Synthesis of porous polymer based on acrylonitrile and 1-allyl-3-methylimidazolium by seed swelling polymerisation

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Porous polymer based on copolymer of acrylonitrile and the ionic liquid 1-allyl-3-methylimidazolium can be prepared by free radical polymerisation and then turned into porous particle by a two-step swelling method. The CO_2 absorption of the product was investigated.

Keywords: acrylonitrile, 1-allyl-3-methylimidazolium, porous polymer, ionic liquids, two-step swelling

Ionic liquids, organic salts that are liquids at low temperatures, have been explored as nonvolatile and reversible CO_2 absorbents because of their high CO_2 solubility.[1–3] Recently, polymers from ionic liquids have been reported to have even higher CO_2 sorption capacity than room temperature ionic liquids with faster sorption/desorption rates.[4,5] Most significantly, their sorption and desorption are very fast, and the desorption by vacuuming is completely reversible. These characteristics make the polymers exceptionally promising as solid absorbent and membrane materials for CO_2 separation. The CO_2 sorption capacities depends on the chemical structure and the surface area of the polymers.[6] This indicates that polymers from ionic liquids adsorption materials with well-developed porous structure have good adsorption performance. To the best of our knowledge, this is first synthesis of porous polymers from ionic liquids by seed swelling polymerisation. The seed swelling polymerisation technique is an effective method to prepare mono-dispersed microspheres with large diameters developed in recent years.[7] Moreover, a two-step swelling method can be more effective, in a first step, relatively small monodisperse polymer particles are swollen with a component and then with monomer or monomer mixtures, followed by polymerisation.[8]

We now report the detailed syntheses of polymer from ionic liquids with a porous structure. First, 1-allyl-3-methylimidazolium tetrafluoroborate ([amim]BF_4) was synthesised as a monomer (Scheme 1).[9] The copolymer was prepared from ionic liquid monomer by free radical polymerisation (Scheme 2).[10] Then the porous polymers were prepared from ionic liquids by the seed swelling method, using the copolymer as seed.

Experimental

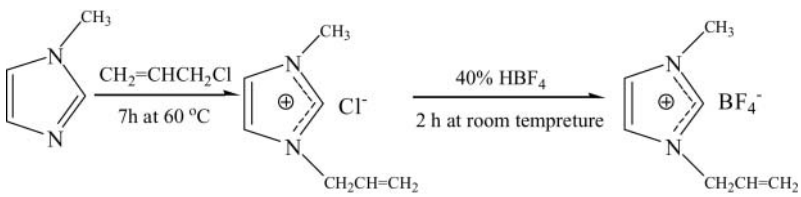
The IR spectra were obtained by using a Thermo Scientific Nicolet 380 IR spectrometer. The morphologies were examined on S-30000N scanning electron microscope. The adsorptive capacity of CO_2 was obtained on Quantachrome Autosorb-1-MP.

Acrylonitrile (AN) was distilled and the 767–77 °C fraction was collected for the experiment. Dimethyl sulfoxide (DMSO) was dried through CaO and then purified by vacuum distillation. 2,2′-Azobis(isobutyronitrile) (AIBN) was recrystallised in acetone. All other chemicals used were of analytical reagent grade.

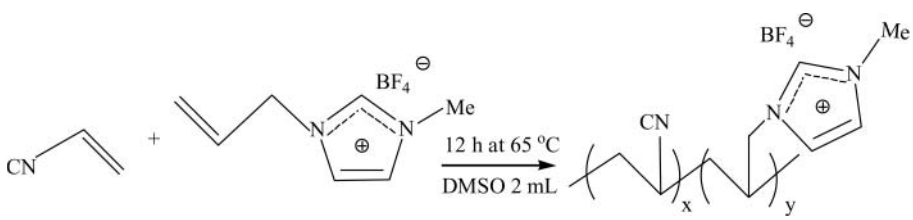
1-Allyl-3-methylimidazolium tetrafluoroborate ([amim]BF_4) as a monomer was prepared according to described procedures,[9] and the copolymer of acrylonitrile and [amim]BF_4 was prepared by free radical polymerisation.[10]

Preparation of porous particle by seed swelling method

The copolymerisation seed particles (0.4 g) were emulsified in the aqueous medium (25 mL) including 0.25% (w/w) sodium dodecyl sulfate (SDS) as the emulsifier. For emulsification, the mixture was sonicated for 15 min in an ultrasonic water bath at the room. Dibutyl phthalate (DBP) (1.4 mL, 5.26 mmol) as swelling agent was added into the SDS emulsion. The resulting dispersion was stirred at room temperature (25 °C) for 24 h for the absorption of DBP by the copolymerisation seed particles. Then heptane (10 mL, 0.069 mol) as pore-forming agent was added at room temperature while stirring for 24 h. In the next step, a monomer phase comprised of [amim]BF_4 (4.53 g, 0.021 mol) and benzoyl peroxide (BPO) (0.1 g, 0.41 mmol) was then mixed with the aqueous dispersion of DBP swollen-seed particles. The obtained emulsion was stirred at the room temperature for 24 h for the absorption of monomer phase by the DBP swollen copolymerisation seed particles. At the end of this period, an aqueous solution (22 mL/1.05 g) containing 5.0% (wt.) polyvinyl alcohol (PVA) as the stabiliser was added into the resulting emulsion. The polymerisation of monomer phase in the swollen seed particles was performed



Scheme 1 Synthesis of ionic liquid monomer.



Scheme 2 Copolymerisation of AN with [amim]Cl.

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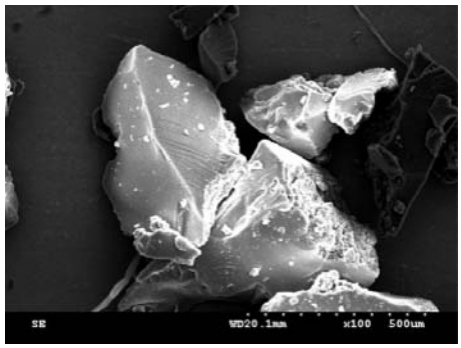

Fig. 1 SEM of copolymerisation (×100).

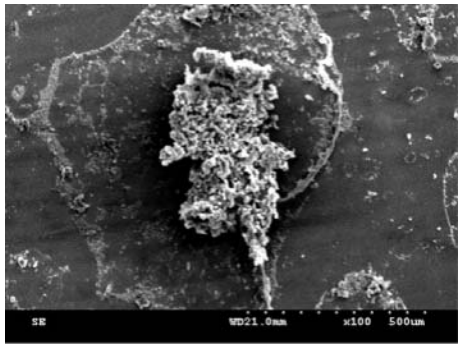

Fig. 2 SEM of porous micro-spheres particle (×100).

at 70 °C for stirring 10 h. The low-sized particles formed in the repolymerisation as a by-product were removed by applying a centrifugation-decantation procedure. The precipitated white powder was washed with deionised water and methanol extensively. Finally, the particles were dried under vacuum at room temperature (0.31 g, 77.5%).

CO_2 capture of porous polymer from ionic liquids

The fine powder of the porous particles was dried and degassed at 100 °C under vacuum for 3 h to remove moisture or other volatile contaminants. Then the adsorption capacity of CO_2 on porous polymer particles was measured.

From Figs 1 and 2, we can see clearly that copolymerisation particles were the nonporous structure. While particles treated by seed swelling method were the porous structure. Besides, CO_2-adsorption experiment showed that, when 1.0 g of the sample was exposed to dry CO_2 at 0 °C and 1 atm, a mass gain was 3.18 mg (0.318 wt %) for copolymer, 8.40 mg (0.84 wt %) for porous particle. The CO_2 solubility in porous particle is found to be higher than that in copolymer at the same temperature and pressure.

The authors would like to thank the National Natural Science Foundation of China (Grant No. 20807056), the Foundation of Key Laboratory of Coal Processing and Efficient Utilization of Ministry of Education (Grant No. CPEUKF08-09) and Young Scholars of China University of Mining And Technology (Grant No.OH060102 and No.OH080254) for financial support.

Received 29 December2009; accepted 9 February 2010
Paper 100936 doi: 10.3184/030823410X12659622957537
Published online: 24 March 2010

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