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# Thermomechanical Formation-Structure-Property Relationships in Photopolymerized Copper-Catalyzed Azide-Alkyne (CuAAC) **Networks**

Austin Baranek, Han Byul Song, Mathew McBride, Patricia Finnegan, and Christopher N. Bowman\*

Department of Chemical and Biological Engineering and Materials Science and Engineering Program, University of Colorado Boulder, Boulder, Colorado 80309-0596, United States

**S** Supporting Information

ABSTRACT: Bulk photopolymerization of a library of synthesized multifunctional azides and alkynes was carried out toward developing structure-property relationships for CuAAC-based polymer networks. Multifunctional azides and alkynes were formulated with a copper catalyst and a photoinitiator, cured, and analyzed for their mechanical properties. Material properties such as the glass transition temperatures  $(T_g)$  show a strong dependence on monomer structure with  $T_g$  values ranging from 41 to 90 °C for the series of CuAAC monomers synthesized in this study. Compared to the triazoles, analogous thioether-based polymer networks exhibit a 45-49 °C lower  $T_g$  whereas analogous monomers composed of ethers in place of carbamates exhibit a 40 °C lower T<sub>g</sub>. Here, the formation of the triazole moiety during the polymerization represents a critical component in dictating the material properties of the ultimate polymer network where material properties such as the rubbery modulus, cross-link density, and  $T_{g}$ 



all exhibit strong dependence on polymerization conversion, monomer composition, and structure postgelation.

# INTRODUCTION

The development of the photoinduced copper-catalyzed azidealkyne cycloaddition, or photo-CuAAC reaction, represented a significant milestone as an important new photopolymerization technique.<sup>1</sup> The advantages of photoinitiating this reaction complement its already significant value within synthetic methodologies, bioconjugation, labeling, surface functionalization, dendrimer synthesis, polymer synthesis, and polymer modification<sup>2-7</sup> by adding spatial and temporal control.<sup>8,9</sup> Scheme 1 illustrates the traditional CuAAC reaction, where the key component allowing this reaction to occur on a reasonable time scale is the copper(I) catalyst. In the absence of Cu(I), the reaction proceeds as much as 7 orders of magnitude more slowly.<sup>10,11</sup> Traditionally, by the nature of what this reaction has

Scheme 1. General Scheme for the Proposed Mechanism of the CuAAC Reaction<sup>4</sup>



<sup>a</sup>A reducing agent is first used to reduce Cu(II) to Cu(I) followed by Cu(I) catalysis of the 1,3-dipolar cycloaddition. Various photoreduction methodologies have been developed to enable photochemical control of the Cu<sup>+1</sup> generation.

been used for in synthetic chemistry, these reactions have been generally performed in a solvent to solubilize the copper(II) salts and with a reducing agent such as sodium ascorbate used to reduce the copper from a + 2 to a + 1 oxidation state. The use of a homogeneously soluble reducing agent precludes spatial and temporal control of the reaction, as the reduction of copper will generally commence upon addition of the reducing agent.

Successfully implementing photochemical approaches to reduce the copper to its +1 oxidation state enables enhanced control over the reaction that is particularly useful in materials science. Broadly, two approaches have been used to photochemically reduce Cu(II) to Cu(I) and initiate the CuAAC reaction.

Both ligand metal charge transfer utilizing an amine complex and the photochemical formation of radicals from a conventional radical photoinitiator have been used to facilitate photoinitiation of the CuAAC reaction.<sup>8,9,12-19</sup> In particular, with the use of a photoinitiator, the reduction of copper can be triggered upon exposure to either UV or visible light (Figure 1A), depending on the specific photoinitiator used and its absorption spectra.<sup>1,20</sup> Adzima et al. showed that the photo-CuAAC reaction can be applied in an aqueous environment to perform photolithography and postpolymerization modification of hydrogels.<sup>1</sup> However, for this reaction to be truly considered as one of only a handful of photopolymerization techniques,

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Figure 1. General scheme for the proposed mechanism of the photocatalyzed CuAAC polymerization. A photoinitiator is first used to generate radicals, which reduce Cu(II) to Cu(I). The transiently generated Cu(I) then catalyzes the 1,3-dipolar cycloaddition. In the presence of the multifunctional azide and alkyne monomers, the photo-CuAAC reaction forms a cross-linked network, where " $\bullet$ " represents a triazole linkage.

bulk polymerizations must be considered. Few examples of this reaction exist in a bulk system due to the heat of reaction of the CuAAC reaction and the safety concerns with neat azides.<sup>21</sup> Both Diaz et al. and Sheng et al. pioneered bulk CuAAC polymerizations with significant success; however, because polymerization occurred spontaneously upon mixing, these systems lacked spatial and temporal control.<sup>22–24</sup> Gong et al. studied a small group of synthesized multifunctional azide and alkyne monomers and successfully formed networks using light as the stimulus for polymerization (Figure 1), forming highly cross-linked, high glass transition temperature networks.<sup>25</sup> Additionally, photo-CuAAC has been accelerated using tertiary aliphatic amine ligands as an electron transfer species to reduce Cu(II) upon irradiation while also functioning as an accelerating agent and as protecting ligands for the Cu(I).<sup>12</sup>

The advantages of the CuAAC photopolymerization include not only facile control over the reaction with light but also the benefits of having large quantities of the triazole adduct present within the material postpolymerization. Triazoles formed during this reaction have excellent thermal and chemical stability, and the added rigidity from the heterocycle leads to higher glass transition temperatures, as shown previously.<sup>25</sup> In addition, the step-growth nature of the CuAAC polymerization allows higher conversion of the monomers, as gelation occurs much later in the reaction, forming a more homogeneous network with fewer unreacted chain ends. This behavior leads to a more uniformly cross-linked material with a sharp glassy to rubbery transition. Finally, the triazoles are also able to participate in numerous secondary-bonding interactions such as  $\pi - \pi$  stacking and hydrogen bonding which may also improve the toughness of these materials.

In other considerations of the photo-CuAAC reaction, compared to other catalysts, the copper catalyst is both longlived and may freely diffuse previtrification. In the case of a radical-mediated reaction, even if provided sufficient mobility, radicals will only continue to react for a short time due to the prevalence of rapid termination reactions. In contrast, the copper catalyst remains in the +1 activated state for much longer, extending the dark cure potential and enabling continued polymerization without continuing irradiation. One major concern in bulk CuAAC polymerizations is the solubility of the copper catalyst in the resin. Finding an appropriate ligand, which allows dissolution of the catalyst in the resin, is not only desirable to prevent phase separation or precipitation of the copper but also necessary to enable the polymerization to occur within a reasonable time scale. The same can be said for the photoinitiator, as both are required to create the copper(I) catalyst. Figure 1 is a schematic of the CuAAC photopolymerization accompanied by an illustration of a structural element of the network formed from a 2-3functional azide—alkyne resin system.

Despite several published examples of bulk CuAAC reactions, little is known about the materials produced using this technique, particularly the formation-structure-property relationships that underlie the behavior. Given the novelty and potential for these materials, it is critical to assess and understand these relationships. In particular, the triazole adducts formed during polymerization have been shown to improve mechanical properties;<sup>25</sup> however, the extent of this phenomenon is still unknown as is an ability to design materials with desired behavior. Here, we report simple protocols for synthesis of a variety of both multifunctional azide and alkyne monomers with different structural characteristics (Figure 2) that constitute a library of monomers from which to achieve a wide range of properties. Systematically integrating different moieties into the monomers and comparing the differences in the resulting polymers aid in determining the impact of each moiety on the overall mechanical behavior of the network. To polymerize these materials, CuCl<sub>2</sub>[PMDETA] (*vide infra*) was used as the catalyst because of its high solubility in the monomer resins and 2,2-dimethoxy-2-phenylacetophenone was chosen as the radical initiator due to its high stability under visible light allowing initiation only under high-intensity UV irradiation. The CuAAC photopolymerization of these monomers results in thermosets with tunable properties, where the thermomechanical properties and their dependence on specific chemical structural elements are reported.

# MATERIALS AND METHODS

1,3-Bis(isocyanatomethyl)cyclohexane, 1,3-Bis(2-isocyanatopropan-2yl)benzene, 4,4-methylenebis(cyclohexyl isocyanate), 4,4'-methylenebis(phenyl isocyanate), bis(4-hydroxyphenyl)methane, 6-chloro-1hexanol, 8-chloro-1-octanol, dibutyltin dilaurate sodium azide, 1,1,1tris(hydroxymethyl)propane, tris-1,3,5-bromomethylbenzene, phloroglucinol, propargyl alcohol, propargyl bromide, allyl bromide, sodium hydride (NaH), sodium sulfate (Na<sub>2</sub>SO<sub>4</sub>), potassium thioacetate, diethyl azodicarboxylate (DEAD), tetrabutylammonium iodide, N,N,N',N''-pentamethyldiethylenetriamine (PMDETA), copper(II) chloride, 2,2-dimethoxy-2-phenylacetophenone (DMPA), triphenylphosphine (TPP), tetrahydrofuran (THF), dimethylformamide (DMF), and dimethyl sulfoxide (DMSO) were all purchased from Sigma-Aldrich and used without further purification. Potassium carbonate (K<sub>2</sub>CO<sub>3</sub>) and hydrochloric acid (HCI) were purchased from Fisher Scientific and used without further purification.

Azide Monomer Synthesis (AZ-(1-4)). Note: organic azides are potentially explosive substances that can decompose with the slightest input of energy from external sources. Additionally, small molecules containing the azido functionality tend to decompose violently which may result in injury if proper safety precautions are not utilized. When designing a target azide, one must keep in mind the azide rule represented in the equation  $(N_C + N_O)/N_N \ge 3$ . This equation takes into account all nitrogen atoms in your azide, not just those in the azido group where N signifies the number of atoms.<sup>10,26</sup>

**Synthesis of Bis(6-chlorohexyl)dicarbamates.** A round-bottom flask purged with argon was charged with the diisocyanate (1,3-bis(isocyanatomethyl)cyclohexane, 1,3-bis(2-isocyanatopropan-2-yl)-benzene, 4,4-methylenebis(cyclohexyl isocyanate), 4,4'-methylenebis(phenyl isocyanate) (0.004 09 mol), THF (3 mL), and dibutyltin dilaurate (3–5 drops). The reaction flask was then cooled to 0 °C by placing in an ice bath. The 6-chloro-1-hexanol (1.17 g; 0.008 60 mol)



Figure 2. Library of azide, alkyne, thiol, and alkene monomers in addition to the catalyst and initiator system used in the CuAAC polymerization ( $CuCl_2$ [PMDETA] and DMPA).

was then added dropwise to the reaction, removed from the ice bath, allowed to equilibrate to room temperature, and reacted for 1-2 h (note: minimal heat (40–50 °C) may be used to reduce the reaction time). Following completion of the reaction, the mixture was diluted with excess THF and flowed through a silica plug to remove the tin catalyst. The product was dried in vacuo to a colorless oil and, if necessary, purified using column chromatography.

Bis(6-chlorohexyl)(cyclohexane-1,3-diylbis(methylene))dicarbamate. Yield 95%. <sup>1</sup>H NMR (CDCl<sub>3</sub>), ppm:  $\delta$  0.50–1.85 (26H, m, CH<sub>2</sub>, CH), 3.03 (4H, t, CH<sub>2</sub>-carbamate), 3.56 (4H, t, CH<sub>2</sub>-Cl), 4.05 (4H, t, CH<sub>2</sub>-carbamate), 4.78 (2H, s, NH, carbamate). <sup>13</sup>C NMR (CDCl<sub>3</sub>), ppm:  $\delta$  25.19, 25.23, 26.54, 28.89, 28.89, 20.42, 32.46, 34.61, (12C, CH<sub>2</sub>), 37.95 (2C, CH), 45.00 (2C, CH<sub>2</sub>-NH, carbamate), 47.19 (2C, CH<sub>2</sub>-Cl), 64.68 (2C, CH<sub>2</sub>-O, carbamate), 156.85 (2C, C=O, carbamate).

Bis(6-chlorohexyl)(1,3-phenylenebis(propane-2,2-diyl))dicarbamate. Yield 98%. <sup>1</sup>H NMR (CDCl<sub>3</sub>), ppm:  $\delta$  1.15–1.85 (28H, m, CH<sub>2</sub>, CH<sub>3</sub>), 3.52 (4H, t, CH<sub>2</sub>–Cl), 3.97 (4H, t, CH<sub>2</sub>–carbamate), 5.07 (2H, s, NH, carbamate), 7.27 (3H, s, CH–aromatic), 7.42 (1H, s, CH–aromatic). <sup>13</sup>C NMR (CDCl<sub>3</sub>), ppm:  $\delta$  26.26, 26.57, 28.95, 29.35 (8C, CH<sub>2</sub>), 32.51 (4C, CH<sub>3</sub>), 45.04 (2C, CH<sub>2</sub>–Cl), 55.37 (2C, C, aliphatic), 64.25 (2C, CH<sub>2</sub>–O, carbamate), 121.28, 123.25, 128.37 (4C, CH, aromatic), 147.20 (2C, C, aromatic) 154.87 (2C, C=O, carbamate).

Bis(6-chlorohexyl) (methylenebis(cyclohexane-4, 1-diyl))dicarbamate. Yield 91%. <sup>1</sup>H NMR (CDCl<sub>3</sub>), ppm:  $\delta$  0.85–2.05 (36H, m, CH<sub>2</sub>, CH), 3.40 [mixture of isomers] (2H, m, NH, carbamate), 3.54 (4H, t, CH<sub>2</sub>–Cl), 4.04 (4H, t, CH<sub>2</sub>–O, carbamate), 4.54, 4.80 [mixture of isomers] (2H, CH–NH, carbamate). <sup>13</sup>C NMR (CDCl<sub>3</sub>), ppm:  $\delta$  25.24, 25.60, 26.53, 28.03, 28.89, 29.69, 33.44, 33.62, 33.72 [mixture if isomers] (18C, CH, CH<sub>2</sub>), 44.04 (1C, cyclohex– CH<sub>2</sub>–cyclohex), 44.97 (2C, CH<sub>2</sub>–N<sub>3</sub>), 53.45 (2C, CH–NH, carbamate), 64.47 (2C, CH<sub>2</sub>–O, carbamate), 155.91 (2C, C=O, carbamate).

Bis(6-chlorohexyl)(methylenebis(4, 1-phenylene))dicarbamate. Yield 94%. <sup>1</sup>H NMR (d-DMSO), ppm:  $\delta$  1.31–1.77 (16H, m, CH<sub>2</sub>), 3.63 (4H, t, CH<sub>2</sub>–Cl), 3.86 (2H, s, Aryl–CH<sub>2</sub>–Aryl), 4.05 (4H, t, CH<sub>2</sub>–O, carbamate), 7.10 (4H, d, CH–aromatic), 7.36 (4H, d, CH– aromatic), 9.51 (2H, s, CH<sub>2</sub>–NH, carbamate). <sup>13</sup>C NMR (d-DMSO), ppm:  $\delta$  25.21, 26.51, 28.79, 32.43 (8C, CH<sub>2</sub>), 40.53 (1C, Aryl–CH<sub>2</sub>– Aryl), 44.97 (2C, CH<sub>2</sub>–Cl), 65.02 (2C, CH<sub>2</sub>–O, carbamate), 118.89, 136.07 (8C, CH, aromatic), 129.38, 136.23 (4C, C, aromatic) 153.78 (2C, C=O, carbamate).

**Synthesis of Bis(6-azidohexyl)dicarbamates.** A round-bottom flask fitted with a reflux condenser was charged with bis(6-chlorohexyl)dicarbamates (0.004 15 mol) and dissolved in 30 mL of DMF. Sodium azide (1.08 g; 0.0166 mol) was then added and allowed to react overnight at 80 °C. The reaction flask was then cooled to ambient temperature, and the product was extracted with ethyl acetate followed by water washes to remove DMF and the excess sodium azide. The organic phase was dried with Na<sub>2</sub>SO<sub>4</sub> and dried *in vacuo* to colorless oil and, if necessary, purified using column chromatography.

Bis(6-azidohexyl)(cyclohexane-1,3-diylbis(methylene))dicarbamate (AZ-1). Yield 89%. <sup>1</sup>H NMR (CDCl<sub>3</sub>), ppm:  $\delta$  0.50– 1.90 (26H, m, CH<sub>2</sub>, CH), 3.04 (4H, t, CH<sub>2</sub>-carbamate), 3.29 (4H, t, CH<sub>2</sub>-N<sub>3</sub>), 4.06 (4H, t, CH<sub>2</sub>-carbamate), 4.76 (2H, s, NH, carbamate). <sup>13</sup>C NMR (CDCl<sub>3</sub>), ppm:  $\delta$  25.19, 25.50, 26.40, 28.75, 28.91, 30.42, 34.62 (12C, CH<sub>2</sub>), 37.96 (2C, CH), 47.19 (2C, CH<sub>2</sub>-NH, carbamate), 51.35 (2C, CH<sub>2</sub>-N<sub>3</sub>), 64.66 (2C, CH<sub>2</sub>-O, carbamate). 156.85 (2C, C=O, carbamate).

Bis(6-azidohexyl)(1,3-phenylenebis(propane-2,2-diyl))dicarbamate (AZ-2). Yield 93%. <sup>1</sup>H NMR (CDCl<sub>3</sub>), ppm:  $\delta$  1.15– 1.75 (28H, m, CH<sub>2</sub>, CH<sub>3</sub>), 3.28 (4H, t, CH<sub>2</sub>–N<sub>3</sub>), 3.99 (4H, t, CH<sub>2</sub>– carbamate), 5.10 (2H, s, NH, carbamate), 7.30 (3H, s, CH–aromatic), 7.44 (1H, s, CH–aromatic). <sup>13</sup>C NMR (CDCl<sub>3</sub>), ppm:  $\delta$  25.46, 26.36, 28.89, 29.27 (8C, CH<sub>2</sub>), 28.72 (4C, CH<sub>3</sub>), 51.33 (2C, CH<sub>2</sub>–N<sub>3</sub>), 55.30 (2C, C, aliphatic), 64.17 (2C, CH<sub>2</sub>–O, carbamate), 121.22, 123.20, 128.31 (4C, CH, aromatic), 147.15 (2C, C, aromatic), 154.82 (2C, C=O, carbamate).

Bis(6-azidohexyl)(methylenebis(cyclohexane-4,1-diyl))dicarbamate (AZ-3). Yield 88%. <sup>1</sup>H NMR (CDCl<sub>3</sub>), ppm:  $\delta$  0.90– 2.05 (36H, m, CH<sub>2</sub>, CH), 3.25 (4H, t, CH<sub>2</sub>–N<sub>3</sub>), 3.27, 3.75 [mixture of isomers] (2H, s, NH, carbamate), 4.02 (4H, t, CH<sub>2</sub>–carbamate), 4.60, 4.83 [mixture of isomers] (2H, CH–NH). <sup>13</sup>C NMR (CDCl<sub>3</sub>), ppm:  $\delta$  25.49, 26.38, 28.02, 28.72, 28.90, 29.68, 32.00, 32.55, 33.41, 33.60, 33.70 [mixture of isomers] (18C, CH, CH<sub>2</sub>), 46.89 (1C, cyclohex–CH<sub>2</sub>–cyclohex), 50.28 (2C, CH<sub>2</sub>–N<sub>3</sub>), 51.31 (2C, CH– NH, carbamate), 64.42 (2C, CH<sub>2</sub>–O, carbamate), 155.92 (2C, C=O, carbamate). Bis(6-azidohexyl)(methylenebis(4,1-phenylene))dicarbamate (AZ-4). Yield 85%. <sup>1</sup>H NMR (CDCl<sub>3</sub>), ppm: δ 1.38–1.74 (16H, m, CH<sub>2</sub>), 3.29 (4H, t, CH<sub>2</sub>–N<sub>3</sub>) 3.91 (2H, s, Aryl–CH<sub>2</sub>–Aryl), 4.17 (4H, t, CH<sub>2</sub>–O, carbamate), 6.63 (2H, s, CH<sub>2</sub>–NH, carbamate), 7.12 (4H, d, CH–aromatic), 7.31 (4H, d, CH–aromatic). <sup>13</sup>C NMR (CDCl<sub>3</sub>), ppm: δ 25.50, 26.40, 28.75, 28.80 (8C, CH<sub>2</sub>), 40.54 (1C, Aryl–CH<sub>2</sub>– Aryl), 51.36 (2C, CH<sub>2</sub>–N<sub>3</sub>), 65.01 (2C, CH<sub>2</sub>–O, carbamate), 118.86, 135.99 (8C, CH, aromatic), 129.42, 136.29 (4C, C, aromatic) 153.74 (2C, C==O, carbamate).

Alkyne Monomer Synthesis (AL-(1-4)). 1-(Prop-2-yn-1-yloxy)-2,2-bis((prop-2-yn-1-yloxy)methyl)butane (AL-1). To a roundbottom flask 1,1,1-tris(hydroxymethyl)propane (1.972 g; 14.7 mmol) and 15 mL of dimethyl sulfoxide (DMSO) were charged. Following dissolution of the 1,1-tris(hydroxymethyl)propane, 10 mL of a 40% w/ w solution of NaOH in water was added and allowed to stir for 1 h at ambient temperature. Propargyl bromide (8.9 mL of an 80% solution in toluene; 44.8 mmol) was then slowly added, and the reaction was allowed to stir for 3-5 days. The reaction was extracted with diethyl ether and washed with excess water. After the separation, the organic phase was gathered, dried with anhydrous Na2SO4, filtered, and concentrated. The crude product was then purified using column chromatography to obtain a clear oil. Yield 72%. <sup>1</sup>H NMR (CDCl<sub>3</sub>), ppm: δ 0.90 (3H, t, CH<sub>3</sub>), 1.45 (2H, q, CH<sub>2</sub>-CH<sub>3</sub>) 2.42 (3H, t, alkyne–H), 3.43 (6H, s, CH<sub>2</sub>), 4.14 (6H, d, CH<sub>2</sub>–alkyne). <sup>13</sup>C NMR (CDCl<sub>3</sub>), ppm:  $\delta$  7.48 (1C, CH<sub>3</sub>), 22.71 (1C, CH<sub>2</sub>), 42.73 (1C, C, core), 58.58 (3C, CH2-alkyne), 70.26 (3C, CH2), 74.05 (3C, CH, alkyne) 80.13 (3C, C, alkyne).

1,3,5-tris((prop-2-yn-1-yloxy)methyl)benzene (AL-2). A 60% NaH (0.18 g, 4.51 mmol) oil dispersion was added to a solution of propargyl alcohol (0.25 g, 4.51 mmol) in DMF (15 mL) at 0 °C under N2. After 10 min of mixing at 0 °C, tris-1,3,5-bromomethylbenzene (0.5 g, 1.4 mmol) was added, and the resulting solution was stirred overnight at ambient temperature. The reaction was quenched with methanol and water in that order to neutralize the excess NaH. The reaction mixture was extracted with CH2Cl2 and washed with excess water. After the separation, the organic phase was gathered, dried with anhydrous Na<sub>2</sub>SO<sub>2</sub>, filtered, and concentrated. The crude product was then purified using column chromatography to obtain a colorless oil. Yield 67%. <sup>1</sup>H NMR (CDCl<sub>3</sub>), ppm:  $\delta$  2.50 (3H, t, CH, alkyne), 4.21 (6H, d, CH<sub>2</sub>-alkyne), 4.63 (6H, CH<sub>2</sub>-aromatic) 7.32 (3H, CH, aromatic). <sup>13</sup>C NMR (CDCl<sub>3</sub>), ppm:  $\delta$  57.32 (3C, CH<sub>2</sub>-alkyne), 71.28 (3C, CH<sub>2</sub>-O), 74.79 (3C, CH, alkyne), 79.54 (3C, C, alkyne), 127.17 (3C, CH, aromatic), 137.91 (3C, C, aromatic).

1,3,5-Tris(prop-2-yn-1-yloxy)benzene (AL-3). Phloroglucinol (10 g, 0.0793 mol) and K<sub>2</sub>CO<sub>3</sub> (65.8 g, 0.476 mol) were charged into a twoneck round-bottom fitted with a reflux condenser and dissolved in DMF (500 mL). The mixture was purged with N<sub>2</sub> followed by the slow addition of propargyl bromide (53 mL of an 80% w/w solution in toluene). The reaction was heated to 80 °C for 24 h before extracting with ethyl acetate and washing with a 1 M NaOH solution followed by excess water. After the separation, the organic phase was gathered, dried with anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated. The crude product was then purified using recrystallization in methanol to obtain a white crystalline powder. Yield 82%. <sup>1</sup>H NMR (CDCl<sub>3</sub>), ppm: δ 2.56 (3H, t, CH, alkyne), 4.67 (6H, d, CH<sub>2</sub>–alkyne), 6.29 (3H, CH, aromatic). <sup>13</sup>C NMR (CDCl<sub>3</sub>), ppm: δ 55.96 (3C, CH<sub>2</sub>–alkyne), 77.75 (3C, CH, alkyne) 78.25 (3C, C, alkyne), 95.44 (3C, CH, aromatic), 159.34 (3C, C, aromatic).

3,3-Bis((prop-2-yn-1-yloxy)methyl)heptane (AL-4). To a roundbottom flask 2-butyl-2-ethyl-1,3-propanediol (11.77 g, 73.45 mmol), tetrabutylammonium iodide (300 mg, 0.81 mmol), potassium hydroxide (27 g, 481 mmol), and 250 mL of THF were charged and fitted with a reflux condenser. Following dissolution of the 2-butyl-2-ethyl-1,3-propanediol, 32.7 mL of propargyl bromide (80% solution in toluene; 293.8 mmol) was then slowly added, and the reaction was allowed to stir for 24 h at 70 °C. The reaction was cooled to room temperature and extracted with ethyl acetate and washed with excess water. After the separation, the organic phase was gathered, dried with anhydrous  $Na_2SO_4$ , filtered, and concentrated. The crude product was then purified using column chromatography to obtain a light yellow oil. Yield 88%. <sup>1</sup>H NMR (CDCl<sub>3</sub>), ppm:  $\delta$  0.84, 0.92 (6H, t, CH<sub>3</sub>), 1.29 (8H, m, CH<sub>2</sub>) 2.41 (3H, t, alkyne–H), 3.33 (4H, s, CH<sub>2</sub>), 4.14 (4H, d, CH<sub>2</sub>–alkyne). <sup>13</sup>C NMR (CDCl<sub>3</sub>), ppm:  $\delta$  7.23 (1C, CH<sub>3</sub>), 14.16 (1C, CH<sub>3</sub>), 23.54, 23.67, 25.81, 30.56 (4C, CH<sub>2</sub>), 40.70 (1C, C, core), 58.48 (2C, CH<sub>2</sub>–alkyne), 72.29 (2C, CH, alkyne) 73.82 (2C, CH<sub>2</sub>), 80.33 (2C, C, alkyne).

Thiol Monomer Synthesis. Bis(6-mercaptohexyl)(1,3phenylenebis(propane-2,2-diyl))dicarbamate (2-SH). To a roundbottom flask fitted with a reflux condenser was charged potassium thioacetate (0.47 g, 4.15 mmol) dissolved in 10 mL of DMF. Following the dissolution of the potassium thioacetate, a solution of bis(6-chlorohexyl)(1,3-phenylenebis(propane-2,2-diyl))dicarbamate (1 g, 1.88 mmol) in 3 mL of DMF was slowly added and heated to 60 °C for 12 h. The solution was cooled to ambient temperature, and the product was extracted with ethyl acetate followed by washing with excess water. The organic layer was then concentrated and redissolved in ethanol (5 mL of ethanol per gram of thioacetate). An equal molar equivalence of NaOH to thioacetate was added using a 7 M NaOH solution in water. The reaction was heated at 80 °C for 3 h before allowing it to be cooled to room temperature and neutralized using a 2 M HCl solution in water. Once neutralized, the reaction was extracted with diethyl ether and washed with excess water. After the separation, the organic phase was gathered, dried with anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated. The crude product was then purified using column chromatography to obtain a colorless oil. Yield 69%. <sup>1</sup>H NMR (CDCl<sub>3</sub>), ppm:  $\delta$  1.25–1.75 (30H, m, CH<sub>2</sub>, CH<sub>3</sub>, SH), 2.53 (4H, q, CH<sub>2</sub>-SH), 3.99 (4H, t, CH<sub>2</sub>-carbamate), 5.07 (2H, s, NH, carbamate), 7.30 (3H, s, CH-aromatic), 7.44 (1H, s, CH-aromatic). <sup>13</sup>C NMR (CDCl<sub>3</sub>), ppm:  $\delta$  24.53, 25.36, 27.96, 28.92, 29.30 (10C, CH<sub>2</sub>), 33.85 (4C, CH<sub>3</sub>), 55.32 (2C, C-NH, carbamate), 64.27 (2C, CH<sub>2</sub>-O, carbamate), 121.21, 123.21, 128.34 (4C, CH, aromatic), 147.14 (2C, C, aromatic) 154.85 (2C, C=O, carbamate).

Trialkene Synthesis. 1-(Allyloxy)-2,2-bis((allyloxy)methyl)butane (1-ene). To a round-bottom was charged 1,1,1-tris(hydroxymethyl)propane (1.972 g, 14.7 mmol) and 15 mL of dimethyl sulfoxide (DMSO). Following dissolution of the 1,1-tris(hydroxymethyl)propane, 10 mL of a 40% w/w solution of NaOH in water was added and allowed to stir for 1 h at room temperature. Allyl bromide (5.1 mL, 58.8 mmol) was then slowly added, and the reaction was allowed to stir for 3-5 days. The reaction was extracted with diethyl ether and washed with excess water. After the separation, the organic phase was gathered, dried with anhydrous Na2SO4, filtered, and concentrated. The crude product was then purified using column chromatography to obtain a clear oil. Yield 79%. <sup>1</sup>H NMR (CDCl<sub>3</sub>), ppm:  $\delta$  0.88 (3H, t, CH<sub>3</sub>), 1.46 (2H, q, CH<sub>2</sub>-CH<sub>3</sub>), 3.35 (6H, s, CH<sub>2</sub>), 3.97 (6H, 2t, CH<sub>2</sub>-alkene), 5.15-5.31 (6H, m, CH<sub>2</sub>, alkene), 5.86–5.96 (3H, m, CH, alkene). <sup>13</sup>C NMR (CDCl<sub>3</sub>), ppm: δ 7.72 (1C, CH<sub>3</sub>), 23.03 (1C, CH<sub>2</sub>), 43.16 (1C, C, core), 70.71 (3C, CH<sub>2</sub>alkene), 72.24 (3C, CH2-O), 116.12 (3C, CH2, alkene) 135.31 (3C, CH, alkene).

1,3,5-Tris((allyloxy)methyl)benzene (2-ene). A 60% NaH (0.18 g, 4.51 mmol) oil dispersion was slowly added to a solution of allyl alcohol (0.25 g, 4.51 mmol) in DMF (15 mL) at 0 °C under N<sub>2</sub>. After 10 min of mixing at 0 °C, tris-1,3,5-bromomethylbenzene (0.5 g, 1.4 mmol) was added, and the resulting solution was stirred overnight at ambient temperature. The reaction was quenched with methanol and water in that order to neutralize the excess NaH. The reaction mixture was extracted with CH2Cl2 and washed with excess water. After the separation, the organic phase was gathered, dried with anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated. The crude product was then purified using column chromatography to obtain a colorless oil. Yield 86%. <sup>1</sup>H NMR (CDCl<sub>3</sub>), ppm: δ 4.05, 4.07 (6H, t, CH<sub>2</sub>), 4.55 (6H, s, CH<sub>2</sub>), 5.22-5.36 (6H, CH<sub>2</sub>-alkene) 5.97 (3H, m, CH, alkene) 7.29 (3H, s, CH–aromatic). <sup>13</sup>C NMR (CDCl<sub>3</sub>), ppm: δ 71.28, 71.95 (6C, CH<sub>2</sub>), 117.22 (3C, CH<sub>2</sub>-ene), 126.29 (3C, CH, aromatic), 134.70 (3C, CH-ene), 138.69 (3C, C, aromatic).

**Diazide–Ether Synthesis.** *Bis*(4-((8-azidooctyl)oxy)phenyl)methane (**AZ-4-ether**). To a round-bottom flask was charged bis(4hydroxyphenyl)methane (1 g, 9.98 mmol), 8-chloro-1-octanol (2.47 g, 14.98 mmol), and triphenylphosphine (TPP) (3.93 g, 14.98 mmol)



Figure 3. Plots of (a) tan  $\delta$  vs temperature and (b) storage modulus vs temperature for a series of azide monomers (AZ-(1-4)) with a single alkyne monomer (AL-1). All resins were composed 2 mol % CuCl<sub>2</sub>[PMDETA] and 4 mol % DMPA and were cured with 10 mW/cm<sup>2</sup> UV light. Representative curves are presented as the third cycle in the DMA.

dissolved in 5 mL of THF. Diethyl azodicarboxylate (DEAD) (6.82 mL of a 40% w/w solution in toluene, 14.98 mmol) was added dropwise while under sonication at 0 °C. Once all the DEAD was added, the reaction was allowed to equilibrate to room temperature and sonicated for an additional 2 h. The reaction was extracted with ethyl acetate and washed with excess water. After the separation, the organic phase was gathered, dried with anhydrous Na2SO4, filtered, and concentrated. The crude product was then purified by first crystallizing out the excess TPP followed by column chromatography. Following purification, the dichloro intermediate was then exchanged to the diazide using the previously reported procedure for AZ-(1-4). Yield 93%. <sup>1</sup>H NMR (CDCl<sub>3</sub>), ppm:  $\delta$  1.35–1.84 (24H, m, CH<sub>2</sub>), 3.29 (4H, t, CH<sub>2</sub>-N<sub>3</sub>) 3.89 (2H, s, Aryl-CH<sub>2</sub>-Aryl), 3.95 (4H, t, CH<sub>2</sub>-O), 6.84 (4H, d, CH-aromatic), 7.11 (4H, d, CH-aromatic). <sup>13</sup>C NMR (CDCl<sub>3</sub>), ppm: δ 26.00, 26.67, 28.84, 29.10, 29.25, 29.29 (12C, CH<sub>2</sub>), 40.16 (1C, Aryl–CH<sub>2</sub>–Aryl), 51.47 (2C, CH<sub>2</sub>–N<sub>3</sub>), 67.89 (2C, CH2-O), 114.43, 129.71 (8C, CH, aromatic), 133.59, 157.42 (4C, C, aromatic).

 $CuCl_2[PMDETA]$  Complex. A 1:1 molar mixture of CuCl<sub>2</sub> and PMDETA (*N*,*N*,*N'*,*N''*-pentamethyldiethylenetriamine) in acetonitrile was stirred overnight at room temperature and dried under vacuum to a blue-green solid.

**Film Preparation.** Resins were mixed in equal molar ratios of azide to alkyne based on functional groups with 2 mol % CuCl<sub>2</sub>[PMDETA] and 4 mol % DMPA. Methanol was used to homogenize the resins but was removed prior to polymerization to below 0.5% w/w to limit plasticization. 75–125 mg of the resins was placed in the center of a RainX coated 75 × 50 mm glass slide. Spacers (250  $\mu$ m) were inserted on the sides of the glass slide, and a second RainX coated 75 × 50 mm glass slide was gently placed on the top, making sure bubbles were excluded when "sandwiching" the monomer. The glass slides were clamped together, and the sandwiched resin was placed under 5–10 mW cm<sup>-2</sup> UV light. The resins were irradiated for 3–5 min, followed by annealing in a preheated oven at 75 °C for 24 h.

**Characterization and Measurements.** <sup>1</sup>H NMR and <sup>13</sup>C NMR measurements were performed in deuterated chloroform (CDCl<sub>3</sub>) and dimethyl sulfoxide (*d*-DMSO) to determine the purity and degree of functionalization of the synthesized molecules, using a Bruker Avance-III-400 NMR spectrometer. The number of transients for <sup>1</sup>H and <sup>13</sup>C is 16 and 256, respectively, and a relaxation time of 1 s was used for the integrated intensity determination of <sup>1</sup>H NMR spectra. NMR spectra of all the synthesized monomers can be found in the Supporting Information (Figures S1–S12).

Polymerization conversions were analyzed using a Fourier transform infrared spectroscopy (FTIR) instrument (Nicolet 8700) incorporated with a heating stage to monitor the real-time functional group conversions in transmission mode. Irradiation was performed using a light guide connected to a mercury lamp (Acticure 4000) with a 365 nm bandgap or other filter, as noted. Samples were placed between NaCl plates, and the azide peak was monitored in the absorption range between 2300 and 2000 cm<sup>-1</sup> having the alkane C–H stretching bonds as a reference peak between 2980 and 2840 cm<sup>-1</sup> with 12 scans s<sup>-1</sup> and 2 cm<sup>-1</sup> resolution. In addition, grazing-angle attenuated total reflectance mode FTIR (gATR-FTIR) with a VariGATR accessory (grazing angle 65°, zinc selenide crystal; Harrick Scientific) was used to provide an indication of the functional group conversions of thick samples (100–250  $\mu$ m) postannealing. Spectra were collected with a resolution of 4 cm<sup>-1</sup> by accumulating a minimum of 64 scans per sample (spectra shown in Supporting Information, Figures S13–S16).

Dynamic mechanical analysis (DMA) was performed on a TA Instruments Q800 DMA in tension film mode with a heating rate of 3 °C min<sup>-1</sup> to a maximum temperature of 150 °C at a frequency of 1 Hz. E''/E', i.e., the ratio of the loss and storage moduli, gives the tan  $\delta$ , a dampening term, which relates to the energy dissipation relative to the energy stored in the material upon deformations where the  $T_g$  is assigned here as the peak of the tan  $\delta$  curve. Samples were prepared using the sandwich method previously described to create 250  $\mu$ m thick films, which were cut into bars ranging from 5 to 7 mm wide. DMA experiments were thermally cycled and replicated three times, and the representative curves are presented as the third heating cycle. Note: DMA experiments for samples annealed at lower temperatures (30 °C) can be found in the Supporting Information (Figures S17–S20) and represent the progression of the  $T_g$  over each of the three DMA cycles.

# RESULTS AND DISCUSSION

Thermomechanical Properties. Thermomechanical transitions of the cured CuAAC resins were investigated using dynamic mechanical analysis (DMA) in tension mode. Figure 3 shows the DMA results for a series of four synthesized azide monomers (AZ-(1-4)) with a single trialkyne cross-linker (AL-1). Relatively cyclohexane-based monomers show a consistently lower  $T_{g}$  as compared to their aromatic analogues. In both examples, similar aromatic and nonaromatic cyclic monomers show a 14–16 °C difference in the  $T_g$  as a result of the increased stiffness and additional secondary interactions associated with  $\pi - \pi$  stacking. Interestingly, the increase in  $T_{\sigma}$ going from a single aromatic to a double aliphatic cyclic core, specifically comparing azide monomers AZ-2 and AZ-3, cannot be explained with additional secondary interactions, as cyclohexane rings do not contribute to such forces. A possible explanation is that there is an increase in the stiffness of the monomer and polymer structures with azide monomer (AZ-3) as compared to AZ-2. Additional data including the glassy and rubbery modulus along with the estimated molecular weight between cross-links  $(M_c)$  are summarized in Table 1. In the glassy state all these materials exhibit high modulus values

Table 1. Summary of DMA Results for a Series of Azide Monomers (AZ-(1-4)) with a Single Alkyne Monomer (AL-1) Composed 2 mol % CuCl<sub>2</sub>[PMDETA] and 4 mol % DMPA and Cured with 10 mW/Cm<sup>2</sup> UV Light<sup>*a*</sup>

	alkyne cross-linker (AL-1)			
azide monomer	AZ-1	AZ-2	AZ-3	AZ-4
$T_{g}$ (°C)	57	67	73	81
<i>E</i> <sub>30 °C</sub> (GPa)	1.7	2.2	1.1	1.4
$E$ at $T_{\rm g}$ + 40 °C (MPa)	3.9	3.4	1.8	2.1
$ ho (g/cm^3)$	$\sim 1.1$	~1.2	$\sim 1.1$	$\sim 1.1$
$M_{\rm c}$ (g/mol)	~1200	~1500	~2600	~2300

 ${}^{a}\rho$  is the density of the material estimated from the dimension and mass of the sample;  $M_{\rm c}$  is the molecular weight between cross-links calculated from the equation  $M_{\rm C} = 3\rho RT/2E$  where R is the gas constant.

between 1.1 and 2.2 GPa; however, the lower MW azides (AZ-1, AZ-2) have a higher rubbery modulus as compared to the higher MW azides (AZ-3, AZ-4) due to a corresponding reduction in cross-link density. To ensure these material properties are accurate and not a result of different conversions of the monomers, FTIR spectra of the resin and annealed polymers are included in the Supporting Information and show near-quantitative conversion of the azide moiety as highlighted by the peak disappearance at 2100 cm<sup>-1</sup>.

A similar trend is observed in the  $T_{\rm g}$  values for the series of synthesized trialkyne monomers AL-(1-3) when polymerized with a single azide monomer (AZ-2) (Figure 4a). The material with the lowest  $T_g$  of this series is made with the larger molecular weight aromatic trialkyne (AL-2). One would expect that having an aromatic core would result in a higher  $T_{g}$ ; however, the opposite is observed, likely as a result of a higher molecular weight monomer and reduced  $\pi - \pi$  interactions. This correlation also holds true for trialkyne (AL-3) as it has the lowest molecular weight, which leads to the greatest cross-link density and shows the highest Tg. The opposite is observed when comparing trialkyne monomers AL-1 and AL-2 with azide monomer AZ-4 (Figure 4b). An increase in the  $T_{g}$  with trialkyne AL-2 is likely a result of improved  $\pi - \pi$  stacking from the azide monomer AZ-4 that contains two aromatic rings incorporated through the para position. Additionally, as shown in Table 2, in these materials the glassy moduli ranges from 1.4 to 2.2 GPa; however, changing the alkyne monomer for AZ-2 had little effect on the rubbery modulus with values for the various alkynes used here ranging only  $\pm 300$  MPa. One would expect that more significant changes to the equivalent weight per alkyne functional group in the monomer would beyond the limited range used here would lead to a change in the cross-link density and corresponding rubbery modulus value. In contrast, for AZ-4 the rubbery modulus significantly increases from  $\sim 2.1$ 



**Figure 4.** Plots of tan  $\delta$  vs temperature and storage modulus for a series of alkyne monomers **AL**-(1-3) with a single azide monomer ((a) **AZ-2**, (b) **AZ-4**). All resins composed 2 mol % CuCl<sub>2</sub>[PMDETA] and 4 mol % DMPA and were cured with 10 mW/cm<sup>2</sup> UV light. Representative curves are presented as the third cycle in the DMA.

Table 2. Summary of DMA Results for a Series of Alkyne Monomers AL-(1-3) with a Single Azide Monomer (AZ-2 or AZ-4) Composed 2 mol % CuCl<sub>2</sub>[PMDETA] and 4 mol % DMPA and Cured with 10 mW/Cm<sup>2</sup> UV Light<sup>*a*</sup>

	azide monomer (AZ-2)			
alkyne cross-linker	AL-1	AL-2	AL-3	
$T_{g}$ (°C)	67	63	73	
$E_{30^{\circ}\mathrm{C}}$ (GPa)	2.2	1.9	1.8	
E at $T_g$ + 40 °C (MPa)	3.4	2.9	2.1	
$\rho (g/cm^3)$	~1.2	~1.1	$\sim 1$	
$M_{\rm c}$ (g/mol)	~1500	~1600	~2100	
	azide monomer (AZ-4)			
	azid	e monomer (A2	L-4)	
alkyne cross-linker	AL-1	e monomer (AZ	AL-3	
alkyne cross-linker T <sub>g</sub> (°C)	AL-1 81	e monomer (A2 AL-2 90	AL-3 -	
alkyne cross-linker T <sub>g</sub> (°C) E <sub>30°C</sub> (GPa)	AL-1 81 1.4	e monomer (A2 AL-2 90 1.8	AL-3 – –	
alkyne cross-linker $T_{g}$ (°C) $E_{30 \circ C}$ (GPa) $E$ at $T_{g}$ + 40 °C (MPa)	AL-1 81 1.4 2.1	e monomer (A2 AL-2 90 1.8 6.7	AL-3 - - -	
alkyne cross-linker $T_{g}$ (°C) $E_{30 °C}$ (GPa) $E$ at $T_{g}$ + 40 °C (MPa) $\rho$ (g/cm <sup>3</sup> )	AL-1 81 1.4 2.1 ~1.1	e monomer (A2 AL-2 90 1.8 6.7 ~1.3	AL-3 - - - - -	

 ${}^{a}\rho$  is the density of the material estimated from the dimension and mass of the sample;  $M_c$  is the molecular weight between cross-links calculated from the equation  $M_C = 3\rho RT/2E$ , where R is the gas constant; (–) represents no data collected because AZ-4 and Al-3 are both solid monomers and no resin was formulated.

MPa for AL-1 to ~6.7 MPa for AL-2 likely due to improved  $\pi-\pi$  stacking as discussed above.

Lastly, a single resin was formulated without the addition of the radical initiator (DMPA), and instead, the copper was chemically reduced using hexylamine. Through this process, no spatial or temporal control was achieved; however, the mechanical properties are within error of the same resin cured photolytically (i.e., through a radical reduction of copper) (Figure S21). This outcome verifies that the structure of the triazole-containing polymer is dictating the behavior in contrast to the initiation method used to form the polymer.

In addition to the cores of the monomer structures imparting mechanical performance and characteristics, the triazoles themselves can interact with both  $\pi - \pi$  stacking and H-bonding<sup>27-29</sup> that is unique to the CuAAC polymerization. To study the effect of the triazole secondary interactions on mechanical behavior, alternative analogous monomers (2-SH and X-ene, shown in Figure 5b) were synthesized to create thiol-ene networks in which all else (i.e., backbone, cross-link density, etc.) is equivalent to the CuAAC networks, but the triazoles are effectively replaced by thioethers. It is hypothesized that a CuAAC-based network has the potential for improved thermomechanical behavior as compared to other "click" and especially photo-"click"-based polymeric systems. The triazole adduct, compared to a thioether produced from a thiol-ene or thiol-Michael "click" reaction, for example, produces a stiffer material; however, only minimal attempts to observe this have been conducted. Gong et al. compared a CuAAC-based network to a thiol-Michael network of similar cross-link density; however, the structural dissimilarities of the



**Figure 5.** (a) Plots of tan  $\delta$  vs temperature and storage modulus vs temperature for analogous materials made from either the (a) thiol–ene or CuAAC reactions and (b) the generalized polymeric structure. The thiol–ene resin composed 4 mol % DMPA and the CuAAC resin composed 2 mol % CuCl<sub>2</sub>[PMDETA] and 4 mol % DMPA, and both were cured with 10 mW/cm<sup>2</sup> UV light. Representative curves are presented as the third cycle in the DMA.

Table 3. Functional Group (FG) Ratios of Three Different Monomers (AZ-2, AL-1, and AL-4) Used To Create an Off-Stoichiometric Resin with Excess Azide Functionality with the Resulting Azide Conversions and Material Properties Including  $T_g$  and Molecular Weight between Cross-Links ( $M_c$ ) As Calculated from Rubber Elasticity Included

AZ-2 monomer (FG eq)	AL-4 monomer (FG eq)	AL-1 monomer (FG eq)	theor azide conv (%)	measd azide conv (%)	$T_{g}$ (°C)	$M_{\rm c}~({\rm g/mol})$
1 eq	0.5 eq alk	0.25 eq alk	75	74	46	~85000
1 eq	0.4 eq alk	0.4 eq alk	80	83	51	~20000
1 eq	0.2 eq alk	0.7 eq alk	90	91	59	~9000
1 eq	0 eq alk	1 eq alk	100	~99	67	~1600
(a) 2.5 2.0 1.5 1.5 0.5 0.0 0.5	her $T_9 = 41 ^{\circ}C$ rbamate $T_9 = 81 ^{\circ}C$ 25 50 75 100 1	(b) CuAA $= 0 - AL-1 - CuAAA$ $= 0 - AL-1 - CuAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAA$	AC - Ether	<sup>1</sup> (0,1,1,1,0) 0 1(0,1,1,1,0)\\1(0,1,1,1,0)\\1(0,1,1,1,0)\\1(0,1,1,1,0)\\1(0,1,1,1,0)\\1(0,1,1,1,0)\\1(0,1,1,1,0)\\1(0,1,1,1,0)\\1(0,1,1,1,0)\\1(0,1,1,1,0)\\1(0,1,1,1,0)\\1(0,1,1,1,0)\\1(0,1,1,1,0)\\1(0,1,1,1,0)\\1(0,1,1,1,0)\\1(0,1,1,1,0)\\1(0,1,1,1,0)\\1(0,1,1,1,1,0)\\1(0,1,1,1,1,0)\\1(0,1,1,1,1,0)\\1(0,1,1,1,1,0)\\1(0,1,1,1,1,1,0)\\1(0,1,1,1,1,1,1,1,1,1,1,1,1,1,1,1,1,1,1,		- Na
10000 =	Temperature (°C)	CuA/	AC - Carbamate		~ ~ r	
orage Modulus (MPa)	— Ethe	AL-1		о ни ни о о о о о о т	н м о о т т т т с о с о т с о с о с о с о с	r
<b>ö</b> 1	25 50 75 100 1: Temperature (°C)	25 150 N <sub>3</sub>	~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~	N N N N N N N N N N N N N N N N N N N	$\sim$	N <sub>3</sub>

Figure 6. (a) Plots of tan  $\delta$  vs temperature and storage modulus vs temperature for comparing analogues materials made from monomers with and without carbamates and (b) the generalized polymeric structure. Both resins composed 2 mol % CuCl<sub>2</sub>[PMDETA] and 4 mol % DMPA, and both were cured with 10 mW/cm<sup>2</sup> UV light. Representative curves are presented as the third cycle in the DMA.

monomers limit the comparison<sup>25</sup> and as shown previously have a significant impact on material properties. Here, a thiol and ene monomer are synthesized with the specific intent of directly comparing the relative impact of the triazole and thioether moieties. Figure 5 shows the comparison between nearly identical CuAAC and thiol—ene-based networks, where a significant increase in  $T_g$  of nearly 50 °C was observed as a result of the triazole presence. Additionally, an additional thiol—ene-based resin was formulated, cured, and analyzed using the alkene analogue of AL-2 and showed a similar drop in  $T_g$  of about 45 °C when comparing the CuAAC network to a thiol—ene analogue (Figure S22). These results point to the dramatic impact of the triazole moiety within the network structure.

The difference in material performance is purely a result of the polymerization, forming the triazole adducts which are rigid and capable of both  $\pi-\pi$  and H-bonding interactions. Few polymerization techniques and no other photopolymerization techniques possess this capability, making these materials

unique as a significant portion of the desirable material performance arises directly from the moiety formed during the photopolymerization. In particular, it would be desirable to perform polymerizations at different conversions and observe the evolution of the mechanical behavior of the material at those different extents of reaction. Unfortunately, this approach is dificult in CuAAC-based networks since, as the partially cured networks are heated, the catalyst becomes more mobile allowing conversion to increase. Here, we use off-stoichiometric experiments as mimics of the evolution of conversion. In particular, we synthesized AL-4, which is a difunctional analogue of the trialkyne, AL-1, but with one alkyne replaced with a saturated alkyl chain. By systematically replacing a portion of the AL-1 with AL-4, we alter the azide-alkyne stoichiometry such that at complete conversion of the alkyne, the network mimics a network with incomplete conversion.

Here, however, no additional CuAAC reaction occurs upon heating since no residual alkyne is present. Thus, these offstoichiometry studies were designed and performed to observe the buildup of material properties as the concentration of triazoles increases during polymerization within a network structure that remains largely the same other than the extent of cross-linking/triazole formation. Table 3 presents the resulting material properties achieved when AL-4 is systematically substituted for AL-1 in such a manner that mimic a 75%, 80%, and 90% azide conversions were achieved. As the AL-4 monomer is reduced and the ratio of alkyne to azide functional groups approaches a 1:1 molar ratio, the  $T_g$  increases as a result of the increasing triazole concentration and the molecular weight between cross-links ( $M_c$ ) significantly decreasing. The DMA curves for these samples are provided in the Supporting Information (Figures S23–S25).

Lastly, a major contributor to the mechanical performance likely results from the carbamate structures inherently incorporated into the network via the monomer synthesis approach broadly used here. To investigate this relationship, a monomer containing no carbamates (4-ether, shown in Figure 6b) that is structurally similar to AZ-4 was synthesized. Figure 6 shows the modulus and glass transition temperature for networks both with and without the carbamates. A significant dependence on the carbamate presence is observed as a decrease in glass transition temperature of ~40 °C occurred upon removal of the carbamates from the analogous networks. Within these networks, the carbamates improve the mechanical performance through hydrogen bonding and the formation of hard segments, generally resulting in an increase in  $T_{g}$ . For all of these resins, FTIR was used to confirm near-quantitative conversion of the polymerizable functional groups following the thermal cycles.

# CONCLUSIONS

In summary, the materials developed using the photoinitiated CuAAC polymerization show vast tailorability of mechanical properties, and the unique ability to form a high glass transition temperature material, which is shown to occur from the step growth photopolymerization itself. Both the monomer structure and the polymerization technique utilized have a significant impact on the material properties where the monomers are easily changed and tailored as a result of the simple and scalable synthesis techniques utilized. Lastly, the triazoles generated during the polymerization and the carbamates incorporated into the monomers drastically increase the  $T_{\rm g}$  by 45–49 and 40 °C, respectively, due to secondary interactions (H-bonding,  $\pi - \pi$  stacking, and chain stiffness). Few polymerization techniques and particularly no other photopolymerization techniques possess the capability for altering the material properties so directly from the moiety formed during the photopolymerization. Of all the photopolymerization techniques, the photo-CuAAC-based materials show the highest potential for creating glassy step growth materials with spatial and temporal control over the reaction.

#### ASSOCIATED CONTENT

#### **S** Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.macro-mol.6b00137.

<sup>1</sup>H NMR and <sup>13</sup>C NMR along with supporting FTIR and DMA results are detailed (PDF)

# AUTHOR INFORMATION

#### **Corresponding Author**

\*E-mail christopher.bowman@colorado.edu (C.N.B.).

#### Notes

The authors declare no competing financial interest.

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