Published in final edited form as:

Polymer (Guildf). 2014 November 5; 55(23): 5880–5884. doi:10.1016/j.polymer.2014.08.001.

Photo-Mediated Copper(I)-Catalyzed Azide-Alkyne Cycloaddition (CuAAC) “Click” Reactions for Forming Polymer Networks as Shape Memory Materials

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Abstract

The formation of polymer networks polymerized with the Copper (I) – catalyzed azide – alkyne cycloaddition (CuAAC) click reaction is described along with their accompanying utilization as shape memory polymers. Due to the click nature of the reaction and the synthetic accessibility of azide and alkyne functional-monomers, the polymer architecture was readily controlled through monomer design to manipulate crosslink density, ability for further functionalization, and the glass transition temperature (55 to 120°C). Free strain recovery is used to quantify the shape memory properties of a model CuAAC network resulting in excellent shape fixity and recovery of 99%. The step growth nature of this polymerization results in homogenous network formation with narrow glass transitions ranges having half widths of the transition close to 15°C for these materials resulting in shape recovery sharpness of 3.9 %/°C in a model system comparable to similarly crosslinked chain growth polymers. Utilization of the CuAAC reaction to form shape memory materials opens a range of possibilities and behaviors that are not readily achieved in other shape memory materials such as (meth) acrylates, thiolene, thiol-Michael, and poly(caprolactone) based shape memory materials.

Keywords

Shape Memory Polymers; Click Chemistry; Azide; Alkyne; Photo-“Click”

Introduction

Shape memory polymers (SMPs) are a class of smart, actuating materials that have the ability to hold a temporary shape while returning to a desired permanent shape rapidly and with great fidelity upon exposure to a specific stimulus. These smart materials have found a variety of applications including biomedical devices[1], functional surfaces[2], textiles[3], and aerospace structures.[4] The traditional thermally activated shape memory cycle in

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polymers requires heating the material above a transition temperature associated with the polymer network such as a glass transition (T_g) or melting temperature (T_m) followed by the deformation of the material into a temporary shape followed by cooling below the transition temperature to fix the temporary shape. Finally, when exposed to a temperature above or close to the transition temperature, the permanent shape of the material is restored. A permanent network structure, usually in the form of chemical bonds or strong physical crosslinks, is required to “remember” the original shape, which can be restored after heating through the transition.[5] Recent focus in the field has shifted towards engineering SMPs to achieve desired properties like high glass transitions[6], soft shape memory[7], triple and even multiple shape memory[8], and light induced shape memory[9, 10] among others.

An impressive collection of work in the smart materials arena has focused on implementing a range of various chemistries for polymer structure and formation including polyurethanes[11], poly(caprolactone)[12–14], (meth)acrylates[15–17], ionomers[8], and thiol-ene chemistry[18]. In considering the possibility for using distinct polymerization reactions to form smart materials, the click paradigm represents a significant leap forward in its capacity for enabling molecular design that would improve the control of various macroscopic physicochemical properties. Kolb, Finn, and Sharpless first introduced the click chemistry concept in 2001 describing it as clean, versatile, and efficient chemistry that proceeds in facile reaction conditions with high yields and no byproducts.[19]

Click chemistry has previously been used in crosslinking and functionalization of SMPs. For example, thermoreversible Diels-Alder click chemistry was used to crosslink crystallizable segments to create triple-shape memory materials that have the advantage of being reconfigurable at high temperatures and acting like a crosslinked network at lower temperatures.[20] The CuAAC reaction in particular has been used to chemically modify dynamic surfaces of a SMP by incorporating azide-containing monomers into the backbone that were then further functionalized with alkyne dyes.[2] CuAAC has also been used to chemically crosslink an otherwise linear polyphenol resin by functionalizing the resin with alkynes and reacting them with a bisphenol A based di-azide.[21] In this approach the crosslinked polymer could be used for shape memory because it now had a permanent network structure.

In work related to the approach taken here, other click reactions have been used as a step-growth polymerization reaction to form polymer networks as SMPs. A primary advantage of step growth networks is that they inherently have a more uniform distribution of crosslinks that leads to a sharper glass transition, corresponding to a reduced half width of the glass transition peak. In particular, thiol-ene and thiol-Michael click chemistries have been used to form crosslinked SMPs via a step growth polymerization with excellent shape fixity, free strain recovery and recovery sharpness.[18] As demonstrated in the thiol-Michael reaction, the click reaction paradigm has an additional advantage of self-limiting, stoichiometric reactions. In the implementation of the thiol-Michael reaction with a thiol-acrylate step growth polymerization[22], the click reaction used a stoichiometric excess of the acrylate to leave residual acrylate functional groups that are available for a subsequent, triggerable reaction. In the case of the thiol-Michael reaction, the residual acrylate moieties were used

for triggering a second polymerization stage that increased the modulus and crosslink density.

Among all of the click reactions that exist, the CuAAC reaction is often referred as “the” click reaction due to its desirable characteristics and ubiquitous implementation. It is a robust reaction with easily accessible reactive groups, making it a simple method for modifying and controlling polymer architecture and physicochemical behavior.[23] Although this reaction is used extensively, little work has employed it as a bulk polymerization reaction mechanism to form crosslinked networks. Recent work that enabled photoinitiation of this reaction has expanded the utility of this reaction by enabling spatiotemporal control over the CuAAC, making bulk polymerizations of this type relatively trivial in comparison with traditional CuAAC initiation methods.[24, 25] By enabling the CuAAC-based reaction to be used as a polymerization reaction in the formation of crosslinked polymers, a wide array of monomers and orthogonal chemistries are readily incorporated into the ultimate polymer structure. When a multifunctional azide and alkyne are reacted (Figure 1), a polymer network is formed with relatively independent control over the crosslink density (by monomer functionality), T_g (by monomer stiffness and molecular weight), solvent interactions (monomer core), and secondary interactions (monomer core) as well as other physicochemical attributes. In particular, the formation of a stiff triazole ring structure dramatically increases the modulus and glass transition temperature of these materials relative to other conventional step growth polymers.[26] Additionally, the CuAAC reaction (analogous to the thiol-Michael example highlighted above) is able to leave residual azide or alkyne groups that are useful for subsequent clickable modifications of the SMP.

The goal of this work is then to contribute to the toolbox of polymerization reactions available to engineer the mechanical and chemical properties of SMPs by examining the shape memory properties of click polymer networks formed from the CuAAC reaction. The shape memory behavior of model CuAAC networks formed by photopolymerization is examined and structure-property relationships are discussed. A major distinction in this approach to form CuAAC-based SMP networks is that the CuAAC click reaction is used as the polymerization reaction that forms the basic SMP network and not just as a means of postpolymerization crosslinking or functionalization. By using it as the polymerization reaction to form the parent network of the polymer, uniform networks are formed, and mechanically and chemically tunable SMPs are readily developed.

Methods

Materials

Triethylamine, propargyl acrylate, propargyl bromide (80 wt% in Toluene), 1,1,1-tris(hydroxymethyl)propane, potassium hydroxide, sodium azide, bisphenol A diglycidyl ether, lithium perchlorate, CuCl_2 , and N,N,N',N',N'' -pentamethyldiethylenetriamine (PMDETA), dimethylsulfoxide (DMSO), ethyl acetate, acetonitrile, t-butyl acrylate (tBA), tri(ethylene glycol)dimethylacrylate (triEGDMA), poly(ethylene glycol) diacrylate (MW~575) were obtained from Sigma Aldrich and used as received. Pentaerythritol tetra-3-mercaptopropionate (PETMP) was donated by Evans Chemetics. CuCl_2 /PMDETA, 1-(prop-2-ynyloxy)-2,2-bis(prop-2-ynyloxymethyl)butane, and bisphenol A di(3-azido-2-

hydroxy propan-1-ol) ether **3** are prepared according to a previous procedure.[26] The SMP control or comparison materials comprised of a chain growth, tBA + triEGDMA + PEGDA (MW~575), was chosen because this composition has a comparable glass transition and rubbery modulus to the targeted materials produced here.

Synthesis of 8,12-Dioxa-4,16-dithianonadecanedioic acid, 7,13-dioxo-10,10-bis[[1-oxo-3-[[3-oxo-3-(2-propyn-1-yloxy)propyl]thio]propoxy]methyl]-, 1,19-di-2-propyn-1-yl ester (PETMP tetra-yne) **1**

PETMP tetra-yne was synthesized similar to a procedure reported previously.[27] Pentaerythritol tetra-3-mercaptopropionate (PETMP, 7.89 g, 16.1 mmol) and a catalytic amount of triethylamine (TEA, 600 μ L) were mixed together in a round bottom flask. Then, propargyl acrylate (7.11 g, 64.6 mmol) was added dropwise and the reaction mixture was allowed to stir at ambient temperature overnight. TEA was then removed under high vacuum to afford the resulting PETMP tetra-yne **1** as a slightly yellow liquid (15 g, 16.1 mmol, 99%), which was directly used without further purification. ^1H NMR (CDCl_3 , 400 MHz): δ 4.71 (d, 8H, $J = 4$ Hz), 4.15 (s, 8H), 2.81 (m, 16H), 2.66 (m, 16H), 2.51 (t, 4H, $J = 4$ Hz).

Sample Preparation

Samples that include the PETMP tetra-yne **1** were prepared by dissolving $\text{CuCl}_2/\text{PMDETA}$ (2 mol%) and DMPA (4 mol%) into BPA-diazide **3** with a SpeedmixerTM DAC 150 (Flacktek, Inc.), followed by the addition and mixing of the PETMP tetra-yne **1** in approximately a 1:1 mole ratio based on the two functional groups. Polymer sheets with thicknesses of 0.25 mm were irradiated with 5 mW/cm² light intensity (Black-Ray Model B 100 AP) for 5 to 10 minutes then annealed at 100°C for 1 hour to achieve high functional group conversion.

Samples that include the trialkyne **2** were prepared by using approximately 20 wt% methanol to homogenize the 2 mol% $\text{CuCl}_2/\text{PMDETA}$, 4 mol% Irgacure 651, and monomer **2** and **3** followed by removal of methanol under vacuum and irradiation with 5 mW/cm² (Black-Ray Model B 100 AP) at 80°C for 5 minutes and annealing at 100°C for 3 hours.

SMP control samples that were used to provide a comparison based on a common, previously used formulation were prepared by mixing 80 wt% tBA, 15 wt% triEGDMA, and 5 wt% PEGDA575 with 0.7 wt% DMPA. The mixture was pressed between two glass plates with 0.25 mm spacers and irradiated with 5 mW/cm² light intensity (Black-Ray Model B 100 AP) for 5 to 10 minutes followed by annealing at 100°C for 1 hour. This system was chosen because it has a comparable glass transition and rubbery modulus (i.e., crosslink density) as the model CuAAC system.

Dynamic Mechanical Analysis (DMA)

DMA experiments were performed in tension on a TA Instruments Q800 DMA with rectangular sample dimensions of 15×5×0.25 mm. For temperature dependent viscoelastic property measurements, the sample was ramped at 3°C per minute from 10 to 90°C with a frequency of 1 Hz and a strain amplitude of 0.025%. The glass transition (T_g) was assigned

as the maximum of the tan delta curve, and the width was defined as the full width at half height (FWHH) of the tan delta peak. For shape memory evaluations, the free strain recovery test was performed in vertical tension clamps by heating the sample to $T_g + 30^\circ\text{C}$, holding for 5 minutes, and deforming at a constant stress rate of 0.1 MPa/min to a stress corresponding to 10–20% tensile strain. The sample was held at constant stress for 5 minutes and rapidly cooled at $20^\circ\text{C}/\text{min}$ to -10°C and held for 5 minutes to determine the maximum strain (ϵ_m). The force was then released to 0.001 N and held for 5 minutes to determine the fixed strain after unloading (ϵ_u). The sample was then heated at $3^\circ\text{C}/\text{min}$ to 90°C and held for 5 minutes where the final recovered strain was measured (ϵ_p). The length of the sample was measured at 20°C , and the resulting strains at higher temperature were between 2 and 5% due to thermal expansion. One thermal cycle was required to reach steady state, and shape memory parameters were calculated from the third cycle. The shape fixity was defined $R_f (\%) = (\epsilon_u/\epsilon_m) \times 100$, and the free strain recovery was defined as $R_r = (\epsilon_u - \epsilon_p) / (\epsilon_m - \epsilon_p) \times 100$. The sharpness of the recovery was defined as $v_r = R_r / T$ where T is the width of the recovery starting from the onset temperature to the temperature when the sample is finished recovering.[5]

Results and Discussion

Mechanical Behavior of CuAAC Polymers

Shape memory behavior was determined for polymer networks polymerized by CuAAC click reactions. The model network chosen is formed by photo“clicking” the multifunctional PETMP tetra-yne **1** and BPA diazide **3** monomers (Figure 2) together into a network. Previous work demonstrated a facile approach to photoinitiate this reaction in the presence of a radical photoinitiator (DMPA or Irgacure 819) which reduces Cu(II) to Cu(I) *in situ* to catalyze the reaction with spatiotemporal control. Traditional approaches to forming CuAAC networks which consist of direct addition of Cu(I)[25] were fraught with challenges because of the spontaneous reaction nature associated with CuAAC reactions. These particular monomers were chosen because they highlight the ease with which both the azide and alkyne functional groups are incorporated into multifunctional monomers. However, it is of note that caution must be applied in designing azide monomers at high azido concentrations; low molecular weight or highly functional azide molecules are potentially dangerous, particularly in bulk or in large quantities. Thus, for this study, **diazide 3** was chosen because the (C + O/N) ratio is safely above 3 and the bisphenol A backbone offers additional stiffness and toughness along with hydrogen binding potential from the hydroxyl moieties. PETMP tetra-yne **1** is trivially synthesized in large quantities from commercially available PETMP in high yields using thiol-Michael click chemistry[29]; however, there are also a variety of ways to synthesize multifunctional alkynes and azides from organic halides, epoxies, isocyanates and alcohols, enabling monomers with tunable backbone structure and number of functional groups to be created with ease. In addition, to highlight the enhanced mechanical properties that are achieved, the CuAAC aliphatic tri-alkyne **2** was chosen because the lower monomer molecular weight contributes to an increase in both the crosslink density and increased glass transition temperature of the network.

The glass transition temperature of the polymer formulated from the PETMP tetra-yne **1** and BPA diazide **3** is observed to be 55 ± 5 °C. The full width at half height (FWHH) of the tan delta peak is used to quantify the homogeneity and sharpness of the glass transition. The FWHH of this system is 15 ± 2 °C similar to other step-growth networks based on thiol-ene chemistry which range from 10 to 20 °C.[18, 30] The CuAAC polymerization, however, has the added advantage of forming an aromatic triazole linkage instead of a flexible thio-ether bond, which affects the mechanical properties by significantly increasing the glass transition temperature.[26] Although thiolene monomers can be designed with rigid cores, giving high glass transition materials, the thioether linkage does not inherently contribute to increasing the glass transition whereas triazoles form a stiff, aromatic linkage that will contribute significantly to an increase in the glass transition. Thus, CuAAC-based approaches enable homogenous polymers networks to be formed with glass transition temperatures above 100 °C by replacing PETMP tetra-yne **1** with the lower molecular weight aliphatic tri-alkyne **2** while still maintaining a narrow glass transition temperature, FWHH of 11 ± 3 °C (Figure 3)

Additionally, the CuAAC click chemistry-based approach to forming SMPs also enables further post-functionalization of the polymer networks. The CuAAC is orthogonal to a myriad of reactions useful for postpolymerization modification. Functional moieties can be included in the polymer by appropriate monomer design. Additionally by formulating a polymer based on a non-stoichiometric ratio of alkyne to azide, residual azides or alkynes remain in the network and are available for any subsequent reactions, thus exploiting the self-limiting nature of the reaction in a similar approach to the one taken by Nair and coworkers[22]. Traditionally, azides and alkynes are used commonly to modify polymer backbones chemically because the reaction proceeds efficiently under dilute conditions[2, 31]. Thus, by implementing the CuAAC click reactions to build a SMP network, the material is also inherently amenable to subsequent chemical modification.

Shape Memory Attributes

The shape memory properties of the polymer network formed from PETMP tetrayne **1** and BPAdiazide **3** were characterized by quantifying the free strain recovery (Figure 4). Implementing the protocol developed by Mather et al.[5], the sample was heated to 90°C and deformed into a temporary shape followed by cooling to preserve the shape. Upon heating, the recovery profile that was achieved is presented in Figure 4. Bulk photopolymerized, step growth networks form uniformly forming a homogeneous network with a sharp glass transition. The mobility in the polymer changes dramatically over a short temperature range, imparting the added benefit of allowing the temporary shape to be stable closer to the transition temperature than would otherwise be possible while also minimizing the required heating necessary to recover the permanent shape. The shape memory properties of the CuAAC polymer network and chain-growth control system are shown in Table 1. The CuAAC exhibits repeatable shape memory cycles with both the recovery ratio and shape fixity above 99%, similar to the (meth)acrylate control; however, the observed recovery occurs over a narrower temperature range that results in a higher recovery sharpness. To demonstrate visually the shape memory behavior, a flat ribbon was heated in a water bath at 85°C and deformed into a coil (Figure 5). The coil was stable at ambient temperature and recovered back to its flat shape in less than a second when immersed in an

85°C water bath. Figure 6 demonstrates the stability of the temporary shape. A coil was set at 85°C followed by rapid cooling to ambient temperature where it was allowed to remain for 1 month with no discernable shape change.

Conclusions

This work has demonstrated a facile methodology for implementing the CuAAC reaction to build polymer networks with outstanding shape memory attributes. Working on the hypothesis that the inherent click, and therefore step growth, nature of the CuAAC reaction should translate to highly desirable material properties for SMPs, polymer networks with shape fixity and recovery ratio of at least 99% with sharper transitions than comparable chain growth systems were developed. Additionally, the CuAAC networks had the added benefit of being tunable with regards to their physicochemical behavior. The step-growth nature of this reaction results in uniform network formation and sharper recovery than in comparable chain growth networks. Azide and alkyne monomers with different structures and functionalities are readily synthesized by a variety of methods, making the high diversity of achievable network mechanical and chemical properties possible.

Acknowledgments

This research was funded by the National Science Foundation (NSF) DMR 1310528, National Institute of Health (NIH) U01 DE023774, a fellowship from the National Science Foundation Graduate Research Fellowship (NSF GRFP), and a fellowship from the Department of Education Graduate Assistance in the Areas of National Need (GAANN) in the area of functional materials.

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- Shape memory attributes of CuAAC polymer networks are studied
- Polymers are developed with T_g 's ranging from 55 to 114°C using the CuAAC
- Polymerization with the CuAAC reaction offers control over the final properties

Figure 1.
Schematic illustration of photoinitiated polymerization of tri-alkyne and diazide monomers to form a crosslinked network.

1 (PETMP tetra-yne)

2 (Aliphatic tri-yne)

3 (BPAdiazide)

Figure 2.

Model CuAAC monomers used to demonstrate the general shape memory behavior of a CuAAC-based network. **(1)** 8,12-Dioxo-4,16-dithianonadecanedioic acid, 7,13-dioxo-10,10-bis[[1-oxo-3-[[3-oxo-3-(2-propyn-1-yloxy)propyl]thio]propoxy] methyl]-, 1,19-di-2-propyn-1-yl ester (PETMP tetra-yne). **(2)** 1-(prop-2-ynyloxy)-2,2-bis(prop-2-ynyloxymethyl)butane (Aliphatic tri-yne). **(3)** Bisphenol A di(3-azido-2-hydroxy propan-1-ol) ether (BPA-diazide).

Figure 3.

Storage Modulus (Top) and Tan Delta (Bottom) of two CuAAC polymer networks made using a stoichiometric combination of BPAdiazide and either PETMP tetra-yne (Red) or aliphatic tri-yne (Black). The T_g , designated as the peak of the tan delta curve, is controlled over a wide range from 55 to 114°C with narrow transitions.

Figure 4.

Free strain recovery of a polymer made from a stoichiometric mixture of PETMP tetra-yne **1** and BPA diazide **3** (A, T_g=55°C) and the control (meth)acrylate polymer (B) over 3 cycles. The sample was heated to 90°C and stressed in tension at a rate of 0.1 MPa/min to a corresponding strain between 10 and 20% strain. The stress was held while the sample was cooled to -10°C. Once at -10°C, the stress was released and the chamber was heated at 3 °C/min to 90°C while the sample recovered. At least 5 minutes were allowed in between

each step to reach steady state, and shape memory parameters in table 1 were calculated from the third cycle.

Figure 5.

Shape fixing and recovery of a CuAAC polymer network. **(A)** A ribbon of the stoichiometric mixture of PETMP tetra-yne **1** and BPAdiazide **3** in its permanent shape (left) is heating and deforming into a coil (middle) followed by immersion in an 85°C water bath to recover the original shape (right). **(B)** The recovery of the flat shape from a coil in 85°C water bath occurs in less than a second.

Figure 6. Coiled temporary shape is stable for extended periods of time. The coil was formed by heating the polymer made from PETMP tetra-yne **1** and BPA diazide **3** to 85°C, deforming, and rapidly cooling to ambient temperature. Left: Initial coil, Right: after 2 days.

Table 1

Onset temperature (T_{onset}), recovery width (T), shape fixity (R_f), free strain recovery (R_r), and recovery sharpness (v_r) of BPAdiazide **3**/PETMP tetra-yne **1**, BPAdiazide **3**/aliphatic tri-yne **2** and (meth)acrylate chain growth control determined from the free strain recovery.

Polymer Network	T_{onset} (°C)	T (°C)	R_f (%)	R_r (%)	v_r (%/°C)
BPAdiazide 3 + PETMP tetrayne 1	39 ± 1	26 ± 1	99 ± 1	99 ± 1	3.9 ± 0.1
BPAdiazide 3 + aliphatic triyne 1	94 ± 3	30 ± 2	99 ± 1	99 ± 1	3.3 ± 0.2
tBA + triEGDMA + PEGDA (MW=575)	46 ± 1	33 ± 1	99 ± 1	99 ± 1	3.0 ± 0.1