

# Rapid Synthesis of Block and Cyclic Copolymers via Click Chemistry in the Presence of Copper Nanoparticles

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**ABSTRACT:** A new method for the rapid and efficient coupling of homopolymers to yield diblock and triblock copolymers as well as cyclic polymers using the  $3 + 2 \pi$  Huisgen copper catalyzed cycloaddition reaction has been developed. This facile method utilizes commercially available Cu nanoparticles that are tolerant to  $O_2$ , easily removable and recyclable.

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**KEYWORDS:** block copolymer; click chemistry; cyclic polymers; heterogeneous catalysis; living free radical polymerization

**INTRODUCTION** The copper-catalyzed Huisgen-dipolar cycloaddition reaction of azides with alkynes (CuAAC), which follows all of the original tenants of click chemistry as detailed by Sharpless,<sup>1</sup> has emerged as an important synthetic tool in the preparation of functional materials. This robust and efficient coupling reaction has been exploited in a wide range of different polymer platforms<sup>2,3</sup> for the preparation of functionalized materials<sup>4</sup> in areas ranging from semiconductor processing<sup>5</sup> to drug delivery.<sup>6</sup> The efficiency of this process offers particular appeal for a major challenge in polymer synthesis—the coupling of chain end functionalized homopolymers to give block copolymers and cyclic polymers in high yield.<sup>7–9</sup> Prior work has demonstrated success in the synthesis of block copolymers by CuAAC; however, the reduced reactivity of polymeric chain ends leads to long reaction times, oxygen poisoning, and difficulty in removing the ligands/copper catalyst.<sup>7,8,10</sup> This lowered reactivity limits many of the examples in the literature to low molecular weight block copolymers, typically 5–10 kDa with selected examples as high as 20 kDa being reported.<sup>7,8,10</sup> As a result, there is a need to optimize the efficiency of CuAAC chemistry for polymer chain end coupling and to develop systems that operate under atmospheric conditions with facile removal of the Cu catalyst. Herein, the use of commercially available and recyclable copper nanoparticles (CuNPs) in combination with microwave reaction conditions leads to the fast and efficient synthesis of high molecular weight block and cyclic copolymers.

## RESULTS AND DISCUSSION

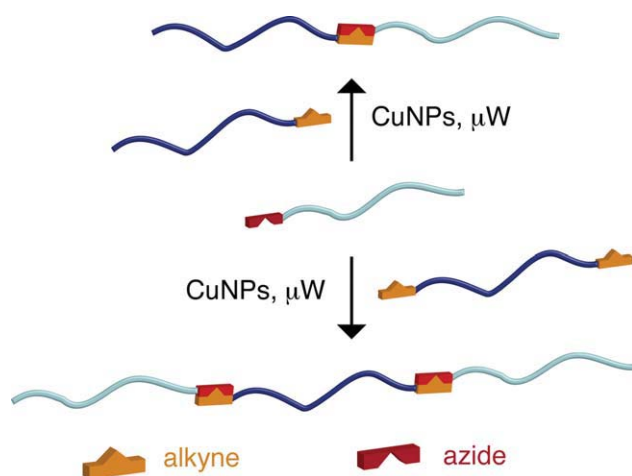
Following the discovery that copper metal can be a source of catalytic species for CuAAC,<sup>11</sup> increasing attention has been

devoted to the application of solid or supported Cu species as catalytic entities to reduce both the catalyst loading and the reaction times.<sup>12–17</sup> In this study, commercially available Cu nanoparticles (nominal size < 50 nm)<sup>18</sup> that can be removed by centrifugation and have low sensitivity to oxygen are shown to be a versatile and robust catalyst for producing advanced macromolecular architectures such as block and cyclic copolymers.

Scheme 1 shows the general procedure for production of macromolecular architectures, such as diblock and triblock copolymers, using click chemistry with microwave irradiation in the presence of CuNPs. Key to the success of these strategies is the preparation of well-defined, chain end functionalized macromolecules prepared by either living radical or ring-opening polymerization (Scheme 2). In a typical diblock copolymer synthesis (Scheme 2), 5.0 kDa poly(ethylene glycol)-acetylene (PEG-alkyne, **1**) and 6.5 kDa polystyrene-azide (PS-N<sub>3</sub>, **5**, 1.2–1.5 eq) homopolymers were dissolved in anisole (1 mL/50 mg PEG). CuNPs (2 mg/50 mg PEG) were added, and the reaction mixture was subjected to microwave irradiation. As the reaction is unaffected by atmospheric oxygen, no purging or inert atmosphere is required and the conversion of the coupling reaction can be easily monitored by gel permeation chromatography (GPC). GPC traces for the CuNPs catalyzed reaction of **1** and **5** demonstrates that full conversion is achieved after only 10 min (Fig. 1). Furthermore, the use of CuNPs simplifies purification as the CuNPs can be easily removed by centrifugation at 3000g for 5 min (Fig. 2), followed by decantation, with the block copolymer (**9**) being isolated in ~90% yield after precipitation. The successful coupling of PEG and PS blocks was

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**SCHEME 1** Schematic representation of the synthesis of diblock and triblock copolymers via chain end coupling of azide and alkyne homopolymers in the presence of CuNPs.

confirmed by multidetector GPC as well as  $^1\text{H}$  nuclear magnetic resonance (NMR) spectroscopy, which showed the expected resonances that are unique for each block. Additionally, the level of residual copper in the purified products was examined by atomic absorption spectroscopy and shown to be less than 200 ppm, which is significantly lower than that observed for both traditional soluble and insoluble catalysts (ca. 500–2000 ppm)<sup>4</sup> and represents removal of >97% of the copper with a single centrifugation step.

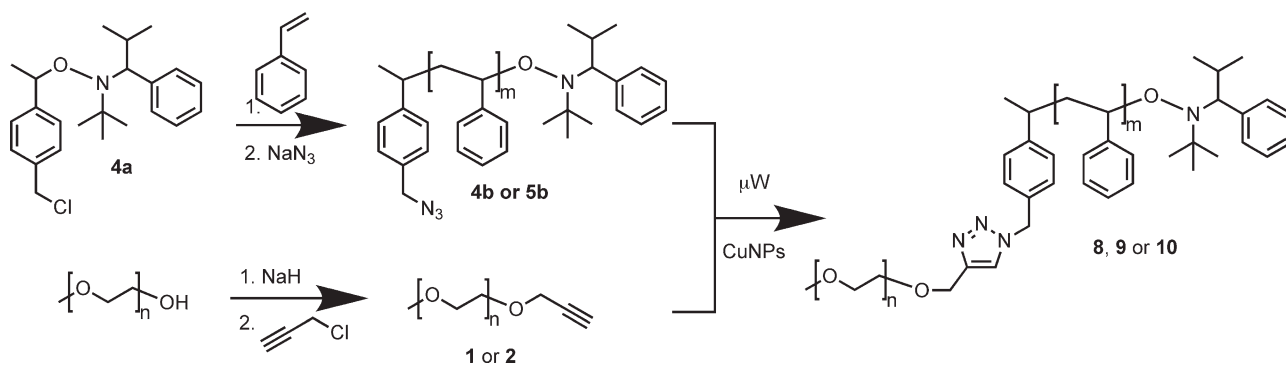
The success of this initial block copolymer coupling reaction prompted an examination of the synthesis of higher molecular weight PEO-*b*-PS and PS-*b*-PMMA diblock and triblock copolymers using CuNPs and microwave irradiation. As shown in Table 1, formation of diblock and triblock with moderate molecular weights (ca. 8–24 kDa) typically required irradiation for 10 min to reach completion (**8–11**). In the case of the higher molecular weight, PS-*b*-PMMA diblock copolymer, **12**, longer reaction times (4 h) were required to achieve high coupling yields due to the low concentration and steric hindrance of chain end groups.

Another advantage of the CuNPs is their tolerance to atmospheric and dissolved oxygen, which allows for catalyst recy-

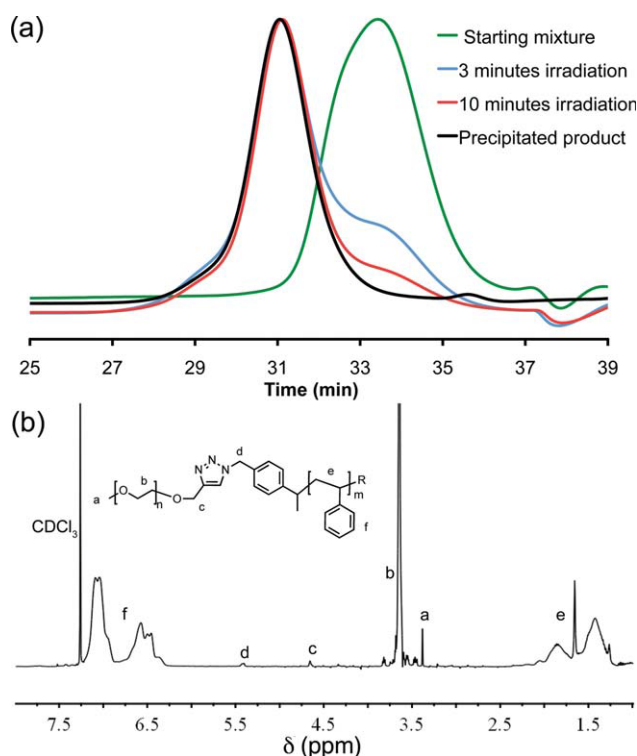
cling. To examine the level of insensitivity of the reaction to oxygen, the coupling of **5** and **1** in the presence of recycled CuNPs was examined (Table 2). Recycling of the catalyst was performed by centrifugation of the initial reaction solution, removal of the supernatant, addition of additional aliquots of the starting homopolymer reaction mixture to the CuNP residue, stirring to redisperse followed by repetition of the microwave irradiation. Significantly, no decrease in reaction rate was observed after four recycling reactions. In addition, control reactions without CuNPs were performed and negligible coupling was observed demonstrating the absence of any background thermal reaction under these conditions (Fig. 3). Interestingly, addition of CuNPs to these previously irradiated control samples led to essentially complete coupling under standard reaction conditions, demonstrating that both the azido and acetylene chain ends are stable under microwave irradiation and do not undergo reaction in the absence of the CuNP catalyst (Fig. 3).

The efficiency and recyclability of CuNPs for the synthesis of diblock and triblock copolymers also suggested their use in the formation of cyclic polymers (Scheme 3). The suitability of Cu nanoparticles for cyclic polymer formation arises from the heterogeneous nature of the catalyst, which may allow the acetylene or azide chain end to bind to the nanoparticle surface with cyclization being favored due to the partial immobilization of the chain. Additionally, the insensitivity of the CuNPs to deactivation permits stepwise or continuous addition of a concentrated hetero-bifunctional linear polymer solution to the reaction mixture.<sup>19,20</sup> The speed of the reaction coupled with the inert nature of the cyclic product then alleviates the ultradilute conditions normally required for cyclic polymer formation. By recycling the catalyst and repetitively adding more aliquots of linear polymer every 15 min, moderate to high yields could be achieved in a few hours. This allows for higher concentrations and shorter reaction times providing significant advantage over the conventional click route to cyclic polymers, which requires large amounts of oxygen-sensitive CuBr complex and extremely dilute solutions.<sup>21</sup>

When compared with prior batch approaches, this repetitive addition strategy leads to increased final cycle concentrations coupled with a dramatic improvement in the time



**SCHEME 2** Synthesis of end-functionalized homopolymers and the resultant diblock copolymer.



**FIGURE 1** (a) GPC elution profiles for coupling of 5.0-kDa PEG-acetylene, **1**, and 6.5 kDa PS-N<sub>3</sub>, **5**, to yield PEG-*b*-PS, **9**. (b) <sup>1</sup>H NMR spectrum of polymer **9**.

needed for cycle formation. For example, approximately 15–20 mg of cyclic polymer could be produced in 5–10 mL of solvent in <1 h under our conditions. In direct contrast, it takes more than 24 h to produce less than ~5 mg of cyclic polymer per 10 mL of solvent using the traditional high dilution strategy.<sup>21</sup> Recently, Lonsdale et al. have produced cyclic polymers in higher concentration using homogenous catalysts and preparative GPC.<sup>22</sup> Characterization of the products (Table 3) obtained from the repetitive addition of hetero-bifunctional linear PEG



**FIGURE 2** Representative image showing separation of CuNPs by centrifugation.

**TABLE 1** Results for the Formation of Diblock and Triblock Copolymers

| No. | Polymer  | $M_n$ (Da) <sup>a</sup> | $M_w$ (Da) <sup>a</sup> | PDI <sup>a</sup> | Time   |
|-----|--|-------------------------|-------------------------|------------------|--------|
| 1   | PEG <sub>5k</sub> -alkyne  | 11,400                  | 11,900                  | 1.04             | –      |
| 2   | PEG <sub>10k</sub> -alkyne   | 22,800                  | 24,600                  | 1.08             | –      |
| 3   | Alkyne-PEG <sub>10k</sub> -alkyne  | 23,900                  | 26,100                  | 1.09             | –      |
| 4   | PS <sub>3k</sub> -N <sub>3</sub>   | 3000                    | 3900                    | 1.30             | –      |
| 5   | PS <sub>7k</sub> -N <sub>3</sub>   | 6500                    | 8000                    | 1.24             | –      |
| 6   | PS <sub>44k</sub> -N <sub>3</sub>  | 44,000                  | 56,600                  | 1.29             | –      |
| 7   | PMMA <sub>60k</sub> -alkyne  | 60,800                  | 78,200                  | 1.29             | –      |
| 8   | PS <sub>3k</sub> - <i>b</i> -PEG <sub>5k</sub>                               | 14,200                  | 15,400                  | 1.08             | 10 min |
| 9   | PS <sub>7k</sub> - <i>b</i> -PEG <sub>5k</sub>                               | 18,300                  | 20,600                  | 1.13             | 10 min |
| 10  | PS <sub>7k</sub> - <i>b</i> -PEG <sub>10k</sub>                              | 25,200                  | 29,900                  | 1.19             | 10 min |
| 11  | PS <sub>7k</sub> - <i>b</i> -PEG <sub>10k</sub> - <i>b</i> -PS <sub>7k</sub> | 32,800                  | 39,600                  | 1.21             | 10 min |
| 12  | PS <sub>44k</sub> - <i>b</i> -PMMA <sub>60k</sub>                            | 83,100                  | 11,000                  | 1.32             | 4 h    |

<sup>a</sup> GPC calibrated to PS standards.

showed the products to be pure cyclic polymer with little or no evidence of unreacted linear polymer or higher molecular weight materials by a combination of GPC, NMR, and matrix assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectrometry (Figs. 4 and 5).

As shown in Figure 5(a), NMR spectroscopy showed the complete disappearance of resonances for the acetylene and azide end groups of the starting linear polymer and appearance of the expected triazole resonance at 7.80 ppm. Similarly, comparison of the MALDI mass spectra for the starting linear polymer with the cyclic product revealed the expected conservation of molecular weight [Figs. 4(b) and 5(b)] while high-resolution MALDI analysis [Fig. 5(c)] shows loss of N<sub>2</sub> for the linear polymer with an azide end group and only the molecular ion for the cyclic analog. Final confirmation of cyclization was obtained by comparison of the GPC elution profiles for the linear and cyclic polymers that showed the characteristic longer retention time for a cyclic polymer when compared with its linear analog [Fig. 4(a)].<sup>23,24</sup>

## EXPERIMENTAL

### Materials

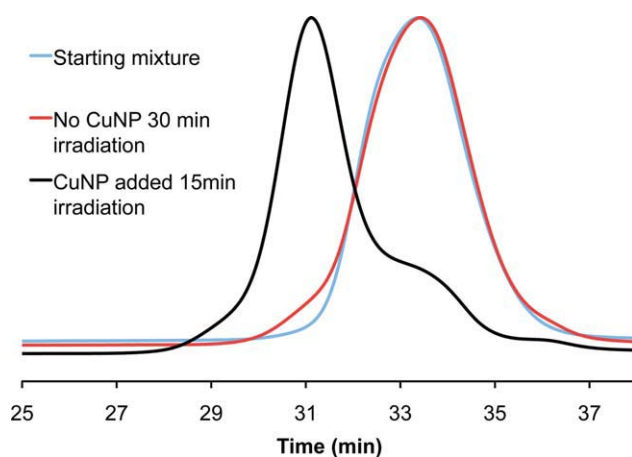
Chemicals were purchased from Sigma-Aldrich (St. Louis, MO) and used without further purification unless otherwise

**TABLE 2** Results for Click Reactions with Recycled Copper Catalyst

| No.  | Polymer  | $M_n$ (Da) <sup>a</sup> | $M_w$ (Da) <sup>a</sup> | PDI <sup>a</sup> | Time (min) <sup>b</sup> |
|------|--|-------------------------|-------------------------|------------------|-------------------------|
| 13.1 | PS <sub>3k</sub> - <i>b</i> -PEG <sub>5k</sub> | 14,500                  | 15,400                  | 1.06             | 15                      |
| 13.2 | PS <sub>3k</sub> - <i>b</i> -PEG <sub>5k</sub> | 14,400                  | 16,500                  | 1.15             | 15                      |
| 13.3 | PS <sub>3k</sub> - <i>b</i> -PEG <sub>5k</sub> | 14,200                  | 16,000                  | 1.13             | 15                      |
| 13.4 | PS <sub>3k</sub> - <i>b</i> -PEG <sub>5k</sub> | 14,200                  | 16,000                  | 1.13             | 15                      |

<sup>a</sup> GPC calibrated to PS standards.

<sup>b</sup> Essentially complete conversion was observed.

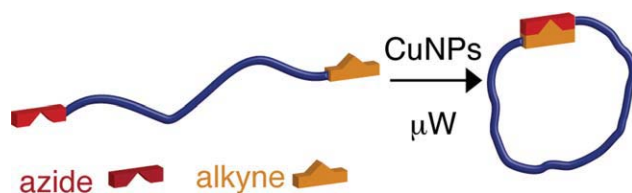


**FIGURE 3** GPC elution profiles for the control reaction of 5.0-kDa PEG-alkyne (**1**) with 6.5 kDa PS-azide (**5**, 1.2 eq) at 160 °C without CuNPs (30 min, crude) followed by addition of CuNPs and reaction at 160 °C (15 min, crude).

stated. Functionalized PEG derivatives were obtained from Intezyme Technologies, (Tampa, FL). PEG-alkyne,<sup>5</sup> chloro-functional NMP initiator **4a**,<sup>25</sup> alkynyl RAFT agent,<sup>26</sup> and 4-pentynoic anhydride<sup>27</sup> were prepared as reported previously.

### Instrumentation

Polymeric materials were characterized by <sup>1</sup>H NMR spectroscopy using a Bruker 500-MHz spectrometer with the residual solvent signal as an internal reference. GPC was performed in DMF on a Waters system (Millford, MA) equipped with four 5-mm Waters columns (300 × 7.7 mm) connected in series with increasing pore size (10<sup>2</sup>, 10<sup>3</sup>, 10<sup>4</sup>, and 10<sup>6</sup> Å). Waters 410 differential refractometer index and Waters 996 photodiode array detectors were used. The molecular weights of the polymers were calculated relative to linear PS or PEG standards. MALDI-TOF mass spectroscopy was conducted on a Bruker UltraFlex MALDI-TOF MS with SCOUT-MTP Ion Source (Bruker Daltonics, Bremen) equipped with a N<sub>2</sub>-laser (337 nm), a gridless ion source and reflector design. All spectra were acquired using a reflector-positive method with an acceleration voltage of 25 kV and a reflector voltage of 26.3 kV. The detector mass range was set to 1000–9000 Da to exclude high-intensity peaks from the lower mass range. The laser intensity was set to the lowest value possible to acquire high-resolution spectra. The obtained spectra were analyzed with FlexAnalysis Bruker Daltonics, Bremen, version 2.2. The instrument was cali-



**SCHEME 3** Schematic representation of CuNP-catalyzed cyclization of polymers.

**TABLE 3** Results for Click Reactions with Recycled Copper Catalyst

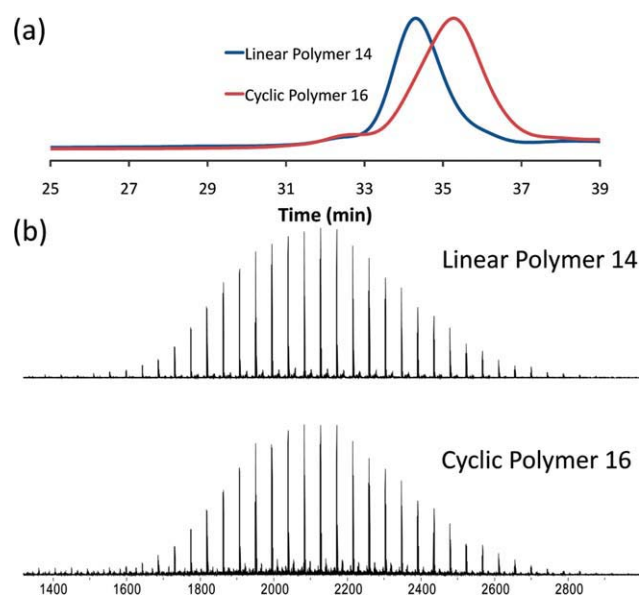
| No. | Polymer                                     | $M_n$ (Da) <sup>a</sup> | $M_w$ (Da) <sup>a</sup> | PDI <sup>a</sup> | Time       |
|-----|---|-------------------------|-------------------------|------------------|------------|
| 14  | N <sub>3</sub> -PEG <sub>2k</sub> -alkyne   | 2100                    | 2400                    | 1.14             | –          |
| 15  | N <sub>3</sub> -PEG <sub>4.5k</sub> -alkyne | 4400                    | 4600                    | 1.05             | –          |
| 16  | Cyc-PEG <sub>2k</sub>                       | 1500                    | 1800                    | 1.20             | 9 × 10 min |
| 17  | Cyc-PEG <sub>4.5k</sub>                     | 3400                    | 3800                    | 1.12             | 5 × 20 min |

<sup>a</sup> GPC calibrated to PEG standards.

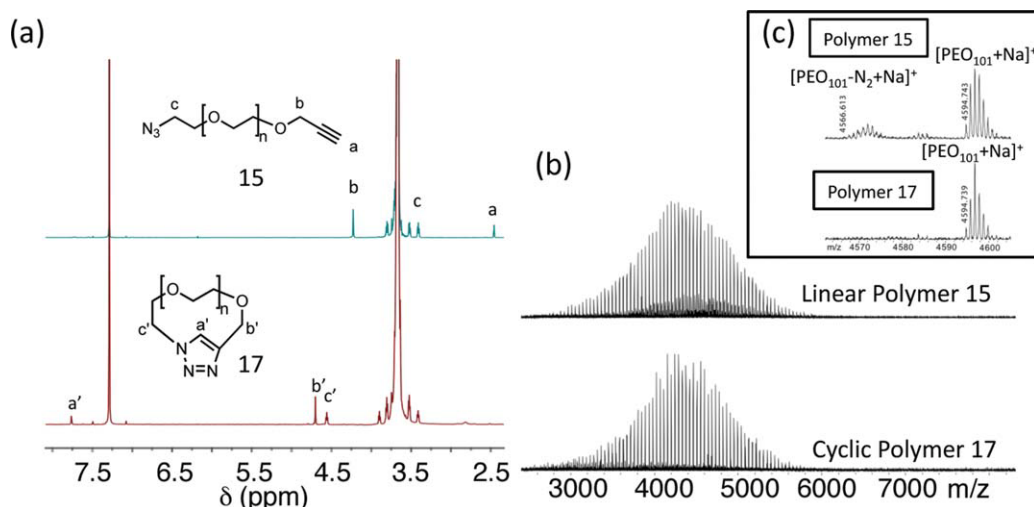
brated using SpheriCal™ calibrants. The calibrants were purchased from Polymer Factory. Infrared spectra were recorded on a Perkin Elmer Spectrum 100 with a Universal ATR sampling accessory.

### PS-N<sub>3</sub>

All PS-N<sub>3</sub> polymers (**4**, **5** and **6**) were synthesized under similar conditions. For example, chloro-functional NMP initiator **4a**<sup>25</sup> (377 mg, 1.01 mmol) was dissolved in styrene (10.0 g, 96 mmol) degassed via three freeze-pump-thaws and heated at 125 °C for 1.5 h to 30% conversion and then precipitated into methanol to achieve PS<sub>3k</sub>-Cl (**4b**, 2.83 g). Polymer **4b** (2.44 g, 0.8 mmol) and NaN<sub>3</sub> (230 mg, 3.5 mmol) were dissolved in 7 mL DMF and heated at 50 °C overnight. The reaction was diluted with dichloromethane (DCM) and extracted with water (3×), dried over MgSO<sub>4</sub>, and precipitated in MeOH, yield 1.57 g (64%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.26–6.30 (m, 5Ar-H), 4.31–4.25 (m, CH<sub>2</sub>-Cl), 3.54–3.50 (m, NCH(Ph)*i*Pr), 2.25–0.90 (m, CH and CH<sub>2</sub> of polymer backbone). FTIR, ν (cm<sup>-1</sup>): 3025, 2922, 2097, 1492, 1451, 754, 695. GPC  $M_n$  3000,  $M_w$  3900, PDI 1.30 (PS standards).



**FIGURE 4** Cyclization of 2 kDa PEG: (a) GPC traces and (b) full MALDI spectra showing conservation of molecular weight for the linear precursor (**14**) and cyclic (**16**) polymer.



**FIGURE 5** Cyclization of 4.5 kDa PEG: (a) NMR spectra, (b) full MALDI, and (c) zoomed-in MALDI spectra showing change in end groups, conservation of molecular weight and transformation of the azide group for linear (**15**) to the triazole ring of the cyclic (**17**) polymer.

### PMMA<sub>60k</sub>-alkyne (**7**)

AIBN (0.82 mg, 0.005 mmol), acetylene-RAFT agent<sup>26</sup> (16.3 mg, 0.05 mmol), and MMA (10.0 g, 100 mmol) were mixed in a schlenk flask and deoxygenated by three freeze-pump-thaws and heated at 70 °C for 12 h followed by precipitation into methanol to yield 5.6 g of polymer **7**. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 3.62 (br, CH<sub>3</sub>O), 1.88–1.56 (m, CH<sub>2</sub> of polymer backbone), 1.09–0.79 (m, CH<sub>3</sub> of polymer backbone). FTIR, ν (cm<sup>-1</sup>): 2950, 1724, 1435, 1145. GPC  $M_n$  60,800,  $M_w$  78,200, PDI 1.29 (PS standards).

### PS<sub>3k</sub>-*b*-PEG<sub>5k</sub> (**8**)

All click polymer-coupling reactions were performed under similar conditions for the times denoted in Table 1. For example, PS<sub>3k</sub>-N<sub>3</sub> **4** (405 mg, 0.135 mmol), PEG<sub>5k</sub>-alkyne **1** (450 mg, 0.090 mmol), and CuNPs (20 mg) were dissolved in 10 mL of anisole in a microwave tube, sealed and reacted in a Biotage microwave reactor for 10 min at a nominal temperature of 160 °C. The Cu nanoparticles were then separated by centrifugation at 3000*g* for 5 min and the supernatant precipitated into cyclohexane, yield 594 mg (83%).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.87–7.63 (m, triazole-H) 7.26–6.27 (m, 5Ar-H), 5.46–5.36 (m, Ar-CH<sub>2</sub>-triazole), 4.71–4.60 (m, O-CH<sub>2</sub>-triazole), 3.64 (br, CH<sub>2</sub> of PEG backbone), 3.38 (s, CH<sub>3</sub>O), 2.40–0.87 (m, CH and CH<sub>2</sub> of PS backbone). FTIR, ν (cm<sup>-1</sup>): 3025, 2884, 1492, 1452, 1342, 1279, 1241, 1104, 962, 842, 756, 696. GPC  $M_n$  14,200,  $M_w$  15,400, PDI 1.08 (PS standards).

### N<sub>3</sub>-PEG<sub>2k</sub>-alkyne (**14**)

Commercially available Boc-NH-PEG<sub>2k</sub>-N<sub>3</sub> (1.12 g) was deprotected in 10% (TFA/DCM) solution overnight, concentrated and precipitated in diethyl ether and dried on high vacuum to give TFA-NH<sub>2</sub>-PEG<sub>2k</sub>-N<sub>3</sub> (1.00 g, 89%). TFA-NH<sub>2</sub>-PEG<sub>2k</sub>-N<sub>3</sub> (372 mg) was dissolved in 2 mL DCM and 100 μL TEA was added followed by 80 mg 4-pentynoic anhydride and let stir overnight followed by 2× washes with NaHSO<sub>4</sub> and 1×

wash H<sub>2</sub>O. The organic phase was then concentrated, precipitated in ether, and dried under high vacuum to give N<sub>3</sub>-PEG<sub>2k</sub>-alkyne (210 mg, 57%).

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 6.55 (br, NH), 3.87–3.46 (br, CH<sub>2</sub> of PEG backbone), 3.41 (t, *J* = 5.1 Hz, CH<sub>2</sub>N<sub>3</sub>), 2.58–2.53 (m, alkyne-CH<sub>2</sub>CH<sub>2</sub>-), 2.44 (t, *J* = 7.3 Hz, -CH<sub>2</sub>CH<sub>2</sub>-CONH-), 2.04 (t, *J* = 1.8 Hz, alkyne-H). FTIR, ν (cm<sup>-1</sup>): 2886, 2099, 1654, 1339, 1278, 1239, 1100, 1059, 945, 840. GPC  $M_n$  2100,  $M_w$  2400, PDI 1.14 (PEG standards).

### N<sub>3</sub>-PEG<sub>4.5k</sub>-alkyne (**15**)

Starting with the acetylene-PEO derivative (476 mg) and following the reported procedure<sup>28</sup> of mesylation and then reaction with sodium azide, 235 mg of polymer **15** was obtained (overall yield = 50%).

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 4.22 (d, *J* = 2.4 Hz, alkyne-CH<sub>2</sub>O), 3.58 (br, CH<sub>2</sub> of PEG backbone), 3.41 (t, *J* = 5.1 Hz, CH<sub>2</sub>N<sub>3</sub>), 2.46 (t, *J* = 2.4 Hz, alkyne-H). FTIR, ν (cm<sup>-1</sup>): 2880, 2098, 1341, 1279, 1240, 1100, 1059, 946, 841. GPC  $M_n$  4400,  $M_w$  4600, PDI 1.05 (PEG standards).

### Cyclic PEG<sub>2k</sub> (**16**)

CuNPs (1.0 g) were dispersed in 10 mL of anisole in a microwave tube. 18.6 mg N<sub>3</sub>-PEG<sub>2k</sub>-alkyne (**14**) was dissolved in 900 μL anisole and 100 μL aliquots of this solution sequentially added to the reaction mixture followed by irradiation at 160 °C for 10 min. The reaction mixture was purified by centrifugation at 5000*g* for 5 min to remove the CuNPs, the supernatant was then decanted and solvent was removed in vacuo.

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.56 (s, triazole-H), 6.54 (br, NH), 4.51 (t, *J* = 5.2 Hz, triazole(N)-CH<sub>2</sub>), 3.90–3.38 (br, CH<sub>2</sub> of PEG backbone), 3.07 (t, *J* = 7.4 Hz, triazole(C)-CH<sub>2</sub>), 2.63 (t, *J* = 7.4 Hz, -CH<sub>2</sub>CH<sub>2</sub>CONH-). FTIR, ν (cm<sup>-1</sup>): 3445, 2868, 1651, 1348, 1297, 1249, 1101, 948, 849. GPC  $M_n$  1500,  $M_w$  1800, PDI 1.20 (PEG standards).

**Cyclic PEG<sub>4.5k</sub> (17)**

CuNPs (0.50 g) were dispersed in 10 mL of anisole in a microwave tube. Aliquots of 4.0 mg of N<sub>3</sub>-PEG<sub>4.5k</sub>-alkyne (15) dissolved in 100  $\mu$ L of anisole were added to the microwave tube for five consecutive microwave reactions at 160 °C for 20 min (total of 20 mg). The reaction mixture was then purified by centrifugation at 5000g for 5 min and the supernatant decanted and solvent removed in vacuo.

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.77 (s, triazole-*H*), 4.71 (s, triazole(C)—CH<sub>2</sub>), 4.56 (t, *J* = 5.1 Hz, triazole(N)—CH<sub>2</sub>), 3.93–3.40 (br, CH<sub>2</sub> of PEG backbone). FTIR,  $\nu$  (cm<sup>-1</sup>): 2861, 1348, 1288, 1259, 1098, 949, 859. GPC *M<sub>n</sub>* 3400, *M<sub>w</sub>* 3800, PDI 1.11 (PEG standards).

**CONCLUSIONS**

In conclusion, we have introduced an easy and simple method for the formation of diblock and triblock copolymers, as well as cyclic polymers using Cu nanoparticles as a catalyst system coupled with microwave irradiation. Advantages of this procedure are the speed of the reaction, its tolerance to O<sub>2</sub>, and the ability to easily separate and recycle the Cu nanoparticles.

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