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Porous Polymerized Organocatalysts Rationally Synthesized from the Corresponding Vinyl-Functionalized Monomers as Efficient Heterogeneous Catalysts

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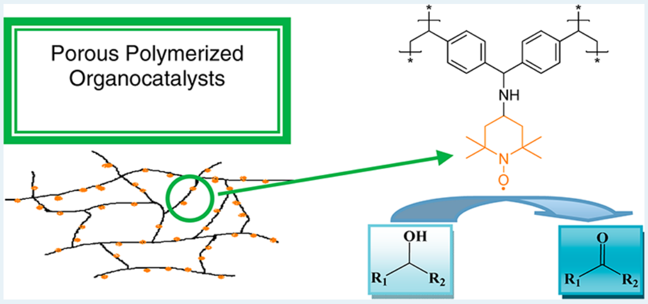
Supporting Information

ABSTRACT: Porous polymerized organocatalysts (PPOs) have been successfully synthesized from the corresponding vinyl-functionalized monomers under solvothermal conditions. These PPOs have high surface areas, large pore volumes, hierarchical porosity, and good stability. Utilized as a typical organocatalyst, the porous polymerized 2,2,6,6-tetramethylpiperidine-1-oxyl (PPO-TEMPO) with stable free radicals shows high activities and excellent recyclabilities in selective oxidations of a variety of alcohols to the corresponding aldehydes or ketones. This synthesis method may open a new door for developing heterogeneous catalysts with high activity and good recyclability in the future.



KEYWORDS: *porous polymerized organocatalysts (PPOs), vinyl-functionalized monomers, TEMPO, oxidation of alcohols, heterogeneous catalyst*

Small organic molecular catalysts, providing an alternative to metal- and enzyme-catalyzed transformations as a result of their distinct activity and selectivity, have been attracting continuous attention over the past decade.[1−15] Despite fruitful advancements in academia, like many homogeneous catalytic systems, they cannot be more extensively applied because of difficulties in separation of the catalysts from the products. To solve this problem, the immobilization of the organocatalysts via covalent bonding interactions with insoluble solid supports such as mesoporous silica, polystyrene, and metal organic frameworks (MOFs) has been performed.[16−27] Notably, the mesoporous silica support is normally sensitive to the alkaline media,[28] the polystyrene support often has relatively low surface area, and the MOFs usually have relatively low stability.[29] These shortcomings strongly hinder their applications in heterogeneous catalysis. More recently, the permanent immobilization of organocatalysts on the textile nylon under ultraviolet irradiation has been developed, giving excellent stability, activity, and recyclability.[30] If the organic functionalized monomers have structure-building abilities, the porous organic functionalized polymers could be obtained.[25,31] Here, we show an alternative route for preparing highly active and excellently recyclable organocatalysts with hierarchical porosity, which could efficiently function as a combination of both catalyst and support. The porous polymerized organocatalysts (PPOs) with high surface area, large pore volume, hierarchical porosity, and superior chemical stability have been directly and rationally synthesized via a mild solvothermal polymerization reaction of the corresponding vinyl-functionalized organocatalyst monomers.[32,33]

Scheme 1 shows the structures of PPOs in this work, including the porous polymerized 2,2,6,6-tetramethylpiperidine-1-oxyl (PPO-TEMPO), porous polymerized (R)-1,1′-binaphthyl-2,2′-diylhydrogen phosphate (PPO-BNPA), and porous polymerized α,α-diphenylprolinol[34] (PPO-DPP). Chosen as a typical example, the PPO-TEMPO was selected for subsequent studies in detail. The PPO-TEMPO was prepared from polymerization of vinyl-functionalized 2,2,6,6-tetramethylpiperidine monomer (V-TEMP) in the presence of azobisisobutyronitrile (AIBN) at 100 °C, followed by oxidation with *m*-chloroperbenzoic acid (*m*-CPBA) at 0 °C (Scheme S1). The V-TEMP and its polymer have been confirmed by NMR spectroscopy (Figure S1 and Figure 1D).

Figure 1A shows N_2 sorption isotherms of the PPO-TEMP and PPO-TEMPO, giving typical curves of type I plus type IV. The adsorption at low pressure ($P/P_0 < 0.01$) is due to filling of micropores, and the hysteresis loops at higher relative pressure ($P/P_0 = 0.2−0.9$) are assigned to the presence of mesoporosity in the sample. Correspondingly, the pore size distribution (Figure S2) is centered at 1.2, 3.4, and 8.6 nm, respectively, as calculated by the nonlocal density functional theory method (NLDFT). The BET surface area and pore volume of PPO-TEMPO are estimated at 289 m^2/g and 0.21 cm^3/g, respectively. Figure 1B,C shows transmission electron micrograph (TEM) and scanning electron micrograph (SEM) images

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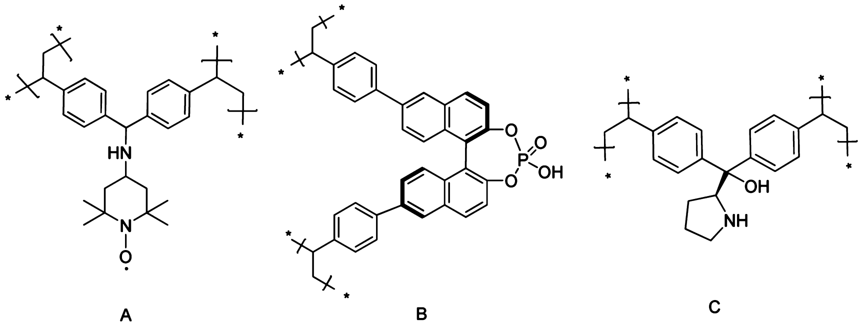
Scheme 1. Structures of Porous Polymerized Organocatalysts of (A) PPO-TEMPO, (B) PPO-BNPA, and (C) PPO-DPP



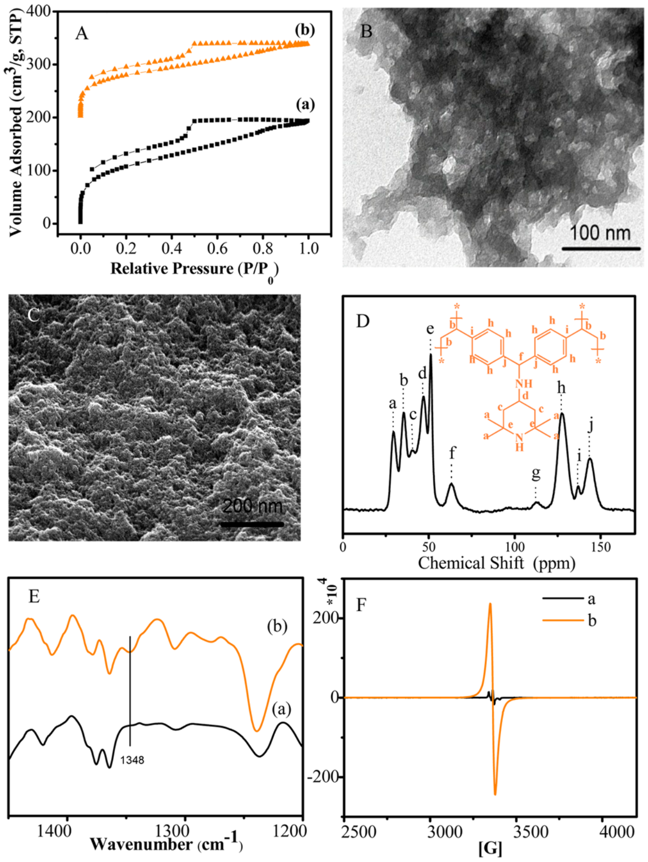


Figure 1. (A) N_2 sorption isotherms, (B) SEM image, (C) TEM image, (D) ^{13}C MAS NMR spectrum, (E) IR spectrum, and (F) ESR spectrum of (a) PPO-TEMP and (b) PPO-TEMPO samples (line b in A has been offset by 200 cm^3/g along with the vertical axis for clarity).

of the PPO-TEMPO, confirming the presence of hierarchical porosity in the PPO-TEMPO. Compared with V-TEMP monomer (Figure S1), the ^{13}C MAS NMR spectrum of the PPO-TEMP shows an additional band at 35 ppm associated with the polymerization of vinyl groups in the V-TEMP monomers (Figure 1D).[35] In addition, the IR spectrum of PPO-TEMPO (Figure 1E) shows a new band at 1348 cm^{-1}, which is reasonably related to the N−O free radicals.[36] Figure 1F shows the electron resonance (ESR) spectrum of the PPO-TEMPO, exhibiting a g value at 2.0049, which is very similar to that of conventional TEMPO monomer (2.0056).[37] This value confirms the presence of the N−O radical moiety in the sample. Element analysis shows that the oxygen weight in the PPO-TEMPO is ∼3.97%, indicating the concentration of the nitroxyl radicals at ∼2.5 mmol/g.

It is well-known that TEMPO is a typical and expensive organocatalyst for selective oxidations of primary and secondary alcohols to the corresponding aldehydes and ketones.[38−40] To evaluate the efficiency of the PPO-TEMPO, alcohol oxidations as model reactions have been carried out. As presented in Table 1, a series of alcohols could be oxidized to the corresponding aldehydes and ketones with very high conversion and selectivities over the PPO-TEMPO catalyst.[41] These excellent activities and selectivities are potentially important for industrial production of aldehydes and ketones from oxidations of alcohols.[42] For example, benzyl alcohol can be fully converted into benzyl aldehyde with very high selectivity (98%) in a very short time (3 min) over the PPO-TEMPO catalyst (entry 3). In contrast, the TEMPO immobilized on MCM-41 (TEMPO-MCM-41, Scheme S2) shows much lower conversion (88%) with a much longer reaction time (5 min, entry 4). A similar phenomenon could also be found in the case of the oxidation of 1-octanol (entries 11−14). Particularly, even in the absence of the cocatalyst KBr, the PPO-TEMPO still gives very high conversion (>99%) and selectivity (99%) after 20 min (entry 12). In contrast, the TEMPO-MCM-41 exhibits lower conversion (90%) and selectivity (85%), even after a much longer reaction time (45 min, entry 14).

In the case of oxidation of 4-methoxybenzyl alcohol, the PPO-TEMPO shows much better catalytic activity and selectivity than TEMPO in homogeneous catalysis. 4-Methoxybenzyl alcohol can be almost converted to methoxybenzyl aldehyde with very high selectivity (98%) over PPO-TEMPO after 10 min (entry 16), while homogeneous TEMPO gives a conversion of only 62% with very low selectivity (30%), even after a very long reaction time (45 min, entry 17). This phenomenon might be related to the enrichment of the reactant in the pores of the PPO-TEMPO catalysts, as reported previously.[43] Furthermore, the oxidation of benzyl alcohol has been performed over the PPO-TEMPO at various ratios of substrate to catalyst (S/C). When the S/C ratio is increased from 100 to 1000 and 2000, the results show very similar conversion (>99%) and selectivity (98%) under reaction times of 10 and 20 min, respectively (entries 5 and 6). Moreover, when divinylbenzene monomer is copolymerized in the hierarchical porous samples (PPO-DVB-TEMPO-x) to increase the catalyst surface areas (Table S1, 434−489 m^2/g), the same conversion (>99%) and selectivity (98%) are still observed in the short reaction time (3 min, entries 9 and 10). These results confirm the excellent properties of the PPO-TEMPO catalyst.

More importantly, the PPO-TEMPO catalyst shows excellent recyclability. After recycling five times, there is no loss of activity (>99%) and selectivity (98%, entry 7). The recycled PPO-TEMPO does not show any change in the ESR spectra

Table 1. Catalytic Data in Oxidation of Alcohols to Corresponding Aldehydes and Ketones over the PPO-TEMPO and TEMPO-MCM-41 Catalysts[a]

entry	substrate	catalyst	time (min)	conversion (%)[b]	selectivity (%)[b]
1	benzyl alcohol		3		
2	benzyl alcohol	TEMPO	3	>99	98
3	benzyl alcohol	PPO-TEMPO	3	>99	98
4	benzyl alcohol	TEMPO-MCM-41	5	88	85
5[c]	benzyl alcohol	PPO-TEMPO	10	>99	98
6[d]	benzyl alcohol	PPO-TEMPO	20	>99	98
7[e]	benzyl alcohol	PPO-TEMPO	3	>99	98
8[f]	benzyl alcohol	PPO-TEMPO	3	>99	98
9	benzyl alcohol	PPO-DVB-TEMPO-3	3	>99	98
10	benzyl alcohol	PPO-DVB-TEMPO-5	3	>99	98
11	1-octanol	PPO-TEMPO	3	>99	>99
12[g]	1-octanol	PPO-TEMPO	20	>99	>99
13	1-octanol	TEMPO-MCM-41	20	89	90
14[g]	1-octanol	TEMPO-MCM-41	45	90	85
15	4-methylbenzyl alcohol	PPO-TEMPO	5	>99	>99
16	4-methoxybenzyl alcohol	PPO-TEMPO	10	>99	98
17	4-methoxybenzyl alcohol	TEMPO	45	62	30
18	1-phenylethyl alcohol	PPO-TEMPO	5	>99	98
19	3-phenylpropanol	PPO-TEMPO	5	>99	96
20	1-nonanol	PPO-TEMPO	10	>99	>99
21	cyclohexanol	PPO-TEMPO	10	>99	98
22	4-chlorobenzyl alcohol	PPO-TEMPO	5	>99	98
23	1-heptanol	PPO-TEMPO	5	>99	>99
24	*m*-nitrobenzyl alcohol	PPO-TEMPO	3	>99	>99
25	2-octanol	PPO-TEMPO	5	>99	98
26	2-nonanol	PPO-TEMPO	5	>99	>99

[a] Reaction conditions: 0.8 mmol of substrate, 3 mg of PPO-TEMPO (1 mol % nitroxide radicals), 2 mL of CH_2Cl_2, 0.16 mL of 0.5 M KBr solution (10 mol %), 0.14 g of $KHCO_3$, 2.86 mL of 0.35 M hypochlorite solution (1.25 equiv), and 0 °C. [b] Conversion and selectivity determined by GC using dodecane as internal standard. [c] S/C = 1000. [d] S/C = 2000. [e] Recycling for 5 times. [f] Treated with boiling water for 48 h. [g] Without addition of cocatalyst KBr.

(Figure S4), suggesting its stable radicals in the catalyst. In contrast, TEMPO-MCM-41 could not be reused under alkaline conditions because siliceous MCM-41 would be dissolved, leaching the active radicals.[44] In addition, being after treated in boiling water for 48 h, the PPO-TEMPO still exhibits a surface area (280 m^2/g, Figure S5) very similar to that of the fresh sample (289 m^2/g). The oxidation of benzyl alcohol over the treated PPO-TEMPO still give high conversion (>99%) and selectivity (98%, entry 8). These results demonstrate the extraordinary hydrothermal stability of the sample, which is very favorable for potential applications of these oxidations in the future.

The other samples of PPO-BNPA and PPO-DPP (Scheme S4 and S5) are also characterized by N_2 sorption isotherms (Figure S7). Both samples have high surface areas and large pore volumes. Their textural parameters are summarized in Table S1. The catalytic activity of PPO-DPP in asymmetric reduction of phenyl methyl ketone with BH_3 was tested, which gives the yield at about 99% with 70% ee (Table S2). The catalytic properties of PPO-BNPA are still under investigation.

In conclusion, we have successfully synthesized porous polymerized organocatalysts with high surface area, hierarchical porosity, and superior chemical stability. As a typical example, the PPO-TEMPO as an efficient heterogeneous catalyst exhibits high activities and excellent recyclability in selective oxidations of alcohols to the corresponding aldehydes or ketones. The PPO catalysts synthesized in this work might open a new door for developing heterogeneous catalysts with high activity and good recyclability in the future.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The following file is available free of charge on the ACS Publications website at DOI: 10.1021/acscatal.5b00008.

> Details of synthesis methods of PPOs and characterization, including ^{1}H NMR and ^{13}C NMR spectra, pore size distribution, and the oxidation testing (PDF)

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Notes

The authors declare no competing financial interest.

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