

動的共有結合を有する可溶性分子内架橋高分子の合成と分子間架橋反応

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Synthesis of single-chain nanoparticles with dynamic covalent bonds and their intermolecular cross-linking reactions (*Department of Chemical Science and Engineering, Tokyo Institute of Technology*) ○Gota Tomono, Hirogi Yokochi, Daisuke Aoki, Hideyuki Otsuka

Bis(2,2,6,6-tetramethylpiperidin-1-yl)disulfide (BiTEMPS) can reversibly dissociate to the corresponding radicals at disulfide bond by moderate heating¹. In this work, we developed a new approach based on bond exchange reactions of BiTEMPS to synthesize single-chain nanoparticles (SCNP).

Cross-linked polymers containing BiTEMPS moieties at the cross-linked points were synthesized by free-radical polymerization of vinyl monomers in the presence of BiTEMPS cross-linkers. Heating the resulting cross-linked polymers under dilute conditions, SCNP intramolecularly cross-linked by BiTEMPS was successfully obtained. We investigated the structural reorganization of network structure in SCNP by the changes in elastic modulus of their SCNP upon heating and found that intermolecular cross-linking reactions based on dynamic covalent chemistry were induced by heating.

Keywords : Polymer reactions, Dynamic covalent chemistry, Single-chain nanoparticles (SCNP), Cross-linked polymer, Disulfide linkages

ビス(2,2,6,6-テトラメチルピペリジン-1-イル)ジスルフィド (BiTEMPS) は穏和な熱的刺激により均一開裂し、可逆的な結合交換反応を起こす (Fig. 1a)^[1]。本研究では、動的共有結合の結合交換特性を利用し、架橋点に BiTEMPS を有する架橋高分子から可溶性分子内架橋高分子 (SCNP) へと変換する手法の開発を目的とした。

まず、BiTEMPS 含有架橋剤とメタクリレートモノマーのフリーラジカル共重合により、架橋点に BiTEMPS を有する架橋高分子を合成した。得られた架橋高分子を希釈条件下で加熱し、BiTEMPS の結合交換反応によって可溶性分子内架橋高分子 (SCNP) へと変換した (Fig. 1b)。さらに、SCNP の動的粘弾性測定から、加熱によって分子間架橋反応を誘起できることを確認した。

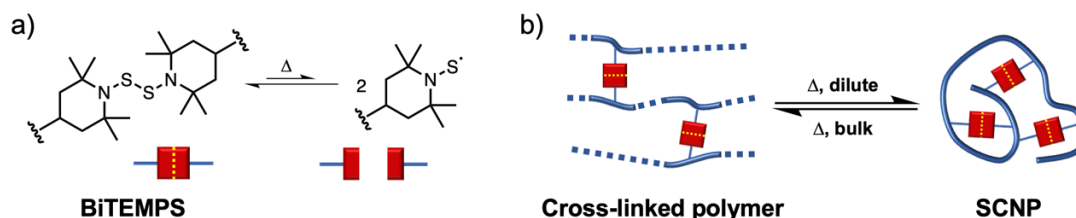


Figure 1. a) Reversible dissociation of a BiTEMPS unit and b) interconversion between a cross-linked polymer and SCNP based on exchange reactions of BiTEMPS units.

[1] H. Otsuka *et al.*, *Angew. Chem. Int. Ed.* **2017**, *56*, 2016–2021