

One-Pot Solvothermal Synthesis of Hypercrosslinked Porous Ionic Polymer and Its Catalytic Activity¹

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Abstract—The hypercrosslinked porous ionic polymer has been synthesized via one-pot polymerization and quaternization of vinyl pyridine and chloromethyl styrene under solvothermal condition. The effects of solvents and synthetic process on the polymer structure were investigated. Polymer from *n*-butanol showed the highest BET surface area of 555.6 m²/g. The catalytic activities were investigated through the aza-Michael addition and the results showed that the polymer owned even higher activity than homogenous ionic liquid. The high BET surface area, high catalytic activity and high stability made the polymer hold great potential for green chemical processes.

Keywords: hypercrosslinked ionic polymer, one-pot solvothermal synthesis, aza-Michael addition

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1. INTRODUCTION

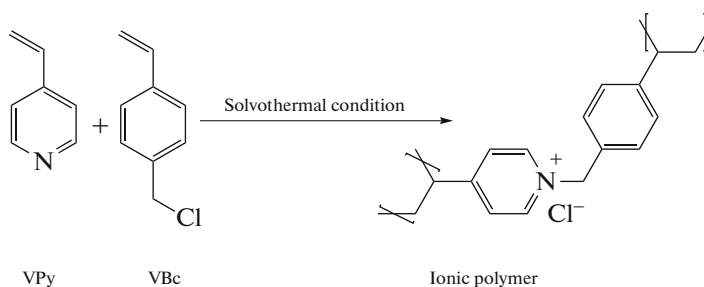
Ionic liquids (ILs) owned excellent properties, such as non-volatility, wide liquid range, excellent solubility and structure tenability, which were widely used in various fields [1–5]. However, ILs suffered from several drawbacks, which restricted their practical application in chemical industry. The high solubility caused the difficulty in recycling ILs from reaction mixture. The large ILs dosage added the process cost. The unendurable viscosity was another problem. The poor biodegradability and toxicity were also the concerns. Some ILs were even more toxic than the reagents that they were aiming to replace. Immobilization of ILs was a good choice to solve the abovementioned problems [6]. The resulting supported ionic liquid phases catalysts (SILPCs) combined the advantages of solid catalysts and ILs with easy separation and high activities. The preparation and application of SILPCs attracted much attention. The solid supports were very important for the SILPCs. The cheap commercial silica gel with high surface area was widely used. The imidazolium-based ILs supported on silica showed high activity for epoxidation of olefins [7]. The sulfonic acid functionalized IL modified silica gel was very efficient for the hydrolysis of cellulose [8]. However, the ILs loading amount was low (below 1.0 mmol/g). Pescarmona grafted bisvinylimidazolium IL onto silica gel to form multilayered SILPCs to improve the IL loading amount [9]. But the internal layer ILs were useless.

Mesoporous molecular sieves such as SBA-15 [10] and MCM-41 [11] were used as supports. The molecular sieves added the cost and their amorphous pore wall was instable. The periodic mesoporous organosilica with alkylimidazolium IL moiety in framework was synthesized [12]. The synthetic process was quite complex. Compared to inorganic supports, the organic polymer owned the high affinity with ILs. The immobilization could be achieved via the simple copolymerization. The IL grafted onto highly crosslinked polymer showed high activity for CO₂ cycloaddition [13]. The nanoporous polydivinylbenzene (PDVB) with superhydrophobicity and superoleophilicity was widely used as support for ILs [14, 15]. Our group grafted the acidic IL onto the PDVB and used for biodiesel synthesis from waste oils [16]. The novel porous polymer containing ionic liquid structures was synthesized *via* quaternization and condensation of 4-vinylpyridine and *p*-xylylene dichloride in our previous work [17]. Although the SILPCs showed high activities for various reactions, the bulky IL molecules would decrease the surface area and cause pore blocking. The IL loading amount was restricted greatly.

The novel porous hypercrosslinked ionic polymer was synthesized *via* one-pot polymerization and quaternization of 4-vinyl pyridine (VPy) and 4-chloromethyl styrene (VBc) at solvothermal conditions (Scheme).

Compared to the grafting structure, the IL moieties were embedded in the polymeric framework with more than two chemical bonds, which avoided the pore blocking. In addition, the active IL in pore walls was

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Scheme. The synthesis of hypercrosslinked ionic polymer.

easily accessible to reactants. The catalytic activity was investigated through aza-Michael addition. The results showed that the polymer showed even higher activity than IL with additional advantage of easy recovery.

2. EXPERIMENTAL

All organic reagents were commercial products of the highest purity available and used for the reactions without further purification.

2.1. Synthesis of Hypercrosslinked Ionic Polymer

4-Vinyl pyridine (1.05 g, 10 mmol), 4-chloromethyl styrene (1.52 g, 10 mmol), solvent (20 mL) and azobisisobutyronitrile (AIBN, 0.01 g) were mixed and stirred at room temperature (25°C) for 2 h. Then, the solution was transferred to the stainless-steel autoclave and solvothermally treated at 140°C for 12 h. The obtained solid was filtered and washed with acetone. The ionic polymer was obtained after drying at 80°C in an oven for 12 h.

2.2. The Procedure for Aza-Michael Addition

Amines (20 mmol) and alkenes (24 mmol) were mixed and stirred at RT. Then, catalyst (20 mg) was added and reacted for certain time. The reaction process was monitored by GC analysis. After reactions, the catalyst was recycled by filtration. The recycled polymer was washed with ethanol and dried at 80°C overnight in an oven. The recycled catalytic activity was investigated. The product was separated by column chromatography using neutral alumina as stationary phase and (petroleum ether/ethyl acetate 95 : 5) as eluent.

3. RESULTS AND DISCUSSION

3.1. Characterization of the IL based Polymer

The rigid hypercrosslinked polymeric network was essential to form the porous structure [18], which would restrict the shrinkage during the drying process and maintain the pore structure. Here 4-vinyl pyridine and 4-chloromethyl styrene were used as raw materials. The quaternization of 4-vinyl pyridine and 4-chloromethyl

styrene formed the rigid aromatic ionic monomer with double vinyl groups, which could form the hypercrosslinked structures. In order to avoid the ionic oligomers precipitating, the polymerization and quaternization were carried out simultaneously. The solvents hold great importance to the polymer structure, which should well swell the polymeric chains and act as porogen [19]. *n*-Butanol, acetone, dioxane and isopropanol were used respectively.

The scanning electron microscope (SEM) images of the polymers from different solvents were quite different (Fig. 1). The polymer from acetone showed relatively large particle size of 2–5 μ (Fig. 1a). The particles gathered together with sphere particles embedded in bulky blocks. The ionic monomer was not well soluble in acetone. The monomer was also polymerized in acetone, which formed the bulky blocks (Fig. 1b). The ionic oligomers precipitated at the very beginning of the reaction. The initial formed nuclei became the reaction centers and the further reactions occurred around them, which increased the particle size and resulted in the bulky blocks.

As to butanol (Fig. 1c), the polymer showed much smaller particle size of about 10 nm. *n*-Butanol owned proper solubility for ionic monomer. Therefore, the reaction intermediates could be well solvated by butanol. The nuclei formed at the late period of the reaction and precipitated simultaneously with large amount, which formed the smaller particle size. Also, the ionic monomer was polymerized in butanol (Fig. 1d). The results showed the polymer with larger particle size of 200–500 nm. Compared to the one-pot process, the ionic monomer owned higher polarity, which moved up the precipitation. The further reactions occurred around these precipitates and added the particle size. Also, 4-vinyl pyridine and 4-chloromethyl styrene were polymerized in *n*-butanol respectively, which formed the homogeneous polymer solution. These further confirmed the good solubility of butanol for the reaction. The poly (vinyl pyridine) and poly (chloromethyl styrene) were also reacted with chloromethyl styrene and vinyl pyridine respectively (Figs. 1e and 1f). The results showed that the polymerization was important for the polymer structure. The prepolymer formed large particles with the size more

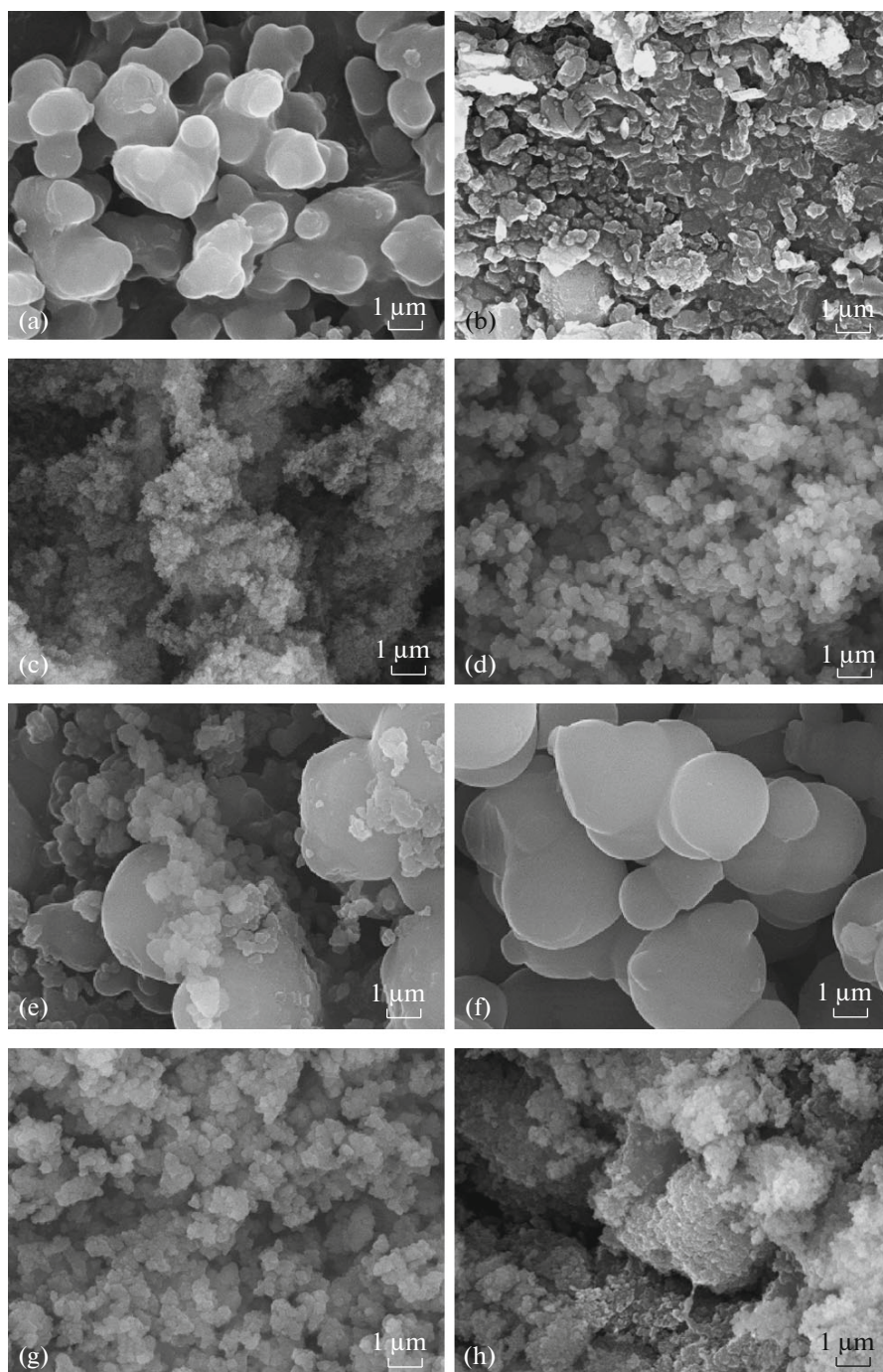


Fig. 1. The SEM images of the polymer from different solvents: (a) polymer from the one-pot synthesis in acetone; (b) polymer from the polymerization of [VBcVpy]Cl ionic monomer in acetone; (c) polymer from the one-pot synthesis in *n*-butanol; (d) polymer from the polymerization of [VBcVpy]Cl ionic monomer in butanol; (e) polymer from the poly Vpy and VBc in butanol; (f) polymer from the poly VBc and Vpy in butanol; (g) polymer from the one-pot synthesis in dioxane; (h) polymer from the one-pot synthesis in isopropanol.

than 10 μm . The prepolymer owned long polymeric chains and the chain growth was quicker, which would pack up during the reaction process. As a result, the particle sizes increased. For poly (vinyl pyridine),

there were some small particles formed, which indicated the vinyl pyridine oligomers with short chains in the prepolymer solution. These further confirmed that the one-pot process was more suitable for the polymer

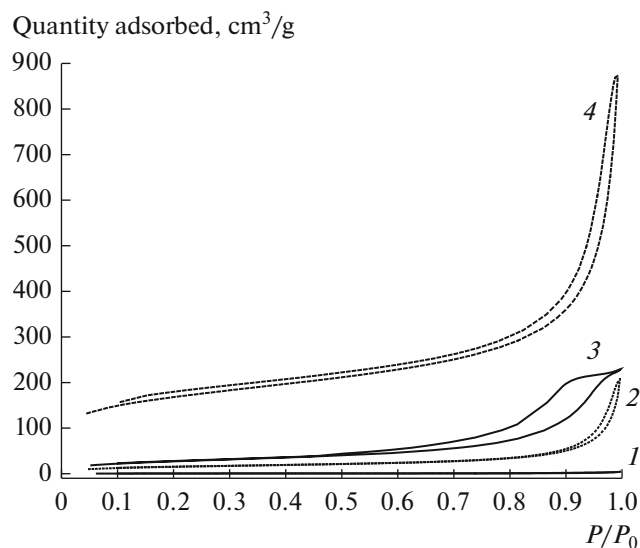


Fig. 2. The N_2 adsorption–desorption isotherms of polymers from different solvents.

synthesis. The polymerization and quaternization occurred at the same time, which effectively avoid the fast chain growth and dense packing.

Dioxane owned lower solubility with reaction intermediates and the polymer with particle size of 200–500 nm was formed (Fig. 1g). The result was similar to acetone, but the particle size was much smaller due to the better solubility.

As to isopropanol, the particle size of 50 nm was obtained (Fig. 1h). Isopropanol owned higher solubility than butanol. The polymeric chain became much longer when the precipitation occurred. The situation was quite similar to prepolymer.

The BET analysis of the ionic polymers was also carried out (Fig. 2, Table 1). The results further indicated that the great effect of solvents on polymers, which acted as porogen [15]. The polymer from acetone owned very low BET surface area of 1.4 m^2/g . Acetone owned poor solubility for the reaction and the solvent could not well swell the polymer network. As a result, the densely packed polymer with low BET surface area was obtained. Butanol owned the proper solubility for both IL and oligomers. The polymeric

chain was short and the residue monomer amount was low when precipitating from the reaction system, which avoided the chain twinning and particle size growth. The ionic polymeric chains were relaxed and solvated by butanol, which formed the highly swollen network. The homogeneous polymeric gel was obtained from butanol, which also confirmed the well interaction between butanol and polymer. The rigid hypercross-linked polymeric network prevented the structure shrinkage during the drying process. The space butanol occupied became the pores in polymer. The polymer owned the high BET surface area of 555.6 m^2/g . The mesopore size of 12.3 nm benefited the mass transfer. As to isopropanol, the BET surface area reduced to 99.8 m^2/g . The isotherms showed the typical type IV (the fourth type) pattern, which indicated the mesoporous structure. The mesopores made the active sites easily accessible to big molecules. Polymer from dioxane showed relatively low BET surface of 52.6 m^2/g . The BET surface areas agreed well with particle sizes, these results indicated the packing pores was the main reason for the BET surface area.

The FT-IR spectra of the polymers from different solvents were also carried out (Fig. 3). All ionic polymers showed the similar IR spectra, which indicated the similar chemical bonds in the polymers. The peaks at 2900–3100 cm^{-1} were assigned to Ar–H and C–H absorption, which was the aromatic rings and methylene from the polymerized double bonds. The strong absorption at 1423 cm^{-1} was the C–H stretching vibration, which indicated the methylene groups from the chloromethyl styrene and the polymerized double bonds. The strong peak at 1135 cm^{-1} was the C–N absorption, which confirmed the quaternization reaction. The strong double bonds adsorption at 1578 cm^{-1} confirmed the high aromatic rings content in the polymer. The peaks at 1636 cm^{-1} was the C=C absorption, which was the residual double bonds. Acetone showed the strongest double bonds absorption, which indicated the large residual double bonds amount. Polymer from butanol showed weak peak, which indicated that the polymerization occurred more completely.

The element analysis of the ionic polymer from *n*-butanol was carried out. The results showed C 75.1%, H 6.1%, N 5.3% (found), C 74.6%, H 6.2%, N 5.4% (calculated). The results agreed well with the

Table 1. Physical properties of the polymers from different solvents

Solvent	Surface area, $m^2 g^{-1}$	Pore volume, $cm^3 g^{-1}$	Average pore size, nm
Butanol	555.6	1.17	12.3
Isopropanol	99.8	0.36	14.4
Dioxane	52.6	0.28	21.8
Acetone	1.4	0.01	14.3

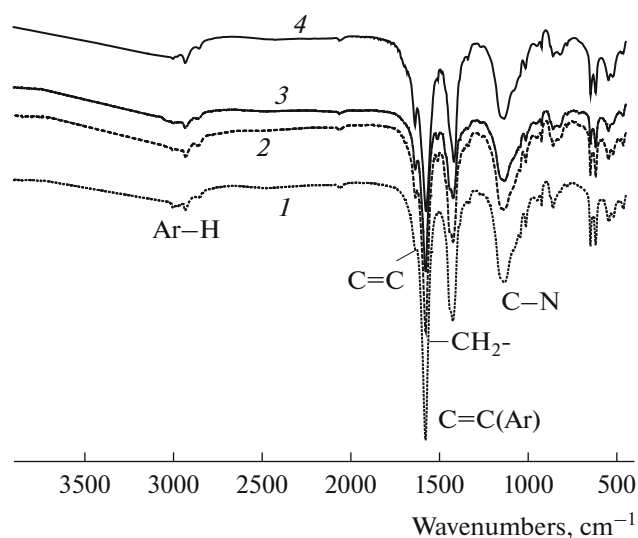


Fig. 3. The FT-IR spectra of the polymer from different solvents.

structure given in scheme. Also, the ions exchange was carried out and the Cl^- was titrated, the result showed the result of 3.82 mmol/g, which was almost the same as the IL amount of 3.88 mmol/g (Calculated). The result further confirmed that quaternization occurred effectively, which formed the dense active sites. The EDX analysis of the polymer showed that the Cl element was evenly dispersed in the polymer, which provided the easily active sites to reactants (Fig. 4).

3.2. The Catalytic Activity for Aza-Michael Addition

The catalytic activities of the ionic polymers were investigated via the aza-Michael addition (Table 2). The reaction condition was optimized to choose the proper reaction condition. The reaction process was monitored by GC analysis and the optimal reaction time was chosen. For the reaction between methyl piperazine and acrylonitrile with low steric hindrance,

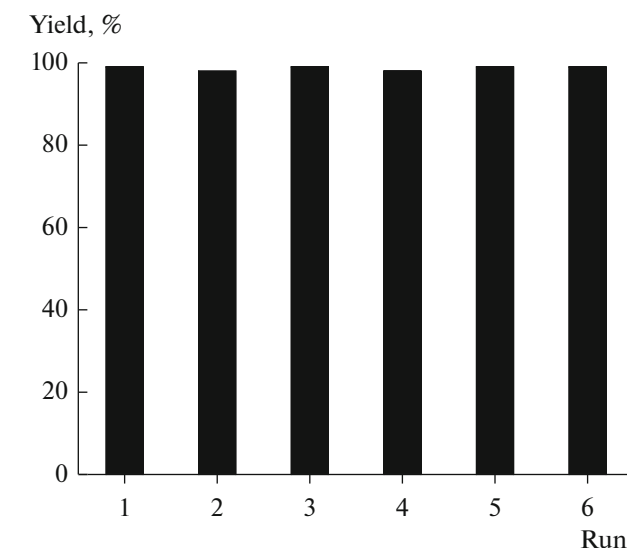
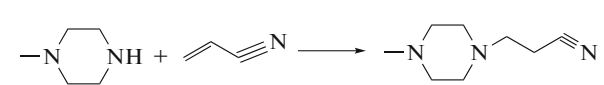
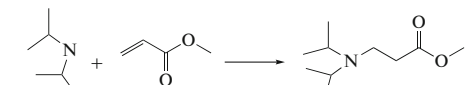


Fig. 4. The recycled catalytic activities of IL based polymer.

the ionic polymer from butanol showed the highest activity with the yield of 99% only after 4 min. The high BET surface area benefited the mass transfer efficiency. The polymer from acetone also showed the high yield of 95% when prolonging the reaction time to 15 min. Although the polymer owned low surface area, the high ion amount (3.8 mmol/g) provided enough active sites. The reactions could be activated around the polymer surface. As to isopropanol and dioxane, polymers owned relatively high surface area and the yield of 98% was obtained. The catalytic activities agreed well with the BET surface area, which further confirmed that the active ionic sites were evenly distributed around the polymer.

The IL from the quaternization of pyridine and benzyl chloride was also used here. The high yield of 98% was obtained after 5 min, which was still lower than the ionic polymer from butanol. Furthermore, IL

Table 2. The catalytic activities of different catalysts for aza-Michael addition

Catalyst				
	reaction time, min	yield, %	reaction time, min	yield, %
Butanol	4	99	7	99
Isopropanol	8	98	10	99
Dioxane	10	98	15	97
Acetone	15	95	30	88
IL	5	98	15	95

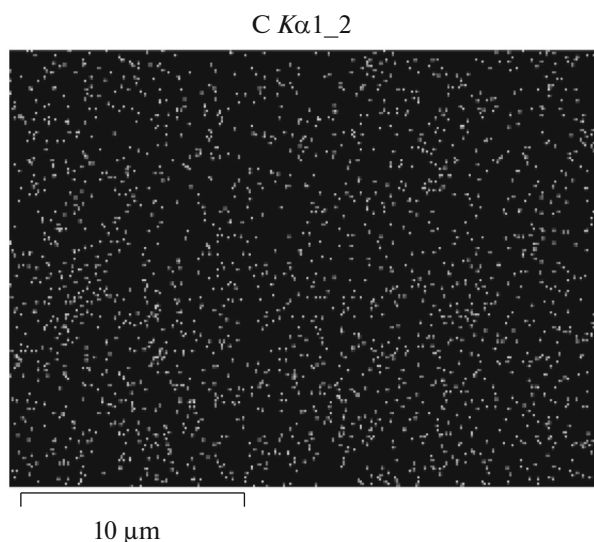


Fig. 5. The EDX analysis of Cl element in ionic polymer from *n*-butanol.

was soluble in the reaction system, which added the separation difficulty.

The reaction between diisopropylamine and methyl acrylate with high steric hindrance was also investigated. The polymers also showed even higher activities than IL. The polymer from butanol showed the yield of 99% after 7 min. The reaction time was longer due to the higher steric hindrance. The polymer from isopropanol also gave the high yield of 99% after 10 min. The mesoporous structure was quite suitable for big molecules and diisopropylamine molecules could easily enter into the mesopores and interact with the active sites. As a result, the ionic polymer from isopropanol showed highest yield even though the BET surface area was low. The polymer from acetone showed lowest activity due to the low BET surface area. The bulky reactant molecules could hardly interact with the active sites inside and the reaction was carried out only around the accessible external surface, which accounted for the low activities.

For IL, the reaction was carried out homogeneously, but the yield was still lower than the heterogeneous polymer. The polymer with organic polymeric framework showed high affinity with reactants, which caused the enrichment effect of reactants.

3.3. The Recycled Activity of the Catalyst

The polymer could be recycled by simple filtration. The recycled activity of polymer from butanol was investigated using the reaction between methyl piperazine and acrylonitrile (Fig. 5). The ionic polymer owned high BET surface area and the reaction mixture would be enriched in polymer. The polymer was washed by acetone and the washing solution was also investigated. The results showed the composition of

the washing solution was quite similar to the reaction mixture. The product content was even higher due to the bigger molecule size, which would be adsorbed in the polymer more strongly. Combined with the little catalyst amount, the absorption attached little importance to the yield. The recycled activities showed that the polymer owned high stability with the yield remained after being recycled for six times. For fresh catalyst, the intermediate yield of 85% was obtained after 2 min, while the yield of 84% was obtained for the recycled polymer. The result further confirmed the high stability of the polymer. The polymer owned the hypercrosslinked structures with the bulky cations embedded in framework, which effectively avoided the active sites releasing and pore blocking. High BET surface area and large pore volume benefited the mass transfer and avoided the carbon deposition. The recycled polymer still showed the similar BET surface area of 546 m²/g to the fresh catalyst. The FT-IR spectrum also showed the no changes, which indicated that the structure was well kept during the catalytic process.

4. CONCLUSIONS

The novel porous ionic polymer was synthesized from the simple one-pot polymerization and quaternization of 4-vinyl pyridine and 4-chloromethyl styrene. The solvents were very important for the polymer structures, which acted as the porogen. The polymer from *n*-butanol owned high BET surface of 555.6 m²/g and large pore volume, which provided the easily accessible active sites to reactants. The ionic polymer showed even higher activity for aza-Michael additions than the IL. High activity, high BET surface area and high stability were the key properties of the ionic polymer, which combined the advantages of solid catalysts and IL. The simple one-pot synthetic route and high IL loading amount made the polymer hold great potential in green chemical processes.

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