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A polymeric chain extension driven by HSCT interaction†

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In this paper, targeting a high-molecular-weight supramolecular polymer, the chain extension of low-molecular-weight polymers (LMWPs) is achieved *via* the 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 naphthalene (Np)-ended LMWP PDMA or PNIPAm. UV-vis spectra, ITC and NMR prove that the guest Np connected to the LMWP does not affect its complexation with guest viologen and CB[8]. The viscosity measurements clearly demonstrate the formation of a supramolecular polymer, as the viscosity of the LMWP PDMA (DP 52) after complexation exceeds that of PDMA (DP 300). Np-ended LMWP PNIPAm shows a similar chain extension. The resultant PNIPAm supramolecular polymer shows peculiar LCST behavior with a remarkably different variation in concentration from its polymeric precursor.

Introduction

Supramolecular polymers (SPs), as a newly emerging type of polymer architecture, feature non-covalent linkages between monomers instead of the covalent bonds in traditional polymers. In the past decade, the research field of SPs grew dramatically with remarkable achievements.[1–11] Compared to traditional polymers, SPs have great advantages in controllable degradability, self-healing and processability because of the dynamic nature of the non-covalent bonds. To date, metal–ligand,[12] hydrogen bonding,[13,14] π–π[15,16] and host–guest interactions[17,18] are all involved in constructing SPs. Most SP chains are constructed from small molecules, because of the synthetic accessibility and the significant contrast of the 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 linkages) have been developed to construct SPs with special designs.[19] It has been reported that an appropriate spacer between the reactive groups, together with charge repulsion, can suppress the formation of cyclic species.[20]

However, there is still much room for the development of SPs. The versatility of traditional polymers stems from the tunability of their crystallinity, mechanical strength and thermal stability, which is still unattainable by SPs due to their limited chemical structures. Currently, a practical way to build

SPs with more "polymeric" properties has emerged, in which covalent low-molecular-weight polymers (LMWPs), instead of small molecules, are used as building blocks. A few such SPs composed of LMWPs by supramolecular chain extension (*i.e.* macro-supramolecular polymers, MSPs) have been reported.[21–25] For example, a MSP with a multi-block copolymer structure composed of two different kinds of polymeric "monomers" bearing hydrogen bond donors or acceptors 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 polymers as building blocks is still quite limited compared to SPs constructed from small molecules,[28–37] and of which, attention is rarely paid to host–guest interactions.[23,38,39]

Using LMWPs as building blocks of SPs exhibits some advantages over the use of small molecules. It has been shown that the polymeric precursor could facilitate the extension of supramolecular chains by suppressing the possibility of ring closure.[26,29] Moreover, SPs constructed from small molecules include a high content of functional groups, resulting in limited solvent solubility.[25] This drawback, which may hinder the further application of SPs, is more pronounced in some host–guest systems. For example, SPs resulting from 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 the popular host molecules, CB[n] (n = 5–10), a family of highly symmetrical pumpkin-shaped molecules, has variably-sized cavities accessible by certain guests through hydrophobic and ion–dipole interactions.[41] CB[8] is an

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outstanding member of 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 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 oligomers,[46,47] followed by the first SP built from small molecules by Zhang *et al.*[20] and, very recently a crystal structure of CB[8]-mediated SP was obtained by Scherman *et al.*[48] However, all of these remarkable SPs based on HSCT were developed from small molecules, where LMWP was not involved.

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

Results and discussion

To prepare the functional LMWPs, we synthesized a new CTA (chain transfer agent, Scheme S1,† characterization in
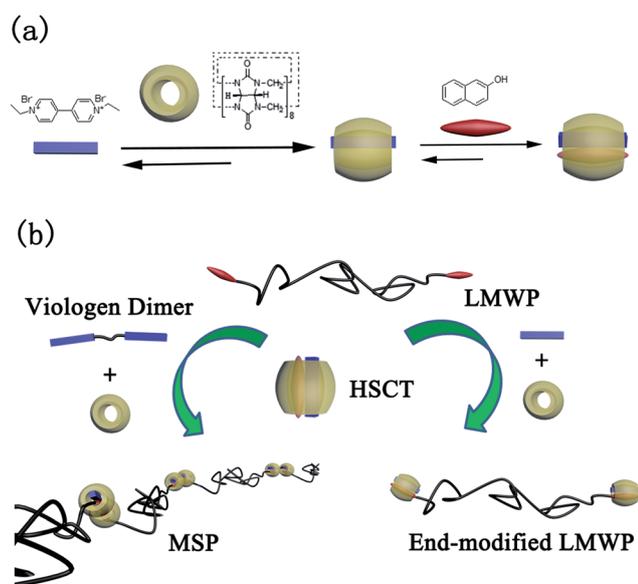
Scheme 1 Schematic representation of (a) the two-step binding process of cucurbit[8]uril in water. (b) Preparation of MSPs and end-modified LMWPs through the addition of CB[8] and an electron-deficient first guest (viologen dimer and viologen, respectively) to the Np-ended LMWPs.

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^{-1}) and Np–PNIPAm–Np (**P2**, Scheme S3,† $M_n = 7.0 \times 10^3$ g mol^{-1}) were synthesized with a designed low DP (degree of polymerization) and narrow molecular weight distribution (PDI < 1.2), and characterized by GPC (Gel Permeation Chromatography) with PEG as the standard (Fig. S5 and S6†). 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 the aminolysis reaction of **P1** or **P2** with their chain-cleavage products, characterized by GPC (Fig. S5 and 6†). A small ditopic guest **3** was obtained through the two-step ionization of nitrogen in viologen (Scheme S4,† ^{1}H NMR shown in Fig. S9†). For control experiments, the monotopic 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.

With these components in hand, the HSCT interactions at the end of the LMWP chains was first examined 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 example, as shown in Fig. 1a, the UV-vis spectra of **P1** (red line) and **3** (black line) alone had no appreciable absorption bands beyond 400 nm, while their equimolar 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 the 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 the concomitant emergence of another CT band beyond 500 nm (cyan line), indicating the formation of a ternary complex. The
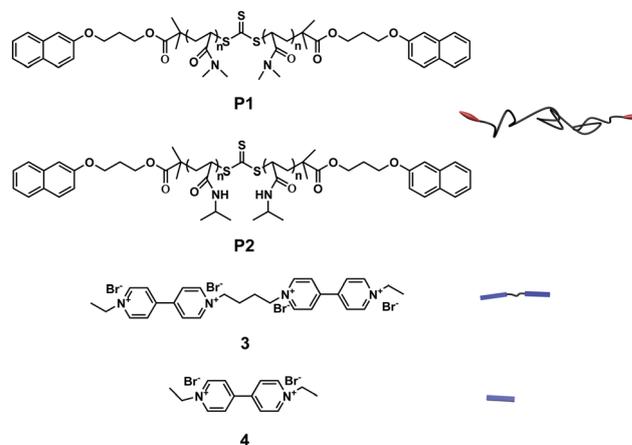
Scheme 2 Chemical structure of the building blocks involved in the construction of MSPs.
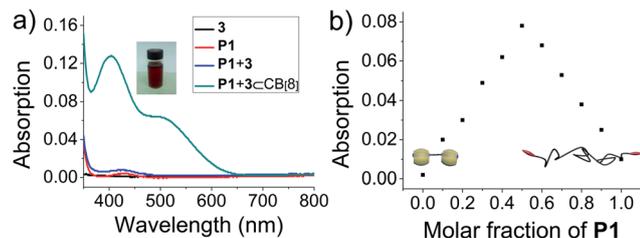
Fig. 1 (a) UV-vis spectra of **P1**, **3**, **P1** + **3** and **P1** + **3**⊂CB[8] (**P1**: 0.125 mM, **3**: 0.125 mM, CB[8]: 0.25 mM). (b) Job's plot of **P1** and **3**⊂CB[8] (total concentration of **P1** and **3**⊂CB[8] was fixed at 0.25 mM, absorption intensity measured at 495 nm).

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

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 a 2 : 1 molar ratio to form the **3**⊂CB[8] complex first, in order to dissolve as much of CB[8] in water as possible. 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** varying from 0 to 1. The absorption at 495 nm was plotted, showing the maximum absorbance at a molar ratio of 0.5, which indicated that 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 for **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 the 1 : 2 stoichiometry of **P1** to **4**⊂CB[8] (Fig. S11†). The above experimental results show that Np groups connecting to the polymer chain do not affect its complexation ability with viologen in CB[8] even in a quantitative sense.

The binding behavior forming the ternary complex was further measured by ITC (Isothermal Titration Calorimetry). In the experiments, an aqueous solution of **P1** (0.5 mM) was continuously titrated into a 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 is 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.

^{1}H NMR was employed to study the molecular state of **P1** + **3**⊂CB[8]. After the addition of CB[8] to the mixture of **P1** and **3** (Fig. 2c), the peaks related to the 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, a 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
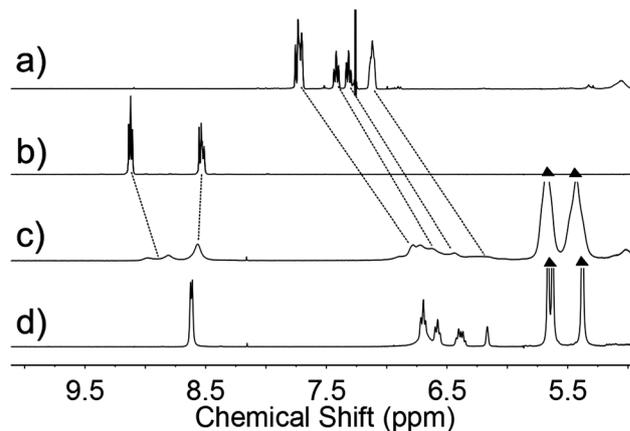
in the latter, indicating the feature of long polymeric chains in the former. A similar phenomenon has been reported for SPs formed from small molecules.[20,50]

High viscosity is one of the macroscopic characteristics of traditional polymers 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 maximum viscosity appeared at the molar ratio of 2, *i.e.* equal molar ratios 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 a transmittance decrease (Fig. S13†), suggesting the formation of large particles upon the supramolecular chain extension of LMWPs, which will be discussed in detail later. In Fig. 3b, the relative viscosity of the **P1** + **3**⊂CB[8] solution was plotted against the concentration of PDMA, 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 that the majority was the unconnected LMWPs in the
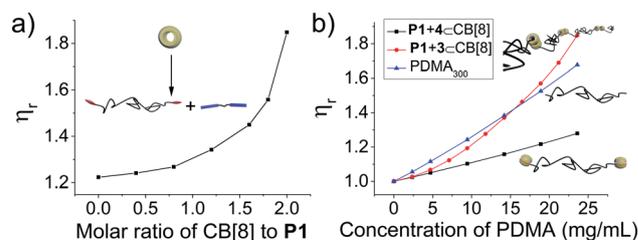

Fig. 3 (a) Relative viscosity of the mixture of **P1** and **3** (4 mM) with different molar ratios of CB[8] to **P1** (20 °C in H$_2$O). (b) Relative viscosity of **P1** + **3**⊂CB[8], **P1** + **4**⊂CB[8] and covalent polymer PDMA$_{300}$ *vs.* the weight concentration of PDMA segments in water at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

mixture of **P1** + **3**⊂CB[8]. When the concentration was increased (>9.4 mg mL^{-1}, calculated as **P1**), the viscosity increase of the **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 a relatively high viscosity, the viscosity drastically decreased, showing the dynamic nature of the **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 a reference. From Fig. 3b, where PDMA$_{300}$ and **P1** + **3**⊂CB[8] kept the same concentration of DMA, 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^{-1}), but the latter showed much higher viscosity than PDMA$_{300}$ at high concentrations (>15 mg mL^{-1}), with the cross point at around 15.5 mg mL^{-1}. 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 SPs is generally non-linear with the concentration of its monomers.[26] With the current MSPs, the observed viscosity variation of the **P1** + **3**⊂CB[8] complex with a concentration of 25 mg mL^{-1} (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 chains, *i.e.* an 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 the **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 of around 3 nm, that of a common synthetic polymer (Fig. S16†), indicating the absence of interactions between **P1** and **3**. However, when CB[8] was added, even when 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 the co-existence of smaller particles 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 the turbidity tests supported this DLS result. As the concentration of **P1** + **3**⊂CB[8] was increased from 2.4 mg mL^{-1} to 23.6 mg mL^{-1} (calculated as **P1**), the transmittance of the solution kept decreasing, indicating the formation of large particles (Fig. 4c). However, the 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 LMWPs.

Temperature-sensitive supramolecular polymers were constructed *via* the same strategy. Here, **P2**, *i.e.* LMWP PNIPAm as the backbone was employed to form the **P2** + **3**⊂CB[8] ternary complex. Similarly, an 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 the **P1** + **3**⊂CB[8] complex (Fig. 4). The TEM image revealed the particles of **P2** + **3**⊂CB[8] as random aggregates of MSPs (Fig. S19†). The aggregation could be attributed to the tight association between CB[8] themselves, which was observed previously in crystals and supramolecular gels.[20,51] As this aggregation was exposed after the MSPs formed longer polymeric chains, CB[8] units along the long chains should have a higher local concentration and thus promote 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 properties. Thus, MSPs based on PNIPAm seem promising to retain this character. Here, **P2** + **4**⊂CB[8] was chosen as a control, which had a 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^{-1}, 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^{-1} (calculated as **P2**), the LCST temperature of **P2** + **3**⊂CB[8] was observed to be lower than that of **P2** + **4**⊂CB[8] (Fig. 5b). Their LCST variation *vs.* concentration is shown in Fig. 5c,
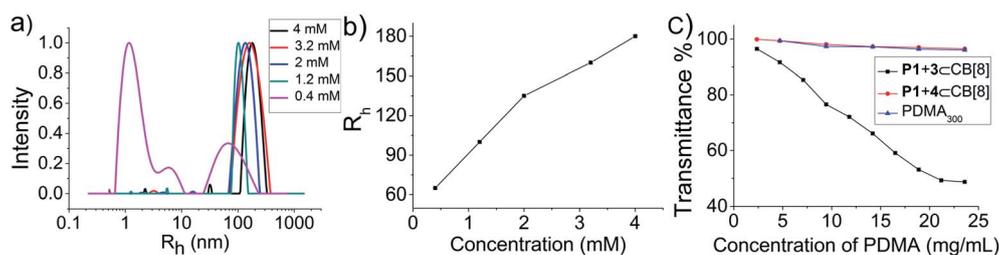

Fig. 4 (a) <R_h> distribution of the **P1** + **3**⊂CB[8] complex at different concentrations. (b) Dependence of <R_h> of the large peak on concentration. (c) Transmittance (data collected at 800 nm) of **P1** + **3**⊂CB[8], **P1** + **4**⊂CB[8] and PDMA$_{300}$ at different concentrations.
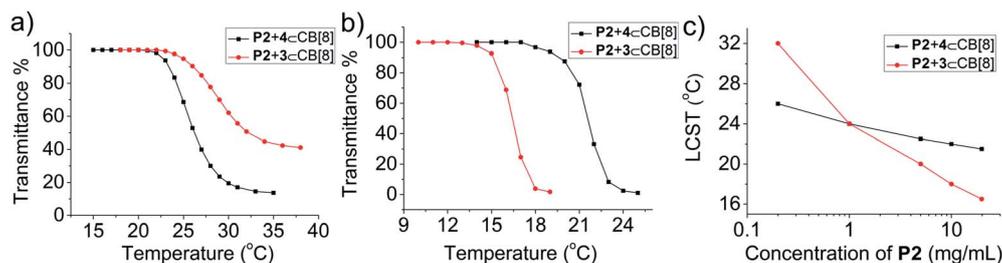
Fig. 5 Temperature dependence of the optical transmittance at 800 nm obtained for ternary complexes **P2** + **4**⊂CB[8] and **P2** + **3**⊂CB[8] at various concentrations of **P2**: (a) 0.2 mg mL^{-1}, (b) 19.8 mg mL^{-1}. (c) Concentration dependence of the LCST of ternary complexes **P2** + **4**⊂CB[8] and **P2** + **3**⊂CB[8]. Here LCST is defined as the temperature corresponding to a 50% decrease of the transmittance.

indicating a sharp LCST decrease of **P2** + **3**⊂CB[8] from 32 °C to 16 °C compared to that of **P2** + **4**⊂CB[8], with a cross point at around 1.0 mg mL^{-1}. This significant concentration dependence of the LCST is unexpected for covalent PNIPAm, where the molecular weight or polymer concentration did not affect the 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,† as 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^{-1}), the temperature-dependent phase transition process almost remained (Fig. S21†), showing that the positive charge from the viologen guest did not have a significant effect on the phase transition process. Thus our current results indicate very different LCST behavior of the MSPs containing PNIPAm compared to the covalent polymer, which might come from the structural differences between **P2** + **3**⊂CB[8], **P2** + **4**⊂CB[8] and covalent PNIPAm. We speculate that 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 the MSPs formed longer polymeric chains, which should facilitate the aggregation of CB[8] together with the PNIPAm. Nevertheless, this is the first LCST behavior observed for supramolecular polymers.

Conclusion

The SP formed in this way from LMWP PDMA (DP 52) shows a higher viscosity than the reference of high MW PDMA (DP 300), which indicates the success of extending polymer chains *via* such HSCT interactions. Furthermore, when PNIPAm was used as a building block, the resultant SP not only inherited the LCST properties of PNIPAm but also showed an apparent effect on the LCST values. This method is expected to be a general strategy to extend polymer chains.

Acknowledgements

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