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Chemical and Physical Tailoring of Guanidine-based Covalent Adaptable Networks

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KEYWORDS

Polymers, guanidine, covalent adaptable networks

ABSTRACT

We present the synthesis of two different guanidine-based CAN materials which, unlike traditional thermoset polymer networks, can undergo an exchange reaction called thermal guanidine metathesis (TGM) and be reprocessed. Thermosets, which are polymer networks characterized by permanent covalent crosslinks between chains, have a myriad of commercial applications. However, a major drawback to thermosets is their inability to be reprocessed. To develop a more sustainable thermoset-like material, CANs exhibit breaking and reforming of crosslinks under certain conditions that enable reprocessing. To elucidate the effects of varied guanidine structure on the rheological and mechanical properties of these dissociative CANs, we synthesized two guanidine-based CANs via reaction of a carbodiimide-containing polymer with two bifunctional amines. We found that the CAN with a more sterically congested guanidine was able to relax stress more quickly than the less sterically hindered CAN, supporting the influence of steric bulkiness on the kinetic and thermodynamic properties of the TGM reaction in guanidine-based CANs.

INTRODUCTION

In general, much of the plastic materials we interact with in a food and packaging context are recyclable. These thermoplastics—which are traditional linear polymers consisting of individual chains with no inter-chain covalent bonds—remain in high usage due to their capacity for recycling and ease of synthesis. Contrastingly, polymeric networks called thermosets possess inter-chain covalent crosslinks and are used in a wide variety of applications such as epoxies, adhesives, and composites due to their durability.[1] While these traditional thermosets are widely

variable in their commercial applications, the formation of molecularly permanent crosslinks during the curing process prohibits any ability to be reprocessed.[2] Given the environmental impact of these materials, efforts in material science have been focused on the development of materials that have the equivalent potential for widespread application but that can be recycled. Covalent adaptable networks (CAN) – polymeric materials which have reversible crosslinking capabilities – are a quickly developing solution to recyclable thermoset plastics, as demonstrated by well-defined examples of materials that can be reversed via Diels-Alder and transesterification, among others.[3]

    In our research, we aimed to create a guanidine-based CAN. The guanidine functional group consists of a sp^2-hybridized carbon surrounded by three nitrogen atoms and is a common functionality in both synthetic and biological contexts.[4] We developed this novel guanidine CAN system due to characteristics of guanidines established in previous small molecule studies by Melchor-Bañales et al: the guanidine functionality, when in the presence of an primary or secondary amine at high temperatures, can undergo a dissociative exchange reaction called thermal guanidine metathesis (TGM; Figure 1).[5] This exchange reaction and its kinetic and thermodynamic properties have been found to be affected primarily by the relative steric hinderance of the three substituents of the guanidine.[6] The changes in kinetic and thermodynamic properties due to guanidine structure as well as changes with temperature enables the possibility of a N, N', N''-substituted guanidine-containing polymeric material that can be altered to have certain mechanical properties as well as the crucial ability to be reprocessed at elevated temperatures. In our project, we successfully synthesized a novel carbodiimide (CDI) monomer, CDI and styrene copolymer, and a guanidine-based CAN system that can undergo TGM exchange at higher temperatures and exhibits reprocessability. The straightforward replacement

of substituents in the guanidine provides an avenue to develop new dynamic polymeric materials

with varied mechanical and rheological properties with promising recyclability.
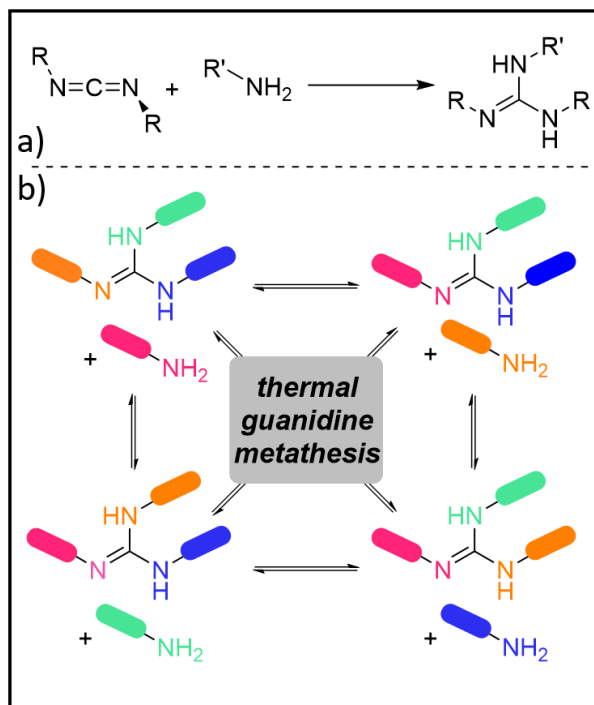

Figure 1. Representative scheme of Thermal Guanidine Metathesis. (a) the guanidine functionality is initially formed via the reaction of a carbodiimide (left) with an amine (right). (b) upon heating, amine substituents exchange via thermal guanidine metathesis.

In order to incorporate a tunable guanidine functionality into a polymeric material, we first

developed a novel CDI monomer, copolymerized it with styrene via free-radical polymerization,

then reacted it with a bifunctional amine to create a fine-tunable guanidine-based CAN. We then

tested the physical and mechanical properties of guanidine-based **CAN4** and **CAN5** via Dynamic

Mechanical Analysis (DMA) and rheology and found that the material has thermal stability when

remolding, as well as that bulkier *N*-substituents around the guanidine result in overall lower

relaxation times at all temperatures tested, consistent with previous small molecule studies
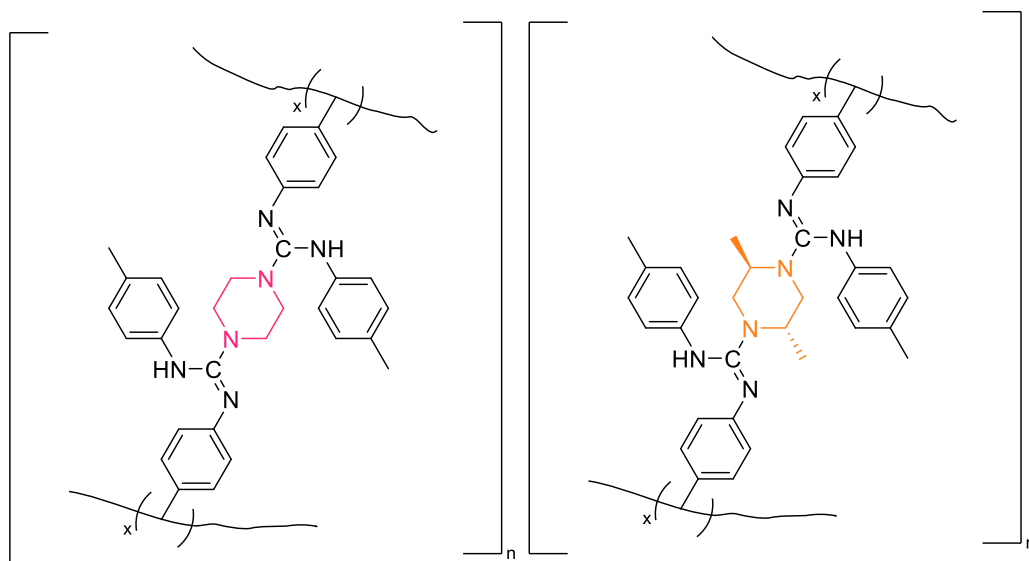
(Figure 2).

Figure 2. Guanidine-based crosslink structure of **CAN4** (left) and **CAN5** (right).

RESULTS AND DISCUSSION

To ultimately synthesize a *N,N',N''*-trisubstituted guanidine-based CAN, we first began

by synthesizing a novel thiourea **1** with aryl-aryl substitution, a para-tolyl group, and a styrenic

handle for further reactivity. **1** was prepared by the addition of p-tolyl isothiocyanate to 4-

aminostyrene in ambient conditions with yields of ~90%. **1** then subsequently underwent

thiourea dehydrosulfurization to produce an aryl-aryl substituted carbodiimide (CDI) monomer **2**

upon addition of Mukaiyama's reagent and triethylamine under N_2 with yields of ~80%.[7]
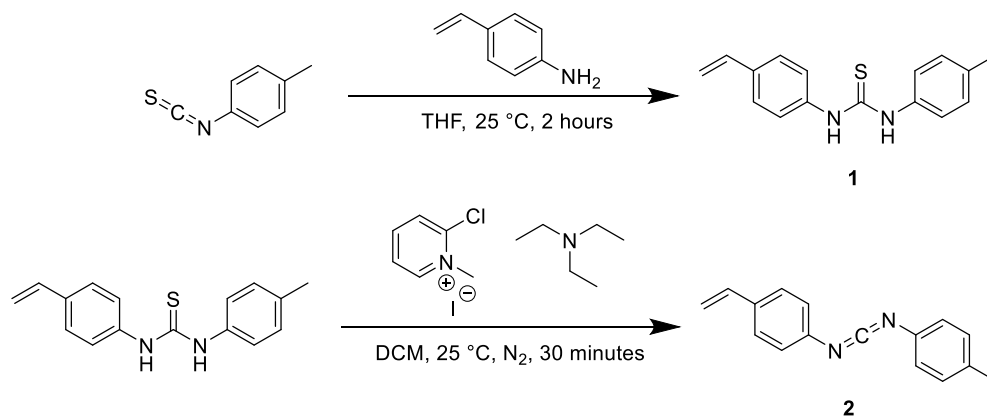
Figure 3. Synthesis of novel aryl-aryl substituted carbodiimide via thiourea dehydrosulfurization.

Utilizing the styrenic handle present on **2,** the CDI monomer was then copolymerized with styrene via free-radical polymerization in a 20:1 stoichiometric ratio to form poly(styrene-co-CDI) (**poly 3**, Figure 4).[8] Copolymerization with styrene was implemented at a 20:1 stoichiometric ratio due to side reactions in linear homopolymers with **2** that rendered the polymers insoluble. To determine the ratio of repeat units of styrene:CDI, ^{1}H NMR spectroscopy was performed and integrations of the aromatic region compared to the para-tolyl group present on the CDI subunit resulted in approximately 17:1 styrene:CDI. To determine the millimoles of carbodiimide per milligram of **poly 3**, ^{1}H NMR spectroscopy was performed with a known mass of polymer along with a known mass of internal standard (*1,3,5*-trimethoxybenzene; Figure 5). Relative millimoles of carbodiimide in each mg of polymer was determined by integration of the internal standard compared to the p-tolyl group at 2.34 ppm and was found to be $\sim 4 \times 10^{-4}$ mg CDI/mg **poly3**.
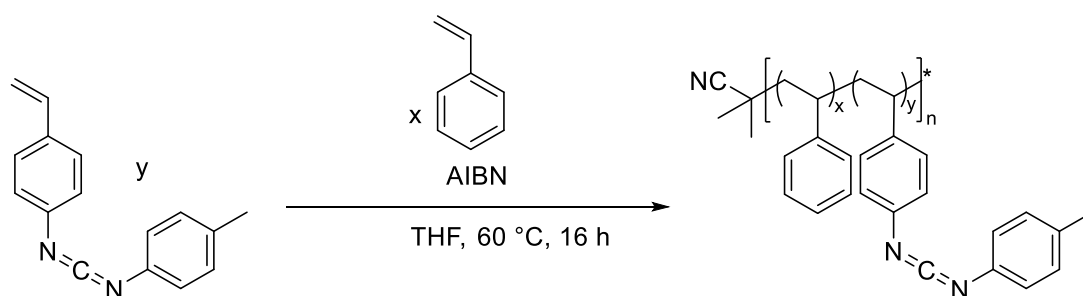

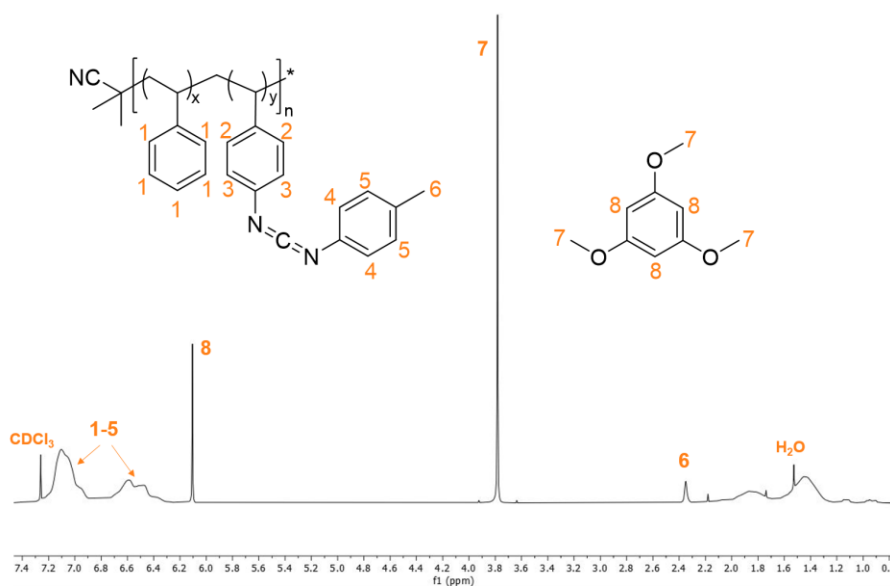**Figure 4.** preparation of poly(styrene-*co-CDI*) **poly3**.

Figure 5. ^{1}H NMR spectrum of 20:1 poly-styrene-co-CDI spiked with known amounts of *1, 3, 5*-trimethoxybenzene. For relative styrene:CDI loading, the integration of the p-tolyl peak of the CDI subunit at 2.34 ppm was compared to the 6.4-7.2 ppm aromatic region. For mmoles CDI/mg **poly3**, the integration of a *1,3,5*-trimethoxybenzene peak at 3.8 ppm was compared to the p-tolyl peak of the CDI subunit at 2.34 ppm.

In the final synthesis step to form a guanidine-based CAN, **poly 3** was reacted with a bifunctional amine, piperazine, in ambient conditions to form a guanidine-based **CAN4** that precipitated into solution. In order to compare the effects of *N,N',N''*-guanidine substitution on the mechanical and physical properties of these polymeric CAN materials, we also reacted **poly3** with trans-2,5-dimethylpiperazine to form guanidine-containing **CAN5** that also precipitated out of solution. (Figure 6). We consistently produced each material on multigram scales with yields of 90%.
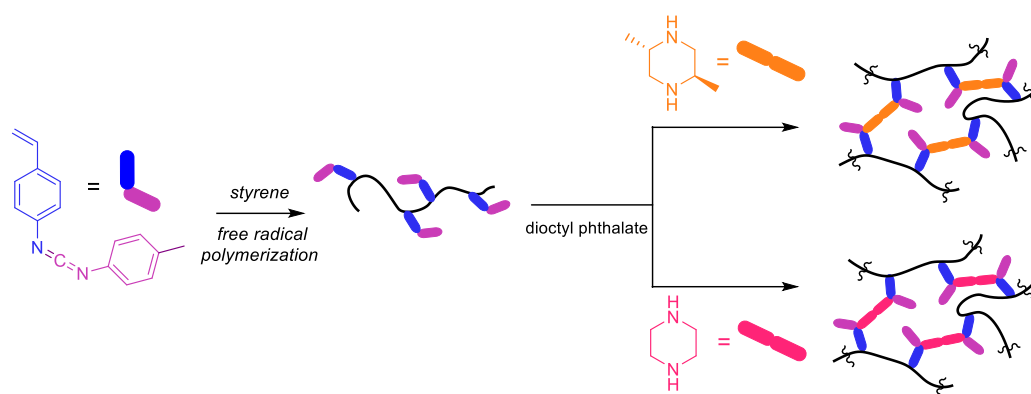
Figure 6. Synthetic scheme of formation of **CAN4** (pink) and **CAN5** (orange).

To ensure that all the carbodiimide subunits in **CAN4** and **CAN5** reacted to form a guanidine in the network, FT-IR spectroscopy confirmed the disappearance of a strong peak at a wavenumber of 2100 cm^{-1} representative of a C=N stretch (Figure 7). Although these materials were reliably forming guanidines as seen via FT-IR spectroscopy and gel fractions were ~85%, preliminary reprocessing data via Dynamic Mechanical Analysis (DMA) and compromised solubility of these materials indicated permanent crosslinking upon heating in excess at 190 °C, thus reducing the application of these adaptive thermoset-like materials. To improve the recyclability of **CAN4** and **CAN5**, we added a plasticizer dioctyl phthalate to both materials which lowered T_g and improved reprocessability.
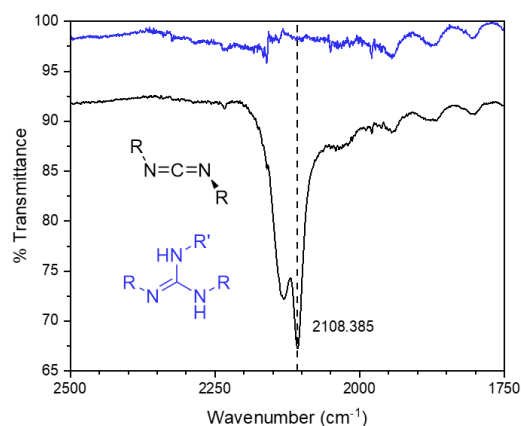
Figure 7. FT-IR spectrum of **poly3** before and after addition of bifunctional amine piperazine (**CAN4**). 16 scans, auto baselined.

Once we established improved thermal stability of the CANs, we examined the effects of guanidine substitution on chemical and physical properties by melt pressing rectangular samples of **CAN4** and **CAN5** for temperature ramps performed by DMA (Figure 8a). Melt pressing did not change the character of the CANs as indicated by FT-IR spectroscopy. Temperature ramps from 40-190 °C at 3 °C/min of **CAN4** and **CAN5** established glass transition temperatures (T_g) of 123 °C and 121 °C, respectively. Despite varied guanidine crosslink structure, comparable T_g indicates that **CAN4** and **CAN5** have similar crosslink densities and that differences in their properties can be attributed to other differences of the materials such as guanidine substituents.[9]

We then compared temperature ramps on singly-melt pressed materials to remolded samples and confirmed that the addition of plasticizer increased thermal stability of **CAN4** so that it could be remolded repeatedly and maintain similar thermal properties (Figure 8). Initial storage moduli of **CAN4** were within the range of 1500-2500 MPa consistently through all three remolds of **CAN4** and tan δ peaks were between 120-123 °C.
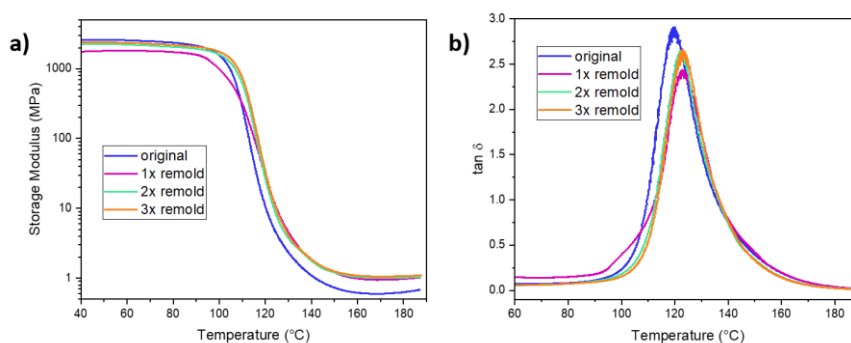

Figure 8. Reprocessing studies of **CAN4**. **(a)** DMA thermograms of *E'* vs temperature 40-190 °C after **CAN4** was reprocessed up to three times. **(b)** Tan δ versus temperature from 60-190 °C of same samples. T_g for each reprocessing was determined by temperature at which maximum tan δ was reached.

To determine the rheological properties of **CAN4** and **CAN5** and the effects of guanidine substituents on these properties, stress relaxation experiments were performed on singly-melt pressed 25 mm diameter samples on a shear rheometer. **CAN4** was tested at 5 °C isotherms from 150-175 °C at 1% strain, and relaxation modulus was measured over 20 min (Figure 9c). The initial relaxation modulus of **CAN4** increases from 150-160 °C, then decreases from 160-175 °C, indicating that there are changes in crosslink density with temperature due to increased dissociation of the guanidine, a change that is not seen in traditional thermosets. In addition, the decrease in initial storage modulus indicated that thermodynamic control—as confirmed via small molecule studies— is maintained in these systems.[5] The relaxation time τ at each temperature was derived from a stretched exponential decay function: $E' = G * e^{(-(x/\tau)^B)}$. An Arrhenius plot was constructed from these relaxation times (Figure 9d). The linear relationship between relaxation time and temperature is indicative that this material's ability to flow is likely controlled by a chemical reaction, which is generally only seen in these dynamic polymer networks .[10] The activation energy in this temperature range for **CAN4** derived from the slope of the Arrhenius plot was found to be 99 ± 2 kJ/mol.

To support that these materials are governed by the dissociation of the guanidine into its carbodiimide and amine parts, we compared this activation energy to previous small molecule kinetic studies. We found that the dissociation of *N,N'*-di-*p*-tolylpiperidine-*1*-carboximidamide (complementary to **CAN4**) has an activation energy of 64 ± 6 kJ/mol; Given the approximate 1.5 difference in activation energy between the small molecule and the polymeric **CAN4**, this difference is consistent with the Semenov-Rubenstein model for crosslinked materials which states that the activation energy of dissociative polymer networks reflect both the dissociation and the diffusion to find new binding partners in the network.[11] This relationship between the

small molecule and **CAN4** supports the function of TGM in the mechanical transition of
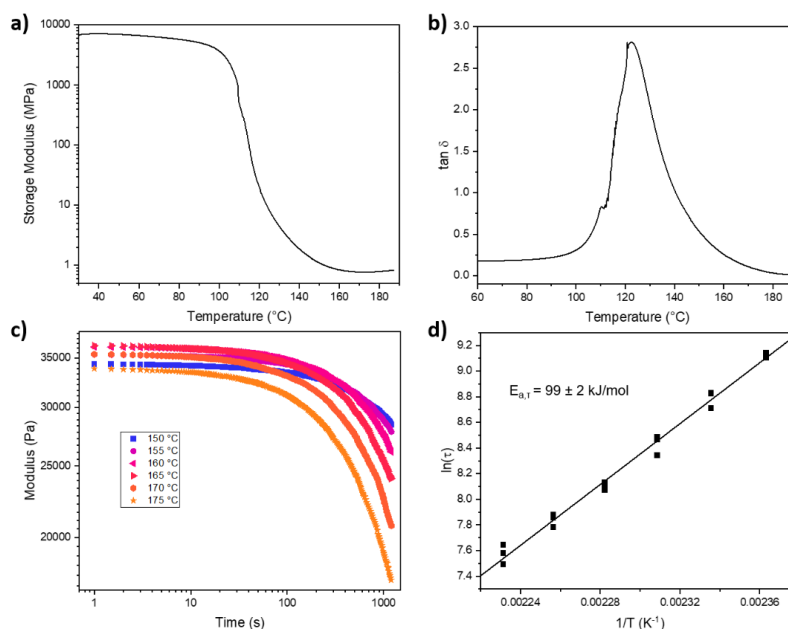
CAN4.[11].

Figure 9. Rheological analysis of **CAN4**. (a) DMA thermogram of E' versus temperature. (b) tan δ curve from same sample, T_g of 123 °C determined by temperature at which maximum tan δ is observed. (c) Representative stress relaxation experiment of G' versus time collected at 1% strain. (d) Arrhenius plot derived from stress relaxation experiments. Relaxation times were determined by fitting relaxation data to a stretched exponential function. $\ln(\tau^*)$ calculated from relaxation times for each isotherm. $E_{a,\tau} = 99 \pm 2$ kJ/mol, calculated by line of best fit ($R^2 = 0.989$).

Similarly, stress relaxation tests over the same temperature range were performed on

CAN5, which differs from **CAN4** due to the presence of two methyl groups located on the

adjacent carbons to the crosslinking substituent of the guanidine CAN (Figure 2). The initial

storage modulus of **CAN4** consistently decreased from 150-175 °C, confirming the dynamic

nature of this material and a more favorable dissociated state of the TGM reaction. The

relaxation time τ was derived identically as above, and an Arrhenius plot was constructed (Figure

10d). The linear relationship between relaxation time and temperature is indicative that this

material is also dynamic and has nearly an identical activation energy as **CAN4**. The activation

energy in this temperature range for **CAN5** derived from the slope of the Arrhenius plot was

found to be 106 ± 5 kJ/mol, slightly more than 1.5 times larger than its complementary small

molecule dissociation of 2-methyl-N,N'-di-p-tolylpiperidine-1-carboximidamide, which has an

activation energy of 56 ± 4 kJ/mol. Investigation into the slight deviation from the Semenov-

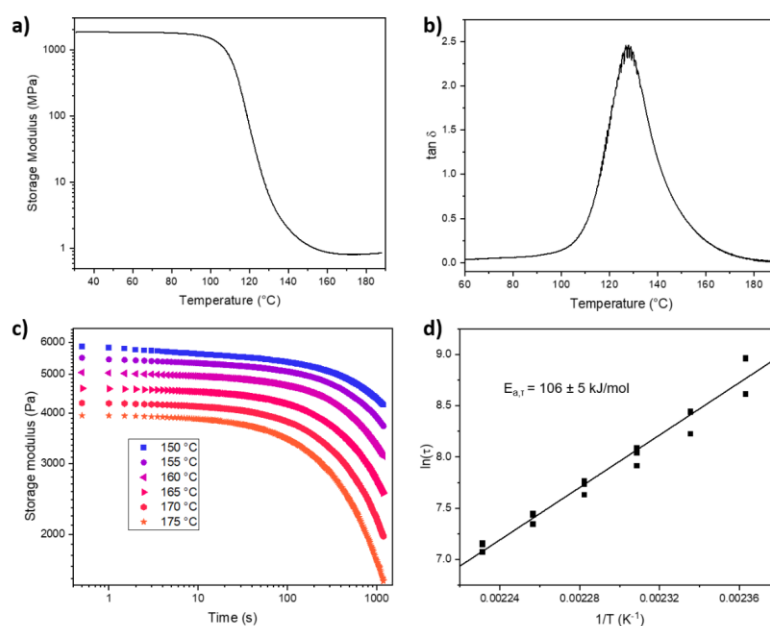Rubenstein model will be addressed in further work.

Figure 10. Rheological analysis of **CAN5**. (a) DMA thermogram of E' versus temperature. (b) Tan δ curve from the same sample. T_g of 121 °C determined by temperature at which maximum tan δ is observed. (c) Representative stress relaxation experiment, showing relaxation modulus versus time collected at 1% strain. (d) Arrhenius plot derived from stress relaxation experiments. Relaxation times were determined by fitting relaxation data to a stretched exponential function. $\ln(\tau^*)$ was calculated from relaxation times for each isotherm. $E_{a,\tau} = 106 \pm 5$ kJ/mol, calculated by line of best fit ($R^2 = 0.969$).

Additionally, despite similar activation energies seen between **CAN4** and **CAN5** (99 ± 2

and 106 ± 5 kJ/mol respectively), a notable difference between the dissociation of these materials

are the absolute relaxation times, in which **CAN5** relaxes stress ~39% faster than **CAN4** at all

temperatures. As the primary difference between **CAN4** and **CAN5** is the presence of a bulkier

N' substituent with two methyl groups, the lower relaxation times seen at all temperatures tested

confirms that these guanidine-based CANs exhibit similar changes in properties as in small

molecules undergoing TGM; guanidines with bulkier *N'* substituents favor dissociation more

than their less sterically hindered counterparts.[6]

CONCLUSION

Here we present the preparation of two guanidine-based CANs that undergo the TGM reaction at

higher temperatures and display similar kinetic and thermodynamic properties as seen in small

molecule studies. We developed these CANs via the synthesis of a novel CDI monomer that was

copolymerized with styrene at a 20:1 ratio to form a novel statistical copolymer. We found that

the kinetic and thermodynamic properties of guanidines shown in small molecules is primarily

reflected in the speed at which the material can relax stress, in which more sterically congested

guanidine crosslinks will relax faster. We hope to further investigate the effects of steric

hindrance on the mechanical and rheological properties of these CAN materials. Additionally,

in future studies we hope to investigate the effect of crosslink density on the properties of these

CANs, as these effects have not been previously studied in dissociative systems. Some previous

studies of CANs have proposed that increasing crosslink density lowers relaxation times,

whereas others have found that increased crosslink density has increased relaxation times.[12] The

answer to this question will enable further fine-tuning of these dynamic polymeric materials with

the promise of wider applications than their unrecyclable thermoset counterparts.

EXPERIMENTAL METHODS

General Information

^{1}H NMR spectra were recorded on a Bruker Avance III 500 MHz Fourier Transform NMR spectrometer. Chemical shifts are reported in parts per million (ppm) with tetramethylsilane as an internal standard (CDCl$_3$, ^{1}H: 7.26 ppm). FT-IR spectroscopy was performed with a Thermo iS10 FT-IR with single bounce diamond ATR. Gel permeation chromatography was performed with a Malvern CP3800 GC with Low Angle & Right Angle (LALS and RALS) and Refractive Index (RI) detectors using polystyrene standards (1300 Da, 3000 Da, 4000 Da, 17.5 kDa, 65 kDa, and 150 kDa). Dynamic mechanical analyses (DMA) were performed on a TA Instruments Q800 with tensile clamps. For temperature ramps, a 0.025% tensile strain was applied to samples. Each sample was heated from ambient conditions to 190 °C at a rate of 3 °C/min. All experiments were conducted at a frequency of 1 Hz and the glass transition temperature (T_g) was taken as the peak of tan δ. For stress relaxation experiments, a 1% strain was applied to samples, and the time at the third measurement was taken as t = 0. After this, a sampling interval of 2 sec was used for acquisition of data. Samples were melt pressed using a hydraulic Carver press equipped with heated plates (see below for sample preparation)

Synthesis and purification of 1-(p-tolyl)-3-(4-vinylphenyl)thiourea

4-aminostyrene (5 mL, 42.67 mmol, 1 equiv.) and *para*-tolylisothiocyanate (6.55 mL, 44.81 mmol, 1.05 equiv.) were dissolved in tetrahydrofuran (30 mL) and reacted while stirring for 2 hours in ambient conditions. To precipitate the product out of solution, 20 mL of hexanes were added to the reaction mixture then filtered. The product was placed in a glass dish and covered until solvent evaporated. The purified thiourea was produced in reliable yields of ~90% and characterized by ^{1}H NMR (Figure 11).
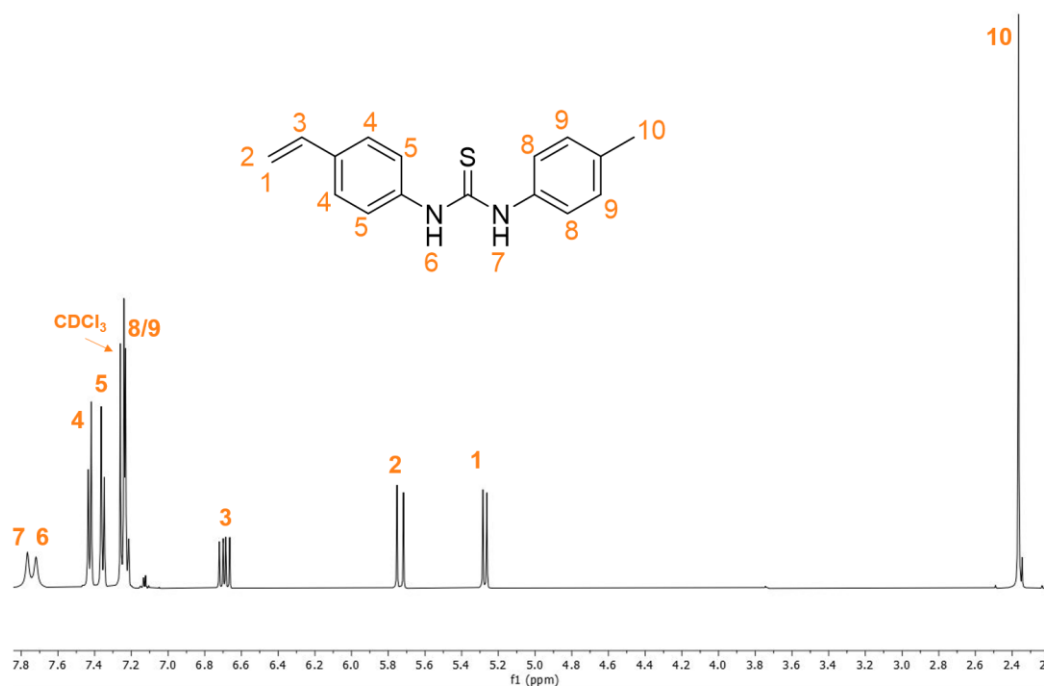
Figure 11. ^{1}H NMR spectrum of 1-(p-tolyl)-3-(4-vinylphenyl)thiourea. ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.77 (bs, 1H), 7.72 (bs, 1H), 7.45 – 7.40 (m, 2H), 7.36 (d, J = 8.6 Hz, 2H), 7.27 – 7.18 (m, 4H), 6.69 (dd, J = 17.6, 10.9 Hz, 1H), 5.73 (d, J = 17.6 Hz, 1H), 5.27 (d, J = 10.9 Hz, 1H), 2.37 (s, 3H).

Synthesis and purification of novel carbodiimide monomer via thiourea dehydrosulfurization:

1-(p-tolyl)-3-(4-vinylphenyl)thiourea (3.5 g, 13 mmol, 1 equiv.) and 2-chloro-1-methylpyridinium iodide (4.04 g, 15.6 mmol, 1.2 equiv.) were dissolved in dry dichloromethane (30 mL). Triethylamine (3.5 mL, 39 mmol, 3 equiv.) was administered and the reaction proceeded for 30 minutes while stirring at room temperature under N$_2$. Completion of the reaction from thiourea to carbodiimide (CDI) was established via TLC in a 2:1 hexanes:ethyl acetate mixture. Solvent was then removed by rotary evaporation. The reaction components were redissolved in minimal 2:1 hexanes to dichloromethane solution and eluted through a silica plug

with 350 mL of the same 2:1 hexanes to dichloromethane eluent. The CDI product (N-(p-tolyl)-N-(4-vinylphenyl) methanediimine) was isolated from the flow through of the silica plug via rotary evaporation of the solvent, reliably producing yields of approximately 90%. The purified CDI product was analyzed by ^{1}H NMR (Figure 12).
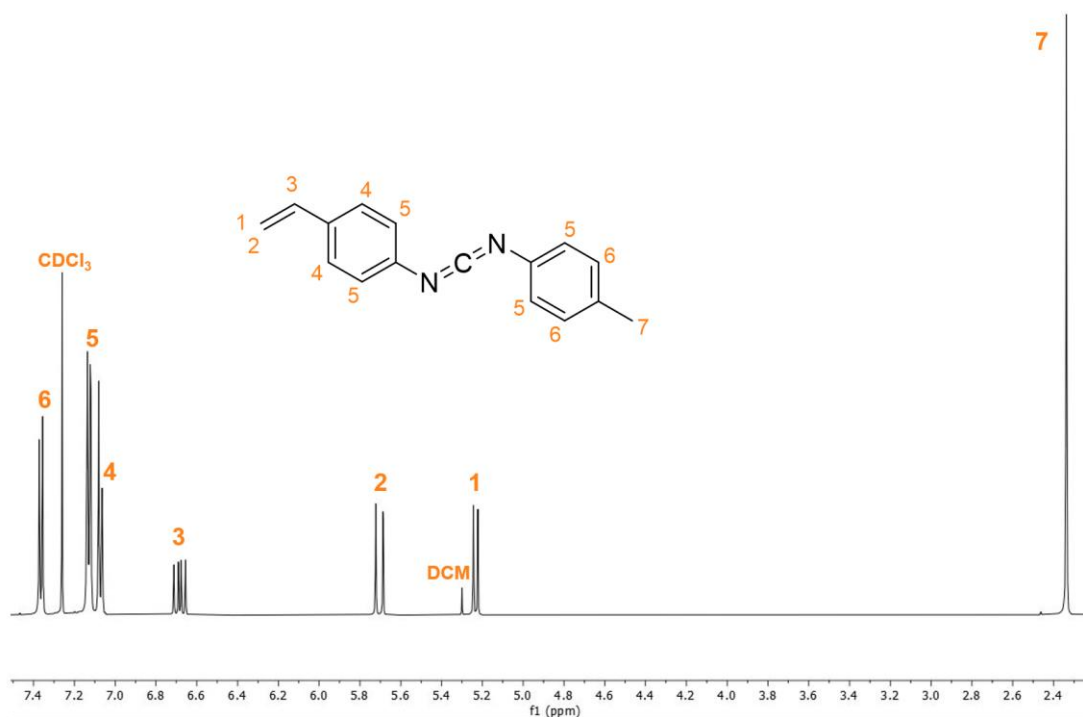

Figure 12. ^{1}H NMR spectrum of N-(p-tolyl)-N-(4-vinylphenyl) methanediimine. ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.40 – 7.33 (m, 2H), 7.16 – 7.10 (m, 4H), 7.10 – 7.05 (m, 2H), 6.68 (dd, J = 17.6, 10.9 Hz, 1H), 5.70 (dd, J = 17.6, 0.8 Hz, 1H), 5.26 – 5.20 (d, J = 11.0 Hz 1H), 2.34 (s, 3H).

Free-radical copolymerization of styrene and CDI monomer in 20:1 stoichiometric ratio:

In a dry Schlenk flask, aluminum oxide-filtered styrene (25.64 mL, 233.04 mmol, 18.9 equiv.), carbodiimide monomer (2.45 mL, 11.1 mmol, 0.9 equiv.), and 2,2-azobis(2-

methylpropionitrile) (2.0247 g, 12.33 mmol, 1 equiv.) were dissolved in 30 mL of

tetrahydrofuran. The mixture was then exposed to three freeze-pump-thaw cycles to remove

residual gas. Once thawed and backfilled with N_2, the reaction proceeded for 16 hours in an oil

bath at 60 °C while stirring. The reaction was terminated via exposure to air. Once terminated,

the reaction mixture was precipitated dropwise into 500 mL chilled methanol with 1% deionized

water. The solution was then filtered, and the crude polymer was collected and redissolved in 20

mL tetrahydrofuran. Once dissolved, the solution was once again precipitated into 500 mL

chilled methanol with 1% deionized water. After filtering, the polymer product (Figure 4) was

collected and put on a high vacuum line overnight at 40 °C. Polydispersity, Mn, and Mw of the

polymer was determined via Gel Permeation Chromatography (GPC) with polystyrene standards

of 1300 Da, 3000 Da, 4000 Da, 17.5 kDa, 65 kDa, and 150 kDa. Polydispersity was ~1.9, with
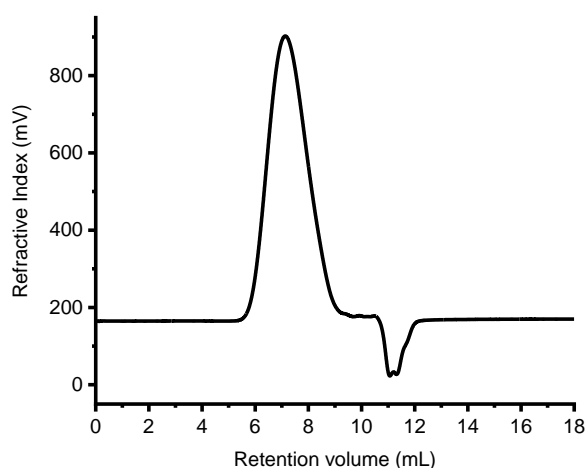
Mn ~7000 Da and Mw ~ 12000 Da (Figure 13).

Figure 13. Gel permeation chromatogram of 20:1 (poly-styrene-co-CDI) **poly3.** Mn = 7000 Da, Mw = 12000 Da, Mn/Mw = 1.89. Polystyrene standards used were 1300 Da, 3000 Da, 4000 Da, 17.5 kDa, 65 kDa, and 150 kDa.

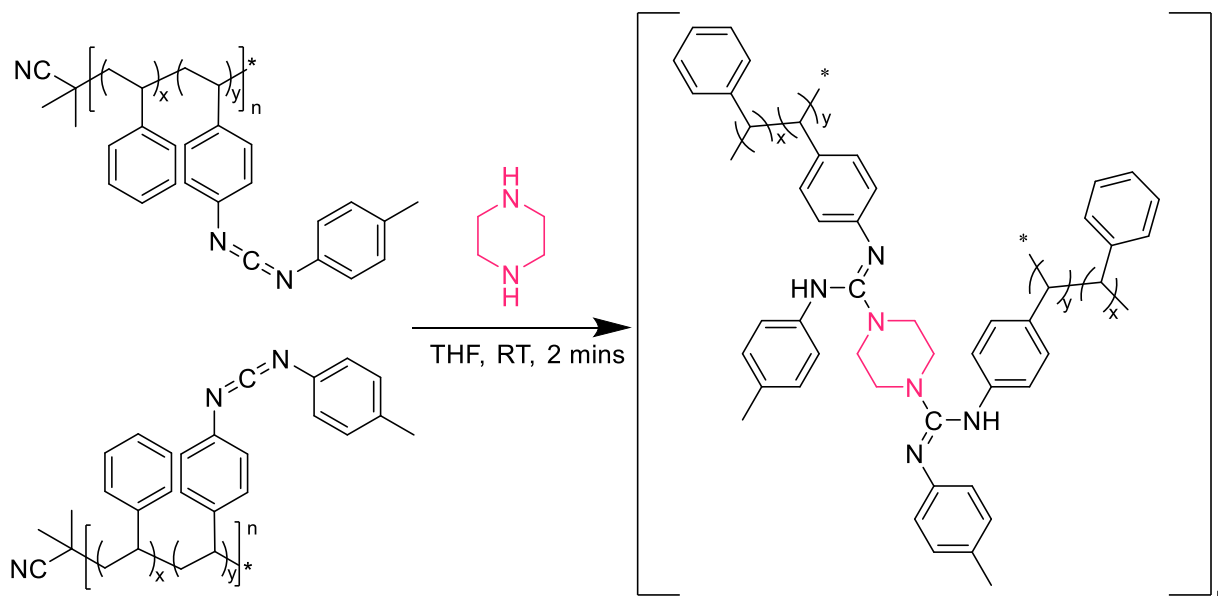**Preparation of covalent adaptable network via reaction of poly-styrene-co-CDI with bifunctional amines**

Figure 14. Representative synthesis of **CAN4**.

Purified and dried poly-styrene-co-CDI with 4×10^{-4} mmol CDI/mg **poly3** (5 g, 2.97 mmol, 2 equiv.) was dissolved in 20 mL tetrahydrofuran while stirring. Either anhydrous piperazine (256.5 mg, 1.52 mmol, 1.025 equiv.) (**CAN4**) or trans-2,5-dimethypiperazine (133.1 mg,1.52 mmol, 1.025 equiv.) (**CAN5**) was dissolved in 10 mL tetrahydrofuran while stirring. Once dissolved, dioctyl phthalate (0.265 mL, 5 % w/w) was added to the piperazine solution, and this was subsequently added to the polymer solution. Once agitated, the product was poured into glass dishes, covered, and left to precipitate out of solvent overnight as a gel. The product was then removed from the glass dish, broken into smaller pieces, and placed on a high vacuum line at 100 °C overnight (Figure 14). The product was then crushed into a finer powder via mortar and pestle and placed in a vacuum oven for 2 hours at 100 °C.

Preparation of rheological and DMA samples:

For rheology, approximately 700 mg of either guanidine network **CAN4** or **CAN5** was ground into a fine powder via a mortar and pestle and was put in 25 mm metal dry pressing die set. The mold was heated in the melt press at 150 °C for 20 minutes with no pressure, then 5000 psi was applied. After 20 minutes, the mold was removed to the benchtop and cooled for 20 minutes at ambient temperature then extracted from the mold. For DMA, approximately 500 mg of crushed guanidine network **CAN4** was weighed and placed in rectangular (30 mm × 5 mm × 2.5 mm) metal molds with aluminum plates on either side. The mold was placed in a hydraulic Carver press at 150 °C and 5000 psi of pressure was immediately applied for 40 minutes. The mold was then immediately moved to a hot plate at 150 °C, and the samples were pushed out from the mold using a preheated rectangular dye. Sol gel analysis of pieces of these samples yielded 86%, consistent with pre-melt pressing samples of **CAN4** and **CAN5**. DMA samples that were reprocessed were crushed again with a mortar and pestle and re-inserted into the melt press molds as described above.

Dynamic Mechanical Analysis:

Temperature ramps from 140-190 °C were performed on processed rectangular samples as prepared above on a TA Discovery Dynamic Mechanical Analyzer Q800. The temperature dependence on the tensile storage (E') and loss (E'') moduli were measured at 1 Hz frequency and 3 °C/min ramp rate. The maximum strain amplitude was 0.025%. T_g was determined by the point at which the loss tangent (E''/E') was at its maximum value.

Rheology:

Rheological samples as prepared above were tested in an Ares-G2 shear rheometer. Stress relaxation experiments were performed at 1% strain after determining that this strain % was within the linear viscoelastic region for both CANs. The testing temperature range was from 150-175 °C in 5 °C intervals with a 60 second soak time, followed by 20 minutes of relaxation time. The Arrhenius plot relaxation time for each temperature was derived via an exponential decay function applied to each isotherm: $E' = G * e^{\left(-(x/\tau)^B\right)}$. Approximate parameters values were G ~ 15,000, x ~ 100, B ~ 0.8, τ ~ 2000. $R^2 = 0.999$ for all temperatures 150-175 °C.

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