ABSTRACT

XU, JINGCHAO. Investigating the Synthetic Methodology for Fused, Nitrogen-containing Aromatic Ladder Polymer. (Under the direction of Dr. Christopher B. Gorman).

Since the discovery of conducting organic polymers in the 1970's, researchers have investigated many types of materials for use in a variety of organic devices. Among these conductive materials is the class of aromatic ladder polymers. We have devised a route for obtaining a novel aromatic ladder polymer, and proposed a method that converts soluble precursor oligomers to cyclized isoquinoline-type conjugated products. The focus of the work presented here is the investigation of cyclization conditions and the synthesis of the soluble precursor polymer. An optimized polymerization condition was obtained.

Investigating the Synthetic Methodology for Fused, Nitrogen-containing Aromatic Ladder Polymer

by
Jingchao Xu

A dissertation submitted to the Graduate Faculty of
North Carolina State University
in partial fulfillment of the
requirements for the degree of
Master of Science

Chemistry

Raleigh, North Carolina

2014

APPROVED BY:

_____	_____
Christopher B. Gorman Committee Chair	Edmond F. Bowden
_____	
Felix Castellano	

DEDICATION

To my parents, Xu Xu and Lijun Zhang, who gave me my life and taught me when I was young. They spent everything to give me a better life and sponsored my study abroad.

BIOGRAPHY

Jingchao Xu was born in Zhejiang, China on April 27th, 1989. He completed his Bachelor's degree in the Chemistry Department of Zhejiang University in 2011. Then he chose to start his master study in the Chemistry Department of North Carolina State University, working with Dr. Christopher B. Gorman on the conductive aromatic ladder polymer project.

ACKNOWLEDGMENTS

I would like to acknowledge Dr. Christopher B. Gorman, who took me into, and supported me for the past three years on a research assistant grant. I appreciate your endless patience in providing guidance on my work. You have taught me how to write and overcome my lack of experience in the field of synthetic chemistry. A special thanks to my committee, Dr. Bowden, and Dr. Franzen, for giving me a lot of guidance and helping me quickly schedule my defense.

Then I want to thank Menglong Hu, Molly Brannock, Jenelle Willett who taught me a lot lab work and gave me help on my project, Xingfang Hu and Jiancheng Zhu who offered lots of guidance on my academic study and other group members who ever helped me.

Last, I want to thank my parents and my friends. Thank for their unconditional support and understanding during study and daily life.

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A. Introduction

1. Organic Conducting Materials

When we talking about the conductive materials, the first thing come to our mind is metals, such as copper, iron and aluminum. These are widely used in our daily life. Though the metals are very easy to get and also some of them are quite cheap, they still have some disadvantages. They can be heavy, don't have very good flexibility, and need very harsh conditions to manufacture.

Beside metals, there are also some nonmetallic, conductive materials. Carbon can be very good conductor. Graphene, composed of sheets of hexagonal, fused, sp^2 hybridized carbon, is one of the hottest research materials being studied right now. It is the thinnest and strongest material in the world. And also, it has very high electric mobility (15000 $cm^2/V \cdot s$). [1]

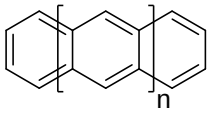
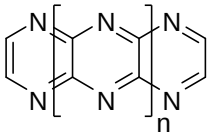
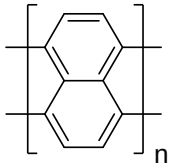
The perfect 2-dimentional hexagonal structure of graphene offers great thermal stability and tremendous conductivity of heat and electricity.[2] Similar structures can be obtained in many organic compounds. These conducting organic materials have been researched for several decades. The conjugated, p_z orbitals overlap to form a molecularly wide, delocalized set of orbitals and thus a fully conjugated structure. This structure offers these electrons in the delocalized orbitals the potential to have a high mobility. The delocalized π-orbitals will also lower the band gap of the molecule.

Organic polymers offer a lot of advantages compared to traditional conducting materials. The organics are lighter than the metals, and they also offer milder processing conditions. Fully conjugated aromatic polymers, like graphene, have a 2-dimensional hexagonal structure, which also offers tolerance to mechanical deformation. Because of these

advantages, the organic conducting materials can be applied on many areas, such as OLED, OFET manufacture, flexible screen and solar cells.[3]

This thesis focuses on synthesis of a fully aromatic polymer. A nitrogen-containing, aromatic polymer has been chosen as the project. A fully aromatic polymer has the possibility to display properties similar to those in graphene including thermal stability and high electrical conductivity, as the result of charge mobility[4–7] and a small band gap (Table 1-1).[8–11]

Table 1-1 Ladder polymer with calculated ionization potential (IP) in eV, and bandgap energy in eV

Structure	IP, eV	Eg, eV
	5.8-6.0	0.0-0.2
	8.1	0.0
	4.0	0.3

2. Direct writing

Moore's law is the trend that the number of transistors on integrated circuits will double approximately every two years over the history of computing. It was first been described in

1965 by Intel the co-founder Gordon E. Moore. Since 1971, this trend has been followed. Currently, the number of transistors on integrated circuits is over a billion (Figure 1-1).

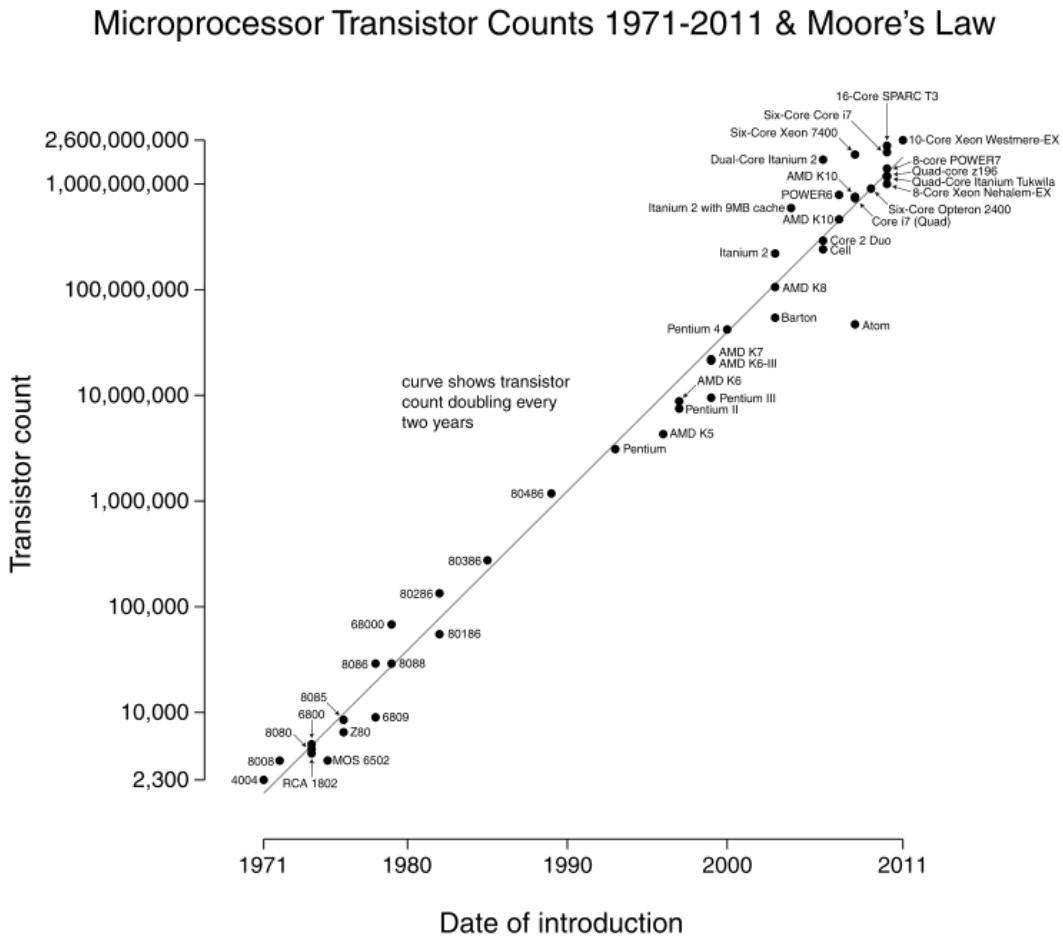


Figure 1-1: Moore's Law & Microprocessor Transistor Counts. Taken from Wikipedia

However, the Moore's law is just a prediction. Even though the trend has been followed to date, it is not a natural law. Currently, there are so many electronic elements on a chip that the size of the transistors the comprise them is less than 100 nm. The manufacture of the microchips right now is becoming more and more difficult. The 2010 update to the

International Technology Roadmap for Semiconductors predicts a slowing of growth at the end of 2013. Continued reduction in transistor size is one of the major challenges being faced right now.

The current approach for nano-sized manufacturing is photolithography. This process is relatively complex, requiring six fundamental steps (cleaning, preparation, photoresist application, exposure and developing, etching, photoresist removal). Organic conductive polymers potentially offers new manufacturing approaches. However, they are insoluble and not melt processable. The only viable approach that has emerged for exploiting these materials is fabrication and/or patterning via a precursor polymer. The most attractive precursor would be convertible from an insulator to a metallic conductor directly under the application of some form of patterning radiation. With this kind of precursor, a new technology named "Direct-Writing" has been proposed (Figure 1-2). The soluble precursor polymer would be spin-coated on the surface of the chip. Then a patterning radiation would be applied to convert the precursor polymer to a patterned, electrically conductive polymer which should be insoluble and ideally will be attached firmly to the surface. In a final step, the remaining, unirradiated precursor polymer would be washed from the surface leaving a patterned conductive "circuit".

Figure 1-2: Illustration of direct writing

With "Direct-Writing" technology, the traditional photolithography can potentially be replaced by this more efficient procedure which only requires two steps. Combining this approach with the advantages of organic conducting materials, this is definitely a promising research and application area.

B. Previous work

1. Proposed aromatic ladder polymer

There are lots of well-defined routes to aromatic ladder polymer have been published (Table 1-2). None of these, however, are amenable to direct writing as the methodology for conversion of the precursor to the aromatic ladder is not mild or possible with photopatterning.

Table 1-2: Well-defined routes to aromatic ladder polymers, focusing on entirely sp2 hybridized structures containing nitrogen and carbon.

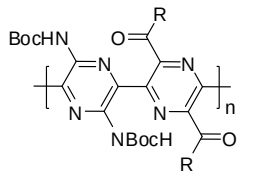
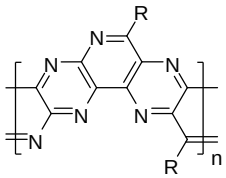
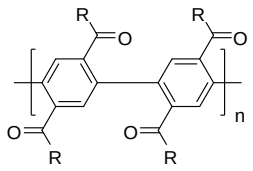
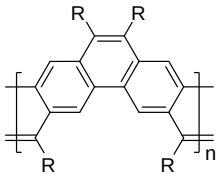
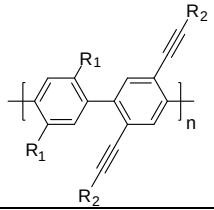
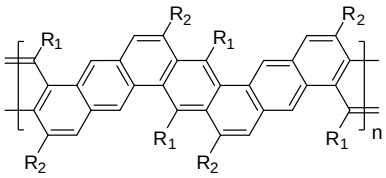
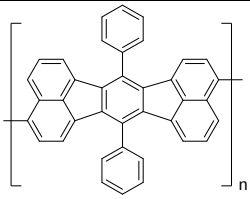
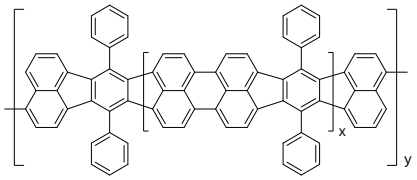
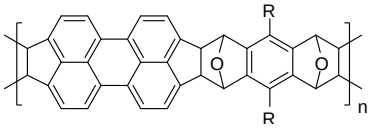
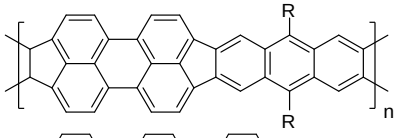
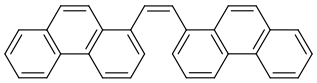
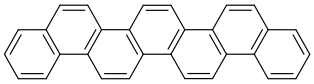
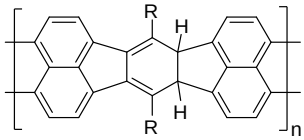
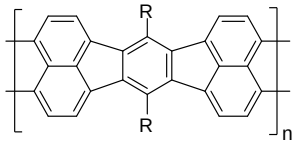
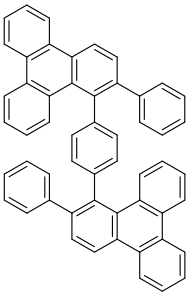
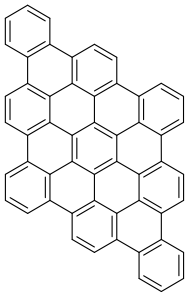
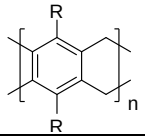
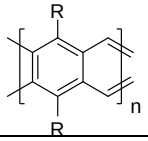
Precursor	Conversion Conditions	Aromatic Ladder	Ref
	$ZnCl_2$ (cat) 105-115 ^oC		12
	B_2S_3 115 ^oC		13
	CF_3CO_2H CH_2Cl_2 Room Temp.		14,15

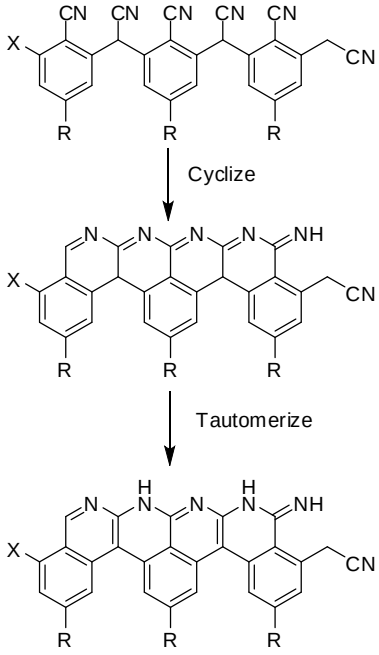
Table 1-2 Continued

Precursor	Conversion Conditions	Aromatic Ladder	Ref
	Elctrochem. Oxidation		16
	xs TsOH Toluene Reflux		17
	hv, I_2		18
	DDQ Room Temp.		19
	$AlCl_3$, $CuCl_2$ Room Temp.		20–22
	DDQ Room Temp.		23,24

The project pursued here is to synthesize a ladder polymer of a fused, isoquinoline structure (Scheme 1-1). Due to the poor solubility of the polymer and precursor, the alkyl group attached will increase the degree of freedom and make it more soluble. The project is divided into two parts. The first is polymerization, and the second is cyclization. In the cyclization part, effective and efficient cyclization conditions which can be applied to the

polymer are sought. In the polymerization part, an efficient way to synthesize long chain precursor polymer is sought.

Scheme 1-1: Route for the synthesis of the proposed, aromatic, ladder polymer

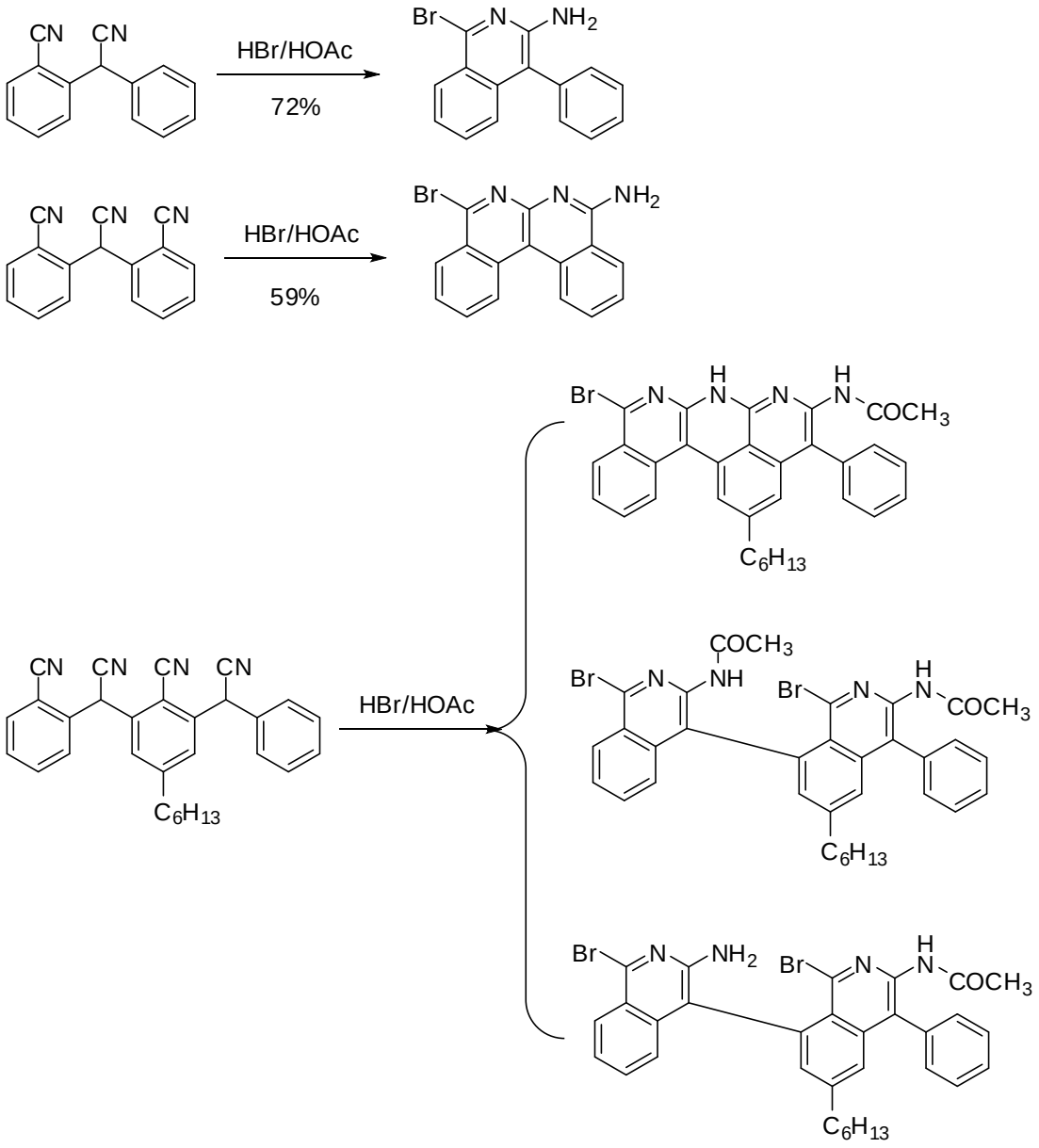


2. Previous work of former group members

Several former group members have studied the cyclization part of this project. Several cyclization conditions have been explored, and some interesting results have been found.

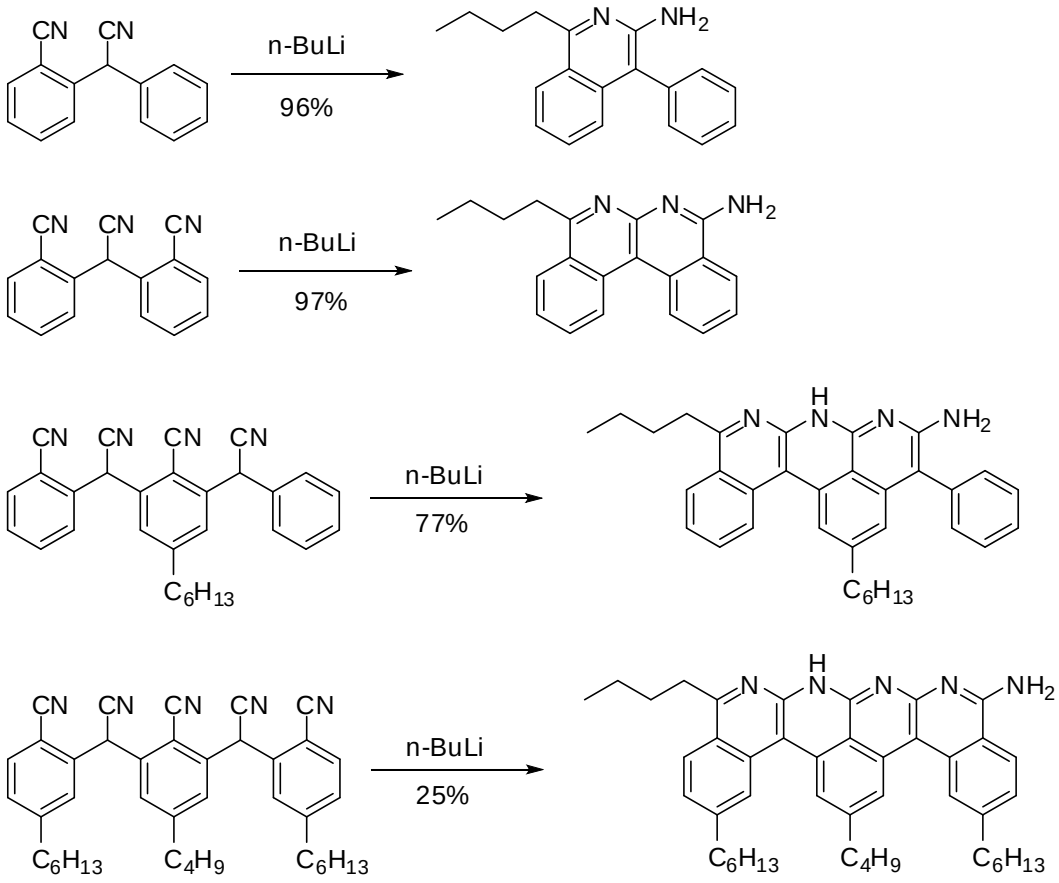
Acid-mediated cyclization led to moderate yield for short oligomers. However, alternative products were obtained in the case of longer oligomers. This approach has limited utility (Scheme 1-2).[25]

Scheme 1-2: Acid-mediated cyclization



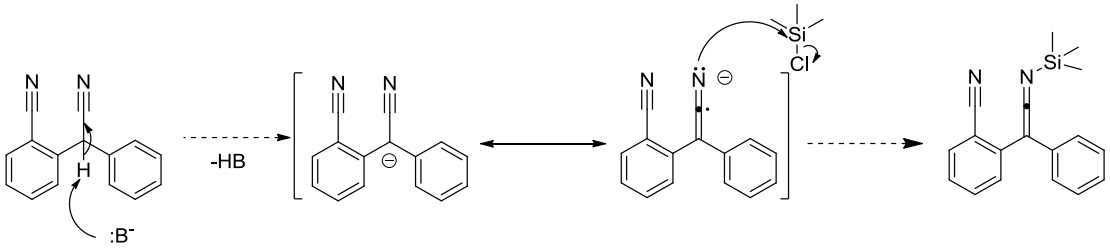
Cyclization mediated by *n*-BuLi –78 ^{0}C also worked well for short oligomers. However, the yield decreased when the length of the oligomers increased. Thus, this approach also had limited utility (Scheme 1-3).

Scheme 1-3: Strong base-mediated cyclization



Silyl ketenimine intermediates were proposed to assist the *n*-BuLi mediated cyclization process (Scheme 1-4). However, attempts to isolate the ketenimine intermediate failed. It was hoped that this ketenimine-based polymer could be used as the precursor and would be able to be cyclized under milder conditions.

Scheme 1-4: Mechanism of ketenimine intermediate



C. Outline of thesis

Based on the proposed approach and the previous work done by former group members, both the cyclization and polymerization were further explored here as follows. Similar to the idea based on formation of silyl ketenimine intermediates, different Lewis acids were explored to form an electrophilic intermediate. It will be explored as to whether this intermediate is stable, able to be isolated, and/or reactive to cyclization under milder conditions. In particular, the use of less reactive nucleophiles will be explored.

The second task is to optimize the synthesis of the precursor polymer. It will be shown that, although some new methodology was previously developed to synthesize the precursor polymer, material with all of the expected spectral signatures of that polymer had yet to be prepared.[26] Efforts to prepare such materials will be described. New approaches to optimize the synthesis of the monomer will also be described.

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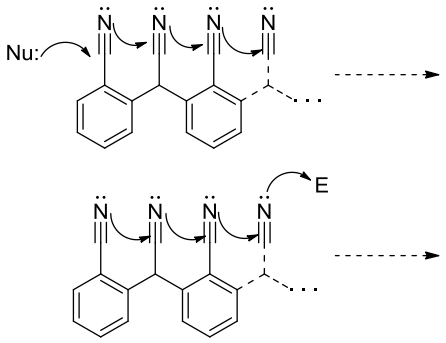
Chapter 2 Investigating ketenimine intermediate

A. Introduction

In the introduction, a precursor polymer route to a completely fused, aromatic heterocyclic ladder polymer has been described. For this approach to be viable, a mild route for cyclization of the precursor polymer is required. As stated previously, the ideal method for cyclization is by generating a catalyst that can perform the cyclization under photochemical irradiation similar to that used in existing photolithographic processes. Identification of a catalyst is one task. Another, however is to determine if there are any alternative methods for cyclization that have more reactive intermediates. Here, we describe synthetic efforts to generate such an intermediate, specifically a ketenimine intermediate.

Scheme 2-1: Depiction of Nucleophile (Nu:) and Electrophile (E) mediated cyclization



The simplest way to catalyze the cyclization is with a nucleophile (attacking the electrophilic carbon on the cyano group) or with an electrophile (activating the cyano group so that it becomes more electrophilic and thus more amenable to attack by the nucleophilic nitrogen on the cyano group). These two options are shown in Scheme 2-1. In either case, the nucleophile or electrophile is envisioned to be photogenerated (e.g. a photogenerated acid or base). Whereas strong, photogenerated acids are known[1–5], the analogous, photogenerated

bases are relatively weak[1,6–13]. Thus, we hypothesized that the molecule might be pre-activated to react with a moderately strong nucleophile.

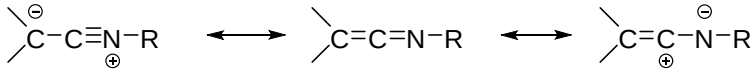
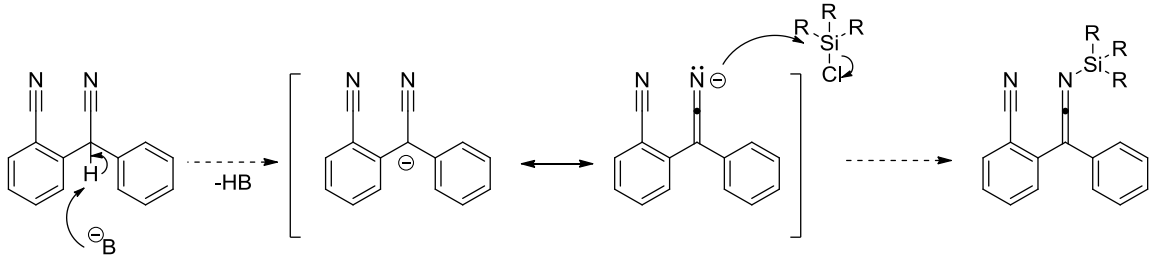


Figure 2-1: Resonance structures of ketenimine

Ketenimines are known to be more electrophilic than the cyano groups from which they are typically derived. Ketenimine has a higher electrophilicity than cyano due to the electron-deficient central carbon (shown in Figure 2-1) which will active or facilitate the nucleophile attack at it.[14–18] Several articles have reviewed this behavior.[19–22] If a stable ketenimine intermediate can be isolated, the intermediate could be used on polymer cyclizations. A polymer which contains ketenimine structures will also offer milder conditions for nucleophilic cascading cyclization. A general route for preparation of a silyl ketenimine is shown in Scheme 2-2. Silyl ketenimine intermediates were proposed and studied previously in the Gorman group.[23] The intermediates did assist the nucleophilic cyclization process, but, attempts to isolate the ketenimine intermediates failed. Here, alkyl ketenimine are studied to see whether similar properties and isolation of intermediates can be obtained.

Scheme 2-2: General route to a model compound containing a silylketenimine

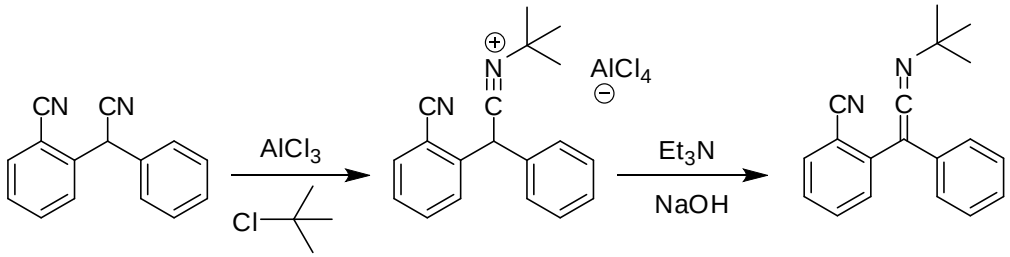


B. Results and Discussion

1. Attempts at formation of a *tert*-butyl ketenimine intermediate

Instead of using a silyl group on the nitrogen of the ketenimine, use of a *tert*-butyl group was explored. The reaction to form the intermediate on a model compound is shown in Scheme 2-3. In the presence of a Lewis acid, the model compound was treated with *tert*-butyl chloride. The resulting salt was deprotonated using a base such as triethyl amine and/or sodium hydroxide.

Scheme 2-3: Route to a tert-butyl ketenimine



1 **2**

The first experiments conducted were to determine which solvent was most efficient for this reaction. Reactions were run in tetrahydrofuran (THF) and dichloromethane (DCM). After the reaction, TLC plates showed that the reaction in THF still had lots of starting material left while the starting materials for the reaction in DCM was completely consumed. The IR spectrum of the crude reaction in DCM also showed a sharp peak at 2014 cm^{-1} which is the characteristic peak of ketenimine. Thus we concluded that DCM was a better solvent than THF for the production of the *tert*-butyl ketenimine derivative.Attempts at isolation of a *tert*-butyl ketenimine intermediate

The second set of experiments conducted were to determine an efficient purification method to obtain pure ketenimine intermediate. Crude products of the reaction in DCM solvent were obtained. According to previous work done by former group members, the ketenimine will break down in silica gel but not in alumina. So, alumina was used as the stationary phase for column chromatography. Alumina was dried at different temperatures (room temperature, 180^0C, 600^0C) and different length of heating time (N/A, 2 hrs, 12 hrs). Elution by solvent mixtures of different polarities (DCM/Hexanes, THF/Hexanes, THF/DCM) was explored. The purified products were characterized by IR and NMR. Most of the products obtained were still mixed with side products or a pure product was obtained that was not the desired product (IR and NMR did not match those expected). From the results, it appeared that the dryness of the alumina is important for acceptable column chromatography results. However, the reaction results in too many side products which have similar polarity to the desired product. Thus, it was not possible to isolate the ketenimine intermediate under these conditions.

2. Cyclization without purification

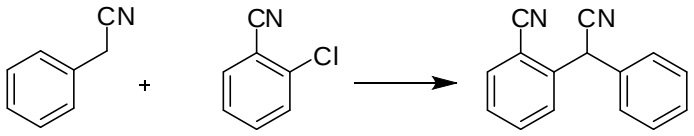
Since ketenimine intermediate was not able to be isolated, will it still be able to assist the cyclization? An experiment was conducted to test it. Same experiment conditions was applied and got the crude product. After IR in which a characteristic peak at 2014 cm^{-1} was observed, the crude product was sent for cyclization. The nucleophile was lithium piperidin-1-ide. After reaction, crude product was examined using IR and 1H NMR. From the IR, the

ketenimine peak at 2014 cm^{-1} already disappeared. From the NMR, the aromatic peak at 8.00 ppm was observed. Thus, the ketenimine intermediate does assist the cyclization reaction.

C. Conclusions

THF is not a suitable solvent for the reaction, but DCM appeared to give the correct product as a crude mixture. However, it is very hard to isolate the desired ketenimine. The crude products are extremely hard purify and are obtained in low yield. The ketenimine appears to be stable at room temperature as evidenced by the the IR of the crude product. The moisture of the alumina stationary phase used will affect the purification. The alumina heated in an oven at 180 ^{0}C and use of 0-20% DCM in Hexanes as the mobile phase offered the best purification, but a completely pure product was not obtained.

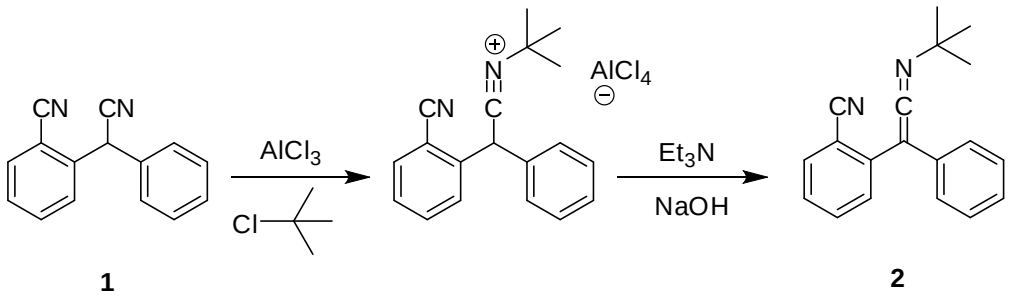
D. Experimental



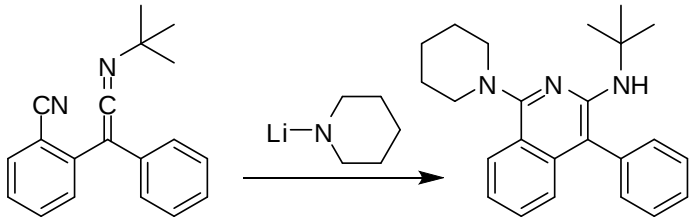
1

Synthesis of 2-(cyano(phenyl)methyl)benzonitrile (1). In a Schlenk flask, 2-phenylacetonitrile (1.879 g, 16.06 mmol), K-O*t*Bu (1.799 g, 16.06 mmol) and DMF (18.5 mL) were added. The solution was cooled to 0 ^{0}C in an ice bath. A solution of 2-chlorobenzonitrile (1.000 g, 7.30 mmol) in DMF (10.1 mL) was prepared and added into the Schlenk flask dropwise. The combined solution was allowed to warm to room temperature overnight. The reaction was quenched using 10% HCl, extracted with EtOAc, rinsed with

brine, and purified by column chromatography on silica gel (0-8% EtOAc in Hexanes) to give the desired product (1.539 g, 96.7%): ^{1}H-NMR ($CDCl_3$): δ= 5.57 (s, 1H), 7.36-7.49 (m, 5H), 7.67-7.71 (m, 4H); IR (KBr): 3067, 3039, 2923, 2227, 1598, 1494, 1454 cm^{-1}.



Synthesis of 2-(2-(*tert*-butylimino)-1-phenylvinyl)benzonitrile (2). In dry box, **1** (218 mg, 1.0 mmol), $AlCl_3$ (293 mg, 2.2 mmol), and DCM (2 mL) were added into a Schlenk flask. The flask was removed from the dry box and put under a nitrogen atmosphere on a Schlenk line. The solution was cooled to -30 ^{0}C in an acetonitrile/dry ice bath. *tert*-Butyl chloride (202 mg, 2.2 mmol) was added and the solution was allowed to stir for 90 minutes. The solution was then cooled to -78 ^{0}C (Acetone/dry ice bath). Triethylamine (152 mg, 1.5 mmol) was added and the solution was allowed to stir for 60 minutes. The reaction was warmed and quenched with 7M NaOH when it reached -40 ^{0}C to -20 ^{0}C, extracted with EtOAc, and the organics were rinsed with brine solution. A peak in the IR at 2014 cm^{-1} was observed which is characteristic of a ketenimine group.[24]



2 **3**

Synthesis of N-*tert*-butyl-4-phenyl-1-(piperidin-1-yl)isoquinolin-3-amine (3). The crude product of **2** (123.5 mg, 0.45 mmol) and THF (1 mL) were added into a Schlenk flask. In a small round bottom flask, lithium piperidin-1-ide (123 mg, 1.35 mmol) and THF (3 mL) were added in dry box. This solution was added to that in the Schlenk flask after both of the solutions were cooled to 0 ^{0}C (ice + water). The resulting mixture was allowed to stir for 2 hours. The reaction was quenched with 10% HCl. Then, NH4OH solution was added into the quenched reaction until the pH reached 7. The resulting solution was then extracted with EtOAc, rinsed with brine, and purified by column chromatography on silica gel (5-20% EtOAc in Hexanes) to give the desired product (0.0969g, 60%). ^{1}H-NMR ($CDCl_3$): δ= 1.27 (s, 9H), 1.84-1.86 (m, 6H), 3.38 (t, 4H), 7.09-7.12 (m, 2H), 7.27 (m, 1H), 7.31-7.34 (d, 2H), 7.50-7.52 (m , 2H), 7.85-7.98 (d, 1H).

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Chapter 3 Investigating milder nucleophilic cyclization conditions

A. Introduction

Efficient cascade cyclization is a major challenge when using a precursor route to make a conjugated or ladder polymer. In the project described here, it would be of interest to initiate the cyclization using light. As stated previously, it is possible to generate only mild bases photochemically.[1–9] Therefore, it is of interest to determine the mildest base/nucleophile that efficiently cyclizes the precursor polymer (or oligomers of it) under study in this thesis. We can then determine whether such a species can be generated photochemically.

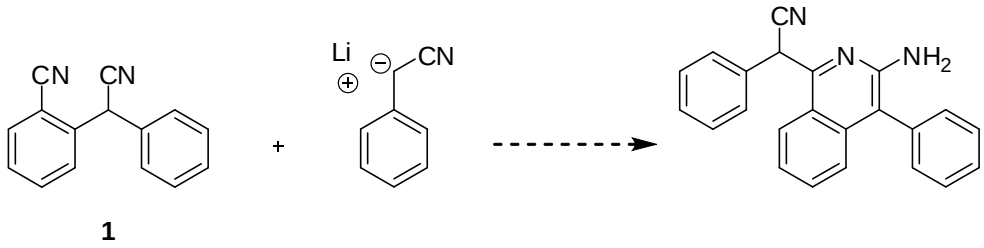
Phenylacetonitrile anion is an interesting nucleophile. It has a similar structure to the monomer in the precursor polymer, and it is also milder than *n*-BuLi, the nucleophile which has been used previously to perform cascade cyclization on model oligomers of our precursor polymer.[10] In this chapter, it is explored as an alternative nucleophile to determine if it can efficiently cyclize a model oligomer of our precursor polymer.

B. Results and Discussion

1. Attempts at cyclization of an oligomer with two cyano groups

The cyclization based on oligomer with two cyano group **(1)** was explored. The first experiments conducted were to determine whether 2-phenylacetonitrile anion (with a lithium or sodium counterion) efficiently initiates the cyclization reaction (Scheme 3-1). 2-Phenylacetonitrile is deprotonated using either *n*-BuLi or NaH to form its anion. A solution containing this anion was then mixed with the model oligomer. Reactions were run at different temperatures (RT/40 ^{0}C /60 ^{0}C).

Scheme 3-1: Cyclization route of oligomer with two cyano group (Lithium base)



In each case, after the reaction was allowed to stir for 12 h, TLC showed that most of the materials were consumed. However, ^{1}H NMR spectra of the crude products and/or purified products did not match that expected for the desired product. Specifically the methine peak in the 1H NMR at 5.57 ppm was still there, peaks at ca. 8 ppm (aromatic region) and 5.06 ppm (a new cyano methine) indicating incorporation of the phenyl acetonitrile initiator were not observed.[11]

After it was determined that the lithium 2-phenylacetonitrile anion was not able to cyclize the material, a stronger nucleophile was explored (Scheme 3-2). TMEDA has an affinity for lithium. Because of the quite stable complex it forms with lithium ion, the 2-phenylacetonitrile anion will be more nucleophilic.[12] Also, sodium is known to be a weaker coordinating cation to carbanion.[13,14] Thus, sodium 2-phenyl acetonitrile anion was also explored as a nucleophile. In this case, sodium hydride was used to deprotonate the 2--phenyl acetonitrile to give the sodium 2-phenyl acetonitrile anion. The same experiment conditions were applied as above. Different reaction temperatures were studied (Table 3-1).

Scheme 3-2: Cyclization route of oligomer with two cyano groups using 2-cyanoacetonitrile anion with Li/TMEDA and sodium cations.

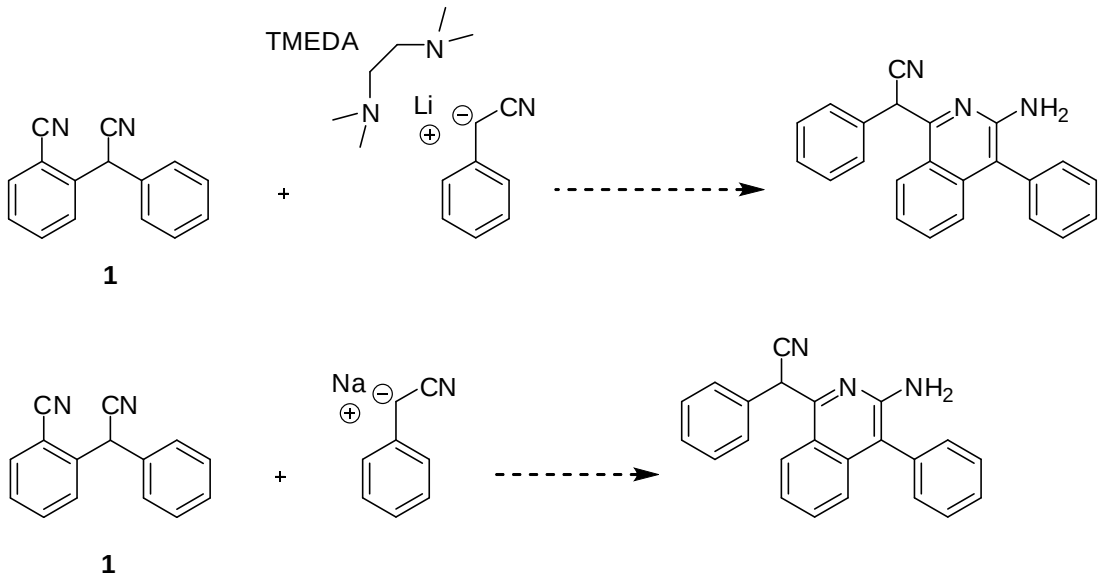


Table 3-1: Experimental conditions for two cyano oligomer

Entry	Base	Temperature	TMEDA
1	BuLi in Hexanes	RT	YES
2	BuLi in Hexanes	40 ^{0}C	YES
3	BuLi in Hexanes	60 ^{0}C	YES
4	NaH	RT	N/A
5	NaH	40 ^{0}C	N/A
6	NaH	60 ^{0}C	N/A
7	NaH	72 ^{0}C	N/A

*Conditions: 1.0 eq. **1**, 10 eq. phenylacetonitrile, 10 eq. base, 10 eq. TMEDA.*

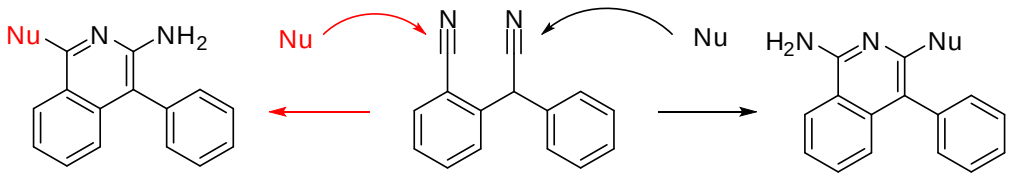
The reactions using TMEDA (Table 3-1, entries 1-3) were examined using ^{1}H NMR. From the TLC, some starting material remained. Also, from the ^{1}H NMR spectra, there was a broad peak close to 6 ppm which was assigned to amine. However, the characteristic aromatic peak and cyano methine peak were not observed at desired region. There was doublet at 7.60 ppm which is quite similar to the desired aromatic peak. Also, a sharp singlet peak was observed at 4.00 ppm. The pure product after column was sent for MS.

Unfortunately, the result did not indicate the desired product. Thus it was concluded that these reaction did not produce the desired product. The reactions using sodium metalated 2-phenylacetonitrile anion (Table 3-1, entries 4-6) showed a better result. From the crude ^{1}H NMR spectrum, a peak close to 5 ppm (new cyano methine) was observed. However, the TLC showed two very close spots which were extremely hard to separate. Thus, the stronger base showed a better result, and this result bears further study.

2. Attempts at cyclization of oligomer with three cyano groups

Using the precursor oligomer with two cyano groups has a disadvantage. If the cascading cyclization can occur at both sides, there will be two different products (Scheme 3-3). The structures of these two products are very similar, which made these harder to be purified. Thus, it was decided to attempt cyclizations using a different model oligomer.

Scheme 3-3: Disadvantage of two cyano oligomer

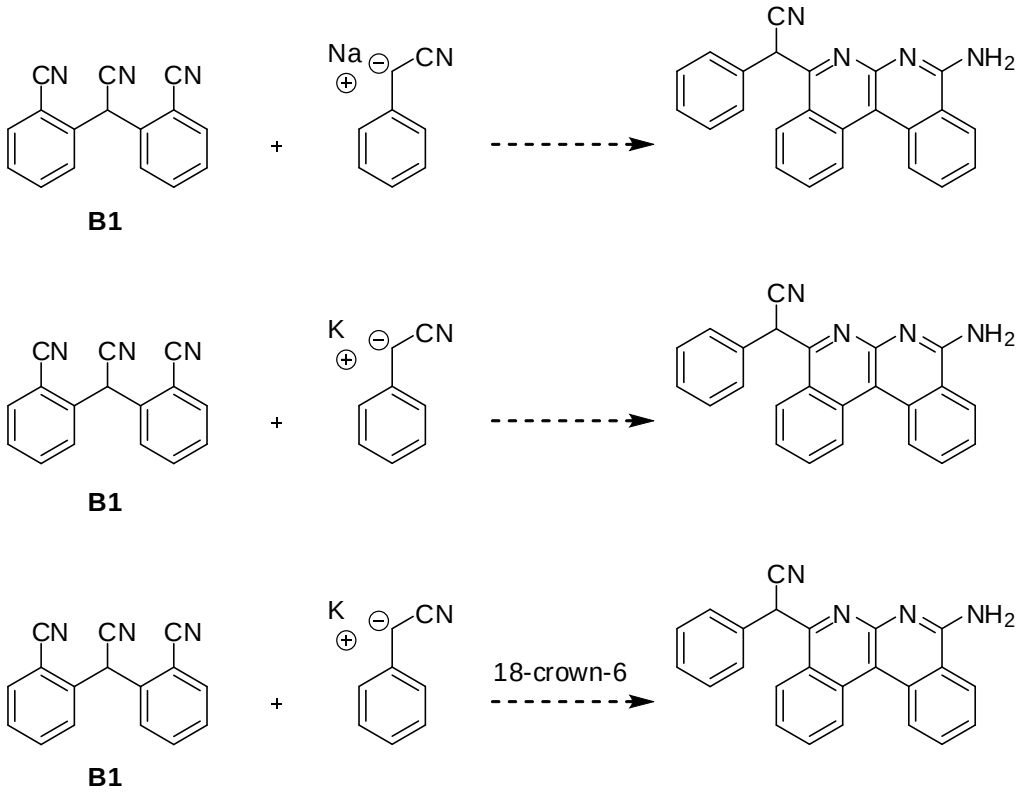


1

Similar experiments were conducted with the oligomer containing three cyano groups (**B1)** as the starting material. From the previous research, the sodium 2-phenylacetonitrile anion showed a better result than the lithium 2-phenylacetonitrile anion. This result suggested that, using a stronger base to make the anion more nucleophilic was more effective in this cyclization reaction. If so, using a stronger nucleophile result in a more efficient

cyclization reaction. Thus, stronger nucleophiles were employed. Cyclization reactions were conducted these optimized nucleophiles (Scheme 3-4).

Scheme 3-4: Cyclization route of oligomer with three cyano group



Nucleophiles based on 2-phenyl acetonitrile were tested at different reaction temperatures (Table 3-2). The 18-crown-6 has same function for sodium cations as TMEDA has for lithium cations used before. It has a particular affinity for potassium cations.[15,16] The complex formed will pull the potassium away from the 2-phenylacetonitrile anion and make the anion more nucleophilic which means easier attack of the cyano group and initiation of the cyclization reaction. TLC was applied to monitor the reaction and ^{1}H NMR was used to characterize the products from the reaction.

Table 3-2: Experimental conditions

Entry	Ratio	Base	Temperature	18-crown-6
1	1:10	NaH	RT	N/A
2	1:10	NaH	40	N/A
3	1:10	NaH	60	N/A
4	1:2	NaH	40	N/A
5	1:10	KH	RT	N/A
6	1:10	KH	40	N/A
7	1:10	KH	60	N/A
8	1:10	KH	RT	YES
9	1:10	KH	40	YES
10	1:10	KH	60	YES

Conditions: 1.0 eq. ***1****, 10 eq. 2-phenylacetonitrile, 10 eq. base, 10 eq. TMEDA.*

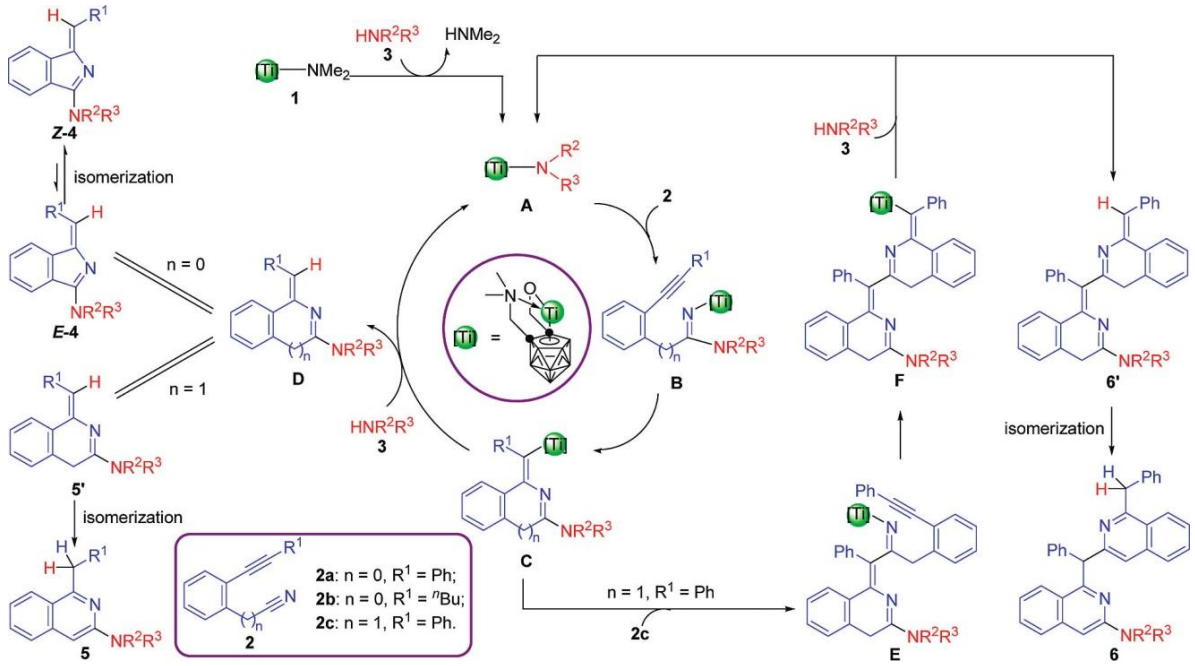
The reaction using a 1:2 ratio of reactant to nucleophile (Table 3-2, entry 4) showed no cyclization according to the TLC. Thus, decreasing the reactant to nucleophile ratio will affect the cyclization. The reactions using NaH (Table 3-2, entries 1-3) were examined using ^{1}H NMR. A peak close to 5 ppm (assigned as a new cyano methine) was observed. One of the characteristic aromatic peaks was observed at 8.0 ppm. However, the integrals of these two peaks showed an incorrect ratio of hydrogens which indicated that it might be not the desired product. Also, a large multiplet was observed around 3.70-4.00 ppm. This peak was not able to be isolated even after column chromatography. The reactions using KH (Table 3-2, entries 5-10) were examined using ^{1}H NMR. The same result was observed as those reactions using NaH. In addition to the peaks at 8 ppm and 5 ppm, peaks in the alkyl region

were observed which should not be present. Thus, it was concluded that the cyclization reaction using 2-phenyl acetonitrile anions didn't work well as no desired products were obtained.

3. Attempts at cyclization in the presence of a titanium catalyst

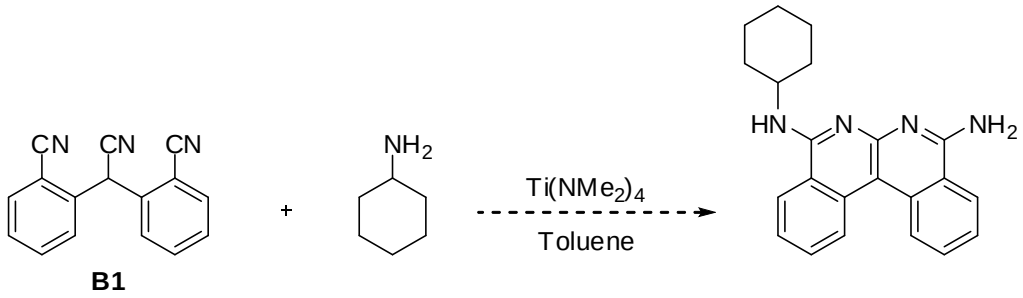
Instead of using stronger nucleophiles to initiate a cascade cyclization, one can envision using a Lewis acid to activate the nitrile groups towards cyclization by milder nucleophiles. In the literature it was discovered that $Ti(NMe_2)_4$ can catalyze cyclizations involving nitrile groups (Scheme 3-5).[17] According to the paper, this method resulted in a high yield of the desired products. The only disadvantages of this method are a longer reaction time and concern over generation of more than one regioisomer of the product. Nevertheless, given the high yields reported (>95%) experiments to try to adapt it to our cascade cyclization of interest were attempted.

Scheme 3-5: Mechanism of $Ti(NMe_2)_4$ catalyzed cascading cyclization. Taken from reference 17



Experimental conditions similar to those reported were employed in our model cyclization[17]. The nucleophile used was cyclohexylamine. The route is shown in Scheme 3-6. TLC was used to monitor the reaction.

Scheme 3-6: Cyclization route catalyzed by $Ti(NMe_2)_4$



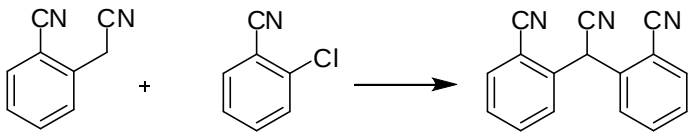
The results from TLC were not good. Starting material still remained after 80 hours of reaction time. Moreover, multiple new spots were observed on the TLC plate, indicating

multiple products. The crude product was examined using ^{1}H NMR. A peak at 6.2 ppm was observed and was assigned to a secondary amine. However, the characteristic aromatic peak close to 8 ppm was not observed. Also, a large multiplet at 4 ppm was observed again. Thus, this reaction didn't provide the desired product. Also, based on the messy TLC obtained, the purification of the crude product likely would be difficult.

C. Conclusions

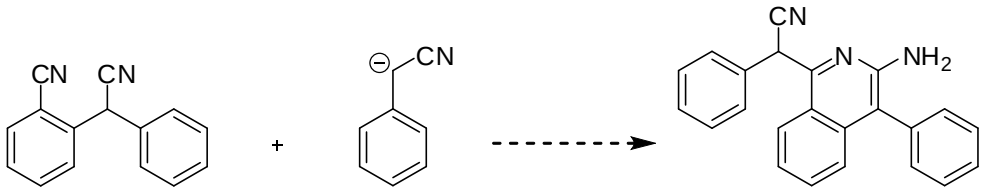
Approaches to perform an efficient, cascade cyclization on model oligomers were studied. Two oligomers were studied. The oligomer with two cyano groups is smaller, but it has an unsymmetrical structure. The nucleophile can attack the cyano group at both sides of the oligomer which will lead to two different cyclized products who have similar polarities. This could result in undesirable difficulties in purification. The oligomer with three cyano groups is larger but doesn't have the disadvantage mentioned for the oligomer with two cyano groups. The crude NMR of the products studied here indicated that the metalated phenylacetonitrile can act as a nucleophile to initiate cascading cyclization reaction. However, none of the reactions studied were efficient. Using a Ti amide catalyst as a Lewis acid to activate the substrate appeared promising. However, it was also not efficient for our model cyclization.

D. Experimental



B1

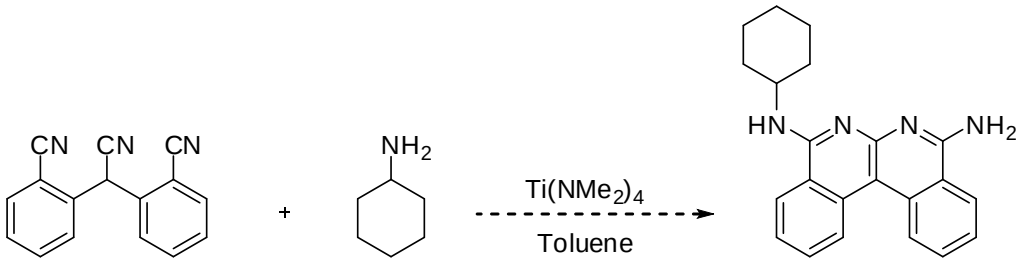
Synthesis of 2,2'-(cyanomethylene)dibenzonitrile (B1). In a nitrogen-filled dry box, 2-cyanomethylbenzonitrile (1.420 g, 10 mmol), K-O*t*Bu (1.232 g, 11 mmol) and DMF (1.5 mL) were added into a Schlenk flask. The resulting solution was allowed to stir for 20 minutes at room temperature. A solution of 2-chlorobenzonitrile (1.370 g, 10 mmol) in DMF (1.5 mL) was prepared and added dropwise into the Schlenk flask. The combined solution was removed from the dry box and attached to a Schlenk line to provide a nitrogen atmosphere. The solution was allowed to heat to 80 ^{0}C and stir overnight. The reaction was quenched using 10% HCl, extracted with EtOAc, rinsed with brine, and purified by column chromatography on silica gel (0-30% EtOAc in hexanes) to give the desired product (1.043 g, 43%). ^{1}H NMR and IR matched the reported value.



1

Attempts at cyclization of 2-(cyano(phenyl)methyl)benzonitrile. In dry box, phenylacetonitrile (117 mg, 1.0 mmol) and THF (0.5 mL) were added into a Schlenk flask.

n-BuLi in hexanes or NaH (1.0 mmol) in THF (0.5 mL) was added into the Schlenk flask dropwise at a given temperature. The solution was allowed to stir for 20 minutes. TMEDA (1.0 mmol) was added after this period in some reactions involving *n*-butyl lithium. 18-Crown-6 (0.1 mmol) was added after this period in some reactions involving potassium hydride. A solution of **1** (21.8 mg, 0.1 mmol) and THF (0.5 mL) prepared in the dry box was then added into the Schlenk flask at a given temperature. The solution was allowed to warm to RT or 40 ^{0}C or 60 ^{0}C or 72 ^{0}C and stir overnight. The reaction was quenched using 10% HCl, then drops of NH_4OH were added to reach pH=7. The solution was then extracted with EtOAc, rinsed with brine and dried with Na_2SO_4. The solvent was evaporated, and the resulting mixture was characterized by TLC and 1H NMR.



B1

Attempts at cyclization of 2,2'-(cyanomethylene)dibenzonitrile with $Ti(NMe_2)_4$. In a dry box, $Ti(NMe_2)_4$ (11.2 mg, 0.05 mmol) and cyclohexylamine (19.8 mg, 0.2 mmol) were added into a Schlenk flask. The flask was removed from dry box, put on a Schlenk line under nitrogen, and allowed to stir for 2 hours at RT. The solution was concentrated under vacuum to a volume of 10 mL. The flask was moved into the dry box, and a solution of **B1** (122 mg, 0.5 mmol) and cyclohexylamine (79.2 mg, 0.8 mmol) in toluene (5 mL) was added into the Schlenk flask. The reaction was moved from dry box, put on a Schlenk line under nitrogen

and allowed to stir for 80 hours at 115 ^{0}C. The reaction was quenched using 10% HCl, extracted with EtOAc, rinsed with brine and dried with $MgSO_4$. The solvent was evaporated, and the resulting mixture was characterized by TLC and ^{1}H NMR.

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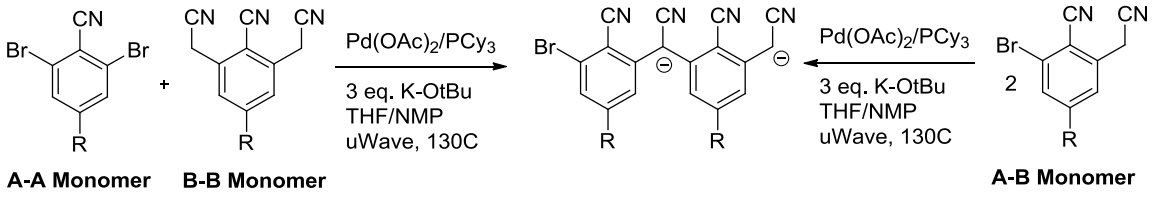
Chapter 4 Synthesis of A-B monomer and initiator assisted synthesis of cyano-containing precursor polymer

A. Introduction

Previous work in the Gorman group has shown that polymerization of the proposed monomer has some significant challenges.[1,2] These are summarized below. The goal of this work is to overcome these challenges and produce the proposed, precursor polymer with a reasonable molecular weight (> 10 kDa) and yield.

Scheme 4-1: Polymer synthesis pathways

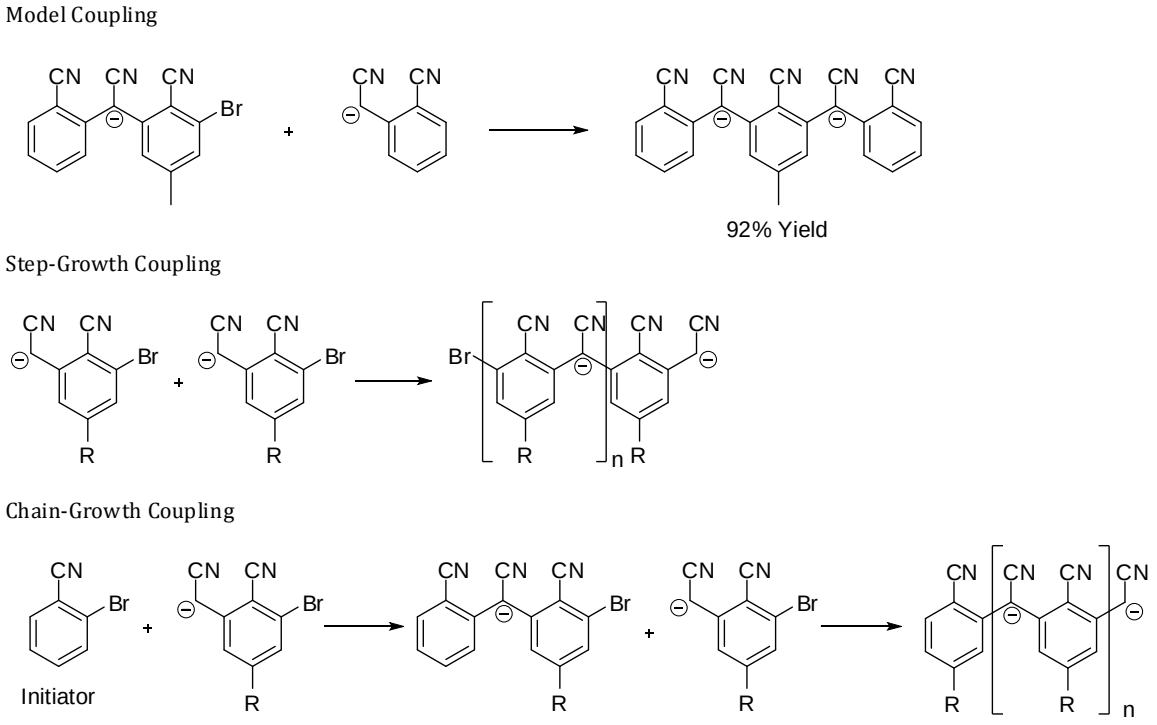


Two conceivable pathways exist for the synthesis of the polymer. The first of these reacts an aryl di-halide (an A-A monomer) with a bis-benzylic nitrile (a B-B monomer) (Scheme 4-1, left). This pathway has been explored previously by other group members, but the synthesis of the B-B monomer has proven problematic.[2–7] The other pathway reacts a monomer that contains both an aryl halide and a benzylic-nitrile (an A-B monomer, Scheme 4-1, right). The A-B monomer pathway only requires one monomer molecule and is thus more convenient. This method is pursued here.

The A-B monomer pathway, however, does have a challenge. The polymerization turns out to be quite different from model couplings studied before.[1] In a model coupling, the model aryl halide contains an additional benzonitrile, which likely results in differential reactivities between the model aryl halide and the monomeric aryl halide (the A-B monomer). With an acidic proton on the diarylmethane linkage, it is thought that deprotonation would

happen quickly, and subsequent coupling would have to occur on a formally anionic species. This anion is, however, able to be delocalized by the additional electron withdrawing benzonitrile, resulting in a substrate that is electron-poor enough to undergo oxidative addition. Scheme 4-2 shows the difference in the electrophilic components for each type of coupling.

Scheme 4-2: Comparing the different coupling method



This problem has been circumvented by the use of an initiator-assisted, chain-growth method. Here, an 'initiator' monomer that lacks one of the two functional groups is added to provide a site that is not deactivated by the second functional group. This approach provides a more comparable electrophile to that used in the model reaction. A previous group member, Molly Brannock, showed that this approach could work to produce the desired polymer.[1]

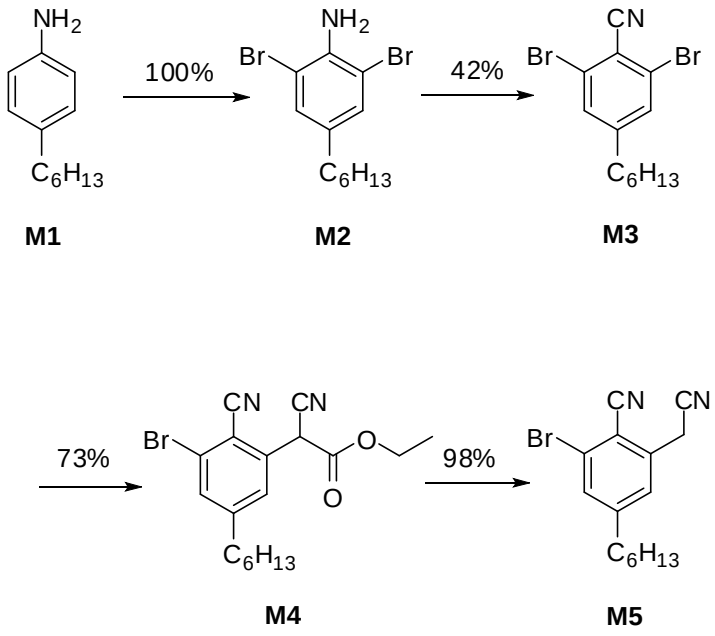
This route, however, still provided relatively low yields of polymer, and the material was colored, suggesting side products as the proposed route should yield non-conjugated, uncolored material. Thus, the goal of this project has been to optimize this reaction.

B. Results and Discussion

1. Optimization of monomer synthesis

The monomer synthesis sequence shown in Scheme 4-3 has been carried out before.[1,2] Some of the steps, however, are challenging or result in low yields. Thus, these reactions were re-examined in order to make the synthesis more efficient.

Scheme 4-3: Synthesis route for the monomer



The monomer synthesis began with 4-*n*-hexylaniline (**M1**) as the starting material. It is commercially available. Bromination to give **M2** is relatively straightforward and proceeds in

essentially quantitative yield.[8,9] The bottleneck in yield is step 2 (**M2** to **M3**). According to the literature, the maximum yield of similar reaction is about 50%.[10] Reaction of 4-cyano hexyl benzene with bromine was considered as an alternative. However, the nitrile group is *meta* directing group, and the hexyl group is *ortho, para* directing. Thus, this alternative molecule is not set up for bis-*ortho* bromination. Thus, the method from the literature was followed.

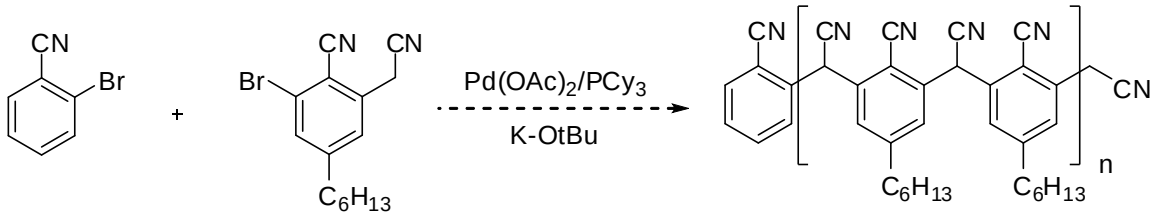
For the step 4, the typical method is thermal heating. However, due to the small scale and high temperature (165 ^{0}C) of the reaction, the small amount of the water required may easily evaporate and would then not be available for the hydrolysis reaction. Moreover, the reaction from literature requires more than 7-12 hours.[11] In order to solve this problem, microwave heating was used. However, the reaction did not work well under these conditions. The color of product was dark and the crude NMR of the product showed nothing in the aromatic region. The temperature of the experiment was lowered to 120 ^{0}C as reported for similar reactions using microwave heating.[11] The crude product was monitored by TLC and purified by column chromatography. One product was observed by TLC, and the NMR agreed with that of the desired product. By using this method, the reaction time was shortened to less than 1 hour and the yield of step four was raised to 98%. Under these revised conditions, the overall yield of this four step sequence is about 30%.

2. Optimization of chain-growth polymerization

As we proposed before, with the help of an initiator, the resulting delocalized anion should make the substrate more electrophilic and the reaction more efficient. However, the

polymerization under these conditions was not very successful (Scheme 4-4). According to the predicted ^{1}H-NMR spectrum of 2,2'-(cyanomethylene)dibenzonitrile, the methine hydrogen should be around 5.9 ppm. Also, for the polymer, there should be a broad signal in the aromatic region. Over several trials, the ^{1}H-NMR spectrums of the products obtained did not have a signal around 5.9 ppm, and peaks in the aromatic region were minimal. In addition, the yield of recovered material was very low (ca. 5 %).

Scheme 4-4: Polymerization route



M5

To make sure the signals of the recovered material were not so broad as to be unobservable, and to make sure the product was sufficiently soluble for ^{1}H-NMR, the product was dissolved in deuterated dimethyl sulfoxide (DMSO-d_6), and ^{1}H-NMR spectra of this sample were acquired at 80 ^{0}C and 100 ^{0}C. The results were the same as those obtained when the spectrum was collected at room temperature.

Next, the ratio of base to monomer and the solvent used to quench the reaction were varied. As the reaction involves excess, strong base, after the reaction, it is important to neutralize the solution and re-protonate the methine carbons in the product polymer which presumably become deprotonated during the reaction. Reactions were run with 1.1

equivalents of base per monomer unit and with three different quench solutions (methanol, methanol & H_2O and methanol & H_2O & HOAc). Based on ^{1}H-NMR spectra of the isolated materials, quenching with the solution containing HOAc offered the best result as it was the only one that showed a signal due to the methine proton expected in the product. The methine and aromatic peaks were sharp, however, not broad as would be expected for polymer. It was speculated that the lower ratio of base to monomer (1.1:1) was not conducive to forming long chain polymer.

3. Attempts to synthesize higher molecular weight polymer

The results presented above are a feasible polymerization route. The next step was to optimize yield and molecular weight. To do this, we focused on changing the ratio of the initiator to the monomer. A 1:20 ratio provides an efficient synthesis with a yield of 95 %. However, the polymer synthesized is too short. Thus, a larger initiator to monomer ratio was explored. After reaction, NMR and GPC were used to characterize the polymerization product (Table 4-1).

Table 4-1: GPC result for different ratio polymerization

I:M Ratio	Mn	Mw	PDI	Yield
1:20	2524	3305	1.310	95%
1:40	4874	8617	1.768	90%
1:60	1490	4567	3.064	100%
1:80	1625	44337	27.280	97%

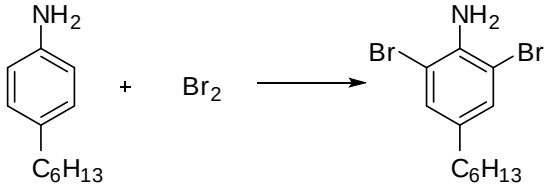
*Conditions: 10 eq. **M5**, 22 eq. K-OtBu, 1 eq. $Pd(OAc)_2$, 2 eq. PCy_3.*

From Table 4-1 we can see that the polymerization gives a high yield at a low initiator to monomer ratios. At higher initiator to monomer ratios, the primary effect was a broadened molecular weight distribution. Nevertheless, this method is the most successful and efficient route developed so far. It required milder reaction conditions and has a relatively high yield (80-100%). It is still need to be further optimized, however.

C. Conclusion

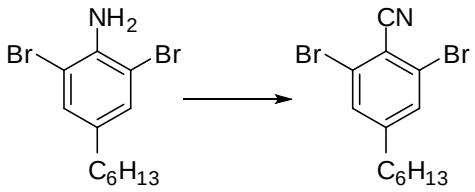
A new method for the synthesis of the monomer was developed starting from 4-*n*-hexylaniline. Under the newly developed conditions, the yield of step 4 increased to almost 100% and required less reaction time by using microwave method. The microwave offers more advantage than regular thermal heating method. Optimized polymerization conditions gave the desired product. It was the first time that ^{1}H-NMR spectra were obtained that matched those expected. In polymerizations with a lower monomer to initiator ratio, this method gave good results. However, this method worked less well when higher initiator to monomer ratios were explored. The method needs further optimization.

D. Experimental



M1 **M2**

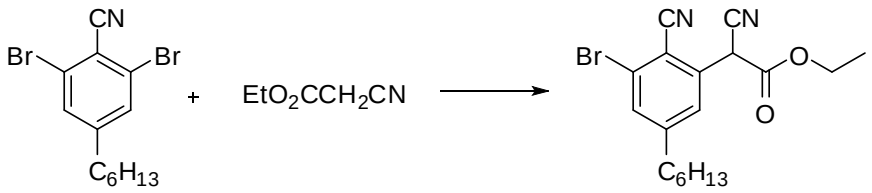
Synthesis of 2,6-dibromo-4-n-hexylaniline (M2). In a 50 mL round bottomed flask, 4-*n*-hexylaniline (**M1**) (1.772 g, 10.0 mmol), methanol (5.9 mL) and dichloromethane (5.9 mL) were added. In another small vial, bromine (1.28 mL, 25.0 mmol), methanol (2.4 mL), and dichloromethane (2.4 mL) were added. The bromine solution was added into the stirring solution in the round bottomed flask dropwise by using a pipet. The solution was allowed to stir for 2 hours. The reaction was quenched using 20% aqueous NaOH, extracted with diethyl ether, dried over Na_2SO_4, and purified by column chromatography on silica gel (0-2% EtOAc in Hexanes) to give the desired product (3.463 g, greater than 100%) which nevertheless was pure enough by ^{1}H-NMR to be used in the next step: ^{1}H-NMR ($CDCl_3$): δ=0.88 (t, 3H), 1.25-1.28 (m, 6H), 1.53 (m, 2H), 2.45 (t, 2H), 7.19 (s, 2H).



M2 **M3**

Synthesis of 2,6-dibromo-4-n-hexylbenzonitrile (M3). In a small vial, **M2** (335 mg, 1.0 mmol), HOAc (2 mL), and H_2SO_4 (0.25 mL, 4.8 mmol) were added. The vial was heated to 60 ^{0}C in an oil bath and the starting material dissolved. While this was heating, $CuSO_4$ (222.6 mg, 1.4 mmol) and H_2O (1 mL) were added into a 25 mL round bottomed flask and stirred to dissolve. After these compounds dissolved, the round bottomed flask was placed into an ice bath. Then a solution of KCN (325 mg, 5.0 mmol) in H_2O (1 mL) was prepared and added into the round bottom flask. After that, a mixture of $NaHCO_3$ (1.680 g, 20 mmol)

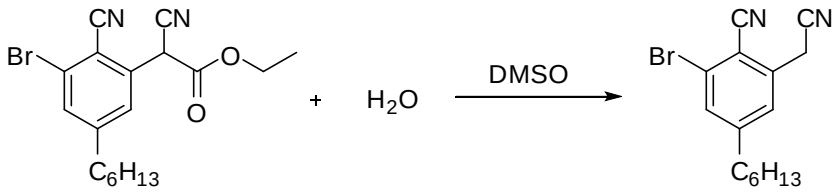
in hexane (4 mL) was added to the round bottom flask. The reaction flask was then heated to 55 ^{0}C. At the same time, the first vial containing the solution of **M2** was cooled in an ice bath. When the reaction flask reached 55 ^{0}C, a solution of $NaNO_2$ (82.8 mg, 1.2 mmol) in H_2O (0.2 mL) was prepared in a small vial, cooled to 0 ^{0}C and allowed to stir until everything dissolved. This solution was then added into the reaction flask drop wise (minimizing foaming) and allowed to stir for 2 hours at 55 ^{0}C. The reaction was quenched with 20% aqueous NaOH, extracted with toluene, rinsed with brine, dried over Na_2SO_4, and purified by column chromatography on silica gel (0-15% EtOAc in Hexanes) to give the desired product (0.143 g, 42%): ^{1}H-NMR ($CDCl_3$): δ=0.88 (t, 3H), 1.25-1.34 (m, 6H), 1.57-1.61 (m, 2H), 2.60 (t, 2H), 7.44 (s, 2H).



M3 **M4**

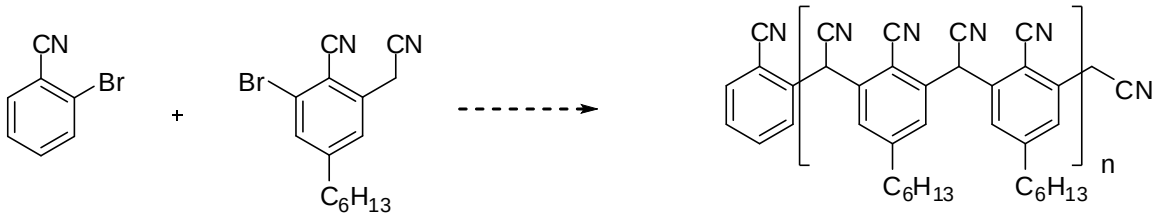
Synthesis of ethyl 2-(3-bromo-2-cyano-5-n-hexylphenyl)-2-cyanoacetate (M4). In a nitrogen-filled dry box, **M3** (120.5 mg, 0.35 mmol) and DMF (0.5 mL) were added into a Schlenk flask. In another 25 mL round bottomed flask, EtO_2CCH_2CN (166mg, 1.47 mmol), K-OtBu (157mg, 1.40 mmol) and DMF (1.65 mL) were added. The two flasks were sealed, removed from the dry box and put under nitrogen protection. Both solutions were allowed to stir for a few minutes until all solids dissolved. Then, the solution in the round bottomed flask was added to that in the Schlenk flask slowly using a syringe. The Schlenk flask was

then heated to 80 ^{0}C and allowed to stir for 18 hours under nitrogen protection. The reaction was quenched with 10% HCl, extracted with EtOAc, rinsed with brine, dried over Na_2SO_4, and purified by column chromatography on silica gel (0-13% EtOAc in hexanes) to give the desired product (0.097 g, 73.13%): ^{1}H-NMR ($CDCl_3$): δ=0.87 (t, 3H), 1.29-1.34 (m, 6H), 1.62 (m, 2H), 2.67 (t, 2H), 4.28-4.32 (m, 2H), 5.13 (s, 1H), 7.45 (s, 1H), 7.55 (s, 1H).



M4 **M5**

Synthesis of 2-bromo-6-(cyanomethyl)-4-n-hexylbenzonitrile (M5). In a microwave reaction tube, **M4** (113.1 mg, 0.3 mmol), H_2O (0.011 mL) and DMSO (0.2 mL) were added. The microwave was set at 200 W and maximum pressure of 150 PSI. The tube was heated to 110 ^{0}C. The heating time was set to 3 minutes and the holding time was 25 minutes. In a small beaker, 10% aqueous HCl and EtOAc were mixed and the reaction solution was added by pipeet to this mixture to quench the reaction. The resulting mixture was extracted with EtOAc, rinsed with brine, dried over Na_2SO_4, and purified by column chromatography on silica gel (0-13% EtOAc in Hexanes) to give the desired product (0.297 g, 98%): ^{1}H-NMR ($CDCl_3$): δ=0.89 (t, 3H), 1.30(m, 6H), 1.60-1.64 (m, 2H), 2.67 (t, 2H), 3.99 (s, 2H), 7.41 (s, 1H), 7.50 (s, 1H).



M5

Synthesis of precursor polymer (1:20 initiator to monomer ratio). In a nitrogen-filled dry box, **M4** (61.0 mg, 0.2 mmol) and THF (0.45 mL) were added into small vial. Potassium *tert*-butoxide (K-OtBu, 49.3 mg, 0.44 mmol) and THF (0.45 mL) were added into a second small vial. $Pd(OAc)_2$ (4.5 mg, 0.02 mmol), PCy_3 (11.2 mg, 0.04 mmol) and 2-bromobenzonitrile stock solution (0.10 M, 0.1 mL) were added into a microwave tube. This tube was pre-heated in the dry box to 60-70 ^{0}C. During this time, the solutions in the two vials were mixed and stirred together. This mixed solution was then added into the microwave tube and allowed to stir until everything dissolved. The microwave tube was sealed and removed from the dry box and placed into the microwave reactor. The microwave was set at 300 W with a maximum pressure of 150 PSI. The tube was heated to 130 ^{0}C with the heating time set to 3 minutes and holding time set to 10 minutes. In a centrifuge tube, a few drops of HOAc were added to a solution of methanol (4-5 mL) and H_2O (4-5 mL). The reaction mixture was then added slowly to this solution by pipette in order to quench the reaction. The mixture was then centrifuged at 5000 RPM for 10 minutes. The supernatant liquid was decanted and the solution was dissolved in THF and collected in a small vial. The vial was placed under vacuum to evaporate the THF and obtain the desired product (58.9 mg,

97%): ^{1}H-NMR (dichloromethane-d^{2}): the characteristic wide peak is around 5.80-5.90 ppm and also wide peak at the aromatic region; GPC (THF): Mn=2524, Mw=3305, PDI=1.310.

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