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Supramolecular Graft Copolymerization of a Polyester by Guest-Selective Encapsulation of a Self-Assembled Capsule

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Abstract: *Repeating guest units of polyesters poly-(R)-**2** were selectively encapsulated by capsule **1**(BF_4)$_4$ to produce supramolecular graft polymers. The encapsulation of the guest units was confirmed by ^1H NMR spectroscopy. The graft polymer structures were confirmed by the increase in the hydrodynamic radii and the solution viscosities of the polyesters upon complexation of the capsule. After the capsule was formed, atomic force microscopy showed extension of the polyester chains. The introduction of the graft chains onto poly-(R)-**2** resulted in the main chain of the polymer having an M-helical morphology. The complexation of copolymers poly-[(R)-**2**-co-(S)-**2**] by the capsule gave rise to the unique chiral amplification known as the majority-rules effect.*

Graft polymers are a unique class of block copolymers in which one or more polymeric side chains are attached to each repeating unit of a linear polymer backbone. Steric interactions between the densely grafted side chains determine the conformational flexibility of a linear polymer backbone, which leads to extension of the main chain.[1] The physical properties associated with the conformation of the main chain can be controlled by varying the grafting density, which leads to potential use in a wide-range of applications such as photoresponsive polymer materials,[2] drug delivery,[3] and nanomaterials.[4] Although covalent synthetic approaches—"graft through," "graft onto," and "graft from"—have been intensively studied for producing graft polymers,[5] multistep synthesis methods are required to obtain graft polymers with a high level of precision in their structure.[6]

Supramolecular polymer chemistry has become an active research area in the field of polymer science,[7] and it offers another option for the construction of graft polymers. Pioneering work on supramolecular graft polymers was reported for the development of liquid-crystalline materials.[8] In addition, complementary multiple hydrogen-bonding motifs were employed for the self-assembly of the side chains of supramolecular graft polymers.[9] Molecular recognition by pillar[*n*]arenes,[10] cyclodextrins,[11] cavitands,[12] cucurbiturils,[13] and crown ethers[14] have been used for the introduction of graft chains. Although many self-assembled capsules have been developed,[15] molecular recognition by self-assembled supramolecular capsules has not been employed for the synthesis of graft copolymers.

It was previously shown that the resorcinarene-based coordination capsule **1**(BF_4)$_4$ encapsulates hydrogen-bonded pairs of carboxylic acids and a variety of other molecular guests within its nanosized cavity (Figure 1 a).[16] The dissymmetric nature of the capsule generates *P* and *M* enantiomers, and a dynamic interconversion of these forms is permitted due to the labile Ag^+-N coordination (Figure 1 b).[17] The encapsulation of a chiral biphenyl guest (*R*)-**G1** biases the interconversion, which leads to the *M* form with an extremely high diastereoselectivity of 98% *de*. We envisioned that such a diastereoselective guest encapsulation could be applied in the synthesis of a graft copolymer. Here, we report a novel synthesis approach to introduce graft side chains onto polymers poly-**2a**–**d** by site-selective encapsulation (Scheme 1 and Figure 1 d). The eight long alkyl chains of the capsule were successfully grafted onto the polymer main chains. Steric interactions between the grafted side chains resulted in a conformational change of polyesters poly-(*R*)-**2a**–**d**, which led to unique morphological transitions. The chirality of a guest unit was efficiently transferred to the helicity of the capsule, which induced a helical organization of poly-(*R*)-**2d** and a chiral amplification of diastereoselective encapsulation by the capsule.

Chiral guest polymers poly-(*R*)-**2a**–**d** were prepared by acyclic diene metathesis (ADMET) polymerization.[18] Monomers (*R*)-**2a**–**d** were subjected to a 2nd generation Grubbs catalyst under the polymerization conditions described by Schulz and Wagener.[19] The ADMET polymerization produced the corresponding polymers, poly-(*R*)-**2a**–**d**, with number-average molecular weights that range from 16300 to 20900, which corresponded to degree of polymerization (DP) values of 19–25 (Table 1).

Table 1: Characterization data for polyesters poly-(*R*)-**2a**–**d**.

Polymer	M_n [g mol^{-1}][a]	M_w/M_n[a]	Yield [%]	DP
poly-(*R*)-**2a**	17000	1.83	90	19
poly-(*R*)-**2b**	20900	1.85	95	25
poly-(*R*)-**2c**	16300	1.58	88	21
poly-(*R*)-**2d**	17400	1.66	83	24

[a] Determined by size-exclusion chromatography.

Supramolecular grafting of poly-(*R*)-**2a** was carried out by encapsulation in capsule **1**(BF_4)$_4$. The encapsulation of a guest unit was monitored by ^{1}H NMR spectroscopy. Figure 2 shows the ^{1}H NMR spectra of poly-(*R*)-**2a** in the presence of two equivalents of **1**(BF_4)$_4$. The acetoxymethyl resonance at $\delta =$

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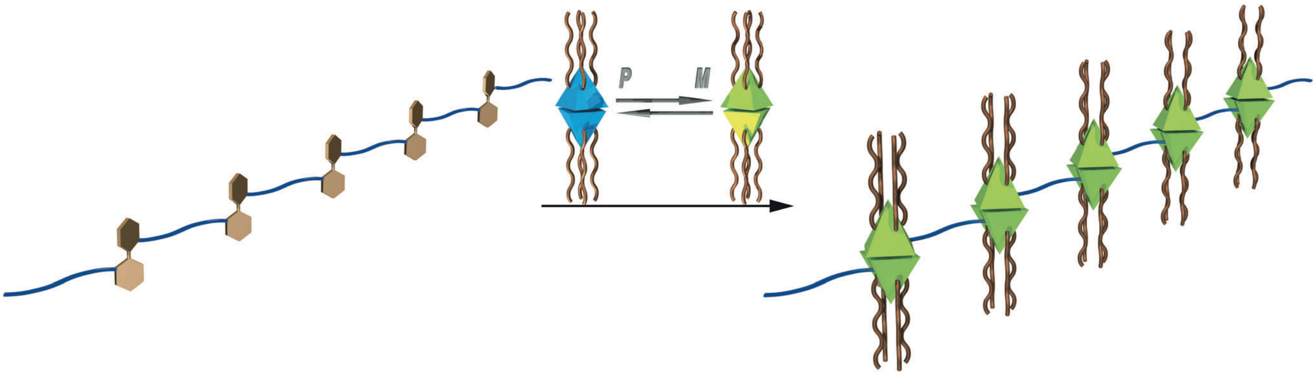

Scheme 1. Schematic representation of supramolecular grafting directed by site-selective guest encapsulation in the self-assembled capsule **1**$(BF_4)_4$.

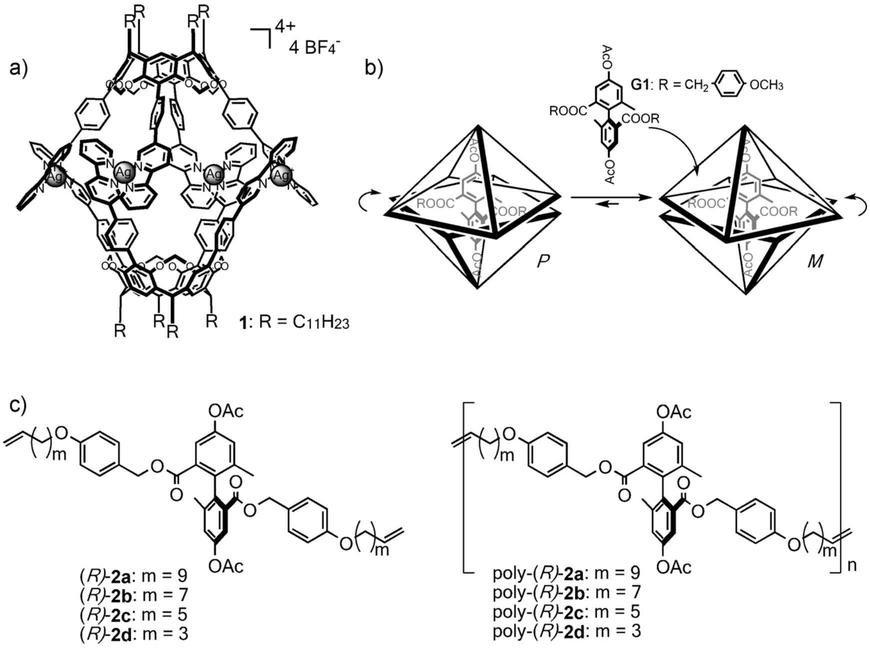

Figure 1. a) Self-assembled coordination capsule **1**$(BF_4)_4$, b) schematic representation of diastereoselective guest complexation to form **G1**$\subset$**1**$(BF_4)_4$, and the structures of c) monomers (*R*)-**2a**–**d** and d) polymers poly-(*R*)-**2a**–**d**.

2.3 ppm moved to a clear window upfield of $\delta = 0$ ppm (Figure 2b).[16a,b] The individual signals of the bound and unbound guest units could be observed at ambient temperature, which supports the idea that a sizeable kinetic barrier exists during the in-and-out exchange process of a guest unit in the capsule. The large complexation-induced shift (CIS) of $\Delta\delta = -3.53$ ppm for the acetoxymethyl signal clearly indicates that these groups are located in a strong shielding region, which is provided by the resorcinarene cavities that are walled by the eight aromatic rings of the cavitands. Thus, the primary axis of each guest unit is located along the C_4 axis of the capsule (Figure 1b). The dominant acetoxymethyl signal of the bound guest unit appeared at $\delta = -1.22$ ppm together with minor signals, and this demonstrates the diastereoselective formation of diastereomeric complexes.[17] Guest units of polymers poly-(*R*)-**2a**–**d** were also encapsulated by the capsule in a diastereoselective fashion. The apparent binding constants of the capsule with the guest units were determined by competition experiments with 4,4′-diacetoxybiphenyl, which has a binding constant K_a of 82000 L mol^{-1}.[16b] Poly-(*R*)-**2a**–**d** showed fairly large binding constants of 33000, 26000, 24000, and 55000 L mol^{-1}, respectively.

Diffusion-ordered spectroscopy (DOSY) estimates the hydrodynamic volume of a molecular aggregate in solution.[20] DOSY experiments for polymers poly-(*R*)-**2a**–**d** were carried out in the presence of capsule **1**$(BF_4)_4$. The diffusion coefficients of the polymers gradually decreased upon the addition of the capsule (Figure 3a). Plots of the diffusion coefficients versus degree of encapsulation of the guest unit generated hyperbolic curves, which saturated when more than 50% of the guest unit was encapsulated. The relative hydrodynamic volume of the polymers can be estimated from the diffusion coefficients. The diffusion coefficient ($D = 2.11 \times 10^{-10}$ m^{2}s^{-1}) of poly-(*R*)-**2a** reduced by 38% when the degree of encapsulation of the guest unit approached 81%. Assuming that all the polymers are hydrospherical, the hydrodynamic volumes of the polymers are 14–15 times larger than those of the polymers without the capsule. These results suggest that the grafting of side chains by guest encapsulation appreciably expands the polymer structures in solution. This structural expansion influenced the viscosity of the polymer in solution.[21] Specific viscosities (η_{sp}) of the polymers were determined with and without **1**$(BF_4)_4$ (Figure 3b). The specific viscosities of poly-(*R*)-**2a**–**d** exhibited a good linear correlation with the polymer concentration. The addition of the capsule to the solution of poly-(*R*)-**2a**–**d** resulted in an increase in the specific viscosities and the generation of curved plots. The clear difference in viscosity is evidence that the graft chains are noncovalently bound to the polymer main chains.

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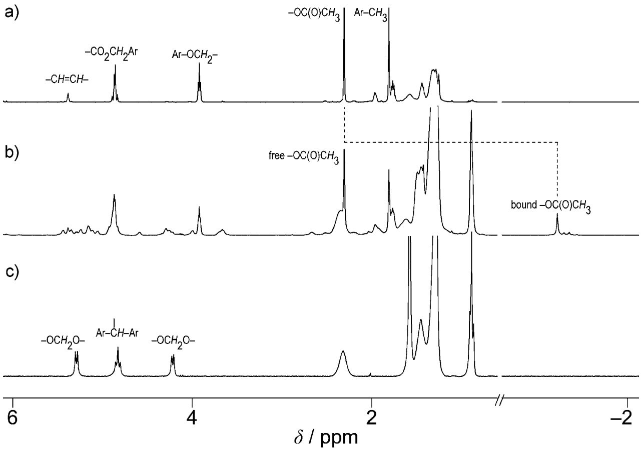

Figure 2. ^{1}H NMR spectra of poly-(*R*)-**2a** (0.053 mmol L^{-1}), poly-(*R*)-**2a** (0.053 mmol L^{-1}) with **1**(BF$_4$)$_4$ (2.0 mmol L^{-1}), and **1**(BF$_4$)$_4$ (2.0 mmol L^{-1}) in CDCl$_3$ at 298 K.

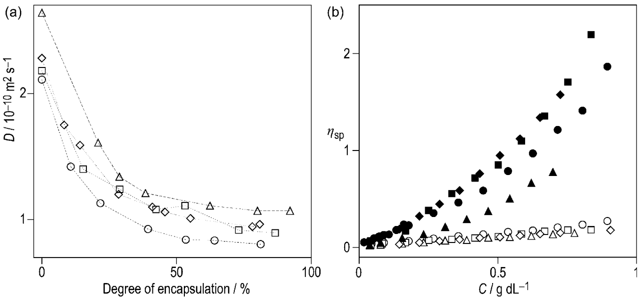

Figure 3. a) Plots of diffusion coefficients (*D*) versus the degree of encapsulation of the guest units of poly-(*R*)-**2** (0.43 mmol L^{-1}; **2a**: ○, **2b**: □, **2c**: △, **2d**: ◇) with **1**(BF$_4$)$_4$ in CDCl$_3$ at 298 K. b) Specific viscosities (η_{sp}) of poly-(*R*)-**2a–d** (**2a**: ○, **2b**: □, **2c**: △, **2d**: ◇) without **1**(BF$_4$)$_4$ and with 1.5 equiv **1**(BF$_4$)$_4$ per guest unit (**2a**: ●, **2b**: ■, **2c**: ▲, **2d**: ◆) in CDCl$_3$ at 298 K.

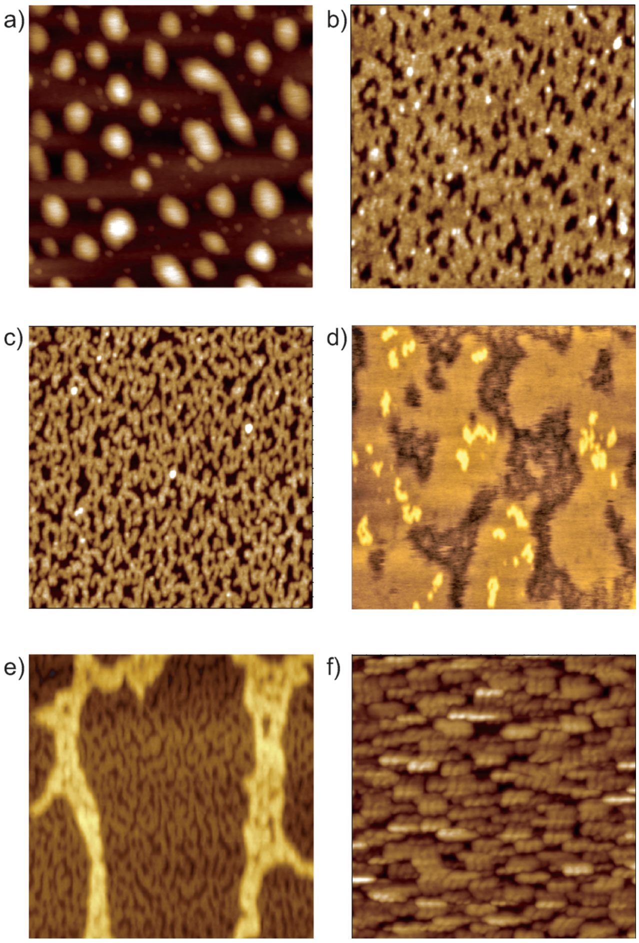

Figure 4. AFM topographic images of a–c) poly-(*R*)-**2a** and d–f) poly-(*R*)-**2d** without **1**(BF$_4$)$_4$ (a,d), with 0.5 equiv **1**(BF$_4$)$_4$ per guest unit (b,e), with 1.5 equiv **1**(BF$_4$)$_4$ per guest unit (c), and 3.0 equiv of **1**(BF$_4$)$_4$ per guest unit (f) on mica. The sizes of the images are (a–d) 1 μm × 1 μm, and (e,f) 500 nm × 500 nm.

AFM measurements showed the conformational changes of poly-(*R*)-**2a** upon the grafting of capsule **1**(BF$_4$)$_4$ (Figure 4). The polymers without the capsule were arranged in random aggregates (Figure 4a). Fibrillar morphologies of poly-(*R*)-**2a** were formed in the presence of the capsule (Figure 4b,c). As the concentration of the capsule increased, the chain extension became apparent. These results indicate that the sterically bulky capsules located on the polymer main chain most likely generate significant steric interactions with neighboring capsules; as a result, the polymer main chain loses its conformational flexibility, which results in main-chain extension. The lengths of the polymer chains were roughly measured from Figure 4c to be (101 ± 10) nm, compared to a length of 4.4 nm for monomer (*R*)-**2a,** obtained from a molecular modeling study conducted using MacroModel V9.1.[22] The DP of poly-(*R*)-**2a** grafted with the capsule was calculated to be 23, which moderately coincides with the observed DP of 19. More apparent morphological differences were observed in the AFM images of poly-(*R*)-**2d** in the absence and presence of the capsule. Poly-(*R*)-**2d** was found to have a random aggregation (Figure 4d). When 0.5 equiv of the capsule was added to the polymer solution, widespread polymer networks were formed (Figure 4e). Further addition of the capsule surprisingly produced helical morphologies, with the *M*-helical configuration being dominant with an average pitch of (15 ± 1) nm (Figure 4f). The presence of the capsule on the polymer chains caused the intermolecular steric interactions between the bound capsules that resulted in a helical morphology.

Induced circular dichroism (CD) was observed when optically active guest units with the *R* configuration were encapsulated within the cavity. An intense absorption of a π-π* transition in the bipyridyl unit was observed at $\lambda = 310$ nm (Figure 5). The addition of poly-(*R*)-**2a** resulted in induced plus-to-minus bisignate CD signals of **1**(BF$_4$)$_4$ emerging at $\lambda =$ 328 and 270 nm, which indicates that the helical interconversion of **1**(BF$_4$)$_4$ is biased. It is known that the plus-to-minus CD signals are characteristic of the *M* configuration, which becomes dominant in the helical interconversion of **1**-(BF$_4$)$_4$.[17a]

Majority-rules experiments demonstrated a unique chiral amplification in the supramolecular graft polymers. Copolymers poly-[(*R*)-**2a**–**d**-*co*-(*S*)-**2a–d**] were prepared to examine

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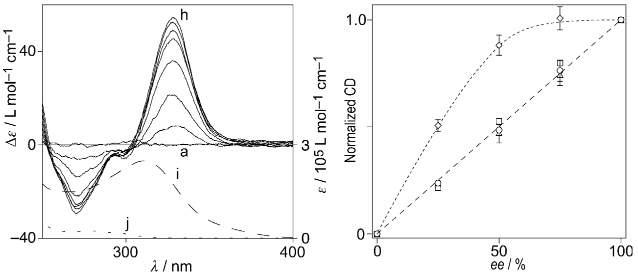

Figure 5. Left: Circular dichroism spectra of **1**$(BF_4)_4$ (9.0×10^{-5} mol L^{-1}) in the presence of poly-(*R*)-**2a** (a–h: [guest unit] = 0.0, 4.5, 9.0, 13.5, 18.0, 27.0, 36.0, 45.0×10^{-5} mol L^{-1}), and UV/Vis absorption spectra of **1**$(BF_4)_4$ (i) and poly-(*R*)-**2d** (j) in chloroform at 298 K. Right: Normalized CD intensities of **1**$(BF_4)_4$ (9.0×10^{-5} mol L^{-1}) in the presence of copolymers poly-[{(*R*)-**2a–d**}$_x$-*co*-{(*S*)-**2a–d**}$_{1-x}$] ($x = 0.500$, 0.675, 0.750, 0.875, and 1.000) ([guest unit] = 45.0×10^{-5} mol L^{-1}) (poly-**2a**: ○, poly-**2b**: □, poly-**2c**: △, poly-**2d**: ◇). Error bars denote standard errors of the means.

the chiral amplification behaviors. The good linear correlation between the normalized CD intensities of copolymers poly-[(*R*)-**2a–d**-*co*-(*S*)-**2a–d**] and their enantiomeric excess indicates that the majority-rules effect is not operative in these polymerization processes (Figure S40). When copolymers poly-[(*R*)-**2a–c**-*co*-(*S*)-**2a–c**] were added to the solution of capsule **1**$(BF_4)_4$, the CD intensities of the capsule were linearly correlated with the enantiomeric excess of the polymers (Figure 5). No chiral amplification was observed in the complexation of the capsule with copolymers poly-[(*R*)-**2a–c**-*co*-(*S*)-**2a–c**]; therefore, the guest chirality is independently transferred to the helicity of the capsule. In contrast, the complexation of poly-[(*R*)-**2d**-*co*-(*S*)-**2d**] to the capsule showed a remarkable deviation from linearity, which indicates that the enantiomer in excess had a disproportionate effect on the helicity of the capsule bound to the polymer main chains. This chiral amplification is clearly associated with the distance between guests. When multiple guest units are encapsulated by the capsule, the bound capsules come closer to each other on the polymer chain. Although the *R*-configured guest unit directs the favorable *M* helicity of the capsule, the favorable subordinate *P* helicity of the capsule with a *S*-configured guest unit was biased to the unfavorable predominant *M* helicity of the capsule with an *S*-configured guest unit (Figure 6). The energetic penalty of the unfavorable diastereomeric complex (*S*)-guest unit$\subset$(*M*)-**1** is most likely compensated by the preferable steric interaction at the exteriors of the neighboring predominant diastereomeric complex (*R*)-guest$\subset$(*M*)-**1**.

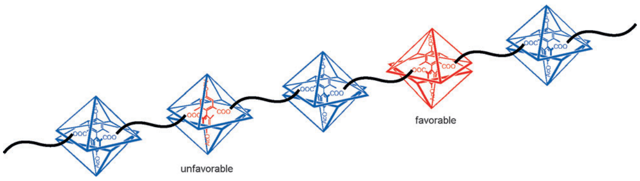

Figure 6. Schematic representation of the chiral amplification of capsule **1**$(BF_4)_4$ with poly-[(*R*)-**2d**-*co*-(*S*)-**2d**].

In conclusion, we have demonstrated the synthesis of supramolecular graft copolymers by guest encapsulation by a self-assembled chiral capsule. The formation of the graft polymers in solution was demonstrated by an upfield shift of the acetoxymethyl resonance, a decrease in the diffusion coefficient, and an increase in the specific viscosity. The introduction of the graft chains resulted in unique morphological changes in the solid state. AFM images confirmed the extended chain structures and the helical chain structures, which were directed through intermolecular steric interactions between the grafted capsules. The chiral guest units of the copolymers determined the helicity of the capsule in solution. The bound capsule was sterically linked to the others, which resulted in a unique chiral amplification known as the majority-rules effect. This study demonstrates that the formation of self-assembled capsules provides a unique method for constructing graft copolymer structures in a noncovalent fashion.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: chiral amplification · majority rules · polymers · supramolecular chemistry

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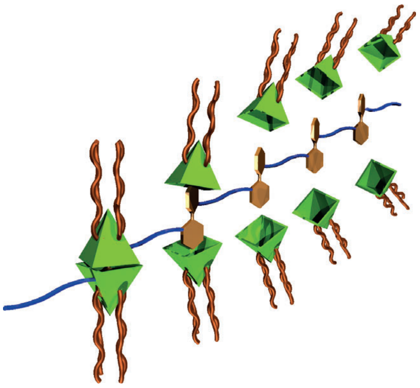
Communications

Supramolecular Polymers

Y. Tsunoda, M. Takatsuka, R. Sekiya,
T. Haino* ________ ■■■–■■■

Supramolecular Graft Copolymerization of a Polyester by Guest-Selective Encapsulation of a Self-Assembled Capsule



Guest of honor: Repeating guest units of polyesters were selectively encapsulated in a self-assembled capsule to produce supramolecular graft copolymers with an induced *M*-helical morphology. A unique chiral amplification was observed in the molecular recognition of the capsule, which is known as the majority-rules effect.

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