Alkyne–Azide Click Polymerization Catalyzed by Magnetically Recyclable Fe$_3$O$_4$/SiO$_2$/Cu$_2$O Nanoparticles

Yizhao Chen, Tianyu Cheng, Anjun Qin,* and Ben Zhong Tang*

The Cu(I)-catalyzed click polymerization fully meets the trend of developing powerful and economic tools for facile synthesis of functional polymers. However, the use of Cu(I) catalyst generally results in polymers with high copper residuals, which complicate the polymer purification and limit their applications. Moreover, these catalysts can only be used one time. Inspired by the report that Fe$_3$O$_4$-based nanoparticles can be used as magnetically recyclable catalysts, these magnetic nanoparticles are used to produce Fe$_3$O$_4$/SiO$_2$/Cu$_2$O catalysts. These magnetic nanoparticles can efficiently catalyze the azide–alkyne click polymerization under mild reaction conditions, producing 1,4-regioregular polytriazoles with high molecular weights in excellent yields. The copper residuals in the polymer products are much lower than those catalyzed by the conventional Cu(I) catalysts. Moreover, the Fe$_3$O$_4$/SiO$_2$/Cu$_2$O can be recycled and reused for at least 12 times. Introducing aggregation-induced emission (AIE)-active tetraphenylethylene unit into the polymer main-chains endows the resultant polymer with AIE feature, too. Thus, this work not only simplifies the polymer purification procedures, but also provides a general strategy to reduce the copper residues in the polymers.

1. Introduction

Polymers are now indispensable materials for human lives. Along with the rapid development of polymer science since 20th century, massive synthetic tools for polymers have been invented. Currently, powerful and sustainable chemistry is required for the polymer synthesis.[1–4] Click chemistry, first proposed by Sharpless et al.,[5] is an innovating concept that fully meets the requirement of sustainable chemistry. Click polymerization, developed

based on click reaction, largely retains its merits, including high efficiency, mild reaction condition, easy access to starting materials, regioselectivity, atom-economic, and simple work-up procedures. Among diversified and prosperous click reactions, Cu(I)-catalyzed azide–alkyne cycloaddition (CuAAC) is well studied[6–11] and has been developed into the Cu(I)-catalyzed azide–alkyne click polymerization, which provides a powerful tool for incorporation of functional groups into the resultant polytriazoles for diverse applications.[12–27]

Our group has been working on the development of powerful and efficient click polymerizations, from which linear and hyperbranched functional polytriazoles have been yielded.[28–37] However, as research advanced, it was found that employing Cu(I) species as catalyst for the click polymerization will bring in Cu residuals in the generated polymers as impurity, which severely defect their functionality and limit their applications, especially in optoelectronic, biological, and medical areas.[38–40] In addition, the use of nonrenewable catalysts will raise economical and environmental concerns.

To confront these problems and to meet the growing tendency of modern chemistry, lots of efforts have been dedicated to further improve catalyst performance for click reaction. For example, photoinduced click reactions[41–46] and electro-click reactions[47] have been reported, which provide the possibility for catalyst reuse and could reduce the copper residuals in the resultant polymers. Alternatively, the immobilized metal catalysts on supporting substrates,[48–78] especially based on magnetic nanoparticles, have been used as heterogeneous catalysts for CuAAC toward the triazole derivatives.[79–85] The advance of these catalysts is that catalytic species could be rapidly and easily separated from the reaction system by a magnet after reaction, but magnetic nanoparticle supported catalysts for click polymerization were rarely reported.

We also successfully used supported Cu(I) catalysts for the azide–alkyne click polymerization.[86,87] However, the separation of the catalysts after the polymerization is complex and the reuse cycles are limited. In this work, magnetic nanoparticles with Cu$_2$O on the surface were prepared and used to catalyze the azide–alkyne click polymerization. The results show that they are highly effective and could be easily segregated from the polymerization system by a magnet. Importantly, these catalysts can be reused for at least 12 times, and the Cu residuals in the resultant polymers are lower than those catalyzed by conventional Cu(I) catalysts.

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2. Experimental Section

2.1. Materials and Instruments

Tetrahydrofuran (THF) was distilled under nitrogen from sodium benzophenone ketyl immediately prior to use. *N,N*-dimethylformamide purchased from Sigma-Aldrich was of extra-dry grade. Diethylene glycol (DEG), tetraethylorthosilicate (TEOS), ammonia aqueous solution, $FeCl_3$, $NaBH_4$, NaOH, hexane, chloroform, ethanol (EtOH), and 1,4-dioxane were purchased from domestic manufacturers. Cupric acetate monohydrate was purchased from TCI (Shanghai). *N*-[3-(trimethoxysilyl)propyl]ethylenediamine was purchased from Energy Chemical. Molecular weights of polymers were estimated by advanced polymer chromatography (APC) with THF as an eluent on the basis of a polystyrene calibration, M_w represents weight-average molecular weight and *Đ* means polydispersity index. FT-IR spectra of polymers were recorded on a Bruker Vector 22 spectrometer as thin films on KBr pullets. ^{1}H and ^{13}C NMR spectra were measured on a Bruker AV500 spectrometer in $CDCl_3$ with tetramethylsilane as internal reference (TMS; $\delta = 0$). Transmission electron micrograph (TEM) was measured by JEM-1200EX transmission electron microscope. The X-ray diffraction patterns (XPS) were recorded on Rigaku SmartLab 3 with Cu *Kα* radiation. *2θ* angle ranged from 10° to 90°. X-ray photoelectron spectroscopy was recorded on Axis Ultra DLD (Kratos, UK) with mono Al *Kα* X-ray as light source. Copper residuals of polymers were measured by atom absorbance spectroscopy (AAS) on Hitachi Z-2000.

2.2. Preparation of Fe₃O₄/SiO₂/Cu₂O Catalyst

The synthetic routes to $Fe_3O_4/SiO_2/Cu_2O$ catalyst are shown in **Scheme 1**.

Fe_3O_4 nanoparticles were prepared by reducing Fe^{3+} in DEG. Anhydrous $FeCl_3$ powder (0.13g, 0.80 mmol) and poly(acrylic acid) (0.58 g, 8.00 mmol, M_n = 3000 g mol^{-1}) were added into a two-necked flask. The flask was repeatedly extracted to vacuum and refilled with N_2 for three times. Then, 34 mL DEG was added. The flask was immersed in 220 °C oil bath and stirred for 1 h with N_2 bubbling into the solution. At the same time, in
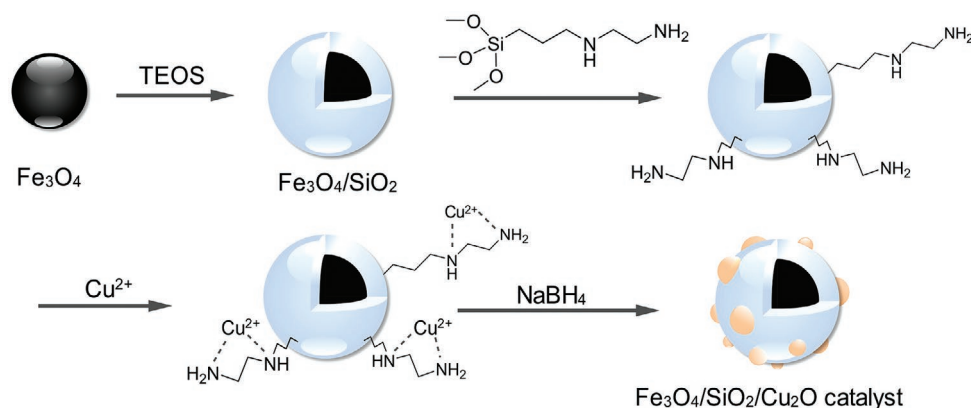
another Schlenk tube, 1.00 g NaOH (25.00 mmol) was added, followed by extracting to vacuum and refilling with N_2 for three times. The Schlenk tube was injected with 10 mL DEG and then immersed in 220 °C oil bath. The NaOH DEG solution was bubbled with N_2 for 30 min; afterward, 1.5 mL of the NaOH DEG solution was extracted with a syringe and rapidly injected into the Fe^{3+} DEG solution. The reaction solution was kept at 220 °C and stirred for 1 h. After cooling to room temperature, the black turbid reaction solution was centrifuged and washed with EtOH for three times.

The as-prepared Fe_3O_4 nanoparticles were encapsulated with SiO_2 immediately. The magnetic nanoparticles were dispersed in a mixture of 320 mL EtOH, 8 mL 25 wt% ammonia aqueous solution, and 20 mL deionized water. The dispersion system was stirred and ultrasonicated for 15 min, followed by adding 0.25 mL TEOS and ultrasonicating for another 1 h. The SiO_2 encapsulated nanoparticles were separated by a magnet, washed with EtOH for three times, and dispersed in 100 mL EtOH. After adding excess amount of 2 mL *N*-[3-(trimethoxysilyl) propyl]ethylenediamine the dispersion was stirred at 60 °C overnight. The amino group–modified magnetic nanoparticles were separated by a magnet and washed with EtOH for three times.

After encapsulating with SiO_2 layer and modifying with amino groups, the magnetic particles were dispersed in 100 mL EtOH. Under mechanical stirring and ultrasonication, 0.10 g (0.50 mmol) cupric acetate monohydrate was added and bubbled with N_2 for 1 h, then the N_2 bubbled $NaBH_4$ (0.074 g, 2.00 mmol) EtOH solution was slowly dropped into the dispersion solution of magnetic particles. The reaction dispersion solution gradually turned to dark black from dark green. After finishing the addition of $NaBH_4$ solution, the reaction system was kept ultrasonicated and stirred for another 1 h. The resultant $Fe_3O_4/SiO_2/Cu_2O$ catalyst sized about 50 nm was washed with N_2 bubbled EtOH for three times, dried under vacuum, and stored under N_2 atmosphere.

2.3. Fe₃O₄/SiO₂/Cu₂O-Catalyzed Click Polymerization

All click polymerizations were carried out under nitrogen atmosphere in Schlenk tubes. Typical experimental procedures yielding **PI** are given below as an example. Into a dry 10 mL

Scheme 1. Synthetic routes to $Fe_3O_4/SiO_2/Cu_2O$.

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Schlenk tube, 30.4 mg (0.10 mmol) of **1a**, 61.4 mg (0.10 mmol) of **2a**, 9.6 mg of $Fe_3O_4/SiO_2/Cu_2O$ (0.015 mmol of Cu), and a magnet connected stirrer were added, and the tube was sealed with a rubber plug. After the Schlenk tube was evacuated and refilled with nitrogen for three times, 2 mL distilled THF was added with a syringe. The Schlenk tube was ultrasonicated for 5 min and stirred vigorously at 70 °C for 8 h. After cooling to room temperature, the reaction solution was diluted with 2 mL distilled THF. A magnet was placed close to the Schlenk tube for 15 min to separate the catalyst. The supernatant was extracted by a syringe and slowly dropped into 100 mL mixture of hexane and chloroform (9:1, v/v) through a cotton filter under stirring. The precipitates were allowed to stand overnight, collected by filtration, and dried under vacuum to a constant weight.

Characterization data of **PI**. Beige powder, yield = 91.7 %, M_w = 45200, Đ = 1.37. FT-IR (KBr), ν (cm^{-1}): 2936, 2864, 1605, 1508, 1467, 1242, 1180, 1011, 829, 699. ^{1}H NMR (500 MHz, $CDCl_3$), δ (TMS, ppm): 1.38, 1.43, 1.62, 1.71, 1.91, 3.84, 4.34, 5.16, 6.59, 6.87, 7.00, 7.04, 7.12, 7.57. ^{13}C NMR (125 MHz, $CDCl_3$), δ (TMS, ppm): 25.56, 26.26, 29.05, 30.18, 31.02, 41.72, 50.32,, 62.14, 67.35, 113.48, 113.58, 114.12, 122.47, 126.15, 127.53, 127.64, 127.79, 131.37, 131.39, 132.52, 136.36, 139.61, 143.62, 144.22, 144.30, 156.13, 157.36.

2.4. Recyclability of $Fe_3O_4/SiO_2/Cu_2O$ Catalyst

After a typical click polymerization, the reaction system was diluted with 2 mL distilled THF and the catalyst was separated and kept in the Schlenk tube by a magnet. The supernatant was extracted and precipitated in a hexane/chloroform mixture to harvest the polymers. In another Schlenk tube, a new batch of **1a** and **2a** were added. After having evacuated and refilled with nitrogen for three times, 2 mL distilled THF was added by a syringe. The Schlenk tube was ultrasonicated to dissolve the monomers. Then, the monomer solution was transfered into the Schlenk tube with the catalyst. After having ultrasonicated for 5 min, the Schlenk tube was stirred at 70 °C for the next cycle of polymerization.

2.5. Measurement of Copper Residuals in the Resultant Polymers

The resultant polymers were first decomposed by concentrated nitric acid. Into the formed dark brown solution, H_2O_2 solution was added, and then the system was heated at 80 °C. Both nitric acid and H_2O_2 aqueous solution were supplemented until the solution became clear and transparent. Afterward, the temperature was raised to 120 °C to expel most of the nitric acid. After adjusting the volume to 10 mL by 3% nitric acid, the aqueous solution was measured by AAS.

3. Results and Discussion

3.1. Synthesis and Characterization of Magnetic $Fe_3O_4/SiO_2/Cu_2O$ Catalyst

The synthesis of the supported magnetic catalyst started from the preparation of Fe_3O_4 nanoparticles, followed by the
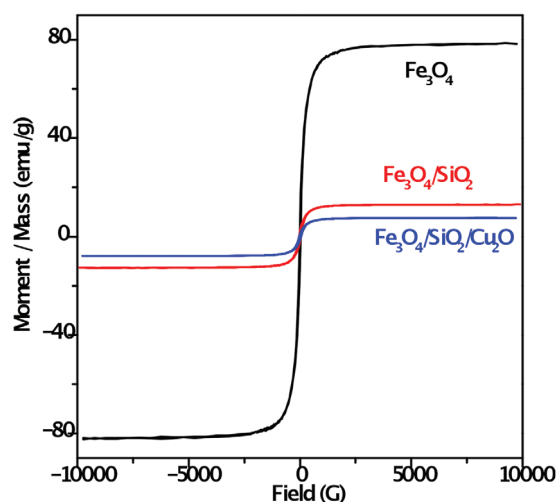

Figure 1. Magnetic hysteresis loops of nanoparticles of Fe_3O_4, Fe_3O_4/SiO_2, and $Fe_3O_4/SiO_2/Cu_2O$.

layer-by-layer encapsulation (Scheme 1). Saturation magnetization intensity of the synthesized Fe_3O_4 nanoparticles was measured to be 78.4 emu g^{-1} under 10000 Gauss magnetic field (**Figure 1**). Acrylic acid and NaOH were added during the synthesis to introduce electrostatic repulsion between the nanoparticles and to avoid flocculation during polymerization. After the SiO_2 layer was formed, saturation magnetization decreased to 13.0 emu g^{-1}. The active catalyst species Cu_2O was immobilized by in situ reduction of Cu(II) coordinated by N-[3-(trimethoxysilyl)propyl]ethylenediamine on the outer layer of SiO_2 as small grains. Finally, the magnetization intensity of the $Fe_3O_4/SiO_2/Cu_2O$ was recorded to be 7.6 emu g^{-1}. The low magnetic remanence of the nanoparticles will help to avoid their flocculation during polymerization. Dried $Fe_3O_4/SiO_2/Cu_2O$ nanoparticles with sizes about 50 nm tend to agglomerate according to TEM image (**Figure 2**), but they could be easily dispersed in organic solvents.

X-ray diffraction patterns of Fe_3O_4/SiO_2 and $Fe_3O_4/SiO_2/Cu_2O$ nanoparticles were recorded and the results are shown in **Figure 3**. The diffraction profile of Fe_3O_4 (Fe_3O_4, PDF # 19–0629, 2θ = 30.095, 35.422, 43.052, 56.942, 62.515) was completely
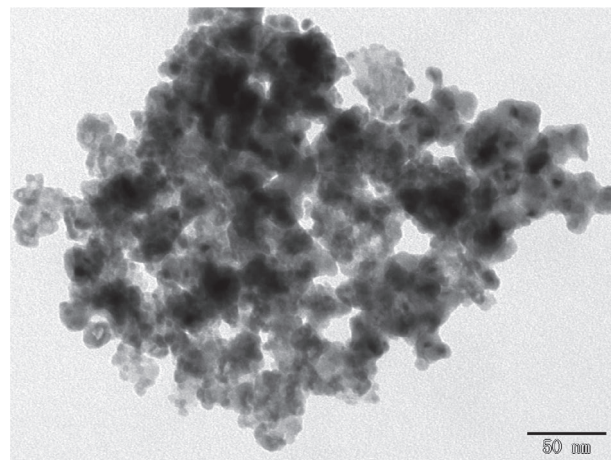

Figure 2. TEM image of $Fe_3O_4/SiO_2/Cu_2O$ catalyst.
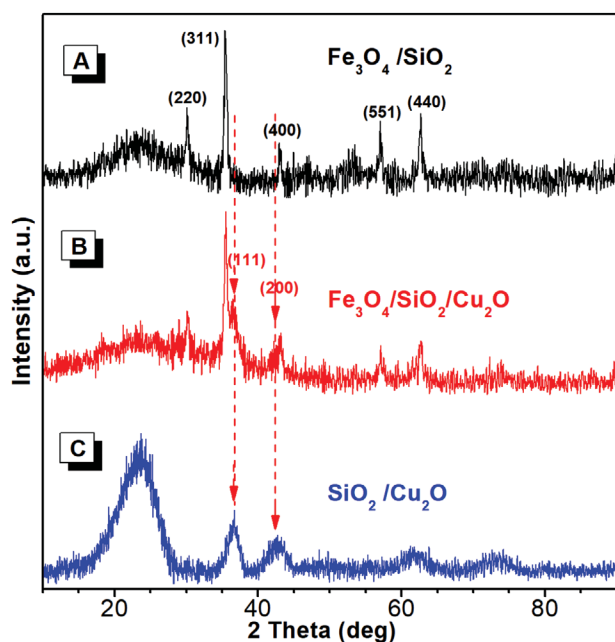
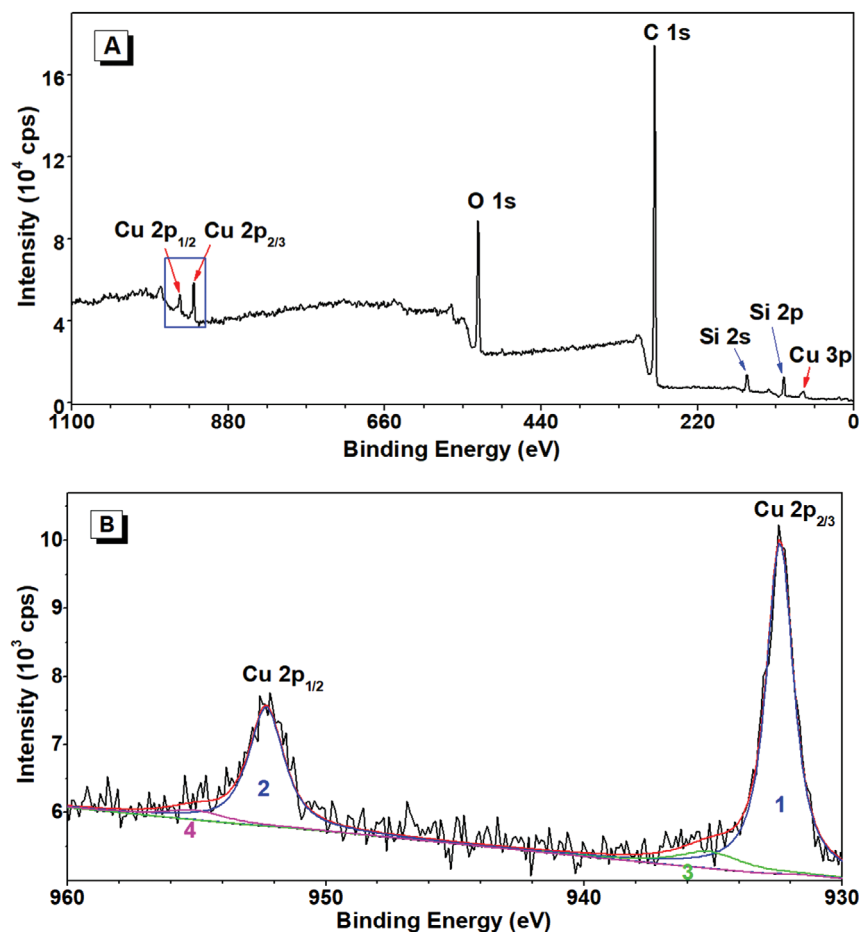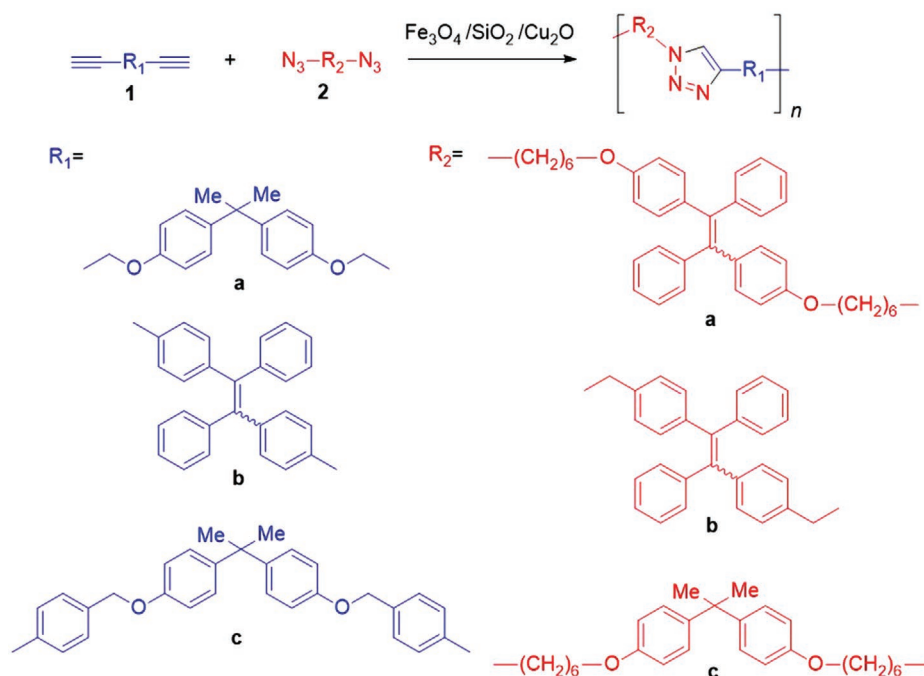**Figure 3.** XRD patterns of A) Fe_3O_4/SiO_2, B) $Fe_3O_4/SiO_2/Cu_2O$, and C) SiO_2/Cu_2O.

Figure 4. A) XPS results for SiO_2/Cu_2O catalyst and B) detailed XPS spectrum of Cu 2p.

retained in the XRD pattern of $Fe_3O_4/SiO_2/Cu_2O$. At the same time, a new peak was observed at $2\theta = 36.4$, which might be the strongest diffraction peak of Cu_2O (Cu_2O syn, PDF #05-0667, $2\theta = 36.418, 42.297, 61.344$). In addition, neither Cu(0) nor CuO diffraction pattern was observed (Cu(0), PDF # 04-0836, $2\theta = 43.297, 50.433, 74.130$; CuO, PDF # 48-1548, $2\theta = 35.543, 38.708, 35.417, 48.716$), verifying the formation of Cu_2O on nanoparticle surface. To assist the characterization of Cu_2O on nanoparticle surface, identical reduction procedure of coordinated Cu(II) using $NaBH_4$ was conducted on amino group–modified SiO_2 nanoparticles and SiO_2/Cu_2O nanoparticles were produced (Scheme S1, Supporting Information). Its XRD pattern clearly supports that Cu(II) species on the nanoparticle surface were reduced to Cu(I), instead of Cu(0) ones (**Figure 3**). Moreover, the photoelectrons from Si, Cu, and O were clearly detected in the XPS spectrum of SiO_2/Cu_2O nanoparticles (**Figure 4**). The Cu 2p photoelectron peaks as shown in Figure 4B suggest that no shakeup line accounted for Cu(II) could be observed, and only a tiny amount of Cu(II) existed, possibly originated from the oxidation during catalyst work-up procedures.

3.2. Click Polymerization

After having succeeded in the preparation of $Fe_3O_4/SiO_2/Cu_2O$ nanoparticles, we applied them to catalyze the azide–alkyne click polymerization (**Scheme 2**). Preliminary investigation of such click polymerization led to an encouraging result. After polymerization of **1a** and **2a**, the catalyst could be easily separated from reaction solution by a magnet and polymers could be acquired by precipitation in hexane/chloroform mixture (volume ratio 9:1). Subsequently, polymerizations under varied reaction conditions were explored, in order to figure out the optimal parameters for the use of catalyst.

The influence of reaction temperature on the yield and M_w of the product can be discerned from **Table 1**. The yields and M_w of products were low at low temperatures (50 °C, Table 1 entry 1), which gradually increased with enhancing temperatures. When the reaction temperature was raised to 80 °C, flocculation of catalyst occurred, resulting in an insoluble polymer–catalyst mixture. As shown in entry 4, Table 1, the M_w of soluble part was low. This is probably because of the unique magnetic property of $Fe_3O_4/SiO_2/Cu_2O$ nanoparticles that intend to agglomerate naturally during the polymerization. We speculated that at the reaction temperature of 80 °C, polymer chains were formed on Cu_2O surface so quickly that the chains were unable to timely detach off, and subsequent reactions between monomers and/or chains deteriorate the polymer chain

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Scheme 2. $Fe_3O_4/SiO_2/Cu_2O$-catalyzed click polymerization of diyne **1** and diazide **2**.

Table 1. Influence of reaction temperature on the polymerization results.

Entry[a]	T [°C]	Yield [%]	M_w[b]	$Đ$[b]
1	50	47.6	9100	2.06
2	60	51.6	12100	1.78
3	70	85.3	79400	1.78
4[c]	80	65.9	22500	1.42

[a]Polymerizations were carried out for 8 h in 2 mL THF. [**1a**] = [**2a**] = 0.050 M. Catalyst concentration [Cu] = 0.0075 M; [b]The weight-average molecular weight (M_w) and polydispersity index ($Đ$) were estimated by APC with THF as an eluent on the basis of a polystyrene calibration; [c]Soluble part.

accumulation and catalyst agglomeration. Furthermore, the triazole rings on the polymer chains might coordinate with the copper species on the nanoparticle surface, leading to larger agglomerates. Such processes generate insoluble mixtures of catalyst agglomerates and polymer gels, which greatly hinder the recycle and reuse of $Fe_3O_4/SiO_2/Cu_2O$ catalyst.

Table 2. Time course of the click polymerization.

Entry[a]	Time [h]	Yield [%]	M_w[b]	$Đ$[b]
1	6	53.5	23500	4.67
2	7	67.1	10400	1.66
3	8	85.3	79400	1.78
4[c]	9	74.1	41800	1.69

[a]Polymerization was carried out at 70 °C in 2 mL THF. [**1a**] = [**2a**] = 0.050 M. Catalyst concentration [Cu] = 0.0075 M; [b]The weight-average molecular weight (M_w) and polydispersity index ($Đ$) were estimated by APC with THF as an eluent on the basis of a polystyrene calibration; [c] Soluble part.

Thus, 70 °C was selected as optimal temperature for further study.

The influence of reaction time on the yields and M_w of polymer products was studied secondly, and the data are provided in **Table 2**. If the polymerization was stopped in 5 h, both the yield and M_w of polymer product were low. Further prolonging the reaction time beyond 8 h also led to flocculation of catalyst. Such flocculation not only severely hampered the harvest of the polymer product, but also rendered the magnetic nanoparticle catalyst difficult to be dispersed into the freshly prepared monomer solution. To avoid such fatal factor for the reuse of catalyst, the optimal reaction time was set as 8 h.

The monomer concentration exerts significant impact on the yields and M_w of the polymer products. Thus, we investigated this parameter thirdly. As shown in **Table 3**, low monomer concentration such as 0.025 M greatly reduced the collision probability of monomers, leading to massive oligomers including cyclic ones with low molecular weights. Increasing the monomer concentration generally enhanced the collision

Table 3. Influence of monomer concentration on the click polymerization.

Entry[a]	[M] [M]	Yield [%]	M_w[b]	$Đ$[b]
1	0.025	47.5	21300	2.00
2	0.030	50.1	15100	2.10
3	0.040	53.8	64500	1.98
4	0.050	85.3	79400	1.78

[a]Polymerization was carried out at 70 °C for 8 h in 2 mL THF. [**1a**] = [**2a**]. Catalyst concentration [Cu] = 0.0075 M; [b]The weight-average molecular weight (M_w) and polydispersity index ($Đ$) were estimated by APC with THF as an eluent on the basis of a polystyrene calibration.

Table 4. Influence of solvent on the click polymerization.

Entry[a]	Solvent	Yield [%]	M_w[b]	Đ[b]
1	THF	85.3	79 400	1.78
2	CHCl$_3$	95.2	30 800	1.98
3	1,4-dioxane	83.2	68 600	1.97

[a]Polymerization was carried out at 70 °C for 8 h in 2 mL solvent. [**1a**] = [**2a**] = 0.050 M. Catalyst concentration [Cu] = 0.0075 M; [b]The weight-average molecular weight (M_w) and polydispersity index (Đ) were estimated by APC with THF as an eluent on the basis of a polystyrene calibration.

probability of the monomers and increased of M_w and yields of the products accordingly. Hence, sufficiently high monomer concentration such as 0.050 M would guarantee to furnish polymers with high M_w in satisfactory yields.

Comparing with conventional Cu(I) catalysts, such as Cu(PPh$_3$)$_3$Br, the as-prepared Fe$_3$O$_4$/SiO$_2$/Cu$_2$O nanoparticles exhibit unique catalytic behaviors in different solvents. The polymerizations conducted in three organic solvents of THF, chloroform, and 1,4-dioxane all could obtain good results as shown in **Table 4**. Considering the highest M_w of product in THF, we chose it as the best solvent.

Moreover, different catalyst dosage also influenced the M_w of products. As shown in **Table 5**, increasing catalyst amount led to higher molecular weights of the products. Interestingly, the yields of the products maintained at same high level, even further enlarging the catalyst dosage. Taking the polydispersity index of the polymer into account, we used 0.0075 M as the best catalyst concentration.

With the optimal polymerization conditions in hand, we tested the universality of the nanoparticles in catalyzing the reactions (Scheme 2). As shown in **Table 6**, the as-prepared nanoparticles are capable of catalyzing click polymerizations of different monomers, including both aromatic and aliphatic alkynes. Polytriazoles with M_w up to 45 200 could be produced in excellent yields (up to 91.7%). These results further confirmed the robustness of our prepared Fe$_3$O$_4$/SiO$_2$/Cu$_2$O nanoparticles in catalyzing the azide–alkyne click polymerization. In addition, the Cu(I) species on and detached from the Fe$_3$O$_4$/SiO$_2$/Cu$_2$O nanoparticles might both serve as the active catalysts for the click polymerization.

3.3. Characterization of Resultant Polymers

The structures of resultant polymers can be definitely confirmed by conventional spectral characterization techniques.

Table 5. Influence of catalyst concentration on the click polymerization.

Entry[a]	[Cu] [M]	Yield [%]	M_w[b]	Đ[b]
1	0.0050	83.2	33 800	1.36
2	0.0075	85.3	79 400	1.78
3	0.0100	85.3	117 400	2.05

[a]Polymerization was carried out at 70 °C for 8 h in 2 mL THF. [**1a**] = [**2a**] = 0.050 M; [b]The weight-average molecular weight (M_w) and polydispersity index (Đ) were estimated by APC with THF as an eluent on the basis of a polystyrene calibration.

Table 6. Fe$_3$O$_4$/SiO$_2$/Cu$_2$O catalyzed click polymerization of different monomers.

Entry[a]	Monomer	Polymer	Yield [%]	M_w[b]	Đ[b]
1	**1a** + **2a**	PI	91.7	45 200	1.37
2	**1b** + **2a**	PII	89.6	35 000	1.36
3	**1a** + **2b**	PIII	91.0	20 000	1.31
4	**1a** + **2c**	PIV	91.8	43 800	1.78
5	**1b** + **2c**	PV	83.7	14 700	1.37
6	**1c** + **2a**	PVI	48.3	12 900	2.26

[a]Polymerization was carried out at 70 °C for 8 h in 2 mL THF. [**1**] = [**2**] = 0.050 M. Catalyst concentration [Cu] = 0.0075 M; [b]The weight-average molecular weight (M_w) and polydispersity index (Đ) were estimated by APC with THF as an eluent on the basis of a polystyrene calibration.

Since the spectral profiles for the polymers are almost same (Figures S1–S14, Supporting Information); herein, the ^{1}H and ^{13}C NMR and FT-IR spectra of **PI** are given as examples and the results are shown in **Figures 5**, **6**, and **7**, respectively.
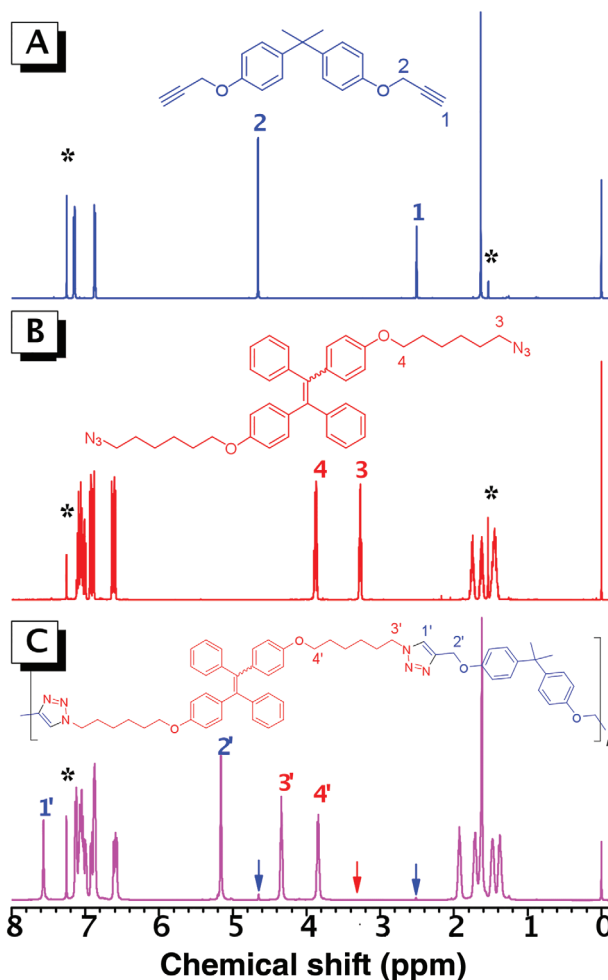

Figure 5. ^{1}H NMR spectra of A) diyne **1a**, B) diazide **2a**, and C) their polymer **PI** in CDCl$_3$. The solvent peaks are marked with asterisks.
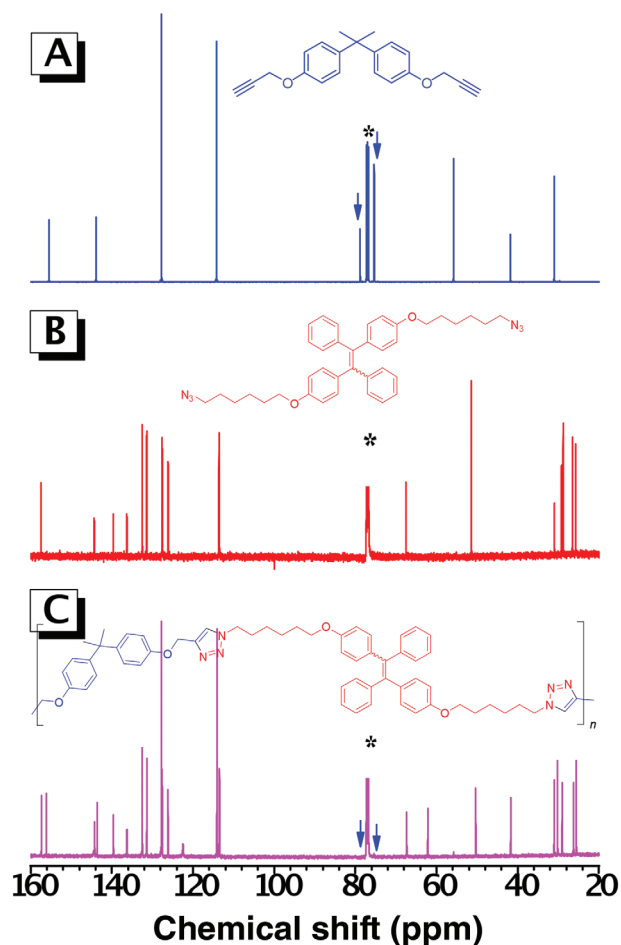
Figure 6. ^{13}C NMR spectra of A) diyne **1a**, B) diazide **2a**, and C) their polymer **PI** in CDCl$_3$. The solvent peaks are marked with asterisks.

With excellent polymerization efficiency, diyne **1a** and diazide **2a** were completely reacted, judging from the disappearance of resonance peaks $\equiv$C$-H$ ($\delta = 2.51$, Figure 5A) and $-CH_2N_3$ ($\delta = 3.27$, Figure 5B) of **PI** in the ^1H NMR spectra
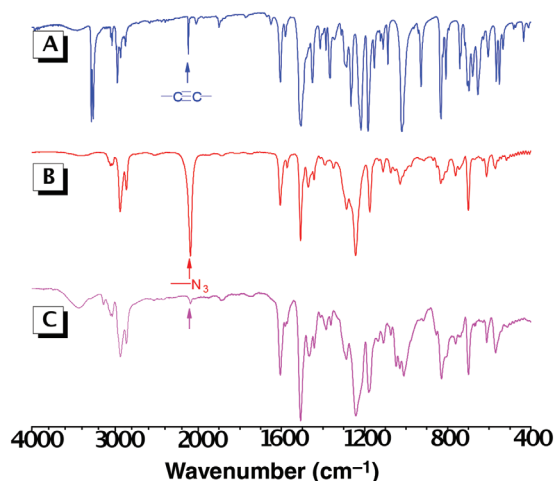

Figure 7. FT-IR spectra of A) diyne **1a**, B) diazide **2a**, and C) their **PI**.

shown in Figure 5C. Moreover, the appearance of peak at $\delta = 7.57$ in the ^1H NMR spectrum of **PI** confirmed the ethynyl and azide groups have been converted into 1,4-triazole rings.

According to the ^{13}C NMR spectra displayed in Figure 6, similar conclusion could be drawn. In Figure 6A, the C$\equiv$C resonance peaks at $\delta = 75.3$ and 78.8 of **1a** were obvious. However, they cannot be found in the ^{13}C NMR spectrum of **PI**. Whereas, comparing with the FT-IR spectra of the monomers in Figure 7, obvious disappearance of the C$\equiv$C (2212 cm^{-1}), $-$N$_3$ (2098 cm^{-1}), and H$-$C$\equiv$ (3286 cm^{-1}) stretching vibration signals indicated that the ethynyl and azide groups have been consumed after reaction. These spectral characterization results unambitiously confirm that Fe$_3$O$_4$/SiO$_2$/Cu$_2$O nanoparticles could successfully catalyze the azide–alkyne click polymerization.

3.4. Recyclability and Reusability of the Catalyst

The recyclability and reusability of Fe$_3$O$_4$/SiO$_2$/Cu$_2$O catalyst was tested using **1a** and **2a** as model monomers. As shown in **Table 7**, the catalyst can be reused for at least 12 times, although prolonging the reaction time from 8 to 12 h was needed after 7th cycle. By simply placing a magnet beside the Schlenk tube, Fe$_3$O$_4$/SiO$_2$/Cu$_2$O catalyst can be attracted on the Schlenk tube wall and segregated from the reaction system, allowing facile extraction of product solution and reload of freshly prepared monomer solution. For the next reusing cycle, the separated magnetic catalyst can be easily re-dispersed in monomer solution by ultrasonication. During each reusing cycle, a polymer can be produced in a high yield. After subsequent reuse for eight cycles, the M_w of resultant polymers decreased owning to the loss of Cu(I) species on the nanoparticles probably due to their coordination with the formed triazole rings.[67,88] The Fe$_3$O$_4$/SiO$_2$/Cu$_2$O nanoparticles offers the great potential for developing a catalytic system that meets the need of powerfulness and economic for the click polymerization and might shine light on other polymerizations.

Table 7. Reuse of Fe$_3$O$_4$/SiO$_2$/Cu$_2$O catalyzed click polymerization.

Cycle[a]	Yield [%]	M_w[b]	Đ[b]
1	82.4	60 700	2.03
2	88.5	132 600	1.78
3	87.6	26 900	1.64
4	92.9	43 800	1.51
5	89.3	27 000	1.33
6	85.7	19 500	1.44
7	88.8	74 700	1.52
8[c]	90.5	96 800	1.61
9[c]	90.5	10 900	1.49
10[c]	91.5	18 600	1.38
11[c]	79.4	37 500	1.46
12[c]	63.0	7300	2.07

Table 8. Cu residuals in the polytriazoles obtained by $Fe_3O_4/SiO_2/Cu_2O$ catalyzed click polymerization.

Polymer	Reaction condition/cycle	Cu residual [ppm]
PIV	70 °C, 8 h/1st	474
PI	70 °C, 8 h/5th	450
PI	70 °C, 12 h/9th	867
PI	60 °C, 8 h/1st	1654
PI	70 °C, 8 h/2nd	389
PI	70 °C, 8 h/3rd	347

Table 9. Cu residuals in the polytriazoles generated by the conventional Cu(I) catalyzed click polymerization.

Cu(I) catalyst[a]	Cu residual [ppm]
CuBr/PMDETA	2741
CuSO$_4$/SA	2913
Cu(PPh$_3$)$_2$NO$_3$	1965
Cu(PPh$_3$)$_3$Br	3987
Cu powder, 14–25 µm	510
Cu nanoparticles, 60–80 nm	340

[a]Polymerization was carried out at 70 °C for 8 h.

3.5. Copper Residuals in Polymers

The copper residuals in the resultant polymers were examined by AAS. The polymers were decomposed in hot HNO_3 and H_2O_2 mixtures, and the aqueous samples were diluted with 3% nitric acid. The total amount of copper species of the polymers retained in acid solution was then measured, and the results are listed in **Table 8**. For comparison, the copper residuals in the products generated by conventional Cu(I)-catalyzed click polymerization are listed in **Table 9**. As can been seen, the polymers obtained by conventional Cu(I)-catalyzed click polymerization have high copper residuals, mostly beyond 2000 ppm. In contrast, $Fe_3O_4/SiO_2/Cu_2O$ catalyst can be easily separated by a magnet from the reaction system, leaving much lower copper residuals in the polymers. Moreover, Cu nanoparticles and small-sized Cu powders could also reduce the copper residuals in polymers, but their catalytic efficiency were low because they will agglomerate and precipitate at the bottom of reaction solution if their surfaces were not modified prior to use. We can conclude that, for the conventional Cu(I)-catalyzed click polymerization, simple work-up procedures of precipitating polymers in poor solvents left large amount of copper species in the polymer products due to the coordination effect of triazole rings with copper ions, resulting in high level copper residuals, which also hindered the reuse of catalyst. In sharp contrast, the copper residuals in our resultant polymers are much lower, suggestive of the advantage of $Fe_3O_4/SiO_2/Cu_2O$ nanoparticles over conventional Cu(I) catalysts in catalyzing azide–alkyne click polymerization.

3.6. AIE Property of PI

The click polymerization is tolerant to functional groups and the AIE-active moiety of TPE could be facilely incorporated into the polymer via the reaction of TPE-containing diyne or diazide monomers. For example, TPE-containing PI could be facilely prepared by the $Fe_3O_4/SiO_2/Cu_2O$ catalyzed click polymerization of diyne **1a** and TPE-containing diazide **2a** under the optimized conditions. The photophysical property investigation showed that PI emits very weakly with a maximum peak at 479 nm in its THF solution (**Figure 8**). However, upon addition of water, especially at a high water fraction (f_w, higher than 70%), the emission of PI in THF/water mixtures enhanced dramatically due to the restriction of intramolecular motion. Notable, when the f_w reached 90%, the emission intensity of the polymer aggregates is 160 times higher than that in its pure THF solution, unambiguously indicative of an AIE feature. Furthermore, the quantum yield measurement of PI also confirmed its AIE feature (Figure 8B).

4. Conclusions

In summary, the $Fe_3O_4/SiO_2/Cu_2O$ nanoparticles were successfully prepared and used to catalyze the click polymerization of alkyne and azide monomers under mild conditions. 1,4-Regioregular polytriazoles with satisfactory M_w and low copper residuals were obtained in high yields. Importantly, $Fe_3O_4/SiO_2/Cu_2O$ catalyst could be reused for at least 12 times and showed excellent performance at each cycle. The polymer prepared by the monomer bearing TPE moiety displayed a typical AIE feature. Such results provide a useful guideline for recyclable catalyst for click polymerization and might shine light on other polymerizations.
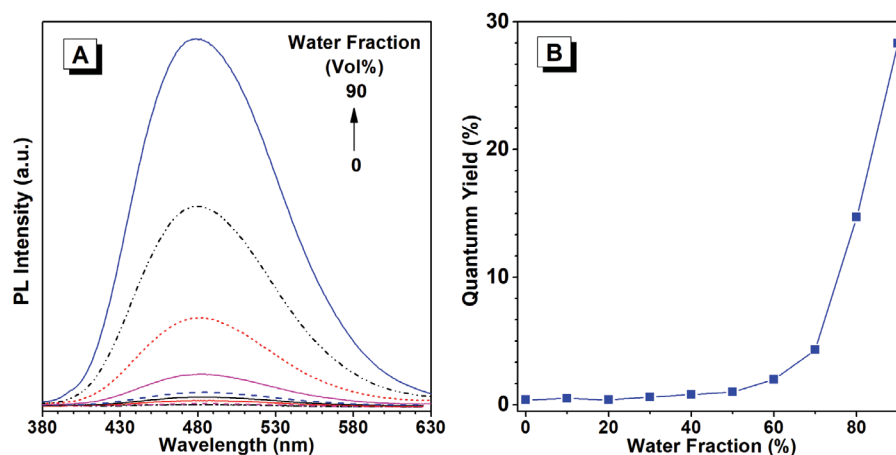

Figure 8. Photoluminescence spectra (A) and quantum yield (B) of PI in THF and THF/water mixtures. Polymer concentration: 10 µM; excitation wavelength: 323 nm.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Conflict of Interest

The authors declare no conflict of interest.

Keywords

click polymerization, copper residuals, magnetic catalysts, recyclability, reuse

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