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# **Synthesis of (1) poly (3-(2-acetoxyethyl)thiophene for gas separation membranes and (2) 3,5-bis(bromomethyl) dimethyl(octyl)silane benzene for solid-state lighting**

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*Andrew Joseph Heinson*

*The University of Texas at Dallas*

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## **Abstract**

Poly (3-(2-acetoxyethyl)thiophene (PAET) is a polymer for gas separation that has the ability to modified or be used in composites to give the membrane different permeability and permselectivity properties. 3,5-bis(bromomethyl) dimethyl(octyl)silane benzene is an intermediate in the synthesis of a meta-PPV derivative which is electroluminescent. The goal is to obtain a polymer that emits light with a wavelength of  $< 420$  nm, because the zeolite NTHU-4 emits white light when excited by light with said wavelength. PAET was synthesized and is currently being characterized. Membranes can now be fabricated and tested so more can be learned about the possibilities PAET has for the gas separation and enrichment industry. 3,5-bis(bromomethyl) dimethyl(octyl)silane benzene was synthesized and can be used to complete the next step in the synthesis of the meta-PPV derivative.

## **Synthesis of (1) poly (3-(2-acetoxyethyl)thiophene for Gas Separation Membranes and (2) 3,5-Bis(bromomethyl) Dimethyl(octyl)silane Benzene for Solid-state Lighting**

### **Introduction**

Synthesis of poly (3-(2-acetoxyethyl)thiophene for gas separation membranes. The application of polymer membranes in the gas separation and purification industry provides numerous advantages over the current methods of distillation and gas absorption.<sup>1</sup> These benefits include an increase in energy efficiency, process flexibility, and utility in the presence of impurities; as well as an increase in the ability to discriminate molecules based on size, shape, polarity, and chemical interaction. The deciding characteristics of gas membranes that allow for an industrial application include selectivity, flux, maintenance cost, and replacement cost.

Poly (3-(2-acetoxyethyl)thiophene (PAET) allows for an increased processibility, brought about by solubility in common solvents,<sup>2</sup> and the ability to modify the surface or be used in composites to give the membrane different permeability and permselectivity properties. PAET membranes also prove to be both strong and durable. Thus, the application of PAET membranes has the possibility of being an effective and efficient material for gas separation and enrichment. The synthesis of PAET was performed following procedures reported in the literature<sup>2, 3, 4, 5</sup> and presented in Figure 1.

Synthesis of 3,5-bis(bromomethyl) dimethyl(octyl)silane benzene. Electroluminescence (EL) is the emission of light from electroactive materials brought about by an electrical current. Processible poly (*p*-phenylenevinylene) (PPV) derivatives and  $\pi$ -conjugated polymers have been widely studied due to their promising optical and electronic properties. These derivatives yield durable and easily processed films, which can be applied over a large area through spin coating due to their solubility in organic solvents. The structure of these polymers can also be modified by adding chemical substituents with different electron withdrawing and donating abilities to the polymer backbone since electron-withdrawing groups tend to shift the emission towards the blue or violet region of the visible spectrum, whereas, the electron-donating groups tend to shift the emission towards the red region. Our goal in this project is to synthesize a PPV derivative that can be used as an initiator for the emission of white light from zeolites or molecular sieves.

The target compound was designed to emit at <420 nm, the deep blue/violet region of the visible spectrum, in order to stimulate a zeolite (NTHU-4)<sup>6</sup> or a molecular sieve, which was reported to emit white light when excited at the said wavelength. Current PPV derivatives normally emit blue light at >420 nm. The PPV derivative poly(2-dimethyloctylsilyl-1,4-phenylenevinylene) (DMOS-PPV) that has been synthesized and studied in the past by the Ferraris group has an EL of about 470 nm. We propose to synthesize the meta-derivative of DMOS-PPV<sup>7, 8</sup> to shift its emission further to the blue

region compared to the para-derivative. This blue shift is brought about by the meta structure interrupting the long range  $\pi$ -electron delocalisation over the length of the polymer; thus, decreasing the conjugation length and increasing the band gap. The synthesis of a co-polymer using pyridine-2,6-dicarboxaldehyde was proposed to further blue shift the emission. Through the use of the meta-PPV derivative, and polymerization with pyridine-2,6-dicarboxaldehyde, a polymer with EL below the target of 420 nm can be synthesized. The synthetic route for the synthesis of the meta-PPV derivative is shown in Figure 2. Intermediate A has already been synthesized in large amounts. This work focused on the next step, which is the bromination of intermediate A.

## Procedure

Synthesis of 2-(3-thienyl)ethylacetate monomer.

Within a three-neck flask, a mixture of 2-(3-thienyl)ethanol (0.156 moles), triethylamine (0.117 moles), acetic anhydride (0.234 moles), and 4-dimethylaminopyridine (DMAP) (0.006 moles) was stirred under nitrogen overnight. The reaction was quenched by first adding 100 mL of ether, then slowly adding 50 mL of 2.0 M HCl. The resulting mixture was placed in a separatory funnel. The aqueous layer, containing HCl was separated from the organic layer, containing the monomer and ether. Ether was added 50 mL at a time to the aqueous layer in order to remove all organic material. The remaining HCl was removed from the organic layer by slowly adding 100 mL of saturated  $\text{NaHCO}_3$  and working up the resulting mixture. The resulting water was removed from the organic solution by adding  $\text{MgSO}_4$  and stirring. The  $\text{MgSO}_4$  was removed through vacuum filtration. The ether in the organic solution was evaporated at reduced pressure. TLC and FT-IR (Fourier Transform Infrared) were used. The product was further purified by column chromatography using a 90:10 hexane:ethylacetate solvent system. The product was characterized by using FT-IR, HPLC (High Performance Liquid Chromatography), and NMR (Nuclear Magnetic Resonance). The solvent was removed by evaporating at reduced pressure.

Polymerization of monomer 2-(3-thienyl)ethylacetate.

In a two-neck flask, the 2-(3-thienyl)ethylacetate monomer (0.059 moles) was mixed with 600 mL of chloroform under nitrogen. To polymerize the monomer,  $\text{FeCl}_3$  (0.235 moles) was added batch-wise over a one-hour period. The solution was stirred for 24 hours at room temperature. The polymer was precipitated in 1500 mL of methanol, stirred for an hour, and then decanted. The polymer was stirred in 500 mL of water for an hour to remove  $\text{FeCl}_3$  and then decanted. The polymer was then dissolved in 300 mL of  $\text{CHCl}_3$  while stirring overnight. The chloroform was evaporated at reduced pressure. Once the polymer was completely dry, a Soxhlet extraction was performed to remove all impurities using methanol, hexane, and chloroform, respectively as solvents.

Synthesis of 3,5-bis(bromomethyl) dimethyl(octyl)silane benzene.

The purified intermediate A (1.0 g) from the first reaction was placed in a three-neck flask, with a condenser, under a nitrogen environment. Carbon tetrachloride (~50 mL) and benzoyl peroxide (0.03 g, 0.2 mmol) were then added. The solution was heated to reflux, allowed to react for 10 minutes, and NBS (3.56 g, 20 mmol) was added. The

solution turned a cloudy orange color and lightened into a pale yellow. The solution was refluxed overnight. In order to quench the reaction, 100 ml of 20% w/w potassium carbonate solution in deionized water was added. The organic layer was then separated from the aqueous layer. The organic layer was then dried over  $\text{MgSO}_4$  and filtered. The crude product was obtained after removing the solvent under reduced pressure.

## Results and Conclusions

Synthesis of poly (3-(2-acetoxyethyl)thiophene for gas separation membranes. The synthesis of the monomer 2-(3-thienyl)ethylacetate began by adding 2-(3-thienyl)ethanol, trimethylamine, acetic anhydride, and DMAP into a three-neck flask. The mechanism of this reaction is shown in Figure 3. DMAP acts as a catalyst and initiates the reaction by reacting with acetic anhydride. The resulting intermediate then reacts with 2-(3-thienyl)ethanol to form the product. This reaction was followed by using thin-layer chromatography (TLC) (90:10 hexane:ethylacetate) by spotting the starting material and the reaction mixture. The reaction was stopped when the starting material was gone.

After work up, the crude product was purified through a silica column. The purity of the product was determined to be ~99% using HPLC (Figure 4). For FT-IR, a background spectrum was obtained from a blank NaCl plate. The sample was then placed on the NaCl plate and the spectrum was obtained. The following peaks were observed ( $\text{cm}^{-1}$ ): 3099 (-CH aromatic), 2955 (- $\text{CH}_3$ , - $\text{CH}_2$ - asymmetric stretch), 1736 (-C=O symmetric stretch), 1383 and 1363 (- $\text{CH}_3$ , - $\text{CH}_2$ - asymmetric bend), 1235 (-( $\text{O}(\text{C}=\text{O})\text{CH}_3$ ) stretch), 1037 (-C-O-C, -C-O-H stretch), 773 (3 neighboring aromatic C-H) (Figure 5). For  $^1\text{H}$  NMR analysis, the monomer was dissolved in deuterated chloroform. The following peaks were observed: 7.27 (dd, 1H), 7.00 (dd, 1H), 6.98 (dd, 1H), 4.28 (t, 2H), 2.97 (t, 2H), and 2.05 (s, 3H) (Figure 6). The six different signals indicate the presence of six different groups of protons. The three aromatic protons on the thiophene ring are coupled (long range) with each other producing doublets of doublets. The protons on the side chain gave triplet signals with the proton close to the oxygen shifted downfield due to the electron-withdrawing effect of the neighboring oxygen. A singlet was observed at 2.05 ppm for the hydrogen with no adjacent protons.

Both the FT-IR and NMR analysis indicated the presence of the desired 2-(3-thienyl)ethylacetate monomer; thus, the polymerization could proceed. In the polymerization process a reduction-oxidation reaction took place. The  $\text{FeCl}_3$  acted as the oxidizing agent and oxidized the monomer to form poly (3-(2-acetoxyethyl)thiophene. The resulting polymer was purified by Soxhlet extraction and currently being characterized using NMR and FT-IR. The molecular weight of the polymer will also be determined using gel permeation chromatography (GPC).

The synthesis of PAET was carried out successfully. The resulting polymer is currently being characterized. Membranes can now be fabricated and tested so more can be learned about the possibilities PAET has for the gas separation and enrichment industry.

Synthesis of 3,5-bis(bromomethyl) dimethyl(octyl)silane benzene.

The synthesis of 3,5-bis(bromomethyl) dimethyl(octyl)silane benzene began with the purification of intermediate A. By HPLC, intermediate A was found to be ~80% pure. Intermediate A was purified using Kügle Rohr vacuum distillation. The desired compound was distilled at reduced pressure, leaving behind the impurities. The resulting purified intermediate A appeared clear. The purity of the intermediate was found to be above 90%, showing one spot with TLC. The bromination began by adding CCl<sub>4</sub> and benzoyl peroxide to the intermediate. The bromination process followed a free-radical mechanism.

The bromination of intermediate A resulted in low yield and low purity, this is however to be expected. In order for the desired product to form, both methyl groups of the aromatic ring must brominate; however, due to the free radical nature of the reaction, the bromination of the other methyl groups of the octylsilane chain also occurs. Another common product is a mono-brominated form; this forms when only one methyl site of the aromatic ring is brominated. Thus, only a fraction of the reactant forms the desired di-brominated form.

The second intermediate of the synthesis of the meta-PPV derivative was carried out. The process has yet to be perfected, and as a result, there is both low purity and low yield, but the product is currently being purified by silica column. When an intermediate with a high purity is obtained, the synthesis of the meta-PPV derivative polymer can continue.

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Synthesis of (1) poly (3-(2-acetoxyethyl)thiophene for Gas Separation Membranes and (2) 3,5-Bis(bromomethyl) Dimethyl(octyl)silane Benzene for Solid-state Lighting

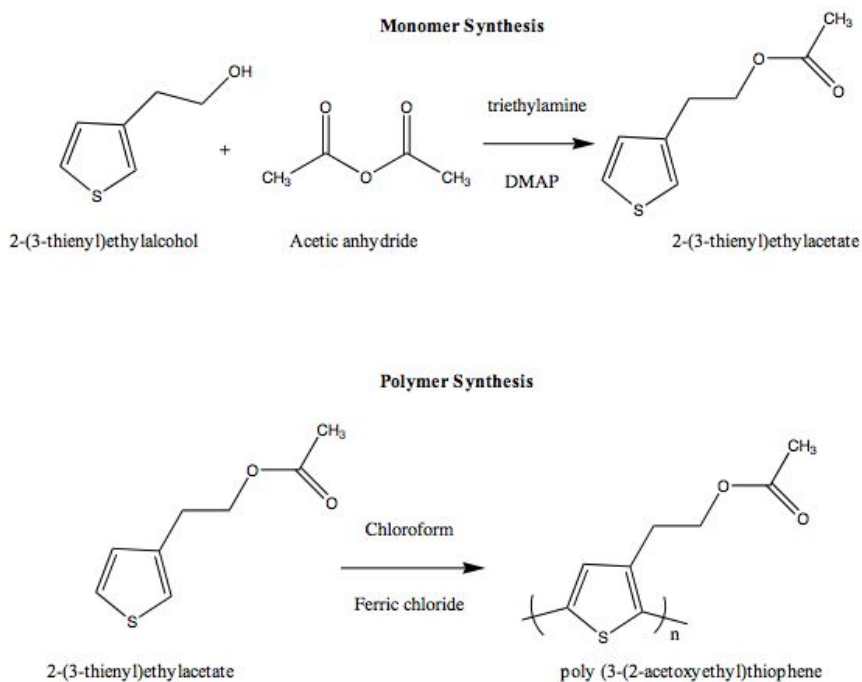


Figure 1. Synthesis of 2-(3-thienyl)ethyl acetate monomer and poly (3-(2-acetoxyethyl)thiophene

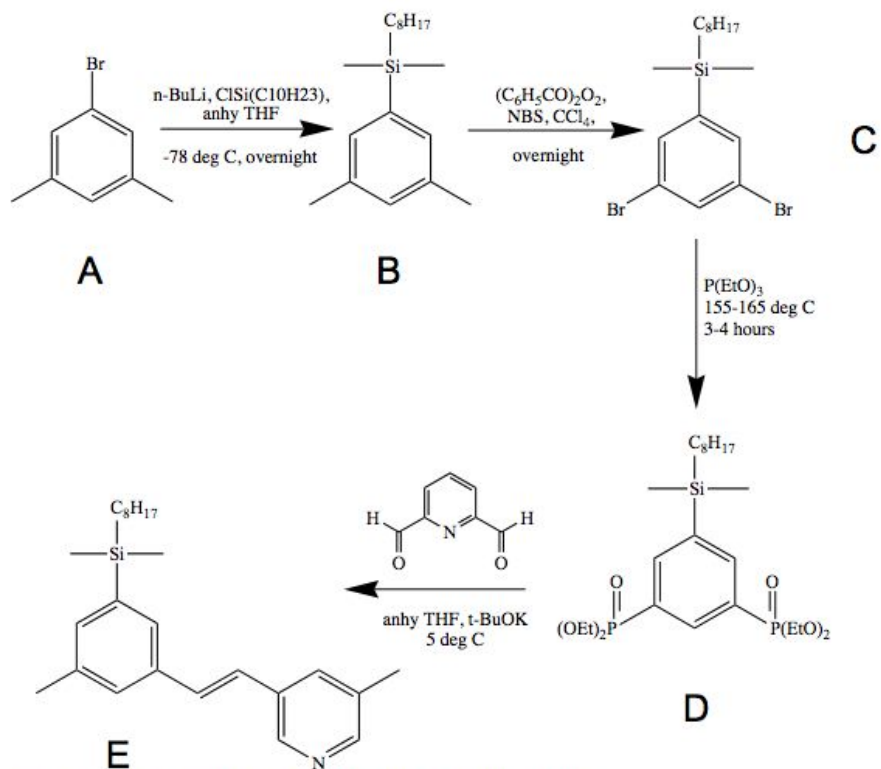


Figure 2. Synthesis of poly(3,5-bis(bromomethyl)phenyl dimethyl(octyl)silane

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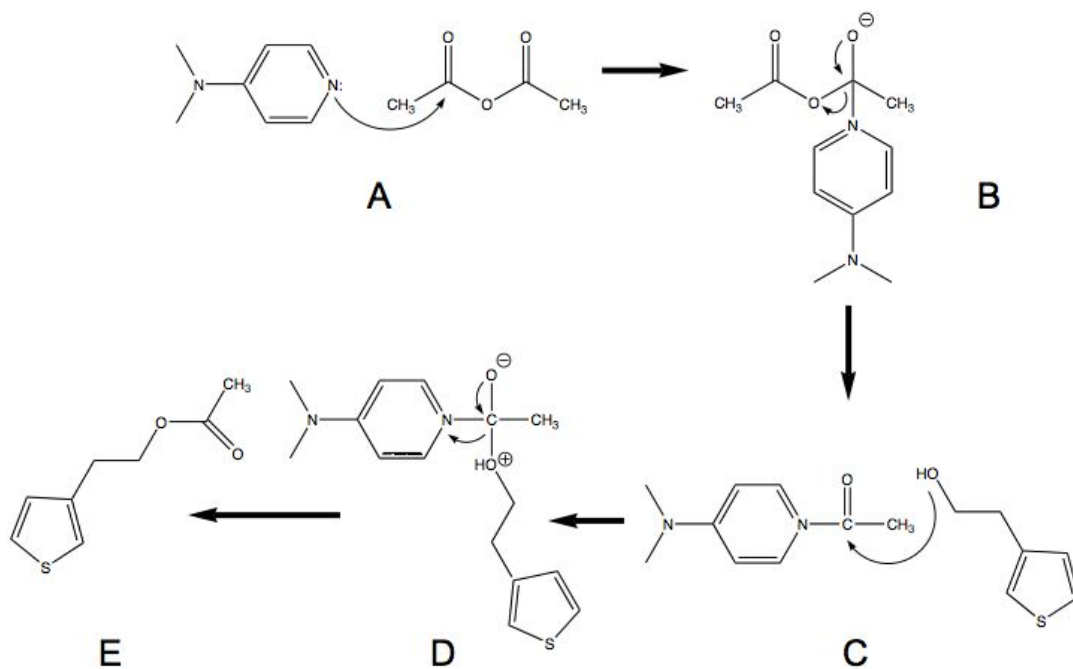


Figure 3. Reaction mechanism for the synthesis of 2-(3-thienyl)ethylacetate monomer

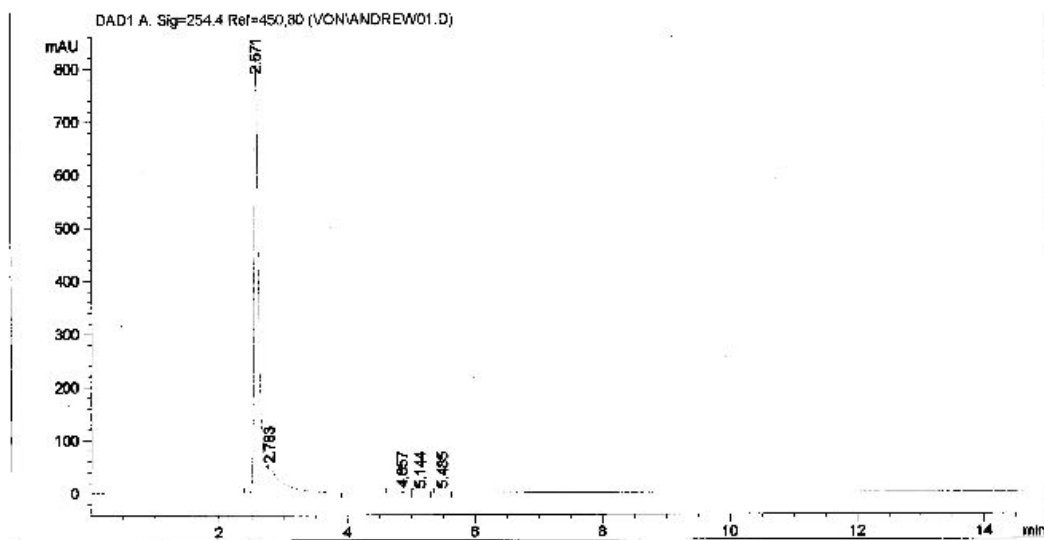


Figure 4. HPLC of purified 2-(3-thienyl)ethylacetate monomer



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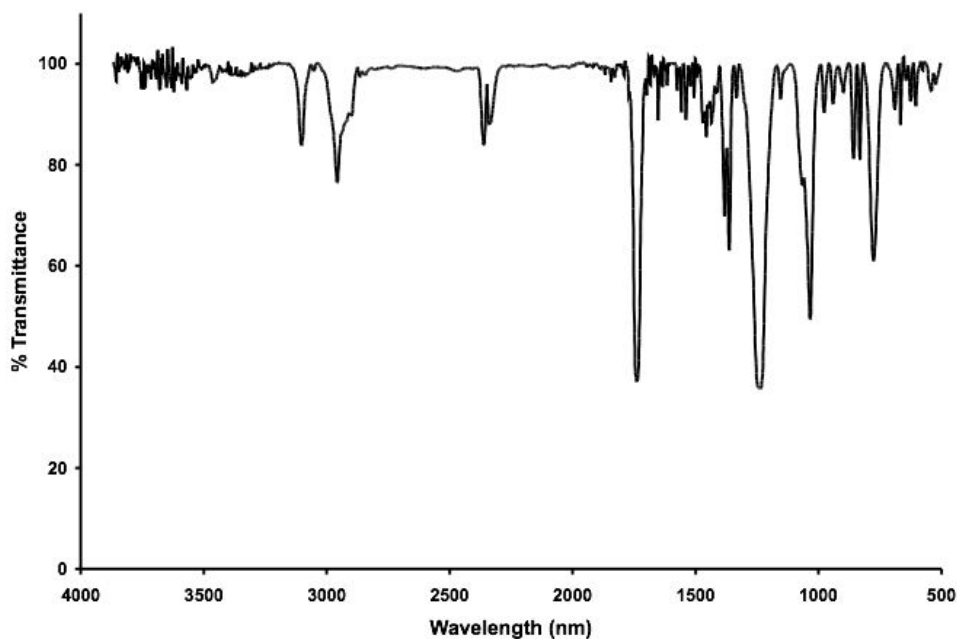


Figure 5. FT-IR spectrum of purified 2-(3-thienyl)ethyl acetate monomer

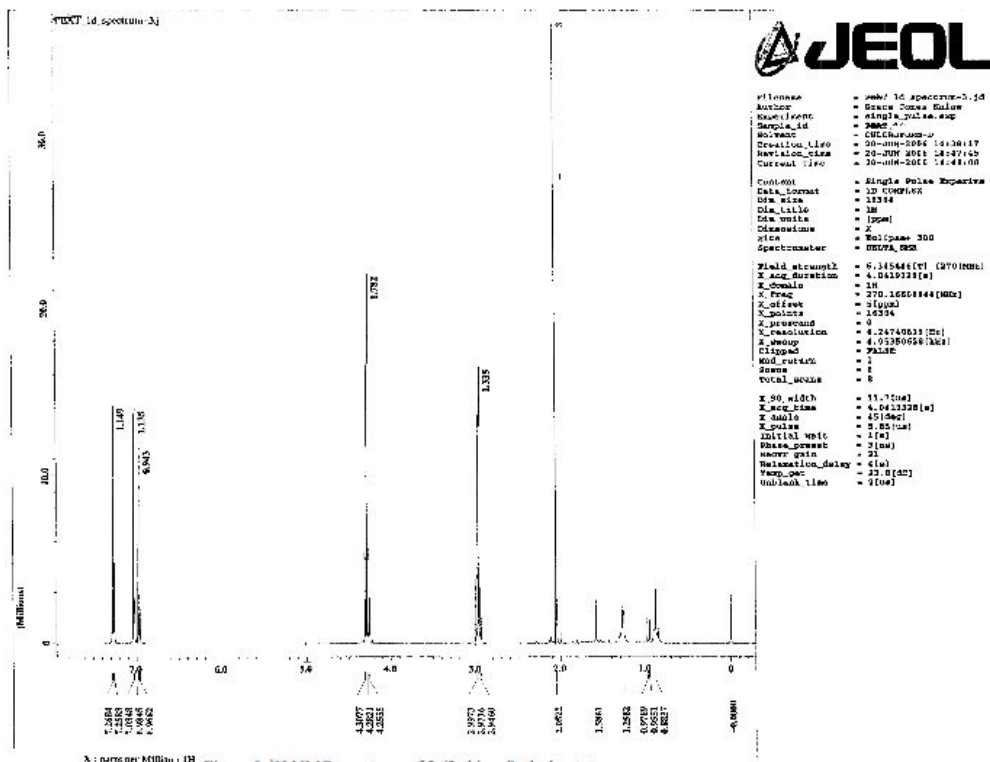


Figure 6. <sup>1</sup>H NMR spectrum of 2-(3-thienyl)ethyl acetate monomer