

Synthesis of double-stranded polymers via controlled crosslinking reaction in coordination nanospaces

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Double-stranded polymers, including DNA, RNA, and polysaccharides, are commonly found and play a vital role in biosystems. Inspired by their elegant structures and functions, several approaches for the preparation of synthetic polymer duplexes have been developed. However, the previous strategies usually require elaborated monomer designs to achieve selective crosslinking between two polymer chains. Herein, we report a versatile methodology to synthesize double-stranded polymers even from common vinyl monomers.^[1] Crosslinking polymerization was conducted within metal–organic frameworks (MOFs), in which the diameter of nanopores was comparable to the two vinyl polymer chains (**Figure 1**). The effective spatial constraint inhibits the unfavorable random crosslinks among multiple polymers, fabricating polymer duplexes.

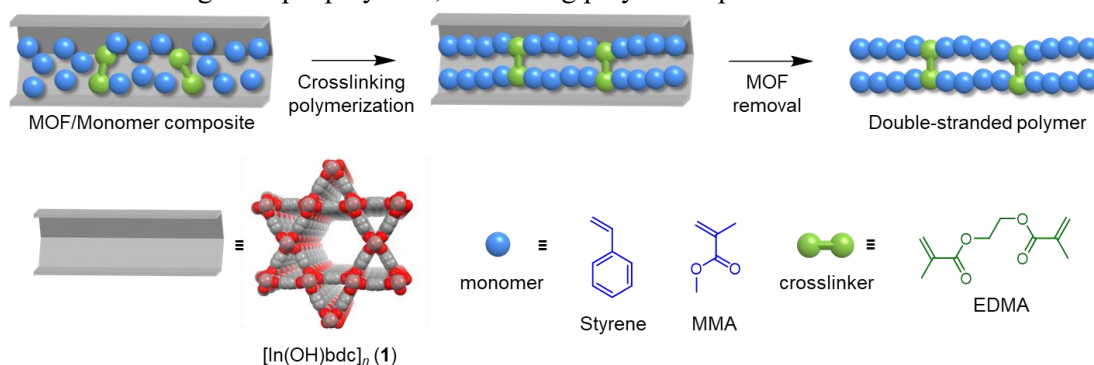


Figure 1. Scheme image for the preparation of double-stranded polymers in nanochannels of **1**.

[In(OH)(bdc)]_n (MIL-68^[2], bdc = 1,4-benzenedicarboxylate, **1**) was employed as a host framework possessing suitable one-dimensional pores to demonstrate our strategy. Vinyl monomers, such as styrene and methyl methacrylate, were encapsulated in **1** with a crosslinker and initiator. The crosslinking radical polymerization within the nanochannel was performed by heating the composite at 120 °C for 24 hours. Soluble crosslinked polymers were obtained after the decomposition of **1** by chelating agents. The double-stranded topology endows the polymers with atypical properties, such as lower intrinsic viscosity and higher glass transition temperature compared to their single-stranded counterparts.

[1] M. Abe, Y. Kametani, T. Uemura, *J. Am. Chem. Soc.* *accepted*. [2] M. Latroche, *et al.*, *Inorg. Chem.* **2008**, 47, 11892–11901.