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A recyclable and reusable supported Cu(I) catalyzed azide-alkyne click polymerization

Haiqiang Wu¹, Hongkun Li¹, Ryan T. K. Kwok³, Engui Zhao³, Jing Zhi Sun¹, Anjun Qin^{1,2} & Ben Zhong Tang^{1,2,3}

¹MOE Key Laboratory of Macromolecular Synthesis and Functionalization, Department of Polymer Science and Engineering, Zhejiang University, Hangzhou 310027, China, ²Guangdong Innovative Research Team, State Key Laboratory of Luminescent Materials and Devices, South China University of Technology, Guangzhou 510640, China, ³Department of Chemistry, Institute for Advanced Study, Institute of Molecular Functional Materials, and State Key Laboratory of Molecular Neuroscience, The Hong Kong University of Science & Technology, Clear Water Bay, Kowloon, Hong Kong, China.

The azide-alkyne click polymerization (AACP) has emerged as a powerful tool for the synthesis of functional polytriazoles. While, for the Cu(I)-catalyzed AACP, the removal of the catalytic Cu(I) species from the resulting polytriazoles is difficult, and the research on the recyclability and reusability of the catalyst remains intact. Herein, we reported the first example of using recyclable and reusable supported Cu(I) catalyst of CuI@A-21 for the AACP. CuI@A-21 could not only efficiently catalyze the AACP but also be reused for at least 4 cycles. Moreover, pronounced reduction of copper residues in the products was achieved. Apart from being a green and cost-effective polymer synthesis strategy, this method will also broaden the application of AACP in material and biological sciences and provide guidelines for other polymerizations with metal catalysts.

Since the generation of chemistry, one of its major goals has been the synthesis of new functional materials, which in turn has promoted the establishment of novel concepts and discovery of new reactions. In 2001, Sharpless and co-workers proposed the concept of click chemistry: a chemical transformation that enjoys such advantages as high efficiency, atom economy, regioselectivity, and functionality tolerance as well as mild reaction conditions, fast reaction rates and simple product isolation procedures¹. One year later, Sharpless' and Meldal's groups independently reported that 1,3-dipolar cycloaddition of terminal alkyne and organic azide could be remarkably accelerated by using Cu(I) catalyst, and solely 1,4-disubstituted 1,2,3-triazole derivatives could be yielded^{2,3}. This Cu(I)-catalyzed azide-alkyne cycloaddition (CuAAC) thus represents the archetypical example of click chemistry and is regarded as one of the most remarkable synthetic trends⁴⁻⁶. Thanks to its great feasibility, the click reaction has found wide applications in the areas of organic synthesis, medicinal chemistry, anion binding, surface modification, as well as bioconjugation etc⁷⁻¹⁶.

This reaction has also been widely utilized in polymer science¹⁷⁻²⁵. Apart from post-functionalization of preformed polymer, it has been developed as an efficient polymerization reaction, *i.e.* the Cu(I)-catalyzed azide-alkyne click polymerization (AACP)²⁶⁻³⁸. However, the Cu(I) catalyst could be used only once and the removal of the copper residues from the resulting polytriazoles is difficult due to the coordination of copper residues with the formed triazole rings. Thus, new Cu(I) catalyst systems, which are environmentally friendly and could greatly decrease the copper residues in the results polytriazoles, need to be further explored. Besides using the strategy of metal-free click polymerizations of activated alkynes and azides or activated azides and alkynes³⁹⁻⁴⁶, we'd like to find the alternative to solve these difficulties.

Generally, most new polymerization reactions, if not all, are derived from the established organic reactions. The strategy used in the latter could provide good reference for the former. During the course of searching new catalytic systems of AACP and new methods to reduce copper residues in the products, we were attracted by an elegant method from the click reaction using supported Cu(I) catalyst (SCC), in which the catalyst was immobilized on a solid matrix. The supported catalysts belong to a catalog of heterogeneous system and possess the advantages of recyclability and easy separation from the reaction mixture⁴⁷. A variety of matrices such as cross-linked polymers^{48,49}, activated charcoal⁵⁰, zeolites⁵¹, alumina⁵², aluminum oxyhydroxide fibers⁵³, and silica⁵⁴ have been used to prepare the supported catalysts. All these supported catalysts could be reused for several times

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Correspondence and requests for materials should be addressed to A.J.Q. (qinaj@zju.edu.cn) or B.Z.T. (tangbenz@ust.hk)

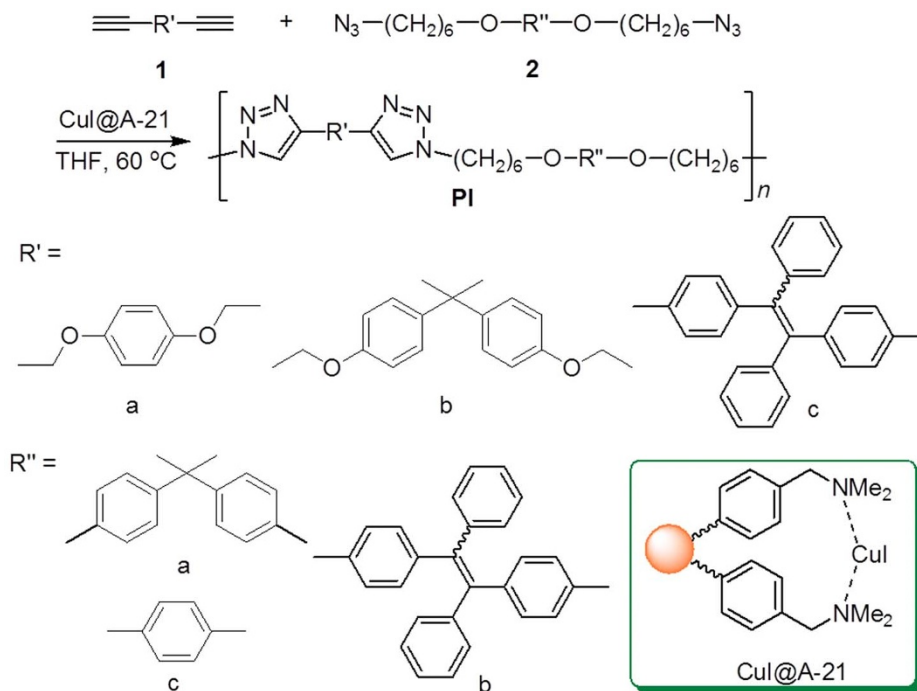


Figure 1 | Synthetic routes to polytriazoles PI by click polymerizations of diynes **1** and diazides **2**.

without decreasing their activities in the organic reactions. Surprisingly, as far as we know, no work on using the SCCs for the AACP was reported.

Recently, Girard and coworkers reported a simple SCC of CuI@A-21, which was prepared by immobilizing CuI onto dimethylamino-grafted cross-linked polystyrene (Amberlyst® A-21 resin). This CuI@A-21 showed high activity and stability, and could efficiently catalyze the reactions of various terminal alkynes and organic azides, and be reused for 4 cycles⁵⁵. Thus, we envision that this SCC is a promising candidate for catalyzing the AACP with high efficiency and recyclability and produce polytriazoles with less copper residues due to the larger coordination constant of dimethylamino than that of the formed triazoles with Cu(I).

Indeed, our experimental results showed that CuI@A-21 could efficiently catalyze the AACP for at least 4 cycles and furnish polytriazoles with copper residues less than 116 ppm, which is 24 times lower than other Cu(I) catalysts, such as CuSO₄/sodium ascorbate (2792 ppm), CuI (3088 ppm) and Cu(PPh₃)₃Br (3197 ppm) when the same copper molar concentration was used.

Results and discussion

Previous studies have shown that the addition of nitrogen-containing ligands to the CuAAC system will not only accelerate the reaction rate but also protect the Cu(I) from oxidation⁵⁶. Thus, it is expected that CuI@A-21 is highly stable and could catalyze the AACP with high efficiency. Moreover, the procedures for immobilizing CuI onto the polystyrene spheres are quite simple and feasible: mixing the CuI and A-21 resin in acetonitrile and stirring at room temperature in dark for 17 h under nitrogen readily furnished CuI@A-21 as light green particles in 94.7% yield. Atomic absorption spectroscopy (AAS) measurement showed that the content of Cu(I) species in the CuI@A-21 is 0.26 mmol/g.

With this SCC in hand, we first investigated its activity by catalyzing the model reaction of phenyl propargyl ether (**5**) and 1,1'-bis(6-azidoethyl)-4,4'-isopropylidenediphenyl ether (**2a**), which was prepared according to the routes shown in Figure S1 (supplementary information). Delightfully, after the mixture was stirred in THF at 60 °C for 12 h, 1,4-disubstituted 1,2,3-triazole **6** was isolated in 96.8%

yield (Figures S2–S4), implying the high activity of this SCC. It is worth noting that even after column chromatography purification, small amount of copper residue (0.44 ppm) was also recorded by AAS in the product of **6**, indicative of the relatively strong coordination interaction between the formed triazole rings and catalytic copper species.

After confirming the activity of SCC, we tried to apply it in catalyzing the AACP. According to our previous results, the reaction time and solvent play crucial roles in the polymerization. We first followed the time course of polymerization of diyne **1a** and diazide **2a** in THF at 60 °C with a monomer concentration of 0.1 M (Figure 1). The yields and molecular weights (M_w) increased accordingly with time (Table S1). However, the products obtained after 12 h became partially soluble. Therefore, 12 h was chosen as the optimum polymerization time.

Next, we evaluated the effect of solvent on the polymerization of **1a** and **2a** at 60 °C for 12 h with a monomer concentration of 0.1 M. The results showed that the products yielded from DMF and toluene were partially soluble, and those from THF and dioxane possessed good solubility in THF (Table S2). Furthermore, the copper residues in the polytriazoles produced in DMF are much higher (1709 ppm) than that in THF (197 ppm). This is because DMF is a highly polar solvent and could dissolve the chelated CuI and dissociate it from SCC, leading to the increased copper content in the resulting polymer. Taking account of the yield, M_w and copper residues in products, we chose THF as the preferable solvent.

Finally, these optimized conditions were employed to polymerize other diynes and diazides (Figure 1). All the polymerizations propagated smoothly, and polytriazoles PI with high molecular weights (up to 69600) and relatively narrow polydispersity (<3.25), in high yields (up to 98.7%) were obtained (Table 1). It is worth noting that the copper residues in the yielded polytriazoles PI are less than 260 ppm, with the smallest value recorded in PIc (82 ppm).

The polytriazoles PI are soluble in commonly used organic solvents, such as THF, chloroform and DMF. The polymers are thermally stable, and the temperatures for 5% weight loss are higher than 367 °C (Figure S5), which indicates their strong resistance to the thermolysis at elevated temperatures. The PI was characterized by

Table 1 | CuI@A-21 catalyzed azide-alkyne click polymerization^a

no.	monomer	polymer	yield (%)	M_w^b	PDI ^b	[Cu] (ppm) ^c
1	1a + 2a	PIaa	98.7	41 000	2.20	197
2	1a + 2b	PIab	82.0	22 100	1.93	102
3	1b + 2a	PIba	83.3	17 900	1.86	260
4	1b + 2c	PIbc	65.1	69 600	3.25	100
5	1c + 2a	PIca	75.2	27 100	2.36	82

^aCarried out in THF at 60 °C for 12 h under nitrogen with a monomer concentration of 0.1 M and catalyst concentration of 0.026 M.
^b M_w and polydispersity (PDI) of polymers were estimated by GPC in THF on the basis of a PS calibration.
^cCopper residue in polymers estimated by atomic absorption spectroscopy (AAS).

infrared, ¹H and ¹³C NMR spectroscopy, and satisfactory results corresponding to their expected molecular structures were obtained (Figures S6–S20). Importantly, the characterization data suggested that the polymer structures were the same as those catalyzed by traditional Cu(I) species.

Another key issue for the supported catalysts is their ability of recovery and reusability, which has economic and ecological implications. We thus evaluated this ability of CuI@A-21 under the similar polymerization conditions. Table 2 summarized the results of AACP of **1a** and **2a**. After finishing the first cycle of reaction, the CuI@A-21 was separated from the reaction mixture by simple filtration, washed with THF twice, and then immediately used for the next cycle. Delightfully, polytriazole with high M_w (22500) could still be obtained in high yield (84.5%) in the 4th cycle, suggesting that the catalyst could be repeatedly used without a significant loss of its activity for 4 cycles. More importantly, the copper residues in the resulting polymer in every cycle is less than 252 ppm (Table 2), displaying the good stability of the SCC. The ability of this catalyst was also confirmed in the AACPs of monomer pairs of **1a** and **2b**, as well as **1b** and **2a**, and 4 cycle recyclability were also realized, suggesting that reusability and recyclability of CuI@A-21 is a universal property instead of being applicable to only a specific azide-alkyne system (Tables S3 and S4).

The advantage of CuI@A-21 over other Cu(I) catalysts was also investigated. Three generally used systems of CuSO₄/sodium ascorbate, CuI, and Cu(PPh₃)₃Br were employed to catalyze the AACP of **1a** and **2a** under exactly the same molar concentration. The results showed that all these Cu(I) species could catalyze the polymerization and polytriazoles with high M_w in high yields were produced (Table 3). Excitingly, the copper residue in the polytriazole synthesized in the presence of CuI@A-21 is only 116 ppm, which is at least 24 times lower than those catalyzed by other Cu(I) species. This result could be explained as that the chelation between copper and nitrogen atoms on the surface of the A-21 has greatly retarded the leaching of copper catalyst into the reaction solution and made the catalyst isolation from the solution easier. Moreover, post-purification of the products by aqueous EDTA solution could further reduced the copper residues in the polymers, while, the value for

Table 2 | Recyclability of CuI@A-21 using in the click polymerization of **1a** and **2a**^a

cycle	yield (%)	M_w^b	PDI ^b	[Cu] (ppm) ^c
1	67.1	80 300	3.21	252
2	96.1	94 400	2.72	162
3	92.8	91 000	2.32	172
4	84.5	22 500	2.51	132

^aCarried out at 60 °C for 12 h under nitrogen using CuI@A-21 as catalyst with a monomer concentration of 0.1 M.
^b M_w and PDI of polymer were estimated by GPC in THF on the basis of a PS calibration.
^cCopper residue in polymers estimated by atomic absorption spectroscopy.

Table 3 | Catalyst effect on the click polymerization of **1a** and **2a**^a

no.	catalyst	solvent	yield (%)	M_w^b	PDI ^b	S ^c	[Cu] (ppm) ^d
1	CuI@A-21	THF	78.0	48 900	1.74	√	116
2	CuSO ₄ /SA ^e	THF	97.4	88 400	1.83	Δ	2792
3	CuI	DMF	69.4	44 800	1.67	Δ	3088
4	Cu(PPh ₃) ₃ Br	THF	86.9	25 700	2.04	√	3197

^aCarried out at 60 °C for 12 h under nitrogen with a monomer concentration of 0.1 M.
^b M_w and PDI of polymer were estimated by GPC in THF on the basis of a PS calibration.
^cSolubility in THF, √ = completely soluble, Δ = partially soluble.
^dCopper residue in the polymer estimated by atomic absorption spectroscopy.
^eSA = sodium ascorbate.

the polymer produced in the presence of CuI@A-21 is still 5 times lower than that yielded from Cu(PPh₃)₃Br (Table S5).

These results indicate that CuI@A-21 could not only efficiently catalyze the AACP for at least 4 cycles but also greatly reduce the copper residues in the obtained polytriazoles, enabling it to find broad applications in optoelectronic and biological fields.

Herein, we show one example to demonstrate the advantage of applying CuI@A-21 over Cu(PPh₃)₃Br in preparation of luminescent polymers. We have proven that **PIab**, which was prepared from diyne **1a** and tetraphenylethene (TPE)-containing diazide **2b**, possesses the unique characteristics of aggregation-induced emission (AIE)^{57–60}. Thus, this polytriazole provides a suitable platform for us to investigate the effect of copper residues on the light emission (Figure 2a). For comparison, we also conducted the Cu(PPh₃)₃Br-catalyzed click polymerization of **1a** and **2b** under the optimized conditions, and polytriazole named **PIab'** with M_w of 27400 (PDI = 2.30) was obtained in 95.5% yield. The AAS analysis showed that copper residue in **PIab'** is as high as 2452 ppm, which is 27.9 times higher than that in **PIab**. The quantum yield (Φ_F) measurements showed that the values of **PIab** are higher than those of **PIab'** in THF/water mixtures, especially with water fraction higher than 60%, well-demonstrating the quenching effect of copper residues (Figure 2b).

Conclusion

In summary, the first example of utilization of supported Cu(I) species to efficiently catalyze the AACP was demonstrated. The supported catalyst of CuI@A-21 could be facilely prepared in excellent yield. CuI@A-21 could effectively catalyze the AACP under heterogeneous conditions without other additives, and regioregular polytriazoles with high M_w and low copper residue contents (<260 ppm) could be produced in high yields. More importantly, this supported catalyst showed a good performance of recyclability, and could be reused for at least 4 cycles without significant reduction of its activity. The TPE containing polytriazoles **PIab** and **PIab'** are AIE-active, and the former possesses larger Φ_F values in THF/water mixture with higher water fraction (>60%) than the latter due to the less copper residues. Thus, our reported method is more suitable for application in optoelectronic and biomedical fields. This strategy could also provide guidelines for other polymerizations with metal catalysts in the polymer science.

Methods

Preparation of CuI@A-21. 2.0 g dry Amberlyst A-21 resin, 190 mg CuI, and 30 mL degassed acetonitrile were added into a 100 mL round-bottom flask. After gently stirring in dark for 17 h under nitrogen, the system was filtered, and the yielded supported catalyst was washed with acetonitrile (15 mL × 2) and dichloromethane (15 mL × 2), and dried in vacuum overnight. CuI@A-21 was obtained as light green particles in 94.7% yield. AAS analysis showed that the content of copper loaded on the A-21 was 0.26 mmol CuI·g⁻¹.

Click polymerization. Click polymerizations were carried out under nitrogen using Schlenk techniques. Typical experimental procedures for the polymerization of **1a** with **2a** are given below as an example.

In a 15 mL Schlenk tube were placed 18.6 mg (0.1 mmol) of **1a**, 47.9 mg (0.1 mmol) of **2a**, and 10.0 mg of CuI@A-21 supported catalyst (0.026 mmol of Cu).

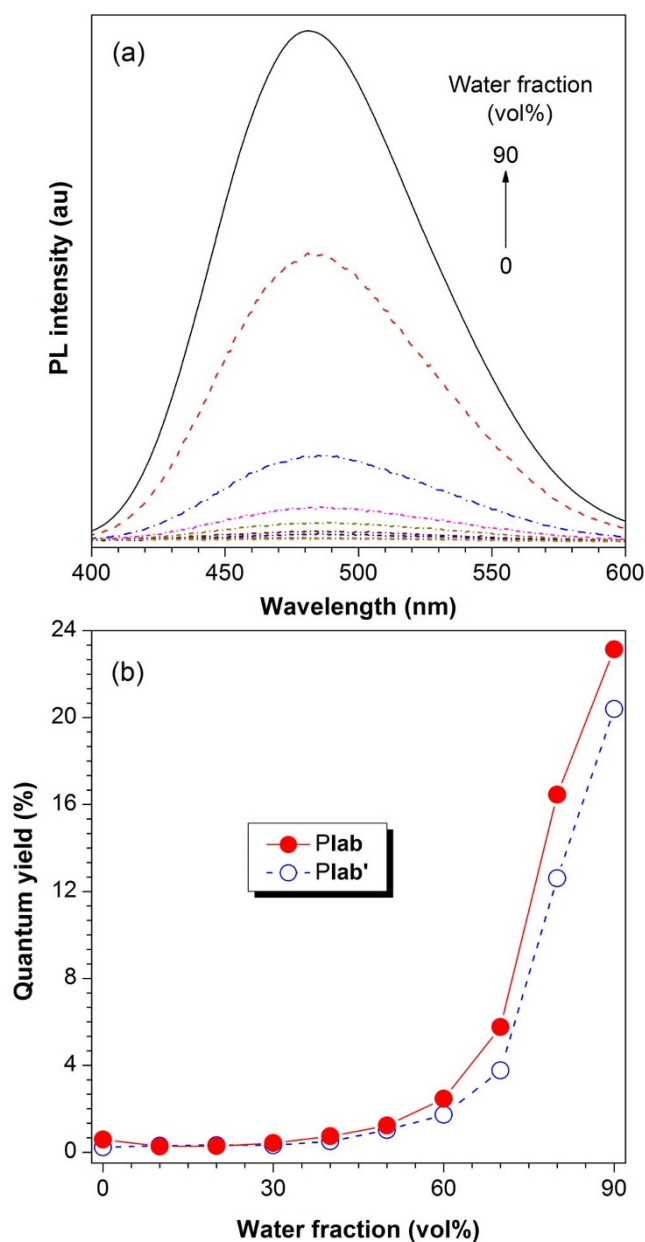


Figure 2 | (a) PL spectra of **PIab** in the THF/water mixtures with different water fractions. Polymer concentration: 10 μM ; excitation wavelength: 326 nm. (b) Variation in the quantum yields (Φ_F) of **PIab** and **PIab'** in the THF/water mixtures with different water fractions. The Φ_F values were estimated using quinine sulfate in 0.1 $\text{N H}_2\text{SO}_4$ ($\Phi_F = 54.6\%$) as standard.

After being evacuated and refilled with dry nitrogen three times, THF (1.0 mL) was then injected into the mixture. After stirred at 60 °C for 12 h, the reaction was diluted with chloroform and added dropwise into 300 mL of a mixture of hexane/chloroform mixture (10 : 1 by volume) through a cotton filter under stirring. The precipitates were allowed to stand overnight, collected by filtration, and dried under vacuum at room temperature to a constant weight. Light yellow solid was obtained in 87.1% yield.

Catalyst reusability. After finishing one cycle of the polymerization, the $\text{CuI}@A-21$ in Schlenk tube was isolated by sucking THF solution out with a syringe and washed with THF (2.0 mL \times 2). After sucking the washing THF, fresh diyne (0.1 mmol) and diazide (0.1 mmol) and THF (1.0 mL) were added immediately, then repeating the click polymerization.

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Author contributions

H.Q.W., A.J.Q. and B.Z.T. conceived and designed the experiments. H.Q.W., H.K.L. and R.T.K.K. conducted synthetic experiments. H.Q.W. and E.G.Z. performed the structure characterization, spectroscopic studies, and AAS measurements. J.Z.S. helped with analysis of the data. H.Q.W., A.J.Q. and B.Z.T. wrote the manuscript.

Additional information

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