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Poly(ionic liquid) Complex with Spontaneous Micro-/Mesoporosity: Template-Free Synthesis and Application as Catalyst Support

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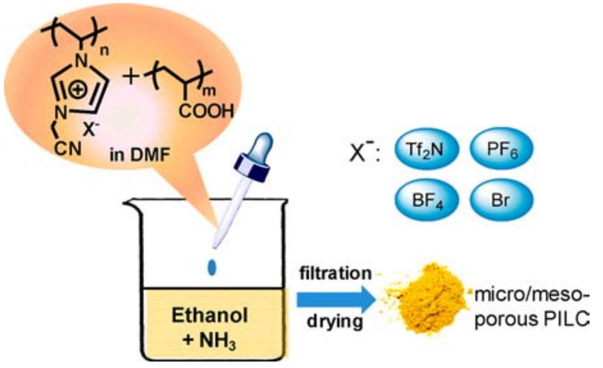
Supporting Information

ABSTRACT: A facile, template-free synthetic route is reported toward poly(ionic liquid) complexes (PILCs) which for the first time exhibit stable micro-/mesoporous structure. This is accomplished via *in situ* ionic complexation between imidazolium-based PILs and poly(acrylic acid) in various alkaline organic solvents. The PILC can be highly loaded with copper salts and can be used as a catalytic support for effective aerobic oxidation of activated hydrocarbons under mild conditions.

Currently, micro- and mesoporous polymers with high specific surface area are receiving rapidly expanding interest, which can be attributed to their importance in both fundamental research and practical applications, such as catalysis, absorption, ion-exchange, separation, and many more.[1−5] Compared to their inorganic counterparts, these polymers are of special interest because of their low bulk density, their extraordinary mechanical properties, and the variability of their monomer building blocks. Additionally, porous polyelectrolytes possess an intrinsically charged character.[6,7] Compared with the simple creation of macropores, preparation of micro- and mesoporous polyelectrolyte materials is far more difficult. A popular yet indirect approach is to chemically modify pre-synthesized nonionic porous polymers, for example the sulfonation of mesoporous poly(divinylbenzene).[8] Another approach is layer-by-layer (LbL) assembly, which has been demonstrated to be capable of creating pores from tens of nanometers (silica template) to several micrometers.[9−12] However, the LbL approach is time-consuming and difficult to scale up, and it involves hazardous chemical etching, let alone the yet unknown specific surface area of the as-prepared materials in these reports. Throughout the polyelectrolyte family, materials of high specific surface area are rarely reported, and their preparation remains a challenge. Apparently an easy-to-make and cost-effective processing approach would be highly welcomed.

Poly(ionic liquid)s (PILs), being a subclass of polyelectrolytes synthesized via polymerization of monomeric ionic liquids (ILs), recently emerged as a new research focus in the polymer and materials communities.[13−29] PILs can alter their physical properties (e.g., glass transition temperature, solubility, etc.) much more broadly than common polyelectrolytes and easily by counterion exchange, an effect well-known to the IL community. PILs offer unique potential as carbon precursors, catalysts, ion conductors, and "smart" stabilizers. In this study, we explore for the first time a new methodology for a template-free preparation of mixed micro- and mesoporous polymeric materials stemming from the complexation of imidazolium-based PILs with poly(acrylic acid) (PAA). We term the resulting structure a poly(ionic liquid) complex (PILC), as it is shown in this contribution that the incorporation of a PIL component into the ionic complexation process brings additional properties and features not available in an ordinary polyelectrolyte complex. Obviously, the large-sized organic cations, with their very high polarizability, create a regiospecific chemical environment that is responsible for unusual physical properties, such as porous structures and metal loading capacity. The synthetic procedure is easy to implement, and the production can be readily scaled up. The high specific surface area up to 330 m^2/g, in combination with a polar surface and shapeable morphology, allowed for some immediate applications; here a PILC is demonstrated as a catalyst support for selective oxidation of sp^3 C−H bonds via copper salts under ambient conditions.

Scheme 1. Synthetic Route to Micro-/Mesoporous PILC Based on PCMVImX PILs and PAA [Tf_2N = Bis(trifluoromethanesulfonyl)imide]



Scheme 1 shows the general pathway toward micro-/mesoporous PILCs, here exemplified with the poly(3-cyanomethyl-1-vinylimidazolium) series (PCMVImX, X = anion) and PAA. PCMVImX PILs with four different counteranions (X = Tf_2N, PF_6, BF_4, or Br) were employed in this study. As an example, PCMVImTf_2N and PAA were dissolved in dimethylformamide (DMF) to form a homogeneous, transparent solution in which only weak complexation occurred, as the majority of the COOH units in PAA chains

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stay in a non-dissociated form. This solution was added dropwise into an excess of ethanol (denoted as complexation solvent) containing 0.5 wt% of NH_3 under ultrasonication. Insoluble PILC aggregates formed immediately (Figure S2). This is because the ammonia turned PAA into a charged state ($PAA^-NH_4^+$) via deprotonation of the COOH groups, initiating the *in situ* ionic complexation between deprotonated PAA and $PCMVImTf_2N$ and producing insoluble PILC materials. The precipitates were collected by centrifugation and dried at 50 °C under high vacuum for 24 h. The FTIR spectrum of the formed $PCMVImTf_2N$−PAA PILC (Figure S3a) confirms that the absorption band at 1700 cm^{-1}, attributed to the C═O bond in the COOH group, shifts to 1550 cm^{-1} due to the ionization of COOH to COO^- groups. X-ray diffraction measurements support that PILC is non-crystalline (Figure S3b).

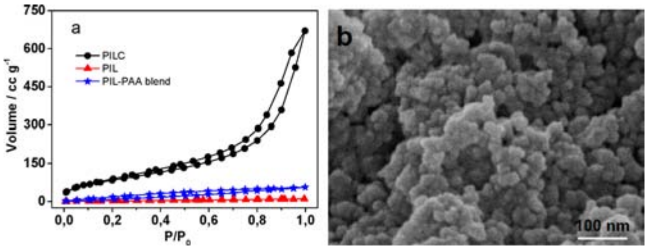


Figure 1. (a) Nitrogen sorption isotherms of $PCMVImTf_2N$, its physical blend with PAA, and the $PCMVImTf_2N$-PAA PILC. (b) SEM image of $PCMVImTf_2N$-PAA PILC (no. 2 in Table 1).

Table 1. Specific Surface Area and Pore Volume of PCMVIm-PAA PILCs Prepared under Various Conditions[a]

PILC	PAA/ PIL[b]	PIL conc (wt%)[c]	solvent[d]	S_{BET} (m^2/g)	pore volume (cm^3/g)
no. 1	0.7	10	EtOH	141	0.26
no. 2	1.0	10	EtOH	310	0.98
no. 3	1.7	10	EtOH	203	1.09
no. 4	3.0	10	EtOH	56	0.29
no. 5	1.0	3	EtOH	143	0.17
no. 6	1.0	5	EtOH	187	0.28
no. 7	1.0	20	EtOH	230	0.68
no. 8	1.0	10	IP[e]	330	1.10
no. 9	1.0	10	acetone	317	1.02
no. 10	1.0	10	butanol	205	0.42
no. 11	1.0	10	THF	109	0.74
no. 12	1.0	10	MeCN[e]	39	0.18
no. 13	1.0	10	EG[e]	6	0.07
no. 14	1.0	10	methanol	11	0.01
no. 15	1.0	10	water	28	0.06

[a] Calculated from nitrogen sorption isothermals. [b] Monomer mole ratio of PAA to PIL in DMF solution. [c] PIL weight concentration in its DMF solution. [d] These organic solvents all contain 0.5 wt% of NH_3. [e] IP, isopropanol; MeCN, acetonitrile; EG, ethylene glycol.

The porous structure of PILC was examined by nitrogen sorption measurements (Figure 1a), which indicated the presence of mesopores as well as a small fraction of micropores. The specific Brunauer−Emmett−Teller (BET) surface area and the pore volume were calculated to be 310 m^2/g and 0.98 cm^3/g, respectively, which stem from the co-existence of micropores and mesopores of random, but supramolecular sizes. Additionally, porous structures of the same PILC are stable when refluxed in ethanol as well as several other organic solvents (80 °C) for 24 h (Figure S3c). One might even speculate that the pore structure is an equilibrium property of this special PILC, allowing optimized charge neutralization of the backbone only in a porous state. On the contrary, neither the pristine $PCMVImTf_2N$ nor its physical blends with PAA are porous (Figure 1a). This result indicates that the ionic complexation between $PCMVImTf_2N$ and PAA plays an important role in the pore formation. An absence or rather low degree of ionic complexation evidently gives nonporous or less porous systems (Table S2). Scanning electron microscopy (SEM) characterization (Figure 1b) reveals the distinctive morphology of the micro-/mesoporous PILC. Particles of 30−50 nm in size were clearly observed as a secondary structure motif. These nanoparticles are believed to be the PILC aggregates built up from mixed PCMVImX and PAA chains via electrostatic interaction, and of course they must be porous in themselves. Nevertheless, the particle superstructure provides a channel system which makes the smaller pores nicely accessible from the outside. Notably, such particles are found neither in the pristine $PCMVImTf_2N$ nor in its physical blend with PAA (Figure S4).

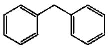
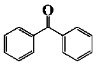
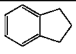
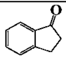
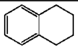
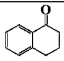
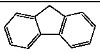
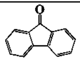
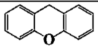
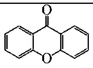
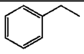
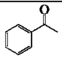
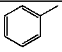
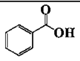
We further studied the effects of various preparation conditions on PILCs' porous structures (Tables 1 and S2). It was found that the ratio of two charged species, the polymer concentration in DMF, and the types of complexation solvents (Table 1) play dominating roles for PILCs' porous structures, while the adding kinetics, the counteranions, and the PAA molecular weight (Table S2) have lesser effects. The optimum specific surface area and pore volume were obtained when the monomer mole ratio of PAA to $PCMVImTf_2N$ was 1:1 at an optimized weight concentration of 10% for $PCMVImTf_2N$ (Table 1, nos. 1−7). This is understandable because, at an equivalent feed ratio, a stoichiometric complexation between $PCMVImTf_2N$ and PAA was found (elemental analysis in Table S1), forming a rigid and fixed solid polyelectrolyte network with minimized chain mobility, which is necessarily required to stabilize the generated micro-/mesopores and to keep them open throughout the drying process.

It should be mentioned that there are many other reports on polyelectrolyte complex systems, but none of them revealed detectable micro-/mesoporosity and large surface area. Most of these systems were prepared by solution mixing or LbL methods under aqueous conditions. Only a few were prepared in organic solvents by adding one polyelectrolyte solution into another.[30−32] For further analysis, $PCMVImTf_2N$−PAA PILCs were also prepared from various complexation solvents (Table 1, nos. 8−15). As observed, PILCs prepared in acetonitrile, ethylene glycol, methanol, and water are apparently nonporous, while those prepared in isopropanol, acetone, butanol, ethanol, and THF are micro-/mesoporous, with the specific surface area ranging from 109 to 330 m^2/g. We noticed that the latter set are poor solvents for both $PCMVImTf_2N$ and PAA, while either PAA or $PCMVImTf_2N$ is soluble in acetonitrile, methanol, ethylene glycol, and water. Furthermore, a unique feature of the PILC system is that $PCMVImTf_2N$ and PAA have already reached a molecular-level mixing state in DMF prior to the ionic complexation. This feature is essential because it facilitates a rapid and complete interchain ionic cross-linking, fixing their nonequilibrium ("frozen") chain conformation *in situ*. It is commonly accepted that the ionic complexation is a kinetically controlled process that produces nonequilibrium structures.[33] This can be also true with our system, especially considering that changing the counterion does not affect the porous PILC system much (Table S2). The correlation between PILCs' porous structures and the solubility of PILs and PAA is valid for several other tested PILs with varied cationic structures (Table S3). Hence, carrying out the ionic complexation between PCMVImX PILs and PAA in their poor solvents rather than good ones is a prerequisite to develop the beneficial micro-/mesoporous structures and surface area.

It is well-known that polyelectrolytes (and even more polymerized ionic liquids) and their zwitterionic complexes can bind and immobilize metal ions, salts, and nanoparticles.[34,35] Combining this feature with the high surface area of our system, these PILCs can be readily used for separation, storage, catalysis, and more. Here as an example, PILCs were applied as a heterogeneous catalyst support for copper compounds for the aerobic selective oxidation of C−H bonds. Traditionally, these processes use metal salts and generate an abundance of noxious, undesired byproducts, which show low selectivity due to the uncontrolled over-oxidation while working under harsh conditions.[36] Aiming at development of active and novel heterogeneous catalysts for such processes, we synthesized the copper-based catalyst using PILC as a support (Cu@PILC) by refluxing micro-/mesoporous PILC with $CuCl_2$ in ethanol overnight. The as-synthesized Cu@PILC catalysts maintained the micro-/mesoporous nature with a reasonable specific surface area of 220 m^2/g (note that massive loading of catalyst always reduces pore volume and surface area). Energy-dispersive X-ray spectroscopy and inductively coupled plasma results show that Cu@PILC contains 12.4 wt% of copper and 13.9 wt% of chlorine, which gives a Cu/Cl atomic ratio of 1:2, in agreement with a $CuCl_2$ structure. The high copper content and the full chlorine preservation in the sample indicate that the binding mechanism is very possibly the multipole-induced ion pair adsorption of $CuCl_2$ onto the local imidazolium-based zwitterions in the PILC matrix rather than the common surface ion exchange. Such a special dipole-binding mode renders a high catalytic activity.[37] The significantly amplified uptake of the copper salt by the imidazolium cation was reported earlier[38,39] (in those systems by a factor of 60 as compared to the polycarboxylates) and is a particular advantage of the imidazolium-based PILCs.

Catalytic tests were performed for the oxidation of various hydrocarbons under mild conditions (50 °C), using Cu@PILC and *N*-hydroxyphthalimide (NHPI) as a combined oxygen-transfer system.[36,40−46] Air, which is the most ubiquitous and available but difficult to activate oxidizing agent, was introduced as the final oxidant. Cu@PILC catalysts afforded an excellent dispersion in the reaction system due to their polar and small polymer nanostructures. Assisted by NHPI, Cu@PILC successfully catalyzed the oxidation of diphenylmethane with 91% conversion and 96% selectivity to diphenyl ketone in 10 h, while NHPI, PILC, or Cu@PILC alone was inefficient for the same reaction (Table 2, entries 2−4). These results illustrate that Cu@PILC and NHPI couple as an efficient catalyst system. The Cu@PILC can be easily recovered by centrifuge and reused for several cycles without losing its activity, which is a prerequisite for practical applications (Table 2, entries 5−8). SEM characterization confirms that morphologies of Cu@PILC were maintained after the catalysis and recycling (Figure S6). To further probe the potential of this new catalyst, a number of aromatic hydrocarbons with methylene such as indane, xanthene, tetralin, fluorene, and ethylbenzene were subjected to the same processes. All the oxidation reactions gave satisfactory conversion and high selectivity for the corresponding ketones (Table 2, entries 9−13). Selective oxidation of the less activated toluene to benzoic acid was also achieved by this system, yet with a moderate conversion (Table 2, entry 14). In general, by coupling with NHPI, the Cu@PILC is highly active and selective, and widely applicable to various C−H bond oxidations. Moreover, the PILCs are resistant to many organic solvents due to the strong internal electrostatic interactions,[33] which is another merit of the specific catalyst system.

Table 2. Aerobic Oxidation of Organic Compounds by NHPI/Cu@PILC Catalyst System[a]

Entry	Substrate	Product	Time/h	Conv.	Sel.
1			10	91%	96%
2[b]			10	14%	97%
3[c]			10	10%	96%
4[d]			10	2%	99%
5			10	80%	95%
6			10	84%	97%
7			10	85%	94%
8			10	82%	96%
9			10	83%	95%
10			14	90%	97%
11			12	98%	97%
12			10	98%	99%
13			14	87%	96%
14			16	48%	96%

[a] Reaction conditions: substrate (5 mmol), NHPI (10 mol%), Cu@PILC (50 mg), CH_3CN (8 mL), air 1 atm, 50 °C. [b] Without Cu@PILC. [c] Without Cu. [d] Without NHPI.

In conclusion, we demonstrate a unique, template-free method to prepare micro-/mesoporous polymer materials via *in situ* ionic complexation of PILs, PCMVImX, with PAA in alkaline conditions in various organic solvents. High specific surface area and large pore volume were found to form spontaneously and stay stable under a variety of conditions. The synthetic procedure can easily be scaled up and is presumably also good for membrane formation. These PILCs, after loading copper salts in an unconventional ion pair binding mode, remained micro-/mesoporous and were used as an effective heterogeneous catalysts for the aerobic oxidation of hydrocarbons under mild conditions. The method developed in the current study provides a facile and distinctive pathway to prepare polyelectrolyte complex materials with inherent micro- and mesoporsity and the interfacial activities of ionic liquids,[47−49] which will propel their applications in catalysis, absorption, nanoparticle growth, and more.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Materials, preparation and characterization of PILCs and Cu@PILC catalyst, and aerobic catalysis reaction. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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