

# Recyclable Cu nanoparticle catalyzed azide-alkyne click polymerization

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Received January 28, 2019; accepted March 15, 2019; published online May 6, 2019

The Cu(I)-catalyzed alkyne-azide cycloaddition (CuAAC) has been developed into a powerful polymerization reaction for the synthesis of new polytriazoles with versatile properties. However, research on recyclable and reusable copper catalyst for click polymerization to meet the requirement of green chemistry was rarely reported. Copper nanoparticles were reported to be capable catalysts for CuAAC. Replacing conventional copper catalyst with copper nanoparticles may realize the recycle and reuse of the copper catalyst in click polymerization. In this paper, copper nanoparticles were prepared and used as an effective catalyst for click polymerization, and soluble polytriazoles with high molecular weights were obtained in excellent yields under optimized reaction conditions. Importantly, the copper nanoparticles can be recycled and reused for up to 11 times for the click polymerization. Moreover, introducing aggregation-induced emission (AIE)-active moiety of tetraphenylethylene into the monomers makes the resultant polymers retain the AIE feature. This work not only provides an efficient recyclable catalytic system for the azide-alkyne click polymerization, but also might inspire polymer chemists to use recyclable copper species to catalyze other polymerizations.

**click polymerization, Cu nanoparticles, recyclability, reusability**

**Citation:** Chen Y, He B, Qin A, Tang BZ. Recyclable Cu nanoparticle catalyzed azide-alkyne click polymerization. *Sci China Chem*, 2019, 62: 1017–1022, <https://doi.org/10.1007/s11426-019-9465-7>

## 1 Introduction

Eco-friendly and sustainable development in chemical industry has received much attention in recent years. Atomic economic, highly efficient, and highly selective chemistry becomes goal that scientists are pursuing. In 2001, Sharpless and co-workers [1] proposed such chemical reactions enjoying the advantages of high efficiency, fast reaction rate, mild reaction conditions, easy product isolation, high selectivity, high atomic economy and good functional group tolerance as “click chemistry”. One year later, Sharpless and

co-workers [2], and Medal and co-workers [3] independently reported that Huisgen 1,3-cycloaddition reaction of alkyne and azide can be accelerated by Cu(I) catalysts, yielding sole 1,4-disubstituted 1,2,3-triazoles. This Cu(I)-catalyzed alkyne-azide cycloaddition (CuAAC) perfectly meets the definition of “click chemistry” and is prospered soon after being reported [4–7]. Thanks to its remarkable advantages, CuAAC is widely applied in biology [8], pharmaceutical chemistry [9], macromolecule synthesis [10–13], synthetic functional polymers [14–16] and many other research frontiers.

Our group has been working on development of new polymerizations based on triple-bond building blocks

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[17,18]. The azide-alkyne click polymerization has also been developed based on the CuAAC, and linear and hyper-branched polytriazoles with versatile properties have been prepared [19–22].

However, conventional Cu(I) catalysts for click polymerization, such as CuSO<sub>4</sub>/sodium ascorbate system can be used only once, which is not environment friendly. Polymer chemists have developed an efficient way to tackle this problem, that is, to recycle and reuse the metal catalyst such as immobilizing active catalytic species on solid supports to facilitate the recovery of the catalyst [23–28]. However the preparation of the catalyst is complicated and tedious. Developing metal-free click polymerization without using any metal catalyst may completely avoid the use of the metal species, but the monomers must be elaborately designed to achieve high reactivity, which limits the structure and applications of resultant polymers [29–35]. An alternative to overcome these shortcomings is to develop a reusable or recyclable metal nanoparticles catalyst.

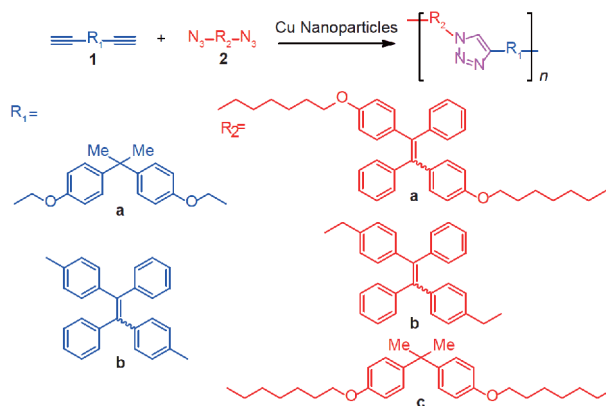
Recyclable nanoparticles that feature large surface area, high reaction efficiency, facile preparation and easy isolation from the products showed distinct advantages over conventional metal catalysts. Lots of work have been focused on nanoparticles catalyzed CuAAC [36–41]. For highly facile synthesis of 1,4-regioregular triazoles, the Cu nanoparticles were found to be very efficient and were easy to be recycled and reused by centrifugation or filtration. However, application of Cu nanoparticles (Cu NPs) as catalyst in polytriazole syntheses was rarely reported. Because Cu NPs can be easily separated and recycled from the reaction system, it is attractive to use them as an efficient and recyclable catalyst for the click polymerization.

In this paper, we report Cu NPs catalyzed click polymerization under mild reaction conditions (Scheme 1). The polymers with high molecular weights were obtained in high yields. This polymerization is also function group tolerant. Polytriazoles with such property as aggregation-induced emission (AIE) could be readily prepared. More importantly, the catalyst system can be easily isolated from the polymerization system and recycled for the next click polymerization cycle, and the number of recycling can be as many as 11 times, which is much higher than that we previously reported [24].

## 2 Results and discussion

### 2.1 Cu NPs catalyzed click polymerization

Click polymerization has attracted much attention due to its high efficiency, excellent selectivity and mild reaction conditions, etc. To make the catalyst more environment friendly, the supported Cu(I) catalyst for the azide-alkyne click polymerization has been developed [24,25]. However, the



**Scheme 1** Cu NPs catalyzed click polymerization of diynes and diazides (color online).

catalyst system can only be reused for 4 times. To make such click polymerization more powerful, we prepared Cu NPs with average diameter of 400 nm to catalyze the click polymerization (Figure S1, Supporting Information online). Delightfully, the preliminary results are positive. Thus we systematically optimized the polymerization conditions using **1a** and **2a** as monomers.

The time course of polymerization of **1a** and **2a** was first studied (Table 1). The yields and molecular weights of the products increased with extension of reaction time from 6 to 10 h. Further prolonging the polymerization time to 12 or 14 h resulted in partially soluble products, and the molecular weights of soluble part appeared to be constant. Because reaction time of 8 h could furnish the product with narrower polydispersity index (*D*) in remarkable yield, it was chosen as optimum reaction time.

Second, the effect of the reaction temperature on the Cu NPs catalyzed click polymerization was investigated, and the results are summarized in Table 2. It can be seen that both the yields and molecular weights of the products increased with elevating the reaction temperatures. However, for the product obtained at 70 °C, it takes 24 h to dissolve in THF. Since the polymerization at 60 °C could produce polymer with considerable high molecular weight and lower *D*, it was

**Table 1** Time course of the click polymerization of **1a** and **2a**<sup>a)</sup>

Number	Time (h)	Yield (%)	<i>M<sub>w</sub></i> <sup>b)</sup>	<i>D</i> <sup>b)</sup>
1	6	68.1	12700	2.31
2	8	84.6	82000	1.69
3	10	70.4	119000	1.88
4 <sup>c)</sup>	12	85.8	86000	2.16
5 <sup>c)</sup>	14	98.1	83000	1.56

a) Carried out at 60 °C in tetrahydrofuran (THF) under nitrogen. The monomer concentration is 0.05 M. Concentration of Cu NPs is 0.05 M. b) *M<sub>w</sub>* and *D* values were estimated by APC (advanced polymer chromatography) with THF as an eluent on the basis of a polystyrene calibration. c) Partially soluble in organic solvents including THF, chloroform, dimethyl sulfoxide (DMSO) and *N,N*-dimethylformamide (DMF).

**Table 2** Effect of temperature on the polymerization of **1a** and **2a**<sup>a)</sup>

Number	<i>T</i> (°C)	Yield (%)	<i>M<sub>w</sub></i> <sup>b)</sup>	<i>Đ</i> <sup>b)</sup>
1	30	60.7	13000	1.85
2	40	73.2	15000	2.04
3	50	75.1	31000	1.98
4	60	84.6	82000	1.69
5	70	79.4	154000	1.76

a) Carried out in THF for 8 h with monomer concentration of 0.05 M. Concentration of Cu NPs is 0.05 M. b) *M<sub>w</sub>* and *Đ* values were estimated by APC with THF as eluent on the basis of a polystyrene calibration.

chosen as the optimum temperature.

Third, the effect of Cu NPs concentration on polymerization was studied while keeping other reaction conditions unchanged (Table 3). The experiments showed that the Cu NPs concentration affected the polymerization results significantly. Low concentration of the catalyst as 0.013 M led to no polymer during work-up, while the concentration of 0.025 M produced polymer with smaller molecular weight in lower yield than that of 0.05 M. If Cu NPs concentration increases to 0.075 M, the molecular weight was still lower than 0.05 M although remarkable yield was achieved. Hence, Cu NPs concentration of 0.05 M was chosen as the most suitable catalyst concentration.

Fourth, the influence of monomer concentration on the polymerization results was investigated. The results show that both 0.025 and 0.05 M of monomer concentrations led to products with high molecular weights (Table 4). Considering *Đ* and yield of the product are better, monomer concentration with 0.05 M was chosen as the best condition.

Fifth, we followed the effect of solvent on the polymerization (Table 5). Polymerizations in THF, chloroform, DMF, DMSO and toluene were carried out under the aforementioned optimal conditions. Both the polymerizations in THF and chloroform produced polymers with high molecular weights in good yields. The product generated from the polymerization in DMF was soluble in commonly used solvents, but the molecular weight and yield were lower than that carried out in THF and chloroform. Whereas, polymer prepared in DMSO, was partially soluble in THF, hence the molecular weight was determined in DMF as eluent on APC. Insoluble pullets appeared when the poly-

**Table 3** Effect of Cu NPs concentration on polymerization of **1a** and **2a**<sup>a)</sup>

Number	<i>M<sub>Cu</sub></i> (M)	Yield (%)	<i>M<sub>w</sub></i> <sup>b)</sup>	<i>Đ</i> <sup>b)</sup>
1	0.013	— <sup>c)</sup>	—	—
2	0.025	34.7	25000	2.21
3	0.050	84.6	82000	1.69
4	0.075	85.1	26000	1.75

a) Carried out at 60 °C for 8 h in THF with monomer concentration of 0.05 M; b) *M<sub>w</sub>* and *Đ* values were estimated by APC with THF as eluent on the basis of a polystyrene calibration; c) no precipitation was obtained when the reaction solution was added into petroleum ether and chloroform mixture.

**Table 4** Effect of monomer concentration on the polymerization of **1a** and **2a**<sup>a)</sup>

Number	[ <i>M<sub>0</sub></i> ] (M)	Yield (%)	<i>M<sub>w</sub></i> <sup>b)</sup>	<i>Đ</i> <sup>b)</sup>
1	0.013	70.2	22600	2.17
2	0.025	77.1	87000	1.92
4	0.050	84.6	82000	1.69
5	0.075	90.4	51000	2.05

a) Carried out at 60 °C in THF under nitrogen atmosphere. Concentration of Cu Nanoparticles is 0.05 M, the reaction time was 8 h. b) *M<sub>w</sub>* and *Đ* values were estimated by APC with THF as eluent on the basis of a polystyrene calibration.

**Table 5** Effect of solvent on polymerization of **1a** and **2a**<sup>a)</sup>

Number	Solvent	Yield (%)	<i>M<sub>w</sub></i> <sup>b)</sup>	<i>Đ</i> <sup>b)</sup>
1	THF	84.6	82000	1.69
2	Chloroform	85.1	92000	1.60
3	DMF	74.3	49000	1.77
4	DMSO <sup>c)</sup>	71.1	53000	1.18
5	Toluene <sup>d)</sup>	—	—	—

a) Carried out at 60 °C for 8 h with Cu NPs concentration of 0.05 M and monomer concentration of 0.05 M, the reaction time was 8 h. b) *M<sub>w</sub>* and *Đ* values were estimated by APC with THF as eluent on the basis of a polystyrene calibration; c) the polymer was partially soluble in THF, and *M<sub>w</sub>* and *Đ* results were estimated by APC with DMF as eluent; d) an insoluble sphere was formed at 2 h which is insoluble in THF and DMF.

merization was carried out in toluene after 2 h, which are insoluble in DMF, DMSO, THF and chloroform. Thus, THF continued to be used as polymerization solvent.

With these optimized conditions in hand, other diyne and diazide monomers were examined to test the universality and robustness of this Cu NPs catalyzed click polymerization. As shown in Table 6, all the polymerization propagated smoothly and polymers with considerable large molecular weights were produced in high yields. These results suggest that our prepared Cu NPs could efficiently and powerfully catalyze the azide-alkyne click polymerization.

## 2.2 Structure characterization

Of the prepared polymers, most of them are soluble in commonly used organic solvents, thus, the polymer structures were characterized spectroscopically using “wet” methods. Since the spectral profiles of the polymers are si-

**Table 6** Cu NPs catalyzed click polymerization of different monomers<sup>a)</sup>

Number	Polymer	Monomer	Yield (%)	<i>M<sub>w</sub></i> <sup>b)</sup>	<i>Đ</i> <sup>b)</sup>
1	PI	<b>1a+2a</b>	84.6	82000	1.69
2	PII	<b>1b+2a</b>	79.6	18800	1.28
3	PIII	<b>1a+2b</b>	76.4	29700	2.21
4	PIV	<b>1a+2c</b>	91.4	20100	2.43

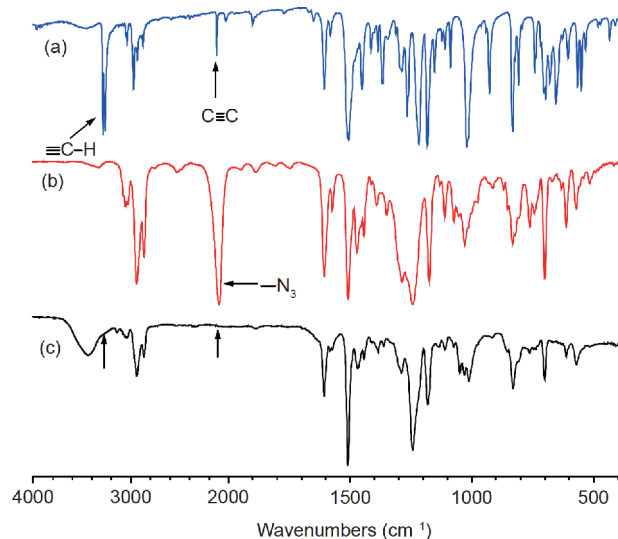
a) Polymerizations were carried out at 60 °C for 8 h with both concentration of Cu NPs monomer concentration of 0.05 M; b) *M<sub>w</sub>* and *Đ* values were estimated by APC with THF as eluent on the basis of a polystyrene calibration.

milar (Figures S2–S4), the Fourier transform infrared spectroscopy (FT-IR) spectra of **PI** and its monomers are discussed here as an example.

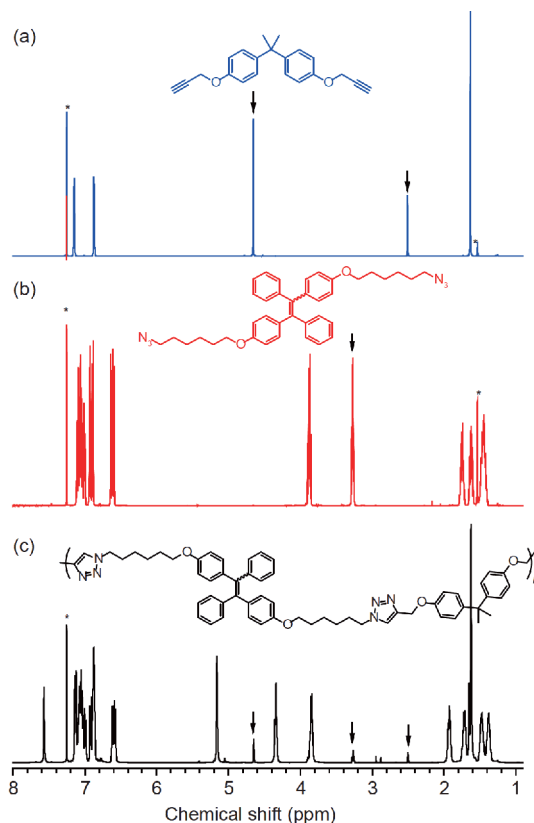
In Figure 1(a), the absorption peaks at 3265 and 2122  $\text{cm}^{-1}$  are attributable to the  $\equiv\text{C-H}$  stretching vibration and  $\text{C}\equiv\text{C}$  vibration of **1a**, respectively. Whereas, the characteristic 2095  $\text{cm}^{-1}$  of  $-\text{N}=\text{N}^+=\text{N}^-$  in **2a** is very abrupt in Figure 1(b). In FT-IR spectrum of **PI**, the entire characteristic absorption peaks of ethynyl and azide groups disappeared, indicative of the occurrence of this click polymerization.

To gain more detail information about the polymer structures,  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of the resultant polymers were measured. The resonance peak of ethynyl proton ( $\delta=2.51$ ) and methylene proton ( $\delta=4.66$ ) adjacent to the ethynyl group of **1a** in Figure 2(a) and methylene proton adjacent to azide group ( $\delta=3.27$ ) of **2a** in Figure 2(b) could be easily designated in the  $^1\text{H}$  NMR spectra. The above characteristic signals could be merely observed in the spectrum of **PI**. At the same time, new peak of triazole rings could be observed at  $\delta=7.57$ . Notably, in  $\text{DMSO-}d_6$ , such new peak of triazole ring proton of **PI** catalyzed by Cu NPs was identical as that of **PI** catalyzed by  $\text{CuSO}_4/\text{ascorbic acid}$ . And no resonance peak assignable to the 1,5-regioregular triazole isomers in the polymer can be observed. Hence it can be concluded that most of the ethynyl and azide groups participated in Cu NPs catalyzed click polymerization, while minority of them was left as terminal groups of polymers.

In the  $^{13}\text{C}$  NMR spectra (Figure 3(c)), very weak resonance peak of acetylene proton ( $\delta=78.8$  and  $\delta=75.4$ ) of polymer **PI** can be observed. New peaks appear at  $\delta=127.8$  and  $\delta=122.4$ , which could be designated as signals of the two carbon atoms on triazole rings. These results verified that most of ethynyl groups have been converted to triazole rings via the click polymerization. In the  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of other



**Figure 1** FT-IR spectra of monomers **1a** (a), **2a** (b) and their polymer **PI** (c) (color online).



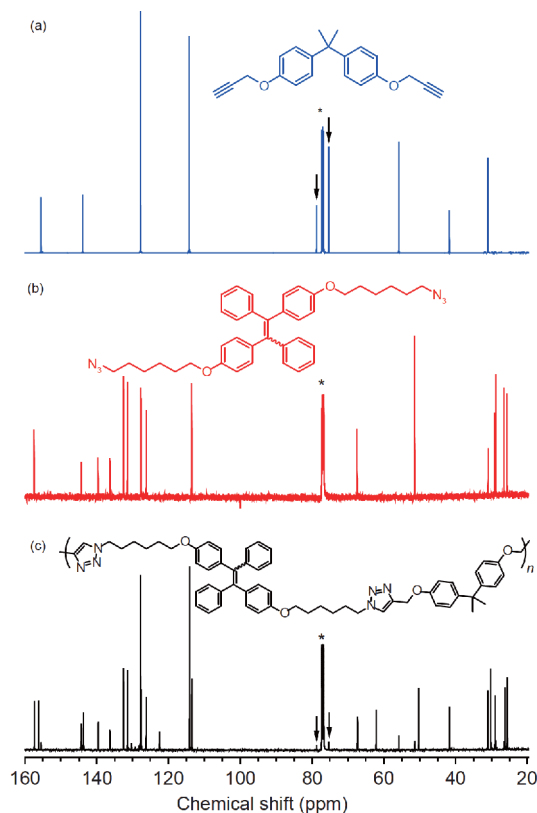
**Figure 2**  $^1\text{H}$  NMR spectra of monomer **1a** (a), monomer **2a** (b) and their polymer **PI** (c) in  $\text{CDCl}_3$ . The solvent peaks are marked with asterisks (color online).

polymers, similar results were also observed (Figures S6–S11).

### 2.3 Reusability of Cu NPs catalyst for click polymerization

Developing reusable and/or recyclable metal catalysts is in accordance with sustainable development strategy. Herein, we focused on the reusability of Cu nanoparticles during carrying out the click polymerization, which could probably provide viable information for the research on nanoparticle catalysts for polymerizations. Reusability of Cu NPs as catalyst for click polymerization was performed under optimal reaction conditions. After each cycle, reaction solvent containing polymer was sucked out by a syringe after centrifugation, while the Cu NPs were washed with THF and re-dispersed in fresh monomer solution for next reaction cycle. The catalyst was successfully reused for 11 cycles and polymer with considerable high molecular weight was produced in high yield even in the eleventh cycle (Table 7). The successful reuse of Cu NPs for click polymerization shows great potential in industrialization owing to its easy separation and reuse.

As long as more cycles were achieved, fewer and fewer catalyst was recycled. At the end of the last cycle, very little catalyst was separated out at the bottom of centrifugation tube.



**Figure 3**  $^{13}\text{C}$  NMR spectra of monomer **1a** (a), monomer **2a** (b) and their polymer **PI** (c) in  $\text{CDCl}_3$ . The solvent peaks are marked with asterisks (color online).

**Table 7** Reuse of Cu NPs for polymerization of **1a** and **2a** in THF <sup>a)</sup>

Number	Cycle	Yield (%)	$M_w$ <sup>b)</sup>	$\bar{D}$ <sup>b)</sup>
1	1	72.0	76,000	1.66
2	2	76.6	136,000	1.68
3	3	87.8	18,000	3.73
4	4	51.6	5,300	1.54
5	5	87.6	34,300	1.84
6	6	42.9	5,500	1.75
7 <sup>c)</sup>	7	88.0	69,400	1.41
8 <sup>c)</sup>	8	93.1	48,000	1.43
9 <sup>c)</sup>	9	82.2	75,000	1.61
10 <sup>c)</sup>	10	80.1	47,300	1.73
11 <sup>c)</sup>	11	80.0	59,900	1.37

a) Polymerizations were carried out at 60 °C for 8 h with both Cu NPs concentration and monomer concentration of 0.05 M. Catalyst was centrifuged and dispersed in fresh monomer solution to start the next cycle. b)  $M_w$  and  $\bar{D}$  values were estimated by APC with THF as eluent on the basis of a polystyrene calibration. c) Polymerizations were carried out at 60 °C for 12 h.

## 2.4 Polymerization mechanism

It was reported that the reaction process takes place on the surface of the nanoparticles [40]. It was believed that the oxidized layer of Cu(I) species on the surface of copper nanoparticles were responsible for the actual catalytic effect

[41]. Such Cu(I) species might be produced by partial oxidation on the surface of Cu nanoparticles during work-up operation, or even during the reaction process because minuscule oxygen might still remain in the monomer solution. Thus, after two polymerization cycles, variation of molecular weight and yield of the product occurred. Bubbling nitrogen gas into monomer solution could not thoroughly eliminate oxygen. Hence evacuating and refilling nitrogen gas for three times at the first cycle led to the results similar with the optimal conditions. Meanwhile, triazole rings were reported to be excellent ligand that sturdily immobilized Cu(I) on solid surfaces [42]. The coordination of triazole rings toward Cu(I) was account for the loss of Cu species during the reuse cycle. Cu residual in **PI** as-prepared was measured by atomic absorption spectroscopy after decomposed in concentrated  $\text{HNO}_3$  which showed similar results to the polymers synthesized by usual copper catalysts such as  $\text{Cu}(\text{PPh}_3)_3\text{Br}$  and  $\text{CuSO}_4/\text{ascorbic acid}$  (Tables S2 and S3, Supporting Information online). This also helped explain the catalyst loss during the reuse of Cu NPs for click polymerization.

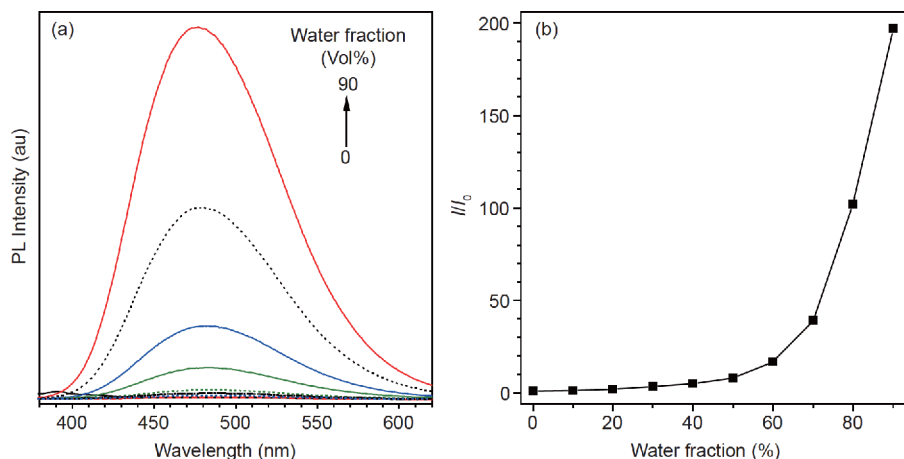
## 2.5 Aggregation-induced emission of polymers

The introduction of AIE-active TPE moiety into the polymer backbones endows the resultant polymer **PI** with the AIE feature, too. As shown in Figure 4, when excited at 323 nm, the photoluminescence (PL) spectrum of the diluted THF solution (10  $\mu\text{M}$ ) of **PI** gives very weak emission. When dissolved in THF/water mixture with 20% water fraction ( $f_w$ ), the polymer exhibits blue-green fluorescence at 481 nm. As  $f_w$  increased, the emission became stronger. The strongest emission was recorded THF/water mixture with  $f_w$  of 90%, which is 197 fold higher than that in pure THF, indicating that **PI** is a typical AIE polymer. It is worthy to note that the maximum emission peaks at 481 nm remained unchanged as  $f_w$  increased. In comparison with conventional aggregation-caused quenching (ACQ) materials, AIE polymers possess great potential applications in bioimaging, sensors, electroluminescence materials and other frontiers.

## 3 Conclusions

In summary, the Cu NPs catalyzed click polymerization of diynes and diazides under mild conditions was successfully developed, and polytriazoles **PI** to **PIV** with high molecular weights were facily produced in high yields in THF after reaction for 8 h. More importantly, Cu NPs could be recycled and reused for up to 11 times, and the click polymerization performed well at each cycle. The polymer prepared by the monomer containing TPE moiety displayed a typical AIE feature. Thus, the results in this paper provide useful





**Figure 4** (a) Photoluminescence spectra of PI in THF/H<sub>2</sub>O mixture with different water fractions. Concentration of PI was 10  $\mu$ M. Excitation wavelength was 323 nm. (b) Plot of the relative fluorescence intensity of PI versus water fraction (color online).

guideline to other polymerizations using metal nanoparticles as recyclable catalysts.

**Acknowledgements** This work was supported by the National Natural Science Foundation of China (21788102, 21525417, 21490571), the National Program for Support of Top-Notch Young Professionals, the Natural Science Foundation of Guangdong Province (2016A030312002), the Fundamental Research Funds for the Central Universities (2015ZY013), and the Innovation and Technology Commission of Hong Kong (ITC-CNERC14S01).

**Conflict of interest** The authors declare that they have no conflict of interest.

**Supporting information** The supporting information is available online at <http://chem.scichina.com> and <http://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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