

Polymerizable Porogens – Direct generation of internally functionalized pores

S. Ramakrishnan

Department of Inorganic and Physical Chemistry, Indian Institute of Science
Bangalore 560012 INDIA
*E-mail: raman@iisc.ac.in

ABSTRACT: Porous polymers have been extensively studied for the past half a century; these have been primarily used as separation media, as adsorbents, and, more recently, designer porous polymers have been tailored for more specific purposes, such as analyte detection, catalysis, stimuli-responsive gates, etc. The control of pore size, shape and their inter-connectivity are key parameters that govern the performance of the porous polymeric materials; these are controlled using porogens, which are often small molecules (or polymers) that serve as place-occupants during the polymerization. Two important approaches have been developed to create porous polymers – one is polymerization-induced phase separation (PIPS) and the other is polymerization-induced microphase separation (PIMS). Whereas in the former the porogen is not linked to the polymer matrix, in the latter the porogen becomes covalently attached to the matrix via RAFT-based chain transfer, and thus the size of pores becomes regulated by the porogen molecular weight; the degradative removal of the porogen leaves behind the porous matrix, which under appropriate conditions generates a continuously linked porous structure, a key feature for improved access to pores and high flux.

To create an alternate single step process to porous crosslinked polymers

wherein the internal walls of the pores are lined with desired functional groups, we embarked on the idea of developing polymerizable porogens, wherein the covalent bond between the polymerizable unit and the porogen is thermally labile; and thus, the porogen can be cleaved from the crosslinked matrix by a simple thermal treatment. By proper design of the thermally cleavable linkage, the desired functional group can be installed on the internal walls. I shall first describe some of the basic ideas associated with the formation of porous polymeric matrices using PIPS and PIMS methods. I shall then contrast our approach that uses a novel polymerizable porogens that also undergoes polymerization-induced microphase separation (PIMS), however with some differences. The thermally labile linkage that we first examined is the carbamate linkage, which under hydrothermal treatment cleaves-and-reacts to leave behind amine functionalities on the internal surface of the pores. Excellent control over the pore-size and surface area is demonstrated by regulating the polymerization-crosslinking process. The effect of various parameters, such as porogen size, polymerization-crosslinking rate, volume-fraction of the porogen and added non-polymerizable porogen, on the structure of the porous polymer will be discussed.

References

1. Rounak Jana and S. Ramakrishnan "Direct Generation of Internally Functionalized Nanoporous Polymers: Design of Polymerizable Porogens" *Macromolecules* **2021**, 54, 9692–9702.