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Synthesis of Supramolecular Graft Copolymer via Specific Guest Encapsulation by Coordination Capsule.

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The graft copolymerization is an effective technique that can modulate the physical properties of polymers, such as morphology and viscosity. Our objective is to develop a new methodology for the preparation of graft copolymers. Resorcinarene-based coordination capsule **1** encapsulates 4,4′-diacetoxybiphenyl derivatives to form stable 1:1 host-guest complexes.[1] This guest recognition can be potential for the construction of graft copolymers via self-assembly of **1** and poly-**2** containing 4,4′-diacetoxybiphenyl units in each repeating unit as shown in Figure 1.

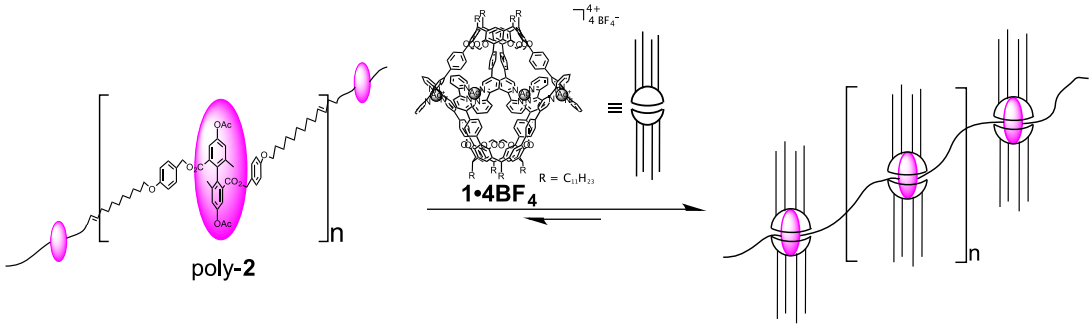

Figure 1. The formation of supramolecular graft copolymer

Poly-**2** was synthesized by ADMET polymerization of a 4,4′-diacetoxybiphenyl monomer in the presence of Grubbs 2nd-generation catalyst. M_n and M_w/M_n of poly-**2** are determined to be 14,000 and 1.76 using SEC analysis.

The graft copolymerization of poly-**2** and **1** was demonstrated by ^{1}H NMR spectroscopy. A new signal, assigned to the acetoxy groups at the 4,4′-positions of the biphenyl moiety, appeared at −1.25 ppm. The significant upfield shift ($\Delta\delta$ = −3.55 ppm) placed the guest moiety within the self-assembled capsule; the guest experienced the shielding effect from the aromatic rings of the capsule (Figure 2a, b).

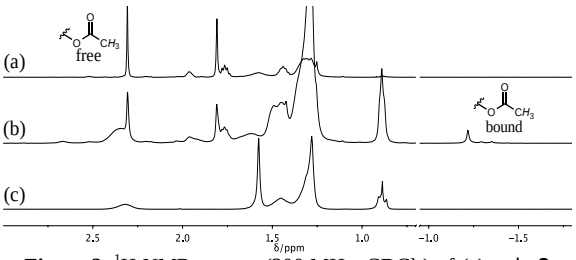

Figure 2. ^{1}H NMR spectra (300 MHz, $CDCl_3$) of (a) poly-**2**, (b) poly-**2** + **1** and (c) **1**.

The morphological transition of the polyesters upon graft copolymerization was studied. Figures 3a and 3b show the AFM images of poly-**2** and a mixture of poly-**2** and **1**. Poly-**2** was agglomerated, whereas the graft copolymers resulted in the highly aligned structure.

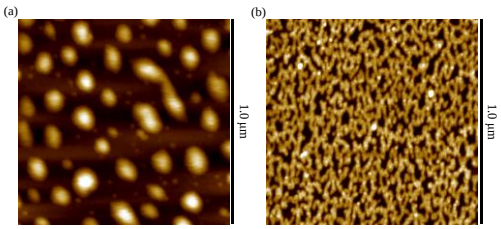

Figure 3. AFM images of (a) **poly-2**, and (b) graft copolymer of poly-**2** and **1**.

The synthesis of the graft copolymers and the morphological transition upon the graft copolymerization will be discussed.

[1] T. Haino, M. Kobayashi, Y. Fukazawa, *Chem. Eur. J.*, **2006**, *12*, 3310-3319.