Polymers with Intrinsic Porosities: Synthesis, Structure, Properties and Applications

Swaminathan Sivaram [1,2], Chilukuri.V. Avadhani [2], Vikas Kumar[2] and Shyambo Chatterjee[2],

([1] Indian Institute of Science Education and Research, Dr. Homi Bhabha Road, Pune, 411008, India

[2]CSIR-National Chemical Laboratory, Dr. Homi Bhabha Road, Pune, 411008, India)

[1]Tel: +91-20-25908434, E-mail: s.sivaram@iiserpune.ac.in

Introduction

Porous polymers are materials containing one or more types of pores, generally classified as microporous (having pores less than 2 nm), mesoporous (having pores between 2 to 50 nm) and microporous (pores greater than > 50 nm) [1]. Pore geometry, pore size, pore surface and the polymer framework structure including composition and topology are important features that determine the property and applications of porous polymers. Porous polymers have attracted significant attention in recent years owing to their potential for applications in areas such as gas adsorption and storage, gas separations, nanofiltration membrane, fuel-cell membranes, battery separators, adsorbents and catalysis. Porosity in polymers can be built either at the time of its synthesis or using a variety of post polymerization methods. Several methods are available for the preparation of porous polymers, namely, "bottoms-up" approach using appropriately designed monomers, Interfacial or solution polymerization followed by phase inversion, high internal phase emulsion polymerization and use of hard (e.g., Nano silica) or soft (porogen) templates with preformed polymers. In our laboratory we have used several of these methods to prepare a diverse class of useful porous polymers (acrylics, poly(acrylonitrile), polybenzimidazoles)

Polymers with Intrinsic Porosities

Polymers with intrinsic micro porosity (PIM's) are a special class of porous polymers which are synthesized using a "bottoms-up" approach [2]. Intrinsic micro porosity in polymers is defined as "a continuous network of interconnected intermolecular voids, which form as a direct consequence of the shape and rigidity of the component macromolecules" [3]. PIM's are amorphous materials having large and accessible surface area. PIM's are synthesized using monomers having rigid and contorted structures which restrict the degrees of conformational freedom available to the polymer chain. This limits their ability to pack efficiently resulting in high fractional free volume. The balance between intra-chain rigidity and inter-chain spacing creates interconnected porous structures. Polymers with intrinsic porosities (prepared either from specially designed monomers are from a "thermal rearrangement" processes) have attracted wide attention in the literature as membranes for gas separations and organic solvent nanofiltration [4].

Synthesis of polybenzimidazoles with Intrinsic Porosities

We have recently reported the synthesis of a family of co-polybenzimidazoles with intrinsic meso-porosities (Figure 1) These family of copolymers are amorphous in nature possess high T_g and exhibit meso-porosities [5].

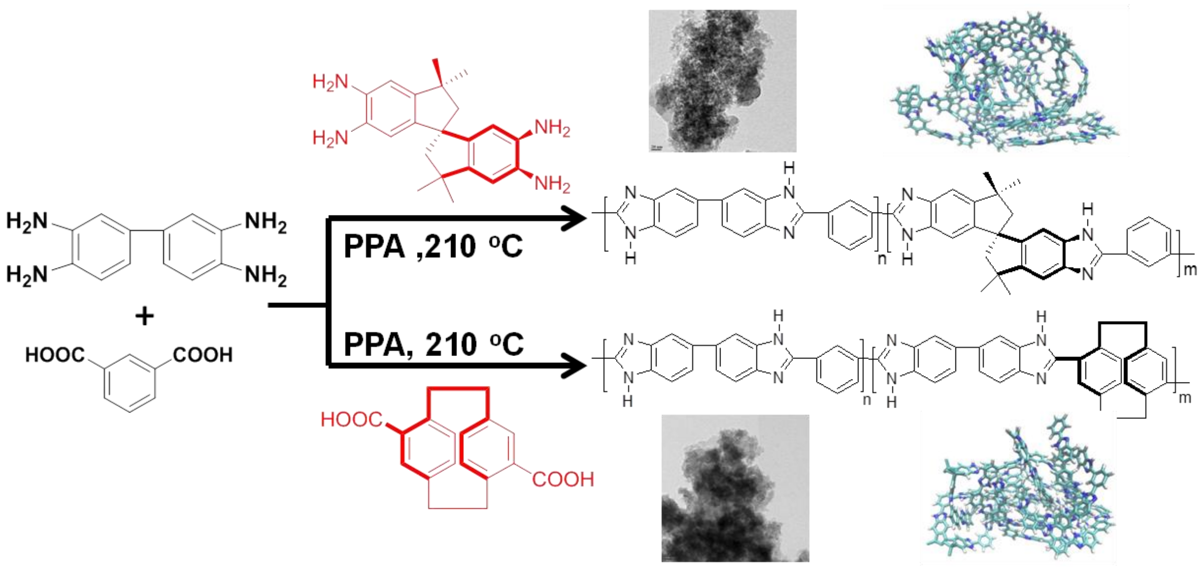

Figure 1: Co - polybenzimidazoles with intrinsic porosities

We have also prepared macroporous polybenzimidazole membranes using a combination of nano-silica or nano-calcium carbonate as a template and phase inversion. The nature of porosities obtained is shown in Figure 2. Using a template along with phase inversion affords a membrane with larger pores.

<u>Application of Porous Polymers as Membranes for Separators in Lithium-ion Batteries</u>

Functional polymers play a key role as advanced materials in many renewable energy applications, for both, generation and storage. Examples are selective proton conducting polymers as membrane electrode assembly for use in fuel cells, selective lithium ion transporting separator membranes and as anodes and cathodes in Li-ion batteries. Separator membrane is a critical component of a battery. It provides a barrier between the anode and the cathode while enabling the exchange of ionic charge carriers from one side to the other. Separators currently used in Li-ion batteries are made of polyolefins, either polyethylene or polypropylene. They are rendered porous by a mechanical biaxial extrusion process. As the battery heats up, the protective layer on the anode breaks down, followed by breakdown of electrolytes into flammable gases. This, in turn, causes the polyolefin separators to undergo catastrophic shrinkages above 120° C leading to shorting of cells causing sparks that ignite the electrolyte resulting in a fire. The inherent safety risks threaten the continued advances of Li-ion battery into applications requiring higher and higher energy density, such as, in smart phones and electric vehicles.

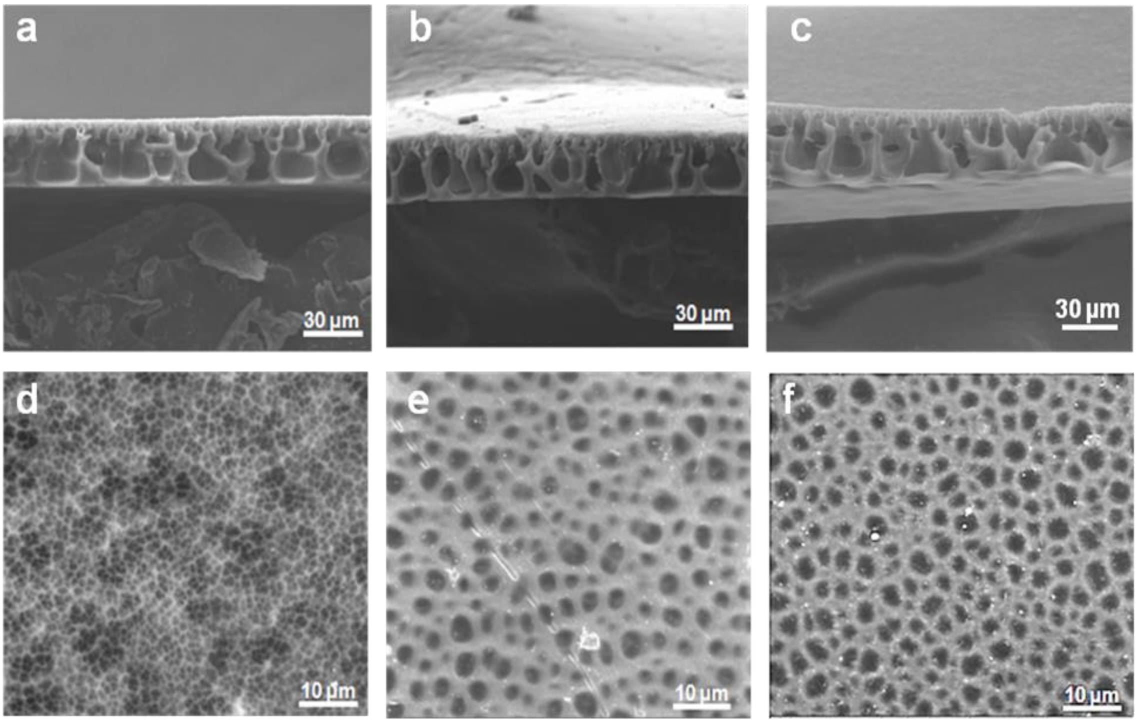

Figure 2: Cross-section (a: Phase Inversion, b: Phase Inversion + Nanosilica, c: Phase Inversion + Nano Calcium Carbonate) and Surface SEM Images (d: Phase Inversion, e: Phase Inversion + Nanosilica, f: Phase Inversion + Nano Calcium Carbonate) of Porous Polybenzimidazole

Porous polybenzimidazoles show useful properties as safe and non-flammable separators for lithium-ion battery applications [6]. The influence of porosity on electrical conductivity and kinetics of lithium ion transport was studied. More detailed understanding of diffusion mechanism of lithium ion across such porous membranes has been derived using Li^{7} NMR and measurement of relaxation time.

References

1) Qiu, S., Ben, T., *Porous Polymers: Design, Synthesis and Applications, Monographs in Supramolecular Chemistry No. 17, The Royal Society of Chemistry, London, UK, 2016;* Wu, D.; Xu, F.; Sun, B.; Fu, R.; He, H.; Matyjaszewski, K. *Chemical Reviews* 2012, *112*, 3959-4015.

2) McKeown, N. B.; Budd, P. M. *Chem. Soc. Rev.* **2006**, *35*, 675-683; Chaoui, N.; Trunk, M.; Dawson, R; Schmidt, J.; Thomas, A. *Chem. Soc. Rev*. **2017**, *46*, 3302-3321.

3) McKeown, N. B.; Budd, P. M. *Macromolecules* **2010**, *43*, 5163-5176.

4) Marchetti, P.; Jimenez Solomon, M.F.; Szekely, G.; Livingston, A.G. *Chem.Rev*.**2014,** 114,10735-10806.

5) Vikas Kumar, Chatterjee, S.; Sharma P.; Chakrabarty, S.; Avadhani, C.V.; Sivaram, S. *J. Polymer. Sci. Polymer Chemistry,***2018,** DOI: 10.1002/pola.28979.

6) Vikas Kumar, Avadhani, C.V.; Sivaram, S. *PCT International Application No. 201711007734,* dated 6 March 2017.