

Alternating Copolymer of Pyridine and 1,4-Diphenyl-1,2,4,5-Tetrazine from *Bis*-1,3-Dipolar Cycloaddition Polymerization

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ABSTRACT: Our manuscript demonstrates a new “click-type” polymerization reaction. We present the synthesis of a new polymer poly(1,4-diphenyl-1,4-dihydro-1,2,4,5-tetrazine-3,6-diyl-2,6-pyridinediyl) through *bis*-nitrilimine intermediates which undergo *bis*-1,3-dipolar cycloaddition polymerization reactions. We synthesized *N,N'*-diphenyl-2,6-pyridindioic(*bis*-hydrazide) and halogenated this precursor to form *N,N'*-diphenyl-2,6-pyridindioic (*bis*-hydrazonoyl dichloride) as a new monomer. The resulting polymeric structure is a high molecular weight alternating copolymer

of pyridine and diphenyltetrazine soluble in a variety of organic solvents. Synthetic preparation and spectral analysis of the synthesis is presented. In addition, we demonstrate coordination of the polymer with cobalt metal salts indicating high complexation capability for these polymers. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 120: 623–630, 2011

Key words: click chemistry; 1,3-dipolar cycloaddition; tetrazine; polytetrazine; *bis*-hydrazonoyl dichloride; metal complexation

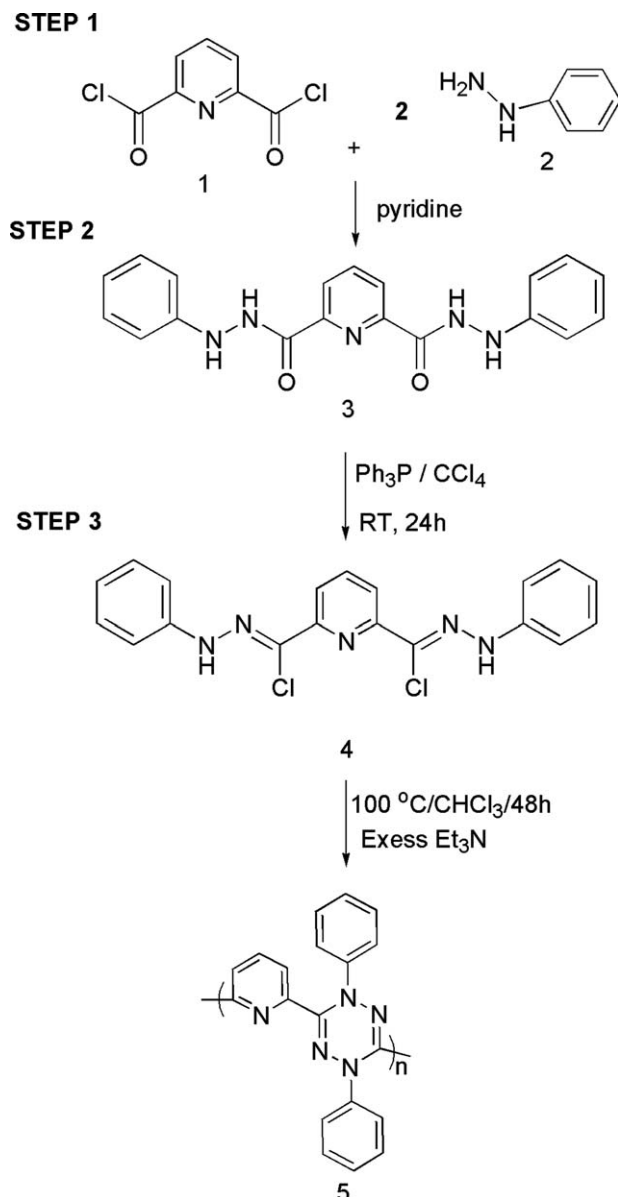
INTRODUCTION

1,2,4,5-Tetrazines are six-membered aromatic heterocycles possessing the highest known nitrogen content, making them exceptional molecules with exclusive properties. The unique properties of tetrazine compounds are derived from their extreme electron deficiency which provides opportunity for complexation, charge transfer, and stimuli-response. The distinctive electronic characteristics of tetrazine compounds have led to numerous studies in a broad range of applications.^{1,2} For example, 3-amino-6-aryl-1,2,4,5-tetrazines have anti-malarial activity,³ hexahydro-*s*-tetrazines display analgesic and anti-inflammatory activity,⁴ and tetrahydro-*s*-tetrazines are known to possess antibacterial and antifungal activity.⁵ Tetrazines are widely known to react as azadienes in the electronically demanding inverse Diels–Alder [4 + 1] cycloaddition reactions allowing versatile synthetic pathways for a number of compounds such as pyridazines.⁶ In addition, tetrazines have been cited to exhibit energetic,⁷ dye,⁸ insecticide,⁹ optical,¹⁰ electrochemical,¹¹ and other biomedically favorable properties.¹²

Fox and coworkers reported a new “click chemistry” based on the reverse Diels–Alder reactions of tetrazines with cyclooctene as retro-[4 + 2] cycloaddition which produces N₂ as condensate.¹³ Hildebrand and coworkers reported a similar reaction which demonstrated a tetrazine based cycloaddition for the pretargeted imaging of living cells.¹⁴ 3,6-Disubstituted tetrazine ligands are frequently used in coordination chemistry. In particular, 3,6-*bis*(2-pyridyl)-1,2,4,5-tetrazine has been demonstrated to have very high complexation capability with a wide variety of metals.¹⁵ Functional tetrazine ligands such as pyridine are stable in multiple oxidation states and have been evaluated in molecular electronic devices.¹⁶

It is surprising to us that tetrazine compounds, which display such diverse chemical and electronic behavior, have largely been overlooked by the polymer community, especially when considering the magnitude of contemporary polymer research focused in areas of metal complexation, charge transfer, biomedical, and stimuli-response applications. As a result, very little evidence of polytetrazine synthetic techniques, or exploration of polymeric tetrazines in similar applications cited for small molecule derivatives is available in the literature. We are reporting the synthesis of a new monomer precursor *N,N'*-diphenyl-2,6-pyridindioic (*bis*-hydrazide), halogenation to a new monomer *N,N'*-diphenyl-2,6-pyridindioic (*bis*-hydrazonoyl dichloride), and polymerization of a new polymer poly(1,

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Scheme 1 Synthesis of poly(1,4-diphenyl-1,4-dihydro-1,2,4,5-tetrazine-3,6-diyl-2,6-pyridinediyl) 5.

4-diphenyl-1,4-dihydro-1,2,4,5-tetrazine-3,6-diyl-2,6-pyridinediyl). The overall reaction is depicted in Scheme 1.

The polymer synthesis presented in this manuscript was motivated from pyridyl-1,2,4,5-tetrazine, which has become a popular small molecule cited for high metal complexation capability.^{17,18} We also demonstrate the efficacy for this polymer to complex with cobalt (II) chloride suggesting polytetrazine compounds maintain favorable electronic interactions cited in small molecule research.

EXPERIMENTAL SECTION

Measurements

Molecular weights (M_n and M_w) and polydispersity index (PDI) of polymers were determined using a

GPC system consisting of Waters Alliance 2695 Separations Module, an on-line multi-angle laser light scattering (MALLS) Detector (MiniDAWNTM, Wyatt Technology) fitted with a Gallium arsenide laser (20 mW) operating at 690 nm, an interferometric refractometer (Optilab DSPTM, Wyatt Technology, Santa Barbara, CA) operating at 35°C and 690 nm, and two mixed DPL gel (Polymer Laboratories) GPC columns (pore size range 50–104 Å, 5 mm bead size) connected in series. Fresh distilled THF served as the mobile phase and was delivered at a flow rate of 1.0 mL/min. Sample concentrations were ~ 7.0–10.0 mg/mL in fresh distilled THF, and the injection volume was 0.10 mL. The detector signals were simultaneously recorded using ASTRA software (Wyatt Technology). FTIR spectra were obtained using a Bruker Equinox 55 FTIR spectrometer using 32 scans at 4 cm⁻¹ resolutions. Monomer and polymer samples were pressed into a KBr pellets at ~ 2% loading levels. Solution ¹H-NMR and ¹³C-NMR spectra were obtained on a Varian 300-MHz spectrometer using 5-mm o.d. tubes with sample concentrations of 5–15% (w/v) in chloroform-d or dimethyl sulfoxide-d₆ containing tetramethylsilane as an internal reference. Thermal gravimetric analysis was conducted using a Thermal Analysis Q500 TGA under dry nitrogen as a purging gas. Tests were conducted from 25 to 600°C at a heating rate of 10°C/min. Differential scanning calorimetry was used to determine the glass-transition temperatures (T_g) for the polymers. Measurements were performed on ~ 10 mg samples using a TA Instruments DSC Q100. Samples were analyzed using the following method: Hold at 20°C for 5 min; ramp at 10°C/min to 200°C; cool at 20°C/min to 20°C; re-heat at 10°C/min to 200°C. The reported T_g values are the mid-point temperatures of the glass-transitions from the second heating cycles.

Materials

The following reagent was used as received without further purification. 2,6-Pyridinedicarbonyldichloride, 97%, triphenyl phosphine, 99%, pyridine ≥ 99%, phenylhydrazine, 97% acetonitrile, 99%, carbon tetrachloride, 99%, anhydrous chloroform, 99%, triethylamine, 99.5%, petroleum ether (reagent grade), anhydrous methanol, 99.8%, tetrahydrofuran (THF) ≥ 99.9%, cobalt (II) chloride 97%, chloroform-d (99.8 atom % D contains 0.03% TMS), dimethyl sulfoxide-d₆ (99.5+ atom % D contains 1% TMS) and cobalt(II) chloride, 97% (all Sigma-Aldrich, St. Louis, MO).

Synthesis of *N,N'*-diphenyl-2,6-pyridindioic (bis-hydrazide) 3

To a dry 500-mL beaker were charged phenylhydrazine 2 (21.63 mL, 0.20 mol) and 100 mL pyridine.

The solution was cooled to 0°C in an ice bath under stirring when 2,6-pyridinedicarbonyldichloride **1** (20.40 mL, 0.10 mol) dissolved in 100 mL pyridine was added dropwise over a period of ~ 1 h. After the addition was complete, the ice bath was removed, and the temperature of the reaction mixture was allowed to warm to room temperature and then held for an additional 1 h under stirring. The mixture was slowly poured (10–15 min) over 500 mL ice water containing ~ 5 mL of 1M HCl and stirring. Once the residual ice had melted the solution was vacuum filtered using a fine fritted glass filter. The *N,N'*-diphenyl-2,6-pyridindioic(*bis*-hydrazide) **3** pale yellow precursor was recrystallized from methanol. Yield (95%); m.p. 260°C; IR (neat, cm⁻¹) 3249 (NH), 3170 (NH), 1701 (C=O), 1685 (C=O); ¹H-NMR (300 MHz, [D₆]DMSO, 25°C) δ = 6.65 (s, 1H, NH), 6.82 (d, *J* = 8.1 Hz, 4H), 7.24 (m, 8H), 8.06 (br, 2H) 8.25 (br, 2H), 11.25 (s, 1H, NH); ¹³C-NMR (300 MHz, [D₆]DMSO, 25°C) 112.73, 119.31, 125.53, 129.46, 140.25, 148.73, 149.68, 163.25.

Synthesis of *N,N'*-diphenyl-2,6-pyridindioic (*bis*-hydrazonoyl dichloride) **4**

To a dry 250-mL round-bottom flask fitted with magnetic stirrer were charged *N,N'*-diphenyl-2,6-pyridindioic(*bis*-hydrazide) **3** (6.88 g, 0.02 mol), triphenylphosphine (13.10 g, 0.05 mol), dry acetonitrile (80 mL), and carbon tetrachloride (4.83 mL, 0.05 mol). Upon addition, the flask was fitted with a rubber stopper, and the mixture was stirred at room temperature for 24 h. After this period, the reaction was complete, and the solvent was evaporated under reduced pressure. The yellow residue was triturated with deionized water (20 mL), and the solid yellow precipitate was vacuum-filtered, washed again with deionized water and dried. The crude yellow product was recrystallized twice from an aqueous 75% methanol/25% deionized water solution as the *N,N'*-diphenyl-2,6-pyridindioic (*bis*-hydrazonoyl dichloride) **4** yellow monomer. Yield (60%); m.p. 210°C; IR (neat, cm⁻¹) 3313 (NH), 740 (C–Cl); ¹H-NMR (300 MHz, [D₆] DMSO, 25°C) δ = 6.90, 7.29, 7.44 (m, 10H, phenylH's); 7.91, 8.04 (m, 3H, pyridylH's) and 10.23 (s, 1H, NH); ¹³C-NMR (300 MHz, [D₆]DMSO, 25°C) 114.28, 120.51, 121.32, 123.52, 129.70, 137.51, 144.21, 150.82.

Synthesis of poly(1,4-diphenyl-1,4-dihydro-1,2,4,5-tetrazine-3,6-diyl-2,6-pyridinediyl) **5**

A representative synthetic procedure for synthesizing poly(1,4-diphenyl-1,4-dihydro-1,2,4,5-tetrazine-3,6-diyl-2,6-pyridinediyl) **5** was as follows: To a dry 100-mL two-neck round-bottom flask fitted with a West condenser were charged *N,N'*-diphenyl-2,6-

pyridindioic(*bis*-hydrazonoyl dichloride) **4** (3.83 g, 10.0 mmol) and anhydrous chloroform (30 mL) with magnetic stirring. The flask containing the yellow solution at room temperature (RT) was immersed into a 100°C preheated oil-bath, and the solution was brought to a reflux condition when triethylamine (5.60 g, 40.0 mmol) was charged into the reactor. The reaction was kept under reflux for 48 h during which time a visible salt precipitated and the yellow solution shifted to a deep brown color. The flask was removed from heating, cooled to RT, and the triethylamine hydrochloride precipitate was vacuum filtered from the solution. Solvent was stripped from the solution under reduced pressure leaving a deep brown tacky residue which was dissolved in 20 mL of chloroform, transferred to a separation funnel and washed three times with 60 mL of deionized water. The chloroform solution was transferred to a dry separation funnel and added dropwise to 300 mL of rapidly stirred petroleum ether. The solid brown polymer immediately precipitated from the stirred solution and the poly(1,4-diphenyl-1,4-dihydro-1,2,4,5-tetrazine-3,6-diyl-2,6-pyridinediyl) **5** was vacuum-filtered and dried under vacuum (24 h at 90°C). IR (neat, cm⁻¹) 1684 (C=N) and 1597 (C=C); ¹H-NMR (300 MHz, [D₆] DMSO, 25°C) δ = 6.91, 7.26, 7.44 (phenylH's); 7.52, 7.65 (pyridylH's); ¹³C-NMR (300 MHz, [D₆]DMSO, 25°C) 113.74, 128.42, 128.58, 129.20, 131.61, 131.98, 132.13, and 133.04.

Cobalt (II) chloride complexation reactions

A representative procedure for the metal complexation of poly(1,4-diphenyl-1,4-dihydro-1,2,4,5-tetrazine-3,6-diyl-2,6-pyridinediyl) with cobalt (II) chloride is as follows: To a dry 100-mL two-neck round-bottom flask equipped with a West condenser and magnetic stirring were charged 0.723 g (0.01 mmol) poly(1,4-diphenyl-1,4-dihydro-1,2,4,5-tetrazine-3,6-diyl-2,6-pyridinediyl) **5** and 40-mL chloroform. The dark-brown solution flask was immersed into a 75°C heated oil-bath and allowed to stir. To a 50-mL addition funnel was charged 0.302 g (0.010 mmol) cobalt (II) chloride dissolved in 10-mL methanol. The cobalt (II) chloride salt solution was added dropwise into the polymer solution over approximately a 30-min period, and we observed a distinct color shift from brown to dark green during this period. The mixture was allowed to stir for 24 h when it was removed from heat and cooled to RT. Solvents were removed under reduced pressure, and the remaining black tacky residue was redissolved in 10 mL of chloroform and washed three times with 30 mL of deionized water. The solution product was dripped into 250 mL of rapidly stirred petroleum ether and polymer-cobalt (II) chloride complexation product

precipitated as a dark-green solid which was vacuum filtered and dried under vacuum (24 h at 90°C).

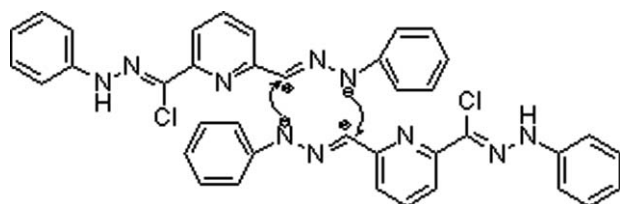
RESULTS AND DISCUSSION

Synthesis

We recently reported the synthesis of high molecular weight *sym*-1,4-diphenyl-1,4-dihydro-1,2,4,5-polytetrazine from *bis*-nitrilimines, which demonstrated the effectiveness of synthesizing polytetrazines through head-to-tail 1,3-dipolar cycloaddition polymerization reactions.¹⁹ Shawali and Sayed previously reported the synthesis of small molecule tetrazine derivatives through 1,3-dipolar cycloaddition reactions of formazans and elucidated the mechanism by confirming the tetrazine ring was formed through nitrilimine intermediates.²⁰ We have extended these teachings to explore polymerization reactions utilizing *bis*-hydrazonoyl dichloride nitrilimine intermediates and found this synthetic approach to be quite efficient to synthesize high molecular weight polymeric tetrazines with unique primary backbone architectures. The polymerization reaction proceeds through *bis*-nitrilimine intermediates which undergo click type *bis*-1,3-dipolar cycloaddition solution reactions to high molecular weight polymer as depicted in Scheme 2.

Our current research demonstrates a new synthetic approach that leads to alternating copolymers of tetrazines with other heterocycles. The ability to alternate a second heterocycle along the main-chain of the polytetrazine provides considerable opportunity to further explore metal-complexation, charge-transfer, and selectivity properties cited for small molecules. We broadened the principles from our previous research to synthesize a series of poly(1,4-diphenyl-1,4-dihydro-1,2,4,5-tetrazine-3,6-diyl-2,6-pyridinediyl) alternating copolymers through *bis*-1,3-dipolar cycloaddition polymerization reactions.

The first step of our approach involved reaction of 2,6-pyridinedicarbonyldichloride **1** with phenylhydrazine **2** to form *N,N'*-diphenyl-2,6-pyridindioic(*bis*-hydrazide) **3** in high yield as depicted in Step 1 of Scheme 1. The chemical structure and purity of the *bis*-hydrazide product **3** was elucidated using ¹H-



Scheme 2 *Bis*-1,3-dipolar cycloaddition polymerization reaction mechanism.

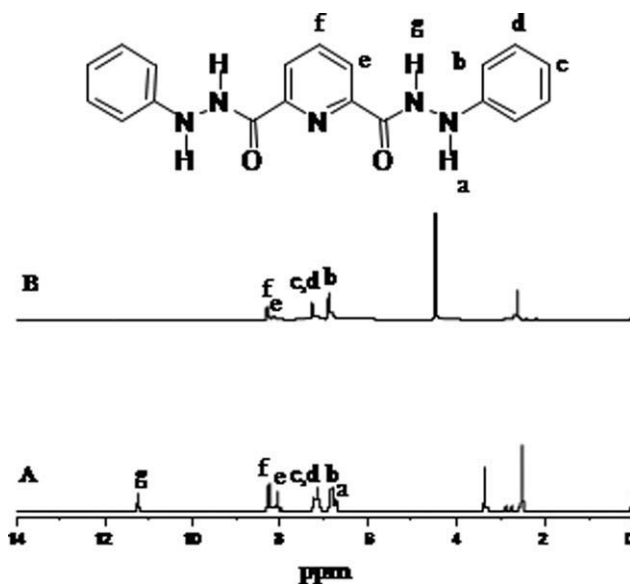


Figure 1 ¹H-NMR of *N,N'*-diphenyl-2,6-pyridindioic(*bis*-hydrazide) **3**.

NMR in DMSO [Fig. 1(A)] and in a 1 : 3 (v/v) D₂O : DMSO mixture [Fig. 1(B)]. ¹H-NMR spectrum for the sample dissolved in DMSO shows two distinct resonances for the secondary amines of the *N,N'*-diphenyl-2,6-pyridindioic(*bis*-hydrazide) at $\delta = 6.65$ ppm and $\delta = 11.25$ ppm. Confirmation of the secondary amine proton assignments was verified using a proton-deuterium exchange with D₂O-DMSO solvent mixture [Fig. 1(B)].

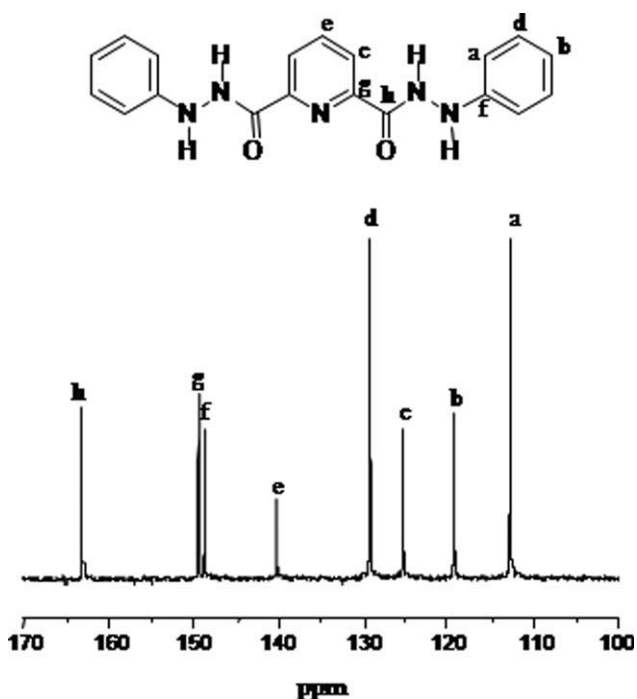


Figure 2 ¹³C-NMR of *N,N'*-diphenyl-2,6-pyridindioic(*bis*-hydrazide) **3**.

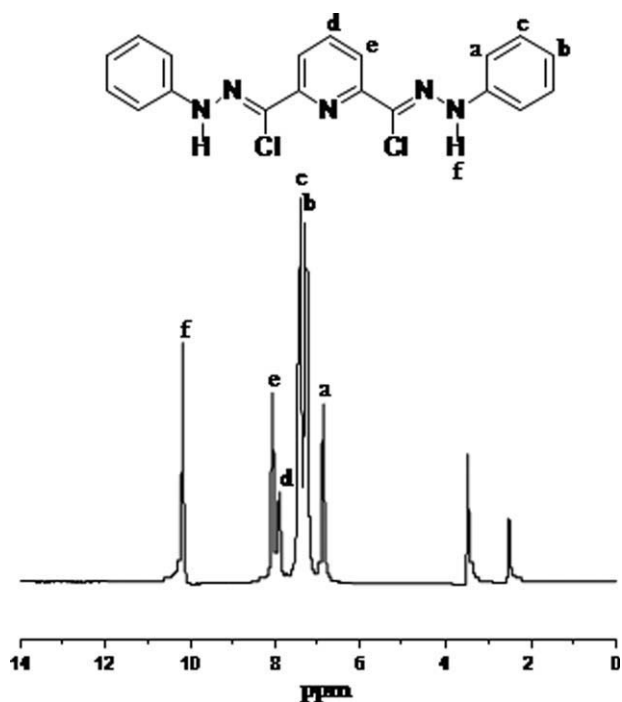


Figure 3 $^1\text{H-NMR}$ of N,N' -diphenyl-2,6-pyridindioic (*bis*-hydrazonoyl dichloride) **4**.

The $^{13}\text{C-NMR}$ spectrum for N,N' -diphenyl-2,6-pyridindioic(*bis*-hydrazide) **3** (Fig. 2) revealed seven distinct aromatic resonances ($\delta = 112.73, 119.31, 125.53, 129.46, 140.25, 148.73,$ and 149.68) and a single resonance at 163.25 ppm assigned to the carbonyl carbon.

Step 2 of the synthesis shown in Scheme 1 depicts N,N' -diphenyl-2,6-pyridindioic(*bis*hydrazide) **3** was reacted with triphenylphosphine in the presence of carbon tetrachloride to form the monomer, N,N' -diphenyl-2,6-pyridindioic (*bis*-hydrazonoyl dichloride) **4**, at 60% yield. Purification of this monomer through several recrystallizations in aqueous methanol was determined to be critical for synthesizing high molecular weight polymer. To our knowledge, this particular pyridine based *bis*-hydrazonoyl halide is unreported in the literature.

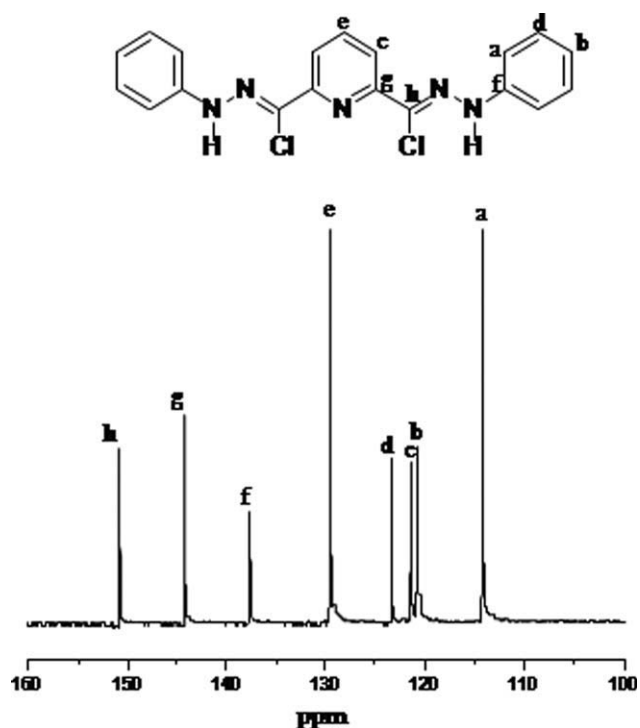


Figure 4 $^{13}\text{C-NMR}$ of N,N' -diphenyl-2,6-pyridindioic (*bis*-hydrazonoyl dichloride) **4**.

Figure 3 shows the $^1\text{H-NMR}$ spectrum of N,N' -diphenyl-2,6-pyridindioic(*bis*-hydrazonoyl dichloride) **4**. The spectrum indicates complete elimination of the amide proton from the *bis*-hydrazide [peak g in Fig. 1(A)] upon conversion to *bis*-hydrazonoyl dichloride. In addition, a significant resonance shift of the secondary amine proton β to the carbonyl of N,N' -diphenyl-2,6-pyridindioic(*bis*-hydrazide) from $\delta = 6.65$ ppm to $\delta = 10.23$ ppm was observed.

Figure 4 shows the $^{13}\text{C-NMR}$ spectrum of N,N' -diphenyl-2,6-pyridindioic (*bis*-hydrazonoyl dichloride) **4**. The spectrum reveals significant shifting for carbon resonances upon conversion of the N,N' -diphenyl-2,6-pyridindioic(*bis*-hydrazide) to the *bis*-hydrazonoyl dichloride product. Most noteworthy is the resonance shift of the carbonyl carbon, labeled h

TABLE I
Summary of Polymerization Reaction Conditions and Analysis

Reaction	Solvent	[Monomer]/ [TEA]	Temperature ($^{\circ}\text{C}$)	Time (h)	Yield (%)	M_n ($\times 10^3$)	PDI	T_g ($^{\circ}\text{C}$)
1	CHCl_3	1 : 2	22	48	65	9	1.32	63
2	CHCl_3	1 : 2	50	48	60	15	1.21	–
3	CHCl_3	1 : 2	75	48	61	40	1.31	–
4	CHCl_3	1 : 2	100	48	63	45	1.21	70
5	CHCl_3	1 : 2	125	48	60	42	1.20	–
6	CHCl_3	1 : 4	100	48	65	72	1.14	85
7	CHCl_3	1 : 6	100	48	65	65	1.13	80
8	THF	1 : 4	100	48	80	22	1.35	–

in Figure 2 from $\delta = 163.25$ ppm to $\delta = 150.82$ ppm upon conversion to halogen (peak h in Fig. 4).

A summary of our syntheses which depict a variety of polymerization reaction conditions is provided in Table I. The polymerizations progressed efficiently in chloroform and triethylamine to form nitrilimine intermediates. We observed that a [monomer]/[TEA] concentration of 4 : 1 provided the most efficient polymerization conditions to form high molecular weight polymer. Reaction temperature and time also influenced molecular weight, and we determined the most efficient conditions for the synthesis of poly(1,4-diphenyl-1,4-dihydro-1,2,4,5-tetrazine-3,6-diyl-2,6-pyridinediyl) was 100°C for 48 h in chloroform. Glass transition temperatures measured by differential scanning calorimetry for the polymers are presented in Table I and observed to be in the range of ~ 63 –85°C depending upon the molecular weights.

Conversion of the *N,N'*-diphenyl-2,6-pyridindioic (*bis*-hydrazonoyl dichloride) to polymer reached around 65% under the reaction conditions we performed in chloroform as shown in Table I. We observed reduced yields in chloroform attributed to increased salt formation of nitrilimine-triethylamine complexation. In an effort to investigate the effect of solvent polarity and nitrilimine-triethylamine complexations, we ran a similar reaction in THF and observed an increase in yield to 80%, but also observed a decrease in molecular weight. The observed increase in yield with the more polar solvent provided further evidence the nitrilimine intermediate complexes with triethylamine forming a salt and reduces the overall yield. Molecular weights for the 1,3-dipolar cycloaddition polymerization of *N,N'*-diphenyl-2,6-pyridindioic (*bis*-hydrazonoyl dichloride) in chloroform approached $M_n = 72,300$ g/mol with surprisingly narrow molecular weight distributions of ~ 1.13 –1.35 as measured by GPC (Fig. 5).

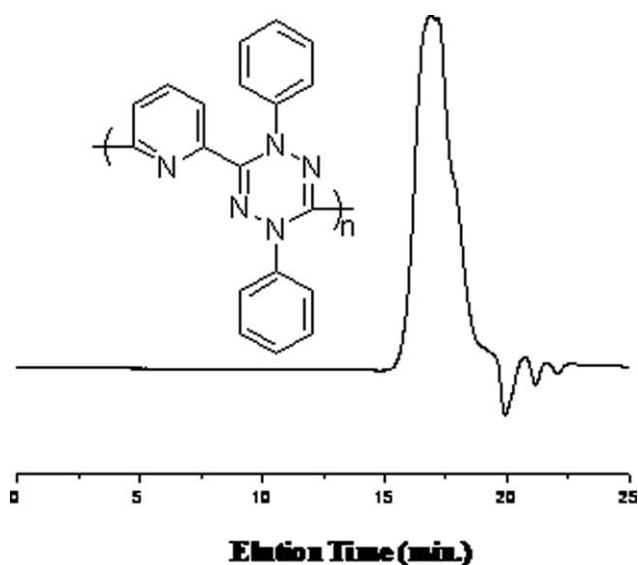


Figure 5 GPC of poly(1,4-diphenyl-1,4-dihydro-1,2,4,5-tetrazine-3,6-diyl-2,6-pyridinediyl) 5.

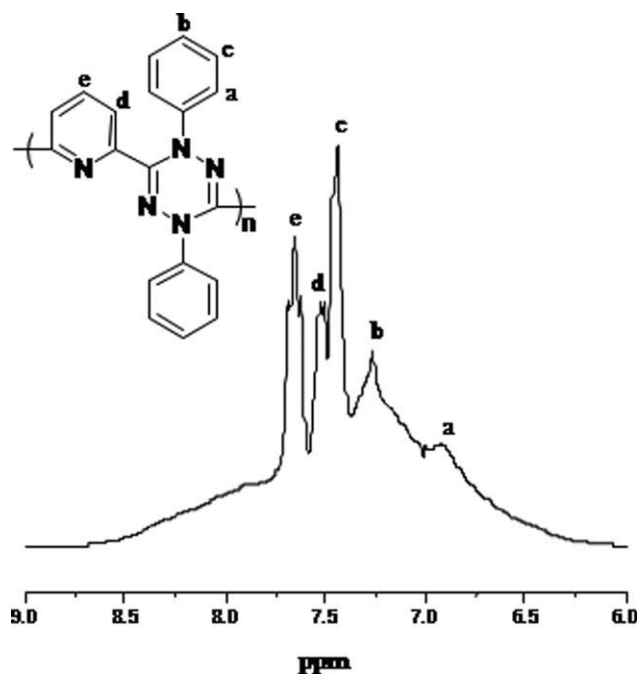


Figure 6 $^1\text{H-NMR}$ of poly(1,4-diphenyl-1,4-dihydro-1,2,4,5-tetrazine-3,6-diyl-2,6-pyridinediyl) 5.

ide) in chloroform approached $M_n = 72,300$ g/mol with surprisingly narrow molecular weight distributions of ~ 1.13 –1.35 as measured by GPC (Fig. 5).

$^1\text{H-NMR}$ spectrum of the polymer is depicted in Figure 6, and we assigned resonance shifts for the polymer at $\delta = 6.91, 7.26, 7.44$ (phenyl H's); $7.52, 7.65$ (pyridyl H's).

$^{13}\text{C-NMR}$ of the polymer product is depicted in Figure 7, and we have assigned resonance shifts for the polymer carbons at $\delta = 113.74, 128.42, 128.58, 129.20, 131.61, 131.98, 132.13,$ and 133.04 .

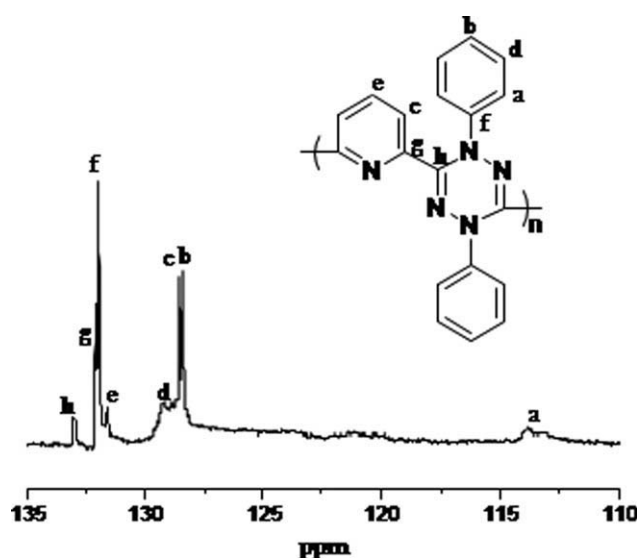


Figure 7 $^{13}\text{C-NMR}$ of poly(1,4-diphenyl-1,4-dihydro-1,2,4,5-tetrazine-3,6-diyl-2,6-pyridinediyl) 5.

The polymerization reaction was further elucidated through FTIR spectroscopy. Figure 8(A) shows the FTIR spectra for the *bis*-hydrazoneyl chloride monomer and contains a secondary amine stretch absorbing at 3317 cm^{-1} . After conversion to polymer, the secondary amine stretch present in the monomer completely disappeared [Fig. 8(B)] confirming loss of proton during the 1,3-dipolar cycloaddition reaction.

Complexation

Tetrazine chemistry has gained significant attention in recent years primarily associated with complexation and coordination chemistries.²¹ Although the basicity of the heterocyclic nitrogen atoms is very low, these compounds demonstrate strong complexation and coordination with metals, as demonstrated with the small molecule 3,6-*bis*-(2-pyridyl)-1,2,4,5-tetrazine.²² We evaluated the metal complexation capability of poly(1,4-diphenyl-1,4-dihydro-1,2,4,5-tetrazine-3,6-diyl-2,6-pyridinediyl) through a series of solution reactions with cobalt chloride to form metal complexes. In these studies, we dissolved the tetrazine based polymers in chloroform and added dropwise a concentrated cobalt chloride solution dissolved in methanol under rapid stirring at 75°C to give the metal complexed polymer. The polymer displayed a distinct color shift from brown to deep

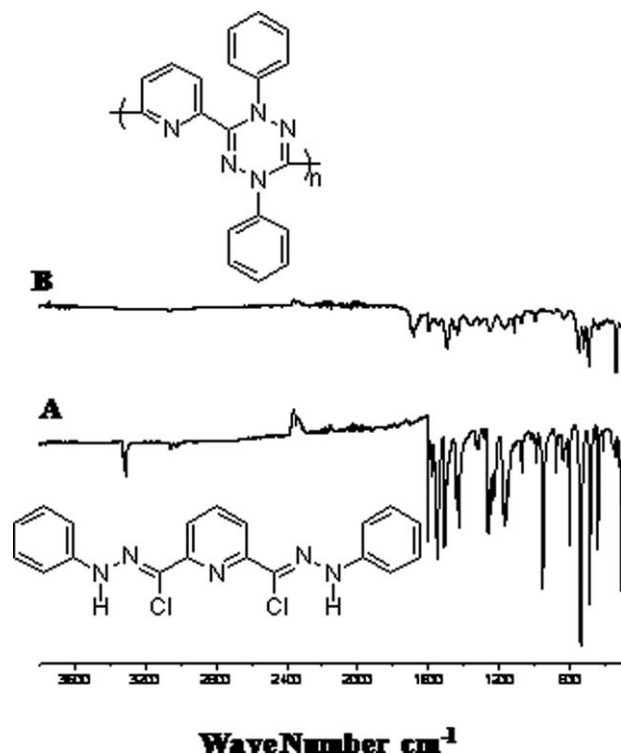
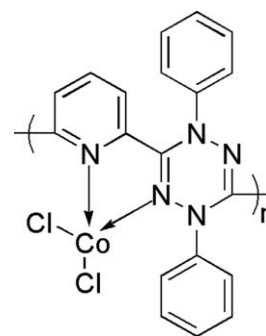


Figure 8 FTIR for *N,N'*-diphenyl-2,6-pyridindioic (*bis*-hydrazoneyl dichloride) **4** and poly(1,4-diphenyl-1,4-dihydro-1,2,4,5-tetrazine-3,6-diyl-2,6-pyridinediyl) **5**.



Scheme 3 Proposed metal complexation of cobalt chloride with poly(1,4-diphenyl-1,4-dihydro-1,2,4,5-tetrazine-3,6-diyl-2,6-pyridinediyl).

green upon reaction with cobalt. Tetrazine compounds generally display distinct colors associated with conjugation, and the color shift is used as an indicator for complexation. These initial studies suggest the tetrazine based polymers have strong complexation capability towards metal salts. Metal complexed polymers were analyzed for thermal decomposition behavior and compared to non-complexed polymers. TGA studies indicated the weight percent of cobalt complexed within the polytetrazine was $\sim 23\text{ wt } \%$ when comparing 600°C remaining mass values for complexed and non-complexed polymers. Although the specific coordination complex for this polymer is not proven, a reasonable polymer-metal complex consistent with citations for small molecule pyridyltetrazine-metal coordination is depicted in Scheme 3.

CONCLUSIONS

Our manuscript presents the synthesis of a new heterohydrazoneyl halide monomer containing pyridine, which we polymerized through *bis*-1,3-dipolar cycloaddition polymerization reactions. Our approach demonstrates the synthesis of a new monomer *N,N'*-diphenyl-2,6-pyridindioic (*bis*-hydrazoneyl dichloride). Preliminary results suggest the monomer undergoes dehydrohalogenation in base to form high molecular weight tetrazine based polymers through *bis*-nitrilimine intermediates. Our synthesis was motivated from numerous research activities citing small molecule tetrazine compound complexation with metals, and the new tetrazine polymers appear to demonstrate similar coordination behaviors. Tetrazines as polymeric materials have been essentially ignored by the polymer community. The significance of this research demonstrates *bis*-1,3-dipolar cycloaddition polymerization applied to new polytetrazine and heterocycle alternating copolymers. The charge complexation capability for these polymers and the preservation of metal binding potential has been demonstrated. These polymers

have the potential for use in charge transfer materials making them attractive to the contemporary polymer science community.

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