Functional group effect on the conformation and rheology properties of novel star-shaped polymer based on metal-organic polyhedra.

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Star polymers are macromolecular structures characterized by multiple linear polymer chains radiating from a central core, forming a star-like architecture. Due to their reduced viscosity and enhanced solubility, star polymers are suitable for applications such as drug delivery, where they can effectively encapsulate active pharmaceutical agents. However, controlling the viscosity of star polymers without changing the polymer chain structure remains a significant challenge.

Here, we demonstrate a strategy to modulate the viscosity of a star-shaped polymer by incorporating various metal-organic polyhedra (MOPs) as the central core while maintaining the polymer chains. MOPs are cage-like supramolecules with a size of a few nm, assembled from metal ions and organic ligands. The accessible open metal sites on the MOPs surface allow functionalized polymer chains to form star-shaped polymers via coordination bond formation [1]. We synthesized four different rhodium-based cuboctahedra as the cores, each formed by twelve dirhodium paddlewheels and twenty-four isophthalate derivates and named RMOP, $[Rh_2(5\text{-}R\text{-}1,3\text{-bdc})]_{12}$ (where 1,3-bdc is 1,3-benzene dicarboxylate and R represents dodecyloxy (C_{12}), hydroxy (OH), *tert*-butyl (tBu) groups or non-functionalized (H)). Star-shaped polymers C_{12}MOP-A_{40}, HMOP-A_{40}, tBuMOP-A_{40}, and OHMOP-A_{40} were formed by tethering 12 equivalent polymer A_{40}, possessing a polyethylene glycol (PEG) chain with coordinative imidazole at one end and a bulky *tert*-octylphenyl group at the other end, to the MOP cores, respectively. Small-and-wide-angle X-ray scattering (SWAXS) measurements revealed the distance between the MOP cores in C_{12}MOP-A_{40} to be 3.44 nm and that in OHMOP-A_{40} to be 8.68 nm, indicating two different polymer conformations: compacted state and stretched state, respectively. Such a difference in conformation should be caused by the interaction between the functional group (R = C_{12} or OH) on the MOP surface and the tethered polymers. These polymer conformation differences resulted in materials exhibiting distinct rheological behavior; compacted C_{12}MOP-A_{40} shows low viscosity, while stretched OHMOP-A_{40} exhibiting high viscosity.

Reference:

[1] P. Han, C. Chuang, S. Lin, X. Xiang, Z. Wang, M. Kuzumoto, S. Tokuda, T. Tateishi, K. Wu, K. Urayama, D. Kang, S. Furukawa. *Nat. Commun.* **2024,** *15*, 9523.