

Porous Porphyrin-containing Polymer Nanoparticles for Gas Separation Applications

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Nanoporous organic polymer materials have gained significant attention lately for applications in gas storage and separation technologies. [1, 2] Among them aromatic polymers containing porphyrin or styrene moieties have been shown to exhibit significantly high surface area and good selectivity for CO₂. [3, 4] In this work, porous polymer nanoparticles were synthesized by free radical emulsion copolymerization of a mixture of styrene (S), tetra-vinyl functionalized 5,10,15,20-Tetrakis (4-hydroxyphenyl)-21H,23H-porphyrin (PO) and divinylbenzene (D) [Figure 1a]. The cross-link density of the polymer particles was varied by increasing progressively the PO content from 1.5 to 5 % with respect to D at a constant S/cross-linker (PO and D) mole ratio of 2:3. The morphology and size of the obtained nanoparticles were characterized by scanning electron microscopy, transmission electron microscopy and dynamic light scattering measurements. After synthesis, the particles were extensively purified by dialysis against water. The samples were then exchanged to ethanol or dimethylformamide and the solvent remaining in the pores was effectively removed by supercritical drying with CO₂ in order to obtain open-pore polymer structures (PO-S-D). The permanent porosity of the PO-S-D materials was confirmed by nitrogen and carbon dioxide adsorption experiments [Figure 1b]. Analysis of the adsorption data using the ideal adsorption solution theory reveals that the PO-S-D sample containing 5% PO has a CO₂/CH₄ separation factor of ~23 and ~12 at -10°C and 0°C, respectively, in the low pressure limit.

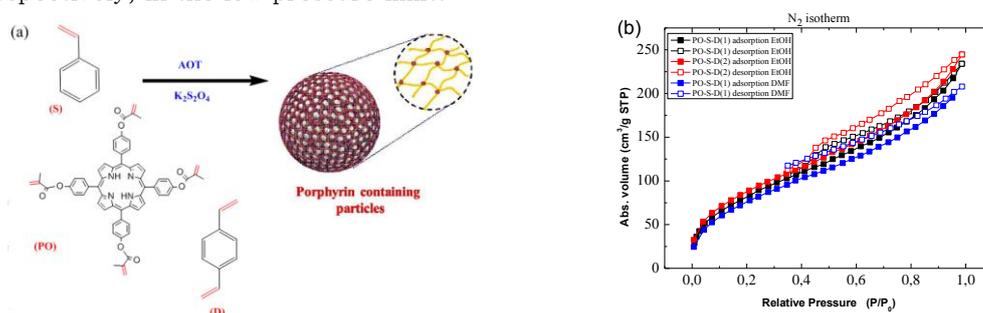


Figure 1: (a) Synthetic process followed for the preparation of the porous porphyrin-containing polymer particles; (b) Nitrogen adsorption and desorption isotherms at -197°C for the solvent-free PO-S-D (1) [1.5 % PO] and PO-S-D (2) [5 % PO] samples treated in ethanol and dimethylformamide.

References

- [1] S. Xu, Y. Luo, B. Tan, *Macromol. Rapid Commun.* **34**, 471–484 (2013).
- [2] M. S. Silverstein, *Polymer* **55**, 304–320 (2014).
- [3] A. Modak, M. Nandi, J. Mondal, A. Bhaumik, *Chem. Commun.* **48**, 248–250 (2012).
- [4] M. Kaliva, G. S. Armatas, M. Vamvakaki, *Langmuir* **28**, 2690–2695 (2012).

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