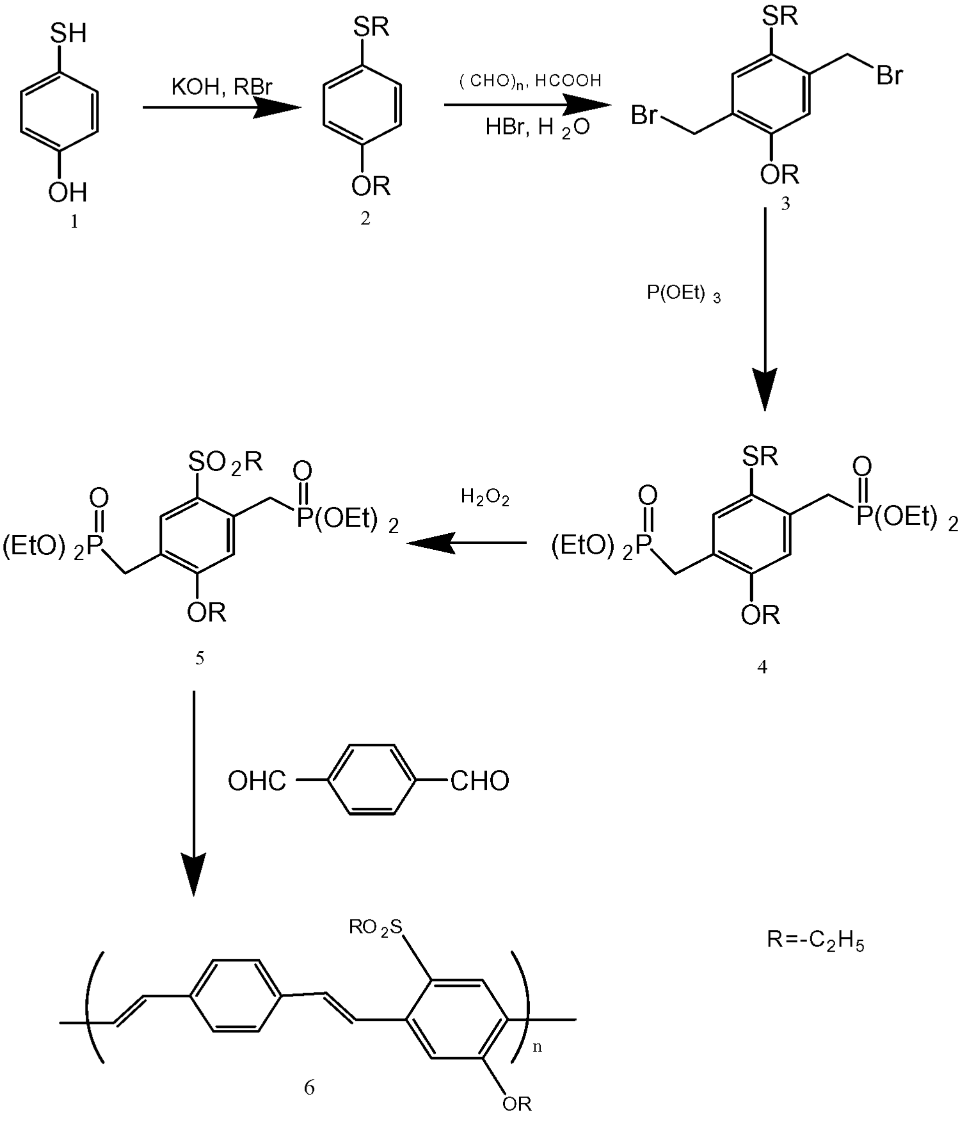


1.1.3 The Advantages of SF-PPV

The electron withdrawing strength of sulfone group is comparable or better to cyno group and the second binding site is useful to attach solubilizing side chains [34]. Compared with fullerene buckyball, the processing advantages of SF-PPV are obvious. By the following synthetic scheme, di-functional ending group containing SF-PPV could be easily coupled with electron-donating non-conjugated bridge or polymers, which is the goal of this project.

1.2 Material Design

Scheme 1.2 Synthetic Scheme of SF-PPV-I



6. SF-PPV-I

Scheme 1.2 shows the synthesis of **6** (SF-PPV-I) with either di-aldehyde or di-phosphate ended functional PPV blocks. Similar synthetic approaches have been used in synthesizing alkyloxy derivatized donor type PPV oligomers and polymers[24]. One advantage of this synthetic scheme is that the synthesized **6** is functional at both ends, and therefore can be further reacted to form block copolymer supramolecular structure.[25-31] In our scheme, 4-mercaptophenol **1** was derivatized first (via Willamson ether coupling) with RO and SR side chains (In our experiments, R is an alkyl units with 2, 8 and 10 carbons) in order to investigate reactivity, process ability and other properties of the materials. Compound **3** was synthesized using a modified dibromomethylation reaction. [32] In this step, compounds with C_2H_5 chains appear having the best reactivity, best yield, and easiest purification, yet the solubility of final PPV blocks were not as good as the C_8H_{17} or $C_{10}H_{21}$ derivatized ones. For instance, the dibromomthylation reaction of **2** with C_2H_5 substituted ones is typically completed in two days, that was in contrast to at least a week for the C_8H_{17} or $C_{10}H_{21}$ ones. This is possibly due to the bulky groups of the C_8H_{17} or $C_{10}H_{21}$, which may have, hinder the dibromomethylation reaction sites nearby the RO or SR chains. For the C_2H_5 substituted compounds, the mono-substituted product is in liquid form and is soluble in formic acid, while the di-substituted product precipitates out of solution as a white solid. The product can be purified conveniently from recrystalization in methanol. For C_8H_{17} or $C_{10}H_{21}$ compounds, chromatography combined with recrystalizations are necessary to purify the product. For the synthesis of **4**, a neat reaction in triphosphite was used. If a solvent is present, the reaction cannot be completed even after 72 hours. A short air-cooled condenser was employed so that the by-product, bromo-ethane can escape from the system. In the last step of monomer **5** synthesis, hydrogen peroxide was used to oxidize the sulfide into sulfone in acetic acid [33]. 4-Mercaptophenol **1** was used as initial material [4]. Through a Williamson ether condensation reaction, side chains were attached to compound **2** to improve the solubility. Compound **2** with different side chains($-C_2H_5$, $-C_4H_7$, $-C_{10}H_{21}$, $-CH_3CH(C_2H_5)C_4H_5$) had been successfully synthesized. However, in step (2), the bromomethylation reaction [5] only succeeded in compounds having the ethyl or decyl side chains. In other cases, mono- and di-substitution products were mixed together, and it was very difficult to separate them. The best result of bromomethylation with compound **2** having 2-ethyl-hexyl side chains showed mono-: di-substitution products was 1:9 based on 1H NMR integration. Compound with ethyl side chains gives the best purity and yield percentage, and the reaction could be completed within one day. In this case, mono-substituted product is liquid, which dissolved in formic acid, but di-substituted product is solid which will precipitated out. By this means, they can be separated. The integration of proton NMR and ^{13}C confirmed that after re-crystallized from methanol, the product is 100% di-substituted. A neat reaction has to be used in step (3). With presence of solvent, the reaction can not be completed even after 72 hours. A short air- cooled condenser was used so that the by-product bromo-ethane can keep escape from the system. The last step [6] of monomer synthesis, hydrogen peroxide oxidized sulfide into sulfone in the acetate acid. Anal, Calcd for (C20H36O9P2S), 514.16. Found: 514.16. The polymer synthesized from the monomer with ethyl side chains can dissolve in THF, DMF, DMSO with a molecular weight up to 2000 (10 benzene ring, 7nm), which is acceptable for making copolymer with alkoxy-PPV in photovoltaic study.

1.3 Experiment Section

All starting materials, reagents and solvents were purchased from commercial sources and used directly except noted otherwise. NMR data were obtained from a Bruker Advance 300 MHz spectrometer with TMS as reference. Elemental Analyses were done at Atlantic Microlab Inc. FT-IR Spectra were collected on a Nicolet Avatar FT-IR or a Bruker IFS66 FT-IR spectrophotometer using 16 scans for each spectrum with background correction. Perkin-Elmer TMA-7/DSC-6/TGA-6 systems were used to characterize the thermal properties of the materials. Molecular weight analysis of polymers was done using a Viscotek T60A/LR40 triple-detector GPC system with mobile phase of THF at ambient temperature (Universal Calibration method is used). UV-VIS-

NIR spectra were collected using a Varian Gary-5 spectrophotometer. Cyclic-Voltammetry was measured by Epsilon-100W CV meter. Luminescence spectra were obtained from an ISA Fluro-max-3 fluorometer. High resolution MASS/MALDI data were obtained from Emory University mass spectroscopy facility.

1.3.1 Synthesis of monomer

1.3.1.1 Monomer with $-C_2H_5$ side chains

Compound (2): 1-Ethoxy-4-ethylsulfanyl-benzene

10g (0.08mol) of 4–Mercaptophenol **1** was mixed with 30g (excess) KOH in 240 ml CH_3CN and 100ml distillated water. After 10 minutes stirring, an ice bath was used to cool the reaction solution to 0°C, then 30ml 2- Ethylene Bromide (excess) was added slowly. The reaction was kept in the original ice bath without adding new ice, and temperature slowly went up until it reached room temperature. Reaction proceeded till TLC test (Hexane:EA=1:1) showed only one spot left(about 24 hours). After the reaction was stopped, the water layer and organic layer separated. Organic layer was collected and directly put onto a rotary evaporator. The residue will have KOH remains, and they can be filtered out. 11.7g light yellow liquid **2** was obtained (yield: 81%). ^{1}H NMR δ: 7.30, (d, 2H, phenyl), 6.85(d, 2H, phenyl), 3.90(m, 2H, $-OCH_2$), 2.95(m, 2H, $-SCH_2$), 1.40(m, 3H, $-CH_3$), 1.2 (m, 2H, $-CH_3$). ^{13}C NMR δ: 14.0, 14.3, 20.0, 63.0, 115.7, 126.5, 132.0,158.2.

Compound (3): 1,4-Bis-bromomethyl-2-ethoxy-5-ethylsulfanyl-benzene

5g (0.0274mol) of **2**, 5g(excess) paraformaldehyde $(CH_2O)n$, 20ml HBr (31%wt in acetic acid), 2ml water, and 150ml formic acid were mixed. The mixture was stirred and heated up to 65°C. A white solid start precipitated out after overnight reaction. Keep the reaction another 24 hours to achieve better yield percent. After the reaction was stopped, the product mixture was poured into water, and the white solid was collected by filtration followed by re-crystallization in methanol twice. 7.11g of **3** were obtained (yield: 71%). Melting point: 130°C. ^{1}H NMR δ: 7.35, (s, 1H, phenyl), 6.95(s, 1H, phenyl), 4.40(s, 2H, - CH_2Br), 4.25(s, 2H, $-CH_2Br$), 3.90(m, 2H, $-OCH_2$), 2.95(m, 2H, $-SCH_2$), 1.40(m, 3H, $-CH_3$), 1.2 (m, 2H, $-CH_3$). ^{13}C NMR δ: 14.0, 14.3, 18.2, 20.0, 22.0, 63.0, 113.5, 127.5, 128.0, 135.8, 141.3, 157.0.

Compound (4): [4-(Diethoxy-phosphorylmethyl)-5-ethoxy-2-ethylsulfanyl-benzyl]-phosphonic acid diethyl ester:

7.11g of **3** (0.0195mol) and 3.23g $P(OEt)_3$ (0.0195mol) were mixed together directly without any solvent, and the temperature raised to 120°C. When temperature reached 80°C, 3 started to melt. A short air-cool condenser was used to allow the by-product bromoethane to escape from the system, so the reaction could be completed faster. After 24 hours, liquid product 4 was further purified by high vacuum to remove remaining by-products. 9.48g of **4** were obtained (yield: 100%). ^{1}H NMR δ: 7.35, (s, 1H, phenyl), 6.95(s, 1H, phenyl), 4.10-3.90(m, 10H, -OCH$_2$ -P(O)OCH$_2$-), 3.45(d, 2H, -CH$_2$P-), 3.25(d, 2H, -CH$_2$P-), 2.95(m, 2H, -SCH$_2$-), 1.40-0.95(m, 18H, -CH$_3$). ^{13}C NMR δ: 14.0, 14.3, 18.2, 26.0, 28.1, 30.1, 32.0, 61.2, 63.0, 67.9, 112.9, 120.5, 126.0, 134.8, 136.5, 156.0.

Compound (5): [4-(Diethoxy-phosphorylmethyl)-2-ethanesulfonyl-5-ethoxy-benzyl]-phosphonic acid diethyl ester:

9.48g (0.0195mol) of **4** and 100ml glacial acetic acid was heated up to 116-120°C, then 3g H_2O_2 (30% in water) was added in 4 times (10mins each time). Temperature was maintained and mixture stirred 12 hours. After the reaction was stopped, acetic acid and excess hydrogen peroxide were removed by the rotary evaporator. The remains were further purified by a short column (about 3cm, chloroform was used as solvent) twice to remove small amount of remaining acetic acid. ^{1}H NMR δ: 7.98, (s, 1H, phenyl), 6.95(s, 1H, phenyl), 4.10-3.90(m, 10H, -OCH$_2$ -P(O)OCH$_2$-), 4.0-3.85(m, 2H, -CH$_2$P-), 3.50-3.25(m, 4H, - CH$_2$P-, -SO$_2$CH$_2$-), 1.40-0.95(m, 18H, -CH$_3$). ^{13}C NMR δ: 14.0, 14.3, 18.2, 26.0, 28.1, 30.1, 32.0, 41.7, 61.2, 63.0, 115.9, 120.5, 129.0, 132.8, 134.5, 160.0. HR-MASS, found: MW=514.16; calculated (C20H36O9P2S): MW=514.16

1.3.1.2 Monomer with –C_8H_{17} side chains

1-(2-ethyl-hexyloxy)- 4-(2-ethyl- hexylsulfide) benzene (2):

10g (79mmol) of 4 – Mercaptophenol and 39.3g (285mmol) K_2CO_3 were mixed in 240 ml CH_3CN. After 10 minutes stirring, 55 ml 2- Ethylhexyl Bromide (285mmol) was added. The reaction solution was heated up to 80°C and maintained this temperature for 24 hours. After the reaction was stopped and cooled to room temperature, the product mixture was added with 200 ml chloroform and washed four times with water. The organic phase was dried over $MgSO_4$ and solvent was removed by a rotary evaporator. The residue was further purified by vacuum distillation. 22.5g brown liquid **2** was obtained (yield: 90%). ^{1}H NMR (CDCl$_3$) δ (ppm): 7.80 (d, 2H, phenyl), 7.00 (d, 2H, phenyl), 3.90 (d, 2H, -OCH$_2$), 2.95 (d, 2H, -SCH$_2$), 1.85 (m, 2H, 3°H), 1.40-1.20 (m, 16H, methylene), 0.95 (m, 12H, -CH$_3$).

[2-(2-ethylhexyloxy)-5-(2-ethyl-hexylsulfide)]-1,4-bis-(chloromethyl)-benzene (3):

3.5g (0.01mol) of **2**, 1.54g (0.05mol) paraformaldehyde (CH_2O)n, 100ml HCl (1M in acetic acid), and 4ml water were mixed. The mixture was stirred and heated up to 90°C, and the reaction kept at 90°C for 7 days. After the reaction was stopped, the product mixture was poured into 10% Na_2CO_3 water solution, and was extracted by 20ml chloroform 3 times. The organic layer was washed by water 3 times, dried over $MgSO_4$, and solvent was removed by a rotary evaporator. 3.83g of **3** was obtained (yield: 85%). ^{1}H NMR (CDCl$_3$) δ (ppm): 7.30 (s, 1H, phenyl), 6.90(s, 1H, phenyl), 4.65(s, 2H, -CH$_2$Cl), 4.50(s, 2H, -CH$_2$Cl), 3.80(d, 2H, -OCH$_2$), 2.80(d, 2H, -SCH$_2$), 1.85 (m, 2H, 3°H), 1.40-1.20 (m, 16H, methylene), 0.95 (m, 12H, -CH$_3$).

[2-(2–ethylhexyloxy)–5-(2–ethylhexylsulfide)]–1,4-bisbenzyl-phosphonic acid diethyl ester (4):

3.83g of **3**(0.0085mol) and 2.822g $P(OEt)_3$ (0.017mol) were mixed together directly without any solvent, raising the temperature to 150°C and stir for 24 hour. The product 4 was further purified by vacuum distillation. 5.5g of **4** were obtained (yield: 100%). ^1H NMR ($CDCl_3$) δ (ppm): 7.50 (s, 1H, phenyl), 6.95 (s, 1H, phenyl), 3.90-3.50 (m, 12H, $-OCH_2-$, *ph*- $CH_2-P(O)(OCH_2R)_2$), 3.15 (d, 2H, *ph*- $CH_2-P(O)(OR)_2$), 2.85 (d, 2H, $-SCH_2$), 1.85 (m, 2H, 3°H), 1.50-1.00 (m, 28H, - CH_2-, - CH_3), 0.95 (m, 12H, $-CH_3$).

[2-(2–ethylhexyloxy)–5-(2–ethylhexylsulfone)]–1,4-bis-benzyl-phosphonic acid diethyl ester (5):

5.5g (0.0085mol) of **4** and 30ml glacial acetic acid was heated up to 116-120°C, then 1.7g H_2O_2 (30% in water) was added in 4 times (10mins each time), Temperature was maintained and stirred for 3 hours. After reaction was stopped, acetic acid and excess hydrogen peroxide were removed by the rotary evaporator. The remains were further purified by a column twice to remove small amount of remaining acetic acid. 5.4g of **5** were obtained (yield: 80%). ^1H NMR ($CDCl_3$) δ (ppm): 7.70 (s, 1H, phenyl), 6.75 (s, 1H, phenyl), 3.90-3.50 (m, 12H, $-OCH_2-$, $-SO_2CH_2-$, $-P(O)(OCH_2R)_2$), 3.15 (d, 4H, *ph*-$CH_2-P(O)(OR)_2$), 1.85 (m, 2H, 3°H), 1.50-1.00 (m, 28H, - CH_2-, - CH_3), 0.95 (m, 12H, $-CH_3$). HR-MASS, found: MW=682.6; calculated (C32H60O9P2S): MW=682.8.

1.3.1.3 Monomer with $-C_{10}H_{21}$ side chains

1-Decyloxy-4-decylsulfanyl-benzene(2):

10g (0.08mol) of 4 – Mercaptophenol **1** and 30g (excess) KOH were mixed in 240 ml CH_3CN and 100ml water. After 10 minutes stirring, 40 ml 1-bromo-decane (excess) was added. The reaction solution was heated up to 80°C and kept at this temperature for 24 hours. After the reaction was stopped and cooled to room temperature, 200ml methanol was added, and a white solid started to precipitate out and was collected by filtration. The crude product was re-crystallized in methanol twice before putting into vacuum oven. 27.6g white solid **2** was obtained (yield: 85%). ^1H NMR ($CDCl_3$) δ (ppm): 7.30 (d, 2H, phenyl), 6.80 (d, 2H, phenyl), 3.90 (m, 2H, $-OCH_2$), 2.85 (m, 2H, $-SCH_2$), 1.75 (m, 4H, $-CH_2$), 1.50-1.20 (m, 28H, methylene), 0.95 (m, 6H, $-CH_3$).

1,4-Bis-bromomethyl-2-decyloxy-5-decylsulfanyl-benzene (3):

8.12g (0.02mol) of **2**, 1.54g (0.05mol) paraformaldehyde $(CH_2O)n$, 20ml HBr (31%wt in acetic acid), and 100ml formic acid were mixed. The mixture was stirred and heated up to 90°C, and the reaction kept at 90°C for 7days. After the reaction was stopped, the product mixture was poured into 10% Na_2CO_3 water solution, and extracted by 20ml chloroform 3 times. The organic layer was washed by water 3 times, dried over $MgSO_4$, and solvent was removed by a rotary evaporator. The remains became black solid after 24hours at room temperature. The black solid was washed with methanol, a white solid was obtained finally. 2.36g of **3** was obtained (yield: 20%). 7.40 (s, 2H, phenyl), 6.80 (s, 2H, phenyl), 4.70(s, 2H, - CH_2Br), 4.50(s, 2H, -CH_2Br), 3.90 (m, 2H, -OCH_2), 2.85 (m, 2H, -SCH_2), 1.75 (m, 4H, -CH_2), 1.50-1.20 (m, 28H, methylene), 0.95 (m, 6H, -CH_3). Melting point: 65°C.

[5-Decyloxy-2-decylsulfanyl-4-(diethoxy-phosphorylmethyl)-benzyl]-phosphonic acid diethyl ester(4):

2.36g of **3** (0.004mol) and 0.66g $P(OEt)_3$ (0.004mol) were mixed together directly without any solvent, raising the temperature to 120°C. The product **4** was further dried by vacuum oven. 2.8g of **4** were obtained (yield: 100%). ^1H NMR ($CDCl_3$) δ (ppm): 7.50 (s, 1H, phenyl), 6.95 (s, 1H, phenyl), 3.90-3.70 (m, 10H, -OCH_2-, *ph*- CH_2 –$P(O)(OCH_2R)_2$), 3.35 (d, 2H, *ph*- CH_2 –$P(O)(OR)_2$), 3.15 (d, 2H, *ph*- CH_2 –$P(O)(OR)_2$), 2.85 (d, 2H, -SCH_2), 1.75 (m, 4H, -CH_2-), 1.50-1.20 (m, 28H, methylene), 0.95 (m, 18H, -CH_2-, -CH_3).

[2-(2–ethylhexyloxy)–5-(2–ethylhexylsulfone)] – 1,4 – bis – benzyl - phosphonic acid diethyl ester (10):

2.8g (0.004mol) of **4** and 30ml glacial acetic acid was heated up to 116-120°C, then 1.7g H_2O_2 (30% in water) was added in 4 times (10mins each time). The temperature was maintained and mixture stirred 12 hours. After reaction was stopped, acetic acid and excess hydrogen peroxide were removed by a rotary evaporator. The crude product was further purified by a short column twice to remove small amount of acetic acid. 2.5g of **5** was obtained (yield: 85%). ^1H NMR ($CDCl_3$) δ (ppm): 8.00 (s, 1H, phenyl), 6.95 (s, 1H, phenyl), 3.90-3.70 (m, 10H, -OCH_2-, *ph*- CH_2 –$P(O)(OCH_2R)_2$), 3.35 (d, 2H, *ph*- CH_2 –$P(O)(OR)_2$), 3.15 (m, 4H, *ph*- CH_2 –$P(O)(OR)_2$, -SCH_2), 1.75 (m, 4H, -CH_2-), 1.50-1.20 (m, 28H, methylene), 0.95 (m, 18H, -CH_2-, -CH_3). HR-MASS, found: MW=738.9; calculated (C32H60O9P2S): MW=738.9.

1.3.2. Synthesis of Polymer

SF-PPV-I (6):

0.268g (0.002mol) of 1,4-benzene-dialdehyde and 1.028g [4-(Diethoxy-phosphorylmethyl)-2-ethanesulfonyl-5-ethoxy-benzyl]-phosphonic acid diethyl ester **5** (0.002mol) were dissolved in 50mL dry THF, and 0.44g (0.004mol) NaH in 20mL anhydrous THF was added drop wise. The resulting reaction mixture was stirred for 24hrs at room temperature. After reaction was stopped, 30ml methanol was added to quench the excess amount of NaH, and subsequently poured into 400ml water. HCl (1M) was added to neutralize the aqueous phase until pH=7. A bright orange color solid was obtained by filtration. After it was dried in the vacuum oven at 60°C overnight, 0.52g polymer **6** was obtained. Mw = 2,000 was measured by GPC. ^1H NMR δ: 8.20-7.90(m, phenyl-H), 7.70-7.50 (m, phenyl-H), 7.40(m, vinyl-H), 7.20-7.00(m, phenyl-H), 7.00-6.80(m, vinyl-H), 3.90(m, -OCH_2-), 3.30(m, -SO_2CH_2), 1.20 – 0.95 (m, -CH_3).

1.3.3 Chemical Characterizations

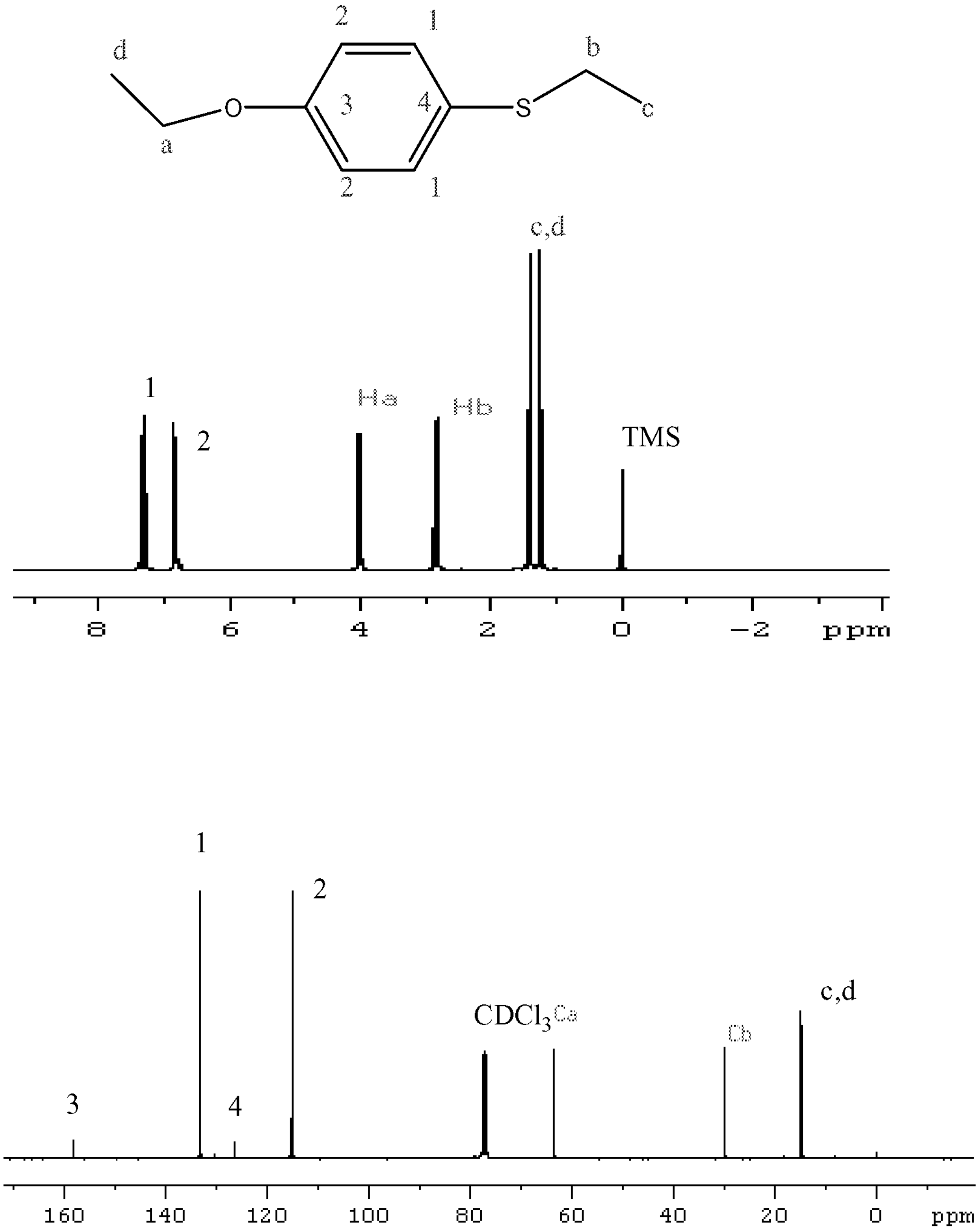


Figure 1.4 NMR Spectra of Compound 2 with $–C_2H_5$

Compound 3 with -C2H5

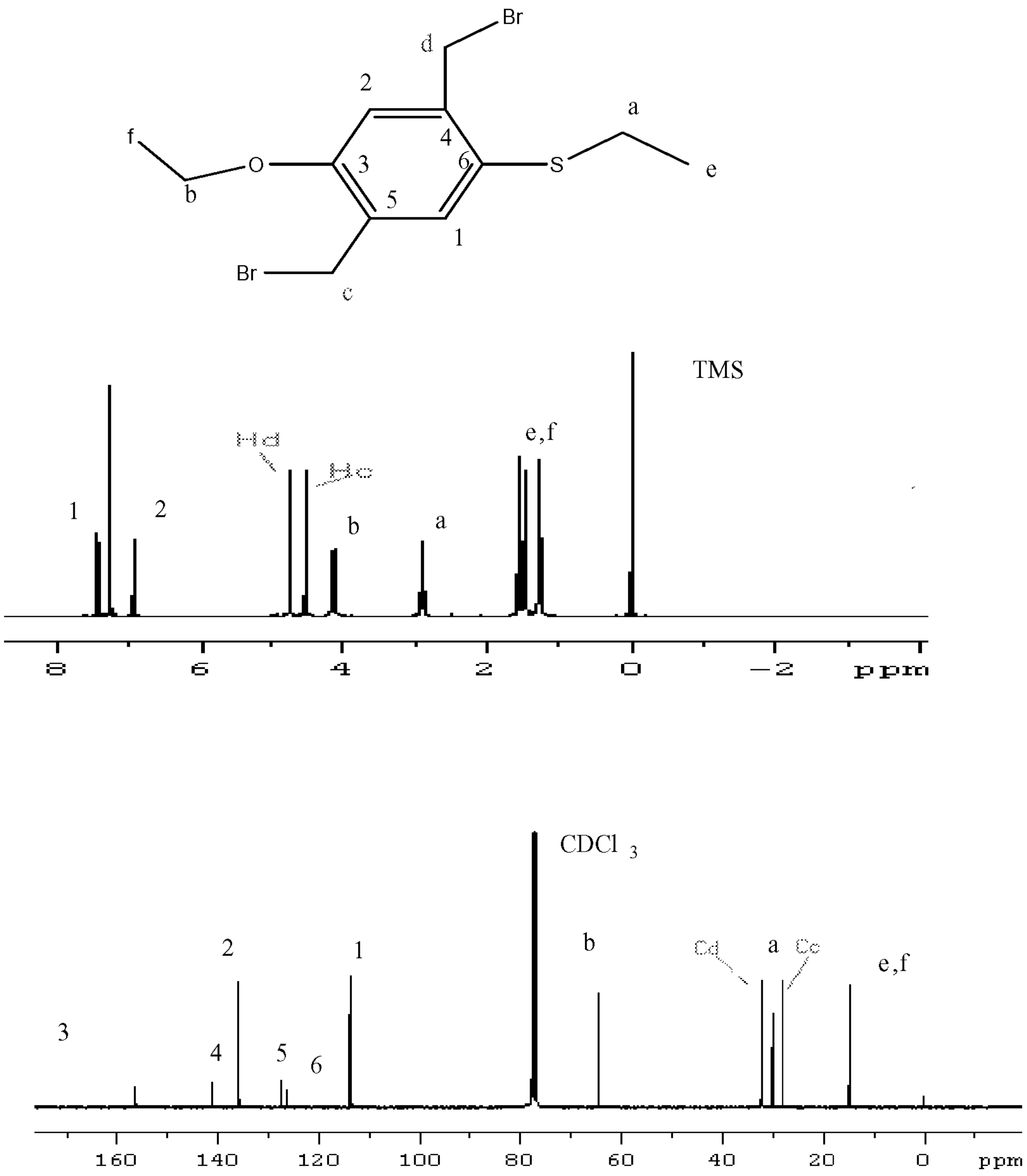
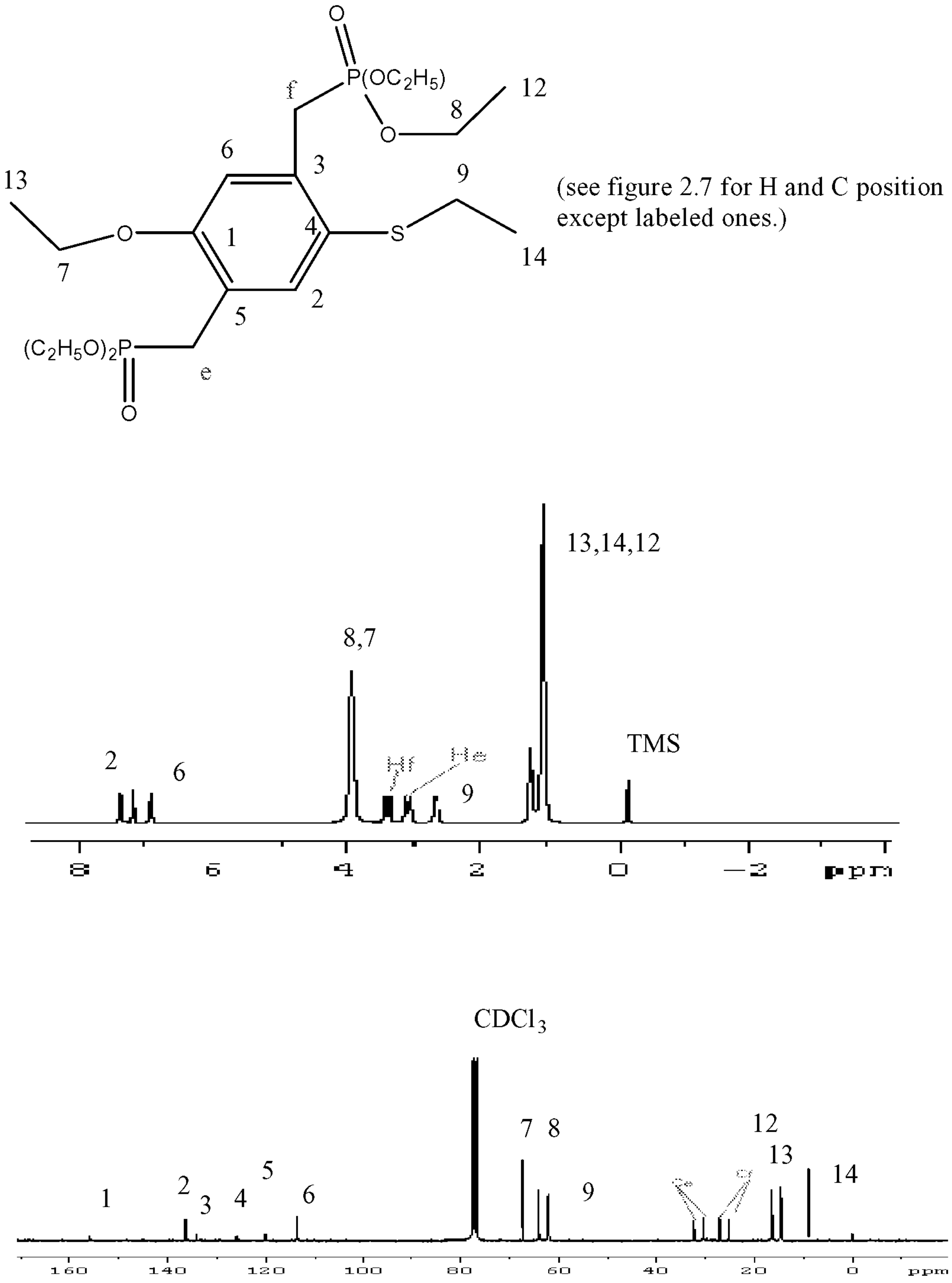
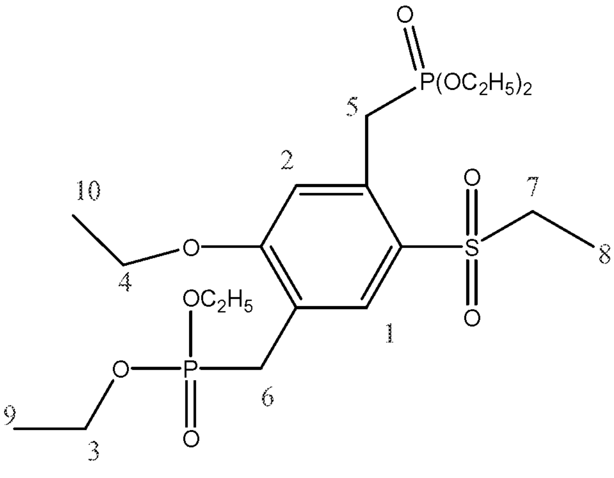


Figure 1.5 NMR Spectra of Compound 3 with –C_2H_5



(see figure 2.7 for H and C position except labeled ones.)

Figure 1.6 NMR Spectra of Compound 4 with $–C_2H_5$



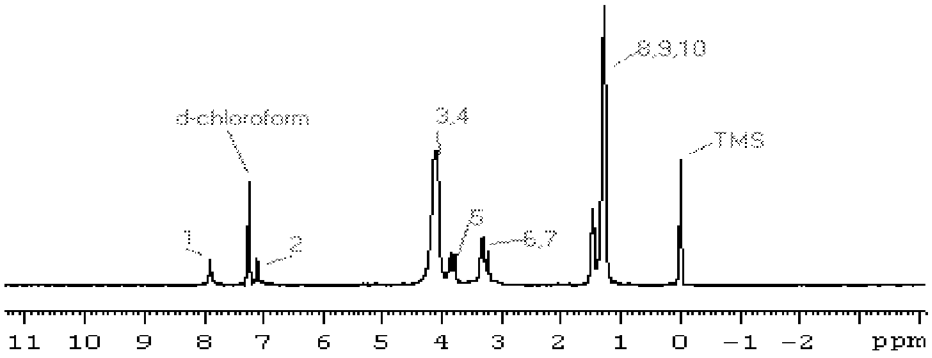


Figure 1.7 (a) ^{1}H NMR Spectra of Compound 5 with $-C_2H_5$

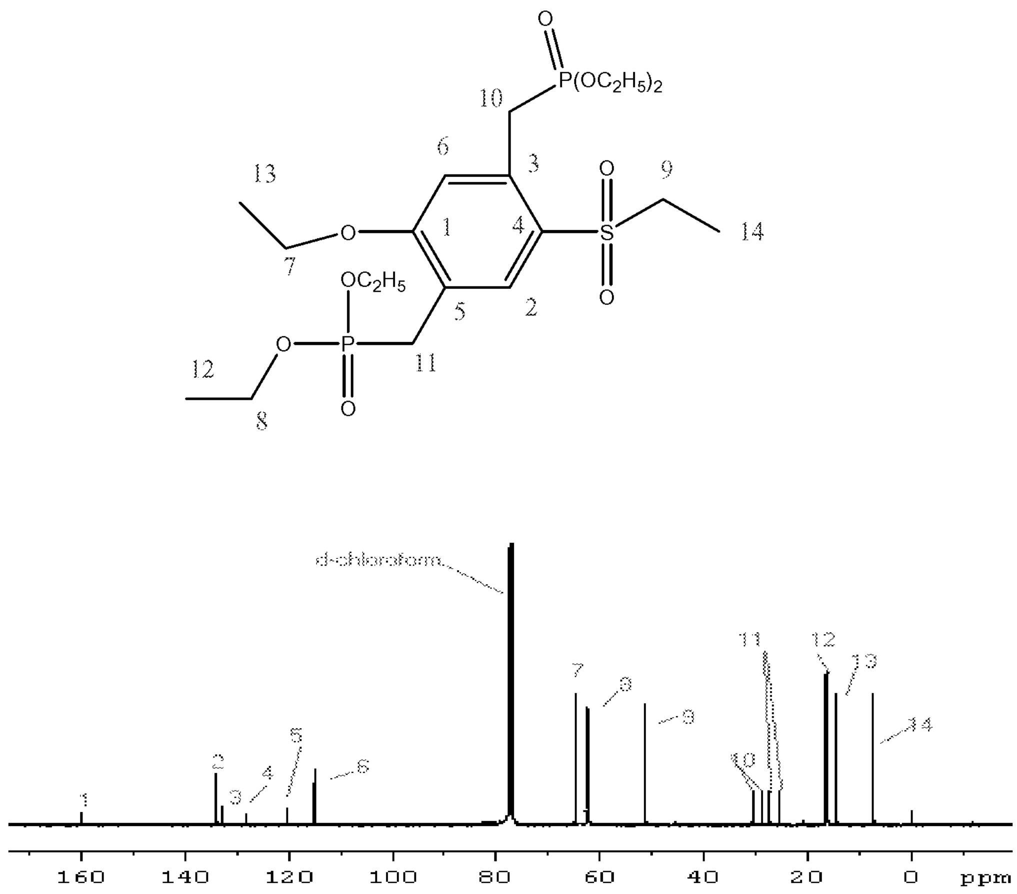
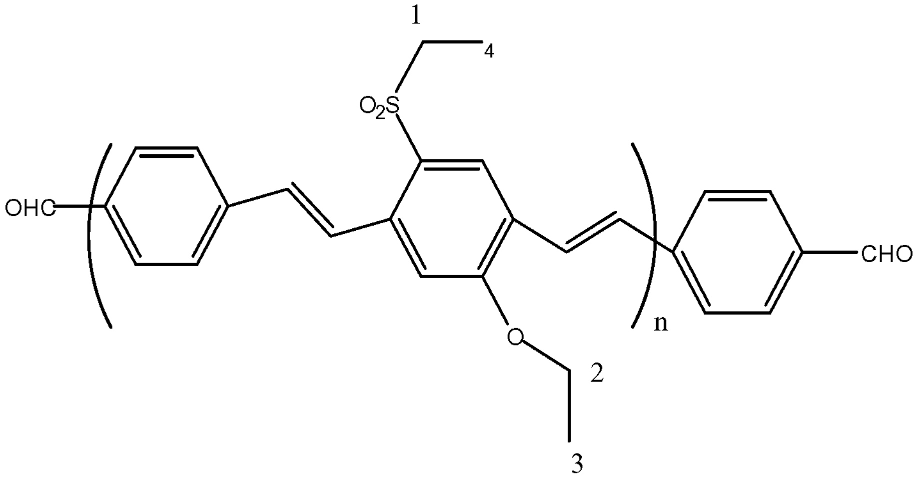


Figure 1.7 (b) ^{13}C NMR Spectra of Compound 5 with $-C_2H_5$



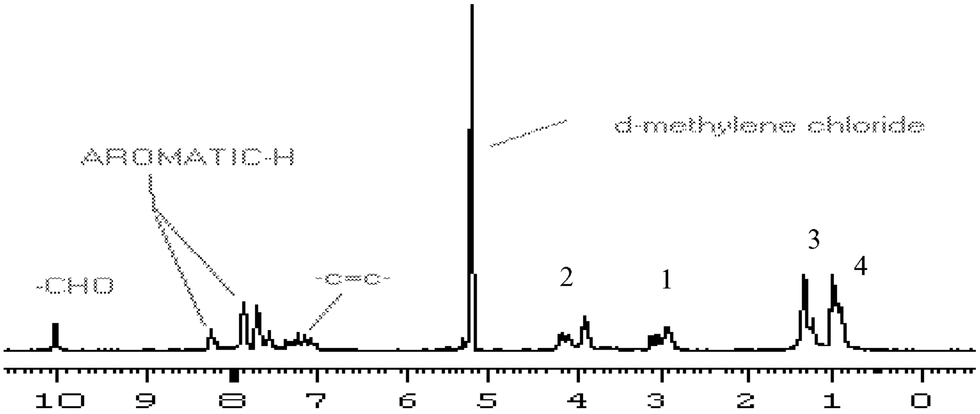


Figure 1.8 NMR Spectra of SF-PPV-I with $-C_2H_5$

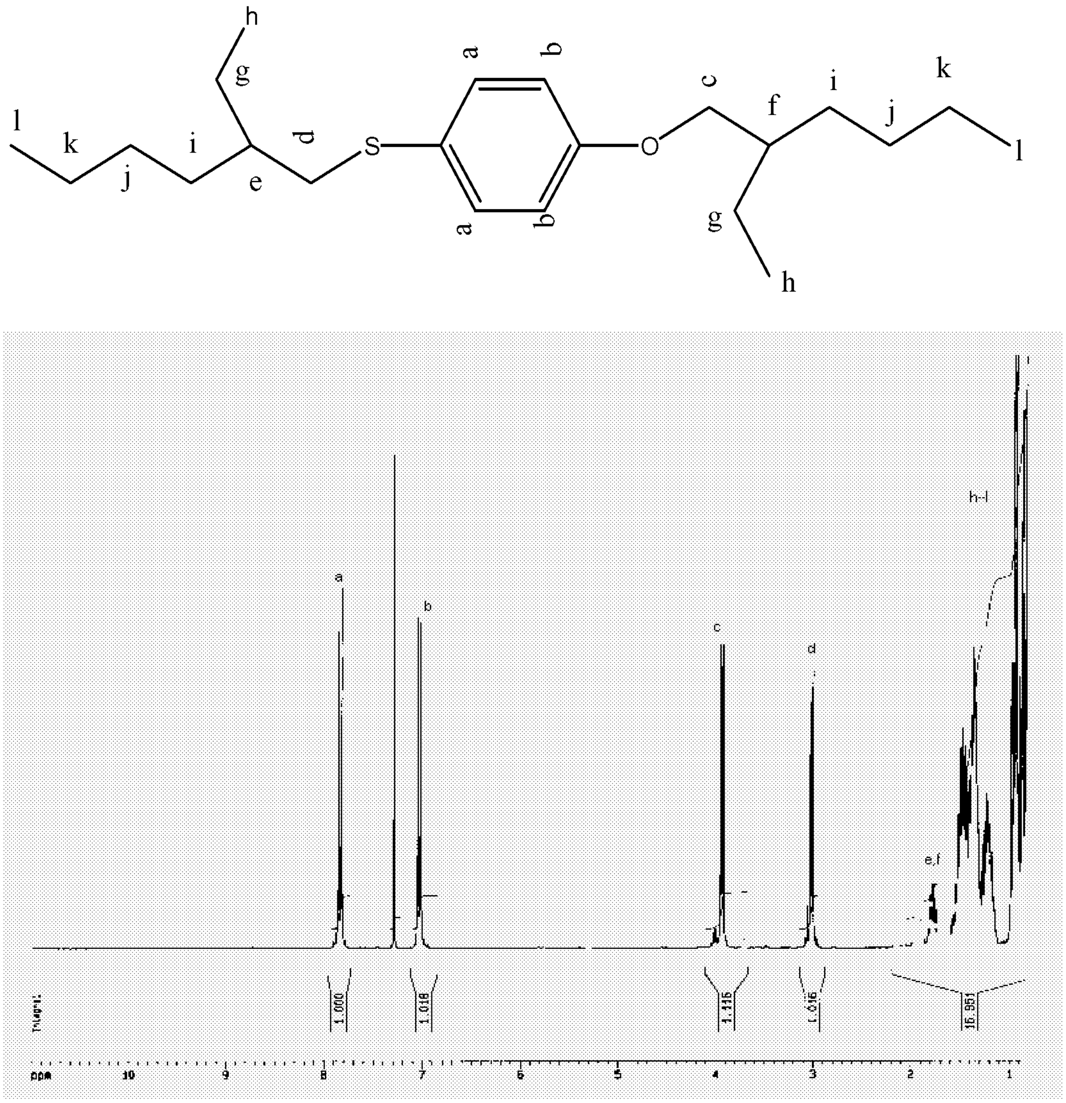
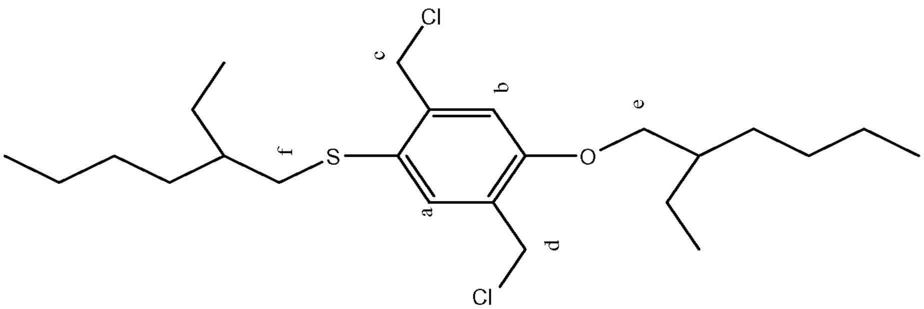


Figure 1.9 NMR Spectra of Compound 2 with $-C_8H_{17}$

Compound 3 with -C_8H_{17}



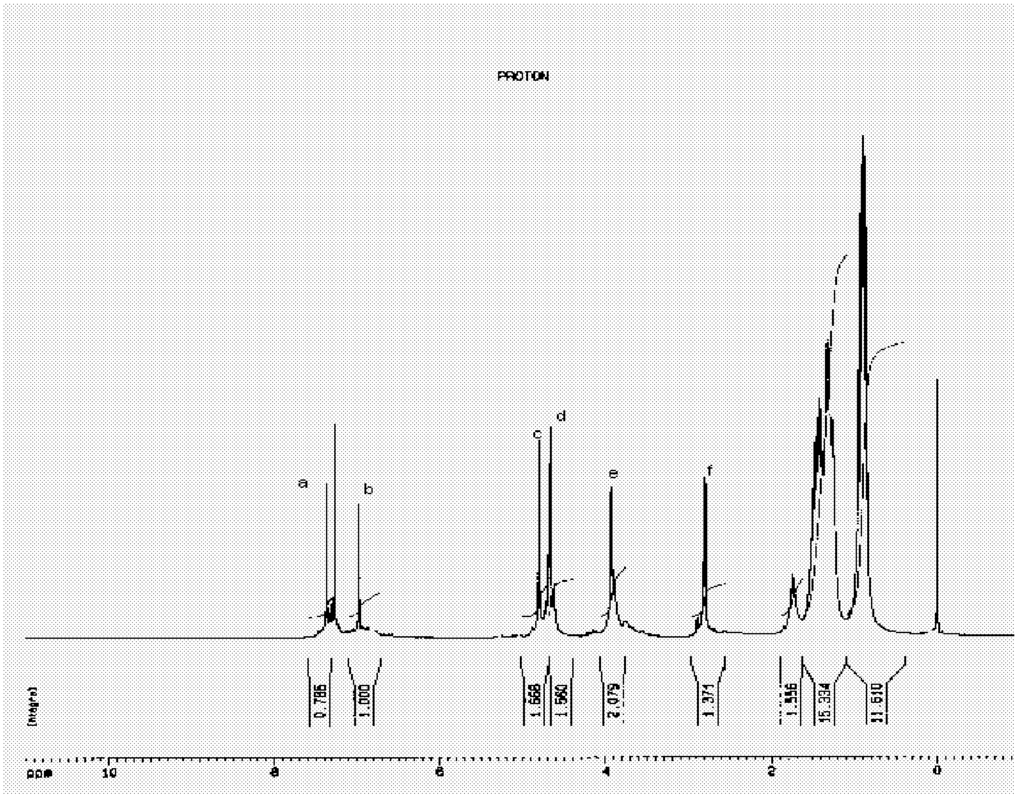


Figure 1.10 NMR Spectra of Compound 3 with C_8H_{17}

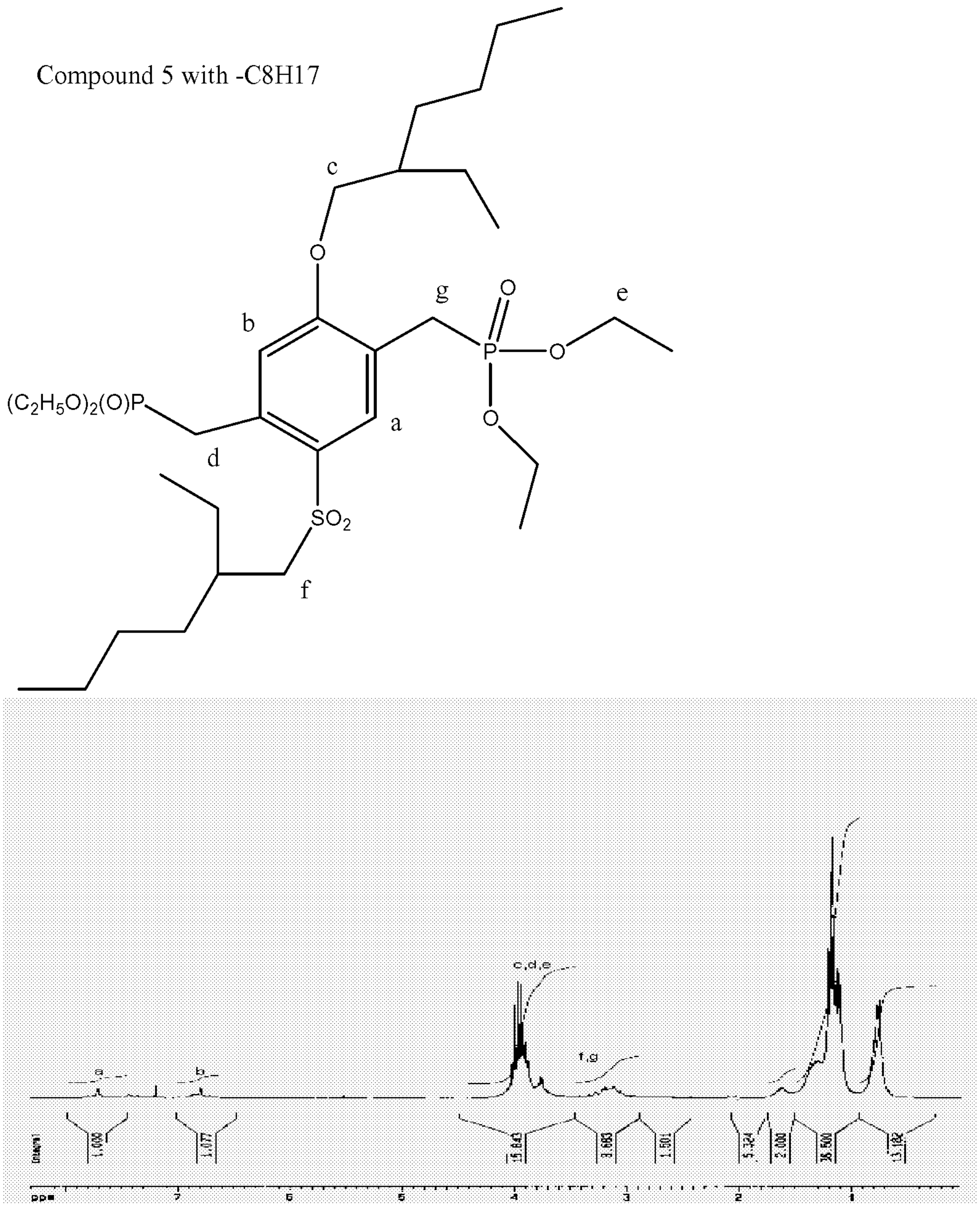
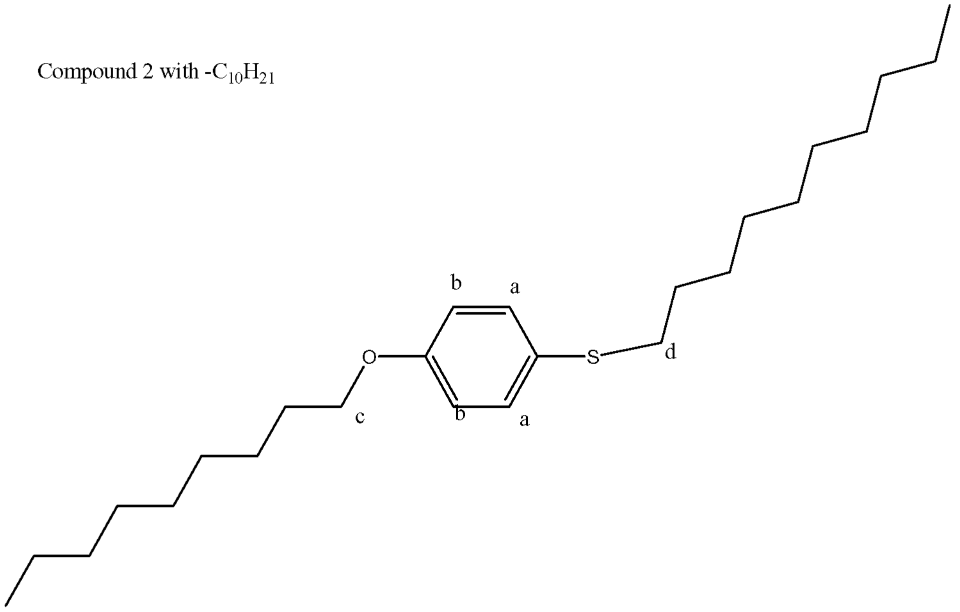

Compound 5 with -C8H17

Figure 1.11 NMR Spectra of Compound 5 with C_8H_{17}

Compound 2 with -$C_{10}H_{21}$



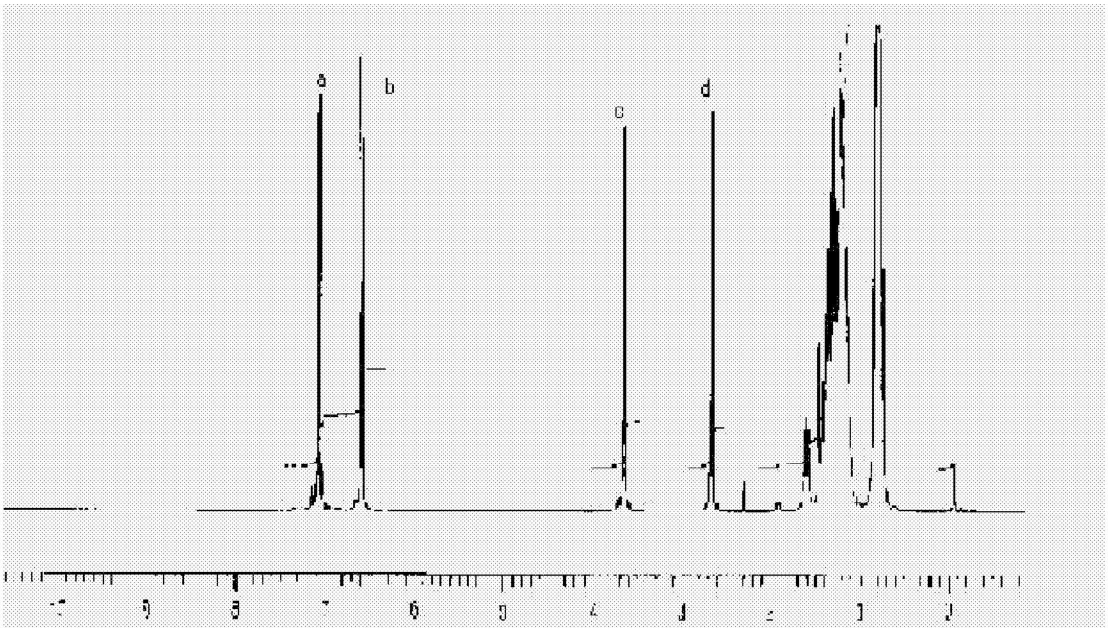
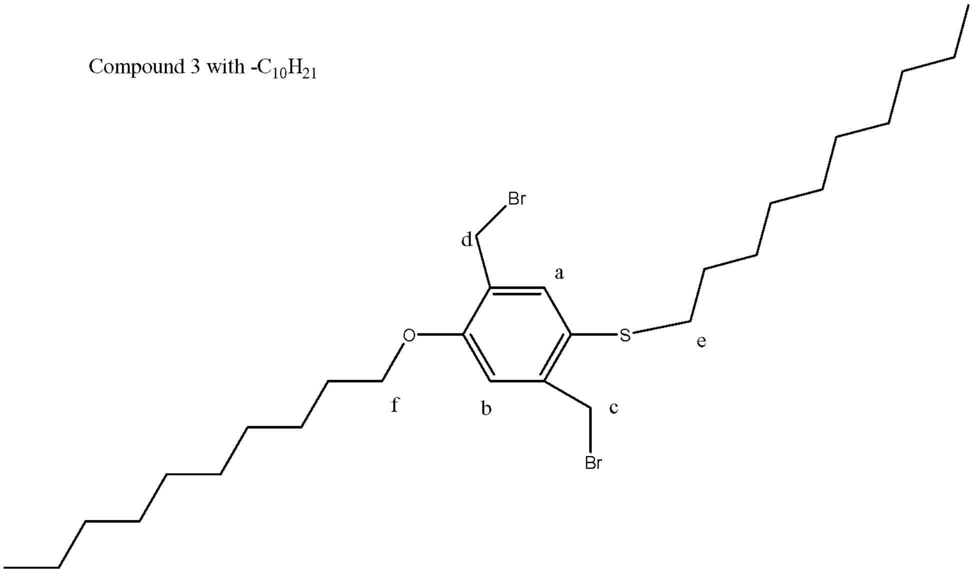


Figure 1.12 NMR Spectra of Compound 2 with $C_{10}H_{21}$

Compound 3 with -$C_{10}H_{21}$



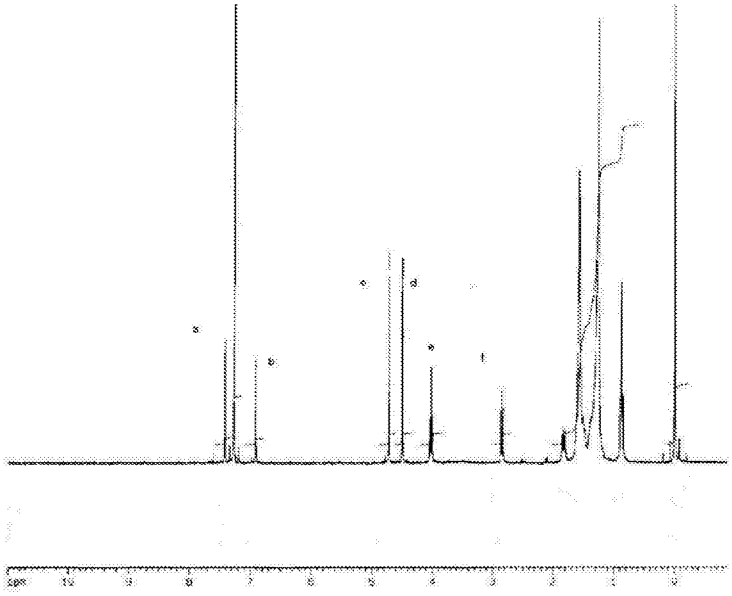
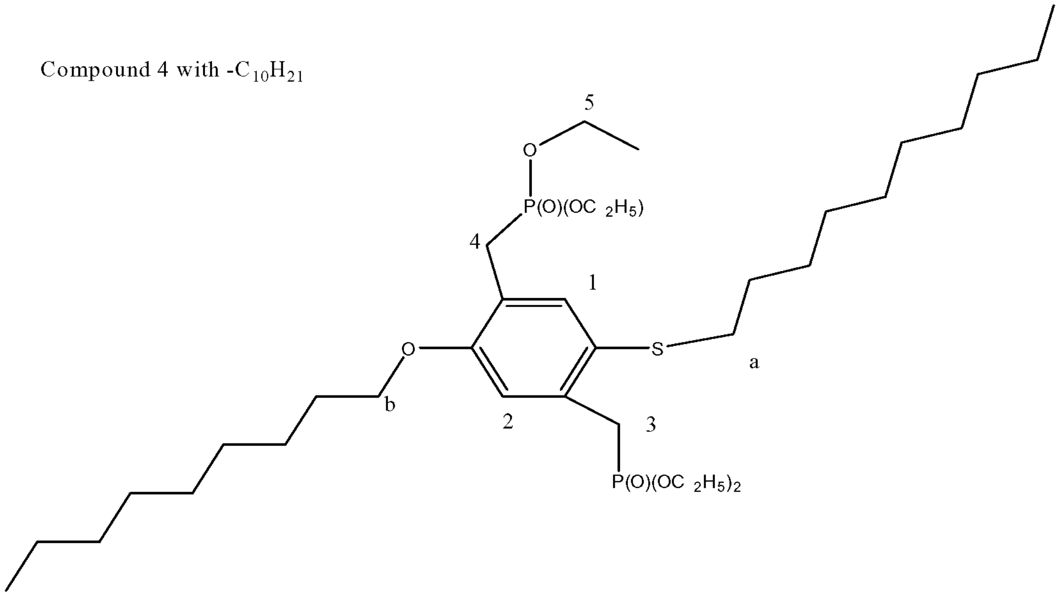


Figure 1.13 NMR Spectra of Compound 3 with $C_{10}H_{21}$

Compound 4 with $-C_{10}H_{21}$



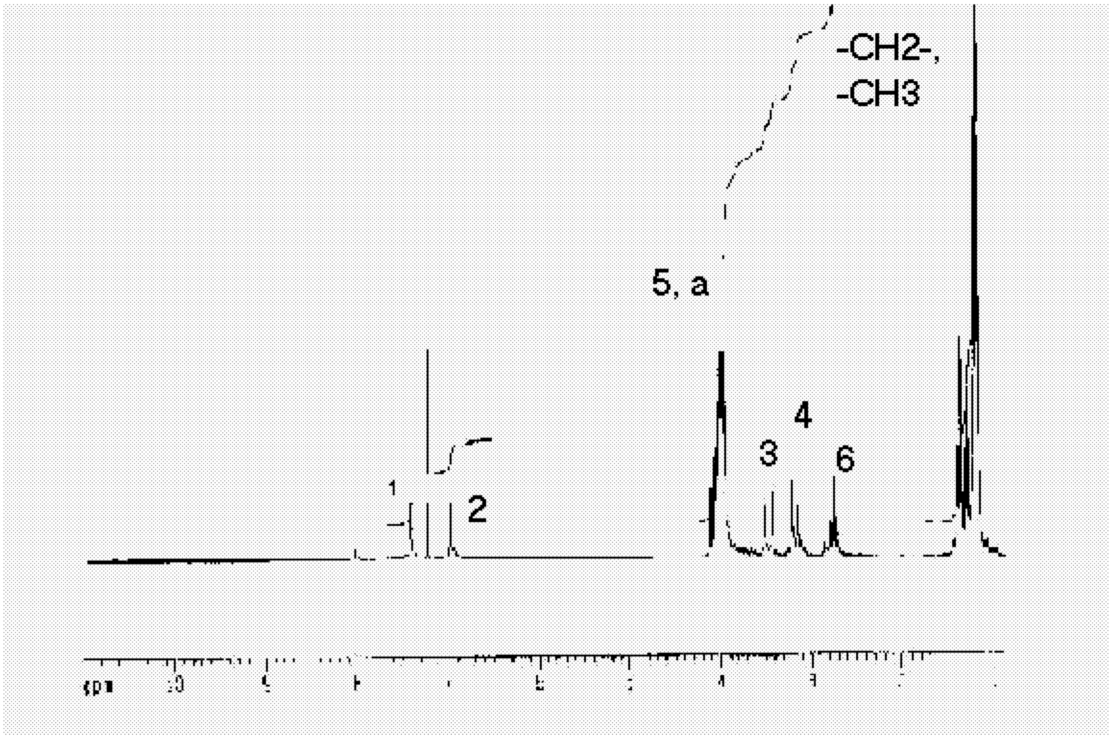
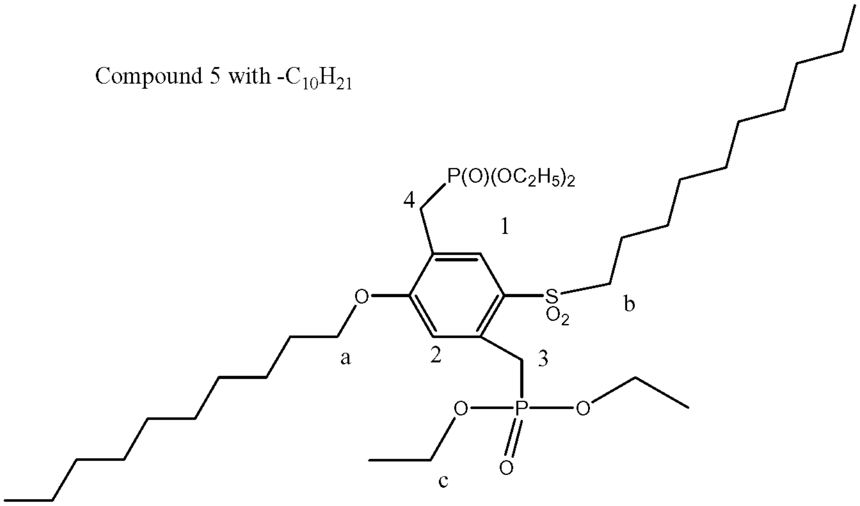


Figure 1.14 NMR Spectra of Compound 4 with $C_{10}H_{21}$

Compound 5 with -$C_{10}H_{21}$



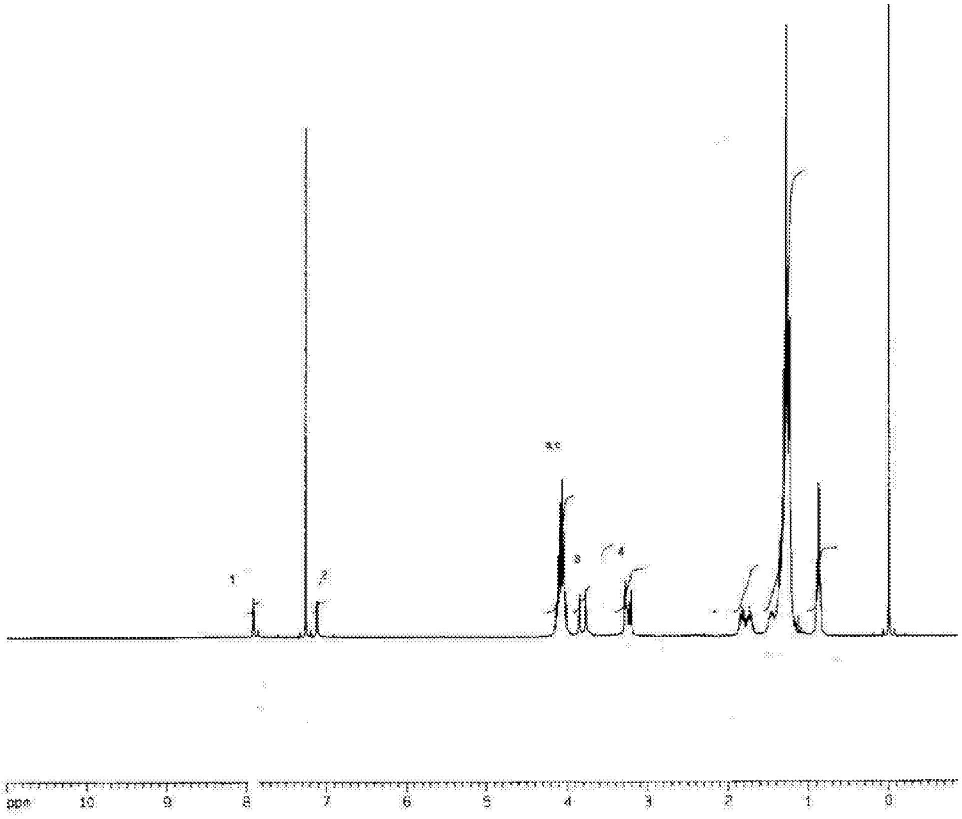


Figure 1.15 NMR Spectra of Compound 5 with $C_{10}H_{21}$

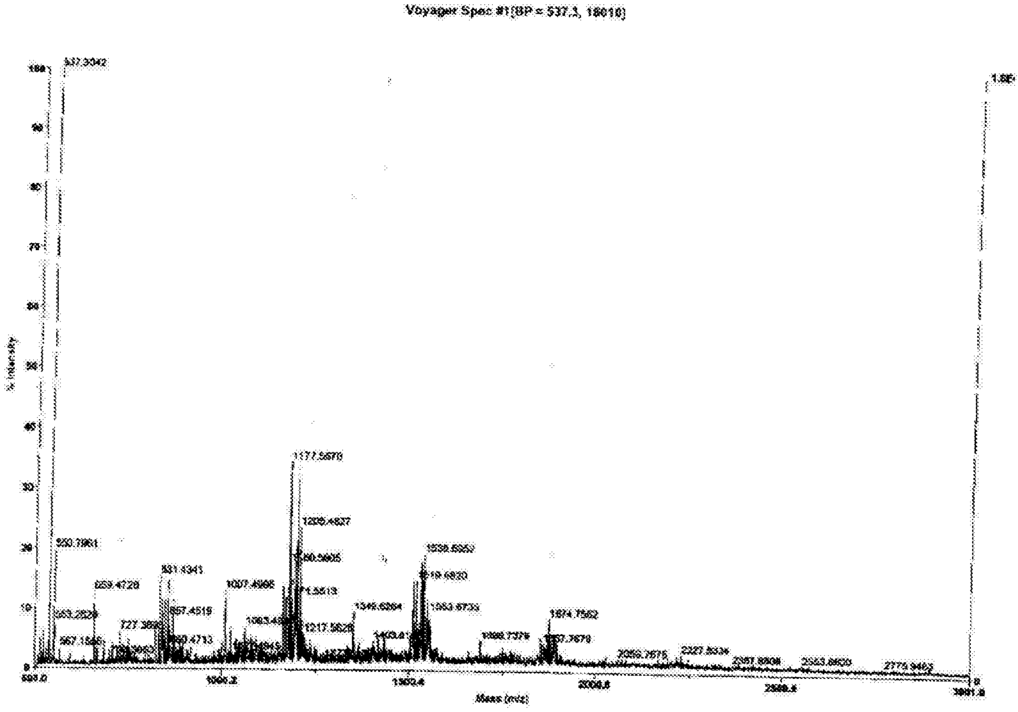
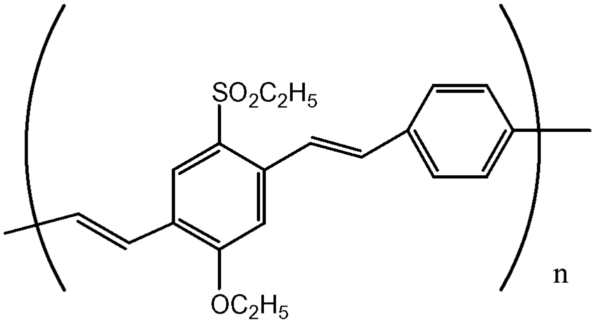
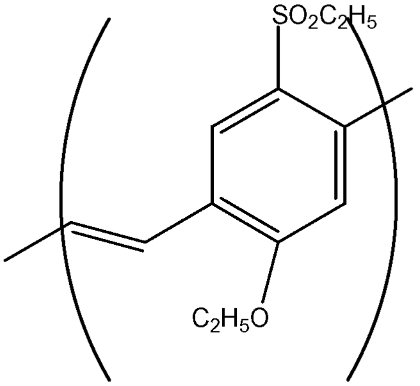


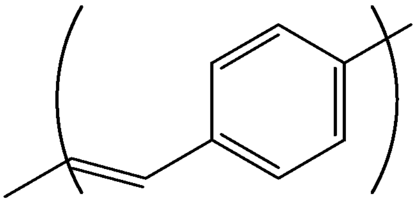
Figure 1.16 MALDI of SF-PPV-I with $-C_2H_5$, Mw ≈ 1,500-2,000



One repeat unit of SF-PPV-I
For one repeat unit $C_{20}H_{20}O_3S$, MW = 340



a



b

MW of unit (a) $C_{12}H_{14}O_3S$ = 238; MW of unit (b) C_8H_6 =102
Peak 857 ≈ 2.52 repeat units, ~ 3.5 nm
Peak 1177 ≈ 3.46 repeat units, ~ 4.9nm
Peak 1538 ≈ 4.52 repeat units, ~ 6.3nm
Peak 1874 ≈ 5.51 repeat units, ~ 7.7 nm

* Note: Dialdehyde is the excess reactant, that is the reason that polymer structure has more unit (b) than unit (a).

1.3.4 Opto-electronic measurements

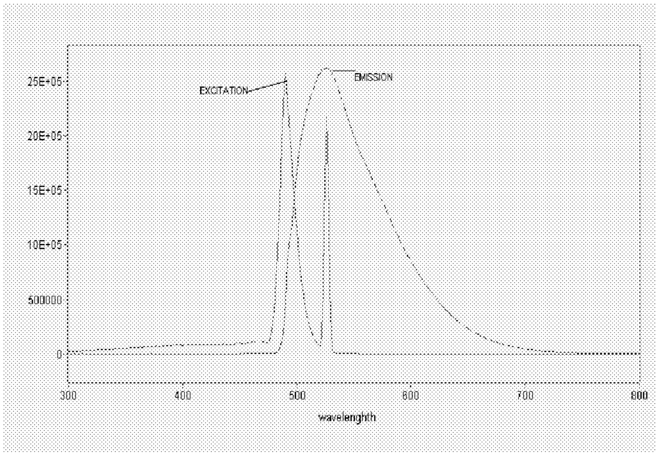


Figure 1.17 PL Excitation and Emission Spectra in Solution (C_2 side chain)

Polymer sample: C2 side chain, Mw= 1500,-2000(4-5 repeat unit, 6-8 nm). Solvent: Methylene Chloride (Note: the sharp spilt at 520nm is due to reflected excitation beam.)

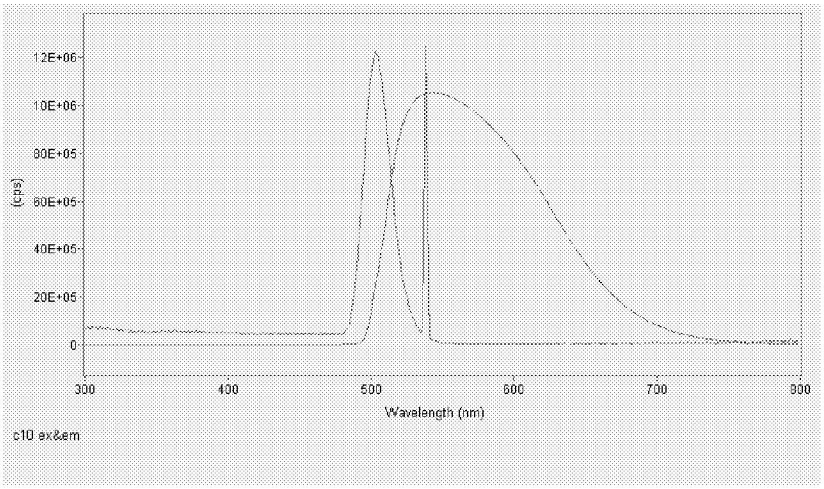


Figure 1.18 PL Excitation and Emission Spectra in Solution (C_{10} side chain)

Polymer Sample: C10 side Chain, Mw=10,000(18 repeat units, 25nm). Solvent: Methylene Chloride.(saturated solution)

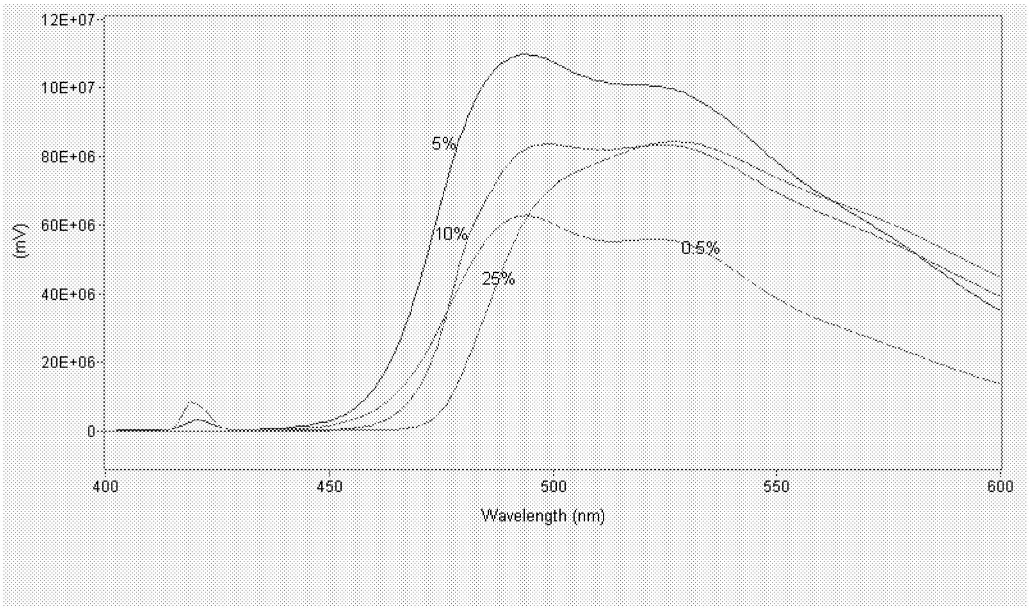


Figure 1.19 Concentration Effects of PL Emission (C_{10} side chain)

Polymer Sample: C10 side Chain, Mw=10,000 (18 repeat units, 25nm)
Solvent: Methylene Chloride.

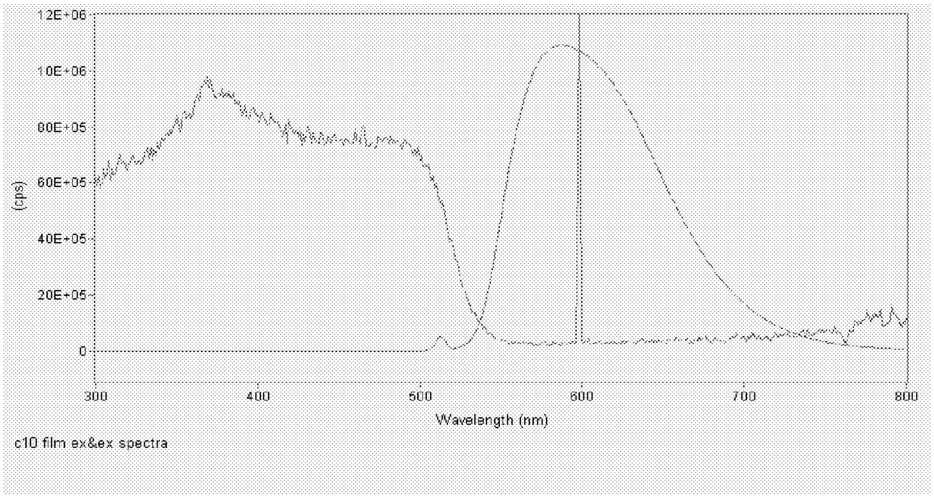


Figure 1.20 PL Excitation and Emission Spectra in Thin Film (C_{10} side chain)

Polymer Sample: C10 side Chain, Mw=10,000(18 repeat units, 25nm), film.

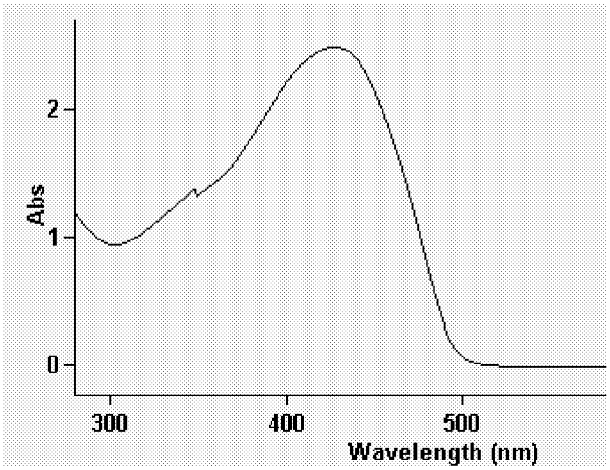


Figure 1.21 UV-Vis absorption spectrum of SF-PPV

Polymer sample: C2 side chain, Mw= 1500,-2000(4-5 repeat unit, 6-8 nm), Solvent: DMF

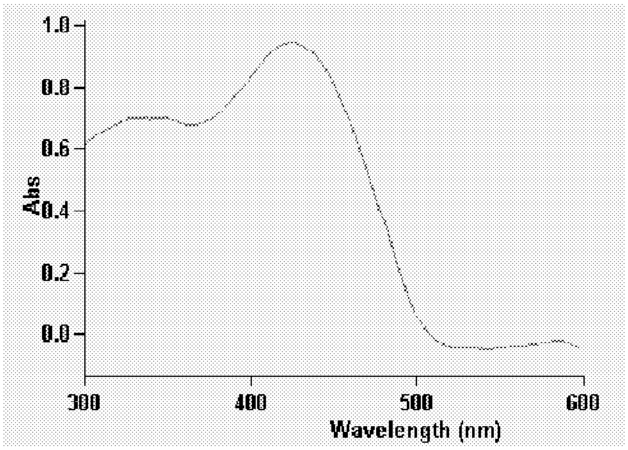


Figure 1.22 UV-Vis absorption spectrum of RO-PPV

Polymer sample: C10 side chain, Mw= 2000,-2500(4-5 repeat unit, 6-8 nm), Solvent: DMF

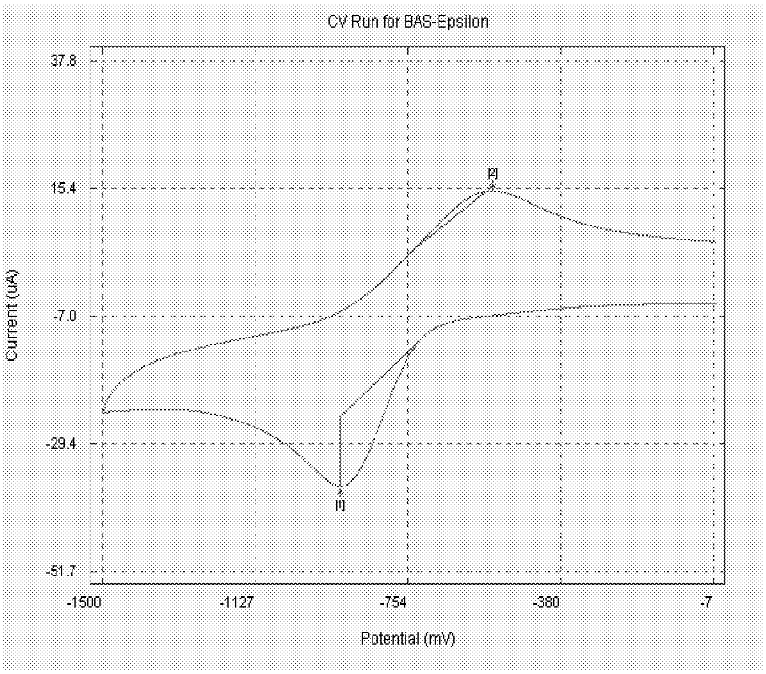


Figure 1.23 Cyclic Voltammogram of SF-PPV-I

Polymer sample: C2 side chain, Mw= 1500-2000(4-5 repeat unit, 6-8 nm), solvent: DMF, concentration: 1mM. First scan.

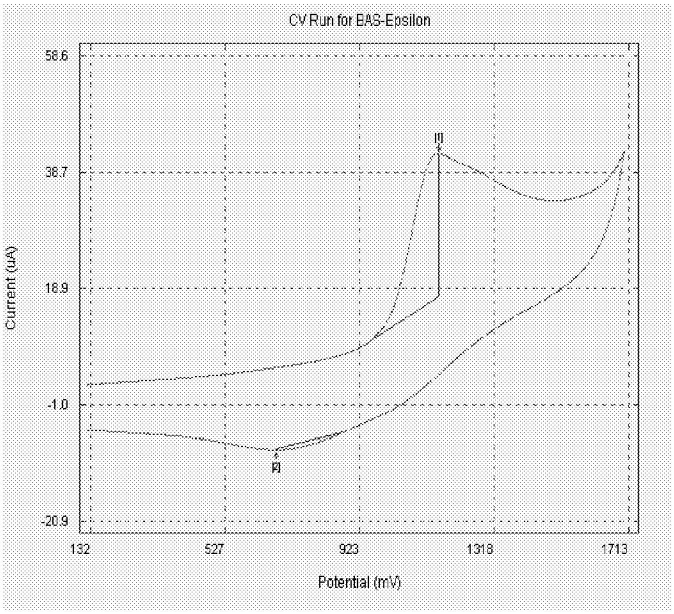


Figure 1.24 Cyclic Voltammogram of RO-PPV

Polymer sample: C2 side chain, Mw= 1500-2000(4-5 repeat unit, 6-8 nm), Solvent: DMF, concentration: 1mM. First scan.

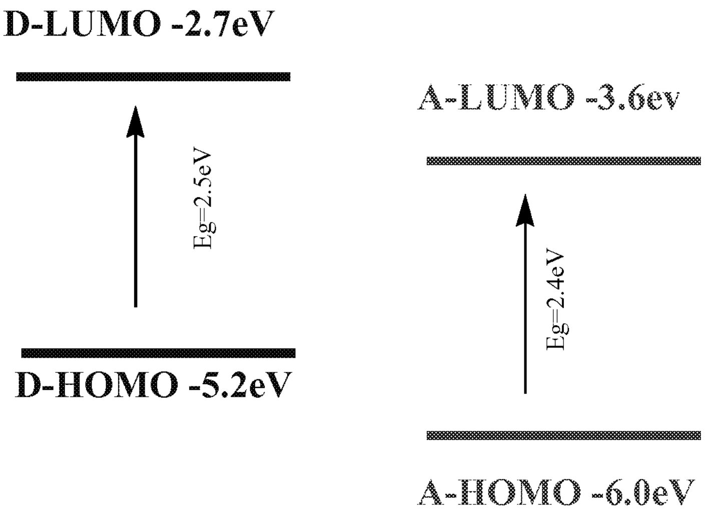


Figure 1.25 HOMO-LUMO levels of SF-PPV-I and RO-PPV

The values shown above are based on acceptor SF-PPV sample: C2 side chain, Mw= 1500-2000(4-5 repeat units, 6-8 nm); donor RO-PPV sample: Mw=2000-3000(4-5 repeat units, 6-8nm).

1.4 Reference

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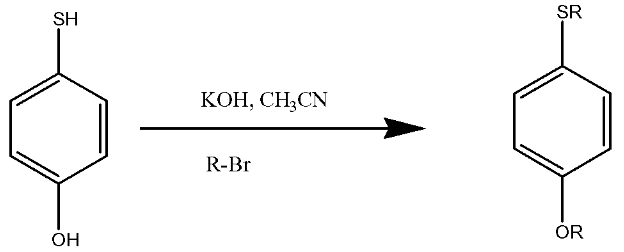
2. RESULTS AND DISCUSSION FOR SF-PPV-I

2.1 Synthesis of monomer

2.1.1 Step 1: Williamson Condensation Reaction



The first step reaction is relatively easy to control. Generally, the product of the reaction has good purity and high yield percentage.

Base

Different bases can be used in this reaction, such as NaOH, KOH, K_2CO_3. The solubility of these bases in acetonitrile is not good, and sometimes the stirrer cannot work properly. To solve this problem, water was added to dissolve the base, and it didn't cause any side reaction.

Solvent

Different solvents have been tried, such as ethanol, acetone, and acetonitrile was found give the best results (shorter reaction time and higher yield percentage.). DMF can be used, but it is hard to completely remove due to its high boiling point.

C_2 side chain

The boiling point of C_2H_5Br is around 50°C, and it is much more active and volatile than Ethylhexyl Bromide and bromo-decane. It should be added slowly and an ice bath has to be used to bring the temperature down, otherwise C_2H_5Br will start to boil and escape from the system. Excess C_2H_5Br should be used to prevent the loss of chemical due to the low boiling point and also to improve the yield percentage of product.

The reaction normally requires two days to complete, and the extent of reaction can be determined by TLC. The separation procedure is different. **Do not** add chloroform and water to extract the product. Once chloroform and water were added, the solution became cloudy and could never be separated into two layers, even after adding salt. The best way to separate the product is simple but effective. After the reaction stops, transfer the mixture into a separation funnel. The mixture will become two layers, one is the water layer (dark color), another is the organic layer(light color). Collect the organic layer, then use rotary evaporator to get rid of the solvent—acetonitrile. The crude product may contain a little amount of white solid, the base dissolved in acetonitrile. It can be filtered out.

C_8 side chain

The temperature for C_8 side chain reaction is about 80°C, which equals to the boiling point of acetonitrile. Excess amount of Ethylhexyl Bromide should also be used, otherwise the reaction cannot be completed even after a week. The separation procedure is the same as the reference paper: add chloroform and wash with water several times to get rid of base. After the organic layer is evaporated by the rotary evaporator, Ethylhexyl Bromide still remains because of its very high boiling point, so a high vacuum distillation should be used, and Ethylhexyl Bromide can be removed at 150-170°C under 10mm pressure.

C_{10} side chain

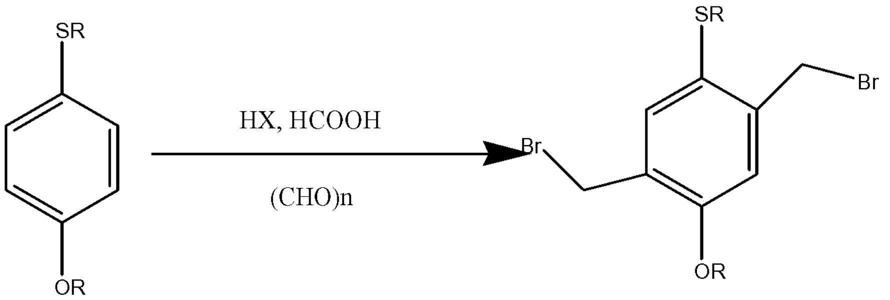
The product with C_{10} side chain is a white solid, so the purification of this compound is relatively easier. Re-crystallization from methanol twice can give a very good NMR result.

Important note

If the excess amount of bromide compound still remains in the product, a peak around 3.5ppm will appear on the proton NMR spectrum. The key points of the proton spectrum are the peaks at 3.9($-OCH_2-$) and 2.7($-SCH_2-$), their integration should be 1:1.

2.1.2 Step 2: Bromomethylation reaction

This is the most difficult part of the monomer synthesis.



HX

Both HCl (1N in dioxane) and HBr (31% wt in acetic acid) can be used, and HBr is the first choice due to its higher HBr content. Once the HBr bottle is opened, it should be put into dry glove box or sealed properly. The reason for several failed experiments were that HBr had been found to undergo some unknown changes (The color became dark).

Solvent

Both formic acid and acetic acid can be used. Formic acid was found better than acetic acid, mainly because it is a stronger acid, which can speed up the reaction, and because the product of this step has poorer solubility in formic acid. Product loss is therefore reduced.

C_2 side chain

The product with C_2 side chain has been successfully synthesized. After mixing all the reactants and reacting at 60-65°C overnight, the clear solution became a solid-liquid mixture. After washing with water, the product of di-substituted compound is obtained as a white solid. The mono-substituted product is liquid, and can be easily removed. A little amount of water was added into the reactant mixture, and it plays an important role in the reaction: prevents the tri-substitution reaction happening. Without presence of water, a black insoluble solid (possibly a polymer) was obtained.

The temperature is critical, and 60-65°C should be maintained. Below 60°C, reaction is very slow, and above 65°C, instead of white solid product, a dark brown color solid was obtained. The NMR spectrum for this brown color solid shows it is a mixture of several unknown chemical structures.

The concentration of reactants also affected the result of the reaction. Higher concentration than the one indicated in the synthesis procedure will cause the failure. Again, in this case, an unknown brown color mixture will be obtained instead of a white solid.

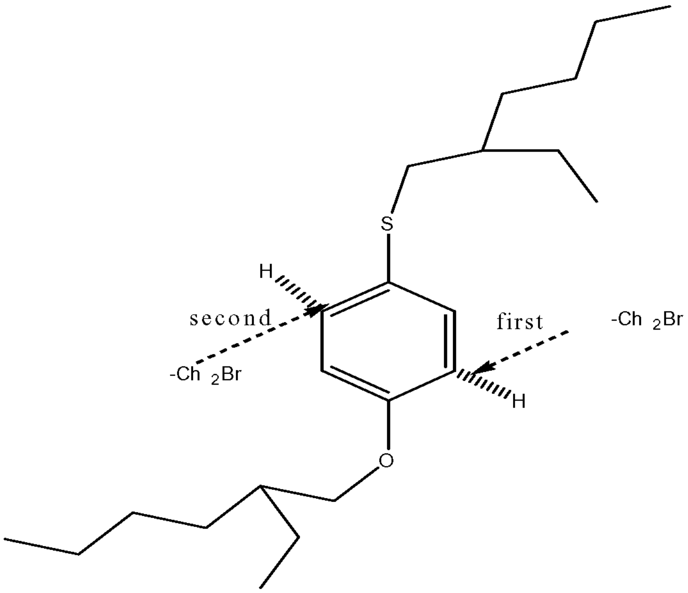
Water washing is good enough to purify the compound, and the resulting product shows a good proton NMR. Unless for the purpose of elemental analysis, re-crystallization in methanol is not necessary (because it will dramatically reduce yield percentage).

C_8 side chain

The 100% pure di-substituted product with C_8 side chain has never been achieved, the reason might be that the ethylhexyloxy group is too big, it hinders the second $–CH_2Br$ from attaching to the benzene ring. During the reaction, the $–CH_2Br$ group always substitutes the aromatic H which is close to the oxygen ($–OCH_2$-). The reason may be because of the larger size of S atom than O atom. When HCl (1N in dioxane) was used, it gave better results than HBr. The final product disubstituted:monosubtitute can reach 90: 10. The reason may be because of the smaller size of $-CH_2Cl$. The disubstituted and monosubstituted product only show one spot on the TLC plate, and they are very high boiling point liquid, so it is very hard to separate them.

C_{10} side chain

Since the decyloxy side chain is a straight chain, even though it is longer than ethylhexyloxy group, the pure disubtituted product still can be obtained as a white solid. Like C_8 side chain, the reaction for C_{10} side chain is extremely slow, usually takes a week to complete. The reaction as well as separation procedures have not been optimized , therefore, the yield is very low The reaction condition is also hard to control, even under same conditions, the reaction may not be repeatable, *i.e.*, one of about 5 trials, maybe one was success.



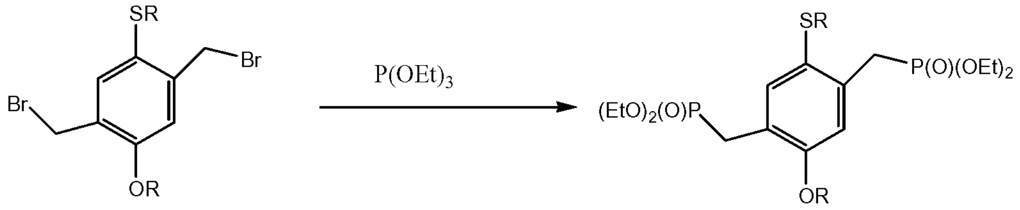
Important notes:

The temperature for this step should be carefully controlled. The ideal condition is that the heat provided from the oil bath should just over the energy barrier for disubstitution but less than that for tri-substitution.

Although there is no reference paper that mentioned about the effects of the sizes of side chains and substitution groups, from the results obtained above, one conclusion can be reached: the smaller size of the substituents, the more ease, more purity and better yield percentage of the final products.

For proton NMR spectra, the important peaks are two $-CH_2Br$ peaks around the 4.5ppm, their integration should be 1:1 ratio.

2.1.3 Step 3 Phosphate Ester Formation

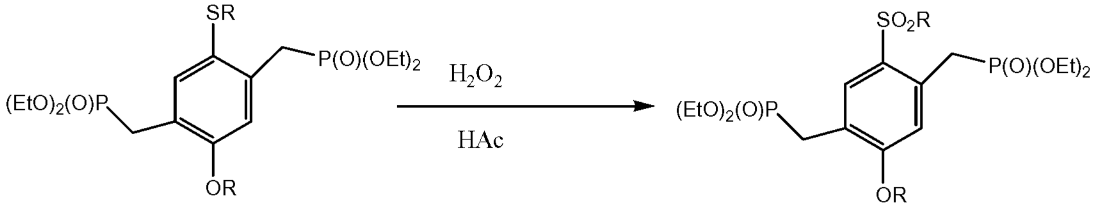


At the beginning, experiments were done according to the procedure from the reference paper. However, a few hours of reaction time was indicated in the reference paper, but the reaction was unable to reach completion even after 3 days. The procedure was modified: the solvent was removed, and a water cooling condenser was replaced by a short air cooling condenser. The by-product of this reaction is bromoethane, since its boiling point is around 50°C, the modification mentioned above, allows the bromoethane to escape from the system, so the chemical balance can never be reached. As a result, this step reaction can be completed within 12 hours. Another reason for using the neat reaction is that the phosphate compound has a very high boiling point, and it is very difficult to remove if excess amount was used.

Important note:

The phosphorous atom has 15 protons and 16 neutrons, so the adjacent H or C peaks on the NMR spectra will be split.

2.1.4 Step 4: Oxidation reaction



The temperature control is the key point of this reaction, and it should be less than 110 °C. Below 110°C, the reaction will not be completed within 12 hours. Formic acid also has been tried as the solvent, the result was not as good as acetic acid. (The reaction was slower.)

After reaction stopped, solvent and excess amount of hydrogen peroxide was directly evaporated. 30-40%wt acetic acid remains in the crude product even after extraction at 100°C under very low pressure. Washing with water is not a good choice, because the product has the sulfonyl group and it partially dissolves in the water. The phosphate group is also sensitive to the water. Product purified by water showed strange peak. The best way to get rid of acetic acid is using a short silicone column (5-7cm), and using chloroform as the solvent. Acetic acid can be removed by going through such a short column twice.

Important notes:

Once reaction is 100% completed, the aromatic hydrogen will show two single peaks on the proton NMR spectrum, one is about 7.9ppm, and another is about 7.0ppm. If the reaction is not 100% completed, four peaks will appears at 7.00-8.00ppm ranges. Hydrogen peroxide needs to be stocked in the refrigerator, and the bottle should be sealed properly. The reason for several failed experiments was found that the hydrogen peroxide was not found kept well, and after changing the new bottle, the problem was solved.

2.2 Synthesis and properties of polymer

2.2.1 Synthesis of polymer

The Wittig-Horner-Wadsworth-Emmons(WHWE) type coupling polymerization reaction was used to synthesize SF-PPV-I. Strong base such as KOBu, NaH, KOH, organic base [1] and polar solvent such as THF, toluene, DMF, dioxane could be used. However, the best combination of NaH and THF was found to have the best results. KOH is too weak to synthesize high molecular weight polymer, however, it still can be used with DMF to make 1-2 repeat units oligomers. KOBu is the strongest base among them, but the purification part is more difficult than NaH. Organic base also has been tried, but the product shows very low photoluminescence emission, and the molecular weight is much lower than NaH.

DMF is too polar, and that reaction is much faster than other solvent. If DMF used, the end –CHO group are not obvious in NMR. Toluene is not polar enough to synthesize high molecular weight polymer, and reaction is very slow. NaH with THF is the best combination. The reaction normally can be completed within 24-72 hours. It is relatively easy to control the polymer size. After reaction is completed, NaH should be quenched by methanol but not water, otherwise a black solid will be formed during the quenching process. Excess NaH should be used, otherwise the reaction will be slow.

The polymer length can be controlled by changing the reaction condition such as temperature, reactant ratio, solvent, and base. Monomer with $-C_8$ side chain coupling with different ratio of dialdehyde under same temperature and solvent has been done.

Table 2.1 Block Size versus Reaction Conditions

Reaction ID	Reactant Ratio (Monomer 5: dialdehyde)	Mw(Dalton, via GPC)	Average repeat units	Average size(nm)
1	1 : 0.80	3,800	6	7
2	1 : 0.85	7,050	14	17
3	1 : 0.95	8,800	17	20

All reactions are under same condition: Solvent : THF
Reaction temperature : room temperature
Reaction time : 24 hours

2.2.2 Polymer properties

2.2.2.1 Solubility

Polymers with different side chains show different solubility. For the SF-PPV-I, the best one is the polymer with ethylhexyl groups. It cannot be to precipitated out from methanol, and can dissolve in most organic solvents, such as chloroform, DMSO, THF, DMF, etc. Such kind of polymer with a molecular weight up to 10,000 at room temperature is still a high viscosity liquid or semi-solid.

The solubility of the polymer with decyl group is also good, even when its molecular weight reaches 10,000, it still can dissolve in chloroform, THF and DMF.

When side chain is $-C_2H_5$, the solubility is poorer than the other two mentioned above. When molecular weight is over 2,000, it will be hard to dissolve in most commonly used organic solvents

.

2.2.2.2 Photoluminescence and UV-Vis spectra [2]

The photoluminescence spectra of SF-PPV in methylene chloride (concentrated solution, Figures 2.17-19) typically have excitation peaks around 480-490nm, and emission peaks around 520-550nm. Polymers with different molecular weight or with different alkyl side chains (*i.e.*, C2, C8 or C10) show little change of the excitation and emission peak positions.

In solvent, at low concentrations, solvent-solute interaction is dominant in comparison to the solute-solute interactions as in thin films. As shown in Figures 2.17-20, in comparison to donor RO-PPV blocks [2,3], a similar trend was observed, *i.e.*, the excitation maximum was blue shifted from about 490 nm (2.53 eV, A in solution) to 420 nm (2.95 eV, BAB in solution), and then further to 370 nm (3.35eV, A film) respectively, yet the emission maximum first blue shifted from about 530 nm (2.34 eV, A in solution) to about 490 nm (2.53 eV, BAB in solution), then red shifted to about 580 nm (2.14 eV, A film). The reasons were explained in ref [2].

The inter-molecular interaction can also be observed in the PL spectra of the different concentration polymer solution. As shown in Figure 2.19, the peak positions and shapes of the PL spectra of polymer solution does not exhibit big shift until the solution concentration reduced to 10% of the saturated one. A new peak appears in shorter wavelength at 490nm. Reduce the concentration to 5%, the 490nm peak becomes higher than 530nm peak. However, even at very dilute concentration, both 490nm and 530nm peaks co-exist with 530nm peak become weaker at lower concentration. We speculate that the 490nm peak is possibly due to single SF-PPV-I chain, and that the 530nm peak is due to molecular aggregates in solution, so that the inter-chain orbital interaction lowers the emission optical gap.

Most of UV-Vis absorption spectra of SF-PPV (in relatively concentrated solution) have an abroad absorption band from 300-520nm (Figures 2.21-22). The offsets of UV-Vis absorption peaks normally are between 500-520nm, which indicate the energy gap of SF-PPVs are about 2.4eV.

2.2.2.3 Cyclic Voltammetry of SF-PPV and RO-PPV

Cyclic voltammetry is the most versatile electrochemical technique for the study of electroactive species, and it is widely used in industrial and research laboratories. Cyclic voltammetry is also a very sensitive measurement, and a small amount of water or impurity will totally change the results.

For the electro-active polymers synthesized in our lab, most times there are no reference data of cyclic voltammetry measurements. To make sure the result is accurate, the anhydrous solvent should be used, and before the experiment, the solvent has to be bubbled with nitrogen gas for at least 20 minutes to remove oxygen. (The presence of water and oxygen will dramatically change the results). The electrode condition is also critical. During the experiment, the compound will slowly deposit on the surface of electrodes, so between the experiments, the surface of the electrodes must be cleaned or polished. 2-10mM Potassium Ferricyanide [$K_3Fe(CN)_6$] in 1M KNO_3 is typically used for a standard cyclic voltammogram and it should be measured before and after polymer measurements to check the cyclic voltammeter performance.

2.2.2.4 Energy levels [3]

One basic method to estimate the energy levels of PPVs is to estimate the optical energy gap from the UV-Vis spectra, and estimate the HOMO or LUMO level by the cyclic voltammograms. The equation to estimate the energy gap (Eg) by UV-Vis absorption spectra is:

Eg (eV) = 1240/ offset of UV-Vis absorption peak (nm) 2.1

In the case of SF-PPV-I, the offset is about 520nm. From the equation above, the estimated Eg is about 1240/520=2.4 eV. For RO-PPV, the offset is about 500nm, the estimated Eg is about 1240/500=2.5eV.

The equations to estimate the HOMO or LUMO levels are [3]:

HOMO level of donor = -{4.3 (potential of Ag/AgCl electrode) + donor anodic peak onset} 2.2

LUMO level of Acceptor = -{4.3 (potential of Ag/AgCl electrode) + acceptor cathodic peak onset } 2.3

In the case of SF-PPV-I, which is an acceptor, LUMO level=-{4.3+(-0.7)}=-3.6 V; for RO-PPV which is a donor, HOMO level =-{4.3+0.9}=-5.2eV. Combined with the estimated energy gap, the HOMO-LUMO level for SF-PPV is about –3.7/-6.0V, and RO-PPV is about –2.7/-5.2V. The results of HOMO-LUMO level confirm that in compassion to RO-PPV, SF-PPV indeed is an electron acceptor.

2.2.2.5 Thermal properties

Polymer with C2 side chains shows higher thermal stability than those with C10 side chains. This is possibly due to the closer inter-chain interaction in C2 then in C10 polymers. DSC and TGA measurements had been done (Figures 2.1-2).

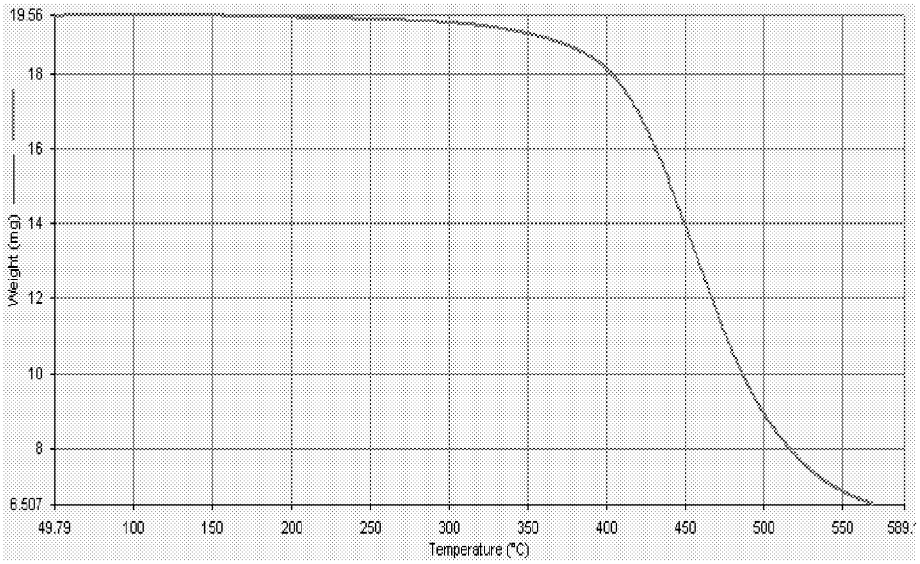


Figure 2.1 TGA of SF-PPV-I with -$C_{10}H_{21}$ Chains

Polymer Sample: C10 side Chain, Mw=10,000(18 repeat units, 25nm)

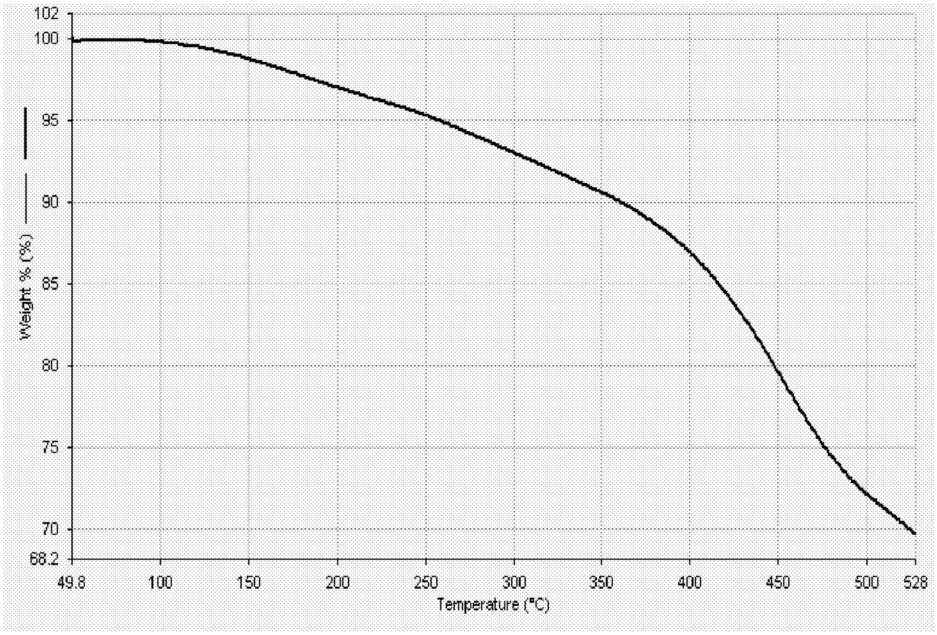


Figure 2.2 TGA of SF-PPV-I with $-C_2H_5$ Chains

Polymer sample: C2 side chain, Mw= 1500 -2000(4-5 repeat unit, 6-8 nm),

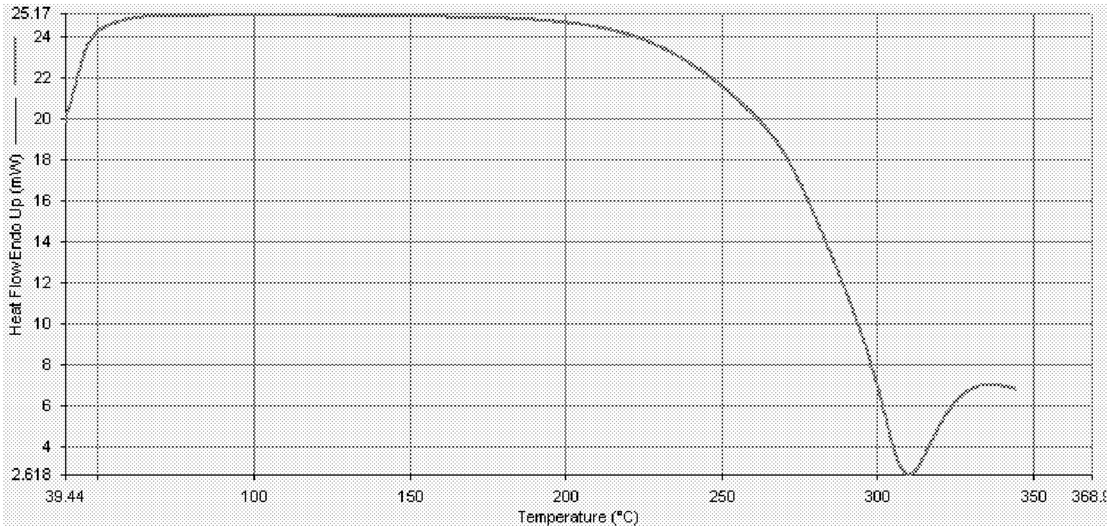


Figure 2.3 DSC of SF-PPV-I with $-C_{10}H_{21}$ Chains

Polymer Sample: C10 side Chain, Mw=10,000(18 repeat units, 25nm)

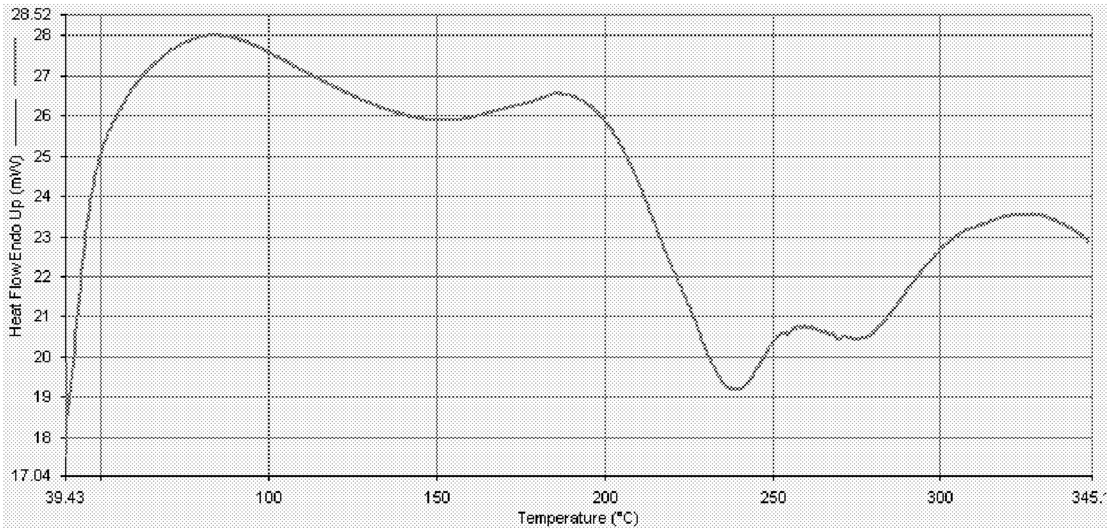


Figure 2.4 DSC of SF-PPV-I with $–C_2H_5$ Chains

Polymer sample: C2 side chain, Mw= 1500,-2000(4-5 repeat unit, 6-8 nm),

2.3 Conclusion [4-8]

In summary, a new processable, terminally functionalized acceptor (n-type) sulfone derivatized conjugated polymer SF-PPV-I has been synthesized and characterized. Since the sulfone group is a well-known stronger electron withdrawing group in comparison to cyano group, the SF-PPV-I is a stronger acceptor polymer alternative than existing CN-PPV. SF-PPV-I is also more processable in comparison to C60. The functional terminals of SF-PPV-I also offer convenience for synthesizing block copolymer nano structures. The average size of SF-PPV-I oligomers can be controlled via synthetic conditions. Finally, the SF-PPV-I can be coupled with donor (p-type) conjugated polymers (such as RO-PPV) to fabricate P/N heterojunction related opto-electronic devices.

2.4. Reference

[1] Simoni, D, et al., *Organic Letter*, **2000**, 2, 24, 3765

[2] Sun, S.; Fan, Z.; Wang, Y.; Taft, C.; Haliburton, J.; Maaref, S.; "Synthesis and Characterization of a Novel –D-B-A-B- Block Copolymer System for Light Harvesting Applications", *SPIE*, **2002**, vol. 4801, in press, and presentation at SPIE 2002 annual convention, Seattle, Washington, July, 2002.

[3] Janietz, S., et al, *Applied Physics Letter*, **1998**, 73, 7, 2453.

[4] Fan, Z., MS Thesis: "Synthesis and Characterization of a Block Copolymer System Containing RO-PPV and SF-PPV Conjugated Blocks", Norfolk State University, Norfolk, Virginia, 2002

[5] Wang, Y., Sun, S.; et al., *Chem. Mater.*, submitted recently

[6] Wang, Y. Fan, Z., Taft, C. and Sun, S., *Poly. Mater. Sci. Eng.*, **86**, 67 (2002).

[7] Fan, Z.; Wang, Y.; Taft, C.; Haliburton, J.; Maaref, S. and Sun, S., *Poly. Mater. Sci. Eng.,* **86***,* 47 (2002).

[8] Sun, S.; Fan, Z.; Wang, Y.; Taft, C.; Haliburton, J.; Maaref, S.; *SPIE Proc.*, **4465**, 121 (2001).

3. BLOCK COPOLYMER SYNTHESIS & STRUCTURE CHARACTERIZAIONS

3.1 General Experimental Information

All starting materials, reagents and solvents were purchased from commercial sources and used directly except noted otherwise. NMR data were obtained from a Bruker Avance 300 MHz spectrometer (TMS as reference). Elemental Analysis was done by Atlantic Microlab Inc. Polymer molecular weight analyses were done using a Viscotek T60A/LR40 triple-detector GPC system with mobile phase of THF at ambient temperature (Universal calibration with polystyrene as standard). UV-VIS spectra were collected using a Varian Gary-5 spectrophotometer. Luminescence spectra were obtained from an ISA Fluoromax-3 luminescence spectrophotometer. For the spectroscopic measurement of polymer solutions, methylene chloride was typically used as the solvent. FT-IR data were obtained from a Nicolet Avatar or Bruker IFS-66 FT-IR spectrometer. Polymer films were prepared from spin coating or drop drying via 0.2 micron filtered methylene chloride polymer solutions on the pre-treated glass slides, and the films were typically dried overnight in heated vacuum oven before any analysis. The thermal analysis was done on a Perkin-Elmer TGA6/DSC6/TMA7 system. The electrochemical data was obtained from a Bioanalytical (BAS) Epsilon100 CV system. In CV measurements, the concentration of polymer solutions (in methylene chloride) was typically 2mM, and the salt $(Bu)_4NPF_6$ concentration was 0.1M. Reference electrode was a standard Silver electrode. The CV scan rate was 100mV/s.

For the final –DBAB- block copolymer, a general synthetic scheme for the synthesis of the polymers (Figure 3.1) is as follows: For instance, in first scheme, one molar quantity of donor block [D] were added slowly and drop wisely into access amount (more than 2 molar quantity) of bridge units [B] in a polar aprotic solvent (such as dichloromethane) under reflux to yield –BDB-. In next step, -BDB- was reacted with about equal amount of donor (D) block yielding final –DBAB- type block copolymers. Alternatively, -BAB- can be synthesized first and then coupled with donor block.

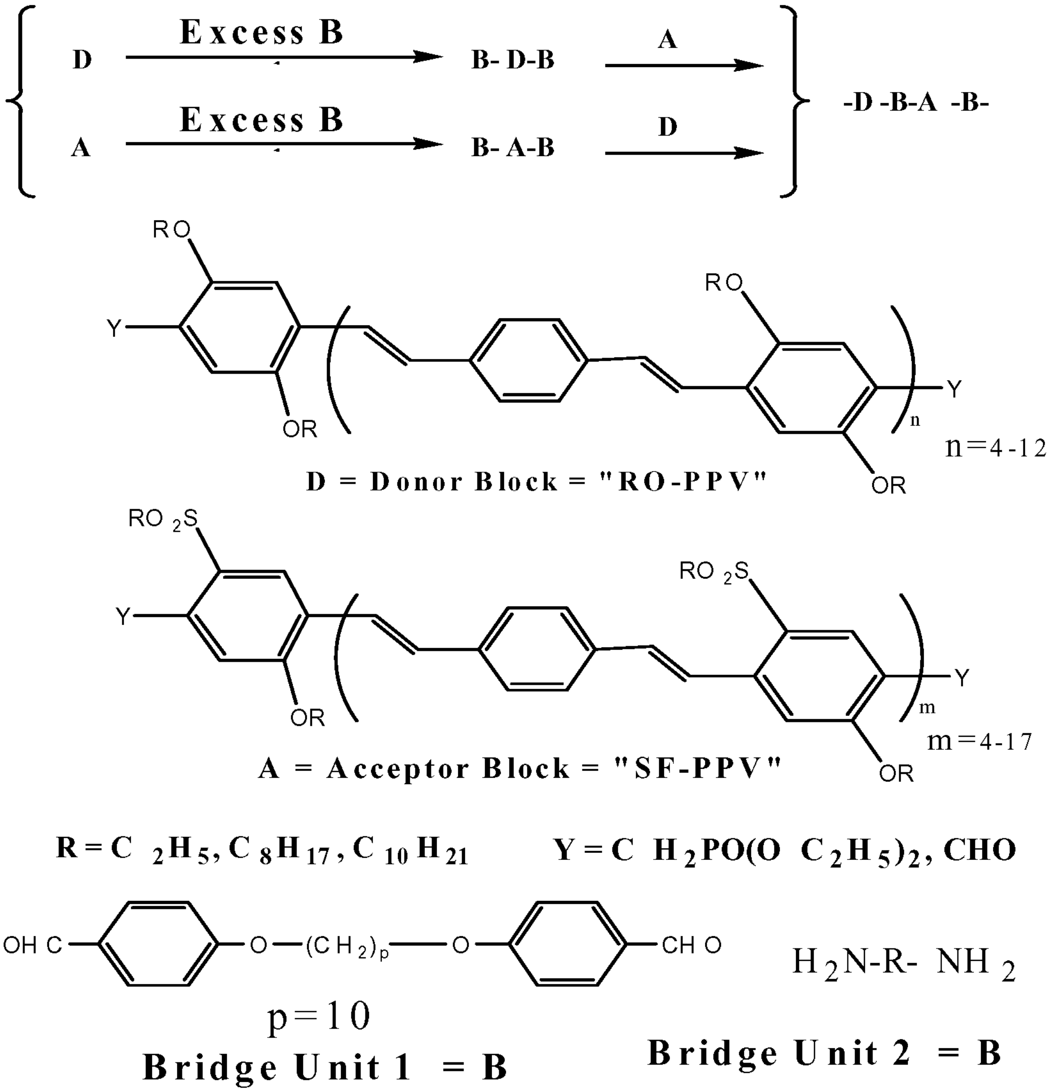


Figure 3.1 Synthetic Scheme of the block copolymers

3.2 Donor Block Synthesis

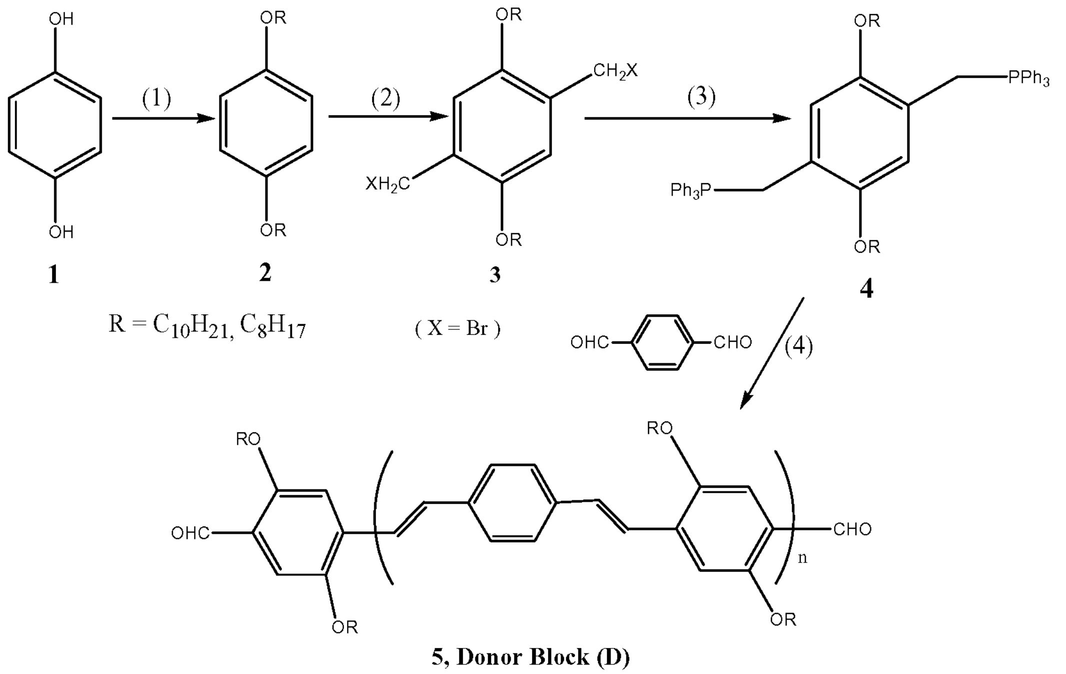
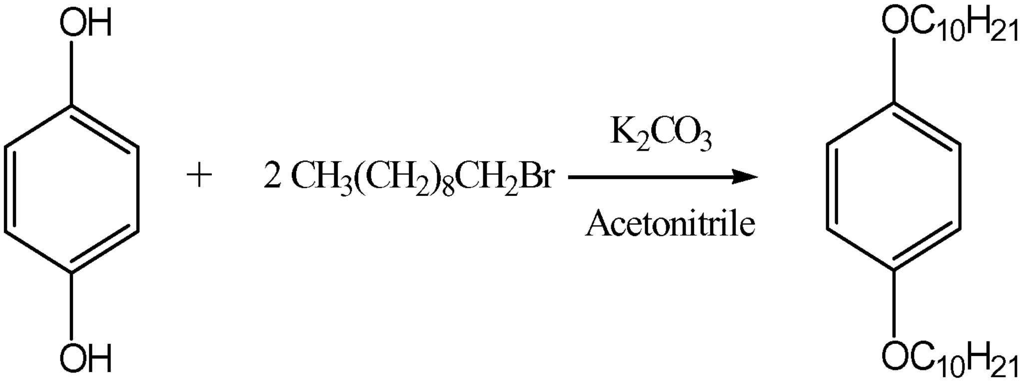


Figure 3.2 Synthetic Scheme of a Donor Block

In the synthesis of donor block, both C_8H_{17} and $C_{10}H_{21}$ were used as different side chain group to the benzene ring. The reaction conditions and scheme are similar. Different lengths of the side chain were proved to affect little of donor block's opto-electronic properties. It will only affect the physical properties of the monomers and donor block, such as the thermal and solubility properties. Below is a detailed procedure to synthesize the donor block with $C_{10}H_{21}$ side chain.

Step (1) Synthesis of 1,4-Bis(decyloxy) benzene (compound 2).

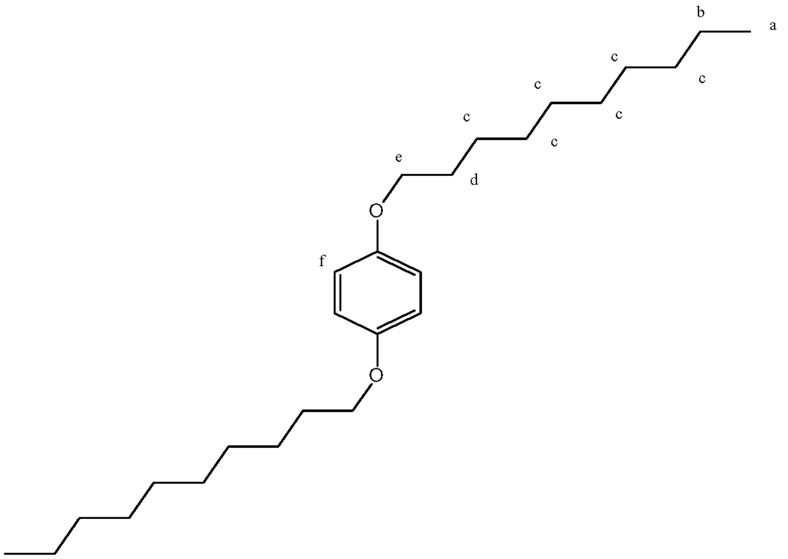


1 **2**

This reaction is a typical Williamson ether synthesis reaction. A suspension of 1,4-hydroquinone **1** (27.5 g, 250 mmol), 1-bromodecane (155ml, 750 mmol), and K_2CO_3 (104.0 g, 750 mmol) in acetonitrile (500 ml) was heated at reflux for two days before being poured into water (600 ml). The precipitates were first collected by filtration and then dissolved in a minimum of hot hexane. Subsequently, the resulting hot solution was poured into methanol (600 ml) to precipitate the product. The precipitates were filtered off and dissolved in hot hexane (200 ml) again. Reprecipitation of resulting solution in methanol then gave 83.0 g pure product **2** as a white solid after filtered and dried under vacuum (85% yield). Melting Point (m.p.) is 66~68°C. ^1H NMR ($CDCl_3$) δ (ppm) 0.88 (t, J=6.86 Hz, 6H, CH_3), 1.27 (m, 12H, $OCH_2CH_2CH_2(CH_2)_6CH_3$), 1.45 (m, 4H, $OCH_2CH_2CH_2(CH_2)_6CH_3$), 1.78 (quintet, 4H, J = 8.14 Hz, $OCH_2CH_2CH_2(CH_2)_6CH_3$), 3.85 (t, J = 6.40 Hz, 4H, $OCH_2CH_2CH_2(CH_2)_6CH_3$), 6.82 (s, 4H, aromatic). Figure 3.3 is the ^1H NMR spectra of compound 2, 1,4-Bis(decyloxy) benzene.

Notes:

In this step, excess amount of 1-bromodecane and K_2CO_3 were used to move reaction forward more quickly and all the 1,4-hydroquinone was reacted. The excess 1-bromodecane and potassium hydroxide can be removed by pouring the reaction solution into water, since both of them are well dissolved in water. The color of the reaction solution changes from bright yellow to brown at the end of reaction. The reaction process was monitored by thin layer chromatography (TLC, a mixture of Hexane and Ethyl Acetate with ratio 2 to 1 as solvent) to ensure the reaction is complete.



Structure of **1,4-Bis(decyloxy) benzene, compound 2**

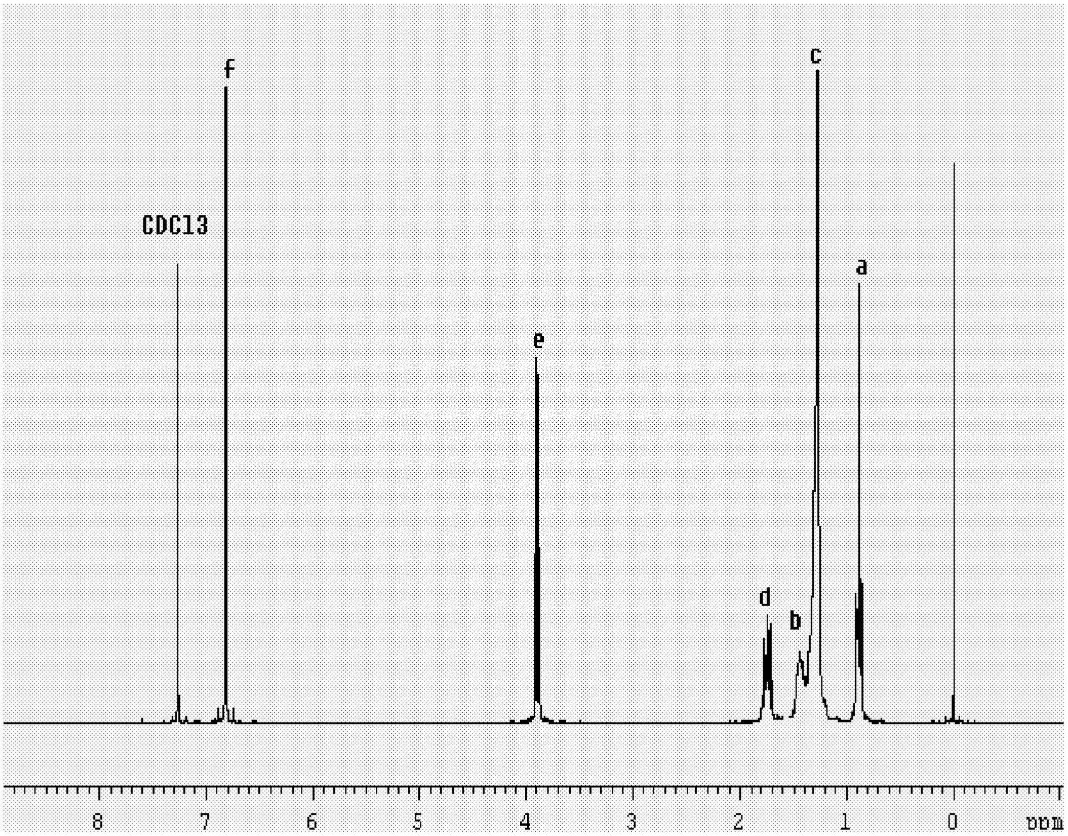
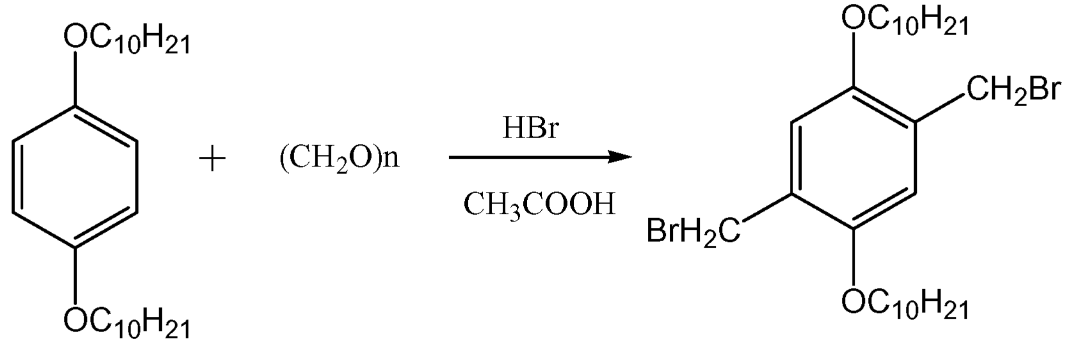


Figure 3.3 ^{1}H NMR spectra of compound **2** (1,4-Bis(decyloxy) Benzene)

Step (2) Synthesis of 2,5-Bis(bromomethyl)-1,4-bis(decyloxy)benzene (compound 3).

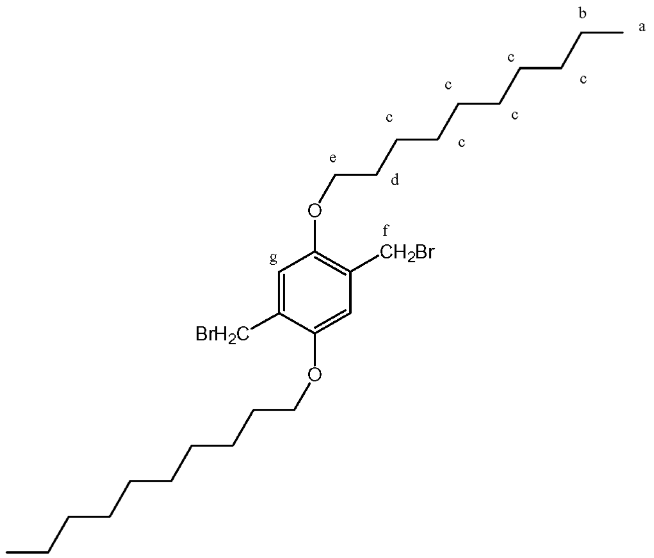


2 **3**

To a suspension of **2** (5.9 g, 15.1 mmol) and paraformaldehyde (0.93 g, 31.0 mmol) in acetic acid (50 ml) was added HBr (6.0 ml, 31 wt % in acetic acid) all at once. This mixture was then heated to 60-70°C with stirring for 2 hours. As the reaction proceeded; the suspension changed to clear solution first and then became a thick suspension again. After cooling to room temperature, this suspension was poured into water (300 ml). The precipitates were filtered and dissolved in hot chloroform. Re-precipitation of resulting solution in methanol then gave **3** (7.5 g, 86.1 % yield) as a white loose solid after being filtered and dried under vacuum. Melting Point (m.p.) is 70~72° C. ^{1}H NMR ($CDCl_3$) δ (ppm) 0.88 (t, J = 6.86 Hz, 6H, CH_3), 1.27 (m, 12H, $OCH_2CH_2CH_2(CH_2)_6CH_3$), 1.49 (m, 4H, $OCH_2CH_2CH_2(CH_2)_6CH_3$), 1.81 (quintet, 4H, J = 8.14 Hz, $OCH_2CH_2CH_2(CH_2)_6CH_3$), 3.98 (t, J = 6.40 Hz, 4H, $OCH_2CH_2CH_2(CH_2)_6CH_3$), 4.52 (s, 4H, CH_2Br), 6.82 (s, 2H, aromatic).

Notes:

In this step, we cannot add more then 2 moles paraformaldehyde to make the reaction goes faster. The ratio of paraformaldehyde to 1,4-Bis(decyloxy) benzene is a key factor to control the final products structure. If the ratio is higher than 2.3, then both di and tri substitution will occur at the end of reaction. That means in addition to the compound **3**, a side product with three bromomethyl groups on the benzene ring will be generated. Since compound **3** has similar structure with that of the side product, it is hard to separate them. Therefore, the only way to avoid this side product is to strictly control the ratio of paraformaldehyde and 1,4-bis(decyloxy) benzene to 2.0 to 2.1. Also, TLC was used to monitor the progress of reaction to ensure the completion of the reaction.



Structure of 2,5-Bis(bromomethyl)-1,4-bis(decyloxy)benzene (compound 3)

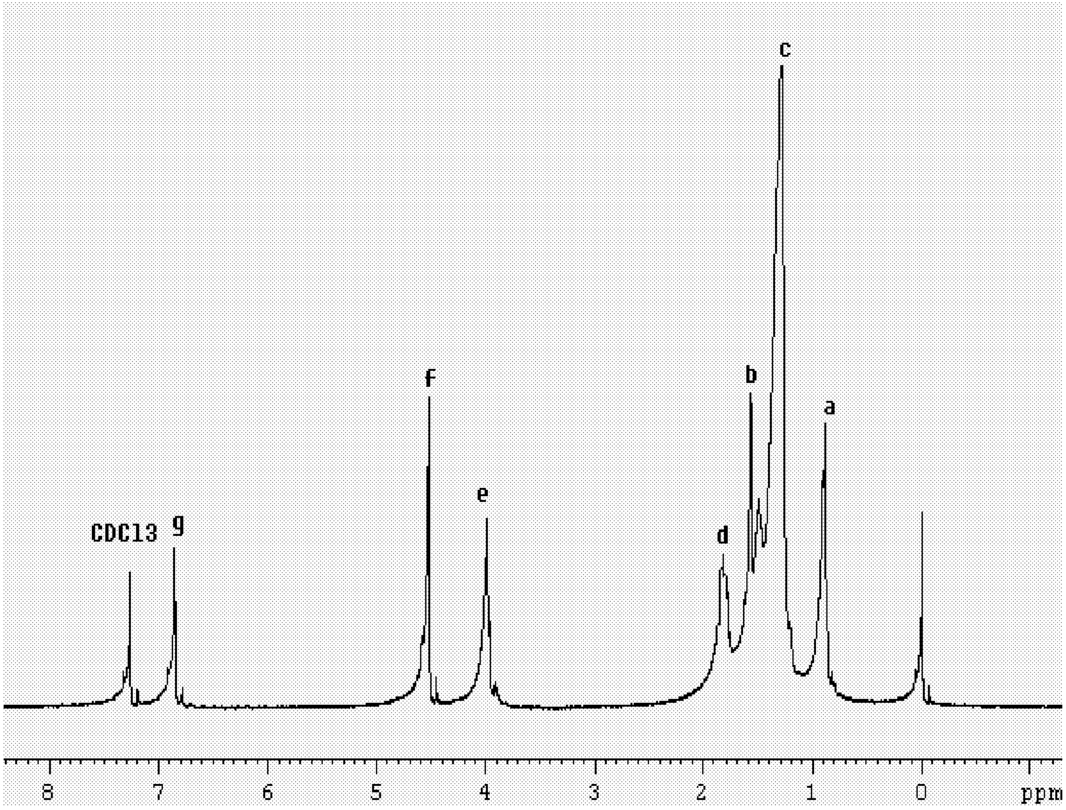
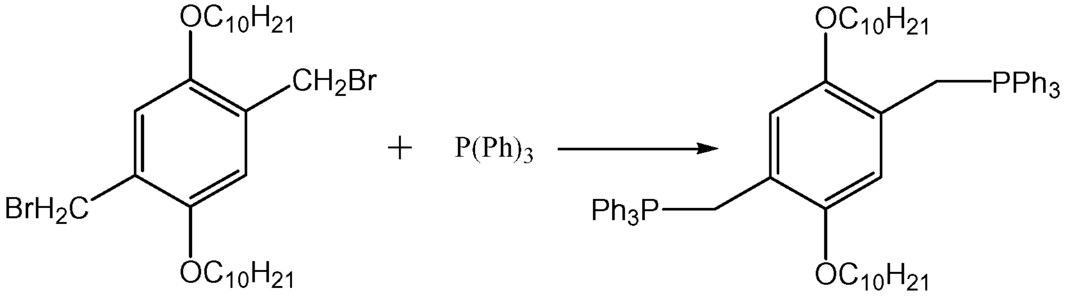


Figure 3.4 ^{1}H NMR spectra of compound **3**.

Step 3 Synthesis of 2,5-bis(decyloxy)-1,4-bis(triphenyl phosphite) benzene



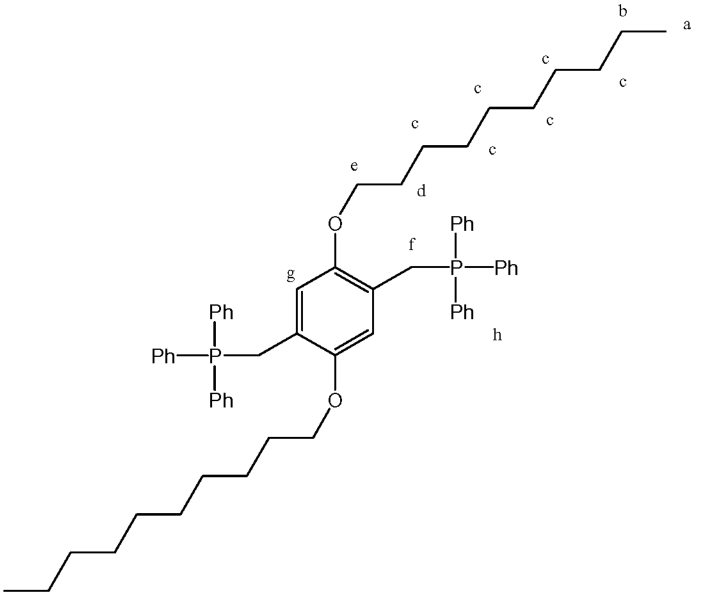
3 **4**

A suspension of compound **3** (0.576 g, 1.0 mmol) and triphenylphosphine (0.550 g, 2.1 mmol) in toluene was heated at reflux for 3 hours. The solvent was then removed from the resulting clear solution under reduced pressure. The resulting residue was then purified by passing through a Gel chromatography column. Melting point (m.p.) is 77~ 79°C. ^{1}H NMR ($CDCl_3$) δ (ppm) 0.88 (t, J = 6.86 Hz, 6H, CH_3), 1.27 (m, 12H, $OCH_2CH_2CH_2(CH_2)_6CH_3$), 1.49 (m, 4H, $OCH_2CH_2CH_2(CH_2)_6CH_3$), 1.81 (quintet, 4H, J = 8.14 Hz, $OCH_2CH_2CH_2(CH_2)_6CH_3$), 2.98 (t, J = 6.40 Hz, 4H, $OCH_2CH_2CH_2(CH_2)_6CH_3$), 5.31 (s, 4H, CH_2PPh_3), 6.82 (s, 2H, aromatic), 7.75 (m, 30H, PPh_3). Elemental analysis result for a not very pure sample gives: C 70.52%, H 6.44%, O 3.56%, calculated: C 69.81%, H 7.14%, O 2.91%. However, high resolution mass of compound **4** with two di ethoxy phosphate groups exhibited a molecular mass at 690.7, which is almost the same with calculated molecular weight (690.8).

Notes:

In step (3), excess amount of tri-phenyl phosphite was used to expedite the reaction. The extra tri-phenyl phosphite can be removed by washing the final solid with methanol. The monomer compound **4** was purified by passing it through a gel chromatography column; the solvent used to pass the column is a mixture of hexane and ethylacetate with ratio 1:2.

In addition to compound **4** with two tri-phenyl phosphite groups on the benzene ring, we also successfully synthesized compound **4** with two di-ethoxy phosphate groups. The procedure is similar. Since the tri-ethoxy phosphite used to do the reaction is a liquid and the boiling point is very low, so no solvent is necessary to do the reaction. This is so called neat reaction and will make it easier to purify the product. . ^{1}H NMR ($CDCl_3$) δ (ppm) 0.88 (t, J – 6.86 Hz, 6H, CH_3), 1.27 (m, 18H, $OCH_2CH_2CH_2(CH_2)_6CH_3$, $PO(OCH_2CH_3)$), 1.49 (m, 4H, $OCH_2CH_2CH_2(CH_2)_6CH_3$), 1.81 (quintet, 4H, J = 8.14 Hz, $OCH_2CH_2CH_2(CH_2)_6CH_3$), 3.23 (d, J = 6.40 Hz, 4H, $OCH_2CH_2CH_2(CH_2)_6CH_3$), 3.85 (d, 8H, $PO(OCH_2CH_3)$), 4.05 (m, 4H, $CH_2PO(OEt_3)$), 6.82 (s, 2H, aromatic).



Structure of the Monomer, compound **4**

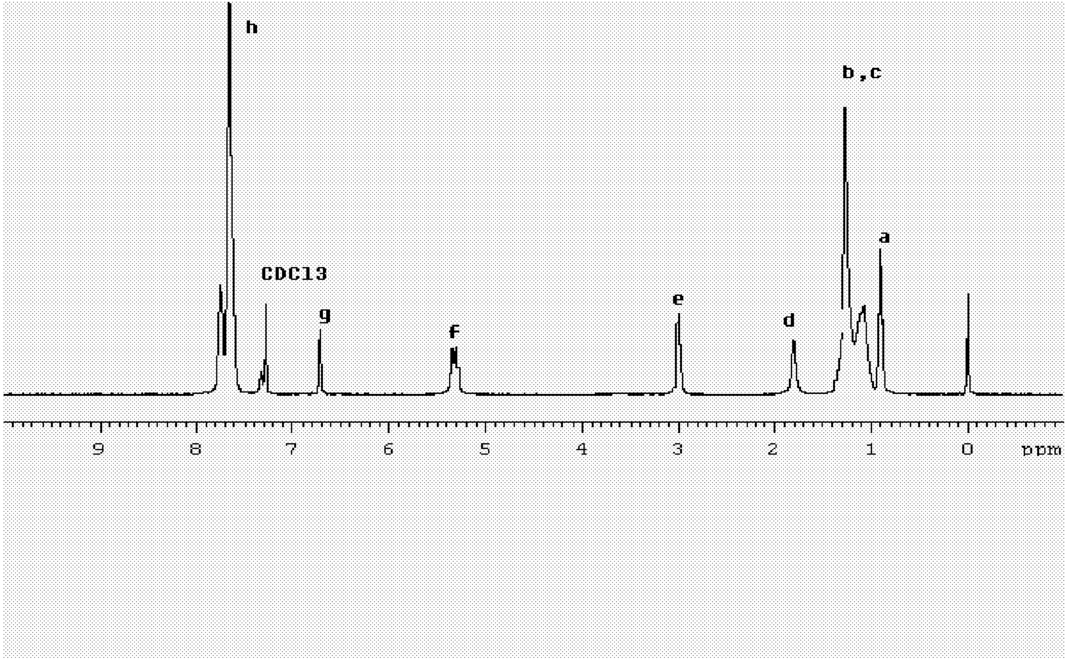
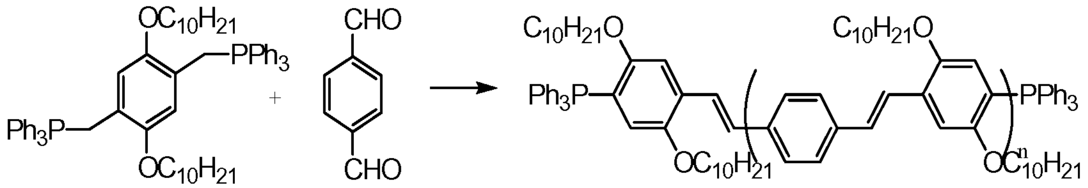


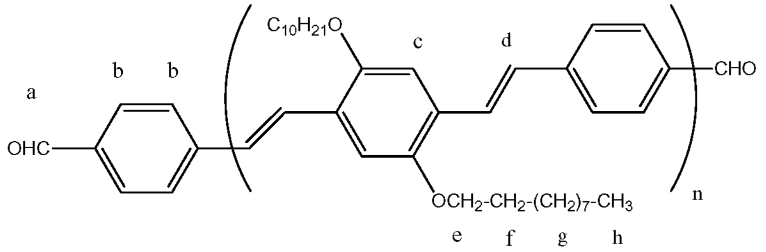
Figure 3.5 ^{1}H NMR Spectrum of Compound **4**

Step 4 Synthesis of 2,5-Bis(decyloxy)-1,4-bis[4-formyl-phenylenevinylene] benzene (donor block 5).



4 **donor block 5**

Compound **4** (1.033 g, 1.1 mmol), along with 1,4-dialdehyde benzene (0.134 g, 1.0 mmol), were dissolved in dry methylene chloride (50 ml). To this solution was added lithium ethoxide solution (4.5 ml, 1.0 M in ethanol) dropwise via a syringe at room temperature. The base should be introduced at such a rate that the transient red-purple color produced upon the addition of base should not persist. The resulting solution was allowed to stir for 12 hours more after the completion of base addition. This solution was then poured into a mixture solvent of dilute aqueous HCl and methanol, adjust the Ph to about 7. The precipitate was separated, washed with water, and dried under vacuum. This afforded 0.66 g of donor block **5** as a redish fluorescent solid. The glass transition temperature (Tg) of a donor block containing 3 repeat units is about 68°C.



Structure of Donor Block 5

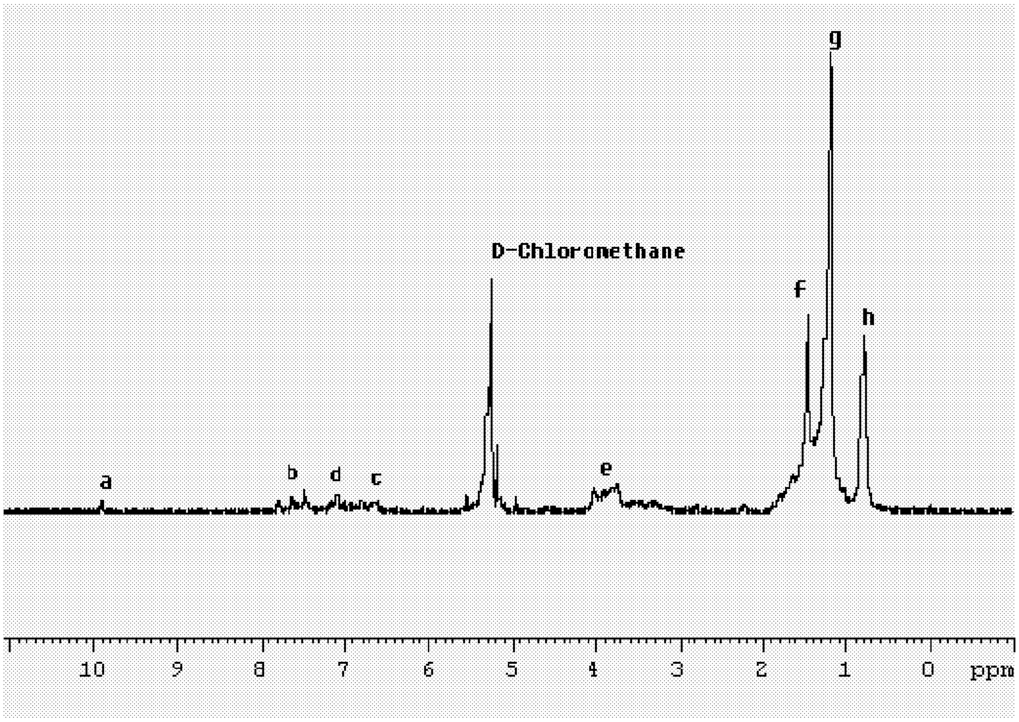


Figure 3.6 ^{1}H NMR Spectrum of **5** (Donor Block)

Notes:

Block **5** was characterized by NMR, GPC and MALDI. Both GPC and MALDI give results of a few thousands molecular weight. The MALDI data also show the distribution of the molecular weight that will be discussed later.

In the synthesis of the donor block **5**, we have tried different reaction conditions to control the donor block's molecular weight, thus we can control the length of the donor block. In general, we use two ways to control the donor block's molecular weight: The first way is to control the two reactants ratio of step (4). Since the two reactants of step (4) have two function groups, in theory, if the ratio of the two reactants is 1:1, the reaction will only stop until the molecular weight is large enough to precipitate out of reaction solution. But if the ratio of two reactants is not 1:1, the reaction will automatically stop at certain stage with the final polymer (or oligomer) ended with the excess function group. For instance, the two reactants we used in step (4) to form the donor block are 2, 5-Bis[triphenyl phosphate]-1, 4-Bis(decyloxy) benzene and 1,4-dialdyhyde benzene, if we use excess amount of 1,4-dialdyhyde benzene in the reaction, then at certain time when the oligomers grow to certain average length, all the triphenyl phosphate were used up and the reaction will stop, leaving the donor block ended with two aldehyde groups.

The second way is to initially use 1:1 reactants ratio but with different reaction conditions to control the block size growth and quench the reaction with a terminator, GPC can be used to monitor the reaction progress. For instance, when the donor block grew to the desired molecular weight, then add some more 2, 5-Bis[triphenyl phosphate]-1, 4-Bis(decyloxy) benzene or 1,4-dialdyhyde benzene to terminated the reaction. Other conditions we can use to control the reaction are reaction temperature, reaction time, the solvent used to do the reaction and the base to initialize the reaction. Normally, the higher the reaction temperature is, the faster the reaction goes. Also, different solvent and base will affect the reaction speed.

Table 3.1 lists some reaction conditions we used to control the reaction, and the molecular weight, donor block length and the average number of repeat unit in the block (C_{10} substituted) we got via the reaction condition control.

Reaction ID	Reaction Condition (monomer 4: 1,4-dialdyhybenzen)	Mw (Dalton, via GPC)	Average # of repeat units	Average Size (nm)	PD
1	30°C for 24 hours (1:1.10)	2250	4	4.8	2.2
2	30°C for 24 hours (1:1.05)	3300	6	7.2	2.7
3	80°C for 24 hours (1:1.05) (DMF as Solvent)	6500	12	14.4	2.9

Table 3.1 Donor Block Size versus Synthetic Condition

3.3 Acceptor Block Synthetic Scheme

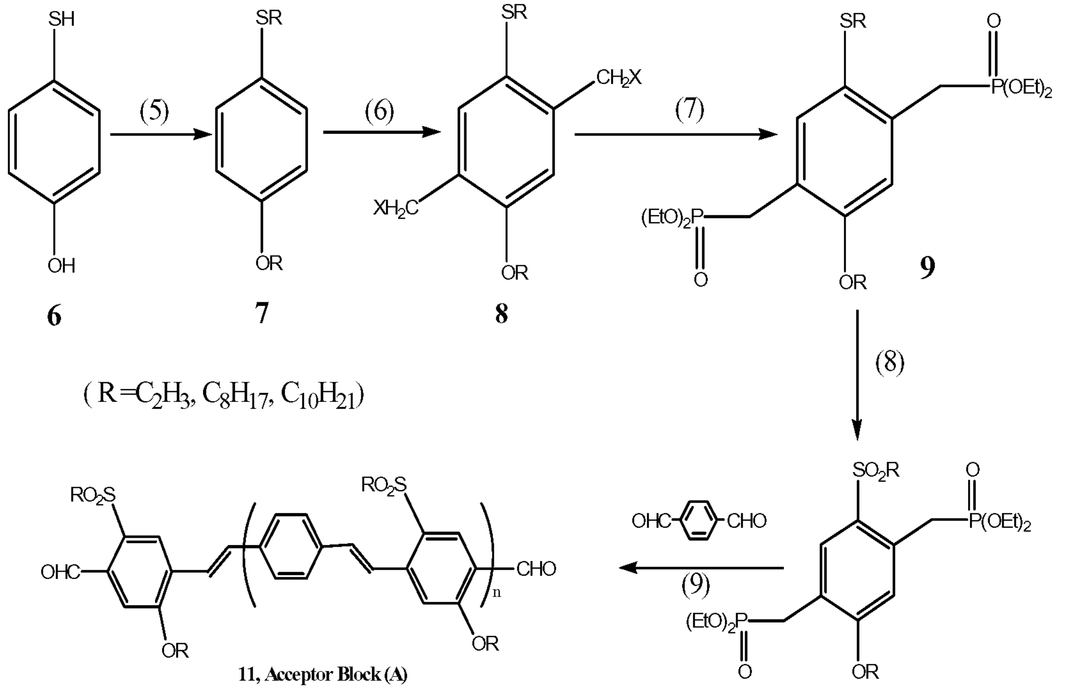


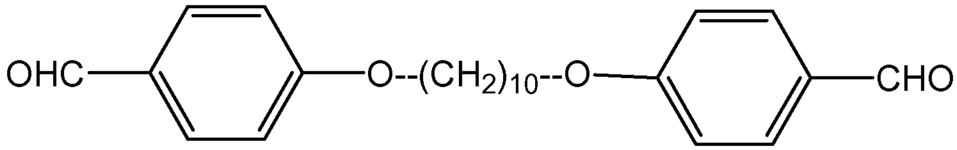
Figure 3.7 Synthetic Scheme of an Acceptor Block (SF-PPV-I)

Acceptor block's synthetic scheme is shown in Figure 3.7. The detailed synthetic procedure of each step and the characterization can be found in previous sections.

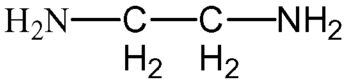
3.4 The Bridge Units

The purpose of using a non-conjugated bridge unit is to separate conjugated donor block from the acceptor block. This will make the electrons at acceptor block and holes at the donor block more difficult to recombine via conjugated main chain. Also, different bridge units may also affect the self-assembly ability as well as the solubility of the final block copolymers.

Figure 3.8 shows the two bridge blocks we have used in our block copolymer system. The di-aldehyde bridge (a) was synthesized in our group. The di-amine bridge (b) was purchased from commercial sources.



(a)



$H_2N{-}\underset{H_2}{C}{-}\underset{H_2}{C}{-}NH_2$

(b)

Figure 3.8 Structures of Bridge Units

NOTE:

We have compared the block copolymers with both bridge units (a) and (b). From table 3.2 shown below, one can see that the solubility and optical properties of the final –DBAB- block copolymers with two different bridge units is almost the same. This is mainly because in comparison to the donor block and acceptor block, the bridge unit is relatively small to affect those properties. λex is the photoluminescence excitation maximum, and λem is the photoluminescence emission maximum.

	H_2N-CH_2-CH_2-NH_2 (B2)	OHC-R_1-CHO (B1)
λex (nm)	480	490
λem (nm)	525	528
Solubility	Good	OK

Table 3.2 Properties versus Bridges

3.5 Block Copolymer Synthesis

a) $$\mathbf{A + 2B \rightarrow B\text{-}A\text{-}B \xrightarrow{D} -(B\text{-}A\text{-}B\text{-}D)-}$$

b) $$\mathbf{D + 2B \rightarrow B\text{-}D\text{-}B \xrightarrow{A} -(B\text{-}D\text{-}B\text{-}A)-}$$

Figure 3.9 General Synthetic Scheme of Block Copolymers

The synthetic strategy of the final –DBAB- block copolymer typically involves using a donor block or an acceptor block to react with excess amount of bridge unit to form the intermediates B-D-B or B-A-B, then equi-molar amount of acceptor block or donor block was added to form the final block copolymer.

For example, 0.5g of donor block **5** (terminated by phosphates) along with excess amount of dialdehyde bridge units were dissolved in dry THF (50 ml). To this solution was added lithium ethoxide solution (4.5 ml, 1.0 M in ethanol) drop wise via a syringe at room temperature. The base should be introduced at such a rate that the transient red-purple color produced upon the addition of base should not persist. The resulting solution was allowed to stir for 48 hours more after the completion of base addition. This solution was then poured into a dilute aqueous HCl, and then poured into 500 ml methanol; the precipitates were collected and washed with water, and dried under vacuum. The –BDB- and the acceptor block (calculated mole ratio is 1:1) were then dissolved in 50 ml dry THF, along with excess amount of t-BuOK. The mixture was stirred under room temperature for 48 hours before poured into 500 ml methanol. The precipitates were collected and dried under vacuum to get a dark redish fluorescent solid, the final –DBAB-type block copolymer.

The above synthetic procedure is for the use of bridge block ended with two aldehyde group. When the bridge unit ended with two amine groups, the synthetic procedure was as below:

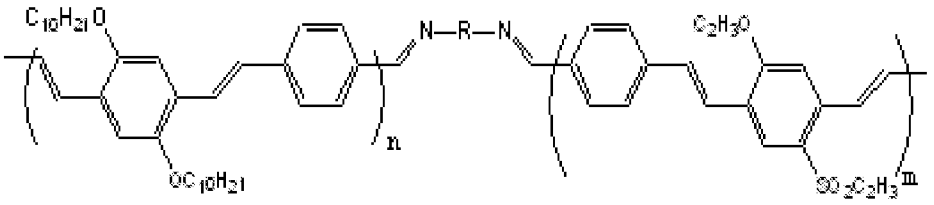
0.5g of **5** along with excess amount of diamine bridge unit were dissolved in dry Toluene (50 ml). The mixture solution was allowed to stir for 48 h more under reflux. This solution was then poured into 500 ml methanol; the precipitates were collected and washed with water, and dried under vacuum. The B-D-B and the acceptor oligomers (calculated mole ratio is between 1:1 and 1:2) were then dissolved in 50 ml dry THF. The mixture was stirred under room temperature for 48 h before poured into 500 ml methanol. The precipitates were collected and dried under vacuum to get a red fluorescent solid, the final donor-bridge-acceptor block copolymer.

Notes:

In the synthesis of the –DBAB- block copolymers, very dry solvent, THF or DMF, are required. If the solvent was not dried enough, the tiny water in the solvents may kill the base, which acts as a catalyst in the reaction. Therefore, the reaction may go very slow or not at all.

Even though the diamine bridge is a liquid, we still can not do a neat reaction without solvent. That is because the boiling point of the diamine bridge is well below the reaction temperature. But the solubility of the donor block and acceptor block in diamine bridge is not good.

Figure 3.10 is the ^{1}H NMR spectra of the final block copolymer with diamine bridge. Compared with the ^{1}H NMR of donor block or acceptor block, the aldehyde peak, which originally appears at around 10 ppm in donor block and acceptor block's ^{1}H NMR spectra, became too weak to see. Also, other peaks that shown in donor block and acceptor block's ^{1}H NMR spectra can be found in that of the final tri-block copolymer and the ^{1}H peak of the bridge was overlapped by those alkene's peaks of donor block and acceptor block. ^{1}H NMR spectra δ (ppm): 0.89 (s, 30H, -CH3), 1.25 (m, 190H, -CH2-), 3.82 (m, 19H, -OCH2-, N-CH2-), 6.68 (s, 8H, aromatic), 7.15(m, 20H, -CH=CH-), 7.46 (t, 15H, aromatic). The ratio of the protons on the benzene ring and the aliphatic protons is somewhat deviate from calculation. Also the aromatic peaks are weak. This may be caused by big volume of the final block copolymer molecules and the bulky size of the side chain that may shield the protons on the benzene ring.



Structure of Donor-Bridge-Acceptor Block Copolymer

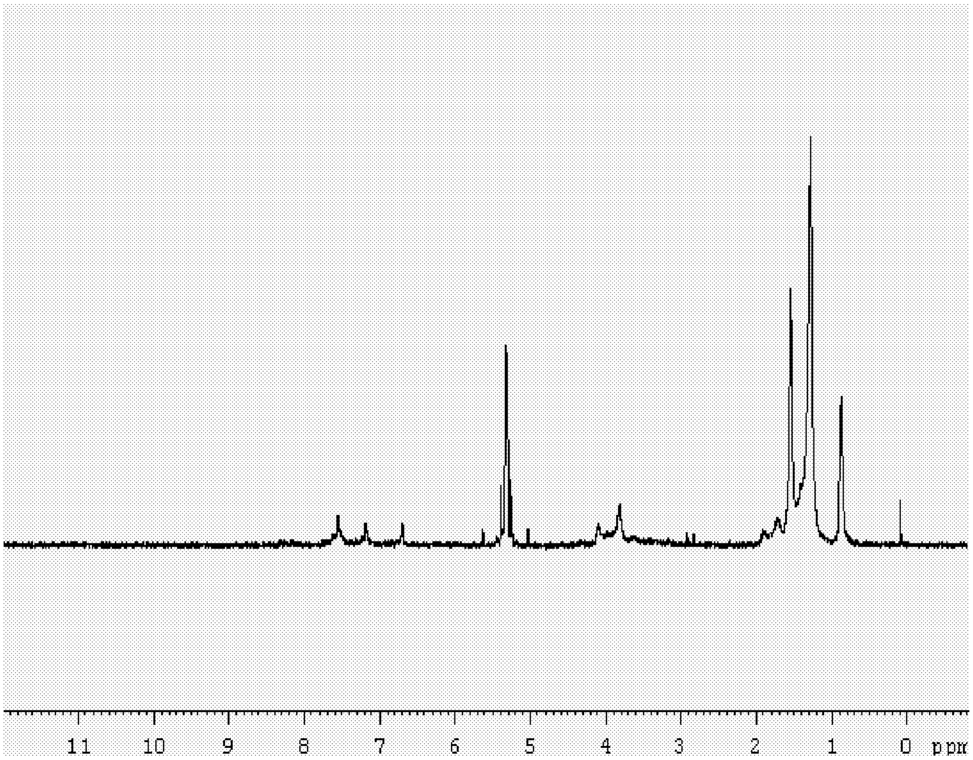


Figure 3.10 ^{1}H NMR Spectra of a Final –DBAB- Block Copolymer

The donor block and acceptor block, as well as the BDB and BAB block, were soluble in THF, while the synthesized BDBA block copolymers is only partially soluble in THF. Most notably, while the donor block or acceptor block were light yellow-reddish color in solid state with very strong luminescence, the synthesized final donor-bridge-acceptor block copolymers were brownish dark color in solid state, and was very weakly luminescence as will be discussed in later section. These also proved the successful coupling of donor block, bridge block and acceptor block.

The final block copolymers were characterized via ^{1}H NMR as well as GPC and MALDI, the MALDI results shows that the molecular weight of a donor-bridge-acceptor block copolymer is almost the sum of the donor block and acceptor block (the MW of bridge unit can be neglected). For example, a donor block was characterized by GPC with molecular weight of 3.2k (6 repeat units, 1 repeat unit is $C_{38}H_{58}O_2$), after coupled with bridge block and acceptor block with molecular weight of 3k (8 repeat units, 1 repeat units: $C_{22}H_{26}O_3S$), the final donor-bridge-acceptor block copolymers was again characterized by GPC, the molecular weight of the final block copolymers is about 6.5k, almost the sum of the donor block and acceptor block. This also verified the successful coupling of donor block, bridge block and acceptor block.

GPC and MALDI analysis shows a polymer molecular weight corresponding to one structure unit of B-D-B-A or B-A-B-D. Since the final block copolymer was only partially soluble in THF, and that filtering (0.2 μm) was applied before the polymer solution was analyzed with GPC, therefore, the GPC results only reflected the soluble part of polymer sample. There might be higher molecular weight block copolymers that are not soluble well in THF and was filtered out. MALDI analysis also confirmed the existence of at least a –D-B-A-B- unit. Though species with higher molecular weight than –D-B-A-B- was not obvious in MALDI data, however, it is also possible that higher molecular weight species may be broke down during laser ablation.

Figure 3.11 is the MALDI data of the donor unit ended with two aldehyde groups. The reaction temperature is room temperature. From figure 3.11, three major peaks can be seen and the difference between two adjacent peaks is 565. The average molecular weight of a donor block repeat unit is about 546 ($C_{38}H_{58}O_2$), which is about 3 % miss to the measured 565. After adding the ending unit, these three peak groups are corresponding to 2, 3, 4 repeat units respectively (Table 3.3). The peaks of 5 repeat units can be also found in the figure. Also, Figure 3.11 shows the polymer distribution of the donor block, this patch of donor block is mainly consist of 3-repeat-unit donor block with about same amount of 2-repeat-unit and 4-repeat-unit donor block and little 5-repeat-unit one.

For the mechanism of MALDI, there is a risk of broken the chemical bond when shinning the laser beam to the molecular. So there might be some high molecular weight polymer in the sample but not shown in GPC or MALDI.

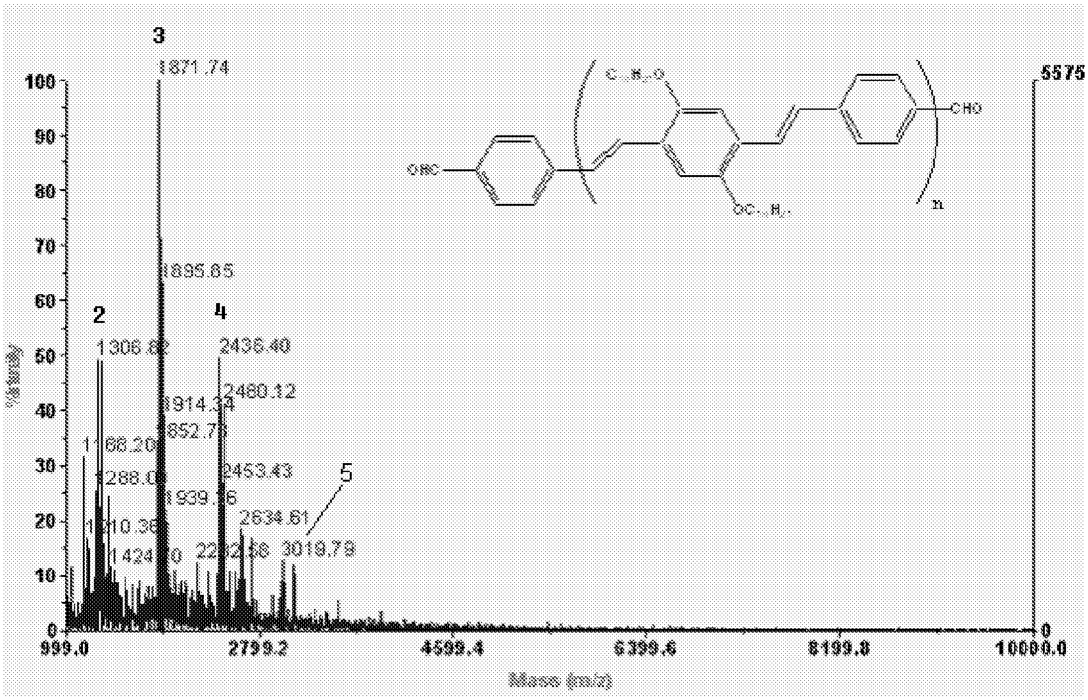


Figure 3.11 MALDI Spectra of a RO-PPV Block

Number of Repeat units	Peak MW	Calculated MW

2	1288	1302
3	1872	1848
4	2436	2457
5	3020	2940

Table 3.3 MW versus Repeat Units

Figure 3.12 is the MALDI spectrum of the final block copolymers. The bridge unit used in this final block copolymers is 1,2-diamine ethylene, and the acceptor block is using the one with -C_2H_3 side chain. The molecular weight of the acceptor block is about 1.2 k (3 repeat units) and the molecular weight of the donor block is about 1.5 k (4 repeat unit). The 1168.22 peak and the 1554.87 peak are the peaks from donor block and acceptor block. The other four peaks, which are labeled a, b, c, d in the figure, are the peaks of the final block copolymers. The difference between any two adjacent peaks is the same. And the biggest peak b (2726), is about the sum of the peaks of donor block and acceptor block. This data also proved the successful synthesis of the final –DBAB- block copolymers. The other a, c, d peaks are about the sum of other donor block and acceptor block.

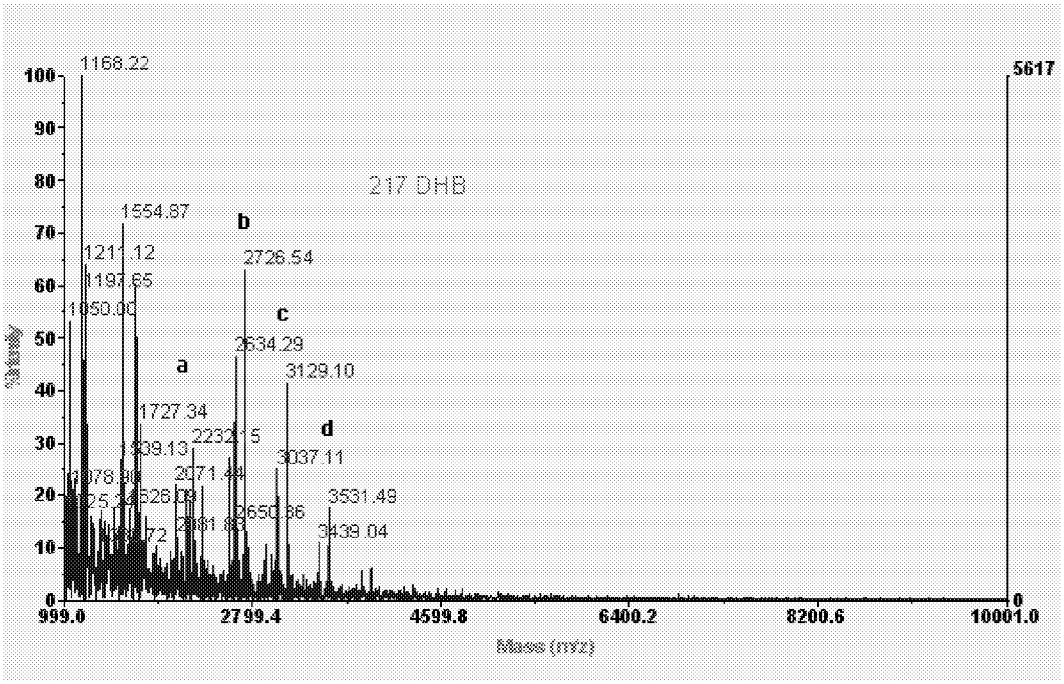


Figure 3.12 MALDI Spectra of a Final –DBAB- block copolymer

4. OPTICAL, ELECTROCHEMICAL, AND MICROSCOPIC STUDIES OF –DBAB- BLOCK COPOLYMERS

4.1 Study of Light Induced Carrier (Free Charge) Generation

In photovoltaic materials, one of the most important properties is the light induced free charge carrier (electrons or holes) generation, it includes the photo-induced electron transfer or charge separation. When a light is irradiated to a photovoltaic material, a photon with certain energy is absorbed, and excitons (electron-hole pairs) were formed. This process is called excitation. Excitons may diffuse in the material within their lifetime, and if they reach a donor/acceptor interface before relaxation, the electrons and holes will separate where electrons will be stabilized in the acceptor phase while the holes will be stabilized in the donor phase. However, if the excitons were not able to diffuse to the donor/acceptor interface during its life time, radiative or non-radiative decay of the excitons will occur. Thus the excitons will decay back to the ground state. In the case of radiative decay, a photon with little longer wavelength then excitation is emitted; this process is called photoluminescence (PL) emission.

Since the main goal of this block copolymers project was to convert efficiently sunlight into electrical energy. By studying the photoluminescence quenching of the material in combination with other techniques, we will know some information about Opto-electronic conversion. Also, by compare the donor or acceptor's photo-luminescence emissions with that of the block copolymers, we will have a better idea on how much excitons are stabilized in the block copolymers system.

Figure 4.1 shows the photoluminescence (PL) excitation and emission spectra of the synthesized RO-PPV donor block dissolved in dichloromethane. In dilute solution, solvent-solute interaction is dominant in comparison to the solute-solute interactions. However, solute-solute interaction (such as in molecular aggregate cases) may not be negligible, particularly at concentrated solutions. As the spectra show, the excitation of the donor block in dichloromethane is at about 480 nm (2.58 eV), and the emission maximum is at about 530 nm (2.34 eV). Interestingly, as shown in Figure 4.2, after coupling with two bridge units, the excitation maximum blue shifted to about 460 nm (2.70 eV), and the emission blue shifted to 515 nm (2.42 eV).

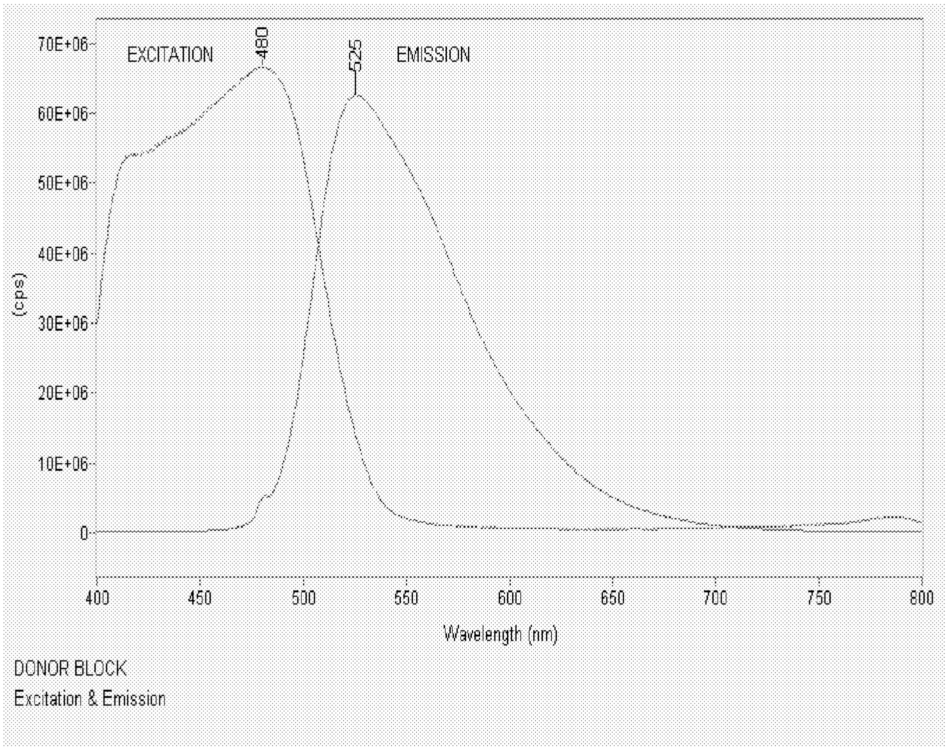


Figure 4.1 PL Excitation and Emission Spectra of RO-PPV in CH_2Cl_2

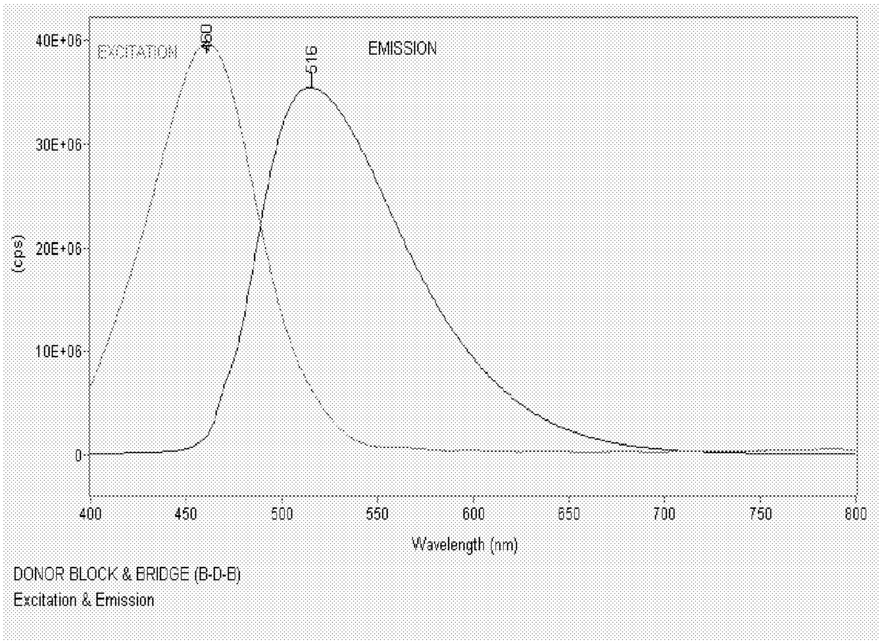


Figure 4.2 PL Excitation and Emission Spectra of BDB in CH_2Cl_2

We speculate that, possibly due to the heavy mass or the long size of the two terminal dialdehyde bridges (a), the effective electronic conjugation of the donor block became shortened due to conjugation backbone distortion, thus optical energy gap increased.

When in thin films states as shown in Figure 4.3, the excitation peak is further blue shifted to about 410 nm (3.02 eV), the emission peak instead red shifted to about 570 nm (2.18 eV). Also, in comparison to solution, thin film peaks become very broadened as expected due to well-known inter-molecular electronic interactions. For the excitation blue shift, one possible mechanism is the electronic conjugation or main chain twist in solid state. For the emission red shift, a well known mechanism is the availability of more vibrational or lattice energy relaxation modes due to solid state molecular interactions.

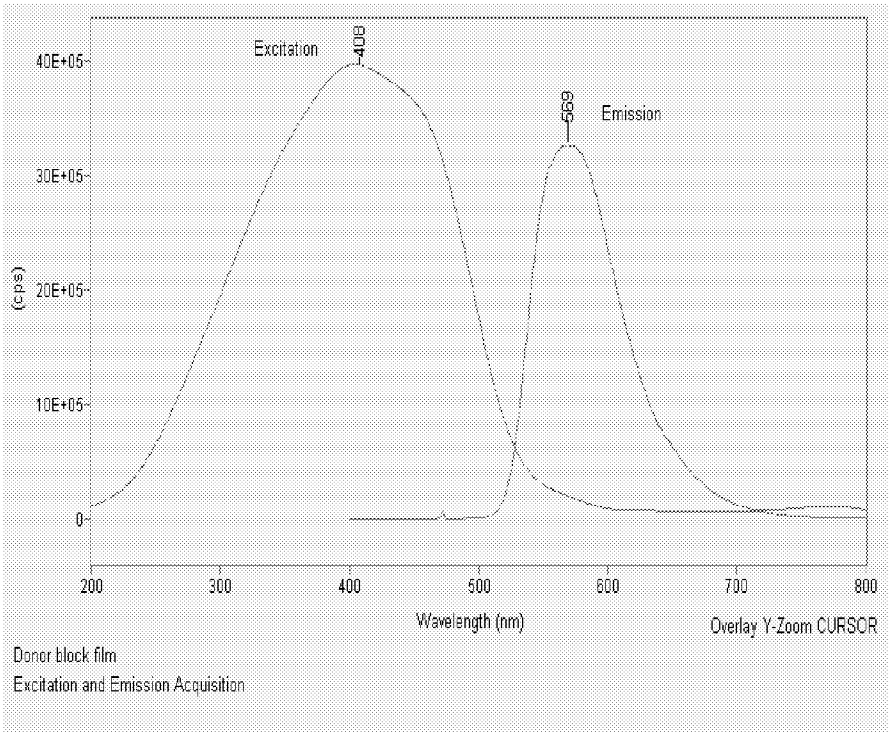


Figure 4.3 PL Excitation and Emission Spectra of RO-PPV film

For optical properties of SF-PPV-I acceptor blocks, as shown in Figures 4.4-4.6, a similar trend was observed, *i.e.*, the excitation maximum was blue shifted from about 500 nm (2.48 eV) to 430 nm (2.88 eV), and then further to 370 nm (3.35 eV) respectively (note the shape of the peak was also affected by film morphology), yet the emission maximum first blue shifted from about 540 nm (2.30 eV) to about 490 nm (2.53 eV), then red shifted to about 590 nm (2.10 eV).

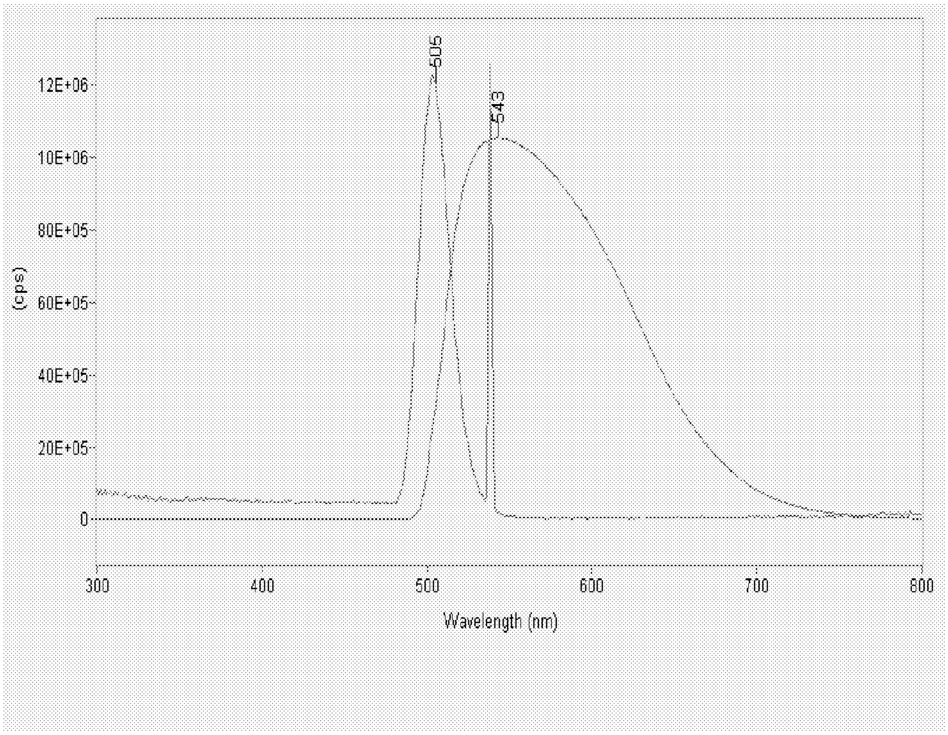


Figure 4.4 PL Excitation and Emission Spectra of SF-PPV-I in CH_2Cl_2

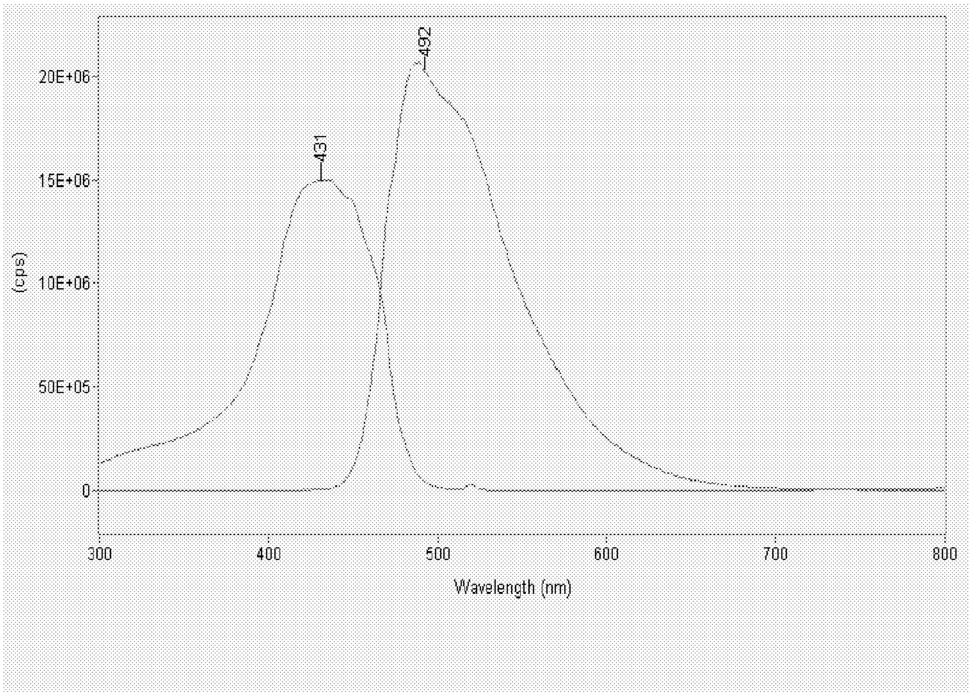


Figure 4.5 PL Excitation and Emission Spectra of BAB in CH_2Cl_2

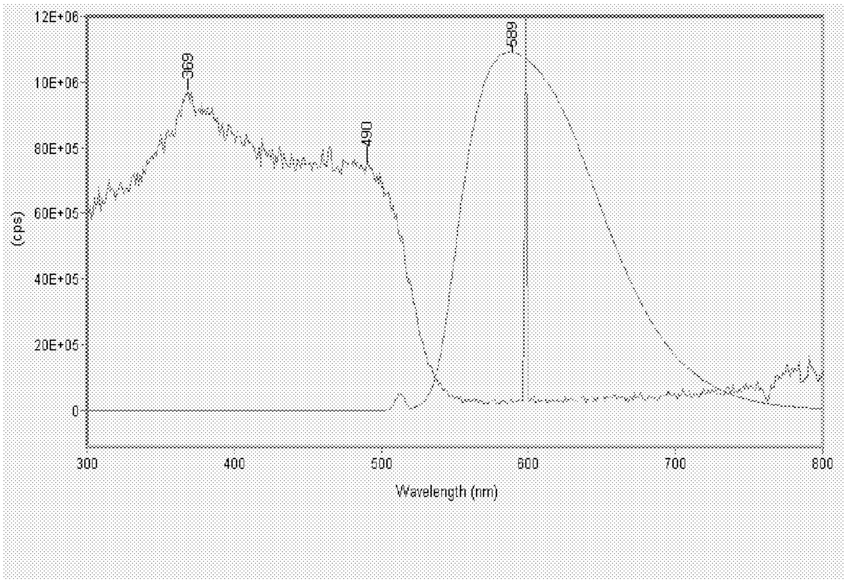


Figure 4.6 PL Excitation and Emission Spectra of SF-PPV-I film

For the final –DBAB- block copolymers, the PL emission was significantly quenched in comparison to the pristine donor or acceptor blocks. Figures 4.7-8 show the emission spectra of the final block copolymers together with those of donor block and acceptor block. Both Figure 4.7 and Figure 4.8 are the simple overlap of three curves, and the peak magnitudes are arbitrary for better view. The actual PL quenching values were derived from molecular density calibrated methods as demonstrated next.

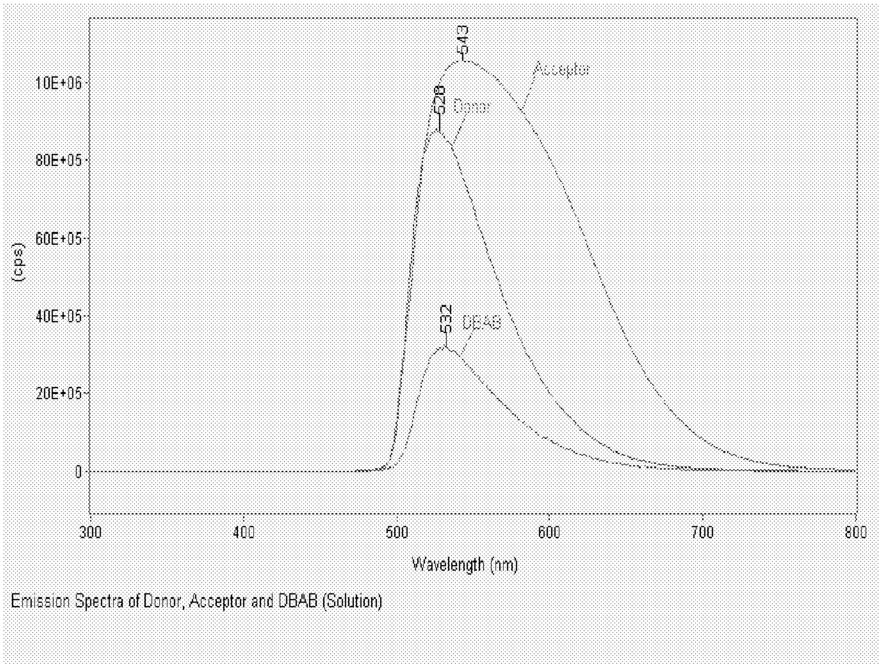


Figure 4.7 PL Emission Spectra of Donor, Acceptor and –DBAB- in CH_2Cl_2

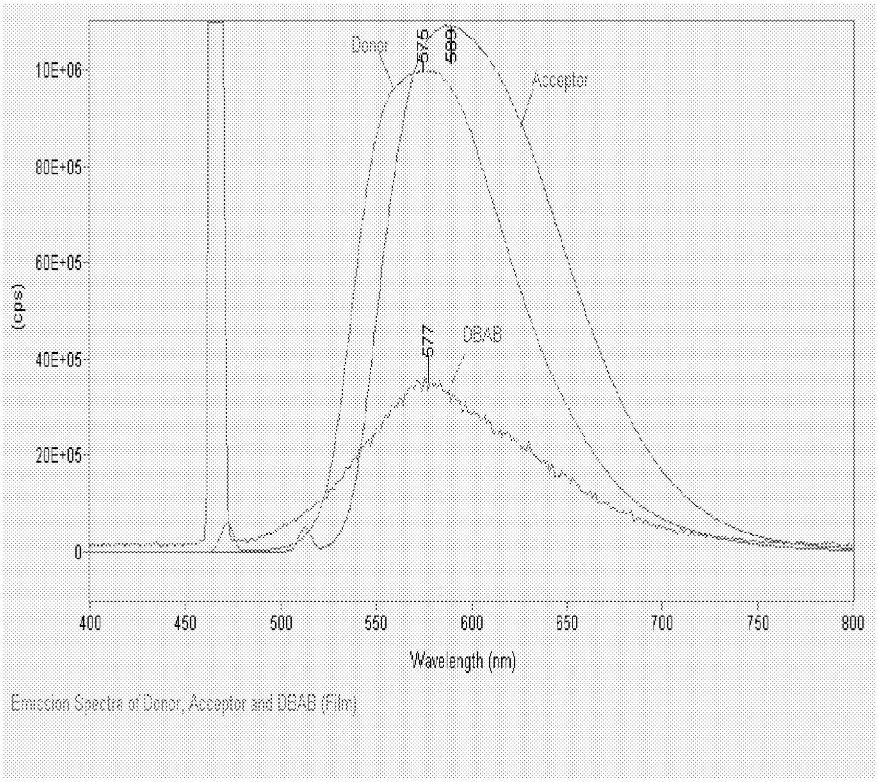


Figure 4.8 PL Emission Spectra of Donor, Acceptor and –DBAB- in film

To estimate the quenching ratio of the final block copolymer versus the pristine donor or acceptor blocks, we first get calibration curves of measured photo-luminescence emission intensity versus densities of donor and acceptor blocks. Then the theoretical PL emission intensity of the final –DBAB- block copolymer can be estimated from densities of both donor (I_D) and acceptor (I_A) inside the final block copolymer. With actual measured PL emission intensity (I_F) of final block copolymer, the quenching ratio η can be calculated out using following equation:

$$\eta = \left(1 - \frac{I_F}{I_D + I_A}\right) \text{x } 100\%$$

I_D : Emission Intensity of Donor from calibration curve

I_A : Emission Intensity of Acceptor from calibration curve

I_F : Measured Emission Intensity of Final Block Copolymers

Table 4.1 PL Emission Quenching Calculation Data

	Density	I_D	I_A	I_F	η
Solution	3.1 mg/ml	62E+06	60E+06	14E+06	~88%
Film	939.92 nm	49E+06	44E+06	32E+05	~97%

Based on the above analytical method, nearly 90% photo-luminescence emission quenching was observed in dichloromethane, and over 97% photo-luminescence emission quenching was observed in –DBAB- films. It demonstrated that the contacts between the donor and acceptor blocks in thin film state are much larger then in solution.

Tables below list the original PL emission data of the acceptor, donor and the final –DBAB- block copolymers in film and in solution respectively.

Film ID	Thickness	S	S/R
A1	531.75nm	943326	32E+07
A2	173.49nm	561229	19E+07
A3	141.87nm	638546	21E+07
D1	740.68nm	354645	71E+06
D2	716.99nm	122639	25E+06
D3	956.02nm	22720	46E+05
Final 1	939.92nm	1310	32E+05
Final 2	358.3nm	5340	48E+05
η			97%

Table 4.2 Thin Film PL Emission Quenching Calibrations

Solution ID	Concentration (mg/ml)	S	S/R
D1	2.4	2.70E+06	6.30E+07
D2	3.2	2.90E+06	6.80E+07
D3	4.2	2.60E+06	6.10E+07
D4	5.2	2.50E+06	5.70E+07
D5	6.0	2.20E+06	5.50E+07
A1	3.28	2.70E+06	5.50E+07
A2	4.52	1.60E+06	3.30E+07
A3	4.92	2.60E+06	5.20E+07
A4	5.94	1.90E+06	3.70E+07
Final	3.1	9.50E+05	1.40E+07
η	-----	-----	88%

Table 4.3 Solution PL Emission Quenching Calibrations

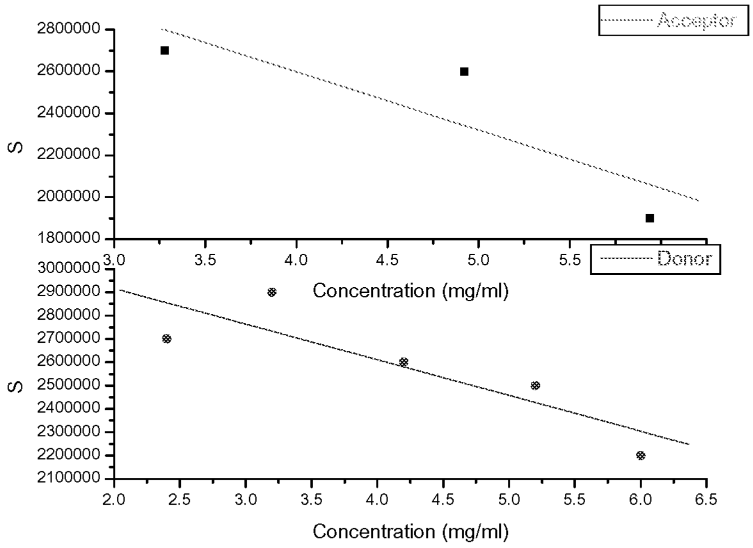


Figure 4.9 Calibration Curves of Donor & Acceptor Blocks (Solution)

Figure 4.9 shows donor and acceptor's solution photo-luminescence emission calibration curves that were built based on the experimental data tables above. The plots are the best linear fit for the original data.

At the same time, the UV-VIS absorptions of final blocks are very similar to a simple overlap of the absorptions of pristine donor or acceptor blocks as shown in Figures 4.10 (dichloromethane) and Figure 4.11 (Thin Film). These data demonstrated that ground state electron transfer were not obvious in –DBAB-. If the photo induced excitons were nearby a donor/acceptor interface, or the excitons diffuse to the donor/acceptor interface during its life time, then electrons and holes will be separated at the donor/acceptor interface with electrons dropped into the LUMO level of acceptor phase, and holes jumped into the HOMO level of donor phase, and this would result the photo-luminescence emission quenching. Once the electrons and holes are effectively separated, the first important process of light harvesting is accomplished. For photovoltaic device purposes, the electrons and holes thus separated will have to move and be collected by respective electrodes having the same or close work function levels to the donor HOMO and acceptor LUMO levels.

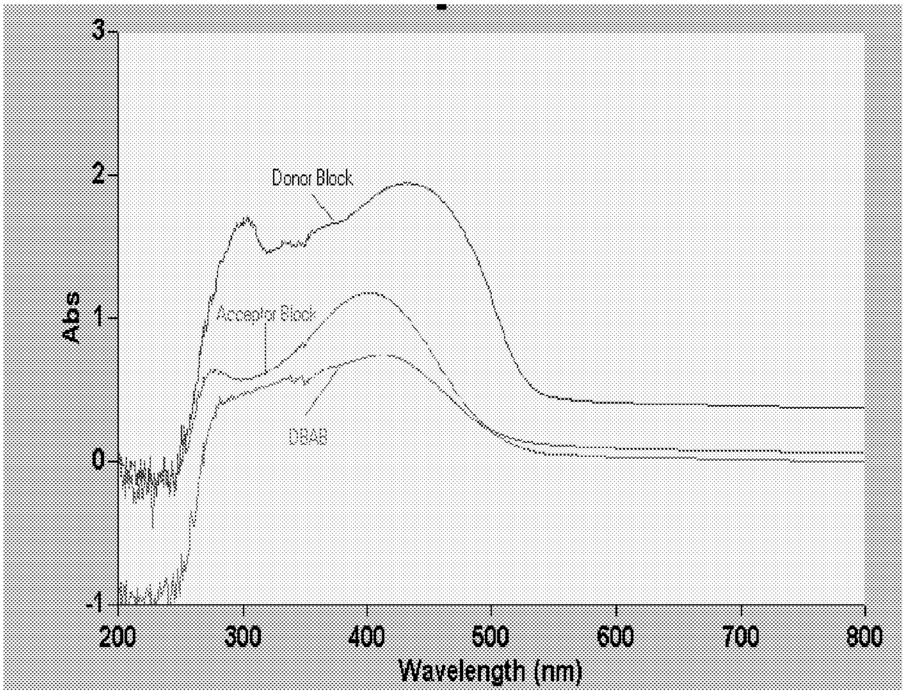


Figure 4.10 UV-VIS Spectra of Donor, Acceptor and –DBAB- in CH_2Cl_2

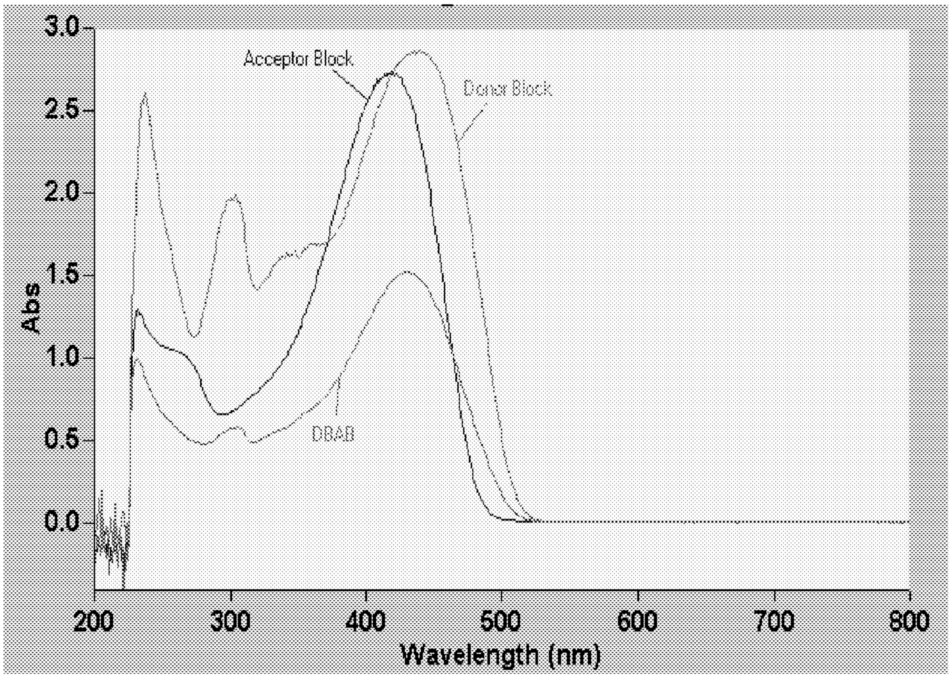


Figure 4.11 UV-VIS Spectra of Donor, Acceptor and –DBAB- Thin Films

Using cyclic voltametry combined with UV-VIS absorption data, the LUMO of RO-PPV is estimated to be –2.7 eV, and HOMO at –5.2 eV. The LUMO of SF-PPV-I is at –3.6 eV, and HOMO is at –6.0 eV. These results indeed confirmed that the RO-PPV is an electron donor and the SF-PPV-I is an electron acceptor in our block copolymer system.

4.2 Study of Thin Film Morphologies

Through the history of organic photovoltaic materials development, one can find that there are many known factors that affect the energy conversion efficiency dramatically. In this project, we are mainly focused on how to improve the donor and acceptor interface. As demonstrated in the project proposal, the bigger the donor and acceptor interface is, the better the charge separation efficiency.

Though the donor/acceptor blend systems possess large D/A interface advantage over bilayer systems, blend systems have intrinsic disadvantages of poor phase morphology and therefore poor charge separation and mobility. Block copolymers are well known for their excellent discontinuous phase separated characteristics. Both morphological pattern and the phase sizes can be easily fine-tuned by the design of each block.

In general, block copolymer molecular chains are randomly packed over the substrate's surface. But under certain conditions, these chains can be well packed and form micro phase separation. In our case, if the final –DBAB- block copolymers can have a uniform, ordered nano-phase separation, the higher charge carrier separation efficiencies are expected due to better phase separation that makes exciton recombination less likely, and/or better continuity of each phase that leads to better charge mobility.

To study the morphology of the final –DBAB- block copolymers, the polymer samples were first dissolved in a solvent, then spin coated or drop-dried onto clean glass substrates or silicon wafers. There are several ways to evaporate the solvent, including vacuum drying or simple heating. Then the films were thoroughly dried in a heated vacuum oven overnight. STEM and AFM are used to study the micro phase separation of the dried films.

When making the film, it is very important to choose the right solvent and the right ways to evaporate the solvent. Rapid solvent evaporation will prevent significant rearrangement of the polymer chains and often quenches a fine phase separation. By varying the solvent, the substrate temperature, the film drying protocol, and the saturation of the atmosphere over the transforming film, the characteristic phase separation length scales could be varied from tens of nanometers or less up to tens of microns.

To make thin film samples, we first dissolve the –DBAB- block copolymers in a mixture of 1:1 dioxane and THF, then drop the solution onto a clean substrate, drying at room temperature for 30 minutes, and then dry under the vacuum for at least one day.

Figures 4.12 and 4.13 are the thin film STEM images of donor block and acceptor block respectively. From the image, we can see that there is no any regular pattern in either block films.

Figure 4.14 is the 100nm x 100nm STEM image of donor/acceptor blend (mixture). As we can see from the image, we can only see the donor block and acceptor block separated poor interface at the bottom, no any regular pattern can be found.

Figure 4.15 is the 200nm x 200 nm STEM image of the final –DBAB- block copolymers. Figure 4.16 is the 7.5 x 7.5 μm AFM top view (non-contact mode) of another final –DBAB- block copolymer sample. In these two images, some regular pattern was observed, and it is possibly due to micro-phase separation in the coupled block copolymers. Compared with the image of D/A blend, the phase size and the continuity of each phase in final block copolymer are much better then in the blend systems.

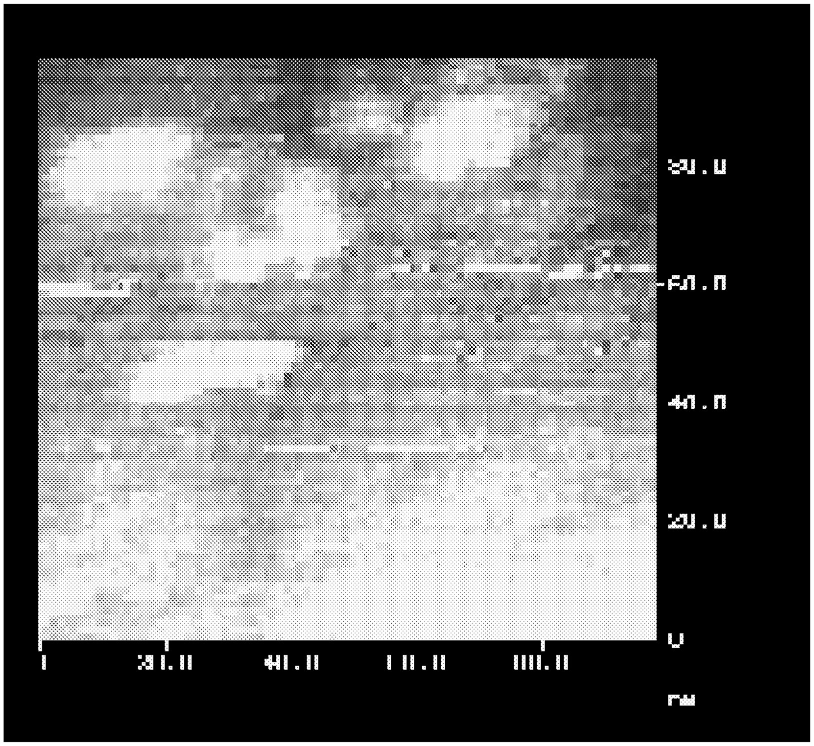


Figure 4.12 STEM Image of a RO-PPV Block Film (100 X 100 nm^2)

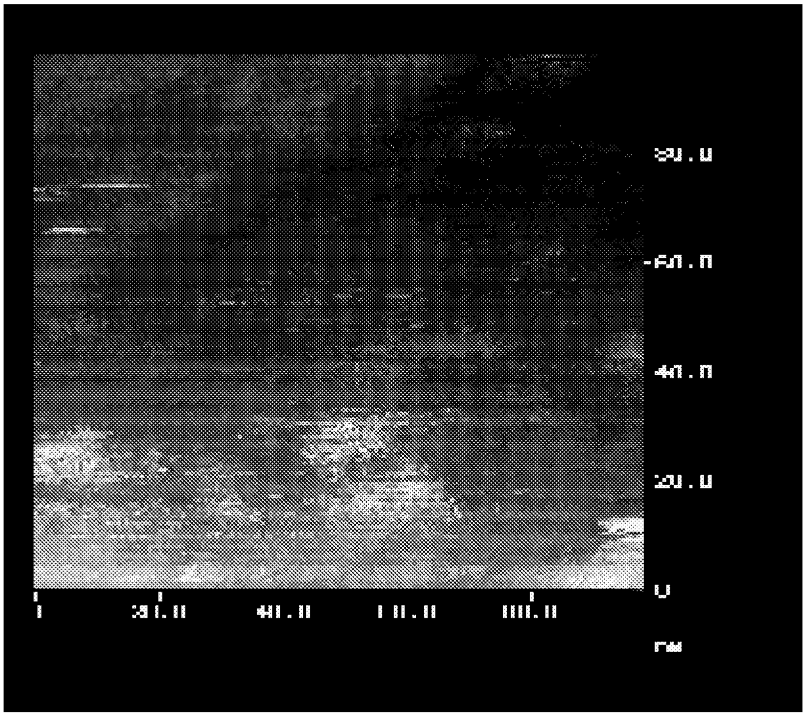


Figure 4.13 STEM Image of a SF-PPV-I Block Film (100 X 100 nm^2)

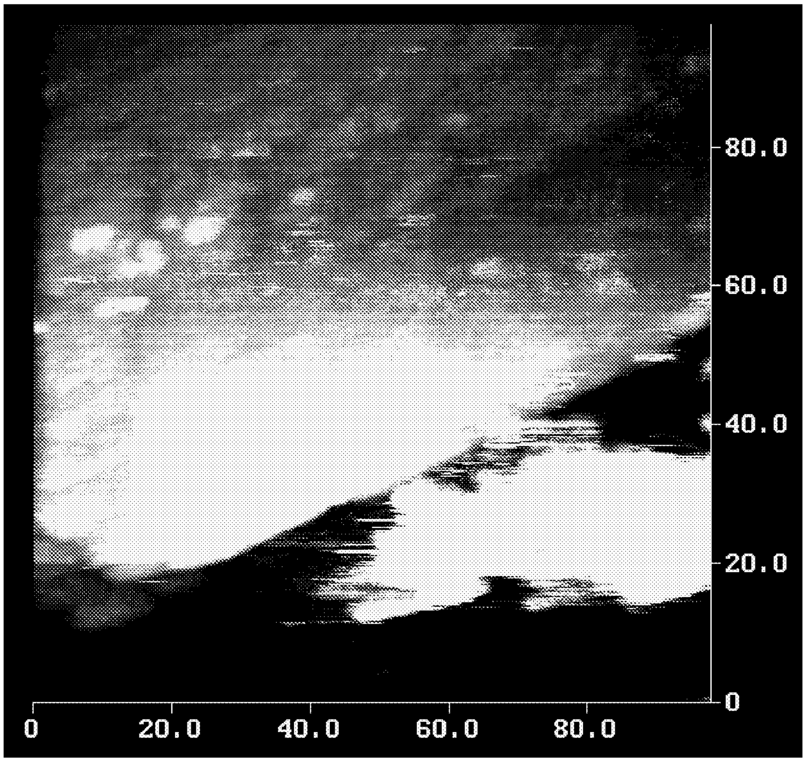


Figure 4.14 STEM Image of a RO-PPV/SF-PPV-I Blend Film (100 X 100 nm^2)**Error!**

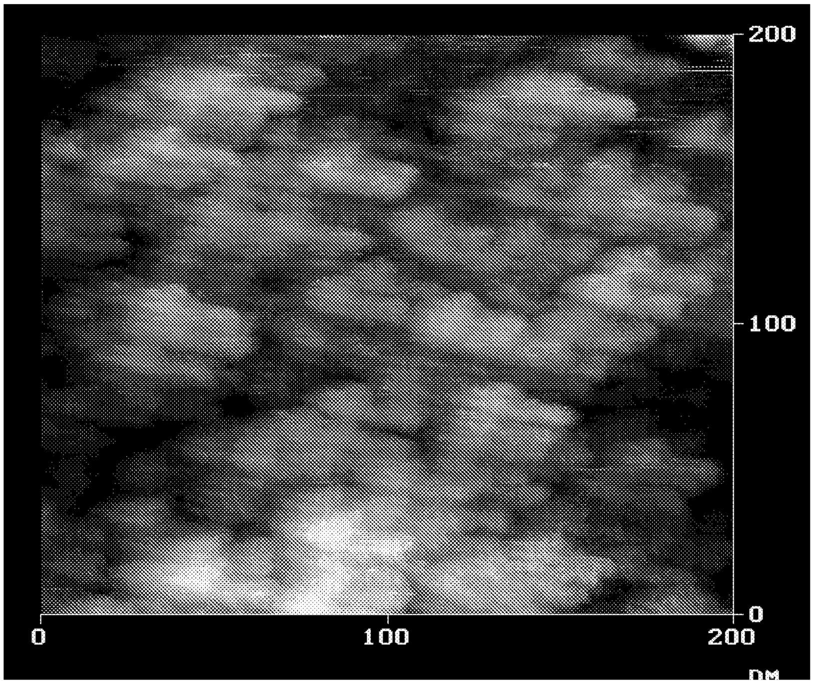


Figure 4.15 STEM Image of a –DBAB- Film (200 X 200 nm^2)

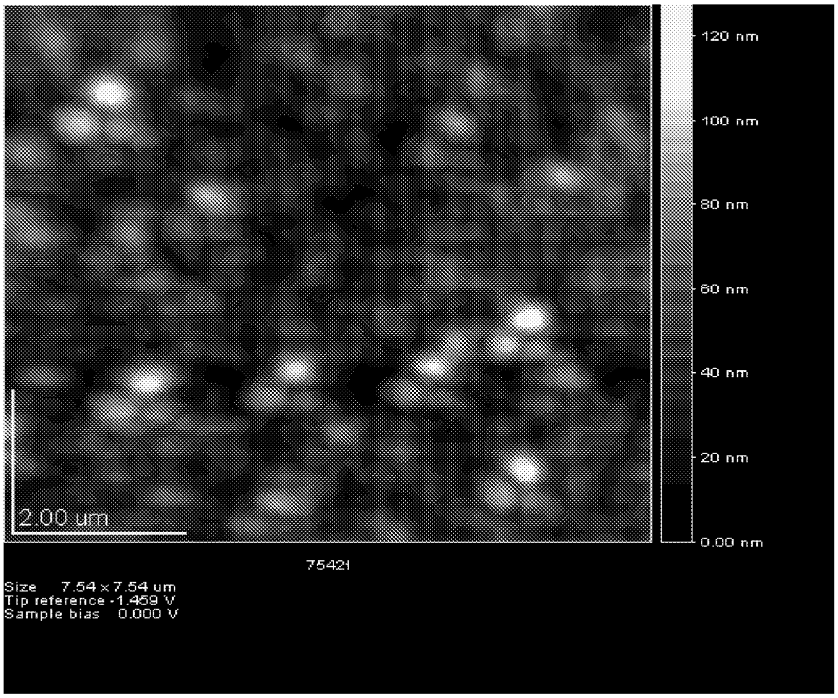


Figure 4.16 AFM Top View of a –DBAB- Film (7.5 x 7.5 μm^2)

4.3 Summary

The design, synthesis and characterization of a novel Donor-Bridge-Acceptor block copolymer system have been studied. Base on previous predictions, this approach or synthetic scheme may be useful for developing high efficient organic opto-electronic materials. Specifically in our system, the donor block contains an electron donating alkyloxy derivative polyphenylenevinylene (RO-PPV), the acceptor block contains an electron withdrawing alkyl-sulfone derivatized polyphenylenevinylene (SF-PPV-I), and the bridge block contains an non-conjugated aliphatic hydrocarbon chain. The key synthetic strategy includes the synthesis of certain sized and functionalized individual blocks first, then couple the blocks together. In this way, the size of the polymer nano phases can also be controlled. While the donor phase stabilizes and transports the photo induced holes, the acceptor phase stabilizes and transports the photo induced electrons, the bridge phase is designed to retard or minimize the electron-hole recombination via conjugated chain. Thus, improved charge separation and transportation are expected with this system. In addition, charge migration toward electrodes may also be facilitated due to the potential nano-phase separated and highly ordered block copolymer ultra-structure.