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ABSTRACT

Due to their high value as flame and heat resistant materials and high cost, improved methods for preparing polybenzimidazoles, particularly those with added substituents to improve processability, are desirable. This project was a proof of principle study to determine if Diels-Alder polymerization of monomers bearing imidazole and thiophene dioxide groups could be used to prepare polybenzimidazoles or related polymers. To this end, several new monomers were synthesized and polymerized. These include the first known bis-thiophene dioxide monomer, which was successfully copolymerized with a diacetylene comonomer, and a bis-imidazole monomer, 1,4-di(1H-imidazol-2-yl)benzene, whose copolymer with the aforementioned bithiophene dioxide monomer was the first polybenzimidazole ever prepared by a Diels-Alder cycloaddition reaction. Despite validation of the project thesis, monomers with more substituents are necessary to achieve the goal of enhanced processability.

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(a) Papers published in peer-reviewed journals (N/A for none)

<u>Received</u>	<u>Paper</u>
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(b) Papers published in non-peer-reviewed journals (N/A for none)

<u>Received</u>	<u>Paper</u>
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TOTAL:

Number of Papers published in non peer-reviewed journals:

(c) Presentations

Number of Presentations: 0.00

Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

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Peer-Reviewed Conference Proceeding publications (other than abstracts):

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Number of Peer-Reviewed Conference Proceeding publications (other than abstracts):

(d) Manuscripts

Received Paper

TOTAL:

Number of Manuscripts:

Books

Received Paper

TOTAL:

Patents Submitted

Patents Awarded

Awards

Congran Guo 1st place (the Arizona Materials Bowl) at the 8th annual ASM International Arizona Chapter meeting in Tempe, Arizona

Graduate Students

<u>NAME</u>	<u>PERCENT SUPPORTED</u>	Discipline
Stephen Budy	0.50	
Zhe Li	0.25	
FTE Equivalent:	0.75	
Total Number:	2	

Names of Post Doctorates

<u>NAME</u>	<u>PERCENT SUPPORTED</u>
Gerald Caple	0.00
FTE Equivalent:	0.00
Total Number:	1

Names of Faculty Supported

<u>NAME</u>	<u>PERCENT SUPPORTED</u>	National Academy Member
Douglas A. Loy	0.00	No
FTE Equivalent:	0.00	
Total Number:	1	

Names of Under Graduate students supported

<u>NAME</u>	<u>PERCENT SUPPORTED</u>	Discipline
Congran Guo	0.00	Materials Science and Engineering
FTE Equivalent:	0.00	
Total Number:	1	

Student Metrics

This section only applies to graduating undergraduates supported by this agreement in this reporting period

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Number of graduating undergraduates who achieved a 3.5 GPA to 4.0 (4.0 max scale):.....	1.00
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Names of Personnel receiving masters degrees

<u>NAME</u>
Total Number:

Names of personnel receiving PHDs

<u>NAME</u>
Total Number:

Names of other research staff

<u>NAME</u>	<u>PERCENT SUPPORTED</u>
Dr. Gerald Caple	0.00
FTE Equivalent:	0.00
Total Number:	1

Sub Contractors (DD882)

Inventions (DD882)

Scientific Progress

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Final Progress Report

"New Polybenzimidazole Architectures By Diels Alder Polymerization"

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Statement of the problem studied

Polybenzimidazoles and polyarylenes are strong polymers with glass transition temperatures over 300 °C and decomposition temperatures higher than any known organic materials. This makes these materials attractive for flame resistant cloth, high strength cable, body armor, and even high performance composites. However, polybenzimidazoles are commercially made in low yields from relatively expensive tetraaminoarenes making their wide commercial application uneconomical. The added difficulty and cost of synthesizing *substituted* tetraaminoarenes in order to improve their solubility and processing has limited the field of commercial polybenzimidazoles to the least substituted system, Celazole. This project was designed to explore a new method for preparing polybenzimidazoles and other polyarylenes that avoids the tetraaminoarenes entirely. This project looked at using the Diels-Alder cycloaddition reaction of three novel monomers to prepare the polybenzimidazoles: bis-thiophene dioxides, bis-imidazoles, and monomers with both thiophene dioxide and imidazole groups. These monomers were designed with sufficient substituents to allow the polymers to remain soluble and processible. The cycloaddition reaction of imidazoles with diene co-monomers has never been used to prepare polybenzimidazoles.

Summary of the most important results

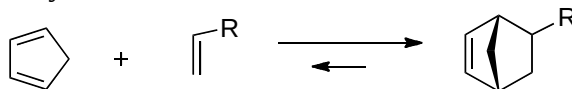
- 1) Prepared 3,4-diphenylthiophene dioxide and copolymerized it with bismaleimide, 1,1'-(1,4-phenylene)bis(1*H*-pyrrole-2,5-dione), to afford the first polymer in the project.
- 2) Prepared a new bis-thiophene dioxide monomer, 4,4'-(1,4-phenylene)bis(3-phenylthiophene 1,1-dioxide), and copolymerized it with 1,4-diethynylbenzene.
- 3) Prepared bis-imidazole monomer, 1,4-di(1*H*-imidazol-2-yl)benzene, and copolymerized it with 4,4'-(1,4-phenylene)bis(3-phenylthiophene 1,1-dioxide) to afford the first polybenzimidazole prepared by a Diels Alder cycloaddition polymerization.
- 4) Investigated new methods for synthesizing bis-imidazole monomers using oxidative coupling.
- 5) Started multistep syntheses of two new AB monomers each bearing thiophene dioxide and imidazole groups

Technical Report

Introduction

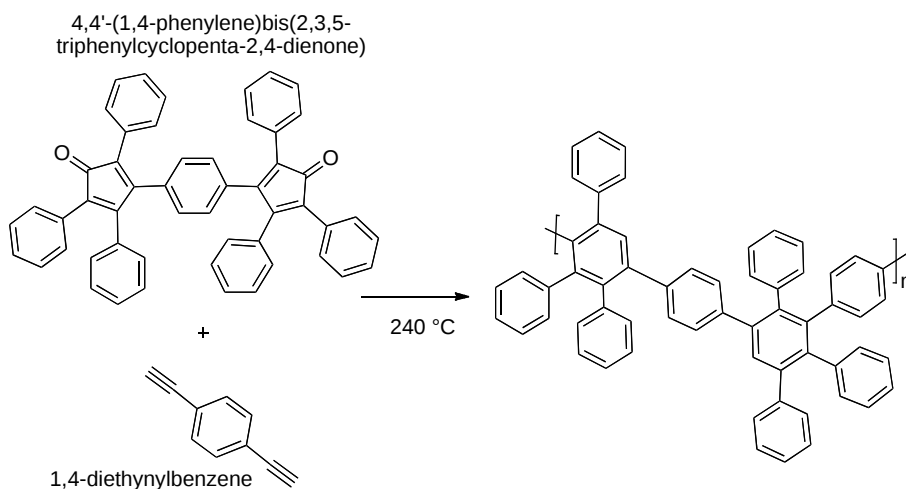
This preliminary research was directed at the Diels-Alder polymerization chemistry of two new classes of monomers, thiophene dioxide as diene monomers and imidazole as dienophile monomers. Diels-Alder reactions are a type of cycloaddition reaction, most often between a diene with four pi electrons in two double bonds and a dienophile with two pi electrons in one double bond (Scheme 1).

Scheme 1. Diels-Alder cycloaddition reaction



The result of the cycloaddition reaction is the formation of a six membered ring with two new sigma bonds and one double bond all made at the expense of the three double bonds in the precursors. The reaction is widely used in organic synthesis,¹ but has also been successfully applied in preparing organic polymers.² Typically, Diels-Alder polymerizations require monomers with at least two reactive groups to allow the formation of linear macromolecules. These can be in monomers with a diene group and a dienophile group in the same molecule (AB monomers) or in co-monomers, one with two diene groups and one with two dienophile groups that must react with each other to afford polymers. A number of Diels-Alder polymerization chemistries have been reported since the 1950's, but one that is still widely investigated today is based on the reaction bis-cyclopentadienone's with bis-acetylenes (Scheme 2).³

Scheme 2. Diels-Alder polymerization of 4,4'-(1,4-phenylene)bis(2,3,5-triphenylcyclopenta-2,4-dienone) with 1,4-diethynylbenzene.



This polymerization reaction, actually [4 + 2] cycloaddition followed by a retro [4 + 2] cycloaddition or chelotropic elimination of carbon monoxide, allows the formation of soluble and processible polyphenylene macromolecules.

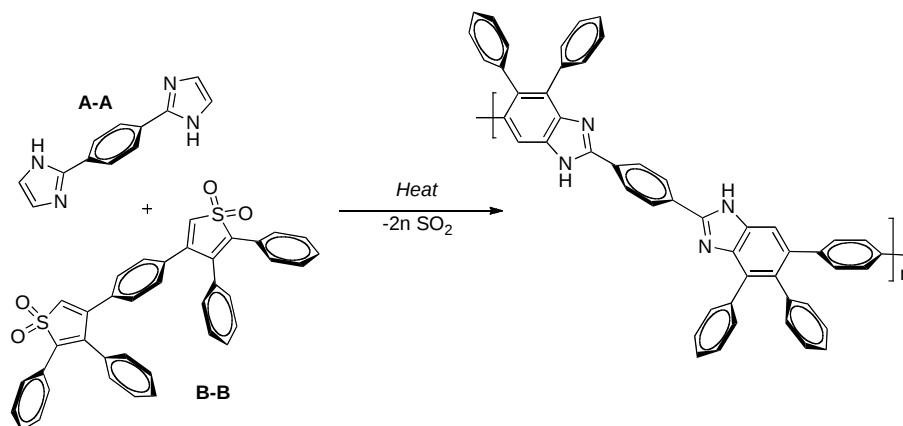
Polyphenylenes have been of interest as strong materials⁴ and semiconducting or conducting polymers.⁵ However, because the polymers are composed of a long chain of phenylene groups in the backbone, they are generally insoluble and intractable, unless substituents are added to twist the phenylene groups out of conjugation. The result is an insulating polymers with glass transition temperatures over 300 °C, thermal stabilities over 500 °C, and toughness second only to ultrahigh molecular weight polyethylene.³ The Diels-Alder polymerizations provide a metal-free reaction to prepare these robust polymers, making them more attractive to applications, such as microelectronics, that cannot tolerate residual metal catalysts.

The most of these Diels-Alder polymerizations have been conducted with the bis-cyclone and bis-acetylene monomers.³ Other monomers, such as those with pyrones as dienes,⁶ have been used but none have proved as versatile or as easy to synthesis as the cyclones. Unfortunately, the bis-cyclones must have four aryl groups attached to the cyclopentadienone ring to prevent it from undergoing a cycloaddition reaction with a second cyclopentadienone ring acting as the dienophile.⁷ This limited the range of materials possible and is one of the main reasons for this work. Despite this limitation, the bis-cyclone/bis-acetylene copolymerization reaction has been widely used and has spun off such important materials as the SiLK low dielectrics for modern computer chips.⁸

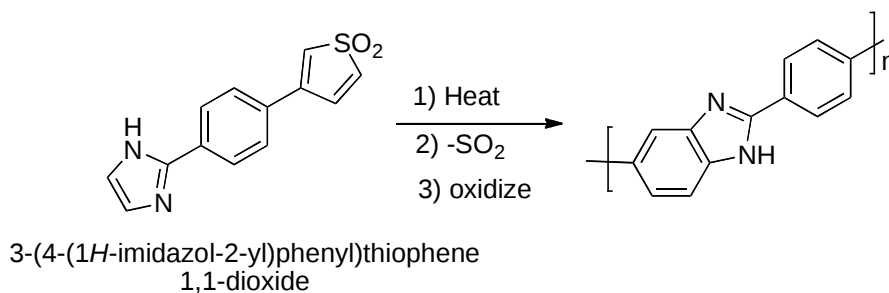
PBI's, first reported in the 1960's, are recognized as being the most thermally, hydrolytically and oxidatively stable organic polymers known.⁹ This class of polymers is aromatic with the heterocyclic benzimidazole group, a five membered imidazole ring annulated to a benzene ring. Their aromaticity coupled with some antioxidant properties of the imidazole are the source of their stability, but their lack of substituents and flat ring structures make PBI's insoluble¹⁰ and difficult to process. While their stability makes them attractive for aerospace applications,¹¹ fire-fighters protective clothing¹² and strong cable, only poly[2,2'-(m-phenylene)-5,5'-dibenzimidazole] (Celazole™) has ever been commercialized due to the difficulties associated with polymerizing and processing the materials.¹³ To date, PBI's have been prepared by condensation polymerizations from either arylene tetraamines and arylene dicarboxylic acids,¹⁴ acid chlorides¹⁵ or esters¹⁶ or of diaminoarylcboxylic acids.¹⁷ None have been prepared by Diels Alder polymerizations.

The targets for this project has been two fold, develop a new diene functionality, the thiophene dioxide, that is easier to prepare and can tolerate fewer substituents without self-cycloaddition and a new dienophile functionality that will allow benzimidazole ring systems to be prepared from the cycloaddition with an imidazole diene. The goals of the project included synthesis of the new monomers and investigation of their Diels-Alder polymerization. While originally we had proposed only the AA, BB copolymerization of monomers with two thiophene dioxides with co-monomers with two imidazole groups (Scheme 3), we also worked towards the synthesis of AB monomers with one thiophene dioxide and one imidazole group per monomer (Scheme 4). We were also interested in the reactivity of both new monomer functionalities with more traditional Diels-Alder polymerization functionalities, such as cyclopentadienonyl and ethynyl groups.

Scheme 3. Copolymerization of 1,4-di(1*H*-imidazol-2-yl)benzene (AA) with 4,4'-(1,4-phenylene)bis(2,3-diphenylthiophene 1,1-dioxide) (BB).



Scheme 4. Polymerization of 3-(4-(1*H*-imidazol-2-yl)phenyl)thiophene 1,1-dioxide, an AB style monomer.



Thiophene dioxides have been known for some time and have been proven to be excellent dienes in the Diels-Alder cycloaddition reaction.¹⁸ This has included enough work to support our hypothesis that the thiophene dioxide diene is less reactive to self-cycloaddition than the cyclopentadienone even with less than four substituents. In fact, it may be possible to prepare the thiophene dioxide with only one substituent and not have it react until a dienophile is introduced. Thiophene dioxides are prepared by oxidizing thiophenes.¹⁹ Thus, we are able to capitalize on the extensive work directed towards modified thiophene structures for organic photovoltaic,²⁰ light emitting diode²¹ and conducting polymers.²² However, most of the AA bis-thiophene dioxide monomers targeted by our group have not been previously reported. To date only one thiophene dioxide has been used in a Diels-Alder polymerization. In a patent in the 1960's, 3,4-diphenylthiophene oxide was shown to polymerize with bismaleimide monomers by two sequential cycloadditions.²³ The resulting thermoplastic material was not fully aromatic as the cycloadditions generated a bicyclic structure in the polymer backbone. The polymers were never described in peer-reviewed literature.

Imidazole groups have demonstrated reactivity as dienophiles to a number of dienes in cycloaddition reactions used in organic synthesis of small organic molecules.²⁴

However, they have not been used to prepare polymers by Diels-Alder polymerizations. Synthesis of imidazoles has traditionally been by reaction of an aldehyde or nitrile or carboxylic acid with a diamine to afford a 4,5-dihydro-1H-imidazole ring followed by oxidative removal of two hydrogens in the five-membered ring.²⁵ Alternatively, preformed imidazole groups have been coupled directly with aryl halides.²⁶ 1,4-Di(1*H*-imidazol-2-yl)benzene, one of the simplest bis-imidazole monomers targeted in this study, has been previously prepared by both methods as part of new methodology development and not as a monomer. Lastly, mixed AB monomers bearing both thiophene dioxide and imidazole have not been previously reported.

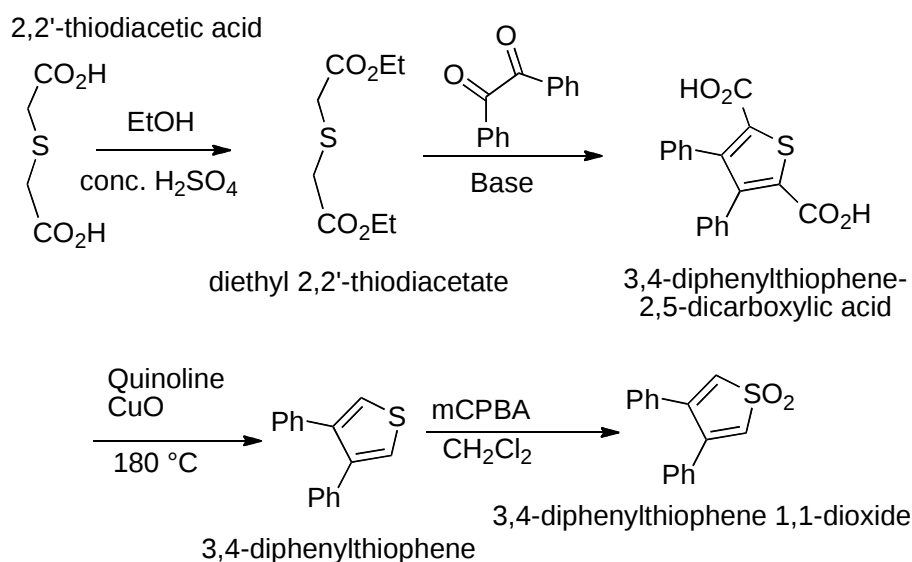
Results & Discussion

The results of the 11 months of research funded in this project will be divided up by monomer. Each monomers synthesis and subsequent polymerization studies will be described starting with the thiophene dioxide monomers, followed by the imidazole monomers, and finishing with the AB monomers.

3,4-Diphenylthiophene 1,1-dioxide monomer

We began with the synthesis of the simplest of the thiophene dioxide monomers to be examined in this study. 3,4-Diphenylthiophene 1,1-dioxide reported in 1964 as part of a US patent.¹⁴ The monomer was synthesized by base catalyzed condensation of diethyl 2,2'-thiodiacetate with benzil, followed by decarboxylation and oxidation of the thiophene (Scheme 5).²⁷ Diethyl 2,2'-thiodiacetate was prepared in 25 gram scale from the disodium 2,2'-thiodiacetate and ethanol by acid-catalyzed esterification. Treatment of the thiodiacetate ester with alkoxide base resulting in the formation of an enolate which condensed with benzil. Elimination of water afforded half of the desired ring and an intramolecular aldol with the enolate from the second acetate group and the second carbonyl in the benzil, followed by loss of water, gave the desired product with two carboxylate groups. The carboxylic acid groups were removed by decarboxylation in quinoline with copper oxide at 180 °C to afford the 3,4-diphenyl thiophene. Oxidation with m-chloroperoxybenzoic acid afforded the 3,4-diphenylthiophene dioxide in good yield.

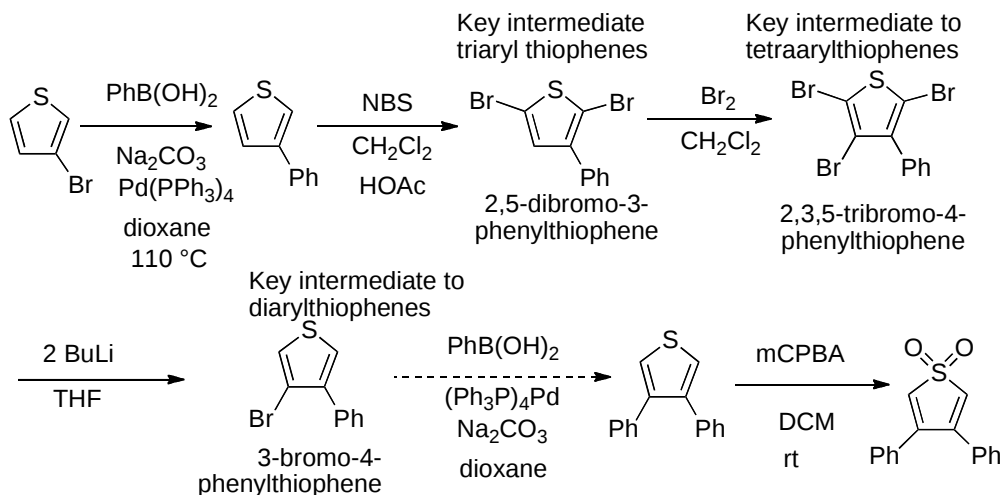
Scheme 5. Synthesis of 3,4-diphenylthiophene dioxide.¹⁸



We also began the preparation of 3,4-diphenylthiophene dioxide from 3-phenylthiophene (Scheme 6) but have not moved past the 3-bromo-4-phenylthiophene at this state. In theory, preparing 3,4-diphenylthiophene dioxide directly from thiophene should be less expensive than the procedure from thiodiacetate (Scheme 5). Scheme 6 represents essentially the same chemistry we would use from thiophene, but with the less volatile bromothiophene as the starting material for the undergraduate on the project to work with. More importantly, this synthetic sequence creates key intermediates for the

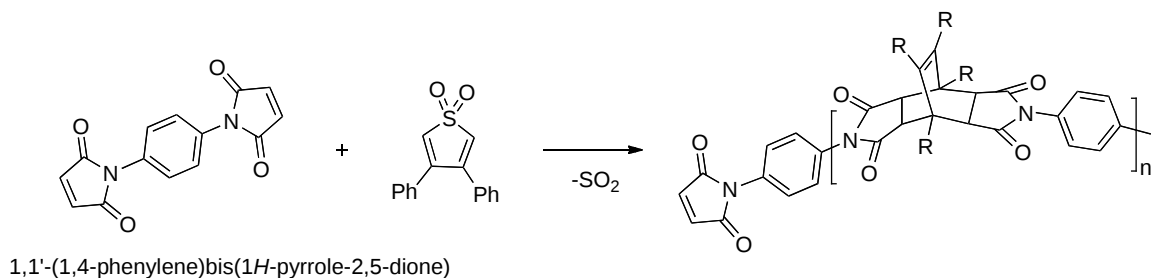
synthesis of future targets with varying levels of substituents: 2,5-dibromo-3-phenylthiophene as a precursor to triaryl substituted monomers, 2,3,5-tribromo-4-phenylthiophene as a precursor to tetra-substituted monomers, and 3-bromo-4-phenylthiophene as a precursor to di-substituted monomers.

Scheme 6. Alternative preparation of 3,4-diphenylthiophene dioxide



3,4-Diphenylthiophene dioxide was copolymerized with the bis-maleimide, 1,1'-(1,4-phenylene)bis(1*H*-pyrrole-2,5-dione) to afford the first polymer in the project (Scheme 7).

Scheme 7. Copolymerization of bis-maleimide with 3,4-diphenylthiophene dioxide.



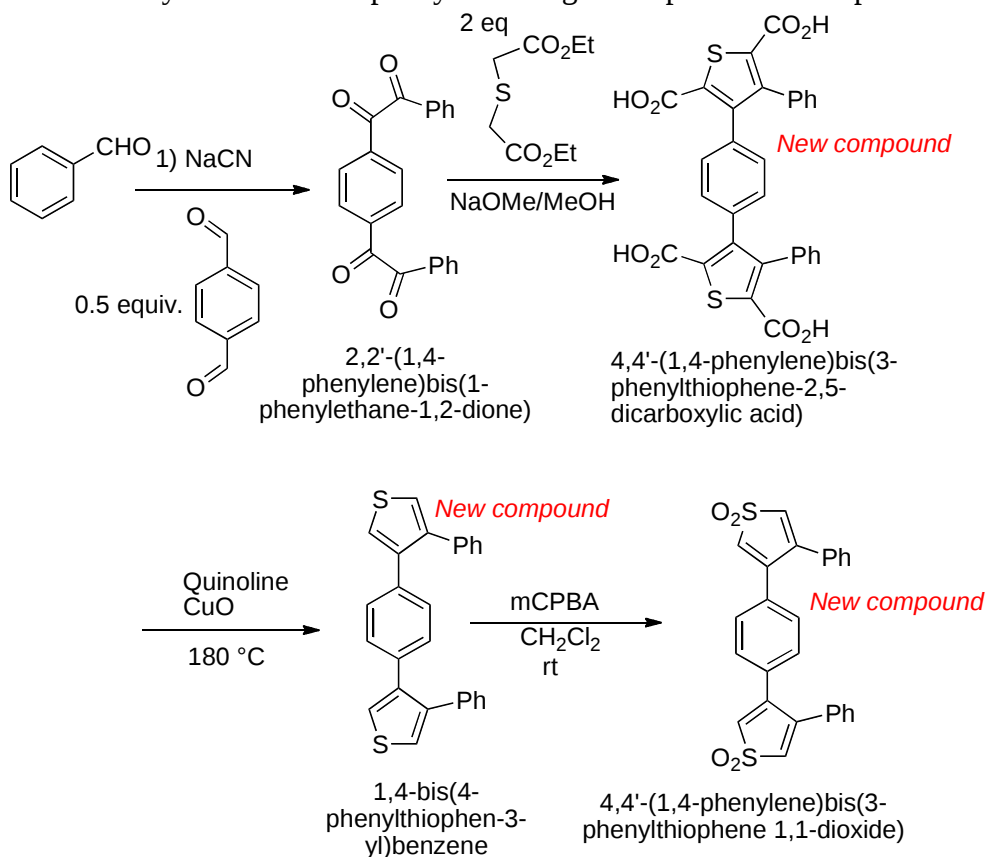
As described by the patent in 1961,¹⁴ the polymer is a thermoplastic. However, what was not described was the dark blue color observed during the polymerization that may have been the result of charge transfer. If this is the case, then it may be possible that the cycloaddition is not proceeding according to a normal pericyclic mechanism as expected. Charge transfer complexes have been observed in cycloadditions before and have been used as evidence for ionic intermediates in a multistep cycloaddition reaction. This effort corroborates the patent report from 1961 and will be reproduced and expanded before reporting the results in a published manuscript. Diels-Alder cycloaddition of 3,4-diphenylthiophene dioxide with commercially available phenyl imidazole as a model

reaction turned deep, dark blue with formation of cycloadduct, just as with the polymerization with the bis-maleimide.

4,4'-(1,4-phenylene)bis(3-phenylthiophene 1,1-dioxide)

This is the first of the monomers prepared with two thiophene dioxide groups attached to a bridging organic group. The preparation mirrored that of the previously described 3,4-diphenylthiophene dioxide save we used 2,2'-(1,4-phenylene)bis(1-phenylethane-1,2-dione) instead of benzil (Scheme 8).

Scheme 8. Synthesis of new phenylene bridged thiophene and thiophene dioxides.

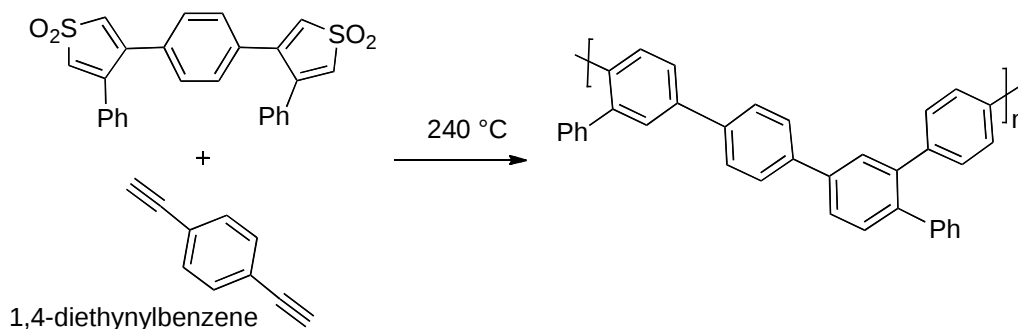


The 2,2'-(1,4-phenylene)bis(1-phenylethane-1,2-dione) was prepared from terephthalaldehyde and benzaldehyde in a direct benzoin condensation. We accidentally prepared a new polymer from terephthalaldehyde and benzaldehyde when we used a 1:1 stoichiometry instead of the desired 1:2 stoichiometry. The polymer formed as a viscous reddish orange mass even in solution suggesting that the molecular weight was fairly high. The polymer appeared to be a thermoplastic when dry, but was not further characterized. With the correct stoichiometry the reaction produced the desired and previously unreported 4,4'-(1,4-phenylene)bis(3-phenylthiophene-2,5-dicarboxylic acid) that we decarboxylated to afford the new bridged thiophene compound, 1,4-bis(4-phenylthiophen-3-yl)benzene. Oxidation with mCPBA in methylene chloride afforded the targeted new monomer, 4,4'-(1,4-phenylene)bis(3-phenylthiophene 1,1-dioxide).

Small scale polymerization of 4,4'-(1,4-phenylene)bis(3-phenylthiophene 1,1-dioxide) was attempted with 1,4-diethynylbenzene in diphenyl ether at 240 °C to afford a creamy white polymer (Scheme 9).

Scheme 9. Copolymerization of 4,4'-(1,4-phenylene)bis(3-phenylthiophene 1,1-dioxide) with 1,4-diethynylbenzene.

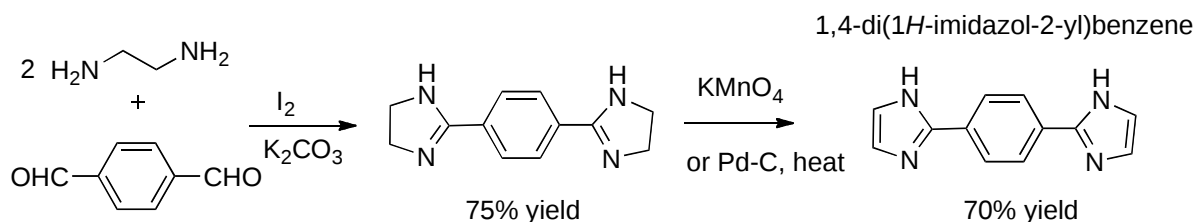
4,4'-(1,4-phenylene)bis(3-phenylthiophene 1,1-dioxide)



1,4-di(1*H*-imidazol-2-yl)benzene

1,4-Di(1*H*-imidazol-2-yl)benzene has been prepared from terephthalaldehyde and diaminoethane to afford the 1,4-bis(4,5-dihydro-1*H*-imidazol-2-yl)benzene that is subsequently oxidized to the desired monomer with either potassium permanganate²⁸ or palladium on carbon.

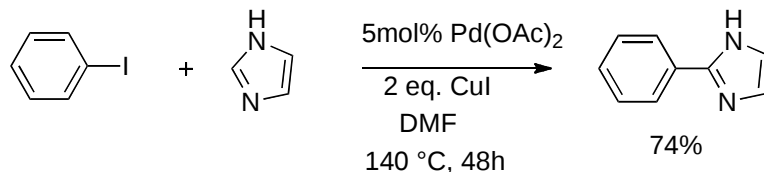
Scheme 10. Synthesis of bis-imidazole monomer, 1,4-di(1*H*-imidazol-2-yl)benzene



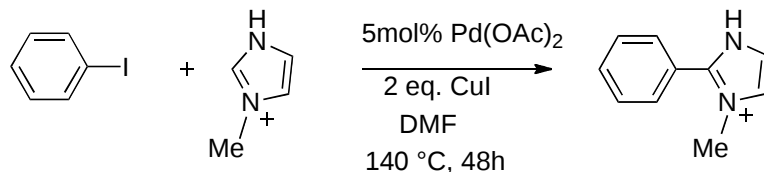
One of our most important discoveries was that the monomer is relatively insoluble. This could lead to lower polymer yields so we have been looking at ways to increase the solubility of the monomer. Generally, solubility of aromatic molecules is improved by changing the regiochemistry of the bridging group from *para* to *meta*. However, we decided to investigate if alkylation at the 2-nitrogen would break up crystal packing and improve the solubility.

We also performed several experiments with palladium-catalyzed oxidative coupling or aryl iodides and imidazoles (Scheme 11) and alkylated imidazoles (Scheme 12) to see if the latter could be made directly. The former reaction has been demonstrated with phenyl iodide and imidazole. The latter reaction has not been reported to date.

Scheme 11. Oxidative coupling of aryl iodides and imidazole.



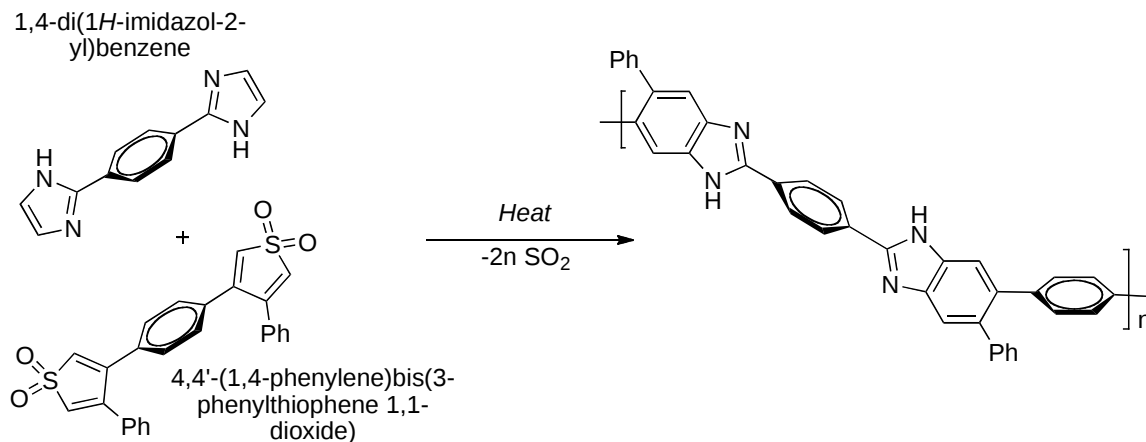
Scheme 12. Oxidative coupling of aryl iodides and N-methylimidazole.



Pure N-methylimidazole has not been isolated at present.

Diels-Alder cycloaddition of phenyl imidazole with 3,4-diphenylimidazole affords a cycloadduct. In comparison, the cycloaddition of phenyl imidazole with tetraphenyl cyclopentadienone undergoes no reaction even up to 260 °C. The phenyl groups are apparently too bulky for the cycloaddition to proceed. Reaction of the bis-imidazole with 4,4'-(1,4-phenylene)bis(3-phenylthiophene 1,1-dioxide) (Scheme 13) affords an insoluble white precipitate. It appears that the two phenyl groups per repeat unit are insufficient to break up intramolecular forces that successfully keep the polymer from dissolving. This hypothesis would require preparation of one of the monomers with three phenyl groups per thiophene dioxide group to test.

Scheme 13. Diels Alder polymerization of 1,4-di(1*H*-imidazol-2-yl)benzene with 4,4'-(1,4-phenylene)bis(3-phenylthiophene 1,1-dioxide).

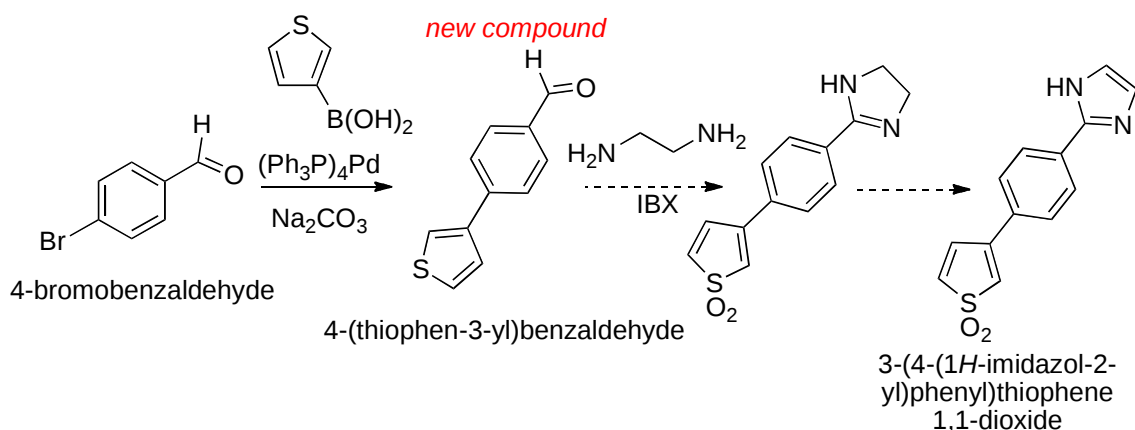


3-(4-(1*H*-imidazol-2-yl)phenyl)thiophene 1,1-dioxide

This is the first AB monomer synthesis to be started in this project. The advantage of AB monomers is that the stoichiometry is set by the molecule. The

disadvantage is that the synthesis can be more complicated. 3-(4-(1*H*-Imidazol-2-yl)phenyl)thiophene 1,1-dioxide has a thiophene dioxide and an imidazole group attached in para regiochemistry about a benzene group. The synthesis (Scheme 14) starts with Suzuki coupling of 4-bromobenzaldehyde with 3-thiopheneboronic acid to afford 4-(thiophen-3-yl)benzaldehyde, a hitherto-now, unknown compound. The next step, which has not been taken yet, is the formation of the diaza ring and oxidation of both it and the sulfur to afford the target monomer. Because conversion of the aldehyde to the diaza ring requires IBX to oxidize the carbon to the oxidation state of a carboxylic acid, it may be possible to combine all of the remaining steps into a single reaction.

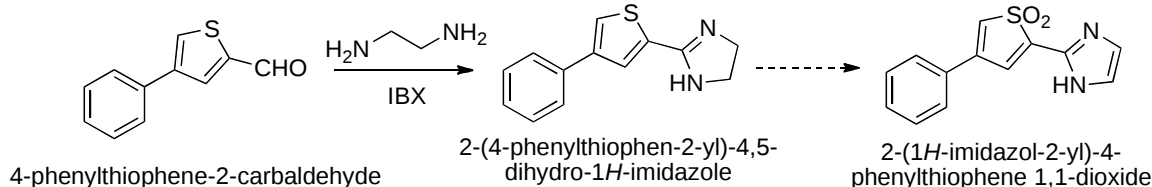
Scheme 14. Synthesis of 3-(4-(1*H*-Imidazol-2-yl)phenyl)thiophene 1,1-dioxide, the first AB monomer. Dashed arrows represent reactions that have not been finished.



2-(1*H*-imidazol-2-yl)-4-phenylthiophene 1,1-dioxide

In parallel to the synthesis of 3-(4-(1*H*-Imidazol-2-yl)phenyl)thiophene 1,1-dioxide, we have also begun the synthesis of 2-(1*H*-imidazol-2-yl)-4-phenylthiophene 1,1-dioxide from 4-phenylthiophene-2-carbaldehyde. At present, we have completed the first step with the formation of 2-(4-phenylthiophen-2-yl)-4,5-dihydro-1*H*-imidazole.

Scheme 15. Synthesis of 2-(1*H*-imidazol-2-yl)-4-phenylthiophene 1,1-dioxide.



Future Directions

Obviously, there are a number of monomers, such as 3-(4-(1*H*-Imidazol-2-yl)phenyl)thiophene 1,1-dioxide and 3-(4-(1*H*-Imidazol-2-yl)phenyl)thiophene 1,1-dioxide, whose syntheses have not been completed. There are also AA monomers with different numbers of phenyl groups that need to be synthesized. The trisubstituted thiophenes are the most urgent targets considering the potential solubility problems observed with the di-substituted thiophene monomer. It would be useful to determine the substituent effects on the reactivity of the thiophene monomers and the solubility of their polymers. Once the AB monomers are finished, their polymerization chemistry would have to be studied. It would be advantageous to conduct polymerizations of both AA-BB and AB monomer systems under high pressure to see if the polymerizations could be conducted at lower temperatures and if thermally unreactive monomers, such as the 4,4'-(1,4-phenylene)bis(2,3,5-triphenylcyclopenta-2,4-dienone) and 1,4-di(1*H*-imidazol-2-yl)benzene system, would polymerize at pressures where Diels-Alder reactions are known to be accelerated. Lastly, it would be useful to prepare sufficient polyarylenes and polybenzimidazoles to examine their oxidative stability, particularly in light of the proposed anti-oxidant characteristics of the dihydrobenzimidazole functionality, and complete a thorough study of their thermo-mechanical properties to gauge the polymers' potential for high temperature applications.

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