SYNTHESIS AND CHARACTERIZATION OF POLYMERIC SCHIFF BASES
FROM 2,5-DIFORMYLFURAN

A Thesis
Present to
The Graduate Faculty of The University of Akron

In Partial Fulfillment
of the Requirements for the Degree
Master of Science

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December, 2012
ABSTRACT

Furan derivatives have the potential to be an alternative resource since it can be obtained from biomass in large scale. Many monomers derived from furfural and 5-hydroxymethylfurfural (HMF), have been used in polymerization investigation in recent years. However, few studies in using 2,5-diformylfuran (DFF) as monomer has been reported, probably due to the limited availability of monomer. Polymeric Schiff bases (or polyimines) is a class of materials containing –CH=N– structural unit, which exhibit good thermal stability, useful mechanical properties. In this work, the polymeric Schiff bases obtained from polycondensation of DFF and aromatic, aliphatic diamines, and more comprehensive characterization study has been carried out. FT-IR and $^{13}\text{C}$ Solid NMR study of products confirmed the formation of –CH=N– structural unit. And MALDI-TOF mass spectrum showed a typical polymer pattern, providing further understanding on the polymerization process. Thermal Analysis had also been carried out for both aliphatic and aromatic polymeric Schiff Bases.
DEDICATION

I would like to dedicate this thesis to my mother, Yumei Jiang, for her love, patience and understanding.
ACKNOWLEDGEMENTS

I would like to thank my advisor Dr. Yi Pang for his guidance, patience that he has shown me through my time here in Akron. None of this work would have been possible if without his help. I would like to thank my co-advisor Dr. Ping Yi, for his kindness support through all my graduate study in all the way. I would also like to extend my gratitude to my lab mates and also my friends in chemistry department, for their support.
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CHAPTER I
INTRODUCTION

Furan is a heterocyclic organic compound, consisting of a five-membered aromatic ring with an oxygen atom. It is the heteroaromatic system when the aromatic system remains both conjugated and isoelectronic with the original hydrocarbons, after heteroatoms were inserted. The furan ring structure has been found in a larger number of industrial products as well as biological materials. Furan and its derivatives could be recognized as ensuing materials, not only because of its research point, but also due to its biological compatibility to the human beings. Furan, pyrrole, pyridine and thiophene and their derivatives are the most common examples of heteroaromatic system, as they could be recognized by their aromatic nature. Furan has a very peculiar chemical behavior which is often not closely related to that of its homologues thiophene and pyrrole, let alone aliphatic and aromatic compounds, and they could be directly prepared from saccharidic renewable resources. Like proposed in Gandini’s review paper in 2010: “The situation is qualitatively different with polymers prepared with furan monomers or through furan chemistry, because the approach here resembles the petrochemical counterpart in the sense that it provides entry to a whole host of monomers and

1
hence a variety of macromolecular structures with different properties.\(^2\) It is so true that currently organic-chemical and polymer industries are heavily depending on fossil fuel resources, which are unsustainable. Thus, furan derivatives have the potential to be an alternative resource since it can be obtained from biomass in large scale. All of these make furan compounds and furan-derived polymers in a special place which could motivate many chemistry-related scientists as well as engineers.

1.5 The furan heterocycle

Like many other five-membered “heteroaromatic” compounds, furan \(1-1\) possesses four resonance-contributing structures as follows (Scheme 1.1). The reactivity of furan is usually substitution reactions at the C2 and/or C5 position, such as alkaylation, halogenatuon, sulfonation and nitrations.

\[
\begin{align*}
\text{1-1} & \quad \longleftrightarrow \quad \text{1-2} & \quad \longleftrightarrow \quad \text{1-3} & \quad \longleftrightarrow \quad \text{1-4}
\end{align*}
\]

Scheme 1.1 Furan resonance structures\(^3\) (Reprinted with permission from reference 3)

The order of aromaticity among furan and the other two common heteroaromatic compounds is followed as thiophene > pyrole > furan, according to the combination of aromatic stabilization energies (ASE) which was obtained from theoretical calculations at MP2/6-31G* and B3LYP/6-31G**, as well as the
magnetic and polarizability criteria. As a planar molecule, the molecular dimensions of \(1-1\) have been determined by Dunlop and Peters from electron diffraction data (Scheme 1.2). The chemical behavior of furan and its derivatives displays a variety of features, depending on both the structure and properties of the heterocycle and the specific nature of the substituent on the ring. Polymerization study based on furan and its derivatives reveals that the mixed aromatic-dienic character plays an important role. The diene property showed in furan compounds makes many of them ideal for the Diels- Alder reaction with variety of dienophiles. On the other hand, furan and its derivatives tend to break their original structure through ring opening, due to the low extent of aromaticity.

\[
\begin{align*}
  a &= 1.46 \text{ Å} & \alpha &= 107\pm4^\circ \\
  b &= 1.35 \text{ Å} & \beta &= 109\pm3^\circ \\
  c &= 1.41\pm0.02 \text{ Å} & \gamma &= 107\pm2^\circ
\end{align*}
\]

Scheme 1.2 Electron diffraction data of furan ring (Reprinted with permission from reference 3)

1.2 Common Furanic Monomers

This section is a brief introduction of the most common furanic derivatives which have already been applied in polymerization study, and most of them could be directly synthesized from biomass.
1.2.1 Furfural

Furfural 2 is called a green compound since it can be directly synthesized from biomass by a process that the hemicellulose fraction is broken down into 5-carbon sugar small molecule unit and then followed by dehydration reaction. German scientists Johann Wolfgang Döbereiner in 1821 obtained it as a byproduct when he was producing formic acid.\(^6\) The reaction sequence (Scheme 1.3) is firstly the hydrolysis of hemicelluloses down to the small molecule xylose 1-7, which then further dehydrated to give furfural 1-9.\(^3\) In 1921, QUAKER OATS COMPANY of cedar rapids, Iowa, initiated massive production of furfural from rolled oats with the redundant pressure cooker. Due to the strong acidic reaction condition, the equipment was corroded badly even after changing to copper reactor\(^7\). Many attempts were made to improve the convention process as well as the yield from xylose 1-7 to furfural 1-9 in the acidic condition. Addition of metal chloride salts to acid solution could promote the formation of 1,2-enediol, which favors the acidic catalyzed dehydration process.\(^9\) Biphasic reactor was used in the production of furfural. The conversion of xylose to furfural in a water/MIBK biphasic reactor had yields up to 85\%.\(^10\) With β-type zeolites (Si/Al = 12) in a siliceous TUD-1 mesoporous matrix, a 74% conversion yield was obtained.\(^11,12\) The conversion yield was improved to 98% when H-mordenite was used in a biphasic (aqueous/toluene) plug-flow reactor.\(^13\) Furfural is the only unsaturated chemical produced massively from carbohydrates, which is used as a selective solvent for separating saturated
from unsaturated compounds in petroleum refining.\textsuperscript{14} It is also applied as a foundry sand linker, and high performance resins are obtained when reacted with other organic compound like pyrrole\textsuperscript{15} and phenol\textsuperscript{3}. The most common application of furfural is the intermediate to synthesis furfuryl alcohol, furan, and tetrahydrofuran.\textsuperscript{16}

![Scheme 1.3 Dehydration process of hemicelluloses to obtain furfural\textsuperscript{3,7,8}](image)

1.2.2 5-Hydroxymethylfurfural (HMF).

5-Hydroxymethylfurfural \textbf{1-10} attracts great attention in recent years, since it is sustainable and can be directly derived from biomass like corn, oats. The reaction process also proceeds firstly through the acid hydrolysis and then dehydration to yield \textbf{1-10}, the same as furfural but the initial sugar compound is mostly fructose \textbf{1-11}\textsuperscript{17}. Many studies are carried out on this synthetic scheme including novel catalysts
and reaction media in the past few years, which brought 1-10 to be considered as a massive producing material in the industry field. However, it is impractical and difficult because 1-10 tends to degradation even under very mild condition, resulting problems like storage and large scale reaction.

![Resonance structures of fructose.](image)

Scheme 1.4 Resonance structures of fructose.

However, 1-12 is a valuable chemical from biomass since it has been applied in resin production, such as in manufacture of phenolic resin by reaction of the aldehyde group and the hydroxymethyl group. More importantly, compound 1-12 is a very useful building block for the production of other molecules such as levulinic acid 1-13 and many 2,5-disubstituted furan derivatives, which can be applied in fine chemical, pharmaceutical, polymer, transportation fuel industries. With different reactions, HMF could be converted into versatile compounds.(Scheme 1.5)

According to the report of U.S. Department of Energy, levulinic acid 1-13 is one of the top 12 valued chemicals from biomass, which has wide applications including lubricants, coatings, electronics, batteries, drug delivery, polymers and so on.
For practical application, a good strategy is to convert unstable HMF to chemically stable 2,5-dimethylfuran 1-15 (DMF) or 2-methylfuran 1-16, which is insoluble in water and maintains to be dry in atmosphere. Furthermore, 2,5-dimethylfuran 1-15 is a very promising substituent for ethanol, which is the only renewable liquid fuel currently produced massively, since that 1-15 maintains a higher energy density (by 40%), a higher boiling point (Ethanol: 78 °C; DMF: 92 °C) as well as insoluble in water. Both 1-15 and 2-methylfuran 1-16 are relatively...
nonpolar chemicals that have potential use as novel component in gasoline blends, which depends typically on ~C5 to C10 hydrocarbons.\textsuperscript{31}

Many investigations have been done for exploring wider application of HMF as polymerization precursor. Same as levulinic acid 1-13, 2,5-furandicarboxylic acid 1-25 is in the list of top 12 valued chemicals from biomass, being a promising candidate for terephthalic or isophthalic acids which are the monomers of useful polymeric materials like polyesters, polyamides and polyurethanes.\textsuperscript{32} Gandini and Ma investigated the processibility and properties of poly(ethylene terephthalate) containing the furan counterpart from 2,5-furandicarboxylic acid 1-25,\textsuperscript{33,34} giving a meaningful guide for further study and application. Roudet reported the first furanic polyester 1-26 by the transesterfication reaction of 1-20, including both crystallinity and photosensitivity information.\textsuperscript{2} 2,5-Bis(hydroxymethyl)furan 1-17 is another widely used monomer to obtain polyester bearing furan ring, at the same time, which already be applied in the production of polyurethane foams.\textsuperscript{35}

With bi-amino functional group at 2, 5-position, the furanic monomers derived from HMF could be used for synthesis of furanic polyamides, polyschiff bases as well as polyurethanes. Most polyamides are obtained by using various diamines that react with 1-18. Among all furanic polyamides, 1-27 displays best properties, which were found to be only soluble in concentrated sulfuric acid and NMP containing 4\% of LiCl. These solutions exhibit a lyotropic liquid crystal behavior. Thermal analysis of this polyamide showed the presence of a minor glass
transition temperature at 325°C and degradation temperature at 385 °C, while $M_w = 10^{5.36}$. Furanic polyschiff bases will be reviewed in chapter 2.

Since 1980s, many systematic studies have been made in the field of furanic polyurethanes synthesis. Cawse et al. carried out the kinetics study of reactions based on 1-24 and its aromatic homologue with aliphatic diols, indicating the latter was more reactive than the former.\textsuperscript{36,37} The spectroscopy and thermal data demonstrated that furanic polyurethane 1-28 obtained from this reaction gave similar properties as its aromatic analogue. More furanic polyurethane had been explored, whose structures were ranging from furanic-aliphatic, furanic-aromatic to fully furanic moieties.\textsuperscript{38} And 1-17 was the most common monomer in these studies, which cover the reactivity of furanic monomers, viscosimetric studies, crystallinity information as well as thermal analysis.

![Chemical structures](image)

1.2.3 Furfuryl alcohol

With the hydroxymethyl group at the 2 position of the furan ring, furfuryl alcohol 1-29 tends to form resin under various conditions. Many investigations have
been devoted to these resulting polymers. Their applications are including cores and moulds for metal casting\textsuperscript{39}, anti-corrosion materials\textsuperscript{40a}, carbonaceous materials\textsuperscript{2}, wood adhesives and binders\textsuperscript{40b}. While the most recent application is the poly(furfuryl alcohol)-coated highly porous polystyrene matrices, which improved the mechanical property for this material.\textsuperscript{41}

The polymerization is usually carried out in acidic condition, while many other methods has been explored in recent years.\textsuperscript{2} The resulting polymer is a cross-linked, black resin which is inert to many chemical environments. However, the first investigation of poly(furfuryl alcohol) was reported over one century ago, and the study of its polymerization mechanisms and characterization of this polymer were taken more than 30 years, without an absolutely precise conclusion. It is quite clear that the first stage of this complicated process is the condensation reactions between hydroxyl group and hydrogen atom at the 5-position on the furan ring, or another hydroxyl group.\textsuperscript{42,43} (Scheme 1.6).

\begin{center}
\includegraphics[scale=0.5]{Scheme1.6.png}
\end{center}

Scheme 1.6 The initial stage of furfuryl alcohol resinification
Choura et al. studied the mechanism of coloration and cross-linking during the polymerization of furfuryl alcohol under acid condition in 1996. This study attempts to unravel this problem based on the investigation of a series of model compounds, and illustrates that the methylene carbon between two furan rings plays a key role. The other aspect, such as the role of water and the effects of hydrolysis products generated under the acidic aqueous medium, has also been cleared up in this paper. The absence of water appeared to not alter the process, and exhibited no effect for the formation of network structures. Choura concludes that it is the methylene hydrogen atoms between two furans that evoke the side reactions which related to color formation in an acidic medium. Choura also claims that the Diels-Alder cycloaddition reaction between a furan moiety (diene) and dihydrofuranic cycle (dienophile) is the reason for cross-linking. However, the synthesis of the ideal poly(furfuryl alcohol) 1-30 with a linear backbone, which is expected to be a colorless thermoplastic polymer, still remains to be a challenge.
1.3 Other Polymers Bearing Furan Ring Not Directly Derived from Monomers above.

There are some polymers bearing furan ring moiety which are not derived from the reactive furanic monomers mentioned above. The synthesis of furanic
polymers with conjugated backbone is still a challenge because which don’t behave as the common heterocycle compounds. Furthermore, the strong diene-like property of the furan ring evokes other reactions like Diels- Alder condensation.

1.3.1 Conjugated Furanic Polymers

Polyheteroaromatic\(^3\) compounds like polypyrrole 1-31 and polythiophene 1-32 received considerable attentions due to their unique and superior properties. Due to its high electrical conductivity and stability, polypyrrole is one of the most frequently studied conducting polymers.\(^44\) Coatings of chemically synthesized polypyrrole can be applied onto organic and inorganic materials that exhibit improved properties. For example, polypyrrole-coated latex maintains a smoother conducting polymer morphology with a more uniform converge, as well as excellent thermal stability, which could be used as model projectiles for assessing the extent of the thermal ablation of organic cosmic dust in aerogel capture experiments.\(^45\) Nystrom et al. created the 50nm thin polypyrrole-coated cellulose fibers. It is a promising, novel approach that extended new possibilities for ecological, low-cost, light-weight energy storage systems.\(^46\) Like polypyrrole, polythiophene has widely applications as well. Polythiophene is suitable to be field-effect transistor,\(^47\) nonlinear optic devices,\(^48\) batteries\(^49\) and so on. When combine the hetero ring with the conjugated C=C moieties or other polymer, organic and inorganic substrates, the new class of material is generated. Gilliard investigated a semifluorinated polymer as
an anion sensor, by incorporating diphenylbithiophene 1-33 and distrylbenzene derivates as chromophoric main chain subunits.50

![Chemical structures](image)

Although pyrrole and thiophene are treated as the homologues of furan, the latter displays quite different properties in exploration of its conjugated heterocycle polymers. Both chemical and electrochemical methods have failed to synthesize polyfuran, which is expected to have the linear structure like 1-34. This critical missing link in the furanic polymerization study might be that the pronounced dienic character of the furan ring resulting several side reactions, including ring opening and unexpected cross-linking.2 Even with self-plasticsing side groups introduced to the furan ring, there is no great improvement for understanding the polymerization process.51 However, progress has been made for furan copolymerization with other substrates, with furan-thiophene copolymer being an example that exhibits interesting opto-electronic properties.52

Indeed, the only processible furanic conjugated polymer should be poly(2,5-furylene vinylene) 1-35. The first attempt was that 2-Methylfurylfuran 1-36 undergo
an aldol-crotonic type of condensation into very strong nucleophiles medium. But the characterization data of the final compound did not provide enough solid evidence for the structure formation. More convincing results were reported in 1987 by applying the “precursor technique”, which is largely based on the synthetic route of its benzene ring analogue. The products were always black brittle films whose intractable nature hinders the characterization of the final polymer. After few years, Gandini’s group reported the correct way to synthesize this polymer by applying monomer 1-36 into the nucleophilic medium at very small flow rate. Despite these reports providing solid data for the formation of this linear conjugated polymer, it is too brittle to allow the casting of films or spinning of fibers, thus leading to further modifications.

1.3.2 Furanic Polycondensation Based on the Diels-Alder Reaction

The furan heterocycle displays a more diene-like property in most specific reactions, compared to its pyrrole and thiophene homologues. So that furan derivatives are undoubtedly the most classic examples representing the Diels-Alder reaction. Despite the stereochemistry in the furan and maleimide adduct could affect the Diels Alder reaction, there is no relevance to the polymerization process. Several scientists have tried to exploit this reaction to prepare linear polymers by step cycloaddition of bimaleimide 1-37 and difuran monomers 1-38, like those shown in Scheme 1.8. The non-linear polycondensation could be achieved by
applying monomers with functionality more than two (Scheme 1.9). This topic was also extended to generate dendrimers $1-42$ or cross-linked structures $1-43$, which are shown in scheme 1.10. The aim of all these studies was to build a material which could be readily reversed to the starting material based on the intrinsic reversibility of Diels Alder reaction. Various materials have been explored, such as shape-memory materials $58$, thermally reversible cross-linked polyamide $59$.

Scheme 1.8 Reversible Diels-Alder Polymerization of maleimide adduct and furanic derivatives. (Linear)$^{55}$

Scheme 1.9 Reversible Diels-Alder Polymerization of maleimide adduct and furanic derivatives. (Non-Linear)$^{56}$
Scheme 1.10 Dendrimers and cross-linked compound derived from Reversible Diels-Alder Polymerization of maleimide adduct and furanic derivatives$^{57, 58}$
1.4 The Monomer Used in This Study: 2,5-Diformyl Furan

As mentioned above, selective oxidation of 2-hydromethylfuran (HMF) leads to 2,5-diformyl furan 1-44, which also named as DFF. There are numerous applications of DFF as a useful chemical platform, such as monomer for polymer synthesis 60,61,62, intermediate of pharmaceuticals 63, antifungal agents 64 as well as ligands 65. It is not very difficult to obtain DFF by oxidation of HMF, while the side reactions and conversion yield should be optimized. Various of classic oxidants have been used in this conversion, including CrO₃-Pyridine, bariummanganate, pyridine chlorochromate (PCC), Pb(OAc)₂-pyridine, TEMPO 66. Catalysts have been developed for this conversion aiming at an environmentally, economical-friendly as well as high-yield route. Carlini and coworkers reported the one-pot conversion of HMF to DFF by using the heterogeneous catalysts based on VOPO₄.2H₂O (VOP) under various conditions in 2005. 67 In the presence of VOP and N,N-dimethylformamide (DMF), the best productivity had been achieved with 95% selectivity but low HMF conversion. Corma et al. provided another aerobic oxidation of HMF to DFF catalyzed by immobilized polymer-bound metal catalysts based on vandayl-pyridine complexes, which gave the best selectivity of DFF as 99% and 82% conversion of HMF at 130°C. 68 Additionally, Halliday et al. announced the first practical, one-pot, two-step oxidization method of fructose into DFF without isolation of HMF as the intermediate, in the presence of vadadium-based catalysts 69. Other metal based catalysts like Mn 66b and Gold 70 were also applied for this
investigation, but none of them gave results far beyond vanadium based catalyst. Recently, Ma and her coworkers report an efficient DFF synthesis from HMF by using a homogeneous mixture of Cu(NO$_3$)$_2$ and VOSO$_4$ catalysts under mild conditions$^{71}$. The conversion and selectivity are both achieved as 99% under room temperature and 0.1MPa O$_2$ (Scheme 1.11)$^{71}$.

In contradiction to the versatile usage of other furan compounds, DFF is rarely reported for its polymerization study. In this work, DFF will be explored as a monomer in direct synthesis of furan based polymers.

![Scheme 1.11 Oxidation of HMF to DFF by Ma et al.]

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CHAPTER II
BACKGROUND OF POLYMERIC SCHIFF BASES DERIVED FROM 2,5-DIFORMYLFURAN

Polymeric materials have an essential and ubiquitous place in everyday life, which has been applied widely, like the synthetic plastic, rubbers as well as cellulose (one of the most common and also important biopolymer is the earth). In these years, researchers starting focus on polymers containing conjugation structure, due to their variety of applications in many fields, such as electronics, opto-electronics, and photonics. There is another class of polymer containing conjugation chain with –CH=N– structural unit, which is known as polymeric Schiff bases (or polyimines). These polymers are mostly synthesized by direct polycondensations between a diamine and hydrazine with a dialdehyde or diketone (Scheme 2.1).

Adam et al. synthesized the first polyimine by condensation reaction between terephthaldehyde and benzidine or o-anisidine in 1923. Then an insoluble and infusible product was made by Steinkophf and Eger, using the reaction of hydrazine.
with terephthaldehyde or isophthaldehyde in 1938. In 1950, Marvel and Hill obtained low molecular weight polyimines by the reaction of aromatic dialdehydes with o-phenylenediamine and hydrazine, because of their insolubility in the reaction medium. In the late 1960s, D’Alelio et al. started to study polyimine for the potential application in aircraft manufacturing on the basis of its thermal stability. He reported various of synthetic schemes, including the polymerization of aromatic dialdehydes and aromatic diamines under melting state, as well as base exchange reactions of Schiff base molecules. In last few years, scientists renewed their interests to the this class of polymer which is the isoelectronic analog of some important and widely studied polymers. For example, aromatic polymeric Schiff base 2-1 and linear polymer 2-3 are the nitrogen-containing analog of poly(p-phenylenevinylene) 2-2 and polyacetylene 2-4 respectively. Aromatic conjugated polymer 2-2 is the first electroluminescent polymer, while linear polymer 2-4 is one of the most known conducting polymer. After replacing carbon by nitrogen, these polymers often gain better thermal stability.

Overall, the polyimines exhibit excellent thermal stability and useful mechanical properties, which could be useful for high strength fibers when contain
aromatic structure in the polyimine backbone\textsuperscript{84}, partly due to a spontaneous alignment of the molecules in the flow direction. And they are also particularly promising electronic materials with semiconducting property\textsuperscript{85}, because they contain the extended electronic states in the molecule structure as in the case of \(\pi\)-conjugated polymers. The metal complexes of Schiff bases are also known for their applications in catalysis and dyes.\textsuperscript{86,87} Moreover, some of the polymers are liquid crystalline materials which can form mesophases under heating or in solution, but it is difficult to characterize and process since these polymers have high melting temperature as well as low solubilities.\textsuperscript{88,89} Due to strong chain-chain interaction arising from the polar C=\(\text{N}\) bond, many polymeric Schiff bases are not soluble. Significant interests exist to improve the processibility of this class of materials, thereby enabling their practical applications.\textsuperscript{90}

Furan-based polymeric materials has received increasing attention in recent years,\textsuperscript{2} due to the growing interests in searching for the sustainable materials and readily available furan-based chemicals from biomass.\textsuperscript{91} Heterocyclic ring is an attractive building block to be used in a wide range of materials containing aromatic structures. The first synthesized polymeric Schiff base containing furan rings was obtained by Chundury and Szmant in 1983. They applied 5-chloromethylfurfuradehyde \textbf{2-5} and 5,5'-(oxybis(methylene))bis(furan-2-carbaldehyde) \textbf{2-6} to react with aromatic diamines.\textsuperscript{2} The result is, however, not desirable since these polymers were insoluble in all solvents tested and the nitrogen analyses of the resulting polymers were not in
consistence with the postulated structures. At the same time, Patel et al. tried to use 5,5'-thio-bisfurfural 2-7 to react with various of diamine, such as o-, m- and p-phenylenediamines, benzidine, 3,3'-dimethoxybenzidine, 3,3'-dimethylbenzidine, 4,4'-diaminodiphenylmethane, 4,4'-diaminodiphenylsulphone, ethylenediamine and hexamethylenediamine.\(^92\) Again these polymers were insoluble but in formic acid, and only polymer 2-8 gave a set of data concerning their electronic conductivity which is very low, and there is no clear structural analysis. In 1990s, Zuen Hui and Alessandro Gandini investigated a series of polymeric Schiff bases bearing furan moieties.\(^93\) In their work, the polycondensation was based on two furanic dialdehyde and different diamines (aromatic, aliphatic and furanic amines). There were four polymers: 2-8, 2-9, 2-10, 2-11, in which polymer 2-9 and 2-11 were less soluble. Due to their higher conjugated structure in the polymer backbone, polymer 2-9 and 2-11 were expected to have low molecular weights. The solubility of the polymer was improved when aliphatic amine was used. Polymers 2-10 and 2-12 were soluble in most polar solvents, while their thermal stability was decreased. In a second investigation, Mealares and Gandini obtained polymer 2-14 with a molecular weight reaching 2000 and thermal stability up to 270 °C without any sign of melting, when 2,5-diformylfuran was condensed with hydrazine.\(^94\) Due to its better solubility, some chemical and physical properties were investigated. Attempts were made to synthesis more amenable structures by introducing soft segments. Then polymer 2-13, a plastic-like soluble product, was synthesized by condensation reaction of 2,5-diformylfuran and an excess
of Jeffamine (an oligo(ethylene) oxide, Mn=600), followed by the reaction with the macromonomer derived from the condensation of an excess 2,5-diformylfuran and hydrazine. This approach improved the molecular weight of furanic polyimine to 20,000, but still need to be optimized.\textsuperscript{94}

As a potentially useful monomer, 2,5-diformylfuran (DFF) contains two aldehyde groups, which can be conveniently transformed into C=C and C=N functionalities.\textsuperscript{95} Like mentioned above, Zuen Hui and Alessandro Gandini are the pioneering scientists who synthesized polymeric Schiff base from DFF. Then this research field seems to be quiet, until Amarasekara et al. reported a new polymer 2-15, 2,5-diformylfuran-urea resin, in 2009.\textsuperscript{62} The novel polymer resin was obtained by the condensation of renewable monomer DFF with urea by melting a solid mixture without catalysts in 90\% yield, which provides insoluble product. In sharp contrast to terephthalaldehyde, only few examples of polymeric furan analogues have been synthesized from DFF in literature.\textsuperscript{60,61,62} Part of the reason for lack of activity is due to the high cost of DFF monomer, which limits its synthetic study. Recent development in catalytic oxidation of 5-hydroxymethylfurfural allows to access DFF in a relative large quantity,\textsuperscript{71} which encourages the further study of its polymerization. It is imperative to understand the fundamental information of these polymeric furan imines and their properties. Herein we studied the synthesis of a few furan-containing polymeric Schiff bases, which add to the existing examples of furan-containing polymer Schiff bases. By using NMR and mass spectrometry, the
study provides further information on the formation and reactivity of –CH=N– functional group, as well as structures of the resulting polymers.
Polymeric Schiff bases were prepared by condensation of 2,5-diformylfuran (DFF) with a series of diamine in solution without any catalyst. The reaction between diamines and dialdehyde appeared to proceed fast at room temperature in dry acetonitrile. And the resulting polymers quickly precipitated from the reaction solution after mixing two monomers, while some polymers of low molecular weights are present in dilute solution. The observation is consistent with the assumption in the synthesis of its benzene analogue, where appreciable polymerization occurs before the polymers begins to precipitate, and the reaction continues more slowly in the suspension.\textsuperscript{84}

3.1 Polymerization of DFF with 1,2-Diaminoethane.

In acetonitrile, the reaction between DFF and 1,2-diaminoethane led to partially precipitate quickly (on a time scale of a few seconds) upon mixing two monomers. In order to examine the reactivity, the condensation reaction was performed in the deuterated acetonitrile and $^1$H NMR spectra were acquired at
different time interval (Figure 3.1). The imine –CH=N– group was formed immediately after mixing, while some residual aldehyde end groups were visible at ~9.5 ppm. At the initial stage of the reaction, three proton signals were detected for imine group at ~8.1 ppm, suggesting the formation of several different species. The sharp signal at ~8.03 ppm was assigned to cyclic molecule, while the broad peaks at 8.12 and 8.22 ppm was attributed to linear species of different length. After the reaction proceeded for 6 hours, the aldehyde became undetectable (Figure 3.1c). Interestingly, the proton NMR showed a clean spectrum with $H_a:H_b:H_c = 1:1:2$ ratio. The proton signals at 1.1 and 3.4 ppm were attributed to ethanol, which was accidently introduced and served as internal reference. A possible explanation is that continuous polymerization led to the growth of linear chain and resulted in precipitation, leaving the cyclic product(s) in solution (detected in Figure 3.1c). The multiple minor signals between 6.2-7.5 ppm were observed from $H_a$ (on furan ring), which are related to the reaction intermediates. Disappearance of these minor furan signals along with –CHO and 1,2-diaminoethane (at~2.8 ppm) supports the assumption, and suggests that the imine –CH=N- bond was formed cleanly during the polymerization.

The solution sample from DFF and 1,2-diaminoethane was further examined by ESI mass spectrometry. The result showed that cyclic trimer 3-2a was predominant in the solution, along with some trace amount of tetramer 3-2b and pentamer 3-2c. The mass spectrum of 3-2a was detected as ions with different
cationizing agents (H\(^+\), Na\(^+\) and K\(^+\)) (Figure 3.2a). The observed isotopic pattern of 3-2a matches the theoretical prediction (Figure 3.2b).

A molecular model study shows that all the imine bonds (–CH=N–) in trimer 3-2a is in anti-geometry. The result is consistent with the single sharp imine signal detected in \(^1\)H NMR at ~8.1 ppm (Figure 3.1c), as anti- and syn-imine proton have different chemical shift.\(^96\) The geometry-optimized conformation of dimer 3-3, however, revealed that one of the –CH=N– bonds must be in the syn-geometry of relative high energy (Figure 3.3), which disfavors the dimer formation and explains its absence in the reaction mixture.

![Scheme 3.1 Reaction of DFF and 1,2-Diaminethane.](image-url)

Scheme 3.1 Reaction of DFF and 1,2-Diaminethane.
Figure 3.1 $^1$H NMR of the DFF and diethylamine in Acetonitrile-d3: (a) immediate after mixing; (b) after mixing for two hours; (c) after mixing 6 hours. The starred signals at 1.1 and 3.4 ppm are attributed to CH$_3$CH$_2$OH, and the signals at 1.93 and 2.1 ppm to residual acetonitrile and H$_2$O.
Figure 3.2 ESI mass spectrum of 3-2a from the same sample that was used for $^1$H NMR in Figure 3.1c. The experimental mass pattern (top) shows the compound with different cationizing agents ($H^+$, $Na^+$ and $K^+$), which matches well with the computer simulation (bottom).

The insoluble polymer 3-1 (as precipitate) was examined by solid state $^{13}C$ NMR (Figure 3.4), which complements the finding from the solution $^1$H NMR. The carbon of imine group was detected at 152 ppm, while the characteristic furan
carbon was found at 122 ppm. The spectrum revealed no aldehyde signal at ~180 ppm, in agreement with the assumption that the reaction proceeded cleanly to form the –CH= N– bonds. The assumed formation of polymeric Schiff base was further supported by the MALDI-TOF mass spectrum. When DFF and diamine were used in 1:1 ratio, the product gave quite complicated mass spectra pattern, due to formation of different chains with both –NH₂ and –CHO as end groups. The reaction was greatly simplified when diamine was used in excess, giving a series of amine-terminated oligomers that were observed as linear sodium-cationated oligomers (Figure 3.5). The representative monoisotopic peaks at m/z = 823.668, 971.613 and 1119.615 correspond to tetramer (n=4), pentamer (n=5) and hexamer (n=6), respectively. On the basis of the observed peaks in MALDI mass spectrum, the polymerization process continuously occurred to form ~ 40-mer (m/z is around 6500)

Figure 3.3 Geometry-optimized dimer 3-3 (by using HyperChem AM1 setting) in top (a) and front view (b). Two front nitrogens are labeled for clarity.
Figure 3.4 CP/MAS $^{13}$C NMR spectra of polymer 3-1, where “ss” indicates spin sideband.

Figure 3.5 MALDI-TOF mass spectra of polymer 3-1 with sodium trifluoroacetate as cationizing agent. Where the region between 5000-6000 is expanded for clarity.
FT-IR spectrum of the insoluble polymer 3-1 showed sharp characteristic absorption for imine \(-\text{CH}=\text{N}^-\) group at \(~1644\ \text{cm}^{-1}\) and furan C–H at \(3069\ \text{cm}^{-1}\) (Figure 3.6), without detecting the aldehyde end group at about \(1676\ \text{cm}^{-1}\). The broad band at \(~3408\ \text{cm}^{-1}\) was mainly associated with water trapped in the product,\(^{93}\) as primary aliphatic amine group would exhibit two moderate peaks at \(~3390\) (for antisymmetric stretching) and \(3340\ \text{cm}^{-1}\) (symmetric stretch).\(^{97}\) The observed pattern was consistent with the mass spectroscopy, where only amine was observed as end groups.

Figure 3.6 FT-IR spectrum of polymer 3-1 in KBr pellet. Broad peak at \(3408\ \text{cm}^{-1}\) is attributed water by-product.
3.2 Polymerization of DFF with 4,4’-Ethylenedianiline.

![Scheme 3.2 The Synthesis of Polymeric Schiff base (3-4)](image)

Reaction of DFF with an aromatic diamine (4,4’-Ethylenedianiline) was also examined in acetonitrile, and polymer 3-4 was formed quickly as yellowish precipitate in high yield (~80-90%) upon mixing two monomers. Attempt to use other solvents (THF, acetone, CH\textsubscript{2}Cl\textsubscript{2}, and toluene) did not improve the reaction, as the polymer was insoluble. When DFF and diamine was reacted in 1:1 molar ratio, mass spectrum of the precipitated polymer 3-4 revealed a series of oligomers (Figure 3.7), with chains terminated by aldehyde-aldehyde (A\textsubscript{n}), amine-amine (B\textsubscript{n}), and amine-aldehyde (C\textsubscript{n}) (Scheme 3.3). While the sample appeared to have peak Mw of about n=6, the higher oligomer up to n=18 was also detected. Observation of all possible combination of end groups in 3-4 clearly indicated that the polymer chain growth was restricted by its insolubility, which hinders the migration of chain ends for further reaction. In consistence with mass spectrum, the IR spectrum of 3-4 (Figure 3.8) also revealed the presence of end groups, as shown by the weak absorption band at 2855 cm\textsuperscript{-1} (C–H of aldehyde) and 1676 cm\textsuperscript{-1} (C=O of aldehyde), in addition to strong imine –CH=N– band at 1621 cm\textsuperscript{-1}.
Scheme 3.3 Oligomer structures with different combination of end groups.

The insoluble polymer 3-4 was further examined by solid state $^{13}$C NMR. Cross polarization magic angle spinning (CP/MAS) $^{13}$C NMR spectra of 3-4 exhibited several aromatic/olefinic carbons between 110-160 ppm, in addition to the aliphatic carbon at ~34 ppm (Figure 3.9a). In the cross polarization experiment, the carbon nuclei are polarized by the proton reservoir at different rates, which depends on the strength of the static $^{13}$C-$^1$H dipolar interaction and can be used to aid the resonance assignment. The resonance signals observed at the smallest contact time (Figure 3.9b) are thus associated with the carbons that have the largest dipolar $^1$H-$^{13}$C interactions, and are assigned to protonated carbons. Comparison of the CP/MAS spectra with different contact times (Figures 3.9a & 3.9b) leads to the identification of non-protonated carbon atoms at 154 and 140 ppm, which are assigned to C-2 and C-4 of 3-4, respectively. Interestingly, the carbon of imine group was detected as two peaks at 150 and 148 ppm, indicating the possible impact of local morphology on the imine group. The broad signals at 40–80 ppm were
attributed to spin side bands of the rigid aromatic carbon atoms (not impurities), as they are moved out of the observation window at MAS=15 kHz (Figure 3.9c, in comparison with Figure 3.9a). The overall clean spectrum indicates that the polymerization was carried out via effective formation of –CH=N– bonds.

Figure 3.7 MALDI-TOF mass spectrum for 3-4 with sodium trifluoroacetate as cationizing agent. Each species is observed as (M+H)⁺ and (M+Na)⁺ cations, which are indicated by thin and thick arrows, respectively. The inset shows the expanded region for m/z = 4200-6000. The oligomers are labeled as Aₙ, Bₙ, and Cₙ, depending on their end groups.
Figure 3.8 FT-IR spectra of polymer 3-4 in KBr.

Figure 3.9 CP/MAS $^{13}$C NMR spectra of polymer 3-4, acquired using a ramped cross polarization pulse sequence with 4 sec relaxation delay and 4.0 ms 90° pulse: a) 3 ms contact time with MAS of 10 kHz; b) 0.02 ms contact time with MAS of 10 kHz; c) 3 ms contact time with MAS of 15 kHz. Spin side band are marked as “SSB.”
3.3 Polymerization of DFF with Benzene-1,3-Diamine

Polymer 3-5 obtained from the reaction of DFF and benzene-1,3-diamine (1:1) in acetonitrile was also examined by solid stated $^{13}$C NMR spectroscopy and MALDI solvent free mass spectrometry. Cross polarization magic angle spinning (CP/MAS) $^{13}$C NMR spectra of polymer 3-5 was showed in Figure 3.11. By using the same method mentioned above in the solid NMR experiment (shorter contact time), the protonated carbons were intensified in the spectra (a), compared to spectra (b) which indicates the furanic carbon 1 located at 153 ppm, while the imine carbon 3 clearly showed up around 148 ppm. The aromatic carbons 4,5,6,7 gave multiple peaks in the region of 105 ppm to 130 ppm without specific resignation, which may due to the rigid morphology of the aromatic ring and the product is a mixture of oligomers. Polymer structure is also confirmed by solvent free MALDI-TOF mass spectrum. In figure 3.10, the mass spectrum shows two main polymer structures An and Bn, which represents two different end groups. And the m/z is detected only up to 2000, which might due to the furan moiety and benzene ring give the most rigid structure in these polymer products. Thus, the FT-IR spectrum of the red brownish product 3-5 shows a fairly declining baseline, while the imine -HC=NH- functional group is still recognizable, as well as the aryl bond (C=C and C-H). Most IR data of polymer 3-5 are in consistence with the previous two polymers. The formation of imine -CH=N- bond gave the absorption peak at 1625 cm$^{-1}$, and the multiple peaks around 1588 cm$^{-1}$ represent the aromatic -C=C- stretching. The broad peak at 3444
cm\(^{-1}\) could also be explained as the overlapping result of primary amine (\(-\text{NH}_2\) stretching) and water trapped in the polymer.\(^93\)

Scheme 3.4 The Synthesis of Polymeric Schiff base (3-5)

Figure 3.10 MALDI-TOF mass spectrum for polymer 3-5 with sodium trifluoroacetate as cationizing agent. Each species is observed as (M+H\(^+\))\(^+\) cations and the oligomers are labeled as A\(_n\) and B\(_n\), depending on their end groups.
Figure 3.11 CP/MAS $^{13}$C NMR spectra of polymer 3-5, acquired using a ramped cross polarization pulse sequence with 4 sec relaxation delay and 4.0 ms 90° pulse: a) 0.02 ms contact time with MAS of 10 kHz, b) 3 ms contact time with MAS of 10 kHz; Spin side band are marked as “ssb.”
Figure 3.12 FT-IR spectrum of polymer 3-5 in KBr.

3.4 Polymerization of DFF with 4,4’-(Ethane-1,2-diylbis(oxy))dianiline

Scheme 3.5 The Synthesis of Polymeric Schiff base (3-8)
This part of the project was aiming to improve the solubility of the furan based polymeric Schiff base by adding a more flexible alkoxy chain into the polymer backbone. This experiment consisted of two steps: (1) the synthesis of an aromatic diamine 3-7, where two amines were connected with an alkoxy bridge; and (2) the reaction of diamine with 2,5-diformylfuran to give the polymeric Schiff base 3-8.

Figure 3.13 ¹H NMR spectrum of 3-6

In step 1, the commercially available starting material 4-nitrophenol reacted with 1,2- dibromoethane to give the product 3-6. In the reaction, the flexible alkane chain was attached to the nitro-phenol moiety. Then, the nitro group was reduced by hydrazine dehydrates in the presence of catalyst Pd/C to yield the 4,4’-(Ethane-1,2-
diylbis(oxy)dianiline 3-7. The $^1$H NMR spectrums of intermediates are shown in Figures 3.13 & 3.14.

There are three types of protons in 3-6 (Figure 3.13). The doublets at 8.2 ppm and 7.0 ppm are corresponding to the aromatic protons. The large separation (~1.2 ppm) of the aromatic signal are due to the attached electron-withdrawing nitro group. The peak showed up in 4.44 ppm is belonging to the aliphatic hydrogen in the alkoxy chain. The formation of 7a is also supported by the integration of these proton peaks, which fits the proton quantities (~1:1:1 ratio).

![Figure 3.14 $^1$H NMR spectrum of 3-7.](image)

The subsequent reaction is to reduce the nitro group to amino group. By refluxing 3-6 and hydrazine dihydrate in the presence of the palladium catalyst
(Pd/C), the aromatic diamine was obtained with high yield. The two resonances (a) and (b) in the aromatic proton region (6.5 ppm to 7 ppm) represent those four protons on the benzene ring (Figure 3.14). In comparison with the $^1$H NMR spectrum of 3-6, the aromatic protons next to the nitro group are upfield shifted because of the electronic effect arising from amino group in 3-7. Due to the same reason, the signal of the aliphatic hydrogen in 3-7 is upfield shifted by about 0.4 ppm (i.e. from 4.48 ppm for 3-6).

In the second step, the aromatic diamine 3-7 reacted with the 2,5-diformylfuran to give the target product 3-8. Polymer 3-8 as the target product of this experiment was obtained in high yield by the reaction of the aromatic diamine 3-7.
with 2,5-diformylfuran at room temperature without applying any catalyst. Unfortunately, the short alkoxy chain didn’t improve the solubility of the polymeric furan Schiff base. The resulting yellow powder still didn’t dissolve in the common organic solvent such as acetone, acetonitrile, methonal, ethanol, THF, DMSO, EtOAc, which limits the property investigation of this polymer. The FT-IR spectrum of polymer 3-8 (Figure 3.15) confirmed the expected imine –CH=N- bond at 1619 cm\(^{-1}\), furan C=C bond at 1578 cm\(^{-1}\), furan ring at 1021 cm\(^{-1}\), the benzene C=C at 1501cm\(^{-1}\) and 1454 cm\(^{-1}\), unsaturated C-H stretching at 3103 cm\(^{-1}\) (for furan C–H), 3069 cm\(^{-1}\) (for phenyl C–H), while the broad peak at 3452 cm\(^{-1}\) could indicate the presence of NH\(_2\) end groups, which is overlapped by the water trapped in the product.\(^\text{93}\)

Polymer 3-8 was examined by the MALDI-TOF mass spectrum. As showed in figure 3.16, there were a series of oligomers with two sets of end groups (\(A_n\) and \(B_n\)). The polymer chain growth was restricted by its insolubility, and the detectable MW was at around 3000 (n=8).
Figure 3.16 MALDI-TOF mass spectrum for polymer 3-8 with sodium trifluoroacetate as cationizing agent. Each species is observed as (M+Na)$^+$ cations, The oligomers are labeled as $A_n$ and $B_n$, depending on their end groups.
3.5 Synthesis of Polymeric Schiff Base (3-11) from 2,5-Diformylfuran and 4,4'-(Decane-1,10-diylbis(oxy))dianiline

Based on the previous experiment, the short alkoxy chain didn’t improve the solubility of the furan-based polymeric Schiff base. Thus in this experiment, we tried to include a longer aliphatic chain into the polymer structure, in order to improve the solubility. The synthetic route is the same as the previous experiment except using 1,10-dibromodecane in the first step.

As it mentioned before, 3-9 derived from the reaction of 4-aminophenol and 1,10-dibromodecane in the basic condition. Potassium iodide was added as the catalyst, because it can accelerate the reaction rate by exchange alkyl chloride or
bromide to alkyl iodide, which typically has better reactivity for substitution in organic solvent than the other two halides.\textsuperscript{99} \textsuperscript{1}H NMR spectrum of 3-9 shown below (Figure 3.17) confirmed the formation of the dinitro compound, where the characteristic proton signal of $-\text{OCH}_2-$ at 4.10 ppm indicates the connection of the alkoxy group. The two sets of doublets shown in the aromatic region (at 7.1 & 8.2 ppm) are attributing to the protons on the benzene ring. The doublet signal at $\sim$8.1 ppm is arising from the protons next to the nitro group, while the doublet at $\sim$7.1 ppm represents the protons close to alkoxy substituent.

By using the same method in the previous part, the nitro groups in 3-9 were reduced to amino groups in the presence of the palladium catalyst (Pd/C) with high yield. The amino protons give the characteristic signal at 4.54 ppm. It is also observed that the aromatic protons were downfield shifted about 1.69 ppm and 0.5 ppm (protons in 1 and 2 position respectively).\textsuperscript{(Figure 3.18)} In the final step, 3-10 reacted with DFF in the acetonitrile at room temperature to yield polymer 3-11. The yellow powder product 3-11 precipitated 5 minutes after mixing the two starting materials. After the final step, the yellow still insoluble product 3-11 was collected. Although adding flexible aliphatic chain to this polymer structure didn’t improve the solubility, the property of this polymer was also investigated, by the same methods mentioned before.

MALDI-TOF mass spectrometry measurements were using trans-2-[3-(4-tert-butylphenyl)-2-methyl-2-propenylidene] malononitrile as the matrix, and silver
trifluoroacetate as cationizing agent this time. The fairly clean mass spectrum of polymer 13 gave the end group information as well as the molecular weight of this polymer (Figure 3.21). The notable m/z is up to 7000, and only one structure with both side aldehyde end groups was detected, as a result of slight excess use of 2,5-diformylfuran in the last reaction step. In the Figure 3.21, the peaks represent the silver cationized oligomers, and no clear protonated oligomers were detected especially in the high molecular weight region, which could be due to the lower ratio of nitrogen atom along the compound structure, compared to oxygen atom.

FT-IR spectrum showed the structure information of polymer 3-11 (Figure 3.19). The formation of imine –CH=N- bond was also confirmed, as the strong peak at 1622 cm\(^{-1}\) was observed. The peaks located at 1672 cm\(^{-1}\) and 2852 cm\(^{-1}\) represent aldehyde end group( -CH=O), in consistent with the end group observed in mass spectrum. The strong absorption peak at 1246 cm\(^{-1}\) is the ether C-O stretching. The polymer exhibited aromatic C-H stretching absorption at 3122 cm\(^{-1}\) (from furan ring) and 3082 cm\(^{-1}\) (from phenyl ring), as well as the C=C stretching at around 1500 cm\(^{-1}\). The aliphatic C-H stretching gave stronger absorption at 2935 cm\(^{-1}\). Typical furan ring absorption at 1020 cm\(^{-1}\) is also observed in this spectrum.

The conformation of polymer 3-11 was further supported by solid \(^{13}\)C NMR spectrum (Figure 3.20). The appearance of new resonance in the spectrum of polymer 13, typical 144 ppm, gave additional evidence of the formation of imine (–CH=N-) connection. It also reveals the end group information as the appearance of
aldehyde group (-CH=O) at 181 ppm, in agreement with the MALDI-TOF mass spectrum. The aromatic carbons showed signal in the region of 100-130 ppm while the aliphatic carbons were detected between 0 to 80 ppm.

Figure 3.17 $^1$H NMR spectrum of 3-9.
Figure 3.18 $^1$H NMR spectrum of 3-10.

Figure 3.19 FT-IR spectrum of Polymer 3-11
Figure 3.20 CP/MAS $^{13}$C NMR spectrum of polymer 3-11.
Figure 3.21 MALDI-TOF mass spectra of polymer 3-11 with silver trifluoroacetate as cationizing agent, where the region between 3500-7000 is expanded for clarity.

3.6 Thermal Analysis.

Thermal analysis of polymers provides property data, which include melting and crystallization characteristics, crystallinity, curing process, and degradation property. These data are useful information that determines the material’s potential applications. Polymeric Schiff bases synthesized in this study can be classified into two kinds: aromatic and aliphatic derivatives. Therefore, two of them (polymers 3-1 and 3-4) are taken to thermal analysis including thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC).
Thermogravimetric analysis (TGA) showed that the weight loss started at about 230°C for 3-1 (Figure 3.22), indicating relative lower decomposition temperature for aliphatic chain. When both ends of –CH=N– were capped with aromatic groups, polymer 3-4 exhibited higher thermal stability, with weight loss starting at 330 °C. At above 330 °C, the weight loss of 3-4 became faster, apparently due to weak -PhCH₂–CH₂Ph- whose cleavage leads to two stable benzylic radicals.¹⁰⁰ No melting was observed when heating both 3-1 and 3-4 up to 300°C. At the same time the polymers became brown when the temperature was increased. DSC scans of 3-1 (from –100 to 180 °C) and 3-4 (from –50 to 300 °C) under nitrogen flow (10 mL/min) only revealed a featureless broad endothermic peak in the first scan, which disappeared in the second scan (Figure 3.23). The thermal behavior is in agreement with polymeric Schiff base with the benzene ring analogue, whose morphology characteristics is susceptible to the sample heating history.⁸⁴ The endothermic peak was not associated with the crystal melting, on the basis of its very broad peak and lack of crystallization. A likely reason is that the trapped trace moisture/solvent was gradually escaped from the inside of the sample. Combined with undetected melting temperature and the likely decomposition phenomenon, this class of polymers is not crystalline but might be amorphous.
Figure 3.22 TGA curves of polymer Schiff bases 3-1 and 3-4 (heating rate: 10 °C/min under N₂ flow).

Figure 3.23 DSC curves for Polymer 3-4 (heating rate 10 °C/min under nitrogen).
3.7 Conclusion

In conclusion, we have synthesized a serial of new polymeric Schiff bases by reaction of a diamine with 2,5-diformylfuran (DFF), a green monomer that can be synthesized conveniently from biomass. By using NMR and Mass spectroscopy, the reaction was found to cleanly and quickly form the imine bond (−CH=N−). In addition to the anticipated linear chains of different lengths, the reaction DFF with 1,2-diaminoethane also leads to a small fraction of cyclic 3-2. The major cyclic product was found to be trimer 3-2a, as all of its −CH=N− bonds can adopt the more stable anti-geometry. Attempts have been made to improve the solubility of this class of polymeric Schiff bases by adding aliphatic chain to the polymer backbone. However, the result is not desirable. Although the insolubility of polymeric Schiff bases hinders their full characterization in solution, the CP/MAS $^{13}$C NMR spectra reveals that the polymer has a regular structure as proposed. Thermal analysis data have also been provided to help understanding of this class of polymeric material. The study thus provides useful fundamental understanding on the formation and reactivity of the furan-based imine −CH=N− bond, which could be a valuable guide for the related material development in future.
3.8 Experimental

In this section, reaction materials and instrumental details have been illustrated, followed by detailed procedures for each reaction steps.

3.8.1 Materials and General Methods.

Unless otherwise noted, all reagents and solvents were purchased from Acros Organics or Alfa Aesar. Aniline was distilled before use, all other reagents were used as received. 2,5-Diformylfuran (DFF) was synthesized as reported in literature. The solvents employed in the synthesis were commercially available chemicals of good quality. UV-vis spectra were acquired on a Hewlett-Packard 8453 diode array spectrometer. FT-IR spectra were recorded on a Digilab Excalibur Series FTS 3000 spectrometer. Matrix-assisted laser desorption ionization time-of-flight mass spectrometry (MALDI-TOF MS) measurements were performed on a Bruker Ultraflex III mass spectrometer (Bruker Daltonics, Billerica, MA), which is equipped with a Nd:YAG laser emitting at a wavelength of 355 nm. Electrospray ionization (ESI) spectra were acquired with a Waters Synapt HDMS quadrupole/time-of-flight (Q/ToF) mass spectrometer (Waters Corp., Milford, MA). Thermogravimetric analysis (TGA) was measured with a TA Instruments Q500 and differential scanning calorimeter (DSC) curves were obtained with TA Instruments Q2000.

Solid-state $^{13}$C NMR spectra were obtained on a Varian VNMR 500 MHz ($^1$H frequency) spectrometer. $^{13}$C chemical shifts were corrected by using
hexamethyl benzene (d_{CH3} = 17.3 ppm) as an external reference. Samples were packed into 4 mm silicon nitride rotors with kel-f end caps. $^{13}$C NMR spectra were acquired using a ramped cross polarization pulse sequence with 4 sec relaxation delay, and 4.0 ms 90° pulse. In order to identify the protonated and non-protonated carbon atoms, ramped cross polarization spectra were acquired at 3 ms and 0.02 ms contact time, respectively. In order to identify the Spin side bands, the CP/MAS spectra were acquired with MAS of 10 and 15 kHz respectively.

3.8.2 Synthesis of Polymeric Schiff Bases Bearing Furan Moieties

This is a three step reaction, explained step by step as following paragraphs. All the procedure details could be found below.

3.8.2.1 Synthesis of Polymeric Schiff Base (3-1) from 2,5-Diformylfuran and 1,2-Diaminoethane

Polymeric Schiff Base was prepared by a literature method. 2,5-Diformylfuran (0.24g, 1.94mmol) was dissolved in 10mL acetonitrile, and placed in a 25mL round-bottom flask equipped with a magnetic stirrer. An equivalent amount of 1,2-diaminoethane (0.35g, 5.82mmol) was separately mixed with a small amount of acetonitrile (about 1 mL). The latter was then added dropwise to the stirred 2,5-
Diformylfuran solution over 10 mins. The reaction mixture was stirred for 12h upon which a creamy precipitate was formed. The precipitates was filtered and washed with the corresponding acetonitrile followed by water, then dried under vacuum. Yield: 90%, and this polymer was analyzed by solid state $^{13}$C NMR (Figure 3.4), MALDI-TOF MS (Figure 3.5), FT-IR (Figure 3.6), TGA (Figure 3.22).

3.8.2.2 Synthesis of Polymeric Schiff Base (3-4) from 2,5-Diformylfuran and 4,4’-Ethylendianiline

4,4’-Ethylendianiline (0.212g, 0.998mmol) was dissolved in 15mL acetonitrileand placed in a 50mL round-bottom flask equipped with a magnetic stirrer. An equivalent amount of 2,5-Diformylfuran (0.124g, 0.998mmol) was separately dissolved in 10mL acetonitrile. The latter was then added dropwise to the stirred 2,5-Diformylfuran solution over 15 mins, during which the color of the solution changed from clear to yellow. The reaction mixture was stirred for 12h upon which yellow precipitates were formed. The precipitates was then filtered and washed with acetonitrile, followed by water, then dried under vacuum. Yield: 85%. This product was analyzed by solid state $^{13}$C NMR (Figure 3.9), MALDI-TOF MS (Figure 3.7), FT-IR (Figure 3.8), TGA (Figure 3.22) and DSC (Figure 3.23).
3.8.2.3 Synthesis of Polymeric Schiff Base (3-5) from 2,5-Diformylfuran and Benzene-1,3-Diamine.

Polymeric Schiff Base 3-5 was prepared by a literature method. 2,5-Diformylfuran (0.08 g, 0.645 mmol) was dissolved in 10mL acetonitrile, and placed in a 25 mL round-bottom flask equipped with a magnetic stirrer. An equivalent amount of benzene-1,3-diamine (0.07 g, 0.6451 mmol) was separately mixed with a small amount of acetonitrile (about 5 mL). The latter was then added dropwise to the stirred 2,5-diformylfuran solution over 20 mins. The reaction mixture was stirred for 12h upon which precipitates were formed. The precipitates were filtered and washed with the corresponding acetonitrile, followed by water, then dried under vacuum. Yield: 85%. This polymer was analyzed by solid state $^{13}$C NMR (Figure 3.11), MALDI-TOF MS (Figure 3.10), FT-IR (Figure 3.12).

3.8.2.4 Synthesis of Polymeric Schiff Base (3-8) from 2,5-Diformylfuran and 4,4'-(Ethane-1,2-diylbis(oxy))dianiline

This is a three step reaction, explained step by step as following paragraphs. All the procedure details could be found below.
3.9.2.4.1 Preparation of 1,2-bis(4-nitrophenoxy)ethane

To a 50mL round-bottomed flask, 4-nitrophenol (3.46 g, 24.9 mmol), potassium carbonate (1.79 g, 13 mmol) and 0.1 g sodium iodide in 30 mL dimethyl formamide (DMF) were added. Then a solution of 1,3-dibromo propane (1.2 mL, 13.9 mmol) in a 5 mL dry dimethyl formamide was added dropwise to the reaction mixture. The reaction mixture was heated for 5h at 120 °C, then cooled and poured onto crushed ice. The precipitated yellow product was collected by filtration, extracted with methylene chloride, then washed successively with sodium hydroxide (2M), hydrochloric acid (1M), and water. The methylene chloride solution was then dried over potassium sulfate and concentrated in vacuum and the product was recrystallized from ethanol. Yield: 75%. This product was analyzed by $^1$H NMR in CD$_3$Cl (Figure 3.13): δ 8.245 (d, 9Hz, 4H), 7.035(d, 9Hz, 4H), 4.48(s, 4H).

3.8.2.4.2 Preparation of 4,4'-(Ethane-1,2-diylbis(oxy))dianiline

In a 100 mL round-bottom flask with a stirring bar, 1,2-bis(4-nitrophenoxy)ethane (12a) (1.5 g, 4.93 mmol) was dissolved in 30 mL ethonal. Then 0.255g (5.1 mmol) hydrazine monohydrate was added. Then 10% Pd/C was added to the reaction mixture, which was heated under reflux for 24 hs. And the reaction progress was monitored by TLC. When the reaction was complete, the reaction mixture was cooled down, and filtered off carefully with the Buchner funnel
apparatus, which was filled up with silica powder. Repeat filtration one more
time until the filtrate was clear enough. The crude product was obtained after removing
the solvent under vacumm, then recrystalized in ethanol. Yield: 80%, this product
was analyzed by $^1$H NMR (Figure 3.14) in DMSO-d$_6$: δ 6.68 (d, 9Hz, 4H), 6.515 (d, 9Hz, 4H), 4.59 (s, 4H, NH$_2$), 4.08 (s, 4H).

3.8.2.4.3 Preparation of polymeric Schiff base 3-8

Polymeric Schiff Base 3-8 was prepared by a literature method. 2,5-Diformylfuran (0.221g, 1.78mmol) was dissolved in 15 mL acetonitrile and placed in a 25mL round-bottom flask equipped with a magnetic stirrer. An equivalent amount of 4,4'-(Ethane-1,2-diylbis(oxy))dianiline was separately mixed with a small amount of acetonitrile (about 5 mL). The latter was then added dropwise to the stirred 2,5-diformylfuran solution over 10 mins. The reaction mixture was stirred for 12h upon under 70 °C which brown precipitate was formed. Thereafter precipitates were filtered and washed with acetonitrile followed by water, then dried. Yield:76% this polymer was analyzed by MALDI-TOF MS (Figure 3.16), FT-IR (Figure 3.15).

3.8.2.5 Synthesis of Polymeric Schiff Base 3-11 from 2,5-Diformylfuran and 4,4'-(Ethane-1,2-diylbis(oxy))dianiline

This is a three step reaction, explained step by step as following paragraphs. All the procedure details could be found below.
3.8.2.5.1 Preparation of 1,12-bis(4-nitrophenoxy)dodecane

To a 100mL round-bottomed flask, 4-nitrophenol (2.0227 g, 14.54 mmol), potassium carbonate (1.773 g, 12.9 mmol) and potassium iodide (0.05 g) were dissolved in 30mL dimethly formamide (DMF). Then a solution of 1,13-dibromo propane (2.06 g, 6.28 mmol) in a 5mL dry dimethyl formamide was added dropwise to the reaction mixture. The reaction mixture was heated for 6h at 120 °C till completion, then cooled and poured onto crushed ice. The precipitated product was collected by filtration, extracted with methylene chloride. Then the collected organic layer was washed successively with sodium hydroxide(2M), hydrochloric acid(1M), and water. The methylene chloride solution was then dried over potassium sulfate and concentrated under vaccum and the product was recrystallized from mixture of ethanol and methylene chloride. Yield: 70%, and this product was analyzed by $^1$H NMR (Figure 3.17) in DMSO-d$_6$: δ 8.185 (d, 9Hz, 4H), 7.125 (d, 9Hz, 4H), 4.10 (m, 4H), 1.73 (m, 4H), 1.25~1.5 (m, 12H).

3.8.2.5.2 Preparation of 4,4’-(dodecane-1,12-diylbis(oxy))dianiline

In a 50 mL round-bottom flask with a stirring bar, 1,12-bis(4-nitrophenoxy)dodecane (8a) (2.1g, 5.046 mmol) was dissolved in 30mL methonal. Then 0.26g (5.2 mmol) hydrazine hydrate was added. Then 10% Pd/C was added to the reaction mixture, which was heated under reflux for 24 hs. And the reaction progress was monitored by TLC. When the reaction is completed, the reaction
mixture was cooled down, and filtered off carefully with the Buchner funnel apparatus, which was filled up with silica powder. Repeat filtration one more time until the filtrate was clear enough. The crude product was obtained after removing the solvent under vacuum, then recrystallized in methanol. Yield: 82%, this product was analyzed by $^1$H NMR (Figure 3.18) in DMSO-d$_6$: $\delta$ 6.625 (d, 9Hz, 4H), 6.495 (d, 9Hz, 4H), 4.54 (m, 4H, NH$_2$), 3.79 (m, 4H), 1.625 (m, 4H), 1.25~1.5 (m, 12H).

3.8.2.5.3 Preparation of polymeric Schiff base 3-11

2,5-Diformylfuran (0.15g, 1.21 mmol) was dissolved in 5 mL methanol, and placed in a 15 mL round-bottom flask equipped with a magnetic stirrer. An equivalent amount of 4,4'-(dodecane-1,12-diylbis(oxy))dianiline (0.269g, 1.1mmol) was separately dissolved in 10mL ethanol. The latter was then added dropwise to the stirred 2,5-Diformylfuran solution over 10 mins. The reaction mixture was stirred for 12h upon under 60 °C which yellow precipitate was formed. Thereafter precipitates was filtered and washed with methonal, acetonitrile, followed by water, then dried. Yield: 85%, this polymer was analyzed by solid state FT-IR (Figure 3.19), $^{13}$C NMR (Figure 3.20), MALDI-TOF MS (Figure 3.21)
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APPENDIX

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