Synthesis and Catalytic Activity of Porous Polymer Containing Ionic Liquid Structures¹

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Abstract – A novel porous polymer containing ionic liquid (IL) structures was synthesized *via* quternization and condensation of 4-vinylpyridine and *p*-xylylene dichloride. The ionic liquid structures were incorporated in the polymeric framework and for this reason bulky IL molecules can hardly block pores and neutralize active sites. The polymer shows a high BET surface area and easily accessible active sites. Catalytically the polymer is very active in Michael additions with averaged yields over 96.0% achieved after short reaction times. The high BET surface, remarkable activity, operational simplicity, wide applicability and improved stability are the key properties of the polymer.

Keywords: porous polymer with ionic liquid structures, high activity, Michael addition **DOI:** 10.1134/S0023158416060082

Ionic liquids (ILs) attracted considerable interest as solvents because of their versatile properties such as non-volatility, wide liquid range, thermal stability and controlled miscibility [1]. Various organic synthesis such as hydrogenation, Suzuki reaction, aldol condensation, Diels-Alder reactions, alkylation, Michael addition and Schmidt reaction have been performed using ionic liquids as environmentally friendly solvents [2]. ILs also perform special functions in materials science, electrochemistry and separation technology [3, 4]. Since the first use of ILs as catalysts for organic synthesis, the potentials of ILs in synthetic applications became considerably wider [5]. Although many efficient processes were developed, the application of ILs in chemical industry is still limited. High solubility favors the interaction between ILs and reactants enhancing catalytic activity. However, it is still difficult to ensure a complete recovery of the ILs from the homogeneous reaction systems. An excessive viscosity is another drawback that is unfavorable for mass transfer and causes the operational difficulties. Furthermore, the ILs are even more toxic than the solvents that they were aimed to substitute. Therefore, the supported ionic liquid phase catalysts (SILPCs) became a good choice [6]. The resulting SILPCs combined the advantages of the solid catalysts and the ILs. As a result, the SILPCs found various applications in heterogeneous catalytic processes. The nature of the support affects both the connection mode and the BET surface; accordingly, supports play an important role in the immobilization of IL. Various supports were

introduced to prepare SILPCs. The commercial silica gel was one of the most used supports. The imidazolium IL with peroxotung state anions were immobilized onto silica gel and the catalyst showed activity comparable with that observed for olefin poxidation in the presence of IL [7]. The acidic ILs anchored to silica gel also showed high activity for hydrolysis of cellulose [8]. Low amounts of IL loaded on the silica gel (below 1.0 mmol/g) resulted in low activities. To increase the loading amounts, the multilayer structure on the support was formed using bis-vinylimidazolium ILs [9]. However, the ILs accommodated in the lower layers could not function during the reactions, which resulted in the loss of the active ILs. Compared to silica gel, mesoporous molecular sieves have higher surface area and the regular system of mesopores and because of these properties, the solids can accommodate high amounts of ILs. SBA-15 functionalized by an acidic IL exhibited high activity in Knoevenagel-Michael-cyclization reactions [10]. MCM-41 was also used to support ILs with phosphomolybdic acid [11]. However, the use of mesoporous molecular sieves increases the catalyst cost. The pore walls in amorphous solids have propensity to collapse during the catalytic process. Bulky IL molecules can block the entrance to the pores. To prevent this phenomenon mesoporous organosilica with alkylimidazolium IL incorprated in the framework was synthesized [12]. However, the use of organosilicon monomer and template needed for the complex synthetic process raises the cost of the catalyst. Furthermore, the expensive linkages are needed to connect the IL and silica. The organic polymers were also applied as supports in the

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simple copolymerization immobilization process. The IL grafted onto the highly cross-linked polymer was efficient for CO_2 cycloaddition [13]. Xiao developed the solvothermal synthesis of the highly porous poly(divinyl-benzene) (PDVB) that was widely used as a support [14, 15]. Our group was able to support the acidic IL on PDVB and applied the catalyst to synthesize biodiesel from waste oils [16, 17]. However, the traditional immobilization was achieved by single chemical bonds formed by grafting the structure of IL

on the surface. The bulky ILs could considerably reduce the BET surface area and in this way significantly affect the amount of loading. On the other hand, many active ILs could not function properly when the support is covered with excessive amounts of ILs due to the increased mass transfer limitations. In order to improve the amount of IL loaded, the novel porous hyper-cross-linked polymer with IL embedded in framework was synthesized from 4-vinylpyridine and *p*-xylylene dichloride (Scheme).

Synthesis of hyper-cross-linked polymer with IL structures



DCE – 1,2-dichloroethane

Scheme.

First, 4-vinylpyridine and *p*-xylylene dichloride were quaternized to form the IL structures. Then, the IL and excess *p*-xylylene were condensed to form the hyper-cross-linked polymer via the $SnCl_4$ -catalyzed alkylation. The ILs were embedded in the framework to act as the pore wall structures and help to avoid the pore blockage. A high surface area facilitates the accessibility of active sites to reactants. The catalytic activities of the polymer were investigated using the aza-Michael addition as a test reaction. The results indicate that the novel polymer has a higher activity than the homogeneous IL with easy recovery as an additional advantage.

EXPERIMENTAL

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

Synthesis of the Hyper-Cross-Linked Polymer with IL Structures

In a typical experiment, 4-vinylpyridine (1.05 g, 10 mmol) and *p*-xylylene dichloride were dissolved in 1,2-dichloroethane (DCE, 20 mL). The solution was stirred for 4 h at 75°C and the mixture became turbid. Then $SnCl_4$ (1 mL) was added to the mixture and reacted at 75°C for another 12 h. The brown gel was

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formed. The product was triply washed with acetone. After drying at ambient temperature overnight and at 80° C in an oven for 12 h, slightly yellow hyper-cross-linked polymer with IL structure was obtained. The amount of residual SnCl₄ in the polymer was examined using ICP technique. The results showed the absence of tin in the polymer indicating total removal of Lewis acid from the catalyst.

The Procedure for aza-Michael Addition

Requisite amounts of amines (20 mmol), alkenes (24 mmol) and catalyst (20 mg) were mixed and reacted for definite time intervals at ambient temperature. The GC analysis was conducted to monitor the reaction process. On completion, the catalyst was recycled by filtration. The recycled catalyst was washed with ethanol and dried at 80°C overnight. Activity of the recycled system was carefully investigated.

RESULTS AND DISCUSSION

Characterization of the Hyper-Cross-Linked Polymer with IL Structures

In order to improve the IL loading amount and BET surface, the ILs structures were incorporated into the polymeric framework. The quaternization of vinylpyridine and *p*-xylylene dichloride was taken to generate the IL structures. Then, the condensation of the



Fig. 1. The SEM images of the polymer with different molar ratio.

ILs and excess *p*-xylylene dichloride were carried out using SnCl₄ to form the hyper-cross-linked polymer. The IL was derived from vinylpyridine and the IL amount could be adjusted by varying the amount of vinylpyridine. However, the reactivity of the aromatic rings in ILs was much lower than p-xylylene dichloride due to the electron-withdrawing effect of pyridinium cations. Using excessive amounts of *p*-xylylene dichloride caused a significant self-condensation leading to an uneven distribution of IL moiety in polymer. The molecular ratio of the reactants greatly affects the polymer morphology (Fig. 1). It appears that the selfcondensation of *p*-xylylene dichloride occurs when the polymer was synthesized with n(vinylpyridine)/n(p-xy|y|ene dichloride) = 0.20. The presence of excessive amounts *p*-xylylene dichloride resulted in considerable self-condensation and formation of the bulky blocks, which represent a typical structure of poly p-xylylene dichloride (Fig. 1a). The polymerization between ILs and *p*-xylylene dichloride yielded polymer in small particles. Although the polymer has a high surface area of 1048 m^2/g , the ILs were distributed unevenly in the polymer. The self-condensation of *p*-xylylene dichloride favors the development of high surface area of the polymer. The amount of IL in the polymer was only 1.02 mmol/g. On the other hand, a prevailing fraction of the surface area was inactive, and could not be involved in catalytic reactions. By contrast, the polymer synthesized using n(vinylpyridine)/n(p-xylylene dichloride) = 0.50showed a uniform particle-size distribution (Fig. 1b). The polymerization produced regular spherical particles with the diameter of about 50 nm without bulky blocks, which indicated that the ILs were uniformly incorporated into the polymeric framework. The nitrogen sorption-desorption analysis indicated a high surface area (667 m^2/g), which could provide sufficient space for mass transfer during the catalytic process. The IL moieties were easily accessible to reactants when a high loading (2.87 mmol/g) was used and the polymer with high surface area was produced. In the agglomerates composed by spherical particles, every particle showed a clear boundary, which further confirmed the uniform pattern of the structure. The proper choice of IL moieties and n(vinylpyridine)/n(p-xylylene dichloride) molar ratio are of great importance for the polymer structure. The ILs imbedded in the polymer bring about electrostatic interactions between particles, which restrict agglomeration and decreases the alkylation reactivity of the particles. As a result, the particles with well-defined spherical shape are formed. With further increase in vinylpyridine amount aimed to reach n(vinylpyridine)/n(pxylylene dichloride) = 1.0, particles become bigger with sizes over 200 nm (Fig. 1c). In addition, the spherical patterns are replaced by particles with a square morphology. Some particles stick together to form clusters without clear boundary. A number of particles was divided into smaller entities with regular spherical patterns. Half of the *p*-xylylene dichloride was involved in quaternization reaction leading to a low cross-linking degree of the polymer. Only half of aromatic rings were alkylated. The hyper-cross-linked structure was not properly formed. The BET analysis showed a surface area of 25.5 m^2/g , which further confirmed a low cross-linking extent of the polymer. On preparing the polymer IL loading was increased to 4.09 mmol/g, but the most active sites were entrapped in the interior due to a low surface area. These active sites could not function during the reaction. Both the IL amount and the surface area affected the catalytic activity. Therefore, the polymer with n(vinylpyridine)/n(p-xylylene dichloride) = 0.5 was chosen, which combined a high amount of IL and a large surface area.

The FT-IR of the polymer with IL structures was also carried out (Fig. 2). The bands at $2921-3012 \text{ cm}^{-1}$ are due to stretching vibrations of Ar–H originated from abundant aromatic rings in polymer. The strong absorption at 1577 cm⁻¹ was assigned to N–C stretching vibrations in pyridinium IL indicating that the quaternization of vinylpyridine smoothly occurred during the synthetic process. The FT-IR also showed the strong absorption at 1421 cm⁻¹, which belonged to the C=C bonds. In order to distinguish the double bonds in aromatic rings from those in vinylpyridine the iodine value analysis was performed. The results showed that the residual contains nearly no vinyl groups. The results confirmed that the polymerization and alkylation was well-completed using SnCl₄ catalyst to form the hyper-cross-linked structures. The C–H stretching vibration at 1137 cm^{-1} confirmed the presence of alkyl groups from *p*-xylylene dichloride and vinylpyridine, which is another evidence that the quaternization and alkylation occurred smoothly. In spectra of the polymer the multiple peaks at 860, 689, 776, 648 and 619 cm^{-1} assignable to the multi-substituted structures of the aromatic rings were observed. The presence of multi-substituted aromatic rings also confirmed the hyper-cross-linked structures, which was essential for the development of pore structure. The resulting polymer with a high surface area greatly improved the mass transfer efficiency.

The elemental analysis gave the following results. Found: C 79.25%, H 6.57%. Calculated for IL structure: C 79.20%, H 6.60%. The agreement between the experimentally found and calculated values for the structure shown in Scheme provides another evidence that the quaternization and alkylation proceed satisfactorily under the conditions chosen for the synthesis. The hyper-cross-linked structures were successfully formed to fabricate the porous polymers with IL incorporated in the framework, which was beneficial for the catalytic activity. The value of the polymer density (0.6 g/cm³) is also indicative of the formation of well-developed pore structure. The polymer showed high thermal stability with the degradation occurring at temperatures beyond 280°C.

The Catalytic Activity for aza-Michael Addition

The catalytic activities of the polymer were investigated via the aza-Michael additions of amines with electron deficient alkenes (Table 1). The reaction condition was optimized to obtain the desired productsin the highest yield using diisopropylamine and dibutyl maleate as model reactants. The polymer showed very high activity for the reactions with high yields obtained in short reaction times. With dimethylamine significant steric hindrance cannot be expected and in reaction with methyl acrylate it was highly reactive with 99.2% yield achieved within 5 min (entry 1). The reactivity decreased when more bulky molecule of diethylamine was used (entry 2). A further reduction in the vield was observed in the reaction between diisopropylamine and methyl acrylate (entry 3). Nevertheless, when the reaction time was increased to 15 min a high yield of 95.6% was obtained. The primary amine was efficiently transformed using the polymer. Ethylamine showed a yield of 98.5% within 6 min (entry 4). The single substituted product was formed under mild reaction conditions. A steric obstacle arising from the presence of the mono-substituted product was much higher than in the case of ethylamine, and that effec-



Fig. 2. The FT-IR spectrum of the polymer with IL structures.

tively prevented a further addition to form the multisubstituted product. On the other hand, the multisubstituted product could be obtained using an increased amount of methyl acrylate at a higher temperature. Also, the diamine could be transformed using the polymer. Both amino groups of ethylenediamine were attacked by methyl acrylate to give 98.1% yield in 11 min (entry 5). With hydroxylamine the product was obtained in a good yield (96.7%) after 13 min, which indicated that the functionalities such as hydroxyl groups remained stable during the reaction (entry 6). The cyclic amines showed a high reactivity due to low steric obstacles caused by the presence of the ring structure (entries 7, 8). The presence of electron deficient alkenes influences the reaction efficiency. Ethyl acrylate showed a lower reactivity than methyl acrylate (entries 9–12). A negligible increase in the steric obstacles caused by the presence of the terminal vinyl structures accounts for weakly decreasing yields. Although high steric hindrances could be expected with dimethyl maleate, the polymer showed high activity yielding 93.2% of diisopropylamine (entry 13). Methyl piperazine showed a high yield of 98.7% in 8 min (entry 14). Due to the presence of the piperazine ring and the ensuing electron donating effect the cyclic amine showed high reactivity to dimethyl maleate with an observed yield of 98.6% achieved within 7 min. By using the polymer high activity was also observed for butyl maleate. Nevertheless, the vields also decreased with increasing steric hindrances caused by the presence of amines (entries 15-17). For methyl piperazine with lower steric obstacles a high yield of 96.7% was obtained within 11 min (entry 17). With diisopropylamine a yield of 91.2% was observed after 21 min providing additional evidence of the high activity of the polymer (entry 16). Involvement of alkenes also affected the yields (entries 18–21). For acrylonitrile low steric hindrances can be expected and diiso-

Table 1. The aza-Michael addition of various amines with electron deficient alke
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$\frac{R_1}{R_2}NH + / \xrightarrow{EWG} \xrightarrow{cat, R.T.} \frac{R_1}{R_2}N \xrightarrow{EWG}$						
Entry	Amine	Alkene	Reaction time, min	Yield, % ^{a, b}		
1	H	COOCH ₃	5	99.2		
2	H	COOCH ₃	8	98.5		
3	\downarrow_{N}	COOCH ₃	15	95.6		
4	∕NH₂	COOCH3	6	98.5		
5	H ₂ N NH ₂	COOCH ₃	11	98.1		
6	HO NH ₂	COOCH3	13	96.7		
7		COOCH ₃	4	99.4		
8	Ο	COOCH ₃	4	99.3		
9	H	COOC ₂ H ₅	9	98.7		
10	H ₂ N NH ₂	COOC ₂ H ₅	13	97.4		
11	\downarrow_{N}	COOC ₂ H ₅	17	94.8		
12		COOC ₂ H ₅	5	99.2		
13	\downarrow_{N}	H ₃ COOC COOCH ₃	23	93.2		
14		H ₃ COOC COOCH ₃	7	98.6		
15	H N	C4H9OOC COOC4H9	18	95.2		
16	\downarrow_{N}	C4H9OOC COOC4H9	27	91.2		
17		C4H9OOC COOC4H9	11	96.7		
18	H N	CN	4	99.3		
19	\downarrow_{N}	CN	5	99.1		
20	H ₂ N NH ₂	CN	7	98.5		
21		CN	3	99.4		

^a The reaction conditions: amino groups 20 mmol, alkene 24 mmol, catalyst 50 mg, RT (25°C). ^b The yield was calculated on GC using an internal standard.

Table 2. The comparison of different catalysts ^{a, b}

Catalyst	Catalyst amount, mg	Reaction time, min	Yield, %
Polymer	50	27	91.2
IL	100	80	84.3
[SO ₃ H-Bmim][HSO ₄]	120	110	82.3
Amberlyst-15	300	210	70.5

^a The reaction conditions: amino group 20 mmol, alkene 24 mmol, catalyst 50 mg, RT (25°C).

^b The yield was calculated on GC using an internal standard.

propylamine was obtained in 99.1% yield within 5 min (entry 19).

Activity of the Recycled Polymer

In view of the possible use of the polymer as a catalyst it was desirable to explore catalytic activity of the recycled polymer. After reactions, the polymer was recycled by filtration. The mass loss of the polymer was guite low with the recycled yield over 90%. The catalyst loss was caused predominantly by absorption of the filter paper. The polymer loss was taken into account and the amount of reactants was correspondingly reduced to maintain the same reaction conditions. The activity of the recycled polymer was investigated in the reaction between diisopropylamine and dibutyl maleate. The results showed that the polymer activity remained stable with 90.3% yield after six cycles whereas the yield with the fresh catalyst was as high as 91.2%. In addition, it was observed that the yields in the presence of the recycled and fresh catalysts after 10 min reaction time were comparable. After six cycles the polymer gave a yield of 65.3%, while with a fresh polymer 66.3% yield was recorded. These results provide another evidence that the polymer recycled for six times retains considerable portion of activity indicating high stability of the polymer. Hyper-cross-linked polymeric network with IL structure incorporated in the framework provide active sites easily accessible for reactants. The ILs embedded in the polymer preserve at least two chemical bonds, which effectively preclude the loss of active sites. Furthermore, due to a high surface area negligible mass transfer limitations and correspondingly insignificant pore blockage can be expected. It can be thus inferred that after multiple recyclization the active sites in the polymer are still accessible for reactants. The surface area of the polymer after six cycles of operation was found to be 651 m^2/g , fairly similar to that of the fresh catalyst (667 m^2/g). It is therefore evident that the pore structure remains nearly intact and easily accessible active sites are available in the recycled polymer. The FT-IR also showed that the same bands characterize recycled and fresh polymers. All these results confirmed the high stability of the polymer.

Comparative Study of Different Catalysts

The catalytic activities of different catalysts were compared in the reactions between diisopropylamine and dibutyl maleate where the effect of steric hindrance is highly probable (Table 2). The IL from the quaternization of pyridine and benzyl chloride was also used for the reaction. Table 2 indicates that the polymer described in this work was the most efficient catalyst for the reaction. The sample of IL containing the same active sites as the polymer was very active with a yield of 84.3% achieved within 80 min. It appears that the IL readily dissolved in the reaction system favors interactions between reactants. However, the separation of the IL from the reaction system was quite difficult. As to the traditional acidic IL [SO₃H-Bmim] [HSO₄], the catalytic activity was even lower than that of IL. It can be suggested that strong acid sites of IL easily enter the interaction with amines to form ammonium salt. As a result, the acid IL showed lower activity. The acidic resin Amberlyst-15 was also used for the reaction. However, the activity was low due to high steric hindrance caused by the reactants. The resin gave 70.5% yield with an increased catalyst amount and longer reaction time. Such behavior can be accounted for by suggestion that the major part of active sites was inaccessible for the reactants. The reason for inaccessibility of active sites can be sought in a low surface area of the resin. Therefore, a higher catalyst amounts were needed to provide an additional portion of accessible active sites for reactants. The polymer showed a high surface area (667 m^2/g) and hydrophobicity of the surface. A combination of active sites embedded in the framework and a well-developed surface provide high rates of mass transfer. The hydrophobic surface showed high affinity to ractants. The reactants accumulated in the polymer promoted the desired reaction. The active sites show a proper activity for the reaction readily activating alkenes to complete the catalytic cycle. All these factors can be taken into account to explain, why the highest activity was observed with the polymer.

CONCLUSIONS

The novel hyper-cross-linked polymer with the IL structure was synthesized *via* the quaternization and condensation of vinylpyridine and *p*-xylylene dichloride. Since ILs were incorporated into the polymeric framework the pore blockage could be avoided and the active sites were accessible for reactant. The polymer containing 2.87 mmol/g of IL showed a high surface area (667 m²/g). The polymer was very active in aza-Michael additions with the average yields over 95% achieved within several minutes. In terms of activity, the polymer is superior to conventional ILs and has an advantage of simple recovery. High activity, a well developed surface and reasonable stability are the key advantages of the polymer that has the potential replace homogeneous catalysts in green chemical processes.

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