Synthesis of 2D crosslinked polymers using MOF templates

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Two-dimensional (2D) network polymers, characterized by their unique topology, are expected to exhibit distinct properties compared to conventional linear polymers. These materials hold promise for applications such as gas separation membranes, anisotropic thermal conductive materials, and coating materials.[1] However, the synthetic methods for polymers with 2D structures are not yet well-established. To date, various approaches such as topochemical polymerization, interfacial synthesis, and synthesis using the interlayer spaces of inorganic layered compounds have been reported.[2] Despite these efforts, a versatile and scalable synthesis method for 2D polymers remains elusive.

In our research, we utilize metal–organic frameworks (MOFs) as templates for polymerization reactions. MOFs are porous materials whose pore sizes and channel dimensions can be precisely designed by the combination of metal ions and organic ligands. Among the diverse types of MOFs, we identified that pillared-layer MOFs with 2D nanopores (thickness 0.7 ~ 1.2 nm) are particularly suitable as templates to synthesize 2D polymers.[3] By polymerizing various monomers and crosslinkers within these MOFs, we successfully synthesized unimolecularly thick 2D network polymers in a simple and scalable manner. The resulting 2D network polymers exhibit unique thermal and mechanical properties distinct from conventional linear polymers, attributed to their 2D molecular structure. Furthermore, our method is applicable to a wide range of vinyl monomers such as styrene,[3] methyl methacrylate,[3,4] acrylonitrile,[5] *N*-isopropylacrylamide, and their copolymers (**Figure**).[6] We discuss the advancements in synthetic methodology and the common chemical and physical properties of the synthesized 2D network polymers.

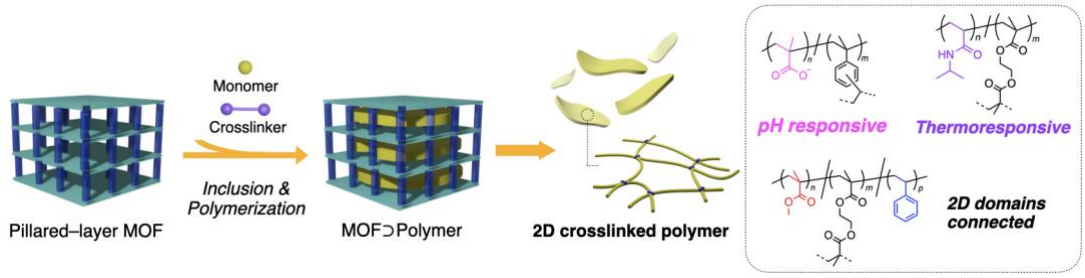

Figure. Schematic illustration of the synthesis of 2D polymer networks.

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