

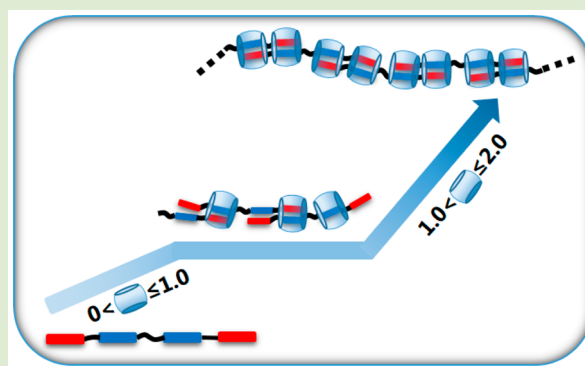
Controllable Supramolecular Polymerization through Host–Guest Interaction and Photochemistry

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S Supporting Information

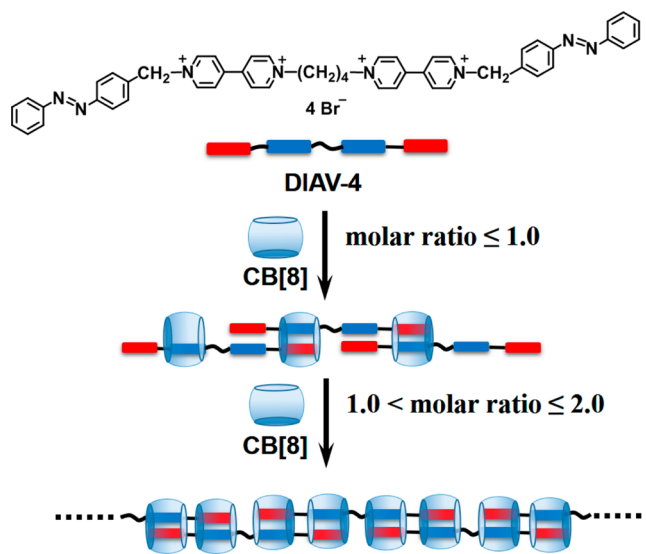
ABSTRACT: A new method for controllable supramolecular polymerization based on ABBA type monomer and cucurbit[8]uril monomer through host–guest interaction and photochemistry is reported. The molecular weight and polydispersity of supramolecular polymers can be well controlled by tuning the molar ratio of these host and guest monomers or by tuning the isomer ratio of azobenzene groups in the guest monomers upon the competitive irradiation of lights. This research provides a general methodology for the control of supramolecular polymerization and the structure of supramolecular polymers.



Supramolecular polymer chemistry has been an important interdisciplinary field that combines supramolecular chemistry and polymer science.^{1–10} With the development of this line of research,^{11–30} the construction of supramolecular polymers is moving toward a controllable process for defined chain structures.^{5,31–34} A well controlled supramolecular polymerization is undoubtedly beneficial to the study of structure–property relationships of supramolecular polymers,³⁵ as well as the rational design of functional supramolecular polymers.^{36–38} Some elegantly designed systems for the precision engineering of supramolecular polymerization have been reported recently. For example, Sugiyasu and Takeuchi et al. reported a living supramolecular polymerization of porphyrin derivatives through seeding the kinetic trapped monomers.^{39,40} Aida and co-workers realized a living chain-growth supramolecular polymerization of corannulene-based metastable monomers upon mixing with initiators.⁴¹ Besenius et al. reported a pH-regulated selectivity of supramolecular polymerization with narrow polydispersity.⁴² We reported a method of supramolecular polymerization which was promoted and controlled by supramolecular self-sorting.^{43,44}

Herein, this communication is aimed to provide a new method of controllable supramolecular polymerization through host–guest interaction and photochemistry. As shown in Scheme 1, an ABBA type monomer DIAV-4 (1',1'''-(butane-1,4-diyl)bis(1-(4-(phenyldiazenyl)benzyl)-[4,4'-bipyridine]-1,1'-dium)) is a guest monomer that contains azobenzene–viologen–viologen–azobenzene structure array. The DIAV-4 monomer with butyl linker was the most suitable candidate for supramolecular polymerization, because the flexible linker longer or shorter than butyl could affect the solubility of the monomers (Section 3 in Supporting Information). One DIAV-

Scheme 1. Schematic Representation of Controllable Supramolecular Polymerization by Tuning the Molar Ratio of CB[8]/DIAV-4



4 monomer can be combined by four cucurbit[8]uril (CB[8]) monomers at most for the formation of supramolecular polymers.⁴⁵ We envisioned that supramolecular polymeric chain structure could be modulated by tuning the molar ratio of CB[8]/DIAV-4, thus, controlling the supramolecular

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polymerization. In addition, the azobenzene moiety can photoisomerize upon UV or visible light, and controlling the isomer ratio of azobenzene might influence the degree of supramolecular polymerization as well. Therefore, this study may provide a new methodology for fabricating supramolecular polymers with controlled molecular weight and distribution through adjusting the molar ratio between the host and guest monomers as well as the irradiation of lights.

To this end, supramolecular polymerization was carried out by adding CB[8] into the DIAV-4 aqueous solution in batches. The supramolecular polymerization was first investigated by asymmetric flow field flow fractionation technique (As4F).^{33,43,46} As shown in Figure 1a, as the ratio of CB[8]

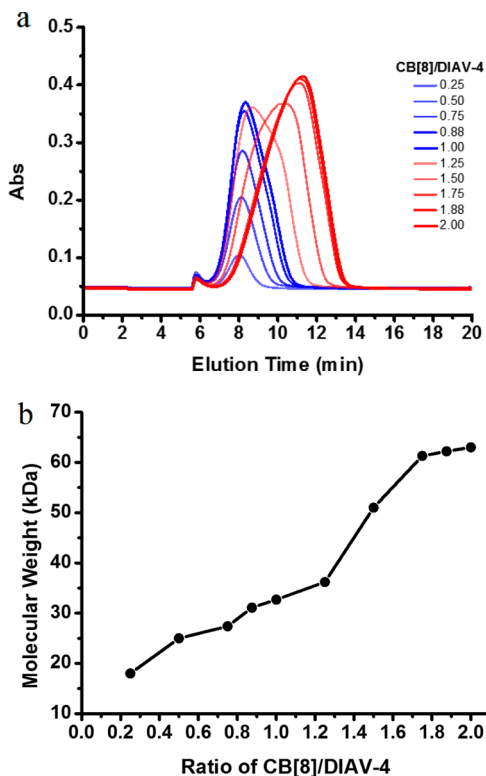


Figure 1. (a) As4F elution curves of supramolecular polymers with different molar ratio of CB[8]/DIAV-4. Elution solvent: HAC-NaAc buffer (50 mM, pH 4.75); concentration, [CB[8]] = 1 mM; injection volume, 100 μ L; semipermeable membrane, PES 5kD. (b) Changes of molecular weight of supramolecular polymers controlled by molar ratio of CB[8]/DIAV-4. The molecular weight was determined by static laser scattering method (Figure S3 in Supporting Information).

to DIAV-4 gradually increased from 0.25 to 1.0, elution peaks with a significant increase of intensity were observed. The detected molecular weight of the supramolecular polymers was relatively low and increased slowly along with the addition of CB[8] (Figure 1b). When the molar ratio of monomers continued to increase from 1.0 to 2.0, the elution peaks showed a right-shift accompanied by a continual rise of peak area (Figure 1a). The molecular weight of supramolecular polymers increased quickly and finally reached a maximum value (Figure 1b). Considering that the increase rate of elution peak area stayed the same during this controllable process of supramolecular polymerization (Figure S4 in Supporting Information), therefore, it suggested a steady increase of monomer conversion as well as the content of supramolecular polymers.

The molecular weight of supramolecular polymers could be varied from 18 to 63 kDa through the process. Moreover, the polydispersity index (PDI) was finally maintained between 1.2 and 1.3 when the molar ratio of CB[8]/DIAV-4 was 2.0 (Table S1 in Supporting Information). Owing to the steric effect of the bulky CB[8] moiety and the repulsive electrostatic interaction, the reactivity of chain end groups might be decreased with the growth of supramolecular polymer chains, leading to an anticooperative supramolecular polymerization. For an anticooperative mechanism, the theoretical PDI value could be much lower than 2.0, which was discussed in the review by Meijer et al.³ Therefore, for this ABBA type monomer, there is a much broader range for tuning the molecular weight and polydispersity, which is distinct from general AB type and AA/BB type monomer systems.⁴⁷

The controllable process of supramolecular polymerization was further confirmed by diffusion ordered spectroscopy (DOSY). As shown in Figure 2, the diffusion coefficient

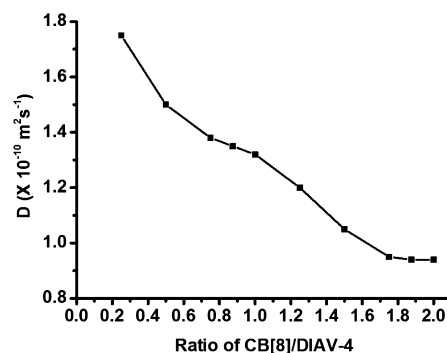


Figure 2. Changes in diffusion coefficient (D) of supramolecular polymers with different molar ratio of CB[8]/DIAV-4. The CB[8] signals were chosen as representatives for the determination of the D value of supramolecular polymers.

decreased step by step, along with the addition of CB[8], suggesting an increase in the average degree of supramolecular polymerization. Interestingly, an accelerated reduction of the diffusion coefficient was observed when the molar ratio of CB[8]/DIAV-4 exceeded 1.0, suggesting a significant increase in the molecular weight of the supramolecular polymers. Therefore, the results of DOSY are consistent with the data of As4F, supporting a controllable process of supramolecular polymerization.

¹H NMR was employed to study the structural changes of the supramolecular polymeric chains behind this process. As the addition of CB[8], peaks of CB[8] (Figure 3), and DIAV-4 monomers (Figure S5 in Supporting Information) broadened, this suggested a formation of supramolecular polymers in aqueous solution.⁴⁵ When the molar ratio of CB[8]/DIAV-4 exceeded 1.0, there was a dramatic enhancement of the peak with $\delta = 5.51$ ppm, accompanied by a gradual decrease in the peak with $\delta = 5.47$ ppm. Meanwhile, these characteristic peaks of CB[8] gradually shifted to the low-field. It means that, when the molar ratio is higher than 1.0, the chemical environment of CB[8] begins to change. Most likely, more DIAV-4 molecules tended to bear two CB[8] molecules on each side, resulting in a close arrangement of CB[8] along the backbone of the DIAV-4 molecule, which was responsible for the change in the ¹H NMR signals. Therefore, the results of ¹H NMR reveal a change in the polymeric chain structure during the process of supramolecular polymerization.

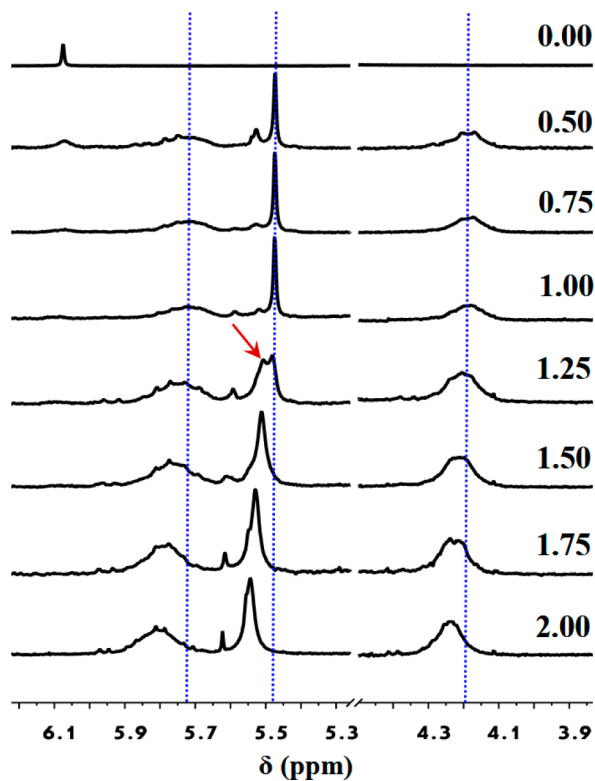


Figure 3. Changes in ^1H NMR spectra of CB[8] with different molar ratios of CB[8]/DIAV-4. The arrow represents a dramatic enhancement of the peak with $\delta = 5.51$ ppm.

We wondered if the photoisomerization of azobenzene^{48,49} in DIAV-4 monomer could be used for fine-tuning the structure of supramolecular polymers. To answer this question, we introduced a competitive input of lights with two different wavelengths (365 and 420 nm). By tuning the relative intensity of the two light beams, the isomer ratio of azobenzene were modulated and stabilized into different states of dynamic equilibrium (Figure 4a). The isomer ratio was quantified by the UV–vis absorption spectra (Section 5 in Supporting Information). Changes in the molecular weight and polydispersity of supramolecular polymers under different equilibrium states were characterized by As4F (Figure 4b). As shown in Figure 4a, the absorption band of *trans*-isomers peaked around 321 nm and then decreased gradually by tuning the relative intensity of the two light beams. The content of *trans*-isomers of the azobenzene can be varied from 30 to 86% (Table S2 in Supporting Information). As shown in Figure 4b, a gradual increase of intensity and right-shift of elution curves with increasing the content of *trans* isomers of the azobenzene was observed by As4F, corresponding to the change of molecular weight from 18 to 41 kDa. It should be pointed out that, only in the case of 100% of *trans*-isomers of the azobenzene, the supramolecular polymers with highest molecular weight can be obtained. The *cis*-isomers of azobenzene are bent structure that can fully occupy the cavity of CB[8] and reject the inclusion of viologen groups, thus inhibiting the formation of supramolecular polymers. In contrast, the *trans*-isomers of azobenzene are extended structure that can form CB[8] ternary complexes with viologen groups from another DIAV-4 molecules, leading to the formation of supramolecular polymers.⁴⁵ Therefore, the *trans*-isomers of the azobenzene favor the supramolecular polymer-

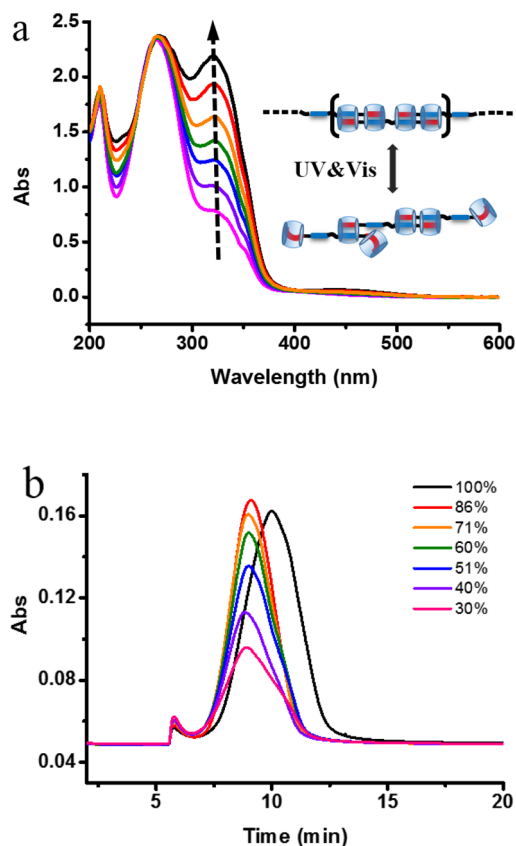


Figure 4. (a) Changes in the UV–vis absorption spectra of supramolecular polymers under the competitive irradiation of two wavelengths of light: concentration, $[\text{CB}[8]] = 1$ mM. Inset: schematic representation of the mechanism of photocontrolled supramolecular polymerization. (b) As4F elution curves of supramolecular polymers with different isomer ratio of azobenzene: elution solvent: HAC–NaAc buffer (50 mM, pH 4.75), concentration: $[\text{CB}[8]] = 1$ mM; injection volume, 20 μL ; semipermeable membrane, PES 5kD.

ization, and the molecular weight of supramolecular polymers can be controlled by tuning the isomer ratio through the competitive irradiation of two wavelengths of light.

In conclusion, we have developed a new method for controllable supramolecular polymerization, which allows for controlling the molecular weight, polydispersity of supramolecular polymers by tuning the molar ratio of monomers, or by tuning the isomer ratio of azobenzene group in the guest monomers. The controllable process of supramolecular polymerization could be described as follows. When the molar ratio of CB[8]/DIAV-4 is lower than 1.0, owing to the insufficiency of CB[8], the DIAV-4 monomers may be partially combined by CB[8], resulting in the termination of supramolecular polymerization and, thus, inhibiting the formation of supramolecular polymers with high molecular weight. When the molar ratio of CB[8]/DIAV-4 is higher than 1.0, the terminals of polymeric chains could be gradually eliminated as further addition of CB[8], leading to a significant growth of supramolecular polymeric chains. For a photocontrolled process, the increase of *trans*-isomers corresponds to the decrease of chain terminals, thus, leading to the growth of supramolecular polymeric chains. This is somehow like a dissipative supramolecular polymerization through the transfer of matter and energy. In addition to the CB[8], other host molecules⁶ such as cyclodextrin,⁵⁰ crown ethers,^{51,52} calixar-

ene,^{49,53} pillar[n]arenes,^{54–57} and even other noncovalent interaction systems^{58–62} are supposed to be available by employing this methodology. Therefore, it is anticipated that this line of research provides a general methodology for controllable supramolecular polymerization.

■ ASSOCIATED CONTENT

■ Supporting Information

Details of synthesis route of monomers, choice of monomers, characterization data of supramolecular polymers with different molar ratio of monomers and isomer ratio of azobenzene, and quantification of isomer ratio of azobenzene. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsmacrolett.5b00266.

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Notes

The authors declare no competing financial interest.

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