Volume 1 | Number 1 | Jan 2013 | Pages 1–100

Polymer Chemistry

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ARTICLE

A Polymeric Chain Extension Driven by HSCT Interaction

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In this paper, targeting at high-molecular-weight supramolecular polymer, chain extension of low-molecular-weight polymer (LMWP) is achieved via HSCT (Host-Stabilized Charge Transfer) of CB[8] (cucurbit[8]uril). Here a combination of ditopic viologen and CB[8] serve as a "supramolecular chain extender" for the first time, to connect the naphathalene (Np)-ended LMWP PDMA or PNIPAm. UV-vis spectrum, ITC and NMR prove that the guest Np connecting to the LMWP does not affect its complexation with guest viologen and CB[8]. The viscosity measurements clearly demonstrate the formation of supramolecular polymer as the viscosity of the LMWP PDMA (DP 52) after the complexation exceeds that of PDMA (DP 300). Np-ended LMWP PNIPAm shows similar chain extension. The resultant supramolecular polymer of PNIPAm shows peculiar LCST behavior with a remarkably different variation on concentration from its polymeric precursor.

Introduction

Supramolecular polymer (SP), as a newly emerging polymer architecture, is featured by non-covalent linkage between monomers instead of the covalent bond in traditional polymers. During the past decade, the research field of SP grew dramatically with remarkable achievements[1-11]. Compared to traditional polymers, SP has great advantages in controllable degradability, self-healing, and processibility because of the dynamic nature of the non-covalent bonds. Till now, metal-ligand[12], hydrogen-bonding[13, 14], π-π interaction[15, 16] and host-guest interaction[17, 18] are all involved in constructing SP. Most SP chains are constructed by small molecules, because of the synthetic accessibility and the significant contrast of properties caused by polymerization. Various molecules with AB type or AA/BB type structure (A and B are complimentary groups, which can form non-covalent linkage) have been developed to construct SPs with special design[19]. It was reported that an appropriate spacer between the reactive groups together with the charge repulsion can suppress the formation of cyclic species[20].

However, there is still a large space for SPs to develop. The versatility of traditional polymer stems from the tunability of material's crystallinity, mechanical strength and thermal stability, which is still unattainable by SPs due to their limited chemical structures. Right now, a practical way to build SPs with more "polymeric" properties emerged, in which covalent low-molecular-weight polymer (LMWP) instead of small molecule is used as building blocks. A few of such SPs composed of LMWPs by supramolecular chain extension (i.e. macro-supramolecular polymer, MSP) have been reported[21-25]. For example, a MSP with multi-block copolymer structure composed of two different kinds of polymeric "monomers" bearing hydrogen bond donor or acceptor was built by Zimmerman et al.[26]. More recently, a MSP formed by metal-ligand linkage on its main chain exhibiting phase separation and self-healing properties, was achieved by Rowan et al[27]. However, the studies on MSP construction with synthetic polymer as building blocks is still quite limited compared to SPs constructed by small molecules[28-37], and of which attention is rarely paid on host-guest interactions[23, 38, 39].

Using LMWPs as building blocks of SP exhibits some advantages than small molecules. It was shown that the polymeric precursor could facilitate the extension of supramolecular chains by suppressing the possibility of ring closure[26, 29]. Moreover, SPs constructed by small molecules include a high content of functional groups, resulting in a limited solvent solubility[25]. This drawback, which may hinder the further application of SPs, is more pronounced in some host-guest systems. For example, SP made of inclusion complexation between CB[8] (cucurbit[8]uril) and two Np (naphthalene) groups, could not reach a high concentration in water because of the limited solubility of the Np-containing small molecule and CB[8][40].

Among popular host molecules, CB[n] (n = 5-10), a family of highly symmetrical pumpkin-shaped molecules, has variable-sized cavities accessible by certain guests through hydrophobic and ion–dipole interactions[41]. CB[8] is an outstanding member in the family since it can encapsulate two different guest molecules in its cavity at the same time[42-45]. In particular, CB[8] can form stable 1 : 1 : 1 ternary complexes with a pair of guests, one electron deficient and one electron rich, such as a viologen and a 2-naphthol, via a stepwise

binding process (Scheme 1a), leading to an enhanced association constant in aqueous buffer. This is named HSCT (Host-Stabilized Charge Transfer). Based on this HSCT, Kim first obtained supramolecular oligomer[46, 47], followed by the first SP built by small molecules from Zhang et al[20] and, very recently a crystal structure of CB[8]-mediated SP was obtained by Scherman et al[48]. However, all these remarkable SPs based on HSCT were developed from small molecules, where LMWP was not involved.
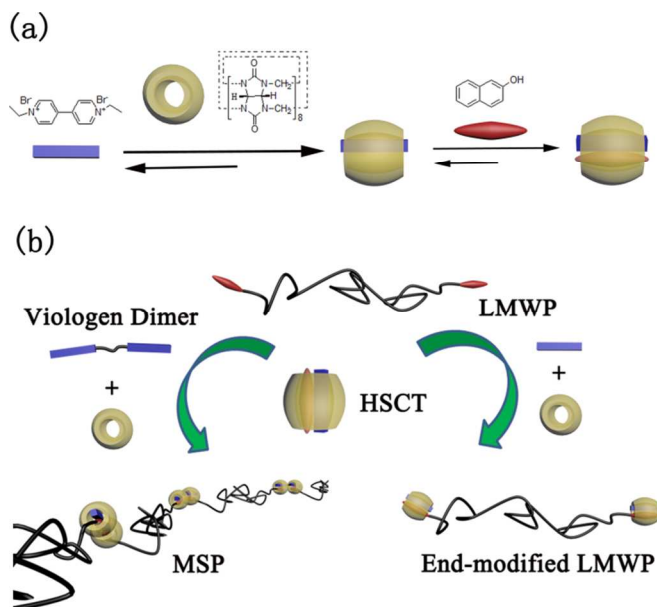

Scheme 1. Schematic representation of (a) the two-step binding process of cucurbit[8] uril in water. (b) Preparation of MSP and end-modified LMWP through addition of CB[8] and electron-deficient first guest (viologen dimer and viologen, respectively) to the Np-ended LMWP.

In this paper, LMWPs are firstly employed to develop MSPs based on the HSCT interaction. After addition of CB[8] and a viologen dimer, LMWP bearing Np groups at its both ends can be extended to a MSP with much larger molecular weight at a relatively high concentration (Scheme 1b). End-modified LMWP is also prepared with a mono-topic viologen as a control. The newly formed MSP exhibited aggregation behavior. Interestingly, the MSP started from PNIPAm shows a remarkably different concentration dependence of LCST (lower critical solution temperature) from its precursor, which is a pronounced property comparing with other SPs made of small molecules.

Results and discussion

To prepare the functional LMWP, we synthesized a new CTA (chain transfer agent, Scheme S1, characterization in Fig. S1-S4) with two Np groups. In the following RAFT (Reversible Addition-Fragmentation chain-Transfer) polymerization, short hydrophilic polymers with two Np ends were obtained. As shown in Scheme 2, the two model LMWPs, Np-PDMA-Np (**P1**, Scheme S2, $M_n = 5.5 \times 10^3$ g/mol) and Np-PNIPAm-Np (**P2**, Scheme S3, $M_n = 7.0 \times 10^3$ g/mol) are synthesized with

designed low DP (degree of polymerization) and narrow molecular weight distribution (PDI < 1.2), characterized by GPC (Gel Permeation Chromatography) with PEG as standard (Fig. S5-6). The effective incorporation of Np groups at both chain ends of the two homopolymers was assessed by ^{1}H NMR (Fig. S7 and S8), showing excellent accordance between the DP calculated by ^{1}H NMR (relative integration of polymer backbone protons to that of Np, 52 for **P1** and 56 for **P2**) and the theoretical values. Further structural confirmation was achieved by aminolysis reaction of **P1** or **P2** with their chain-cleavage products characterized by GPC (Fig. S5-6). A small ditopic guest **3** was obtained through a two-step ionization of nitrogen in viologen (Scheme S4, ^{1}H NMR shown in Fig. S9). For control experiments, mono-topic guest **4** was also synthesized (^{1}H NMR shown in Fig. S10). It should be noted that the solubility of CB[8] in water is very limited, while **P1**, **P2**, **3**, and **4** are water-soluble, which can enhance the water solubility of CB[8] after complexation.
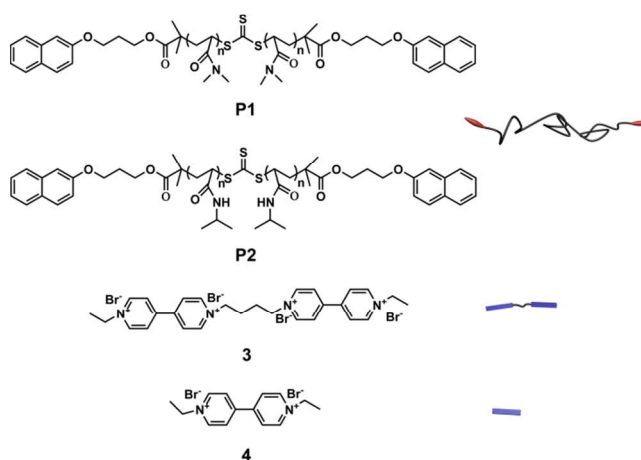
Scheme 2. Chemical structure of the building blocks involved in the construction of MSP.

With these components in hand, the HSCT interaction at the end of LMWP chain was first tested by UV-vis spectra. It is known that the CB[8]-Np-viologen ternary complex based on HSCT exhibits a CT absorption band between 400 and 500 nm in UV-vis spectra[43]. Indeed, in the current polymeric case, as shown in Fig. 1a, the UV-vis spectra of **P1** (red line) and **3** (black line) alone had no appreciable absorption band beyond 400 nm, while their equal molar mixture (**P1**+**3**, blue line) only showed a slight increase in this area, indicating a very weak CT interaction between **P1** and **3**. However, after addition of 2 equiv. of CB[8] to the mixture of **P1**+**3** (**P1**:**3**:CB[8] = 1:1:2), this CT absorption band was greatly enhanced with concomitant emergence of another CT band beyond 500 nm (cyan line), indicating the formation of a ternary complex. The complex is denoted as **P1**+**3**⊂CB[8] with its stoichiometry of binding determined by a Job's plot (Fig. 1b). Here, CB[8] was mixed with **3** in 2:1 molar ratio to form **3**⊂CB[8] complex first, in order to dissolve as much as CB[8] in water. Then **3**⊂CB[8] and **P1** were mixed together with their total concentration fixed at 0.25 mM in the range of the molar ratio of **P1** varied from 0 to 1. The absorption at 495 nm was plotted, showing the

maximum absorbance at the point of 0.5, which indicated the stoichiometry of binding between **P1** and **3**⊂CB[8] was 1:1. In a control experiment, **4** was used instead of **3** where **4**⊂CB[8] first formed in a 1:1 molar ratio. The result of Job's experiment of **4**⊂CB[8] and **P1** showed that the maximum absorption appeared when the ratio of **P1** reached 0.37, which was close to the calculated 0.33 for 1:2 stoichiometry of **P1** to **4**⊂CB[8] (Fig. S11). Above experimental results show that Np groups connecting to the polymer chain does not affect its complexation ability with viologen in CB[8] even in quantitative sense.
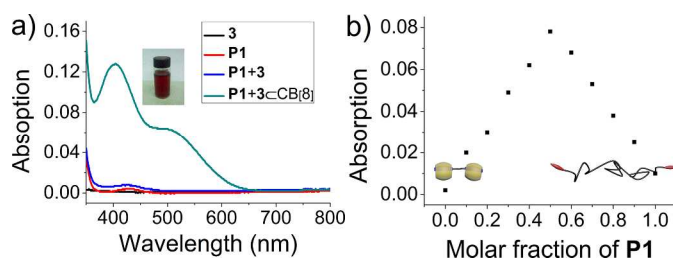

Fig. 1. (a) UV-Vis spectra of **P1**, **3**, **P1**+**3**, and **P1**+**3**⊂CB[8] (**P1**: 0.125 mM, **3**: 0.125 mM, CB[8]: 0.25 mM). (b) Job's plot of **P1** and **3**⊂CB[8] (total concentration of **P1** and **3**⊂CB[8] fixed at 0.25 mM, absorption intensity measured at 495 nm).

The binding behavior forming the ternary complex was further measured by ITC (isothermal titration calorimetry). In the experiment, aqueous solution of **P1** (0.5 mM) was continuously titrated into the solution of **3**⊂CB[8] (0.05 mM, calculated as **3**). The generated heat fits well to the one-set binding mode (Fig. S12a) after calculation, showing an experimental n value of 1.0, which was consistent with the result from the Job's plot (Fig. 1b). Meanwhile, the binding constant of **P1** and **3**⊂CB[8] was calculated as 8.15×10^5 M^{-1}, comparable to the value reported at the small molecular level[49]. As a control experiment, the binding of **P1** to **4**⊂CB[8] was also measured by ITC, which showed an experimental n value of 0.4 (Fig. S12b), close to the expected n value of 0.5. From the above results, we may expect the supramolecular chain extension of **P1** mediated by HSCT interactions.
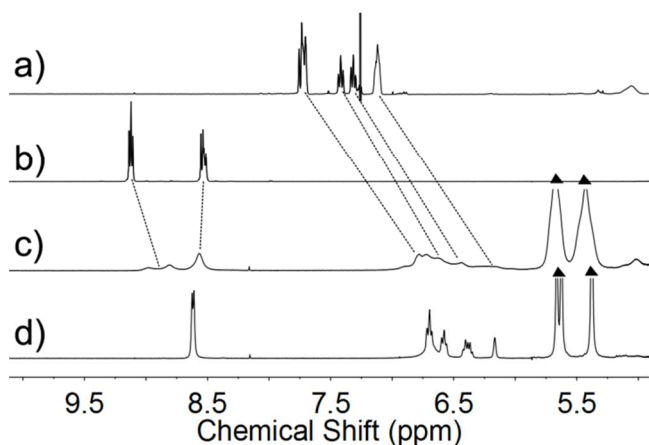

Fig. 2. ^{1}H NMR spectra of (a) **P1** (in CDCl$_3$), (b) **3**, (c) **P1**+**3**⊂CB[8] and (d) **P1**+**4**⊂CB[8] in D$_2$O (Triangle: peaks

belong to CB[8]). Concentrations: **P1** (4 mM), **3** (4 mM), CB[8] (8 mM) and **4** (8 mM).

^{1}H NMR was employed to study the molecular state of **P1**+**3**⊂CB[8]. After addition of CB[8] to the mixture of **P1** and **3** (Fig. 2c), the peaks related to viologen and Np groups underwent pronounced shifts, indicating that the two groups were captured by CB[8]. The mixture of **P1** with 2 equiv. of **4**⊂CB[8] was expected to form an end-modified LMWP as a control sample, which is denoted as **P1**+**4**⊂CB[8]. As shown in Fig. 2, clear difference in the proton signals was observed in the spectra of **P1**+**3**⊂CB[8] and **P1**+**4**⊂CB[8], i.e. the signal in the former was obviously broadened and weakened than that in the latter, indicating the feature of long polymeric chain in the former. Similar phenomenon was found for SPs formed by small molecules[20,50].
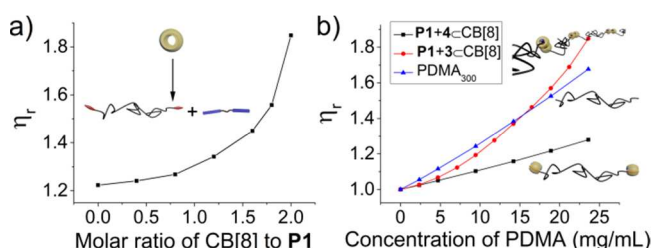

Fig. 3. (a) Relative viscosity of the mixture of **P1** and **3** (4 mM) with different molar ratios of CB[8] to **P1** (20 °C in H$_2$O). (b) Relative viscosity of **P1**+**3**⊂CB[8], **P1**+**4**⊂CB[8] and covalent polymer PDMA$_{300}$ *vs* their weight concentration of PDMA segments in water at 20 °C.

High viscosity is one of the macroscopic characteristics of traditional polymer in solution, thus the formation of MSPs of **P1**+**3**⊂CB[8] could be directly demonstrated by viscometry. The viscosity of **P1**+**3**⊂CB[8] was plotted against the concentration of CB[8] (Fig. 3a). When CB[8] was gradually added to the 1:1 mixture of **P1** and **3** (4 mM), the relative viscosity of the complex first increased slowly. Then the increase rate became faster after the ratio of CB[8]/**P1** exceeded 1. The maxium viscosity appeared at the molar ratio of 2, i.e. equal molar ratio of CB[8], Np and viologen. Thereby, the stoichiometric ratio of the three is a crucial factor leading to long extended chains, which is similar to the feature of condensation polymerization[40]. Meanwhile, this process was accompanied by the transmittance decrease (Fig. S13), suggesting the formation of large particles upon supramolecular chain extension of LMWP, which will be discussed in detail later. In Fig. 3b, the relative viscosity of the **P1**+**3**⊂CB[8] solution was plotted against concentration of DMA with **P1**+**4**⊂CB[8] as a control. At very low concentrations, the relative viscosity of **P1**+**3**⊂CB[8] (red line) was comparative to that of **P1**+**4**⊂CB[8] (black line), indicating the majority was the unconnected LMWPs in the mixture of **P1**+**3**⊂CB[8]. When the concentration was increased (> 9.4 mg/mL, calculated as **P1**), the viscosity increase of **P1**+**3**⊂CB[8] solution was much faster than that of **P1**+**4**⊂CB[8], indicating the formation of extended polymer chains. Furthermore, when **4** was added as a competitive guest to the above MSP solution of **P1**+**3**⊂CB[8]

with the relatively high viscosity, the viscosity drastically decreased, showing the dynamic nature of **P1**+**3**⊂CB[8] polymer (Fig. S14). To semi-quantitatively estimate the M_w and DP of the resultant extended polymeric chain in solution, a
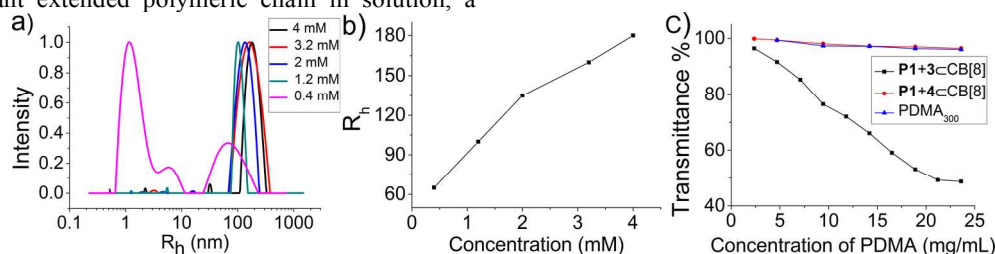
traditional polymer PDMA$_{300}$ (DP 300, PDI 1.21, GPC result in Fig. S15) was used as reference. From Fig. 3b, where PDMA$_{300}$ and **P1**+**3**⊂CB[8] kept the same concentration of DMA,

Fig. 4. (a) $<R_h>$ distribution of the **P1**+**3**⊂CB[8] complex at different concentrations. (b) Dependence of $<R_h>$ of the large peak on concentration. (c) Transmittance (data collected at 800 nm) of **P1**+**3**⊂CB[8], **P1**+**4**⊂CB[8] and PDMA$_{300}$ at different concentrations.

it was found that the viscosity of PDMA$_{300}$ was slightly higher than that of **P1**+**3**⊂CB[8] at low concentrations (< 15 mg/mL), but the latter showed much higher viscosity than PDMA$_{300}$ at high concentrations (> 15 mg/mL), with the cross point at around 15.5 mg/mL. Based on this result, the supramolecular chain extension of **P1** (DP 52) in the mixture of **P1**+**3**⊂CB[8] was confirmed with its viscosity higher than that of the traditional polymer with DP 300. In addition, it is known that the viscosity variation of SP is generally non-linear with the concentration of its monomers[26]. In the current MSP case, the observed viscosity variation of **P1**+**3**⊂CB[8] complex with the concentration 25 mg/mL (calculated as DMA) is different from both its covalent counterpart and the control polymer, showing its supramolecular nature. However, at the highest concentration we measured, the viscosity of **P1**+**3**⊂CB[8] is only slightly higher than that of PDMA$_{300}$. This is understandable due to the dynamic nature of supramolecularly extended chain, i.e. equilibrium always exists between the monomer, oligomers and supramolecular long chains[48].

To examine the structure of the obtained MSP in detail, the solution behavior of **P1**+**3**⊂CB[8] ternary complex was measured by DLS. The mixture of **P1** and **3** (4 mM each) without CB[8] gave an $<R_h>$ (hydrodynamic radius) value around 3 nm as a common synthetic polymer (Fig. S16), indicating the absence of interactions between **P1** and **3**. However, when CB[8] was added, even the concentration of **P1**+**3**⊂CB[8] was as low as 0.4 mM, large particles ($<R_h>$ = 60 nm) were found in the system with co-existence of smaller ones with $<R_h>$ less than 10 nm (Fig. 4a). When the concentration of **P1**+**3**⊂CB[8] was increased to 1.2 mM, the small peaks disappeared and the large peak remained and grew. This large peak even shifted to a much larger $<R_h>$ value as the **P1**+**3**⊂CB[8] concentration further increased (Fig. 4b). Meanwhile, data from turbidity test supported this DLS result. As the concentration of **P1**+**3**⊂CB[8] was increased from 2.4 mg/mL to 23.6 mg/mL (calculated as **P1**), the transmittance of the solution kept decreasing, indicating the formation of large particles (Fig. 4c). However, transmittance of the two control samples, i.e. PDMA$_{300}$ and **P1**+**4**⊂CB[8], almost remained constant, proving that the formation of large particles was related to the supramolecular chain extension of the LMWP.

Temperature-sensitive supramolecular polymers were constructed via the same strategy. Here **P2**, i.e. LMWP PNIPAm as backbone was employed to form **P2**+**3**⊂CB[8] ternary complex. Similarly, obvious viscosity enhancement of **P2**+**3**⊂CB[8] vs concentration was observed (Fig. S17), which was distinctive to that of the control **P2**+**4**⊂CB[8] (**P2**:**4**:CB[8] = 1:2:2). The relative viscosity of **P2**+**3**⊂CB[8] even reached as high as 3.0 at a concentration of 4.5 mM (calculated as **P2**). DLS measurements also supported the formation of aggregates, when concentration of **P2**+**3**⊂CB[8] reached 2.3 mM (Fig. S18), which was similar to the case of **P1**+**3**⊂CB[8] complex (Fig. 4). TEM image revealed the particles of **P2**+**3**⊂CB[8] as random aggregates of MSPs (Fig. S19). The aggregation could be possibly attributed to the tight association between CB[8] themselves, which was observed previously in crystal or supramolecular gel[20,51]. As this aggregation got exposed after MSP formed longer polymeric chain, CB[8] units along the long chains should have a higher local concentration and thus promoted the aggregation. Furthermore, as the aggregation may cause chain collapse and then result in a viscosity decrease, the real polymerization degree of **P1**+**3**⊂CB[8] may be much higher than 300 as estimated from Fig. 3.

PNIPAm is well-known for its thermo-responsive property. Thus MSP based on PNIPAm seems promising to retain this character. Here **P2**+**4**⊂CB[8] was chosen as a control, which had similar chain composition to **P2**+**3**⊂CB[8]. Their LCST behavior was measured at different concentrations. At a rather low concentration (0.2 mg/mL, calculated as **P2**), **P2**+**3**⊂CB[8] exhibited a higher LCST temperature (the temperature at 50% transmittance) than that of **P2**+**4**⊂CB[8] (Fig. 5a). However, when the concentration was increased to 19.8 mg/mL (calculated as **P2**), the LCST temperature of **P2**+**3**⊂CB[8] was observed lower than that of **P2**+**4**⊂CB[8] (Fig. 5b). Their LCST variation vs concentration is shown in Fig. 5c, indicating a sharp LCST decrease from 32 °C to 16 °C of **P2**+**3**⊂CB[8] compared to that of **P2**+**4**⊂CB[8] with a cross point around 1.0 mg/mL. This significant concentration dependence of LCST is unexpected for covalent PNIPAm, where molecular weight or polymer concentration didn't affect LCST singnificantly[52]. A control experiment showed that the HSCT interaction in **P1**+**3**⊂CB[8] solution remained at higher temperature, as shown in Fig. S20 that 90% HSCT absorbance remained when

the temperature was increased from 10 °C to 35 °C. In addition, when **3** (2.8 mM, the highest concentration used in the LCST test) was added to **P2** solution (2 mg/mL), the temperature-dependent phase transition process almost remained (Fig. S21),
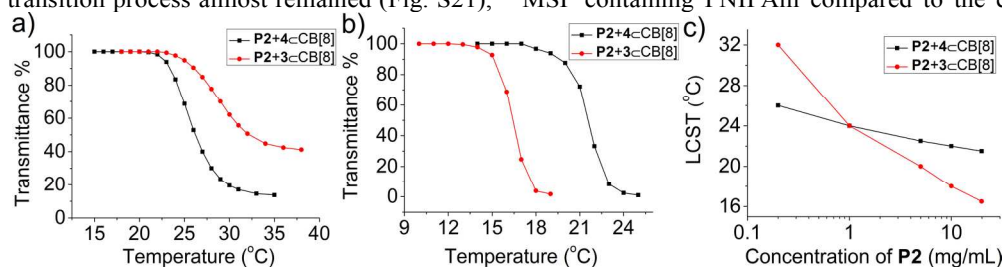
showing that the positive charge from viologen guest did not have significant effect on the phase transition process. Thus our current result indicated very different LCST behavior of the MSP containing PNIPAm compared to the covalent polymer,

Fig. 5. Temperature dependence of optical transmittance at 800 nm obtained for ternary complex **P2**+**4**⊂CB[8] and **P2**+**3**⊂CB[8] at various concentrations of **P2**: (a) 0.2 mg/mL, (b) 19.8 mg/mL. (c) Concentration dependence of LCST of ternary complex **P2**+**4**⊂CB[8] and **P2**+**3**⊂CB[8]. Here LCST is defined as the temperature corresponding to 50% decrease of transmittance.

which might come from the structural difference between **P2**+**3**⊂CB[8], **P2**+**4**⊂CB[8] and covalent PNIPAm. We speculate that here the drastic LCST decrease of **P2**+**3**⊂CB[8] vs concentration is attributed to the aggregation behavior of CB[8]. As mentioned above, the local concentration of CB[8] increased after MSP formed longer polymeric chain, which should facilitate the aggregation of CB[8] together with the PNIPAm. Nevertheless, this is the first LCST behavior observed for supramolecular polymer.

Acknowledgements

Notes and references

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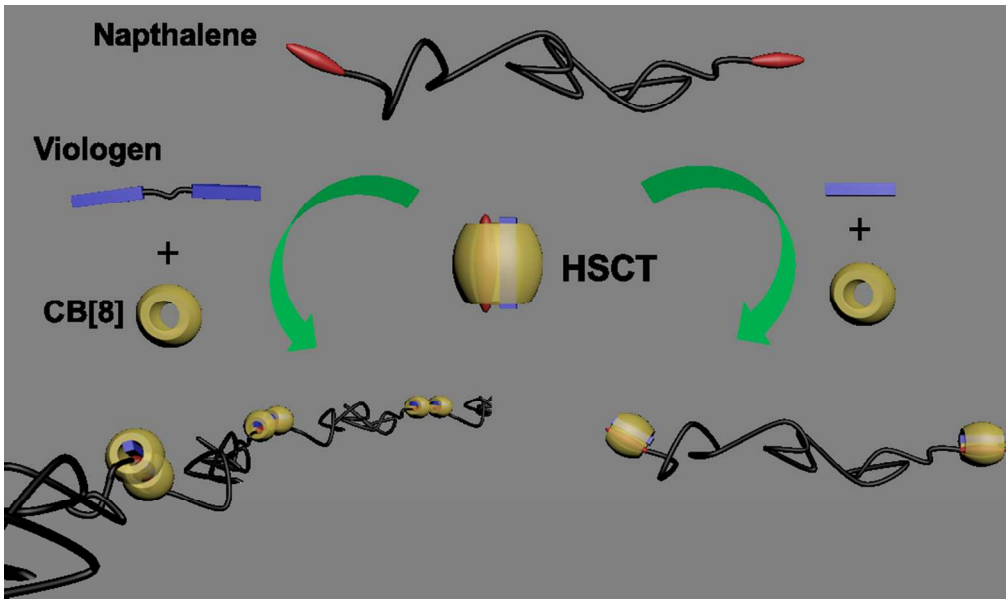
† Electronic Supplementary Information (ESI) available: Experimental details were in the supporting information, including the preparation and characterization of CTA, **P1**, **P2**, **3** and **4**. See DOI: 10.1039/b000000x/

1   C. Fouquey, J. M. Lehn, A. M. Levelut, *Adv. Mater.* 1990, **2**, 254.

2   J. B. Beck, S. J. Rowan, *J. Am. Chem. Soc.* 2003, **125**, 13922.

3   M. Miyauchi, A. Harada, *J. Am. Chem. Soc.* 2004, **126**, 11418.

4   P. Cordier, F. Tournilhac, C. Soulie-Ziakovic, L. Leibler, *Nature* 2008, **451**, 977.

5   F. Wang, C. Han, C. He, Q.; Zhou, J. Zhang, C. Wang, N. Li, F. Huang, *J. Am. Chem. Soc.* 2008, **130**, 11254.

6   G. Gröger, W. Meyer-Zaika, C. Böttcher, F. Gröhn, C. Ruthard, C. Schmuck, *J. Am. Chem. Soc.* 2011, **133**, 8961.

7   L. Zhu, M. Lu, Q. Zhang, D. Qu, H. Tian, *Macromolecules* 2011, **44**, 4092.

8   D. S. Guo, Y. Liu, *Chem. Soc. Rev.* 2012, **41**, 5907.

9   S. L. Li, T. Xiao, C. Lin, L. Wang, *Chem. Soc. Rev.* 2012, **41**, 5950.

10 Y. J. Wang, L. M. Tang, *Prog. Chem.* 2006, **18**, 308.

11 F. Wang, S. Y. Dong, B. Zheng, F. H. Huang, *Acta. Polym. Sin.* 2011, **9**, 956.

12 U. S. Schubert, C. Eschbaumer, *Angew. Chem. Int. Ed.* 2002, **41**, 2892.

13 J. M. Lehn, *Polym. Int.* 2002, **51**, 825.

14 M. Fathalla, C. M. Lawrence, N. Zhang, J. L. Sessler, J. Jayawickramarajah, *Chem. Soc. Rev.* 2009, **38**, 1608.

15 Z. Chen, A. Lohr, C. R. Saha-Moller, F. Würthner, *Chem. Soc. Rev.* 2009, **38**, 564.

16 M. Hasegawa, M. Iyoda, *Chem. Soc. Rev.* 2010, **39**, 2420.

17 A. Harada, Y. Takashima, H. Yamaguchi, *Chem. Soc. Rev.* 2009, **38**, 875.

18 B. Zheng, F. Wang, S. Dong, F. Huang, *Chem. Soc. Rev.* 2012, **41**, 1621.

19 T. F. A. De Greef, M. M. J. Smulders, M. Wolffs, A. P. H. J. Schenning, R. P. Sijbesma, E. W. Meijer, *Chem. Rev.* 2009, **109**, 5687.

20 Y. Liu, Y. Yu, J. Gao, Z. Wang, X. Zhang, *Angew. Chem. Int. Ed.* 2010, **49**, 6576.

21 W. H. Binder, L. Petraru, T. Roth, P. W. Groh, V. Pálfi, S. Keki, B. Ivan, *Adv. Funct. Mater.* 2007, **17**, 1317.

22 B. J. B. Folmer, R. P. Sijbesma, R. M. Versteegen, J. A. J. van der Rijt, E. W. Meijer, *Adv. Mater.* 2000, **12**, 874.

23 Z. Ge, J. Hu, F. Huang, S. Liu, *Angew. Chem. Int. Ed.* 2009, **48**, 1798.

24 R. P. Sijbesma, F. H. Beijer, L. Brunsveld, B. J. B. Folmer, J. H. K. K. Hirschberg, R. F. M. Lange, J. K. L. Lowe, E. W. Meijer, *Science* 1997, **278**, 1601.

25 H. Hofmeier, R. Hoogenboom, M. E. L. Wouters, U. S. Schubert, *J. Am. Chem. Soc.* 2005, **127**, 2913.

26 T. Park, S. C. Zimmerman, *J. Am. Chem. Soc.* 2006, **128**, 13986.

27 M. Burnworth, L. Tang, J. R. Kumpfer, A. J. Duncan, F. L. Beyer, G. L. Fiore, S. J. Rowan, C. Weder, *Nature* 2011, **472**, 334.

28 S. Abed, S. Boileau, L. Bouteiller, *Macromolecules* 2000, **33**, 8479.

29 G. B. W. L. Ligthart, H. Ohkawa, R. P. Sijbesma, E. W. Meijer, *J. Am. Chem. Soc.* 2004, **127**, 810.

30 C. P. Lillya, R. J. Baker, S. Hutte, H. H. Winter, Y. G. Lin, J. Shi, L. C. Dickinson, J. C. W. Chien, *Macromolecules* 1992, **25**, 2076.

31 S. Zou, H. Schönherr, G. J. Vancso, *Angew. Chem. Int. Ed.* 2005, **44**, 956.

32 D. Knapton, S. J. Rowan, C. Weder, *Macromolecules* 2005, **39**, 651.

33 J. R. Kumpfer, J. Jin, S. J. Rowan, *J. Mater. Chem.* 2010, **20**, 145.

34 J. M. J. Paulusse, R. P. Sijbesma, *Angew. Chem. Int. Ed.* 2004, **116**, 4560.

35 S. Schmatloch, A. M. J. van den Berg, A. S. Alexeev, H. Hofmeier, U. S. Schubert, *Macromolecules* 2003, **36**, 9943.

36 S. K. Yang, A. V. Ambade, M. Weck, *Chem. Eur. J.* 2009, **15**, 6605.

37 S. Burattini, B. W. Greenland, D. H. Merino, W. Weng, J. Seppala, H. M. Colquhoun, W. Hayes, M. E. Mackay, I. W. Hamley, S. J. Rowan, *J. Am. Chem. Soc.* 2010, **132**, 12051.

38 Z. Ge, H. Liu, Y. Zhang, S. Liu, *Macromol. Rapid Commun.* 2011, **32**, 68.

39 Y. Hasegawa, M. Miyauchi, Y. Takashima, H. Yamaguchi, A. Harada, *Macromolecules* 2005, **38**, 3724.

40 Y. Liu, R. Fang, X. Tan, Z. Wang, X. Zhang, *Chem. Eur. J.* 2012, **18**, 15650.

41 Y. Xu, M. Guo, X. Li, A. Malkovskiy, C. Wesdemiotis, Y. Pang, *Chem. Commun.* 2011, **47**, 8883.

42 J. J. Reczek, A. A. Kennedy, B. T. Halbert, A. R. Urbach, *J. Am. Chem. Soc.* 2009, **131**, 2408.

43 Y. H. Ko, E. Kim, I. Hwang, K. Kim, *Chem. Commun.* 2007, 1305.

44 E. A. Appel, F. Biedermann, U. Rauwald, S. T. Jones, J. M. Zayed, O. A. Scherman, *J. Am. Chem. Soc.* 2010, **132**, 14251.

45 J. Zhang, R. J. Coulston, S. T. Jones, J. Geng, O. A. Scherman, C. Abell, *Science* 2012, **335**, 690.

46 K. Kim, D. Kim, J. W. Lee, Y. H. Ko, K. Kim, *Chem. Commun.* 2004, 848.

47 Y. H. Ko, K. Kim, J. K. Kang, H. Chun, J. W. Lee, S. Sakamoto, K. Yamaguchi, J. C. Fettinger, K. Kim, *J. Am. Chem. Soc.* 2004, **126**, 1932.

48 J. del Barrio, P. N. Horton, D. Lairez, G. O. Lloyd, C. Toprakcioglu, O. A. Scherman, *J. Am. Chem. Soc.* 2013, **135**, 11760.

49 U. Rauwald, F. Biedermann, S. P. Deroo, C. V. Robinson, O. A. Scherman, *J. Phys. Chem. B* 2010, **114**, 8606.

50 Q. Yan, A. Feng, H. Zhang, Y. Yin, J. Yuan, *Polymer Chemistry* 2013, **4**, 1216.

51 I. Hwang, W. S. Jeon, H. J. Kim, D. Kim, H. Kim, N. Selvapalam, N. Fujita, S. Shinkai, K. Kim, *Angew. Chem. Int. Ed.* 2007, **46**, 210.

52 S. Furyk, Y. Zhang, D. Ortiz-Acosta, P. S. Cremer, D. E. Bergbreiter, *J. Polym. Sci., Part A: Polym. Chem.* 2006, **44**, 1492.

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