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Supramolecular polymerization of supramonomers: a way for fabricating supramolecular polymers

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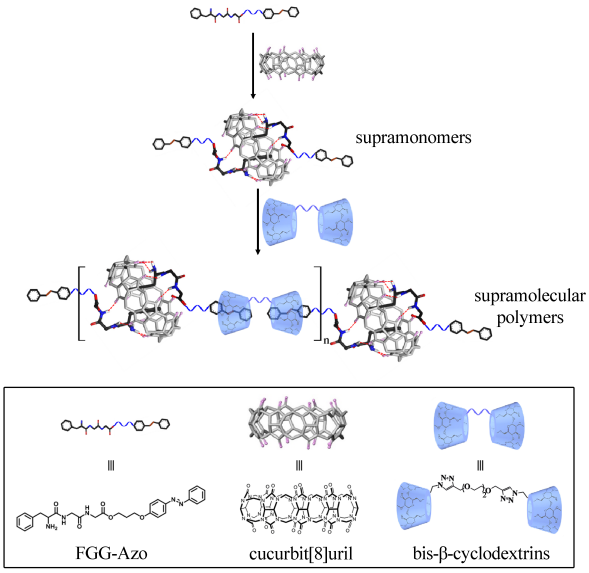
This communication describes a new method of fabricating supramolecular polymers through supramolecular polymerization of supramonomers. To mix building blocks of Phe-Gly-Gly linked with an azobenzene group and cucurbit[8]uril (CB[8]) in a molar ratio of 2:1 in aqueous solutions, supramonomers were obtained by host-guest interaction between tripeptide and CB[8]. Then supramolecular polymers were formed spontaneously by mixing the supramonomers with bis-β-cyclodextrins in a molar ratio of 1:1 in an aqueous solution through noncovalent host-guest complexation of the azobenzene group and β-cyclodextrin. Considering that various noncovalent interactions can be used to drive the formation of supramonomers and the supramolecular polymerization of the supramonomers, this study can enrich the methodology of fabricating supramolecular polymers.

Supramolecular polymers are polymers whose monomers are connected through noncovalent interactions. [1-13] During the supramolecular polymerization process, bifunctional monomers should first be prepared via traditional synthetic chemistry. Then supramolecular polymers can be obtained based on various noncovalent driving forces, including hydrogen bonding, metal coordination, π–π interactions and host–guest interactions. [14-28] In contrast with the fabrication of supramolecular polymers that involves covalent preparation of bifunctional monomers and supramolecular polymerization of the bifunctional monomers, we have proposed a method of fabricating supramolecular polymers by polymerization of supramonomers. Supramonomers refer to monomers which are fabricated via noncovalent interactions, but are able to polymerize through conventional methods of polymerization. [30-31] For example, we have first synthesized the supramonomers with two alkyne functional groups based on the strong supramolecular complexation of cucurbit[8]uril (CB[8]) and a tripeptide derivative. The resultant supramonomers can then be polymerized via a traditional click reaction, the copper (I)-catalysed azide–alkyne cycloaddition reaction. [30] This concept of supramonomers provides a new perspective on the fabrication of supramolecular polymers with controlled compositions and structures.

In this work, we aim to extend the concept of supramonomers, attempting to fabricate supramonomers on the basis of noncovalent interactions and then to fabricate supramolecular polymers through noncovalent supramolecular polymerization of the supramonomers. To this end, as shown in Scheme 1, we first designed and synthesized a guest molecule, Phe-Gly-Gly linked with an azobenzene group via esterification reaction (FGG-Azo). Then the FGG-Azo was allowed to complex with CB[8] in a molar ratio of 2:1 via host-guest noncovalent interaction to give the supramonomers with an azobenzene moiety on each end. The binding constant between FGG and CB[8] has been estimated to be 10^{10} M^{-2}, which is strong enough to ensure the formation of supramonomers. [32-33] Moreover, the acquired supramonomers could be supramolecular polymerized with bis-β-cyclodextrins via noncovalent host-guest complexation of the azobenzene group and β-cyclodextrin. [34-38]



Scheme 1 Supramolecular polymers synthesized by host-guest noncovalent interaction from supramonomers.

The supramonomers were prepared by mixing FGG-Azo and CB[8] in a molar ratio of 2:1 in aqueous solutions. It should be noted that the solubility of FGG-Azo and CB[8] is less than 0.1 mM at room temperature. However, once supramonomers form, the solubility is significantly enhanced and the concentration of the solution can be prepared as high as 4 mM. The change of solubility suggests the formation of supramonomers. In addition, the poor solubility of the building blocks inhibits the supramolecular polymerization directly, and the increased solubility of the supramonomers is advantageous for supramolecular polymerization of the supramonomers as discussed later on.

The formation of supramonomers was confirmed by ^{1}H NMR and electrospray ionization mass spectrometry (ESI-MS). As shown in ^{1}H NMR spectra (Fig. 1), peaks at 7.23 ppm and 7.13 ppm ascribable to aromatic ring of FGG shifted to higher field after the complexation of FGG with CB[8] while no residual signals from free FGG were detected, indicating that FGG-Azo and CB[8] form a complex and the binding ratio should be 2:1. The ESI-MS spectrum (Fig.S5) showed a molecular ion peak with mass/charge ratio of 1182.94, which was in accordance with the calculated molecular weight of supramonomers with two positive charges. Combining the ^{1}H NMR and the ESI-MS results, we are able to confirm that supramonomers are successfully fabricated due to the strong noncovalent interaction between FGG-Azo and CB[8][32].

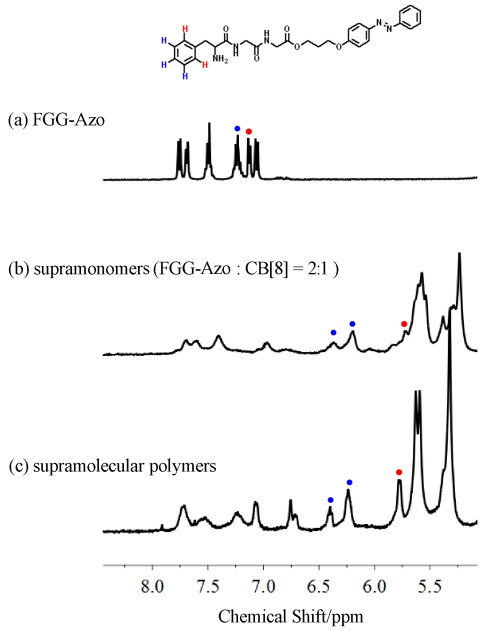


Fig. 1 ^{1}H NMR spectra (D_2O, 25 °C) of (a) FGG-Azo, (b) supramonomers (FGG-Azo and CB[8] complexes), (c) supramolecular polymers (FGG-Azo concentration: 4 mM)

To determine the binding strength between azobenzene moiety on supramonomers and bis-β-cyclodextrins, UV spectroscopic titration experiments were carried out.[39-41] The concentration of the supramonomers was fixed at 0.05 mM, and absorbance at 347 nm decreased upon the addition of bis-β-cyclodextrins (Fig. 2a). It was assumed that the absorbance change was in linear relation with the concentration of host-guest complexes in the solution. In this case, using a nonlinear least-squares curve-fitting method (Supporting Information), the binding constant between the supramonomers and bis-β-cyclodextrins is calculated to be 2.3×10^4 M^{-1} by analysing absorbance change at 347 nm at various concentrations of bis-β-cyclodextrins (Fig. 2b).

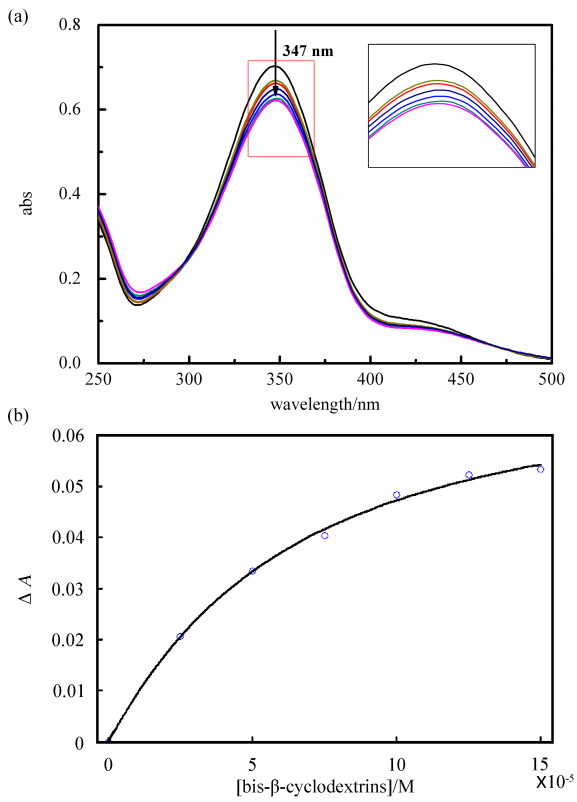


Fig. 2 UV-vis spectroscopic titration results. (a) Typical UV spectral changes of supramonomers upon the addition of bis-β-cyclodextrins in aqueous solution at 20 °C ([supramonomers]=0.05 mM, [bis-β-cyclodextrins]=0, 0.025, 0.050, 0.075, 0.100, 0.125, 0.150 mM, respectively) (b) The nonlinear least-squares analysis of the differential absorbance changes (Δ *A*) at 347 nm against concentration of bis-β-cyclodextrins to calculate the binding constant between supramonomers and bis-β-cyclodextrins.

Supramolecular polymers were constructed by adding bis-β-cyclodextrins into the aqueous solution of the supramonomers in an equivalent molar ratio. From ^{1}H NMR, we can see that peaks belonging to azobenzene group became sharp and shifted to higher field, indicating the complexation of azobenzene and bis-β-cyclodextrins (Fig. 1c). Single-molecule force spectroscopy (SMFS) was employed to provide evidence to support the formation of supramolecular polymers.[42-44] Typical force-extension curves of supramolecular polymers are shown in Fig. S6. After normalizing some characteristic force-extension curves in terms of contour length, we can observe that they superimpose on each other well (Fig. 3a). In addition, the force-extension curves can be simulated using a modified freely jointed chain (M-FJC) model (Fig. S7), which provides Kuhn length of l_k as 0.40 nm and $K_{segment}$ as 50 nN/nm. Gaussian fitting shows that the most probable length is about 21 nm (Fig. 3b). Considering that AFM tip can pick up the supramolecular polymers at various positions along polymer chains, the probable length estimated should be shorter than the practical one. Furthermore, control experiments have been conducted with the solution containing the supramonomers and mono-β-cyclodextrin instead of bis-β-cyclodextrins. No such force curves can be observed. Besides, no signal can be detected with the bis-β-cyclodextrins alone. Therefore, the formation of the supramolecular polymers is clearly indicated by SMFS.

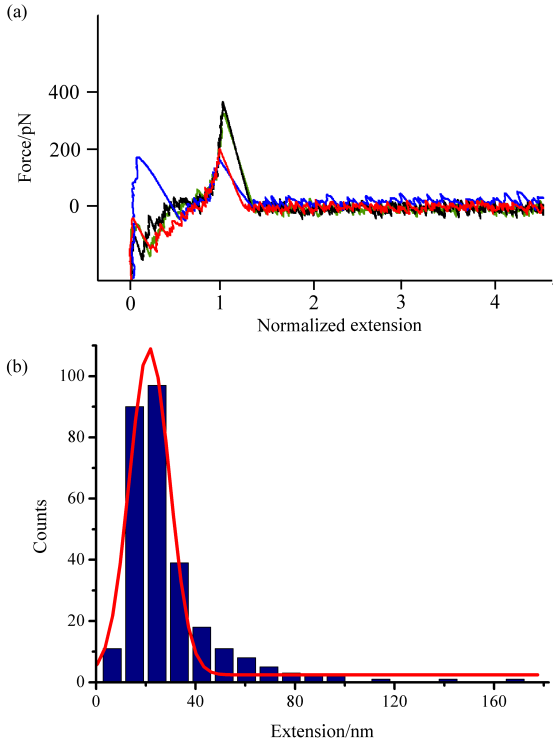


Fig. 3 SMFS results. (a) Normalized force-extension curves. (b) Histogram of the lengths of the force peaks; the most probable length was determined to be 21 nm by Gaussian fitting.

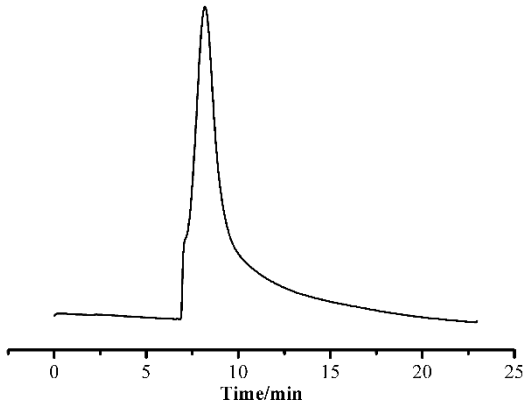


Fig. 4 AsF-FFF elution curve of supramolecular polymers obtained by ultraviolet detector.

The formation of the supramolecular polymers was further confirmed by asymmetric flow field flow fractionation (AsF-FFF), which belongs to a family of field flow fractionation techniques. Compared to gel-permeation chromatography, AsF-FFF is a very mild technique and significantly reduces the probability of the degradation of supramolecular polymer because of the absence of stationary phase. The AsF-FFF has proved to be an efficient technique to characterize the molecular weight and the polydispersity of supramolecular polymers. [45] As shown in Fig. 4, the elution curve of supramolecular polymers was obtained with an ultraviolet detector. The molecular weight is calculated to be 5.4×10^4 $g\cdot mol^{-1}$ with the polydispersity of 1.4.

Due to the dynamic nature of the noncovalent interactions, the supramolecular polymers can be depolymerized under external stimuli. In this case, we wonder if the addition of triethylamine could destroy the complexation between FGG-Azo and CB[8], thus leading to the depolymerization process. To answer this question, triethylamine was added into the aqueous solution of the supramolecular polymers. A large amount of precipitates appeared immediately following the depolymerisation of the supramolecular polymers because the solubility of both building blocks, FGG-Azo and CB[8] were poor and thus precipitated from the solution (Fig. S8). As indicated by ^{1}H NMR, proton signals belonging to the aromatic ring of FGG recovered to lower field, which provided further evidence of depolymerization of the supramolecular polymers (Fig. S9).

The supramolecular polymers can be depolymerized and formed reversibly by alternating irradiation of UV and visible light. As shown in Fig. S10, upon UV irradiation for 5 min, the π to π* band vanished and a new n to π* band appeared instead, revealing that the depolymerization process occurs. The reason behind this depolymerization is UV irradiation induced configuration change of azobenzene from trans-form to cis-form, and the interaction between the cis-form of azobenzene and β-cyclodextrin is too weak to hold the supramolecular polymers. [46-51] After being exposed to daylight for 12 h, the cis-form azobenzene can slowly change back to trans-form, and the interaction between trans-form azobenzene and β-cyclodextrin is strong enough to drive the supramolecular polymerization, which is responsible for the reformation of the supramolecular polymers. Therefore, the formation and depolymerization of the supramolecular polymers can be controlled by light.

Conclusions

In summary, we have successfully achieved supramolecular polymerization of supramonomers via host-guest noncovalent interaction between azobenzene and β-cyclodextrin, thus extending the application of supramonomers for fabricating supramolecular polymers. The obtained supramolecular polymers are of reversible and degradable properties. Although various noncovalent interactions can be used to drive the formation of supramonomers and supramolecular polymers, it should be noted that these interactions should be orthogonal during the entire polymerization process, which means that the interactions should not interfere with each other. It is anticipated that this study will further enrich the synthetic methodology of supramolecular polymers.

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Notes and references

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