Molecular Catalysis 474 (2019) 110422

Contents lists available at ScienceDirect

Molecular Catalysis

journal homepage: www.elsevier.com/locate/mcat

Highly efficient polymer-based nanoreactors for selective oxidation of alcohols in water

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ARTICLE INFO

Keywords:
TEMPO
Nanoreactor
Selective oxidation of alcohol
Recoverable catalyst

ABSTRACT

In this study, we demonstrate the fabrication of thermo-responsive polymer-based TEMPO nanoreactors and their application in the catalytic selective oxidation of alcohols as a highly efficient and recoverable catalyst in aqueous media. First, a diblock amphiphilic copolymer NHS-P(MMA_{25}-*b*-$OEGMA_{75}$) consisting of poly(methyl methacrylate) (PMMA) and poly[oligo(ethylene glycol) methyl ether methacrylate] ($POEGMA_{300}$) with a terminal *N*-hydroxysuccinimide (NHS) activated ester was synthesized utilizing reversible addition-–fragmentation chain transfer polymerization (RAFT) techniques. Free radical 2,2,6,6,-tetramethyipiperidinooxy (TEMPO) was then introduced into the end of the copolymer based on activated ester functionalization to afford the temperature responsive polymer-supported catalyst TEMPO-P(MMA_{25}-*b*-$OEGMA_{75}$). Next, core-shell TEMPO nanoreactors were formed through self-assembly of the amphiphilic block polymers in deionized water. The morphology of the nanoreactors was well characterized by dynamic light scattering (DLS) and scanning electron microscopy (SEM). The nanoreactors were then successfully applied in the selective oxidative of alcohols in water. A variety of aldehydes and ketones were achieved in excellent yields and selectivities in high reaction rates with low catalyst loading. The high efficiency in catalysis of the nanoreactors may attributed to the ideal environment where enhancing the interactions between the catalyst and the alcohol substrate, mimicking the environment of enzymes. The thermo-responsive polymer-based nanoreactors could be conveniently recovered in the temperature above the LCST of the polymer after extraction of product from the reaction mixture. This strategy provides an effective and cleaner way for the selective oxidative of alcohols in organic synthesis and industrial application.

1. Introduction

The oxidation of alcohols into their corresponding carbonyl compounds is of great importance in organic synthesis and industrial processes owing to their wide application in drug synthesis etc. [1]. The development of efficient catalysts for the selective oxidation of alcohols has always been the goal of chemists. In the last decade years, 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) was found to be efficient for the selective oxidation of alcohols in combination with renewable oxidants such as molecular oxygen, hydrogen peroxide or hypochlorite [2]. While, isolation and recovery of catalyst remain key issues for large-scale application just as other homogeneous catalysis. To address these shortcomings, immobilization of TEMPO onto diverse carriers to form recoverable heterogeneous catalysts has been widely reported [3–11]. However, the activity of catalyst often decreases when carrier possessing poor dispersibility was adopted [12]. The development of new polymer carrier, which possesses good solubility or dispersivity combining the benefits of homogeneous and heterogeneous catalysis, such as high activity and recyclability will be very meaningful [13–15].

On the other hand, chemical transformation is often accomplished in nano-sized enzymes and other confined spaces under mild and green conditions in nature. Inspired by nature, chemists attempt to construct various nanoreactors in order to achieve efficient chemical conversion by using the special effects in nanoreactors, such as small size effect, surface effect, confinement effect and synergistic effect etc [16–18]. Usually, nanoreactors have good dispersibility and are easy to recycle and reuse. In addition, the efficiency is much higher than traditional heterogeneous catalysis due to the enhanced local substrate concentration, active catalyst and accordingly the interactions between the substrate and the catalyst when the catalytic reaction is carried out in

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https://doi.org/10.1016/j.mcat.2019.110422
Received 21 March 2019; Received in revised form 21 May 2019; Accepted 22 May 2019

nanoreactors, [19–26].

In recent years, core-shell type polymeric nanoreactors through self-assembly of amphiphilic copolymers have attracted more and more attention. In these nanoreactors, the active catalyst was encapsulated inside the hydrophobic core, which greatly increased its concentration, and accordingly the catalytic activity. Besides, the hydrophilic shell made the nanoreacters evenly dispersed in water, which enabled the catalysis in water [27–33]. In most cases, the active catalyst was introduced to nanoreactors by functionalization of hydrophobic part of amphiphilic block copolymers by chemical reactions with high specificity, or copolymerization of active catalyst-containing monomer into the hydrophobic block. For example, Weck et al. reported a class of shell cross-linked micelles-supported Co(III)-salen complexes, which were prepared by the esterification reaction of hydroxyl group from salen ligand and carboxyl groups from the hydrophobic block, then metalated with Co(II) and oxidized to Co(III)-salen complexes. These supported Co(III)-salen complexes displayed not only high catalytic efficiencies but also an unique substrate selectivity [34]. In O'reilly et al.'s study, copolymerization of monomer with a L-proline moiety in the hydrophobic block of amphiphilic block copolymers, then self-assembly to form nanoreactors for asymmetric Aldol reaction in aqueous media was reported [35].

Herein we wish to report the facile synthesis of an amphiphilic block copolyer with a TEMPO organocatalyst in the terminal of the hydrophobic block, the fabrication of core-shell TEMPO nanoreactors by self-assembly of the amphiphilic block copolymers in water, and the investigation of their catalytic activities and recyclability in the selective oxidation of alcohols. The results demonstrate high efficiency, easy recycling and environmental friendliness of the TEMPO-based nanoreactors, which highlight the potential utility of this catalysis system in organic synthesis and industrial production.

2. Experimental section

2.1. Preparation of NHS-PMMA$_{25}$ (Macro-CTA)

NHS-CEPA was prepared followed by our previous report [36]. Macro-CTA was prepared as below. NHS-CEPA (144.0 mg, 0.4 mmol), methyl methacrylate (MMA) (1.00 g, 10.0 mmol), and AIBN (6.57 mg, 0.04 mmol) were added to dioxane (4 mL) in a 50 mL ampule. The resulting solution was degassed by 3 freeze–pump–thaw cycles and the ampule was refilled with nitrogen and tightly sealed. The RAFT polymerization was carried out at 65 °C for 24 h, after that the reaction mixture was opened to air and cooled down. The polymer was precipitated in cold *n*-hexane (4˜5 °C) to yield Macro-CTA as a yellow oil (Scheme 1). The degree of polymerization was determined by the crude ^{1}H NMR spectroscopy. Molecular weight and dispersity were determined by GPC with THF as an eluent using poly(methylmetacrylate) (PMMA) as standards.

2.2. Preparation of NHS-P (MMA$_{25}$-*b*-OEGMA$_{75}$)

Macro-CTA (286 mg, 0.10 mmol), OEGMA (1.50 g, 7.5 mmol) and AIBN (1.64 mg, 0.01 mmol) were added to 1,4-dioxane (4 mL) in a 50 mL ampule. Similar procedure with the preparation of NHS-PMMA$_{25}$ was adopted for the polymerization. The polymer was precipitated in cold *n*-hexane (4˜5 °C) to yield NHS-P (MMA$_{25}$-*b*-OEGMA$_{75}$) as a yellow oil (Scheme 2). The degree of polymerization was determined by the crude ^{1}H NMR spectroscopy. Molecular weight and dispersity were determined by GPC with THF as an eluent and using poly(methylmetacrylate) (PMMA) as standards.

2.3. Preparation of TEMPO-P(MMA$_{25}$-b-OEGMA$_{75}$)

To a solution of NHS-P(MMA$_{25}$-*b*-OEGMA$_{75}$) (0.5 g, 0.02 mmol) in THF (15 mL), 4-amino-TEMPO (6.85 mg, 0.04 mmol) and TEA (10 µL, 0.072 mmol) was added under nitrogen atmosphere and the resulting mixture was stirred at room temperature for 24 h. The product was precipitated from cold *n*-hexane to yield TEMPO-P(MMA$_{25}$-*b*-OEGMA$_{75}$) as an orange-red viscous oil (Scheme 3).

2.4. Fabrication of polymer-supported nanoreactors

20 mg of TEMPO-P(MMA$_{25}$-*b*-OEGMA$_{75}$) was added to 2 mL of deionized water. The mixture was oscillated continuously to fully dissolve. Nanoparticles formed through self-assembly of the amphiphilic block polymers in water. The size and morphology of the nanoreactors were investigated by dynamic light scattering (DLS) and scanning electron microscope (SEM).

2.5. General procedure of the catalytic oxidation of alcohols

Alcohol (0.8 mmol), NaBr (1.25 mol%), and nanoreactors (20 mg, 0.1 mol%) were added to the mixed solution of NaClO (1.0 mmol, 1.25 mol equil., 2 mL) at 0 °C. The pH value of the aqueous solution was adjusted to 9.1 using NaHCO$_3$. The resulting mixture was vigorously stirred at 0 °C. After completion of the reaction, ether was added to extract unreacted alcohol and product. The conversion and selectivity were analyzed by GC-MS. The catalyst was left in aqueous phase and recovered by heating and centrifugation. And the recycled catalyst was reused for next run after careful washing with cold ether.

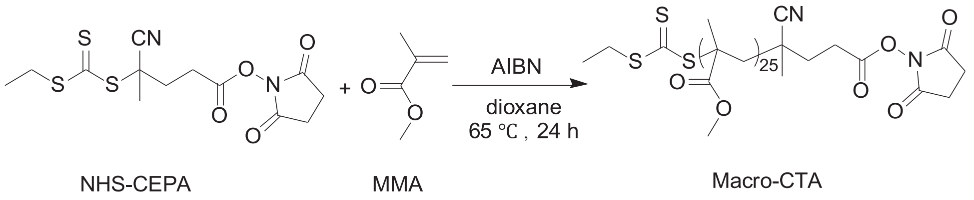
3. Results and discussion

3.1. Synthesis and structural characterization of TEMPO-P(MMA$_{25}$-b-OEGMA$_{75}$)

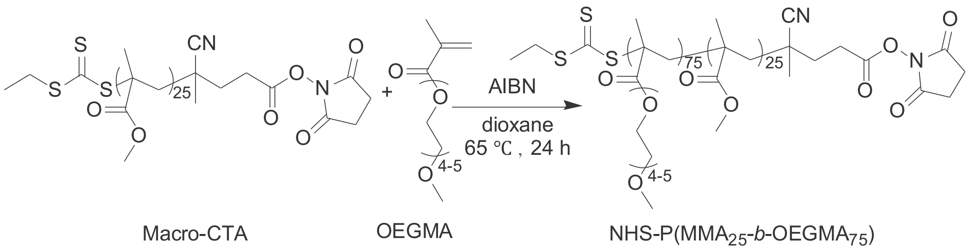
In our study, macro-chain transfer agent NHS-P(MMA$_{25}$) (NHS-CTA) (Mn = 3.16 kg mol^{-1}, PDI = 1.21) (Table 1) with a terminal activated ester functional group was synthesized by RAFT polymerization employing NHS-CEPA as the chain transfer agent. Then, an amphiphilic diblock copolymer incorporating a NHS moiety on the hydrophobic block side was synthesized affording a low dispersity NHS-P(MMA$_{25}$-*b*-OEGMA$_{75}$) (Mn = 23.0 kg mol^{-1}, PDI = 1.22) (Table 1), determined by gel permeation chromatography (GPC) (Fig. S1).

Next, TEMPO was then brought into the end of the amphiphilic diblock copolymer through activated ester functionalization strategy, reaction of the NHS-P(MMA$_{25}$-*b*-OEGMA$_{75}$) with 4-amino-TEMPO to provide TEMPO-P(MMA$_{25}$-*b*-OEGMA$_{75}$) in nearly quantitative yield (Fig. 1).

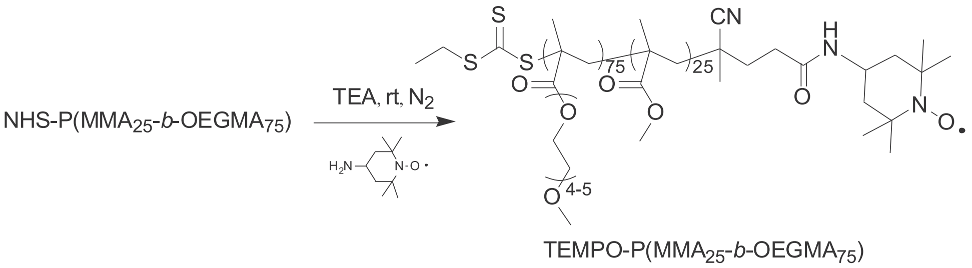
The successfully introduction of TEMPO moiety into the amphiphilic diblock copolymer was confirmed by the ^{1}H NMR spectrum and Electron Spin Resonance (ESR) spectrum. It can be found from ^{1}H NMR spectrum (Fig. S8) that the proton resonance at 2.85 ppm, which is



Scheme 1. Synthesis of Macro-CTA.



Scheme 2. Synthesis of NHS-P(MMA_{25}-b-$OEGMA_{75}$).



Scheme 3. Synthesis of TEMPO-P(MMA_{25}-*b*-$OEGMA_{75}$.

Table 1
Characterization data of the NHS-containing polymers.

Sample	Mn[a]	Mn[b]	PDI
NHS-P(MMA_{25}) (Macro-CTA)	2860	3160	1.21
NHS-P(MMA_{25}-*b*-$OEGMA_{75}$)	25360	22980	1.22

[a] Measured by ^{1}H NMR (in $CDCl_3$, Figures S6, S7).
[b] Measured by GPC (in THF).

corresponded to NHS, completely disappeared after reaction. Meanwhile, it can be seen from EPR spectrum (Fig. 2) that the characteristic triplet signal of TEMPO radical appeared at 3450–3550 G. Comparison of ESR signals of TEMPO-P(MMA_{25}-*b*-$OEGMA_{75}$) and 4-Amino-TEMPO at the same molar concentration (Fig. S9), accompanied by the observation of in ^{1}H NMR, NHS-P(MMA_{25}-*b*-$OEGMA_{75}$) is considered to be fully converted to TEMPO-P(MMA_{25}-*b*-$OEGMA_{75}$).

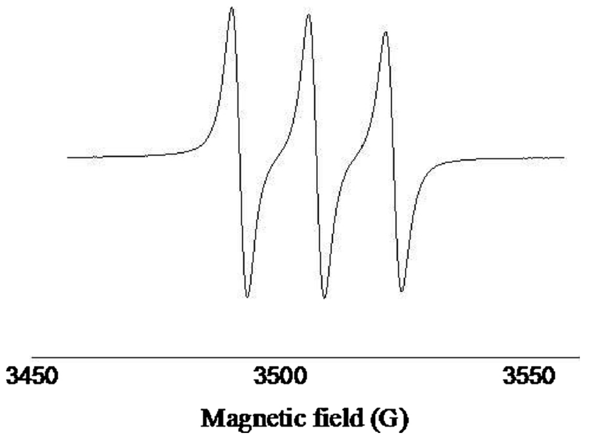


Fig. 2. The triplet signal of TEMPO radical of TEMPO-P(MMA_{25}-*b*-$OEGMA_{75}$).

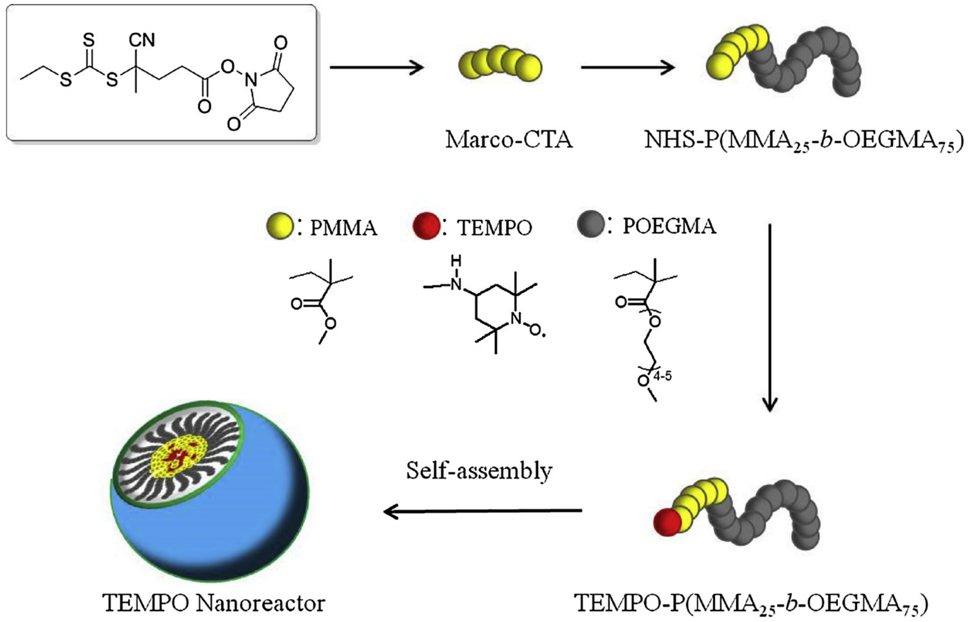


Fig. 1. Schematic illustration of the preparation of TEMPO-P(MMA_{25}-*b*-$OEGMA_{75}$) and formation of TEMPO-based nanoreactors.

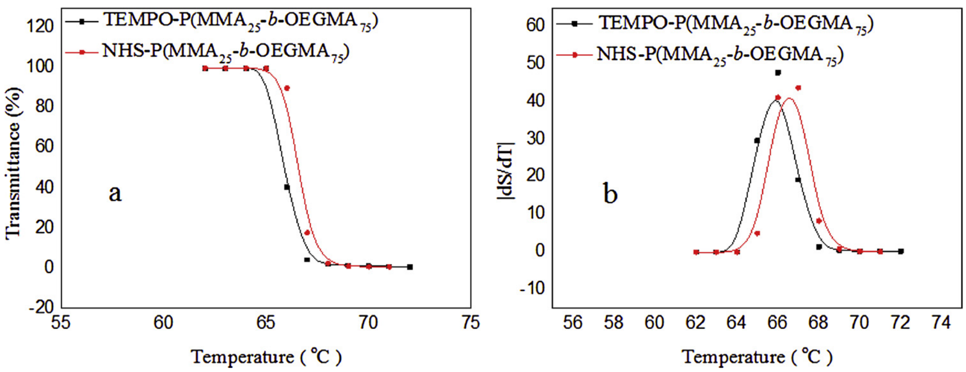


Fig. 3. The percent transmittance of copolymer versus temperature by UV–vis (a), and the derivation absolute value (|△S/△T |) of the curve of transmittance versus temperature (b).

3.2. Determination of the lower critical solution temperatures (LCSTs)

The recycling of thermo-responsive polymer-based catalyst based on its thermo-responsive property is one of the straight forward catalyst recover methods. When the temperature is higher than its LCST in aqueous solution, the thermo-responsive polymer turns hydrophobic, and realizes phase separation from water [37,38]. To understand the thermo-responsive perperty of TEMPO-P(MMA_{25}-*b*-$OEGMA_{75}$), its LCST was investigated. Polymer solutions were prepared in 1.0 mg mL^{-1} of aqueous solution for the UV–vis absorption measurements. Fig. 3 shows the percentage transmittance of the samples at 500 nm probed by UV–vis spectroscopy. By plotting the derivation absolute value with aspect to temperature as a function of temperature (Fig. 3b), It can be seen that the copolymer NHS-P(MMA_{25}-*b*-$OEGMA_{75}$) displayed thermo-responsive property and its LCST is determined as the temperature showing the maximum in the first derivative, which is 66.5 °C. The LCST of TEMPO-P(MMA_{25}-*b*-$OEGMA_{75}$) is 0.5 °C lower than that of NHS-P(MMA_{25}-*b*-$OEGMA_{75}$), which should be attributed to the substitution of NHS with a more hydrophobic TEMPO moiety.

3.3. Preparation and characterization of TEMPO nanoreactors

With the amphiphilic diblock copolymer TEMPO-P(MMA_{25}-*b*-$OEGMA_{75}$) in hand, the copolymer was self-assembled into micelles in water (TEMPO nanoreactors) through direct dissolution method. TEMPO-P(MMA_{25}-*b*-$OEGMA_{75}$) was dissolved into deionized water at room temperature ($T < LCST$), then self-assembled until thermodynamic equilibrium micelles formed (Fig. 1). The size, shape, and distribution of this micelle system were then determined by DLS (Fig. 4a, b) and SEM (Fig. 4c, d). Analysis of the polymeric micelles by DLS at 1.0 mg mL^{-1} in water indicated that nanoparticles with an average hydrodynamic diameter of 240 nm and particle size distribution of 1.20. To further confirm the formation of nanoparticles, the surface topography of TEMPO nanoreactors were characterized by SEM. Nanoparticles with a spherical morphology and average diameter of around 300 nm was being observed, which is generally in line with the results of DLS analysis.

3.4. Application of TEMPO nanoreactors for catalytic oxidation of alcohols in water

To investigate the catalytic activity of the thermo-responsive polymer-supported TEMPO nanoreactors in the catalytic oxidation of alcohols, the oxidation of benzyl alcohol in water was firstly chosen to study their catalytic activity. After optimization, the reaction condition of using sodium hypochlorite as the oxidant and sodium bromide as the co-catalyst at pH = 9.1 and 0 °C were adopted. At the optimized reaction conditions, benzyl alcohol could be selectively oxidized to the corresponding benzaldehyde in excellent conversion and selectivity (Table S1, entry 6). Usually, the catalytic activity of supported catalysts decreases due to the decrease of the dispersion of the catalysts. Previous reports in TEMPO catalysis confirmed this point (Table S1, entries 2˜5). There exists a obvious decrease in catalytic activity of supported catalysts such as TEMPO/magnetic polystyrene nanosphere (TEMPO/MPNs) ($TOF = 0.333\ s^{-1}$) [8], microporous organic nanotube networks (TEMPO/MONNs) ($TOF = 0.199\ s^{-1}$) [11], TEMPO-P(MEO_2MA-*co*-OEGMA), and PEG-supported TEMPO (TOF is up to $0.333\ s^{-1}$) [4], compared to homogeneous TEMPO ($TOF = 0.555\ s^{-1}$) [8]. While, the TEMPO nanoreactors demonstrated remarkably high oxidative activity ($TOF = 2.667\ s^{-1}$). The enhanced reaction rates may attribute to the enzyme-mimic catalyst system, where, the hydrophobic environment within the nanoreactors allowing hydrophobic alcohols can readily transfer into the core of micelles. In addition, the existence of hydrophilic ester bonds in the hydrophobic block makes certain amounts of water, sodium hypochlorite and sodium bromide to diffuse into the catalytic sites to facilitate the catalytic oxidation of alcohols.

3.5. Substrate scope study of the catalytic oxidation of alcohols

Further tests using TEMPO nanoreactors revealed that a variety of alcohols can be oxidated to their corresponding carbonyl compounds (Table 2). The reactions were performed at 0 °C in water for all the substrates. The benzyl alcohols containing electron-withdrawing group in the para position (NO_2-, Br-, Cl-) were quantitatively converted into their corresponding aldehydes within 5 min (Table 2, entries 1–3, $TOF = 2.667\ s^{-1}$), similar to the unsubstituted benzyl alcohol (Table S1, entry 6). It is noteworthy that these nanoreactors were equally applicable in different types of aromatic alcohols such as 4-methylthiobenzyl alcohol, 1-phenylethanol and 1-naphthalenemethanol (Table 2, entries 6–8, $TOF = 2.667\ s^{-1}$), giving their corresponding aldehydes in excellent conversion and selectivity. Significantly, TEMPO nanoreactors displayed extremely high oxidative activities to the benzyl alcohols with electron-donating group (Me-, MeO-, Ph-), offering the respective aldehydes within 2 min (Table 2, entries 4, 5 and 9, $TOF = 6.667\ s^{-1}$). Obviously, the nanoreactor is more effective than the unloaded catalyst, only 45% conversion for the selective oxidation of 4-phenylbenzyl alcohol was achieved when 4-amino-TEMPO was used as catalyst (Table 2, entry 9 in parenthesis). In addition, the nanoreactors also exhibited excellent activities in the oxidation of both secondary benzylic and secondary aliphatic alcohols to yield the corresponding ketones within 5 or 2 min (Table 2, entries 10–14, $TOF = 2.667˜6.667\ s^{-1}$). The sterically hindered alcohols were also effectively oxidized to their corresponding carbonyl compounds in high conversion and excellent selectivity although somewhat longer reaction times were required (Table 2, entries 15–18, $TOF = 1.293˜2.587\ s^{-1}$). Notably, there was no obvious catalytic reaction for 2-adamantanol when 4-amino-TEMPO was adopted as catalyst (Table 2, entries 16 in parenthesis).

3.6. The reuse of the TEMPO nanoreactors

After the preliminary activity study, recovery and recycling of the

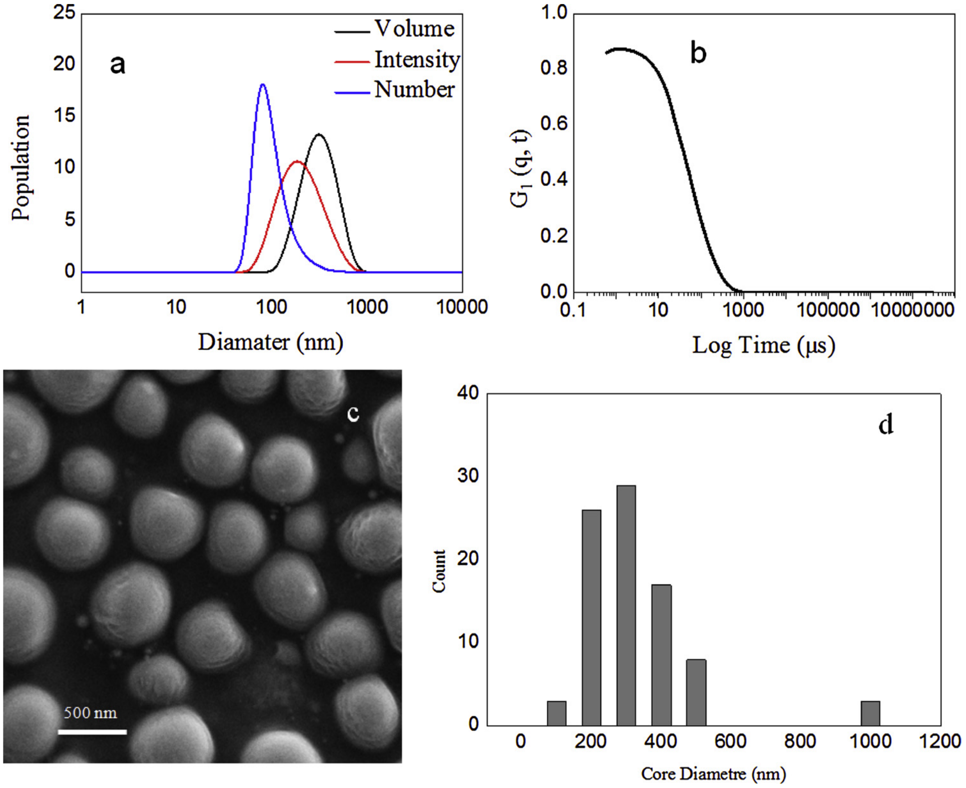
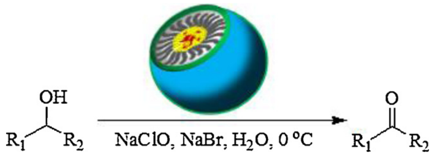
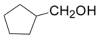
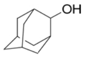
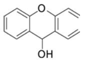
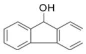


Fig. 4. DLS distribution (a) autocorrelation function (b) SEM characterization (c) and Histogram of particle size distribution obtained by SEM (d) of TEMPO Nanoreactor.

Table 2

TEMPO nanoreactors catalyzed catalytic oxidation of alcohols to the corresponding carbonyl compounds[a].



Entry	R_1 (or alcohol)	R_2	Time (min)	Conv.[b] (%)	Sel.[b](%)	TOF (s^{-1})
1	4-NO_2Ph	H	5	> 99	> 99	2.667
2	4-BrPh	H	5	> 99	> 99	2.667
3	2-ClPh	H	5	> 99	> 99	2.667
4	4-MePh	H	2	> 99	> 99	6.667
5	4-MeOPh	H	2	> 99	> 99	6.667
6	4-MeSPh	H	5	> 99	> 99	2.667
7	Bn	H	5	> 99	> 99	2.667
8	1-Naphthyl	H	5	> 99	> 99	2.667
9[c]	4-PhPh	H	2	> 99 (45)	> 99 (> 99)	6.667
10	Ph	Me	2	> 99	> 99	6.667
11	4-NO_2Ph	Me	5	98	> 99	2.613
12	2-MeOPh	Me	5	> 99	> 99	6.667
13	4-MeOPh	Me	2	> 99	> 99	6.667
14	Ph	Ph	5	> 99	> 99	2.667
15	 CH_2OH		5	95	98	2.533
16[c]	 OH		5	97 (N.R.)	> 99	2.587
17	 O OH		10	99	> 99	1.293
18	 OH		10	99	> 99	1.306

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[a] The reactions were performed with alcohol (0.8 mmol), TEMPO nanoreactors (0.1 mol%), NaBr (1.25 mol %), NaClO aq. (1.25 equiv.), at 0 °C, pH = 9.1.

[b] Determined by GC-MS.

[c] The results in parenthesis were obtained using 4-amino-TEMPO as catalyst.

thermo-responsive polymer-supported TEMPO nanoreactors was next investigated using the catalytic selective oxidation of benzyl alcohol as the model reaction. After the completion of the reaction, the product was extracted by cooled ether. Increasing the temperature of the residual aqueous phase to above the LCST of TEMPO-P(MMA_{25}-*b*-$OEGMA_{75}$) at 70 °C produced the precipitate of catalyst from water. Next, the dispersion was centrifugated with care to recover the catalyst, and it could be reused after careful washing with cold ether. A certain amount catalyst loss was observed, which is about 10% by calculation from UV–vis standard curve of TEMPO-P(MMA_{25}-*b*-$OEGMA_{75}$) (Fig. S2). The loss of catalyst during the recovery should be arise from the incompletely precipitation. Scaling up production probably can reduce the loss. In the next run, the recovered catalyst together with 10% amount of supplement was dissolved into deionized water at room temperature ($T < LCST$) to form nanoparticles, and similar activity was achieved for at least 6 cycles (Fig. S3). Although there is room for further improvement, this strategy represents a straightforward and promising recycling method.

4. Conclusions

In summary, we have successfully introduced a TEMPO organocatalyst to an amphiphilic block copolyers in the terminal of the hydrophobic part. Core-shell type of polymeric nanoreactors were fabricated through the self-assembly of the amphiphilic block polymers in water. The nanoractors were then successfully apllied in the selective oxidative of alcohols in aqueous media. The corresponding aldehydes and ketones were achieved in excellent yield and selectivity. Importantly, higher TOF were achieved with both lower TEMPO loading and less reaction time compared to the previously reported polymer-supported TEMPO catalyst systems, which may attributed to the ideal environment for catalysis where enhancing the interactions between the catalyst and the alcohol substrate, mimicking the environment of enzymes. Furthermore, the temperature responsivity of the nanoreactors facilitated the recovery of the catalyst from the reaction system. The catalyst can be easily recovered utilizing the thermo-responsive characteristic. The thermo-responsive polymer-supported TEMPO nanoreactors combine product selectivity, high efficiency and easy recycling in an environmentally safe medium, which highlights the potential application of this nanoreactor system in the industrial practice of the selective oxidation of alcohols.

Acknowledgments

The financial support from Zhejiang Provincial Natural Science Foundation of China (No. LY17B020013) and Key Technology Research and Development Project of Zhejiang Province (No. 2017C03016) throughout the project is greatly appreciated.

Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.mcat.2019.110422.

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