Monolithic format of porous materials: A polymer chemist's view

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The current monolithic materials were developed more than 30 years ago as a result of the search for bulk polymers that had a highly crosslinked porous polymer matrix with large pores and could be ideal for high-speed flow-through applications. We expected that convection through the pores of the monolith could enhance the mass transport of even large molecules and significantly accelerate processes such as chromatographic separations and catalyzed reactions. Unlike porous polymers produced as beads via suspension polymerization, bulk polymerization has never been studied before. Therefore, we had to carry out numerous experiments to explain the differences between suspension and bulk polymerization, to provide means to closely control the porous properties and morphology and offer methods for the preparation of monoliths with desired chemistries. Since then, we have developed fundamentals describing the mechanism of pore formation and chemistry control. We have also introduced several polymer chemistry-based approaches in the monolithic field such as hypercrosslinking, which resulted in monoliths with a very high surface area, or UV-initiated photografting of functional monomers, which facilitated the preparation of products with pore surface chemistries required for the intended application. Meanwhile, the number of polymerization approaches used worldwide to prepare monoliths has grown significantly. New functionalization methods have also been developed such as the attachment of metal-organic frameworks and nanoparticles to the pore surface. The latter, for example, expands the applications of monoliths in the field of highly selective chromatographic and capture systems, allows reversible functionalization, and provides support for highly efficient enzyme immobilization.