

1,3-Dipolar cycloaddition polymerization reactions of novel macromolecules containing *sym*-tetrazine rings

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Received 5 November 2007; received in revised form 18 February 2008; accepted 23 February 2008

Available online 29 February 2008

Abstract

We report the synthesis of *sym*-1,4-diphenyl-1,4-dihydro-1,2,4,5-polytetrazine through 1,3-dipolar cycloaddition polymerization reactions where bis-hydrazoneyl chloride was converted to a tetrazine based polymer through bis-nitrilimine intermediates. Polymer molecular weights approached 90,000 g/mol under optimized reaction conditions with low polydispersity indices of approximately 1.05. The polymers are soluble in a variety of organic solvents and the reactions were characterized through a series of spectral, thermal and chromatographic techniques. The tetrazine based polymers display high complexation potential with cobalt chloride demonstrating metal complexation capability.

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Keywords: Tetrazine; Polytetrazine; 1,3-Dipolar cycloaddition

1. Introduction

1,2,4,5-Tetrazines are a distinct class of compounds that have been cited in a variety of research applications including *anti*-tumor activity [1], molecular self-assembly [2], fluorescence [3], energetics [4], and conductive materials [5]. Tetrazines are unique since they constitute the most electron deficient aromatic family of compounds, providing unusually high electron affinity and charge transfer potential as conjugated molecules. Tetrazines display brilliant color and their fluorescence can be selectively quenched by electron rich molecules [6]. Tetrazine chemistries have been useful in the molecular recognition of environmental contaminants [7], as anion binders [8] and in metal complexations [9].

Concerns regarding tetrazine thermal and oxidative stability [10] have been overshadowed during the last decade with a significant increase in scientific study and patent

activity as reflected in a recent literature review [11]. Interest in tetrazine exploration is commensurate with a recognized need for materials with selective binding sites driven through research in stimuli-response materials, smart materials and molecular self-assembly chemistries. The unique electronic and structural properties of tetrazines make these products particularly interesting for evaluation in polymeric applications.

Surprisingly little research has been reported for polymers based upon tetrazine or substituted tetrazine moieties contained within the backbone of the molecules. Early reports include tetrazine functionalized polystyrene-*co*-DVB copolymers [12] and self-assembled metal–lattice coordination polymers [13]. The first example of an electroactive polymer containing an oligothiophene substituted tetrazine moiety in the backbone of the polymer was reported by Audebert et al. in 2004 [14]. Stille and Harris reported that dihydrotetrazine polymers can be obtained from the reactions of isophthaloyl and terephthaloyl hydrazoneyl chlorides with triethylamine in refluxing tetrahydrofuran to account for the low molecular weights of polymers obtained in cycloaddition reactions of nitrilimines [15]. Recently, Sagot et al. reported

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the synthesis of linear and hyperbranched tetrazine based polyheterylene assemblies through hydrazine-mediated polycondensation of dinitriles or diimidates to polydihydro-tetrazines [16].

We report the synthesis of *sym*-1,4-diphenyl-1,4-dihydro-1,2,4,5-polytetrazine from bis-hydrazoneyl halide with triethylamine in the absence of dipolarophiles. This research provides new synthetic pathways for incorporating tetrazine moieties into the backbones of polymeric materials to further explore and evaluate polymeric tetrazines for complexation, charge transfer and selectivity properties cited for small molecule compounds.

2. Experimental

2.1. Materials

The following reagents were used as received without further purification. Diethyl oxalate, 99+%, phenylhydrazine, 97%, anhydrous methanol, 99.8%, anhydrous ethanol, 99.5%, dimethylformamide (DMF), 99%, triphenylphosphine, 99%, anhydrous acetonitrile, 99%, carbon tetrachloride, 99%, anhydrous chloroform, 99%, triethylamine, 99.5%, petroleum ether (reagent grade), benzene, 99%, tetrahydrofuran (THF), 99.9%, acetone, 99%, dioxane, 99%, 1-methyl-2-pyrrolidinone, 99%, chloroform-*d* (99.8 atom% D contains 0.03% TMS), dimethyl sulfoxide-*d*₆ (99.5+ atom% D contains 1% TMS) and cobalt(II) chloride, 97% (all Sigma–Aldrich).

2.2. Synthesis of *N,N'*-diphenyloxalic(bis-hydrazide) **3**

To a dry 100 mL two-neck round-bottom flask fitted with a West condenser were charged 3.39 mL of diethyl oxalate **1** (25.0 mmol) and 4.92 mL of phenylhydrazine **2** (50.0 mmol). The flask containing a low-viscosity slightly yellow solution was immersed into a pre-heated oil-bath set at 110 °C and the solution was stirred using a magnetic stirring device for 30 min. During this 30 min period, the low-viscosity solution increased in viscosity to the point at which the reaction product became a slightly yellow solid-plug mass (no significant color change) and the flask was removed from the oil-bath and allowed to cool to room temperature. The reaction product, *N,N'*-diphenyloxalic(bis-hydrazide) **3** was removed from the flask by adding approximately 30 mL of ethanol and using a metal spatula to fragment the glassy solid into size-reduced particles. The solid product was filtered from the ethanol and dried *in vacuo* (2 h at 110 °C). The dry product was recrystallized from DMF and the slightly yellow solid product was collected for analysis [17]. Yield for this reaction was 95% and the melting point for the product was 274 °C. ¹H NMR in DMSO-*d*₆ (δ, ppm): 6.78–7.15 (m, 10H, ArH), 7.90 (s, 1H, NH) and 10.59 (s, 1H, NH). ¹³C NMR in DMSO-*d*₆ (δ, ppm): 112.30, 118.69, 128.49, 148.38, and 159.66. IR ν cm⁻¹, 3344 (NH), 3171 (NH), 1675 (C=O).

2.3. Synthesis of *N,N'*-diphenylethane(bis-hydrazoneyl dichloride) **4**

To a dry 250 mL two-neck round-bottom flask fitted with a West condenser and magnetic stirrer were charged 5.40 g (20.0 mmol) *N,N'*-diphenyloxalic bis-hydrazide **3**, 13.10 g (50.0 mmol) triphenylphosphine, 150 mL acetonitrile, and 4.83 mL (50 mmol) carbon tetrachloride. The mixture was solubilized by immersing the flask into an 80 °C pre-heated oil-bath and refluxed for 10 h during which the solution color changed from slightly yellow to red-brown as the reaction approached completion. The solution was removed from heat, cooled to room temperature and solvents were evaporated under reduced pressure. The dark tacky residue was triturated with 40.0 mL of deionized water and stirred using a spatula to form bright yellow powder slurry. The yellow powder *N,N'*-diphenylethane(bis-hydrazoneyl dichloride) **4** was filtered from the water, washed with ethanol. The final yellow product was recrystallized from acetic acid and dried *in vacuo* (12 h at 80 °C) [18]. Yield for this reaction was 75% and the melting point for the product was 188–190 °C. ¹H NMR in DMSO-*d*₆ (δ, ppm): 6.85–7.34 (m, 10H, ArH), 10.15 (s, 1H, NH). ¹³C NMR in DMSO-*d*₆ (δ, ppm): 113.55, 118.13, 121.26, 129.70 and 144.26. IR ν cm⁻¹, 3317 (NH), 1650 (C=N), 1600 (C=C) and 785 (C–Cl).

2.4. Synthesis of *sym*-1,4-diphenyl-1,4-dihydro-1,2,4,5-polytetrazine **5**

A representative synthetic procedure for synthesizing *sym*-1,4-diphenyl-1,4-dihydro-1,2,4,5-polytetrazine **5** is as follows: to a dry 100 mL two-neck round-bottom flask were charged 3.07 g (10.0 mmol) *N,N'*-diphenylethane(bis-hydrazoneyl dichloride) **4** and 30 mL chloroform. The flask containing a yellow solution at RT was immersed into a 90 °C pre-heated oil-bath and the solution was brought to a reflux condition when 14 mL (100 mmol) of triethylamine was charged into the reactor. The reaction was kept under reflux for 48 h, during which a visible salt precipitated and the yellow solution changed to deep brown. The flask was removed from heat, 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 toluene, transferred to a separation funnel and washed three times with 60 mL of deionized water. The toluene solution was transferred to a dry separation funnel and added dropwise to 300 mL of rapidly stirred petroleum ether in ice bath. The solid brown polymer precipitate was vacuum filtered, washed with water several times and dried *in vacuo* (24 h at 90 °C). Yield for this reaction after purification was 65%. ¹H NMR in CDCl₃ (δ, ppm): 6.07–8.22 (m, ArH). ¹³C NMR in CDCl₃ (δ, ppm): 116.07, 129.14, 138.85 and 142.06. IR ν cm⁻¹ 1683 (C=N) and 1594 (C=C).

2.5. Cobalt(II) chloride complexation reactions

A representative procedure for the metal complexation of polytetrazines 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 0.89 g (0.010 mmol) *sym*-1,4-diphenyl-1,4-dihydro-1,2,4,5-polytetrazine **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 0.444 g (0.010 mmol) cobalt(II) chloride dissolved in 10.0 mL methanol. This cobalt salt solution was added dropwise into the polymer solution over approximately a 30 min period, and 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 residue was re-dissolved 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. The polymer complex precipitated as a dark-green solid was vacuum filtered and dried *in vacuo* (24 h at 90 °C).

2.6. Analysis

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, Inc.) fitted with a Gallium arsenide laser (20 mW) operating at 690 nm, an interferometric refractometer (Optilab DSPTM, Wyatt Technology, Inc.) operating at 35 °C and 690 nm, and two mixed DPL gel (Polymer Laboratories, Inc.) 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 approximately 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, Inc.).

FT-IR spectra were obtained using a Bruker Equinox 55 FT-IR spectrometer using 32 scans at 4 cm⁻¹ resolution. Monomer and polymer samples were pressed into KBr pellets at approximately 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-*d*₆ 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 approximately 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.

3. Results and discussion

Shawali et al. previously reported the synthesis of small molecule tetrazine derivatives through 1,3-dipolar cycloaddition reactions of formazans and elucidated the mechanism for these reactions by showing that the tetrazine ring formation was achieved through a nitrilimine intermediate [19]. Shawali et al. also reported 1,3-dipolar cycloaddition reactions to synthesize substituted tetrazine molecules from hydrozonoyl chlorides using triethylamine as base catalyst [20]. We extended these principles to polymerization reactions using bis-hydrasonoyl chloride and determined that this was an effective method for preparing linear and soluble high molecular weight polytetrazines. Our rationale was to utilize the well-documented formation of nitrilimine intermediates through symmetrical intermolecular 1,3-dipolar cycloaddition reactions of bis-nitrilimines into polymers. Our expectations associated with this polymerization technique were to form polymers with relatively high molecular weights and broad molecular weight distributions through step-growth polymerization reaction mechanisms. We were successful in synthesizing high molecular weight polymer in our reactions up to approximately 90,000 g/mol, but quite surprised to obtain narrow molecular weight distributions of around 1.04–1.05. These PDI results are counterintuitive to what one would expect for a step-growth reaction. Although we are not completely dismissing our results as an unidentified artifact of our procedures, we continue to gain confidence that this unusually narrow PDI is correct, as we have observed consistent results through numerous reaction replications and careful analytical studies. Our only explanation for a narrow PDI outside of an unknown procedural artifact is that the polymerization reaction must proceed through some alternative reaction mechanism that we have not elucidated at this point of our study; this reaction and the mechanism are worthy of continued study.

Irrespective of the reaction mechanism, this research demonstrates new synthetic techniques that are useful for synthesizing relatively high molecular weight polymers which contain tetrazine moieties within the backbones. We have demonstrated that 1,3-dipolar cycloaddition polymerization reactions of bis-hydrasonoyl chlorides have proven to be effective for synthesizing substituted tetrazine based polymeric materials. The first step of our approach reacted diethyl oxalate (**1**) with phenylhydrazine (**2**) to form *N,N'*-diphenyloxalic(bis-hydrazide) (**3**) in high yield (95%). The chemical structure and purity of the bis-hydrazide (**3**) were elucidated using ¹H NMR and ¹³C NMR in DMSO.

In the second step of the reaction *N,N'*-diphenyloxalic(bis-hydrazide) (**3**) was reacted with triphenylphosphine in the presence of carbon tetrachloride to form *N,N'*-diphenylethane(bis-hydrasonoyl chloride) (**4**) at 75% yield after purification through several recrystallizations in methanol. This purification step was determined to be the most critical procedure in the overall reaction for synthesizing high molecular weight polymer. ¹H NMR for the bis-hydrasonoyl chloride product (**4**) revealed essentially a complete elimination for the proton

assigned to the secondary amine α to the carbonyl of bis-hydrazide, upon conversion to bis-hydrazoneyl chloride. We also observed a significant shift of the proton for the secondary amine β to the carbonyl of bis-hydrazide, upon conversion to bis-hydrazoneyl chloride from $\delta = 7.90$ ppm to $\delta = 10.15$ ppm, respectively. ^{13}C NMR revealed significant shifting for carbon resonances upon conversion of bis-hydrazide to bis-hydrazoneyl chloride. Most noteworthy was the shift of the carbonyl carbon from $\delta = 159.66$ ppm to $\delta = 144.26$ ppm upon conversion to halogen.

N,N'-Diphenylethane(bis-hydrazoneyl chloride) was polymerized in the presence of excess triethylamine in chloroform to form the *sym*-1,4-diphenyl-1,4-dihydro-1,2,4,5-polytetrazine. The complete polymerization reaction from starting materials to final product is depicted in Fig. 1. ^1H NMR for the polymer run in CDCl_3 showed a broad resonance between (δ , ppm): 6.07–8.22 (m, ArH). ^{13}C NMR of the polymer product was run in CDCl_3 and we have assigned resonance shifts for the polymer carbons at $\delta = 116.07$, 129.14, 138.85 and 142.06 as depicted in Fig. 2.

A summary of selected polymerization reaction conditions is presented in Table 1. Reactions 1–8 represent our initial studies which incorporated a theoretical equivalent monomer to TEA ratio of 1:2 and investigated time and temperature effects for the polymerization reaction. Reaction temperature and time influenced the final molecular weights of the polymers and we determined that the most efficient condition for

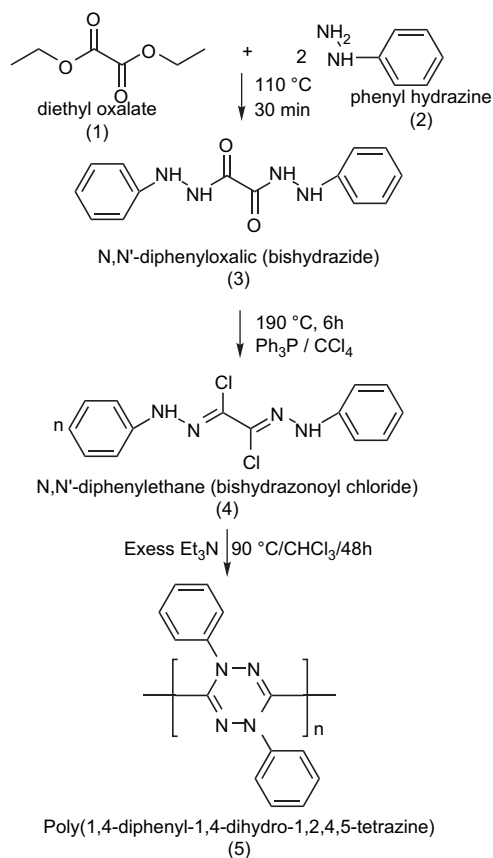


Fig. 1. Synthesis of *sym*-1,4-diphenyl-1,4-dihydro-1,2,4,5-polytetrazine (5).

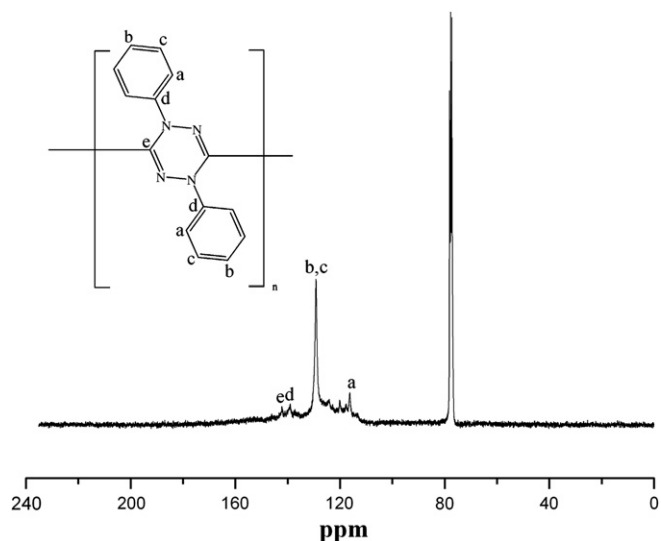


Fig. 2. ^{13}C NMR for *sym*-1,4-diphenyl-1,4-dihydro-1,2,4,5-polytetrazine (5).

the synthesis of *sym*-1,4-diphenyl-1,4-dihydro-1,2,4,5-polytetrazine was the reaction in chloroform at 90°C for approximately 48 h.

Reactions 1–8 were our first results that provided evidence for high molecular weight polymers with surprisingly narrow PDIs. Given the relatively low yields for these reactions, we initially attributed this result to an unknown artifact possibly associated with TEA concentration, or fractionation of our polymer during precipitation. Reactions 9–12 were run to investigate how increasing the molar concentration of TEA and slight modifications to our precipitation procedures would affect our results. Under these conditions we observed an increase in molecular weight from around 60,000 g/mol to 90,000 g/mol but did not detect a change in PDI. In addition, our polymerization precipitation yields increased from around 30% to 45%. Still suspicious of our PDI result, we selected conditions from Reaction 11 to further investigate and optimize our yields with the specific goal of increasing above 50%. Reaction 13 is the basis of the experimental procedures and analytical results presented herein. Contrasting with Reaction 11, we have reproduced our molecular weight/PDI results and increased our polymerization yield to 65%. This result eliminates the possibility of fractionation of the polymer during precipitation leading to a narrow PDI and increased our confidence that the molecular weight observations are correct.

The polymerization progresses efficiently in chloroform and we are assuming the excess base is necessary to effectively act as catalyst for the formation of the nitrilimine intermediate and trap HCl as a salt. We determined that a $[\text{TEA}]/[\text{monomer}]$ concentration of 10:1 (5:1 molar) provided the most efficient polymerization condition to form high molecular weight polymers in chloroform. It is possible that a portion of the nitrilimine intermediates complex with TEA–HCl in the non-polar chloroform, reducing the overall yield. Conversion of *N,N'*-diphenylethane(bis-hydrazoneyl chloride) to polymer did not exceed 65% for the reactions

Table 1
Summary of polymerization reaction conditions and analysis

Reaction	Solvent	[Monomer]/ [TEA]	Temp. (°C)	Time (h)	Yield (%)	M_n ($\times 10^3$)	PDI	T_g (°C)
1	CHCl ₃	1:2	22	12	17	46	1.05	68
2	CHCl ₃	1:2	22	24	20	57	1.08	69
3	CHCl ₃	1:2	22	36	22	60	1.02	—
4	CHCl ₃	1:2	22	48	30	65	1.05	—
5	CHCl ₃	1:2	22	60	30	64	1.09	—
6	CHCl ₃	1:2	70	48	33	59	1.06	—
7	CHCl ₃	1:2	90	48	33	62	1.02	70
8	CHCl ₃	1:2	110	48	20	61	1.09	—
9	CHCl ₃	1:4	90	48	30	76	1.05	72
10	CHCl ₃	1:6	90	48	35	81	1.04	—
11	CHCl ₃	1:10	90	48	45	89	1.04	82
12	CHCl ₃	1:20	90	48	40	88	1.03	—
13	CHCl ₃	1:10	90	48	65	89	1.04	82
14	None	1:10	90	48	No reaction	—	—	—
15	THF	1:10	90	48	70	16	1.12	75

run in chloroform. In an effort to investigate solvent polarity on the reaction and yield we ran a similar experiment (Reaction 15) in THF and observed the yield increased to 70% after purification, but also observed a significant decrease in molecular weight and broadening of PDI. This result suggests that solvent polarity has a significant influence on the polymerization mechanism and possibly effects important solubility considerations as the polymerization reaction progresses.

Glass-transition temperatures measured by differential scanning calorimetry for the polymers are presented in Table 1 and are approximately 70 °C–80 °C depending upon the reaction conditions and molecular weights. We observed a general trend of an increase in T_g with molecular weight for the polymers ran in chloroform. The lower molecular weight and broader PDI polymer from Reaction 15 ran in THF is

an outlier which we attribute to a morphological disparity we have not further investigated.

The polymerization reaction was further elucidated through FT-IR spectroscopy. Fig. 3A shows the FT-IR spectra for the bis-hydrazoneyl chloride monomer and contains a clear secondary amine stretch absorbing at 3307 cm^{-1} and C–Cl stretch at 785 cm^{-1} . After conversion, the secondary amine and C–Cl stretches present in the monomer completely disappeared as seen in Fig. 3B confirming the loss of the protons and chlorines from the monomer during the 1,3-dipolar cycloaddition polymerization.

As discussed, molecular weights for the 1,3-dipolar cycloaddition polymerization of *N,N'*-diphenylethane(bis-hydrazoneyl chloride) in chloroform approached $M_n = 90,000$ g/mol with surprisingly narrow PDIs of approximately 1.04–1.07 as measured by GPC. Fig. 4 shows the GPC trace of the polymerization product from Reaction 13 and plots the cumulative elution mass vs. molar mass for this example. PDI for this product was calculated to be 1.04 and M_n to be 89,000 g/mol.

Tetrazine chemistry has gained significant attention in recent years primarily associated with complexation and

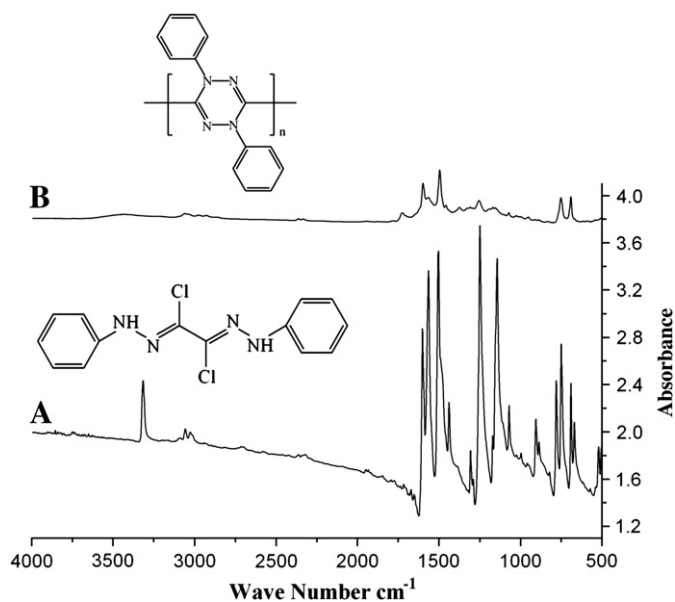


Fig. 3. FT-IR for (A) *N,N'*-diphenylethane(bis-hydrazoneyl dichloride) (4) and (B) *sym*-1,4-diphenyl-1,4-dihydro-1,2,4,5-polytetrazine (5).

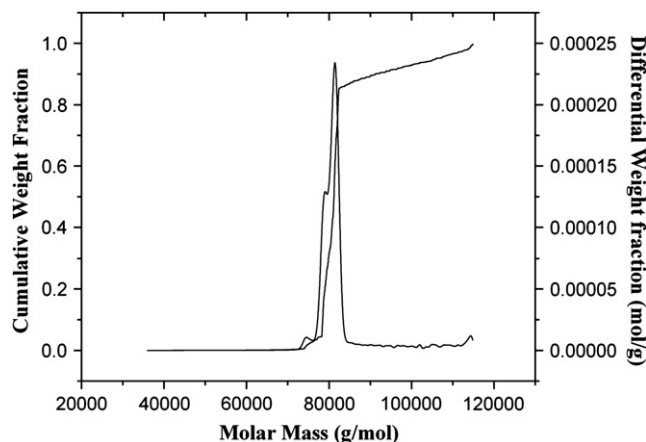


Fig. 4. GPC for *sym*-1,4-diphenyl-1,4-dihydro-1,2,4,5-polytetrazine (5).

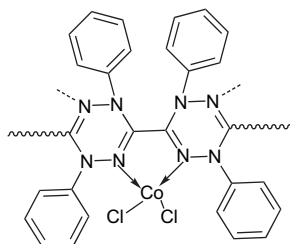


Fig. 5. Theoretical cobalt(II) chloride-substituted tetrazine complexation.

coordination chemistries. We evaluated the metal complexation capability of *sym*-1,4-diphenyl-1,4-dihydro-1,2,4,5-polytetrazine through a series of solution reactions with cobalt chloride to form metal complexes with tetrazine moieties of the polymer. In these studies, we dissolved the tetrazine polymers in chloroform and added dropwise a concentrated cobalt chloride/methanol solution under rapid stirring at 75 °C. We observed a distinct color shift from light brown to a deep green upon complexation of the polymer with cobalt to give the metal complexed polymer depicted in Fig. 5. The specific coordination shown in this schematic is only representative of what one might expect as presented in prior publications [5]. We are currently conducting a more extensive evaluation of the complexation behavior for tetrazine based polymers which will be the subject of a future publication.

This initial result is presented to demonstrate the strong complexation capability these polymers have towards metal salts. It is useful to analyze the polymer–metal complexes using TGA to gain insights into complexation potentials for the materials. It is important to wash the complexed polymers with deionized water to separate non-complexed salts prior to TGA analysis. A typical result from our TGA complexation studies is shown in Fig. 6 for complexed and non-complexed polytetrazines. We observed a shift in the 95% mass retention from 210 °C to 270 °C and 50% mass retention from 310 °C to 450 °C upon complexation with cobalt. These differences are attributed to the cobalt content complexed within the polymer sample. The total weight percent of cobalt in the complexed polymer was calculated at approximately 37.5% by comparing

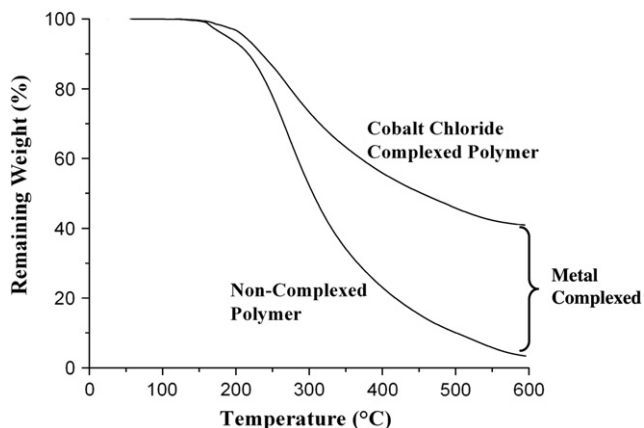


Fig. 6. TGA for non-complexed and cobalt chloride complexed polytetrazines.

the remaining weight values at 600 °C for the complexed vs. non-complexed TGA results.

4. Conclusions

Tetrazines have become important molecules over the last decade when considering stimuli-responsive environments such as molecular recognition, anion binders and metal complexations, but very little work has been reported for tetrazines incorporated into the backbone of high molecular weight polymers. The development of soluble polymers which contain tetrazine moieties within the backbone has far-reaching potential when considering applications including molecular filtration and purification devices, catalysis and other recognition technologies. Tetrazines have an additional benefits associated with their very high electron affinities and charge transfer capabilities allowing potential applications that benefit from high levels of conjugation and charge transfer, such as photovoltaic devices. Our initial studies for tetrazine containing polymers developed 1,3-dipolar cycloaddition polymerization reactions to synthesize polytetrazine materials in high molecular weights and narrow molecular weight distributions. The synthetic techniques described in this work will be useful to synthesize a variety of substituted tetrazine polymers for investigation within future research, and for the synthesis of additional polymers that can be derived through 1,3-dipolar cycloaddition polymerization reactions in the absence of dipolarophile.

Acknowledgement

This work was supported by the MRSEC Program of the National Science Foundation under Award Number DMR 0213883.

References

- [1] Guo WR, Wei XH. *Bioorganic and Medicinal Chemistry Letters* 2006;16(14):3702.
- [2] Hsu CJ, Tang SW, Wang JS, Wang WJ. *Molecular Crystals and Liquid Crystals* 2006;456:201.
- [3] Kim Y, Kim E, Clavier G, Audebert P. *Chemical Communications* 2006;34:3612.
- [4] Talawar MB, Sivabalan R, Senthilkumar N, Prabhu G, Asthana SN. *Journal of Hazardous Materials* 2004;113(1–3):11.
- [5] Kaim W. *Coordination Chemistry Reviews* 2002;230(1–2):127.
- [6] Gong YH, Audebert P, Tang J, Miomandre F, Clavier G, Badre S, et al. *Journal of Electroanalytical Chemistry* 2006;592:147.
- [7] Maekawa M, Konaka H, Minematsu T, Sowa T, Suenaga Y, Munakata M. *Inorganica Chimica Acta* 2005;358:1317.
- [8] Garau C, Quinero D, Frontera A, Costa A, Ballester P, Deya P. *Chemical Physics Letters* 2003;370:7.
- [9] Frantz S, Kaim W, Fiedler J, Duboc C. *Inorganica Chimica Acta* 2004;357(12):3657.
- [10] Sauer J, Sustmann R. *Angewandte Chemie* 1980;92:773.
- [11] Saracoglu N. Recent advances and applications in 1,2,4,5-tetrazine chemistry. *Tetrahedron* 2007;63(20):4199.
- [12] Topp K, Grote M. *Reactive and Functional Polymers* 1996;31:117.

- [13] Erxleben A. *Coordination Chemistry Reviews* 2003;246:203.
- [14] Audebert P, Sadki S, Miomandre F, Clavier G. *Electrochemistry Communications* 2004;6:144.
- [15] Stille JK, Harris FW. *Journal of Polymer Science, Part A: Polymer Chemistry* 1968;6(8):2317.
- [16] Sagot E, Le Roux A, Soulivet C, Pasquinet E, Poullain D, Girard E, et al. *Tetrahedron* 2007;63:11189.
- [17] Bulow C. *Berichte der deutschen chemischen Gesellschaft* 1902;35:3684.
- [18] Grundmann C, Datta SK, Sprecher RF. *Liebigs Annalen der Chemie* 1971;744:88.
- [19] Shawali AS, Abdelkhalak AA, Sayed AR. *Journal of the Chinese Chemical Society [Taipei, Taiwan]* 2001;48(4):693–9.
- [20] Shawali AS, Elwan NM, Awad AM. *Journal of Chemical Research, Synopses* 1997;8:268–9.