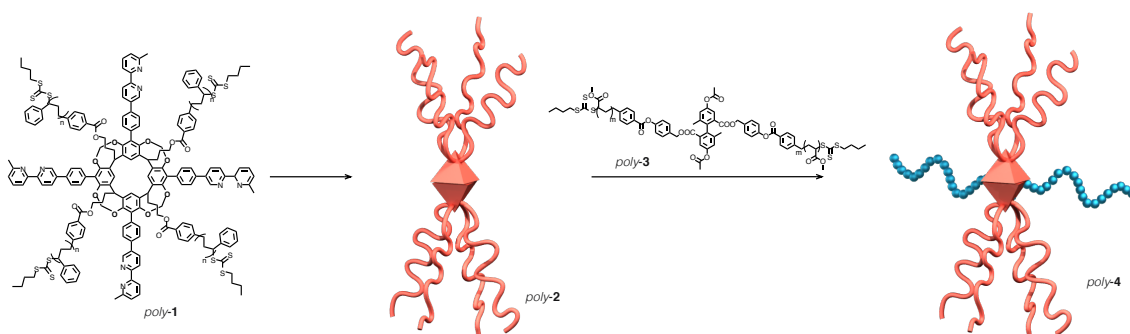


## 1A3b

Facile synthesis of supramolecular A<sub>8</sub>B<sub>2</sub> type star-shaped copolymer via guest complexation of self-assembled capsuleNatsumi Nitta,<sup>1</sup> Ryo Sekiya<sup>1</sup>, Takeharu Haino<sup>1</sup><sup>1</sup> Department of Chemistry, Graduate School of Science, Hiroshima University

Star-shaped polymers, consisting of a core and three or more arms radiating from the core, have attracted much attention due to their highly branched structure and unique rheological properties. The synthesis of star-shaped copolymers generally requires tedious multistep procedures to construct their branched structures. Our group reported a biphenyl guest molecule is encapsulated within a self-assembled coordination supramolecular capsule.<sup>[1]</sup> Here we report the facile synthesis of A<sub>8</sub>B<sub>2</sub> type star-shaped copolymer via the guest complexation within the self-assembled capsule.

Scheme 1. Synthesis of *poly-4*.

We synthesized *poly-1* with polystyrene chain and *poly-3* with poly (methyl acrylate) chain via reversible addition-fragmentation chain-transfer (RAFT) polymerization (Scheme 1). The structures of *poly-1* and *poly-3* were characterized by <sup>1</sup>H NMR. GPC analysis resulted in average molecular weights (*M<sub>n</sub>*) of 5300 (PDI = 1.04) and 5400 (PDI = 1.09) for *poly-1* and *poly-3*, respectively. *Poly-2* was formed by mixing copper ion and *poly-3* in a mixed solution of CH<sub>2</sub>Cl<sub>2</sub> and CH<sub>3</sub>CN, whereas *poly-4* was formed by mixing *poly-2* and *poly-3* in a mixed solution of 1,2-ClCH<sub>2</sub>CH<sub>2</sub>Cl and CH<sub>3</sub>CN. <sup>1</sup>H NMR measurement was carried out to confirm the encapsulation of *poly-3* within *poly-2*. The bound of the acetoxy methyl resonances of *poly-3* shifted upfield at -1.25 ppm (Figure 1), which indicates A<sub>8</sub>B<sub>2</sub> supramolecular star-shaped copolymer *poly-4* was formed through the encapsulation of the 4,4'-diacetoxybiphenyl unit of *poly-3*. Differential scanning calorimetry measurement of *poly-4* gave rise to glass transition temperatures observed at 97 and 12 °C, which are consistent with those observed for *poly-2* and *poly-3*. These results indicate that the PS chains and the PMA chains of *poly-4* were phase separated.

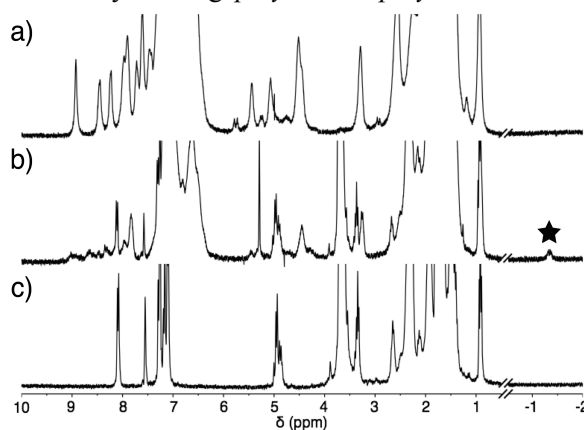


Figure 1. <sup>1</sup>H NMR spectra (300 MHz, CDCl<sub>3</sub>, 293 K) of a) *poly-2*, b) *poly-4*, ★ denotes the signal of the bound of the acetyl group of *poly-3*, c) *poly-3*

[1] T. Imamura, T. Maehara, R. Sekiya, and T. Haino, *Chem. Eur. J.*, **2016**, *22*, 3250-3254.