Hollow and Microporous Organic Polymers Bearing Sulfonic Acids: Antifouling Seed Materials for Polyketone Synthesis

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Supporting Information

ABSTRACT: The reactor fouling is a notorious obstacle in managing continuous synthetic processes of polyketones. The fouling raises synthetic costs and reduces the bulk density of polymers. Thus, efficient seed materials are required for antifouling performance. Hollow microporous organic polymers (HMOPs) were prepared using ZIF-8 nanoparticles as templating materials. Sulfonic groups were incorporated into HMOPs via a post synthetic approach. The resultant HMOP−SO3H (20−90 µg/mL in methanol) showed successful catalyst activation and antifouling performance in polyketone synthesis.

Chemical fixation and conversion of C1 gases such as CO, CO2, and CH4 are important issues in managing global warming.1 CO can be used to synthesize useful chemicals.2 For example, thermoplastic polyketones have been produced in methanol using CO, ethylene, and Pd catalysts (Scheme 1a), in which methanolysis is conducted by Pd catalysts.3 The generated methoxy or hydride ligand initiates polymerization through migratory insertion. The original anionic ligands in Pd catalyst precursors are critical for methanolysis.4 For example, (P−P)Pd(OAc)2, which has poor reactivity in methanolysis can be activated by sulfonic acids to form (P−P)Pd(OSO2R)2 with less coordinating sulfonate ligands (Scheme 1b).4

One of the technical problems in the synthesis of polyketones is the notorious fouling of reactors which is an obstacle in managing continuous synthetic processes.5 Moreover, the fouling raises synthetic costs and reduces the bulk density of polymers. Thus, antifouling technologies are critical for the commercialization of polyketones.6 As an antifouling method, seed materials have been added to the reaction media.5,7 However, further exploration is required to reduce the amount of seed materials. Considering the catalyst activation of (P−P)Pd(OAc)2 by sulfonic acids, we expect that solid materials having sulfonic acids can be used as seed materials in polyketone synthesis.

Recently, various microporous organic polymers (MOPs) have been prepared by the coupling of organic building blocks.8,9 Our research group has shown that hollow MOPs can be engineered using templates.10 These hollow MOPs are highly dispersible in organic solvents including methanol.11 In addition, functional groups can be easily introduced to hollow MOPs through postsynthetic approaches11 due to the short diffusion pathways of reagents. Thus, we believe that antifouling seed materials for polyketone synthesis can be developed based on MOPs. However, as far as we are aware, there have been no reports investigating MOP-based antifouling seed materials in polymer synthesis. In this work, we report nonfouling polyketone synthesis using hollow MOPs with sulfonic acids (HMOP-SO3H) as seed materials.

Figure 1 shows the synthetic route for HMOP-SO3H.

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We used zeolitic imidazolate framework (ZIF-8) particles with a diameter of $473 \pm 21$ nm as templates to engineer HMOP-SO$_3$H (Figures 2a,b). It has been known that ZIF-8 is a good adsorbent and can be disassembled by acetic acid.$^{13b}$ The ($\text{PPh}_3)_2\text{PdCl}_2$ and CuI catalysts were adsorbed in ZIF-8. Using tetrakis(4-ethynylphenyl)methane$^{14}$ and 1,4-diiodobenzene as building blocks, MOPs were formed on the surface of ZIF-8 particles through the Sonogashira coupling (Figure S1 in the Supporting Information, SI). After treating the ZIF-8@MOP with acetic acid for 1 h, the hollow MOP (HMOP) was obtained. As shown in Figure 2c, scanning electron microscopy (SEM) indicated the hollow nature of HMOP.

The sulfonation of HMOP with CISO$_3$H was conducted following the procedure in the literature.$^{15a}$ The SEM analysis of HMOP-SO$_3$H showed hollow polyhedrons with a diameter of $521 \pm 21$ nm (Figures 2d,e). Transmission electron microscopy (TEM) showed a wall thickness of $25 \pm 2$ nm (Figure 2f). The incorporation of sulfonic acids into HMOP resulted in a decrease of the surface area to $232 \text{ m}^2/\text{g}$, matching well with observations in the literature.$^{11,13a}$ Powder X-ray diffraction (PXRD) studies showed the conventional amorphous characteristics of HMOP and HMOP-SO$_3$H (Figure S2 in the SI).$^{8,12,15}$ The infrared (IR) absorption spectroscopy of HMOP-SO$_3$H revealed vibration peaks of sulfonic acids at 3475, 1218, and 1047 cm$^{-1}$ (Figure 2h).$^{15}$ The solid-phase $^{13}$C nuclear magnetic resonance (NMR) spectroscopy of HMOP and HMOP-SO$_3$H showed $^{13}$C peaks of benzyl carbon and phenyl rings at 64 and 110$^{−150}$ ppm, respectively (Figure 2i). The aromatic $^{13}$C peaks changed significantly by the incorporation of sulfonic acid groups to phenyl rings. The similar change of $^{13}$C NMR spectra was reported in the literature$^{13a}$ on the sulfonated MOPs by ClSO$_3$H. The $^{13}$C peaks at $85^{−95}$ ppm disappeared, indicating the acid addition to internal alkynes (Figure 2i). The addition of halosulfonic acid and HCl$^{16}$ to internal alkynes was well reported in the literature.$^{17}$

**Figure 1.** Synthetic scheme and the suggested structure for hollow microporous organic polymers bearing sulfonic acids (HMOP-SO$_3$H) and a photograph of colloidal HMOP-SO$_3$H in methanol.

**Figure 2.** SEM images of (a,b) ZIF-8 particles, (c) HMOP, and (d,e) HMOP-SO$_3$H. (f) TEM image of HMOP-SO$_3$H. (g) N$_2$ adsorption−desorption isotherm curves at 77 K, pore size distribution diagram based on the DFT method (inset), (h) IR absorption spectra, and (i) solid-phase $^{13}$C NMR spectra of HMOP and HMOP-SO$_3$H.
acids (p-TsOH) activated the (domppp)Pd(OAc)$_2$ (entries 2–4). The use of p-TsOH as an activator in the range of 1 to 2 equiv with respect to (domppp)Pd(OAc)$_2$ showed good activities in polyketone synthesis (entries 3–4). However, as expected, the severe fouling of reactor was observed (entries 3–4 and Figure 3). When HMOP-SO$_3$H was used as a catalyst activator for polyketone synthesis, the reaction showed good activity without reactor fouling. Through screening the synthetic conditions, it was found that there is an optimal range of seed concentrations (entries 5–10). When 0.2–0.9 mg of HMOP-SO$_3$H was used in 10 mL of methanol, the systems showed excellent antifouling performances (entries 5–7). When the seed concentration exceeded 180 μg/mL, the catalytic activities gradually decreased (entries 8–10). It is noteworthy that a very small amount of HMOP-SO$_3$H (20–90 μg/mL in methanol) showed successful antifouling performance during polyketone synthesis. In the literature, a relatively large amount (2–6 wt %) of solid seed materials without catalyst activating groups (SO$_3$H) have been used to solve the fouling problem.

According to the stoichiometric consideration, the (domppp)Pd(OAc)$_2$ used in entries 5–7 in Table 1 (2.0 μmol) is in excess to the amount of SO$_3$H groups (0.43–1.9 μmol) in the HMOP-SO$_3$H, implying that some Pd compounds did not participate in the polyketone synthesis. Even when we gradually reduced the amount of Pd catalysts from 1.5 to 0.32 mg (0.43 μmol) with 0.40 mg (0.86 μmol SO$_3$H) of HMOP-SO$_3$H, the catalytic activities were significantly retarded (entries 6 and 11–13). The system of (domppp)Pd(OAc)$_2$ and HMOP-SO$_3$H in this work showed activities of up to 46 kg polyketones/g of Pd (entry 13). The bulk densities of polyketones were measured up to 0.29 g/mL (entries 5–7). When we used HMOP without sulfonic acids (instead of HMOP-SO$_3$H), the catalytic system showed very poor catalytic activity, indicating that the Pd catalyst was activated by the sulfonic acids in HMOP-SO$_3$H (entry 14).

The NMR spectroscopy confirmed the chemical structure of polyketones with major $^{13}$C peaks of carbonyl and ethylene at 212 and 35 ppm, respectively (Figures S4–5 in the SI). The infrared (IR) absorption spectroscopy showed the vibration peaks at 1693 (C=O), 1407 (C–H), and 1334 (C–H) cm$^{-1}$ (Figure S6 in the SI). Elemental analysis of polyketones showed 63.85–64.11% of carbon, 7.01–7.17% of hydrogen, and 28.11–28.38% of oxygen (theoretical values of (C$_3$H$_4$O)$_n$: 64.27%, H: 7.19%, O: 28.54%). The endothermic peaks by the melting of polyketones were observed in a range of 252–260 °C in differential scanning calorimetry (DSC) curves (Figure S6 in the SI). These characterization data match well with those of polyketones in the literature.

To understand the difference in the reaction processes between the homogeneous catalyst system using p-TsOH
(entry 4 in Table 1) and the heterogeneous HMOP-SO$_3$H seed system (entry 6 in Table 1), we investigated the pressure changes during the reactions. As shown in Figure 3a, the homogeneous system with (dompp)Pd(OAc)$_2$ and p-TsOH showed a sharp decrease in the total pressure during the early stage of reaction. In comparison, the HMOP-SO$_3$H seed system showed a gradual decrease in the total pressure, indicating the controlled formation of polymers around the seed materials, as illustrated in Figure S7 in the SI.

It has been reported that the relatively slow crystallization of polyketones induces α packing,$^{22}$ which is denser and more stable than β packing.$^{22}$ Wide-angle XRD study showed a dominant α phase of polyketone obtained using HMOP-SO$_3$H and a β phase of polyketone obtained using p-TsOH (Figures 3e and S8 in the SI), indicating the slower and closer packing in seed-mediated polymerization.$^{22}$ Through centrifugation of polyketone solution in hexafluoroisopropanol (HFIP), we could isolate the minute HMOP-SO$_3$H materials. The SEM studies showed the homogenous decoration of HMOP-SO$_3$H materials with polymers, inducing an increase of diameter and wall thickness from 521 and 25 to 625 and 120 nm, respectively (Figures 3g and S9 in the SI). This observation supports the action of HMOP-SO$_3$H as seed materials.

In conclusion, this work shows that MOP chemistry can be applied to develop the polymerization processes of polyketones by creating efficient antifouling seed materials. The seed-mediated polymerization by HMOP-SO$_3$H showed a more gradual formation of polymers, hence controlling the packing structure of polyketones to a denser α packing, compared with the β packing formed through homogeneous polymerization by p-TsOH. We believe that the strategy in this work can be applied for industrial polyketone processes.$^{23}$ In addition, shape-controlled MOP materials can be further designed and developed as highly efficient seed materials for more diverse types of antifouling polymerization.

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**REFERENCES**


**ASSOCIATED CONTENT**

Supporting Information
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Synthetic procedure, TEM images of ZIF-8@MOP, PXRD patterns, characterization data of polyketones, and SEM images of HMOP-SO$_3$H before and after reaction (PDF)

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**Notes**
The authors declare no competing financial interest.
(16) The HCl is generated during the sulfonation of aromatic groups by ClSO₃H.


(18) The elemental mapping based on energy-dispersive X-ray absorption spectroscopy (EDS) showed the homogeneous distribution of sulfur and oxygen over HMOP-SO₃H (Figure S10 in the SI).

(19) Acid-base titration showed 2.46 mmol SO₃H/g of HMOP-SO₃H.


(21) According to ref 5, 2—6 wt % seed materials were used in industrial applications. In comparison, 0.01 wt % HMOP-SO₃H (entry 6 in Table 1) was used in this work.
