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ARTICLE

Fixable Supramolecular Cyclic Polymer based on Cucurbit[8]uril-stabilized π-π Interaction

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A novel reversible unimolecular cyclization method based on CB[8]-stabilized interaction in aqueous environment has been investigated. The dynamic property of the cyclic PEG chain was monitored by viscometry and DLS. Upon photo-irradiation, the cyclic PEG was covalently fixed and utilized to GPC characterization.

Introduction

Preparation of polymers with different topological structures has been a long-term goal for polymer chemists, as properties of the resulting materials are intimately related to their architectures. With elaborate design and synthesis, a variety of precisely controlled polymer topologies have been attained[1]. Among them, cyclic polymers have attracted considerable interest, owing to their unique physical properties compared to the linear or branched counterparts[2]. Despite the difficulties in synthesis, cyclic polymers with various chemical structures[3] have been realized due to the development of novel synthetic protocols, which mainly based on controlled polymerization techniques as well as coupling reactions with high efficiency. One of the most explored and versatile routes utilized to prepare cyclic architecture is cyclization of a linear precursor, which typically involves a bimolecular or unimolecular end group coupling reaction. In last decades, efforts have been paid to solve problems in ring closure, such as low yields and polycondensation byproduct formation, most of which were based on different chemical reactions forming covalent bonds.

Being a research group devoting on macromolecular assembly, we have great interest in cyclizing polymers via non-covalent bonds, since the property of the resulting materials could be tuned directly by their dynamic topologies, which is quite attractive for novel materials with special applications[3c, 3f, 4]. Although there is a great success of cyclizing polymer via various covalent bonds, non-covalently cyclized polymer with reversible switching between its linear and ring state is still very rare. Two major problems hindered its development: 1) the instability of non-covalent bond to solvent and its concentration-dependency make the resulting polymers hardly be characterized by Gel Permeation Chromatography (GPC) and Maldi-TOF as traditional polymers; 2) a relatively strong non-covalent interaction is required to obtain cyclic polymers in highly diluted solution. Until now, although a couple of supramolecular interactions have been employed, including hydrogen bond[5], inclusion complexation[6], electrostatic interaction[7], as far as we know, there have been only two reported reversible cyclic polymers with a clear GPC evidence of showing a different elution time from their linear precursor, which were formed by dynamic covalent bonds in organic solvents[8]. In fact, such bonds under some circumstances are featured by covalent bonds. Thus it is still quite demanding to employ new supramolecular interactions for efficient polymer cyclization.

The pumpkin-shaped host, Cucurbit[8]uril (CB[8]), has become very popular recently since the convenient synthetic protocol published by Kim[9]. Its cavity is capable of encapsulating two guest molecules at the same time through hydrophobic and ion–dipole interactions, when it is employed to connect two molecules or polymers. A plethora of supramolecular structures have been prepared through the CB[8]-based host-guest complexation, including oligomer[10], supramolecular polymer[11], hydrogel[12], microcapsule[13], micelle[14] and responsive surface[15]. Moreover, the binding motif has induced protein dimerization in a highly diluted solution (20 μM)[16]. Thus, CB[8]-based complexation is quite suitable to construct polymeric ring, concerning its high association constant (10^{10}-10^{13} M^{-2}), as one of the highest ones among all synthetic non-covalent interactions.

Herein, this paper reports a novel reversible unimolecular cyclization method based on CB[8]-stabilized π–π interaction. Ring closure of naphthalene (or anthracene)-functionalized polyethylene glycol (PEG, M_n = 20000) was achieved in highly diluted solution through addition of equimolar amount of CB[8], which brought the two naphthalene (or anthracene) ends to a really close position in its cavity. More importantly, the π–π stacking of anthracene groups was further fixed to covalent bond after irradiation under UV light (Scheme 1). Thus direct characterization on the cyclic polymer by GPC was achieved, which is very rare for this type of polymers linked by supramolecular interactions. It is also worth to note that the whole process happened in water, thus this environmental friendly cyclization may find further applications as a new concept of dynamic topologies and properties.

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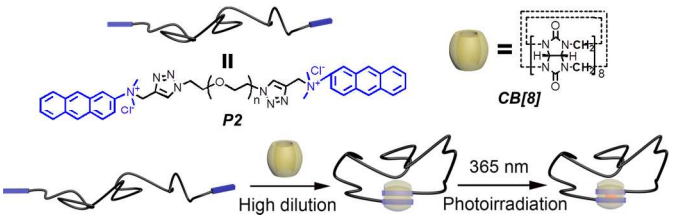

Scheme 1. Schematic representation of reversible cyclization based on CB[8]-stabilized π–π interaction in highly diluted aqueous solution, and the following covalent fixation through photo-irradiation at 365 nm.

Results and discussion

To synthesize naphthalene (Np) end-functionalized PEG (**P1,** Scheme 2, S1), ternary amine terminated PEG chain was achieved through amidation between carbonyldiimidazole (CDI) activated hydroxyl end of PEG and 3-dimethylaminopropylamine (Fig. S1), followed by the electrophilic attack of 2-(bromomethyl)naphthalene. GPC showed the resulting cationic naphthalene telechelic PEG (**P1**, $M_{n,SEC}$ = 14400, PDI = 1.12) shifted to a higher elution volume compared to unmodified PEG ($M_{n,SEC}$ = 19000, PDI = 1.11), probably due to the electrostatic interaction with the stationary phase (Fig. S2). Successful incorporation of Np groups was confirmed by ^{1}H NMR spectroscopy (Fig. S3). The relative peak area of PEG backbone to the Np group indicated that more than 90% hydroxyl end was transferred to Np functionalization. Successive addition of CB[8] into an aqueous solution of **P1** resulted in a decrease of the intensities of the peaks corresponding to free Np and growth of a new set of signals assigned to CB[8]-encapsulated Np, which exhibited a significant broadening and upfield shift (Fig. S4). The peaks of free Np disappeared when the molar ratio of **P1** and CB[8] reached 1 : 1, suggesting the successful formation of CB[8]-based host-guest complexes, in which the opposite alignment of the two singly charged guests was more favorable, although the two Np groups with the same direction could not be fully excluded[17].

To provide more detailed information on CB[8] enhanced π–π interaction, naphthalene derivative *N*,*N*,*N*-trimethyl-1-(naphthalen-2-yl)methanaminium bromide (**M1**, ^{1}H NMR in Fig. S5) was chosen as a model molecule and its binding ability with CB[8] was investigated by isothermal titration calorimetry (ITC)[18]. In the experiment, aqueous solution of **M1** (2 mM) was consecutively titrated into the solution of CB[8] (0.1 mM) at 25 °C (Fig. S6). The binding stoichiometry of **M1** to CB[8] was confirmed to be 2:1, as indicated by the abrupt change in the titration curve. The generated exothermic binding isotherm fitted the two-site binding mode well yielding an overall binding constant of 1.30×10^{12} M^{-2}, which indicated that the host-enhanced π–π interaction between two cationic Np groups promoted by CB[8] could be strong enough for the fabrication of cyclic polymer in highly diluted solution. To further confirm the stoichiometry of the polymer to CB[8], several portions of CB[8] were continuously titrated into the diluted aqueous solution of **P1** (0.25 mg/mL), and the absorption change at 220 nm was recorded, showing a turning point at 0.5 equiv. of CB[8] to Np group (Fig. S7), indicating a 1:1 binding between **P1** and CB[8]. Thus, the CB[8]-stabilized π–π stacking of Np group retained its association at highly diluted solution.

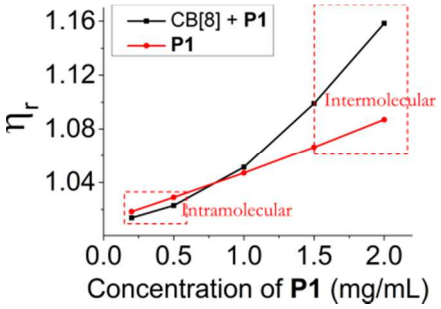

Fig. 1 Relative viscosity of CB[8]+**P1** and **P1** alone at different concentrations.

With the telechelic polymer in hand, the first problem we were facing to was the competition between intramolecular cyclization and intermolecular polymerization, which could be mainly controlled by solution concentration[3b]. The critical concentration for the formation of cyclic polymer was first established via viscometry experiments by varying the concentration of CB[8]+**P1** complex in comparison with **P1** alone as a control. As shown in Fig. 1, at the high concentration region (>1 mg/mL), the CB[8]+**P1** complex provided higher relative viscosity compared to that of **P1**, indicating the favorable intermolecular polymerization. The non-linear plot type of CB[8]+**P1** complex was very similar to our previous results in CB[8]-mediated supramolecular polymerization[19], which also demonstrated the successful incorporation of Np groups at both chain ends of PEG. When the concentration gradually decreased, the relative viscosity of complex CB[8]+**P1** decreased much faster than that of **P1** until 0.5 mg/mL was reached, where the former exhibited relatively lower value than the latter. It is known that the intrinsic viscosity of cyclic polymer was lower than the linear one with same molecular weight. We deduced here the viscosity decrease at low concentrations was caused by the conformation transformation of **P1** from linear to cyclic. The calculated inherent viscosity ratio $[\eta]_{c,exp}/[\eta]_{l,exp}$ of CB[8]+**P1** at 0.5 mg/mL was 0.79, close to but larger than the theoretical value of 0.66[20], probably due to the supramolecular nature of the cyclic PEG

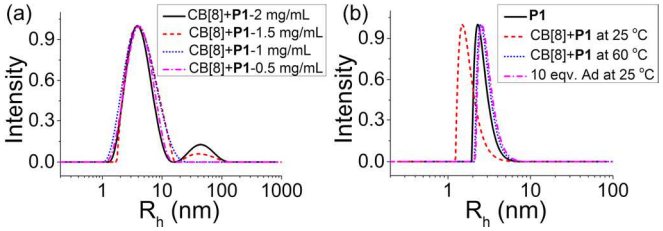

Fig. 2 (a) Unweighted R_h distribution of CB[8]+**P1** complex with different concentrations at 25°C. (b) Number-weighted R_h distribution (0.5 mg/mL) of CB[8]+**P1** and **P1** alone at 25°C, CB[8]+**P1** at 60°C, CB[8]+**P1** at 25°C with 10 equiv. Ad.

The hydrodynamic distribution of the CB[8]-based host-guest complex at different concentrations were examined by DLS. As shown in Fig. 2a, at concentrations of 2 mg/mL and 1.5 mg/mL, in the range giving a high viscosity, besides the main peak around 4 nm, a small peak corresponding to the

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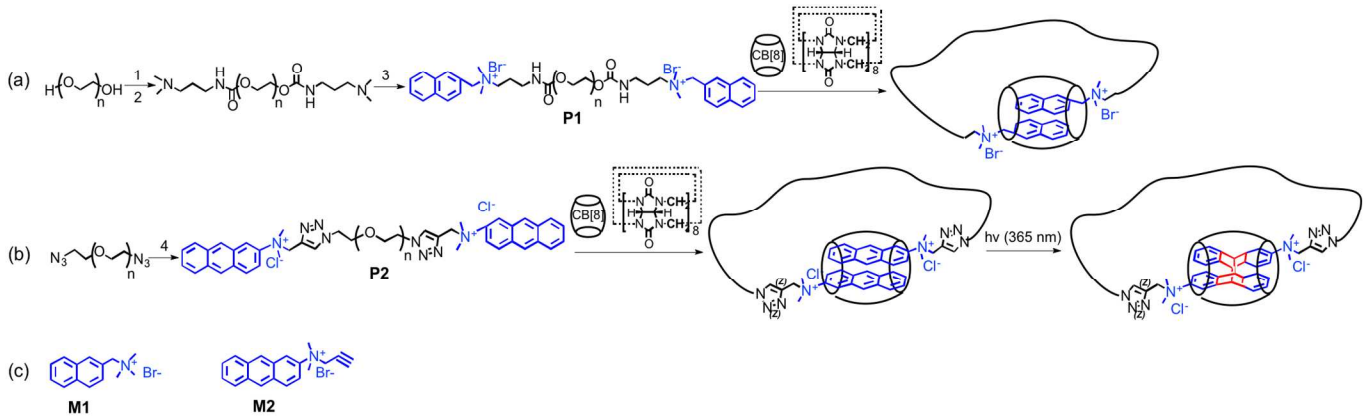

Scheme 2 (a) Synthetic route of **P1** and its cyclization upon addition of CB[8] in highly diluted aqueous solution: (1) CH_2Cl_2, CDI, rt; (2) 3-dimethylaminopropylamine, CH_2Cl_2, 35 °C; (3) 2-(bromomethyl)naphthalene, CH_3CN, reflux. (b) Synthetic route of **P2,** its cyclization and the following photo-irradiation at 365 nm: (4) **M2**, $CuSO_4$, Sodium ascorbate, H_2O, 30 °C. (c) Model molecule **M1** and **M2**.

large-size species was observed, which was obviously corresponding to the intermolecular aggregates[19]. While at concentrations of 1 mg/mL and 0.5 mg/mL, CB[8]+**P1** giving a similar viscosity value to **P1** alone, in the R_h distributions no signal associated with such large species was observed. Then 0.5 mg/mL was selected as a critical concentration for further study of the host-guest complex system. Detailed investigation at this concentration was performed (Fig. 2b). After addition of equimolar CB[8] to 0.5 mg/mL **P1** solution, the number-weighted radius distribution ($<R_h>$) shifted to a lower value, indicating the hydrodynamic volume decrease of CB[8]+**P1** compared to **P1**, which is a typical character of cyclic polymer. Furthermore, the distribution curve of CB[8]+**P1** returned back when the solution was treated by either heating to 60°C or adding 10 equiv. 1-amantadine (Ad). This confirmed the supramolecular nature of the CB[8]-based cyclic polymer.

GPC is one of the most powerful methods in demonstrating cyclization of a linear polymer, as the cyclic one exhibits a longer retention time than its linear counterpart due to the more compact chain structure of the former. However, our attempt to demonstrate the cyclic structure of CB[8]+**P1** in aqueous solution by GPC failed, probably due to the dynamic nature of inclusion complexation which underwent association-dissociation equilibrium under highly diluted conditions. This phenomenon is quite common in other supramolecular systems. Previous work proved that Np groups could be dimerized in the cavity of CB[8] by photo-irradiation[21]. Compared to the lifetime of excited singlet state of Np, the exchange between free and complexed Np can be neglected, thus most molecular state of the non-covalent system should be retained in the resultant covalent system[17]. This encouraged us to perform the photoreaction for transferring the labile non-covalent bond into stable covalent bond. Unexpectedly, the photo-irradiation of CB[8]+**P1** with UV light (wavelength > 280 nm) only resulted in white precipitates from aqueous solution. ^{1}H NMR (Fig. S8) showed that Np groups were cleaved from PEG backbone, leading to the formation of byproduct. We supposed that here the methylene linkage was not suitable for photo-dimerization, as previous works had only shown successful photo-induced dimerization when carbonyl group was utilized[21, 22].

To solve this problem, the cationic Np group was substituted by cationic anthracene (An) group with much higher photo-activity on PEG backbone. The polymer named **P2** for clarity (Scheme 2) was prepared through click reaction between alkyne modified An group and azide-modified PEG (M_n = 20k, Scheme S2, Fig. S9-S12)[23]. To efficiently click An group to the end of PEG_{20k}, PEG_{2k} was first selected as a model reactant. Different reaction conditions were screened. And finally we found that by using chloride as the counter ion for quaternary ammonium and water as solvent after 24 h reaction, no azide was found in Fourier transform infrared spectrum (FT-IR) (Fig. S13). Then the azide-modified PEG_{20k} was charged into reaction under the same condition. The obtained crude product was further loaded into cation exchange column, eluted with aqueous NaCl gradient for purification. ^{1}H NMR of the final product of **P2** showed that more than 90% hydroxyl end was transferred to An group (Fig. S14). ^{1}H NMR of **P2** exhibited a significant upfield shift of the An protons after addition of CB[8] (Fig. S15), very similar to the result of **P1**. Consecutive titration of model molecule **M2** (2 mM) into CB[8] (0.1 mM) at 25 °C indicated a 2:1 binding ratio of An to CB[8] (Fig. S16), yielding an overall binding constant of 1.14×10^{13} M^{-2}. Besides, UV-Vis titration of **P2** (0.25 mg/mL) with CB[8] showed that CB[8]-stabilized π–π stacking of An group was also retained in highly diluted solution (Fig. S17).

Supramolecular cyclization is mainly controlled by the molecular weight of the linear polymer precursor and its concentration. When very similar supramolecular interaction is employed, the dynamic system should exhibit similar property. This assumption was supported by the viscosity test of CB[8]+**P2**, which showed a similar viscosity change vs concentration to that of CB[8]+**P1**, yielding an inherent viscosity ratio $[\eta]_{c,exp}/[\eta]_{l,exp}$ of 0.8 at 0.5 mg/mL (Fig. S18). Then photoreaction of CB[8]+**P2** was conducted in highly diluted solution, with **P2** alone as control at the same concentration. Photo-irradiation of CB[8]+**P2** led to a rapid decrease of the absorbance centred around 254 nm (Fig. S19), resulting from the close stack of two An groups in the cavity of CB[8], while **P2** alone showed a much slower decrease at the same interval (Fig. S20)[23].

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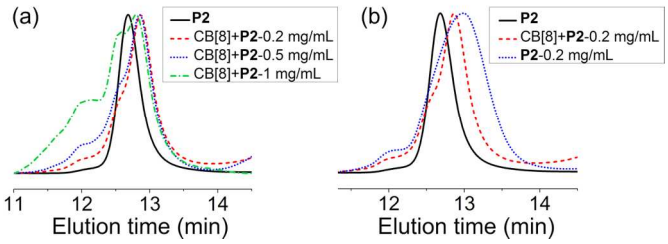

Fig. 3 (a) GPC profiles of P2, product after photo-irradiation of CB[8]+P2 at different concentrations. (b) GPC profiles of P2, product after photo-irradiation of P2 and CB[8]+P2 at 0.2 mg/mL.

The crude product from photo-irradiation was freeze-dried and subjected to GPC characterization. As shown in Fig. 3a, the main peak of photo-irradiated CB[8]+**P2** complex at 0.5 mg/mL ($M_{n,SEC}$ = 15300, PDI = 1.26, M_p = 14000) appeared at a larger elution volume than the **P2** precursor ($M_{n,SEC}$ = 15500, PDI = 1.12, M_p = 17800), which provided a direct evidence of the formation of covalent cyclic polymer from GPC. Besides, there were also a small quantity of oligomers in the final product, due to the relatively long PEG precursor. As predicted by theory, for the same precursor concentration, the long chain length is prone to the formation of oligomers[24]. Here the content of oligomers could be decreased by decreasing precursor concentration to 0.2 mg/mL ($M_{n,SEC}$ = 13900, PDI = 1.19, M_p = 13700). The cyclic *vs* linear ratio of the apparent peak molar mass ($M_{p,c}/M_{p,l}$) from GPC, denoted as ⟨G⟩, was 0.77 at 0.2 mg/mL and 0.5 mg/mL, which agreed well with the value previously reported for cyclic PEG[25]. On the contrary, irradiating CB[8]+**P2** complex at 1 mg/mL as expected led to a great increase in both the content of oligomers and polydispersity ($M_{n,SEC}$ = 20300, PDI = 1.45, M_p = 15100) and meanwhile the cyclization efficiency was apparently decreased.

Fig. 3b showed the GPC profile of photo-irradiated P2 at 0.2 mg/mL without CB[8], which exhibited a much broader molecular weight distribution ($M_{n,SEC}$ = 11400, PDI = 1.40, M_p = 11500), compared to that of cyclized CB[8]+P2 at the same concentration. The apparently decreased M_n and board peak indicated chain cleavage of P2 after photo-irradiation without CB[8]. This was reasonable since in the absence of CB[8], either the intra- or intermolecular dimerization of two An groups was really difficult for the long chain at such low concentration, thus part of energy from excited An groups was transferred to PEG backbone, resulting in polymer structure destruction. ^{1}H NMR result also supported this assumption. The peaks corresponding to aromatic part of reacted P2 in ^{1}H NMR without CB[8] become disordered and weak (Fig. S21). Meanwhile, the ^{1}H NMR (Fig. S15) of photo-irradiated CB[8]+P2 showed a distinctively different result, indicating a typical covalent An dimer in the cavity of CB[8], which was linked to the PEG backbone through the triazole unit (8.2 ppm)[23].

Conclusion

In conclusion, we demonstrated a selective and reversible unimolecular cyclization method based on the CB[8]-stabilized π–π interaction. The detailed molecular structure distribution of the resultant polymers in a labile non-covalent system at various dilute concentrations, was explored for the first time through GPC by photo-irradiation which led to covalent bonds between two An groups at the chain ends of PEG within CB[8] cavity. Viscometry, DLS, NMR and GPC strongly indicated the formation of the cyclic polymer. We believe the idea to tune the property of materials by controlled topological change between cyclic and linear polymer will find further applications in many research field.

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Notes and references

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† Electronic Supplementary Information (ESI) available: Synthesis and characterization of **P1**, **P2** including ^{1}H NMR and GPC results, as well as details of UV-Vis, ITC and photoreaction are all available in supporting information. See DOI: 10.1039/b000000x/

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Graphic Abstract of

Fixable Supramolecular Cyclic Polymer based on Cucurbit[8]uril-stabilized π-π Interaction

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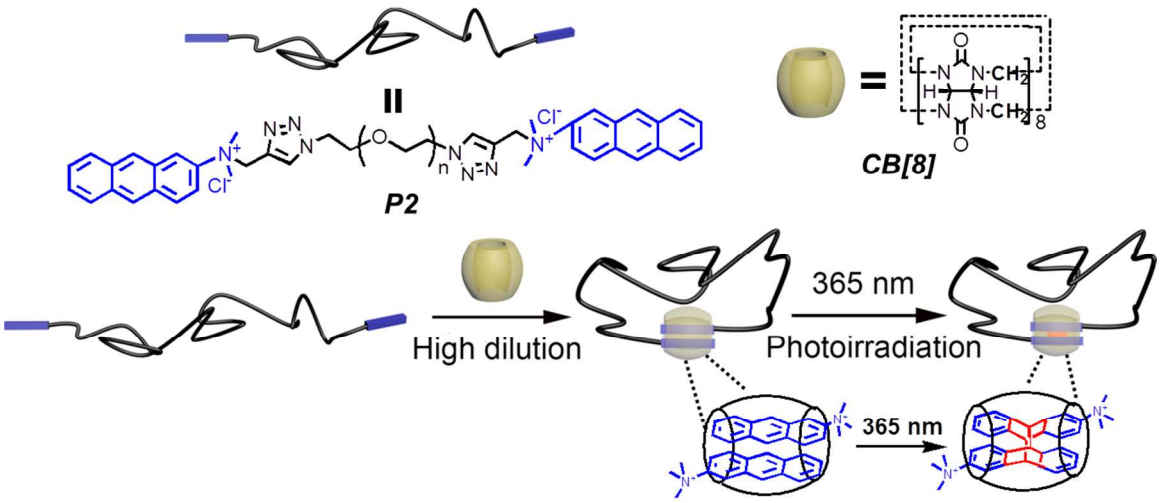

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