

An air-stable supported Cu(I) catalyst for azide-alkyne click polymerization

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An air-stable supported Cu(I) catalyst, CuI@PS-Phen, was designed and synthesized. CuI@PS-Phen can efficiently catalyze the click polymerization of diynes **a** and diazides **b** to produce soluble and thermally stable polytriazoles with high molecular weights (M_w up to 30800), and low copper residue content (down to 190 ppm) in high yields (up to 94.2%) under mild reaction conditions without the exclusion of oxygen.

azide-alkyne click polymerization, copper residue, polytriazole, supported Cu(I) catalyst

1 Introduction

Exploration of new catalytic systems is at the heart of organic and polymer chemistry, especially with respect to the development of new organic and polymerization reactions [1].

One representative example that the catalyst facilitates the reaction is the Cu(I)-catalyzed azide-alkyne cycloaddition (CuAAC). The thermally initiated azide-alkyne cycloaddition was first reported in 1893 by Michael [2] and systematically investigated by Huisgen in the 1960s [3]. However, as a direct method to access triazole rings, this reaction attracted little attention because of the slow reaction rate and lack of regioselectivity. The reaction remained undeveloped until Sharpless *et al.* [4] independently reported that Cu(I) catalysts can greatly enhance the reaction rate

and yield solely 1,4-disubstituted 1,2,3-triazoles. The CuAAC is regarded as a typical reaction of “click chemistry” [5], and has aroused much interest among researchers due to its remarkable features such as high efficiency, regioselectivity, mild reaction conditions, simple product isolation, atom economy, and tolerance to functional groups.

CuAAC has found widespread applications in diverse fields, including polymer science. Along with being used for postfunctionalization of preformed polymers, it has also been developed into an efficient polymerization technique—click polymerization [6,7]. Functional polytriazoles with topological structures have been prepared with this technique.

Unfortunately, the complete removal of copper residues from polytriazole products is difficult, because the formed triazole rings can coordinate with the copper species. These metallic residues have restricted the application of the polymers in fields such as biological and optoelectronic sciences due to their cytotoxicity and fluorescence quenching

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effect [8].

One of the solutions to this problem is to develop click polymerization without using transition metal complexes, i.e., metal-free click polymerization. However, this method usually requires high reaction temperatures and an activated monomeric species [6c]. One alternative to avoid such conditions is to use a supported catalyst. The strong coordination of the copper ions to the supporting substrate could result in fewer metallic residues coordinated to the resultant polymers. In addition, such catalysts could be easily recycled and reused several times, thus meeting the requirements of "green chemistry". With this in mind, we succeeded in establishing a supported Cu(I)-catalyzed click polymerization, in which the catalyst could be reused for total four cycles. More importantly, the copper contents in the polytriazole products were much lower than those catalyzed by other in more Cu(I) species such as CuSO₄/sodium ascorbate and Cu(PPh₃)₃Br [9].

Nevertheless, improving catalyst recyclability and reducing metal residue content in products are our continued goals. Thus, exploitation of new supported Cu(I) catalytic systems in click polymerization is still an important research topic.

It has been reported that phenanthroline can form a stable complex with copper, which has been utilized as a supported catalyst [10,11]. Inspired by these reports, we envisioned that these supported Cu(I) complexes could catalyze the azide-alkyne click polymerization, be recycled and reused, and decrease the copper residues in the resulting polytriazoles.

2 Experimental

2.1 Materials

Unless otherwise stated, all chemicals used were purchased from Sigma-Aldrich (USA) or Alfa Aesar (USA). Tetrahydrofuran (THF), toluene, and 1,4-dioxane were distilled from sodium benzophenone ketyl under nitrogen immediately prior to use. *N,N*-dimethylformamide (DMF) was extra-dry grade. Other solvents were purified by standard methods.

2.2 Instruments

¹H and ¹³C NMR spectra were recorded on a Mercury plus 400 MHz NMR spectrometer using tetramethylsilane (TMS; δ=0 ppm) as internal reference. Atomic absorption spectroscopy (AAS) was conducted on Thermo Elemental Solaar S4 AA (USA). FT-IR spectroscopy was carried out on a Bruker Vector 22 spectrometer (Germany). Thermogravimetric analysis (TGA) measurements were run on TA Q50 under dry nitrogen at 20 °C/min. Average molecular weights (*M_w* and *M_n*) and polydispersity indices (PDI) of the

polymers were estimated with a Waters PL-GPC-50 gel permeation chromatography (GPC) system equipped with an interferometric refractometer detector. A set of mono-dispersed polystyrenes were used as calibration standards and THF as the eluent at a flow rate of 1.0 mL/min.

2.3 Catalyst synthesis

2.3.1 Synthesis of PS-Phen

5-Amino-1,10-phenanthroline (**2**) (0.781 g, 4.0 mmol) and Merrifield resin (0.727 g) were added into a 250 mL two-neck round-bottom flask. After acetonitrile (75 mL) and trimethylamine (1.12 mL, 8.0 mmol) were added, the mixture was refluxed for 36 h with gently stirring. The resultant resin was collected by filtration and washed with methanol (×3) and dichloromethane (DCM, (×3)) to remove the free phenanthroline. After drying under vacuum overnight, brown PS-Phen resin was obtained (1.32 g, 87.4%).

2.3.2 Synthesis of CuI@PS-Phen

In a glovebox with nitrogen atmosphere, PS-Phen resin (200 mg) and CuI (190 mg, 1.0 mmol) were added into a 100 mL round-bottom flask equipped with a stirring bar. The flask was sealed with a rubber plug and removed from the glovebox. Degassed acetonitrile (30 mL) was injected, and the mixture was gently stirred in the dark for 16 h. The resultant solid was washed with acetonitrile (3×15 mL) and DCM (2×15 mL), and dried under vacuum overnight. CuI@PS-Phen was obtained as brown powder (265 mg, 67.9%).

2.4 Click polymerization

A typical procedure for the click polymerization of diyne **a1** with diazide **b1** is given below: in a 15 mL Schlenk tube were placed **a1** (18.6 mg, 0.1 mmol), **b1** (47.9 mg, 0.1 mmol), and CuI@PS-Phen (4.9 mg, 0.008 mmol Cu). THF (1.0 mL) was then injected into the mixture. After stirring at 60 °C for 12 h in air, the mixture was diluted with chloroform (5 mL) and added dropwise into a hexane/chloroform mixture (200 mL, *v/v*=10:1) through a cotton filter under stirring. The precipitates were allowed to stand overnight, and then collected by filtration and dried under vacuum at room temperature to a constant weight. The resultant light pink solid was obtained in 87.1% yield.

2.5 AAS measurement

Polytriazole (10.0 mg) was added into a 20 mL test tube, followed by concentrated nitric acid (5 mL). The mixture was heated to 120 °C for 10 h. After cooling to room temperature, the solution was diluted to 10 mL and the AAS measurement taken.

3 Results and discussion

3.1 Catalyst preparation

The supported catalyst was synthesized according to the route shown in Scheme 1. CuI@PS-Phen was obtained in satisfactory yield by stirring CuI and PS-Phen (prepared from Merrifield resin and 5-amino-1,10-phenanthroline (**2**)) in acetonitrile in the dark for 16 h. The structure of PS-Phen was characterized with FT-IR spectroscopy (Figure S1, Supporting Information online). Enhancement of the peak at 1608 cm^{-1} suggested that additional benzene rings existed on the surface of Merrifield resin. Furthermore, the strong absorption at 1342 cm^{-1} indicated the formation of the C–N bonds in PS-Phen. AAS measurements showed that 1.63 mmol g^{-1} CuI coordinated on the PS-Phen surface, suggesting that the preparation of CuI@PS-Phen had been successful.

3.2 Click polymerization

We first conducted the click polymerization of **a1** and **b1** in the presence of CuI@PS-Phen in THF at 60 °C under nitrogen (Scheme 2), the conditions used in our previous work [9]. However, only trace amounts of the product were obtained after 24 h. Occasionally, we found the polymerization occurred when a small amount of oxygen existed in the reaction system. Therefore, we envisioned that oxygen may be of benefit to the polymerization and thus conducted the reaction in air. To our delight, the polymer product was obtained in a high yield under this condition.

We next investigated the time course of this click polymerization with the same monomers in THF (0.1 mol L^{-1}) at 60 °C under open air (Scheme 2). The weight-average molecular weight (M_w) of the products increased with reaction time, while the yield decreased slightly after 12 h (Table S1, Supporting Information online). Thus, we chose 12 h as the optimum polymerization time.

Solvent effects were then evaluated using THF, DMF, toluene, and 1,4-dioxane. Reactions in THF and DMF can produce polymers with high M_w in high yields. The product was partially soluble in DMF, with the residual copper

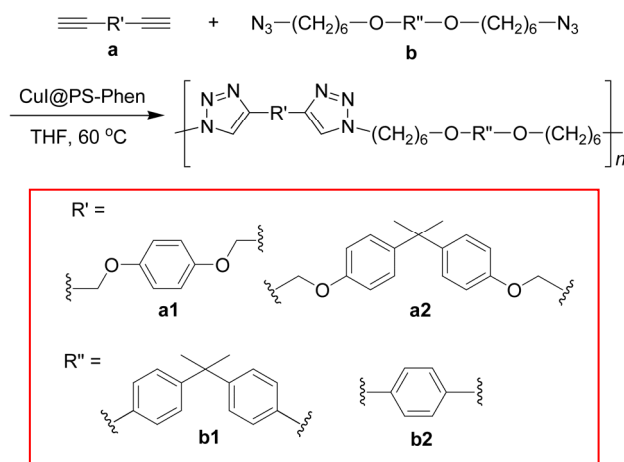
(1602 ppm) at much higher levels than that in THF (394 ppm) (Table S2). Furthermore, when the polymerization was carried out in toluene and 1,4-dioxane, only trace amounts of product were obtained. Hence, THF was selected as the reaction solvent.

With these optimal reaction parameters in hand, we investigated the universality of the CuI@PS-Phen catalyzed click polymerization by varying the diyne and diazide monomers (Scheme 2). All polymerizations propagated smoothly and gave soluble polytriazoles **P1–P3** with high M_w (up to 26500) in high yields (up to 94.2%) (Table 1, Figure S2). More importantly, **P1–P3** had low copper residue content, with the smallest value being recorded as 190 ppm, demonstrating the advantage of using a supported Cu(I) catalyst.

The thermal properties of **P1**, **P2**, and **P3** were evaluated by TGA under nitrogen. The experimental results indicated that all polymers were thermally stable (Figure S3), with temperatures required for losing 5% weight being above 357 °C (Table 1).

3.3 Structural characterization

Structures of **P1–P3** were characterized by FT-IR and NMR spectroscopies. Satisfactory analytical data corresponding to their structures were obtained (Figures S4–S11). Since the

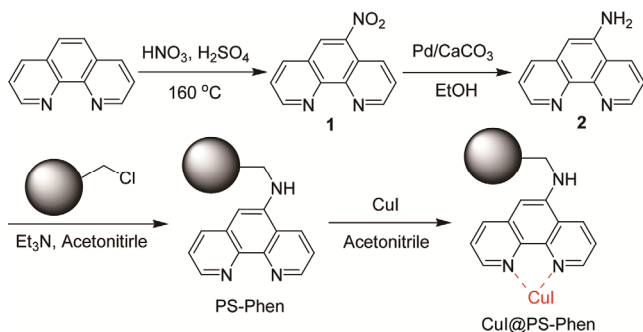


Scheme 2 Synthetic route to polytriazoles by CuI@PS-Phen catalyzed click polymerizations of diynes **a** and diazides **b**.

Table 1 CuI@PS-Phen catalyzed azide-alkyne click polymerization^{a)}

Monomer	Polymer	Yield (%)	M_w ^{b)}	PDI ^{b)}	[Cu] (ppm) ^{c)}	T_d (°C) ^{d)}
a1+b1	P1	92.5	24200	2.60	410	357
a2+b1	P2	94.2	26500	2.27	299	364
a2+b2	P3	79.2	8100	2.58	190	366

a) Reaction carried out in THF at 60 °C in air for 12 h with a monomer concentration of 0.1 mol L^{-1} and a catalyst concentration of 0.008 mol L^{-1} ; b) M_w and polydispersity (PDI) of polymers were estimated by GPC in THF on the basis of a PS calibration; c) copper residue content in polymers estimated by atomic absorption spectroscopy; d) T_d =temperature for 5% weight loss.



Scheme 1 Synthetic route to supported catalyst CuI@PS-Phen.

spectral profiles of P1–P3 were similar, only the analysis of P1 is discussed here as an example. The stretching vibrations of $\equiv\text{C}-\text{H}$ at 3275 cm^{-1} , $\text{C}\equiv\text{C}$ at 2127 cm^{-1} , and $-\text{N}_3$ at 2098 cm^{-1} from the monomer spectra had almost disappeared after the reaction, indicating that most of ethynyl groups in **a1** and azide groups in **b1** had mostly been converted into triazole rings in P1 by the click polymerization (Figure S4).

This conclusion was further confirmed by NMR spectra. The ^1H NMR of P1 and its monomers showed that the resonances corresponding to ethynyl protons in **a1** (2.51 ppm), methylene protons adjacent to the ethynyl group in **a1** (4.63 ppm), and the azide group in **b1** (3.90 ppm) had almost disappeared (Figure 1). In addition, new peaks were observed at 7.66, 5.13, and 4.36 ppm, in which, the first one was assigned to protons in the triazole ring and the other two to the methylene groups neighboring the triazole ring. Moreover, the ^{13}C NMR spectrum showed that ethynyl carbon peaks at 78.7 and 75.3 ppm in **a1** had disappeared completely in P1 (Figure S5). We could thus conclude that polytriazole P1 was obtained in the CuI@PS-Phen catalyzed azide-alkyne click polymerization. Similar conclusions were

drawn for P2 and P3 by analyzing their spectral data.

4 Conclusions

In summary, a new kind of air-stable supported Cu(I) catalyst, CuI@PS-Phen, for azide-alkyne click polymerization was designed and synthesized. Soluble and thermally stable polytriazoles with high M_w and low copper residue contents were obtained in high yields by CuI@PS-Phen catalyzed click polymerization of diynes **a** and diazides **b** in air. Next investigation will focus on further reducing the polymer copper residue contents and exploring the reusability of CuI@PS-Phen.

Supporting information

The supporting information is available online at chem.scichina.com and link.springer.com/journal/11426. The supporting materials are published as submitted, without typesetting or editing. The responsibility for scientific accuracy and content remains entirely with the authors.

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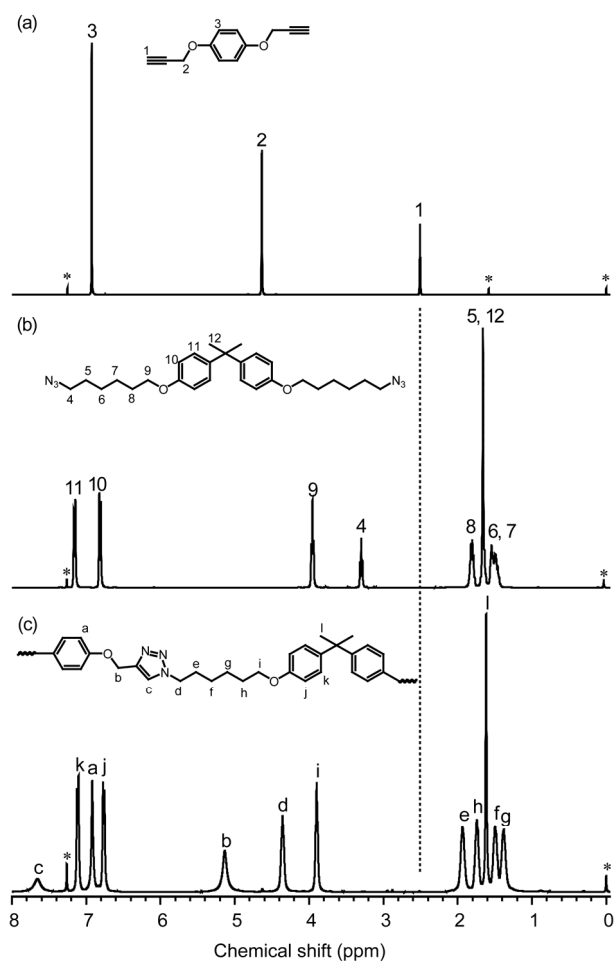


Figure 1 ^1H NMR spectra of (a) diyne **a1**, (b) diazide **b1**, and (c) polymer P1 in CDCl_3 . Solvent and water peaks are marked with asterisks.

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