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# Cross-linked reverse micelles with embedded water pools: a novel catalytic system based on amphiphilic block copolymers†

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Ruihan Liu,<sup>a</sup> Shiping Wang,<sup>b</sup> Jia Yao,<sup>\*a</sup> Weiwei Xu<sup>a</sup> and Haoran Li<sup>a</sup>

Based on the idea of structural design, a novel catalytic system was developed from a block copolymer for the oxidation reaction of 2,3,6-trimethylphenol (TMP). The block copolymer, poly(4-vinylpyridine)-*block*-poly(ethylene glycol)-*block*-poly(4-vinylpyridine) (P4VP-PEG-P4VP), was synthesized *via* anionic polymerization. After self-assembly in water–1-hexanol solution and shell cross linking, the block copolymer formed the shell cross-linked reverse micelles (SCRMs). The CuCl<sub>2</sub> complexed SCRMs were used in the catalytic oxidation reaction of TMP. Through coordinating with metal ions, regulating the distribution of metal catalytic active centers, and with the cocatalysis effect of the immobilized water droplets, this polymer-supported catalyst system demonstrated an efficient catalytic activity and recoverability. This work not only provides a promising catalyst based on mesoscale structure design using block copolymers but is also an example for deeper understanding on the structure effect in catalysis.

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## Introduction

Over the recent years, the development of polymer-supported catalysts<sup>1-4</sup> has attracted widespread attention with the consideration of structure at nanoscopic or mesoscopic levels,<sup>5-8</sup> offering a viable method for catalyst design. The designed catalysts can dramatically alter their reactivity, selectivity, and efficiency by impacting the location and activity of catalytic active centers. However, designing a more effective polymer-supported catalyst with a specific structure is still a challenge because of the lack of knowledge regarding the reaction mechanism and the mesoscale structure.

Micelles from amphiphilic block copolymers have already been developed in catalysis applications.<sup>9-11</sup> In general, micelles are considered to have a hydrophobic core and a hydrophilic shell in polar solvents. However, if the solvent system is less hydrophilic, the core and the shell may be inverted to give reverse micelles (RMs).<sup>12,13</sup> In addition, compared with the selfassembled micelles formed through noncovalent interactions, the formation of shell cross-linked reverse micelles (SCRMs)<sup>7,14-16</sup> can provide reinforcement and stability, even if the environmental conditions change.

The catalytic oxidation of TMP using molecular oxygen as the oxidant is a key step to synthesize vitamins, pharmaceuticals,

and flavors in the chemical industry.17 The homogeneous copper catalyst system can achieve high conversion and selectivity,18-20 but a serious drawback is that almost or even more than a stoichiometric amount of catalyst is required, which is environmentally unfriendly. Polymer-supported metal catalysts<sup>21-25</sup> are considered to be more friendly to the environment. Takaki et al.17 succeeded in the oxidation of TMP with polymersupported copper catalysts. However, it took a long time to complete the reaction and the products could only be obtained under high  $O_2$  pressure (10 atm). The relatively low activity might be because of the simple structure of Takaki's catalyst. Hence, in this paper, a novel catalyst system was designed for the oxidation of 2,3,6-trimethylphenol (TMP) by dioxygen. The catalyst carrier is a kind of cross-linked reverse micelle formed by the self-assembly of block copolymers with an encapsulated water pool. The relationship between the mesoscale structure and catalysis efficiency was investigated. It is worth mentioning that a small amount of water can act as an activator in some catalytic reactions,<sup>26,27</sup> such that the structure of the aqueous cores of RMs, even with water pools embedded, can have a positive effect on promoting reactions.

To prepare the SCRM structure, in this work, an ABA amphiphilic block copolymer poly(4-vinylpyridine)-*block*-poly(ethylene glycol)-*block*-poly(4-vinylpyridine) (P4VP-PEG-P4VP) was synthesized *via* anionic polymerization. P4VP-PEG-P4VP formed RMs in a mixed biphase solution (Scheme 1). The hydrophilic core of P4VP-PEG-P4VP RM consists of PEG blocks, enclosing a water pool, and the P4VP blocks constituting the shell. 1,2-Bis(2-iodoethoxy) ethane (BIEE) was used as a cross-linking agent to selectively quarternize the nitrogen atoms on the pyridine groups in the micelle shell, thus forming SCRMs.

<sup>&</sup>lt;sup>a</sup>State Key Laboratory of Chemical Engineering, Department of Chemistry, Zhejiang University, Hangzhou 310027, PR. China. E-mail: yaojia@zju.edu.cn

<sup>&</sup>lt;sup>b</sup>Key Lab of Applied Chemistry of Zhejiang Province, Department of Chemistry, Zhejiang University, Hangzhou 310027, PR. China

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Scheme 1 Structure of the amphiphilic block copolymer P4VP-PEG-P4VP reverse micelles in 1-hexanol-water mixed solution.

Through the coordination with metal ions,<sup>28-34</sup> CuCl<sub>2</sub>-(P4VP-PEG-P4VP) SCRMs were successfully applied in the catalytic oxidation reaction of TMP in the 1-hexanol media, followed by reusing the catalyst in several cycles.

## **Experimental section**

#### Materials

Poly(ethylene glycol) (PEG,  $M_n = 2000 \text{ g mol}^{-1}$ , Aldrich) was dried under vacuum at 55 °C for 1 h and then stored under nitrogen at -15 °C. 4-Vinylpyridine (4VP, Aldrich) was passed through an activated basic alumina column to remove the stabilizing agents and stirred with a small amount of CaH<sub>2</sub> overnight at room temperature, followed by vacuum distillation. The 4VP was filled with nitrogen and stored in a refrigerator at -15 °C. Tetrahydrofuran (THF) was dried under refluxing over sodium and distilled in a nitrogen atmosphere just before use. Potassium naphthalene was prepared by dissolving naphthalene in dried THF and refluxing the solution over potassium until it turned dark blue. The feed ratio of potassium and naphthalene was 1:1. The 2,3,6-trimethylphenol was donated by Zhejiang NHU Company, Ltd. All the other reagents and solvents were of analytical grade (Aldrich) and were used without further purification.

#### Synthesis of P4VP-PEG-P4VP

Dried PEG (2.0 g) was dissolved in 100 mL of dried THF, and the solution was transferred to a 250 mL round-bottomed flask under nitrogen. 4 mL of a freshly prepared solution of potassium naphthalene in THF (0.5 mol  $L^{-1}$ ) was injected into the round-bottomed flask via a nitrogen-washed injector and stirred until the color of the solution turned light green. The mixed solution was stirred at room temperature for 0.5 h to form the alcoholate macroinitiator. A known amount of freshly distilled 4VP was then charged to the reactor under nitrogen atmosphere at -78 °C. Polymerization was carried out at this temperature for 24 h. The crude copolymer was dissolved in ethanol at 60 °C and precipitated at room temperature. The copolymer was dissolved in ethanol at 60 °C, and then transferred to a dialysis tube to dialyze against water for 1 week to remove small molecules. The diblock copolymer, poly(ethylene glycol)-block-poly(4vinylpyridine) (P4VP-PEG), was synthesized using a similar method for comparison.

# Self-assembly and shell cross-linking of P4VP-PEG-P4VP reverse micelles

Water was added into 1-hexanol to achieve a water content of 50%, forming 100 mL of biphase mixed solution. Then, the block copolymer P4VP-PEG-P4VP was added to the solution at a pH of 4 (polymer weight: 0.15%) and stirred at room temperature for 24 h.

1 mmol of BIEE was dissolved in 10 mL of 1-hexanol. After being stirred and left standing for 24 h, the BIEE solution was added into the abovementioned P4VP-PEG-P4VP solution in a dropwise manner to achieve shell cross linking. The solution was then stirred at a low speed for at least 3 days at room temperature. Several degrees of cross linking were studied, among which the highest was 30%. The solvent was stripped by freeze drying, and the SCRMs dried powder was obtained.

#### Preparation of the CuCl<sub>2</sub>-(P4VP-PEG-P4VP) SCRMs complex

P4VP-PEG-P4VP SCRMs (0.5 mmol) were dissolved in 100 mL 1hexanol. A solution of the appropriate amount of copper salts (CuCl<sub>2</sub>·2H<sub>2</sub>O, Aldrich) in 10 mL 1-hexanol was slowly added, and then the combined solution was mixed under moderate stirring for 12 h. Products were obtained by centrifugation, washing and freeze drying.

# Oxidation of TMP by O<sub>2</sub> using CuCl<sub>2</sub>-(P4VP-PEG-P4VP) as catalyst

Catalytic oxidation of TMP was conducted in all-glass reactor vessels consisting of a 50 mL round-bottomed flask connected reflux condensing tube and ventilation capillary. TMP (136.2 mg, 1 mmol) was dissolved in 1-hexanol (20 mL), and stirring was continued at room temperature under  $O_2$  (1 atm). After the addition of an appropriate amount of H<sub>2</sub>O into the CuCl<sub>2</sub>-(P4VP-PEG-P4VP) SCRMs complex, the morphological characteristic of the complex changed from powder to paste. The catalyst, moist CuCl<sub>2</sub>-(P4VP-PEG-P4VP) SCRMs, was added to the TMP solution and the mixture was stirred under the conditions indicated in Table 1, which was monitored by gas chromatography (GC). The precipitated catalyst was recovered through centrifugation and thorough washing in 1-hexanol. After being dried by lyophilization and wetted again, the catalyst was reused in the next cycle (Table 2).

#### Characterization methods

Transmission electron microscopy (TEM) was performed on a Hitachi HT-7700 at an acceleration voltage of 120 kV. A drop of very dilute solution was applied onto a carbon-coated TEM copper grid. The sample was then immediately frozen by liquid nitrogen and dried by lyophilization.

Dynamic light scattering (DLS) measurements were performed on a Malvern Zetasizer Nano-ZS equipped with a He–Ne laser at a wavelength of 633 nm. The experimental data were analyzed by the CONTIN method, which is based on an inverse-Laplace transformation of the data and provides access to a size





Run	Amine ligand <sup>b</sup> (mmol)	${\rm CuCl_2}^c$ mol%	H <sub>2</sub> O <sup>d</sup> mol%	Conv.%	Product and yield/%			
					2	3	4	Mass balance <sup>e</sup> %
1	_	10	0	No reaction	_	_	_	_
2	—	10	100	tr	tr	tr	tr	tr
3	_	10	1000	100	44	17	tr	61
4	P4VP	10	1000	49	3	0	tr	6
5	P4VP-PEG-P4VP	2	1000	39	2	6	7	38
6	P4VP-PEG-P4VP	10	1000	100	46	tr	tr	46
7	P4VP-PEG-P4VP	50	1000	100	62	6	tr	68
8	P4VP-PEG-P4VP	100	1000	100	74	7	tr	81

<sup>*a*</sup> Reaction conditions: **1** (1 mmol), 1-hexanol (20 mL), O<sub>2</sub> (1 atm, pure oxygen bubbled in from a gas cylinder), reaction time (24 h), 90 °C. <sup>*b*</sup> Ratio of 4VP unit of P4VP to CuCl<sub>2</sub> is unity. <sup>*c*</sup> Based on **1**. <sup>*d*</sup> Based on **1**. <sup>*e*</sup> Total yield of **2–4**.

Table 2 Recycling of catalyst CuCl<sub>2</sub>-(P4VP-PEG-P4VP) in the oxidation of TMP<sup>a</sup>

	Recycle	CuCl <sub>2</sub> mol%	Conv.%	Product and yield/%			
Catalyst				2	3	4	Mass balance <sup>b</sup> %
Non-cross-linked CuCl <sub>2</sub> -(P4VP-PEG-	First	100 <sup>c</sup>	100	78	5	3	86
P4VP)	Second	68.4	100	66	tr	2	68
	Third	52.7	98	57	tr	2	60
30% Cross-linked CuCl <sub>2</sub> -(P4VP-PEG-	First	100	100	74	7	tr	81
P4VP)	Second	95.9	100	88	2	8	98
	Third	83.3	100	87	3	4	94
	Fourth	81.6	100	79	7	1	86
	Fifth	63.3	100	68	tr	1	69

<sup>*a*</sup> Reaction conditions: **1** (1 mmol), 1-hexanol (20 mL), O<sub>2</sub> (1 atm), reaction time (24 h), 90 °C. Ratio of H<sub>2</sub>O to CuCl<sub>2</sub> is 10 in the first reaction, and the amount is fixed in following reactions. <sup>*b*</sup> Total yield of **2–4**. <sup>*c*</sup> Ratio of 4VP unit of P4VP to CuCl<sub>2</sub> is 1 in the first reaction.

distribution histogram for the analyzed micellar solutions. The  $\zeta$  potential of RM nanoparticles was determined by laser Doppler anemometry using a Malvern Zetasizer Nano-ZS. The temperature was set to 25 °C, and the results were normalized with respect to the polystyrene standard solution.

The coordination of Cu(II) and SCRMs was measured by electron paramagnetic resonance (EPR) on a Bruker A300 with X-band frequencies at 108 K. The solution of  $10^{-4}$  M coppercontaining SCRMs in DMSO was transferred to an EPR tube and shock frozen in liquid nitrogen to obtain a transparent, glassy sample.

The yields of all the products obtained from TMP oxidation were determined by GC (Agilent GC-2014) using ethyl benzoate as an internal standard.

## Results and discussion

# Synthesis and characterization of P4VP-PEG-P4VP amphiphilic block copolymer

P4VP-PEG-P4VP was synthesized by anionic polymerization in THF at -78 °C using potassium naphthalene as the initiator. Vamvakaki *et al.*<sup>35</sup> synthesized the poly(ethylene oxide-tertiary amine methacrylate) with potassium naphthalene as a functional initiator. In our study, anionic polymerization was initiated with potassium naphthalene from PEG, and P4VP-PEG-P4VP was obtained by the polymerization of 4VP in a controlled mechanism (Scheme 2).

Analysis of the polymer including <sup>1</sup>H NMR and GPC can be found in ESI Fig. S1 and S2.† The ratio of polymer to monomer



Scheme 2 Synthesis of the P4VP-PEG-P4VP block copolymer.

and the number-average molecular weight could be calculated through <sup>1</sup>H NMR spectrum. Based on the calculation of the NMR spectrum, we found that one P4VP-PEG-P4VP chain had 45 EG units and 50 4VP units, with a  $M_{\text{copolymer}}$  of 7200 g mol<sup>-1</sup>. The  $M_n$  values obtained from NMR and GPC measurements were consistent.

#### Formation of P4VP-PEG-P4VP SCRMs

The shell cross-linked reverse micelles were prepared in two steps. First, P4VP-PEG-P4VP self-assembled into RMs in water-1-hexanol solution (Scheme 1). Then, the solution of crosslinker BIEE was added to the micelle solution under stirring (Scheme 3), forming P4VP-PEG-P4VP SCRMs.

In the first step, the mixed solution of water–1-hexanol was used as the media for P4VP-PEG-P4VP RMs self-assembly in acidic conditions. Because water is a good solvent for the PEG block but not for the P4VP block, the formed core–shell RMs had PEG chains as the core and P4VP chains as the shell. The morphologies of the copolymer self-assemblies were characterized by TEM.

For comparison, P4VP-PEG self-assemblies were prepared under the same conditions, as described in the experimental section. As shown in Fig. 1a, the P4VP-PEG diblock copolymer self-assembled into vesicles with a large exterior diameter of about 2  $\mu$ m, which were loose and unstable. P4VP-PEG-P4VP formed core–shell RMs, partially with a hollow structure (actually a water pool) (Fig. 1b). The folding of the ABA copolymer chain of P4VP-PEG-P4VP enhanced the rigidity of the shell, providing the P4VP-PEG-P4VP micelle with a higher stability than the P4VP-PEG micelle. The P4VP-PEG-P4VP RMs had an average exterior diameter of 100  $\pm$  20 nm with a shell thickness of approximately 50 nm.



**Scheme 3** Intermicellar and intramicellar cross linking of PEG-P4VP-PEG RMs by BIEE.

A small amount of  $CuCl_2$  was used as a staining agent to determine the location of the pyridine group in the RMs. The TEM image in Fig. 1c indicates that the pyridine groups were located on the shell. The small dots near the exterior surface were the coils of P4VP molecular chain, generated by the coordination of  $Cu^{2+}$  and pyridine groups.

The size of the water pool in the RMs could be controlled by the component ratio of the solution.<sup>15</sup> The morphologies of P4VP-PEG-P4VP self-assemblies at different component ratios of solution are illustrated in Fig. 2. ESI Fig. S3<sup>†</sup> shows the particle size distribution of P4VP-PEG-P4VP copolymer selfassemblies according to DLS measurements, and the result is consistent with that obtained from TEM. When only 1-hexanol was used, the polymers could not form a stable aggregation. On increasing the ratio of water in the mixture of water-1-hexanol, micelles can form. When the ratio of water was higher, the water pool in RMs could form more easily. When the mass ratio of water-1-hexanol reached 1 and above (Fig. 2d and e), the coreshell structure micelles could be obtained. As the ratio of water-1-hexanol increased from 1.5 to 4, the water pool inside the RM became bigger. When the solution was pure water, the polymers formed large thin films.

The exterior surface properties of P4VP-PEG-P4VP RMs were investigated by measuring  $\zeta$  potential<sup>36–38</sup> (see ESI Fig. S4 and S5†). At a positive potential, the RMs showed a stable structure. With increasing pH, the potential declined for decreasing degree of protonation of P4VP. The  $\zeta$  potential became negative at pH above 5.4, and the structure of RMs was unstable.

Following self-assembly, BIEE was used to crosslink the shell layer, reinforcing the RM structure through covalent bonding. Scheme 3 describes the formation procedure of P4VP-PEG-P4VP SCRMs. As a cross-linking reagent, BIEE could quarternize the nitrogen atoms on the pyridine group.

Therefore, the self-assemblies of the P4VP-PEG-P4VP RMs in the mixed solution of water–1-hexanol at a concentration of  $2 \times 10^{-4}$  M were stabilized through cross linking reactions between the pyridine groups within the peripheral shell. The morphologies of SCRMs with a different extent of cross linking are shown in ESI Fig. S6.† With increasing content of cross linking at the peripheral shell, the binding among the P4VP-PEG-P4VP micelles became stronger. At 30% degree of cross linking, partial peripheral P4VP segments formed a smooth thin film with interior structures of P4VP-PEG-P4VP micelles located on it separately. The SCRMs remained spherical and well dispersed. In addition, large aggregations of SCRMs could be achieved by increasing the concentration of micelles or BIEE (see ESI Fig. S7†).

# Catalytic application of P4VP-PEG-P4VP SCRMs in oxidation of TMP

To achieve a preferable catalyst for further oxidation of TMP,  $CuCl_2 \cdot 2H_2O$  was added to the maximum micelle loading (Cu: 4VP = 1: 1) corresponding to pyridine units in the P4VP-PEG-P4VP SCRM solution (0.2 mmol  $L^{-1}$ ) (note that the concentration of 4VP in the sample was calculated using  $M_n$  of P4VP-PEG-P4VP, same as the value used for the block ratio





Fig. 1 TEM images of (a) PEG-P4VP, (b) P4VP-PEG-P4VP reverse micelles in mixed solution and (c) with 5 mol%  $CuCl_2$  added into the mixed solution (polymer weight: 0.15%, mass ratio of 1-hexanol-water = 1).



Fig. 2 TEM images of P4VP-PEG-P4VP self-assemblies prepared in a mixture solution of water–1-hexanol: (a) 100% 1-hexanol, (b) 80% 1-hexanol + 20% water, (c) 60% 1-hexanol + 40% water, (d) 40% 1-hexanol + 60% water, (e) 20% 1-hexanol + 80% water, (f) 100% water (polymer weight: 0.15%).

calculation). In general, Cu( $\pi$ ) can form 4, 5 or 6 coordinated complexes with a wide range of ligands. However, because of steric hindrance, a mixture of lower coordination numbers are produced in general.<sup>32</sup> Therefore, the maximum micelle loading at 1 : 1 ratio should be a combination of Cu( $\pi$ ) coordination and the copper ions dissolved in the core of P4VP-PEG-P4VP SCRMs, which was revealed by TEM in ESI Fig. S8a.<sup>†</sup>

The coordination of the Cu( $\pi$ ) can be confirmed directly by EPR in DMSO. When measured at room temperature, the EPR peaks of CuCl<sub>2</sub> were not clearly separated (Fig. 3a). Therefore, the temperature was adjusted to 108 K to improve Cu( $\pi$ ) signals. As shown in Fig. 3b and c,  $g_{\parallel} = 2.3593$  and  $g_{\perp} = 2.0906$  were observed for Cu( $\pi$ ) and  $g_{\parallel} = 2.4050$  and  $g_{\perp} = 2.0914$  for the complexes of CuCl<sub>2</sub>-(P4VP-PEG-P4VP). These indicated the presence of copper( $\pi$ ) d<sup>9</sup> paramagnetic species in this system, as expected. Similar EPR behavior was observed on Cu/P4VP,<sup>39</sup> which validated that the copper ions were indeed located in the P4VP-PEG-P4VP SCRMs.

 $CuCl_2$ -(P4VP-PEG-P4VP) SCRMs were used as catalysts for TMP **1** oxidized to trimethyl-*p*-benzoquinone (TMBQ) **2** by dioxygen (Table 1). In general, the reaction also produces

4-chloro-2,3,6-trimethylphenol (CTP) **3** and 2,2-3,3-5,5hexamethyl-4,4-biphenyldiol (HBD) **4** in the process as detectable compounds by GC. The control experiment without the catalyst did not proceed to any appreciable extent (Table 1, Run



Fig. 3 X-band EPR spectra in the 2.6976-1.9274 g-factor region of (a) CuCl<sub>2</sub> at room temperature (black line), (b) CuCl<sub>2</sub> at 108 K (blue line) and (c) CuCl<sub>2</sub>-(P4VP-PEG-P4VP) at 108 K in DMSO (red line).

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1). Because of the important role played by  $H_2O$  in the oxidation, reaction could proceed with the addition of a small amount of water (Table 1, Run 2 and 3). Then, the oxidation of 1 with CuCl<sub>2</sub>-P4VP and CuCl<sub>2</sub>-(P4VP-PEG-P4VP) (Cu : 4VP = 1 : 1) was carried out under similar conditions (Table 1, Run 4 and 6). After 24 h, only a low yield of 2 was obtained with CuCl<sub>2</sub>-P4VP, indicating a significantly higher activity of CuCl<sub>2</sub>-(P4VP-PEG-P4VP). It was suggested that the hydrophilic segments and the core domain containing water had a positive effect on oxidation. The water pool could dissolve more copper ions, such that the catalytic centers were concentrated and the catalyst became harder to wash off. The mesoscale structure of the SCRM decreased the entropy of the reaction by reducing distances among the substrates, catalytic centers and  $H_2O$ , resulting in efficient catalytic activity for this reaction.

The time course for the oxidation of TMP 1 with CuCl<sub>2</sub>-(P4VP-PEG-P4VP) is shown in Fig. 4. With the consumption of substrate TMP 1, the CTP 3 appeared first and finally changed to the TMBQ 2. A small amount of the HBD 4 was detected after the formation of 2. The reaction system essentially induces several competitive reactions such as C-C and C-O coupling and peroxide formation from phenoxy radicals and dioxygen. Thus, the yield and selectivity of 2 are very sensitive to reaction conditions, particularly to the molar ratio of 4VP to CuCl<sub>2</sub>. At low ratio, the results were unsatisfactory (Table 1, Run 5). Higher copper loading in the ligand increased the conversion of 1 (Table 1, Run 6-8). This oxidation reaction at a relatively high temperature produces a series of higher multimers (hard to be completely detected by GC). When the conversion reached 100%, although the yield of 2 was not high (Table 1, Run 6), the selectivity of 2 increased with increasing copper loading.

With a low cross-linking extent of P4VP-PEG-P4VP RMs, the corresponding catalysts usually cannot be used more than twice because of the mechanical degradation and/or elution of the catalyst. However, this limitation can be overcome by increasing the cross-linking content.<sup>25</sup> Therefore, as a better reaction condition compared to the one using non-cross-linked CuCl<sub>2</sub>-(P4VP-PEG-P4VP) as catalyst, the reaction was repeated using 30% cross-linking content of the CuCl<sub>2</sub>-(P4VP-PEG-P4VP) (Table 2) for five times. After being thoroughly dried and



**Fig. 4** Oxidation of TMP with  $CuCl_2$ -(P4VP-PEG-P4VP). For conditions see Run 6 in Table 1.

treated with nitric acid, the amount of copper in the catalyst was measured by atomic absorption spectroscopy (AAS). The amount of copper in the non-cross-linked CuCl2-(P4VP-PEG-P4VP) declined significantly. In the third reaction, only 52.7% copper was left and the yield obviously decreased, which was because of the destruction in multiple trials at high temperature. The results of 30% cross-linked CuCl<sub>2</sub>-(P4VP-PEG-P4VP) show that the catalyst could be easily recovered and reused without great decrease in the activity. The copper was proven to remain in the catalyst (by the ratio of copper/P4VP-PEG-P4VP) without considerable loss after every recycle. After the fifth reaction, the remaining copper dropped to 63.3% at the same level with non-cross-linked CuCl<sub>2</sub>-(P4VP-PEG-P4VP). The recycle 2-4 (Table 2) brought about reasonable reductions in reaction yields. In the second recycle, 2 yielded a higher percentage than in the first one, possibly because of the absorption of SCRMs catalyst carrier and the redistribution of copper in the first reaction. In addition, the change in the morphologies of CuCl<sub>2</sub>-(P4VP-PEG-P4VP) was investigated in ESI Fig. S8.†

## Conclusion

In this study, a novel catalytic system for the oxidation reaction of TMP was designed and synthesized. First, an amphiphilic block copolymer P4VP-PEG-P4VP was synthesized *via* the anionic polymerization technique. After addition into a water–1-hexanol mixed solution, the block copolymer P4VP-PEG-P4VP self-assembled into reverse micelles. The reverse micelles consisted of a hydrophobic shell of P4VP and a hydrophilic core of PEG, partly with a water pool in the core. Demonstrated by TEM and  $\zeta$  potential, the structure and morphologies of the reverse micelles changed along with the pH of the surroundings. To stabilize the structure, BIEE was used to cross-link the shell by quarternizing the nitrogen atoms on the pyridine groups. SCRMs were reinforced through covalent bonds between P4VP chains to maintain the structure when the environmental conditions changed.

After coordinating with copper ions, the  $CuCl_2$ -(P4VP-PEG-P4VP) SCRMs complex was obtained as a catalyst. The oxidation of TMP used the catalyst system with dioxygen under ambient pressure. Taking advantage of the coordination with metal ions, the distribution of metal catalytic active centers in the structure, and the cocatalysis effect of the immobilized water droplets,  $CuCl_2$ -(P4VP-PEG-P4VP) demonstrated efficient catalytic activity and recoverability. It is indicated that the designed polymeric catalyst carrier has the potential to provide a more reactive and recoverable catalytic system for catalytic oxidation.

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