

Synthesis of High Metal-Complexation Linear Elastomers Containing *Sym*-1,2,4,5-tetrazine Rings

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ABSTRACT: We report the synthesis of polyurethane-urea elastomers containing 1,2,4,5-tetrazine covalently reacted within the main chains of the polymers. Our study investigates the synthesis of 3,6-diamino-1,2,4,5-tetrazine (DAT), the polymerization reaction conditions for reacting DAT into the backbone of segmented polyurethane elastomers, and the metal-complexation capabilities of tetrazine-containing elastomers with cobalt (II) chloride. Tetrazines are highly colored and electro-active heterocyclic moieties, which have a very high electron affinity which make them reducible at high to very high potentials. Upon complexa-

tion with metals, we observed a strong color shift of the polymers from deep red to blue indicating the binding efficacy for the polymers. We quantified the metal-complexation capability of the tetrazine elastomers and determined a molar ratio of approximately two metal atoms per tetrazine allowing us to provide a plausible complexation mechanism for the active polymers. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 114: 3915–3922, 2009

Key words: metal complex; tetrazine; polyurethane; stimuli-response; charge transfer

INTRODUCTION

1,2,4,5-Tetrazines are a distinct class of compounds that have been investigated in numerous research applications including antitumor activity,¹ molecular self-assembly,² fluorescence,³ energetics,⁴ and conductive materials.⁵ Tetrazines are chemically unique since they constitute the most electron deficient aromatic family of organic compounds, providing abnormally high electron affinity and charge transfer potential as conjugated molecules. As a result, tetrazines are highly colored and can be selectively quenched by electron rich species.⁶ As a result, tetrazines have been used for the molecular recognition of environmental contaminants,⁷ anion binders,⁸ and metal complexation.⁹

Surprisingly little research has been reported for tetrazine-containing polymers, yet tetrazine molecular characteristics are relevant for a multitude of contemporary polymer research considerations including stimuli-response, binding, charge transfer, and recognition materials. Reports of polymer research include

tetrazine functionalized polystyrene-*co*-DVB copolymer¹⁰ and self-assembled metal-lattice coordination polymers.¹¹ The first example of an electro-active polymer containing a tetrazine moiety in the backbone of the polymer was reported by Audebert et al. in 2004.¹² We have recently reported the synthesis and metal-complexation capability of *sym*-1,4-diphenyl-1,4-dihydro-1,2,4,5-polytetrazine through 1,3-dipolar cycloaddition polymerization reactions.¹³ These high molecular weight polytetrazines were soluble and demonstrated excellent metal-complexation behavior, but the mechanical properties and film forming capabilities for this polymer was poor due to the highly aromatic and rigid polytetrazine backbone.

Our current tetrazine research demonstrates a synthetic approach for incorporating controlled stoichiometric equivalents of 1,2,4,5-tetrazine directly into the backbone of linear polymers to realize the complexation and selectivity properties inherent for tetrazine derivatives within useful polymeric thin films and membranes. Herein, we report the synthesis, analysis and metal-complexation capability for a tough elastomer that incorporates 1,2,4,5-tetrazine directly into the backbone of the linear polymer and maintains favorable electronic capabilities of the tetrazine. These polymers have excellent membrane properties, are highly colored and display a strong color shift after binding with metals demonstrating for the first time the possibility to preserve the

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desirable attributes of covalently bound tetrazine derivatives within useful polymeric membranes.

EXPERIMENTAL

Materials

The following reagent were used as received without further purification: 1,3-diaminoguanidine monohydrochloride (98%), 2,4-pentanedione (99+%), 2-propanol, methanol, sodium perborate tetrahydrate, tetrahydrofuran, anhydrous *N,N*-dimethylformamide (DMF), anhydrous chloroform, 1,4-butanediol (BD), dibutyltin dilaurate (DBTDL), chloroform-*d*₆ (99.8 atom% D contains 0.03% TMS), (methyl sulfoxide)-*d*₆ (99.5+ atom% D contains 1% TMS) and cobalt (II) chloride (all Sigma-aldrich). poly(butylene adipate) (BA, Bayer Desmophen[®] 2502) were used as received. Dicyclohexylmethane di-isocyanate (H₁₂MDI, Bayer Desmodur[®] W).

Analysis

Gel Permeation Chromatography (GPC) molecular weights and molecular weight distributions (or polydispersity, PDI) of polymers were determined using a GPC system consisting of Waters Alliance 2695 Separations Module, an online multiangle laser light scattering (MALLS) Detector (MiniDAWNTM, Wyatt Technology) fitted with a Gallium arsenide laser (20 mW) operating at 690 nm, and an interferometric refractometer (Optilab DSPTM, Wyatt Technology) 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. Freshly distilled THF served as the mobile phase and was delivered at a flow rate of 1.0 mL/min. Sample concentrations were 7 mg/mL in freshly distilled THF, and the injection volume was 100 mL. The detector signals were simultaneously recorded using ASTRA software (Wyatt Technology). PIB samples (recovered from aliquots removed before addition of styrene) were analyzed using a known dn/dc value of 0.103 mL/g. PIBPS blocks and final PtBA-PIB-PS terpolymers were analyzed using a dn/dc calculated from the refractive index detector response and assuming 100% mass recovery from the columns.

Nuclear Magnetic Resonance 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 5–7% (w/v) in chloroform-*d* and (methyl sulfoxide)-*d*₆ (Aldrich Chemical Co.) containing tetramethylsilane as an internal reference.

Differential Scanning Calorimetry (DSC) was used to determine the glass-transition temperatures (T_g). Measurements were performed on ~ 10 mg samples

using a TA Instruments DSC Q100. Samples were quenched to –60°C, ramped at 10°C/min to 250°C, cooled 10°C/min to –60°C, and reheated at 10°C/min to 250°C. The reported T_g values represent the mid-point temperature for the glass-transition of the second heating cycle.

Thermogravimetric Analysis (TGA) was performed using a Thermal Analysis Q500 instrument Thermo gravimetric Analyzer with nitrogen as purging gas. Tests were conducted from 25 to 600°C at a heating rate of 10°C/min.

Mechanical properties stress vs. strain measurements were conducted using a Material Testing System (MTS) 810 test-frame with alliance RT/10 and analyzed using an MTS Testworks 4.0 software package. Test specimens were clamped using Al 2000N pneumatic grips set at 40 psi, and the tests were conducted using a 2250 lbf load cell operating at 10% range. The strain rate for the experiments was 10 mm/min.

Synthesis of 3,6-diamino-1,2,4,5-tetrazine (4)

3,6-Diamino-1,2,4,5-tetrazine (4) (DAT) was synthesized from a procedure described by Coburn and Ott.¹⁴ To a 2000 mL round-bottom flask equipped with mechanical stirring was charged 128.0 g 1,3-diaminoguanidine monohydrochloride (1) (1.0 mol), 1000 mL of 2-propanol and 100.0 g 2,4-pentanedione (2) (1.0 mol) and allowed to stir for 20 h at ambient temperature to form a yellow sticky semisolid. The mixture was then heated at reflux for 8 h during which time the semisolid completely solubilized and then precipitated as a pale-yellow solid crystal from the solution. This crude crystalline solid, 3,6-diamino-1,2-dihydro-1,2,4,5-tetrazine monohydrochloride (3), was collected by filtration, washed with 2-propanol at ambient temperature, and then refluxed again in 500 mL 2-propanol when 400 mL of water was added slowly to the boiling mixture to form clear solution. Once fully clarified, the hot solution was allowed to cool to room temperature and then placed in a refrigerator) (4°C) to give pure 3,6-diamino-1,2-dihydro-1,2,4,5-tetrazine monohydrochloride (3) (34.8 g, 46%) as glistening pale-yellow crystal plates, the solid product was dried *in vacuo* (5h at 80°C). ¹H-NMR in DMSO-*d*₆ (δ , ppm): 6.77 (s, 2H, NH₂) and 9.19 (s, 2H, NH). ¹³C-NMR in DMSO-*d*₆ (δ , ppm): 155.04. mp 194–195°C.

The final conversion was as follows: To a 2000-mL round-bottomed flask with magnetic stirring was charged 30.1 g 3,6-diamino-1,2-dihydro-1,2,4,5-tetrazine monohydrochloride (3) (0.20 mol), 1000 mL deionized water and 32.3 g sodium perborate tetrahydrate (0.21 mol) at ambient temperature. As the sodium perborate dissolved, the solution turned dark red as deep-red crystals precipitated. The

mixture was allowed to stir at ambient temperature for 2 h then cooled at 4°C overnight. The final product was collected by filtration, washed with ice water, and dried in an oven (24h @ 130°C) to give DAT (4). ¹H-NMR in DMSO-d₆ (δ, ppm): 6.69(s, 2H, NH₂). ¹³C-NMR in DMSO-d₆ (δ, ppm): 162.13 (22.4 g, 100%). mp > 350°C.

Synthesis of linear segmented polyurethane elastomers

A typical segmented urethane (TPU) elastomer formulation is as follows. To a dry 250 mL beaker was charged 10.0 g of 2000 g/mol poly (butylene adipate) (5.0 mmol) and 100 mL of dry DMF. This solution was stirred using a magnetic stirrer for 30 min at ambient temperature to allow complete dissolution. To a dry 250 mL round-bottom flask was charged 100 mL dry DMF, 4.949 g H₁₂MDI (18.87 mmol), 1.200 g 1,4-butanediol (13.32 mmol) and 0.043 g DBTDL (0.06803 mmol). The flask was then submerged into a 50°C oil bath and magnetic stirring. After 15 min the polyol solution was added and the reaction was held at 50°C for ~ 24 h when the reaction was stopped, and the DMF was removed by rotary evaporation. The resulting TPU elastomer polymer was dissolved in a minimum amount of chloroform and poured into a 300 mL PTFE dish. The dish was then placed in a room temperature vacuum oven, and the solvent was removed over a 48 h period to provide well-formed film samples ~ 1mm in thickness. TPU films were used for control experimentation and analysis. Miniature dog-bones samples for mechanical testing were cut using a stamping tool. ¹³C-NMR in CDCl₃ (δ, ppm): 26.13, 28.22, 30.09, 31.96, 34.57, 36.43, 49.88, 52.89, 64.84, 66.34, 158.89, 159.76, and 175.19

Synthesis of linear segmented polyurethane-urea elastomers containing *sym*-1,2,4,5-tetrazine (10)

A typical segmented polyurethane-urea (TPU-U) elastomer (tetrazine) formulation was as follows. To a dry 250 mL beaker was charged 10.00 g of 2000 g/mol poly (butylene adipate) (9) (5.0 mmol) and 100 mL of dry DMF. This solution was stirred using a magnetic stirrer for 30 min at ambient temperature to allow complete dissolution. To a dry 250 mL round-bottom flask was charged 100 mL dry DMF, 0.1490 g 3,6-diamino-1,2,4,5-tetrazine (4) (1.33 mmol), 4.949 g H₁₂MDI (5) (18.87 mmol), and 0.043 g DBTDL (0.068 mmol). The solution was heated for 25 min at 65°C when the temperature was reduced to 50°C. Then 1.080 g of 1,4-butanediol (BD) (7) (11.98 mmol) was charged into the solution and allowed to react. After 15 min, the polyol solution was added, and the reaction was held at 50°C for ~ 24 h when the

reaction was stopped, and the DMF was removed by rotary evaporation. The resulting TPU-U elastomer (10) was dissolved in a minimum amount of chloroform and poured into a 300 mL PTFE dish. The dish was then placed in a room temperature vacuum oven, and the solvent was removed over a 48 h period to provide well-formed deep-red film samples ~ 1mm in thickness. TPU-U films were analyzed for mechanical, thermal and metal-complexation capabilities. ¹³C-NMR in CDCl₃ (δ, ppm): 23.41, 25.04, 27.53, 29.58, 31.62, 33.27, 46.83, 49.71, 62.02, 64.07, 155.29, 156.10, 162.27, and 172.99.

Metal-complexation reactions of TPU-U with cobalt (II) chloride

A typical metal-complexation procedure was as follows: 1.0 g TPU-DAT was fully dissolved in ~ 40 mL of dry chloroform at 60°C. A cobalt(II) chloride solution containing approximately 10× cobalt(II) chloride (based on molar ratio of calculated tetrazine content in given TPU formulation) was dissolved in 15 mL of methanol and slowly added drop-wise over a period of ~ 30 min to the stirred TPU-DAT solution. The polymer-metal mixture was observed to shift color from deep red to blue-green while the cobalt salt was added over this period. We allowed the solution to continue stirring at 60°C for an additional 24 h but generally did not observe an appreciable color change beyond the first hour of reaction. The mixture was cooled to room temperature when 300 mL of deionized water was added under rapid stirring for 1 h to remove noncomplexed cobalt(II) chloride salt from the solution. The organic-layer was separated from the water, and the washing procedure was repeated two additional times. After the final separation the organic phase was poured into a 100 mL PTFE dish and placed into a room temperature vacuum oven, and the solvent was gradually removed over a 48 h period to provide well-formed light-blue film samples ~ 1 mm in thickness. The metal-complexed films were analyzed for thermal and complexation studies. ¹³C-NMR in CDCl₃ (δ, ppm): 27.11, 28.08, 30.09, 31.95, 34.58, 37.18, 49.52, 52.88, 66.71, 80.16, 158.31, 159.88, and 176.19.

RESULTS AND DISCUSSION

We synthesized a series linear polyurethane-ureas (TPU-U) containing varying levels of *sym*-3,6-diamino-1,2,4,5-tetrazine (DAT) rings by replacing stoichiometric equivalents of BD chain extender with DAT to incorporate the electron active tetrazine moieties into tough linear polyurethane membranes. Figure 1 depicts the chemical schematic for the synthesis of DAT. In this procedure, 1,3-

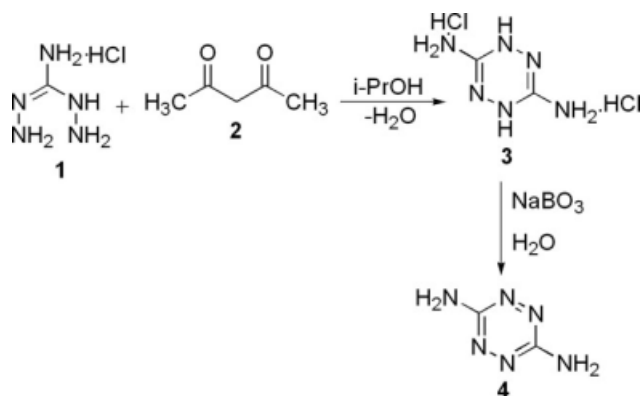


Figure 1 Synthesis of 3,6-diamino-1,2,4,5-tetrazine (DAT).

diaminoguanidine monohydrochloride (1) was reacted with 2,4-pentanedione (2) to form the crystalline intermediate 3,6-diamino-1,2-dihydro-1,2,4,5-tetrazine monohydrochloride (3). This intermediate was subsequently reacted with sodium perborate tetrahydrate. As the sodium perborate dissolved we observed the solution progressively turning dark red as the highly conjugated substituted tetrazine crystals precipitated. Pure *sym*-3,6-diamino-1,2,4,5-tetrazine was collected by vacuum filtration and reacted without further purification or modification before reaction within the TPU-U formulations.

Optimization for the reaction conditions of DAT with H_{12} MDI was necessary to form elastomers with high physical properties since the kinetics for this reaction were observed to be very slow as compared with typical aromatic amine isocyanate reactions. We associate the reduced reaction kinetics of DAT with isocyanate to the very low LUMO (lowest unoccupied molecular orbital) for this aromatic compound leading to a strong electron withdrawing effect and a significant reduction in the amine nucleophilic reactivity. We determined a one-pot and three-step synthetic approach was most effective for synthesizing high molecular weight linear elastomers with high physical properties. This approach was most effective for successfully reacting DAT with isocyanate and subsequent reactions for incorporating the tetrazine moiety into the backbone of the TPU-U elastomers. Figure 2 depicts the prereaction of DAT (4) with a stoichiometric excess of H_{12} MDI (5) to form DAT-urea di-isocyanate (6). The prereaction of DAT with di-isocyanate required more aggressive conditions than normally required for aromatic amine and isocyanate reactions, but still reasonably mild and optimized to prevent isocyanate side reactions. The prereaction allowed the kinetically slower reaction to progress with sufficient time and temperature providing complete conversion of DAT to the DAT-urea di-isocyanate in the absence of competing hydroxyl moieties from BD and polyol. Reaction conditions of 65°C for 25 min

in DMF and 300 ppm tin, followed by a reduction of temperature to 50°C, worked efficiently for incorporating the DAT into the H_{12} MDI substituted tetrazine-urea di-isocyanate (6).

The second step in the synthesis of the TPU-U elastomer shown in Figure 3 involves the addition of BD chain extender (7) into the solution to drive the formation of the urethane-urea “hard-block” component for the elastomer (8) and to stabilize the solubility of the urea within the reaction solution. The DAT ratio varied between 0 and 30% (100–70% BD) stoichiometric equivalent of DAT : BD chain extender to assess the effect of DAT concentration on metal-complexation capabilities for the polymers. A noteworthy observation during this step is careful control of the time-temperature relation of the hard-block reaction. As seen in Figure 3, the urethane-urea hard-block (8) is beginning to build molecular weight, and if too high of molecular weight is achieved, the hard-block will precipitate from the solution. It is important to carefully monitor reaction conditions and sequence additions to maintain solubility throughout the polymerization to achieve high molecular weight and optimized physical properties of the elastomers. Formulations above 30% DAT chain-extender content were difficult to control during the polymerization process due to a rapid precipitation of the hard-block attributed to insolubility of urea within the polymerization medium.

The third and final step of the polymerization reaction, shown in Figure 4 was the addition of the polybutylene adipate diol “soft-block” segment (9) to complete the formation of the segmented linear polyurethane elastomer. We maintained a constant molar ratio of “chain extender to polyol” for all formulations reported in this study, with the chain-extender hard-block segments being comprised of varying molar amounts of DAT and BD. It is important to note that varying molar amounts of DAT were specifically reacted into the hard-block

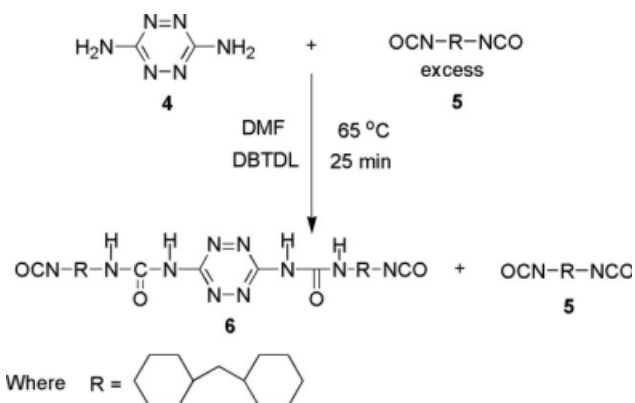


Figure 2 Polymerization step 1: reaction of DAT with H_{12} MDI.

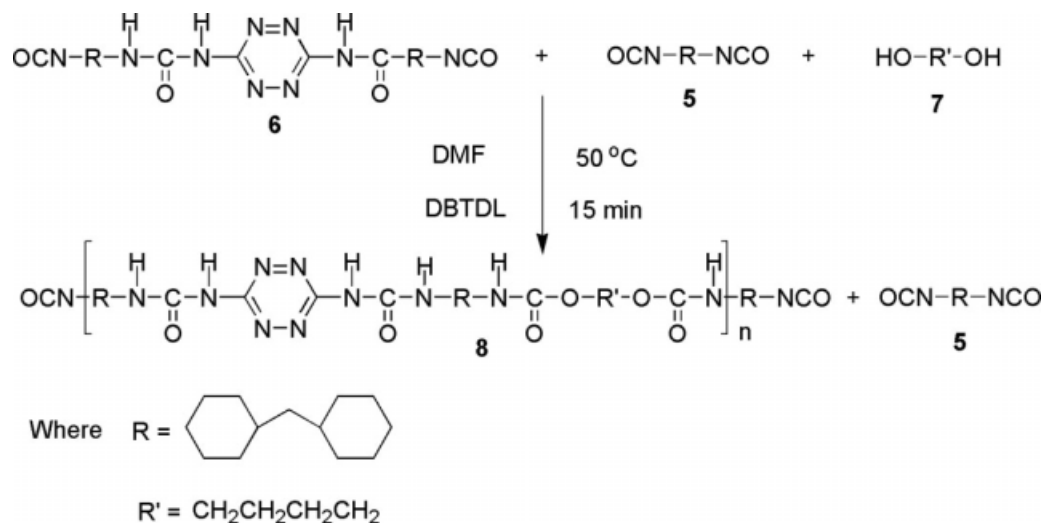


Figure 3 Polymerization step 2: polyurethane hard-block synthesis.

segments of the elastomers. Tracking the deep-red color of the tetrazine moiety incorporated within the polymers was a convenient method for optimizing polymerization procedures to assure the complete reaction of DAT, enhance mechanical properties and minimize urethane side reactions within the polymeric elastomers. In addition, we were able to confirm DAT reaction through selective solvation using chloroform since it is completely insoluble and in this solvent.

Molecular weight and molecular weight distribution analyses for the TPU-U as measured by GPC indicated well-reacted and distributed linear materials. M_n for these polymers were typically between 3.5 and 4.0×10^3 g/mol with a PDI of around 1.3, which is typical of the GPC results for solution

synthesized H_{12} MDI-based TPU elastomers we synthesize in our laboratories. Figure 5 displays a GPC chromatogram for a linear TPU which was formulated with 10 : 90 DAT to BD chain-extender ratio. The smooth chromatogram suggests a well-reacted polymer and complete incorporation of all monomers within the polymer backbone.

The TPU-U polymerization reactions were further characterized by ^1H - and ^{13}C -NMR to assure proper incorporation of the DAT moieties into the backbones of the TPU-U elastomers. We observed spectral evidence by comparison of ^{13}C -NMR spectra for control TPU elastomers and TPU-U formulations that contained varying levels of DAT within the chain extender. A characteristic resonance shift of 161.4 ppm for carbons of the tetrazine rings were

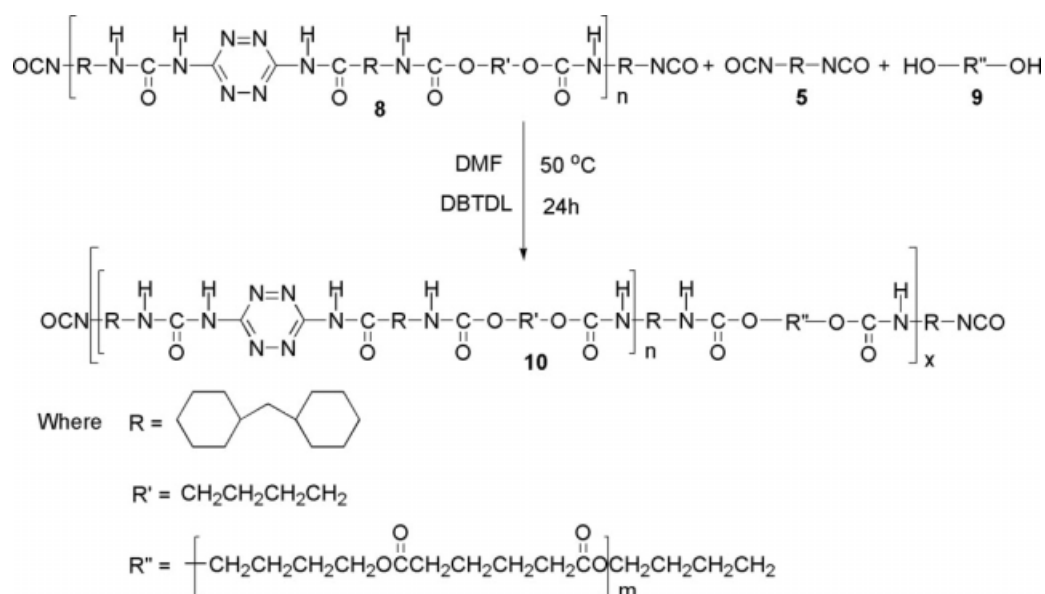


Figure 4 Polymerization step 3: linear segmented elastomer containing 1,2,4,5-tetrazine.

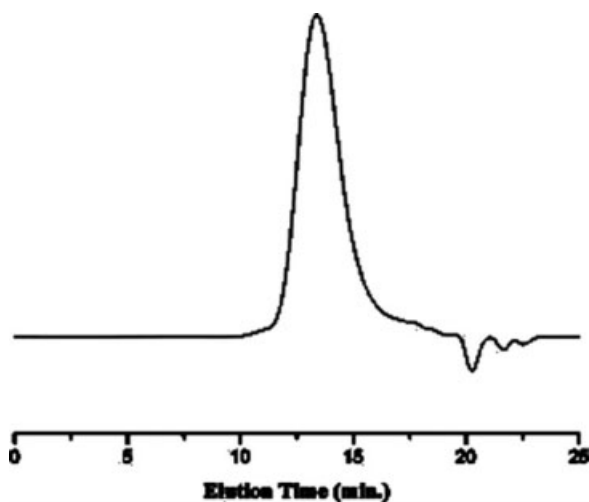


Figure 5 GPC chromatogram of tetrazine based elastomer.

present in the TPU-U spectra indicating the rings were incorporated into the backbone of the polymers.

After confirming the DAT was fully reacted into the backbone of the TPU-U polymers, we proceeded to evaluate metal-complexation capabilities of the polymers and determined the binding efficacy of tetrazine-metal complexes with TPU-U elastomers. Initial metal-complexation studies with the tetrazine indicate these materials have strong complexation capabilities and are active complexation agents for metal ions. We reacted TPU-U with cobalt (II) chloride by dissolving the polymer in chloroform followed by the drop-wise addition of concentrated cobalt (II) chloride/methanol solution with vigorous stirring. Upon reaction, we observed a significant color shift from the characteristic deep-red color attributed to the highly conjugated tetrazine within the TPU-U polymers to blue-green color after complexing with cobalt. This color shift is a strong indicator of deconjugation associated with metal complexation of the tetrazine with the cobalt (II) metal salt. Figure 6 shows a photograph of the 10% chain-extender tetrazine TPU-U film (Fig. 6-1), the 30% chain-extender tetrazine TPU-U film (Fig. 6-2), and the 10% chain-extender TPU-U film after complexation with cobalt (II) chloride (Fig. 6-3). This result is significant and demonstrates the strong color shift from red to blue-green upon metal complexation, which confirms tetrazine moieties incorporated into the backbone of TPU-U maintain a conjugated electronic characteristic in the polymer, and have strong binding capability with metals. By washing the bound polymer-metal complexes with a chloroform–water solution, we were able to extract any noncomplexed cobalt (II) chloride from the mixture and assure all metal was fully-bound to

polymer. For example, by using a large excess of cobalt (II) chloride in our complexation studies we were able to extract the solution and isolate residual nonbound cobalt (II) chloride providing us a convenient method to analyze the complexation capability of the 1,2,4,5-tetrazine in a polymer backbone and provide mechanistic insights to the tetrazine-metal complexation.

We further explored metal-complexation capabilities of TPU-U by varying the DAT : BD chain-extender ratio between 10 and 30% DAT and evaluated metal-complexation levels using TGA. As expected, increasing the tetrazine content in the polymer backbone led to an increase in the total cobalt (II) metal complexed within the polymer. Figure 7 shows some typical TGA traces for cobalt (II) chloride metal-complexed TPU-U polymers. Non-complexed TPU-U completely pyrolyze by around 500°C. Polymer-metal complexes shown in Figure 7 display residual mass at temperatures well-beyond the 500°C condition that we attribute to cobalt metal, which was complexed within the polymer. The samples displayed in Figure 7 shows residual masses between approximately 3, 7, and 11% by weight of the starting mass for the 10% DAT, 20% DAT, and 30% DAT polymers, respectively.

By controlling molar compositions of 1,2,4,5-tetrazine in the polymer backbones during synthesis and comparing molar weight percentages of cobalt (II) chloride complexed within various polymer structures we have consistently observed approximately two metal complexes per tetrazine moiety for all formulations. Regardless of the tetrazine molar content in the starting polymer we observed ~ 200% molar equivalent of cobalt (II) chloride from our TGA experiments suggesting that each tetrazine contained within a TPU-U polymer is capable of complexing

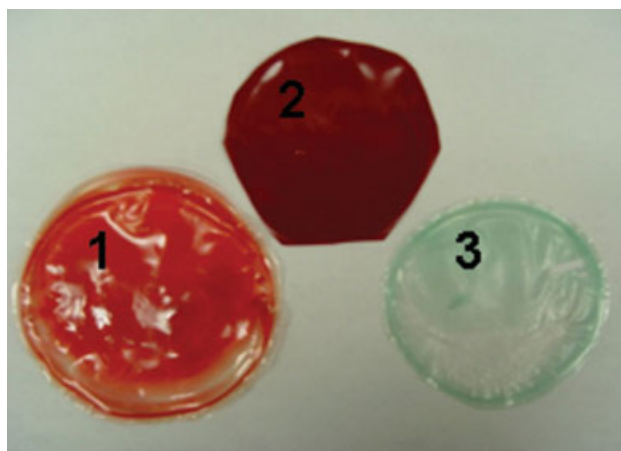


Figure 6 (1) TPU-10%DAT (2) TPU-20%DAT and (3) TPU-10%DAT/CoCl₂ complex. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

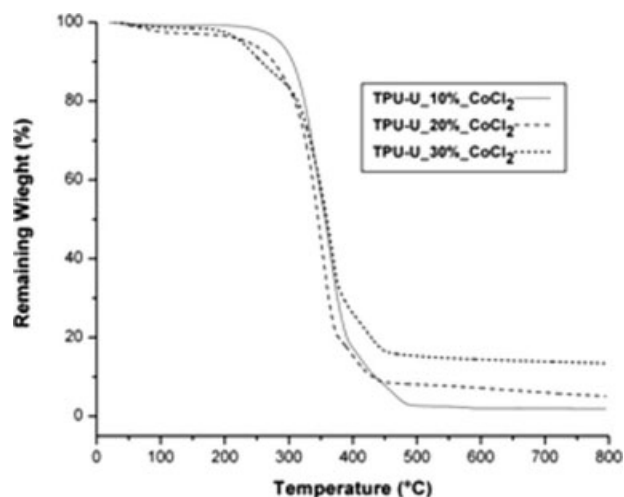


Figure 7 TGA profiles for varying levels of metal complexation.

with two cobalt (II) chloride molecules. This result is important for helping to provide insight into the potential complexation mechanism between the metal salt and polymer backbone, and allows us to derive a plausible complexation mechanism, which we propose in Figure 8. Although tentative and not fully resolved, an intramolecular mechanism as depicted is reasonable since we did not observe a change in polymer solubility as would be expected if a supermolecular interchainmetal-complexation network was formed. Specific metal-complexation mechanisms and further exploration of metal complexes is the subject of continued research in our laboratories.

Segmented linear polyurethane elastomer mechanical properties are controlled by varying the molar ratio of chain extender to polyol for a particular combination of starting materials, and through a broad combination of chemical building blocks. Figure 9 shows the stress versus strain behavior for a traditional linear segmented polyurethane (TPU) elastomer (100% BD chain extender), a 10% DAT and 90% BD chain-extender linear segmented polyurethane-urea (TPU-U_10%) elastomer, and the

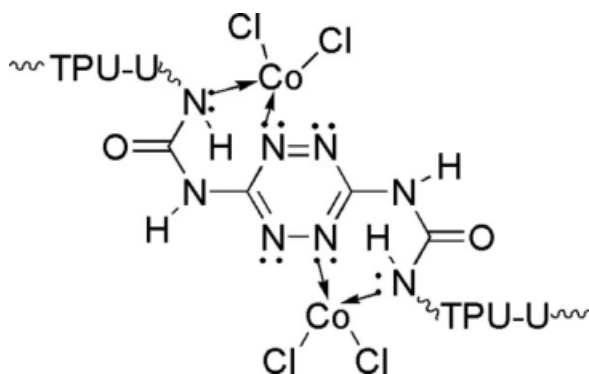


Figure 8 Proposed metal-complexation mechanism.

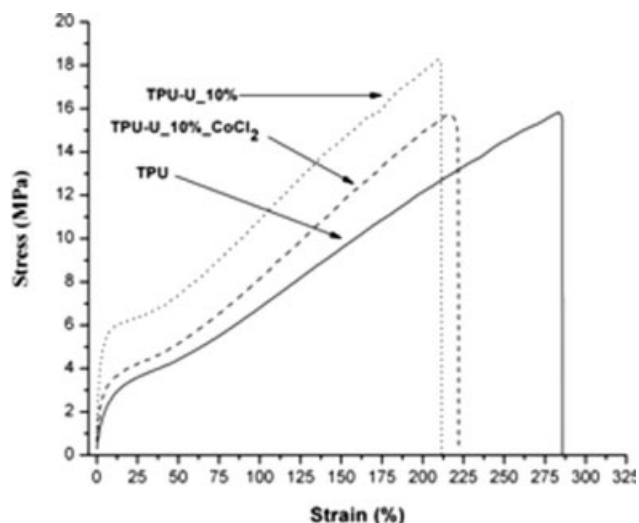


Figure 9 Stress-strain behaviors of polymers.

TPU-U_10% elastomer which has been complexed with cobalt (II) chloride (TPU-U_10%_CoCl₂). The TPU-U_10% increased from 3.2 to 5.9 MPa stress and decreased from 15.8 to 9.7% yield strain as compared with the traditional TPU elastomer. This behavior is classical polyurethane mechanical response for incorporation of urea moieties within the hard-block regions and attributed to increasing hydrogen bonding and rigidity with urea. A very interesting result is the mechanical behavior of the TPU-U_10% complexed with cobalt (II) chloride (TPU-U_10%_CoCl₂). For this elastomer, the yield stress (3.7 MPa) and yield strain (13.9%) more closely resemble the traditional TPU. This result further supports our proposed complexation mechanism and suggests the secondary amine of the urea participates in the metal complexation and reduces (or interferes with) the urea hydrogen bonding within the urethane.

CONCLUSIONS

This research demonstrates the first application for incorporating 1,2,4,5-tetrazine directly into the backbone of a linear segmented elastomer with high mechanical properties and strong metal-complexation capability. This work demonstrates a new application in polymer research and has a high potential benefit given the broad utility of tetrazine compounds cited for medical, metal complexation, charge transfer, and binding affinity. Our preliminary results have shown it is possible to synthesize stable and high molecular weight tetrazine-containing polymers. The very low lying π -orbital associated with tetrazine provides a unique opportunity to investigate polymer films and membranes toward new applications and provides a significant

opportunity for advancing polymer science within the field of stimuli-responsive materials. The importance of polytetrazine derivatives for coordination chemistry is associated multiple binding sites and diverse electronic behavior. Incorporation of the 1,2,4,5-tetrazine into polymer backbones from DAT has demonstrated a significant effect on polymer properties and provides a unique route to prepare a broad range of high-performance tetrazine-containing polymer, which can be considered for a variety of advanced polymer applications.

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