Electronic Supplementary Material (ESI) for Polymer Chemistry.

Polymeric Crown Ethers: LCST behavior in Water and Stimuli-Responsiveness

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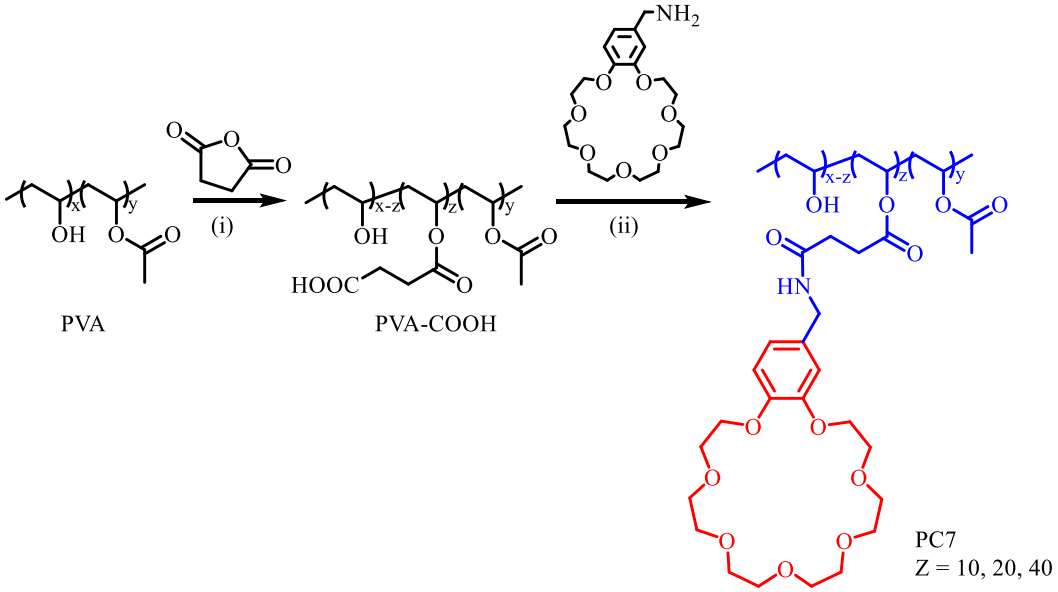
Supporting Information (4 pages)

1. Materials and methods

Succinic anhydride, triethylamine, 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide (EDC), and N-hydroxysuccinimide (NHS) were commercially available and used as received. Poly(vinyl alcohol) (PVA, Mowiol 3−85, M_n = 14000 g/mol) was kindly provided from Kuraray Europe GmbH (Germany). Benzo-21-crown-7 (B21C7) with an amine group was prepared *via* a reported method.[S1] UV/Vis spectra were recorded on a Lambda 950 UV/Vis/NIR spectrometer with a temperature control device at a wavelength at 550 nm. Gel-permeation chromatography (GPC) was carried out on a Shimadzu-GPC/HPLC machine equipped with three PSS Polarsil columns and a differential refractive-index detector using DMF with 3.0 g/L of LiBr and 6.0 g/L of acetic acid as an eluent at a flow rate of 1 mL/min. Cloud points were defined as the temperatures at which the transmittance decreased by 50% (550 nm).

2. Synthesis of B21C7-functionalized PVA

The synthesis of benzo-21-crown-7 functionalized PVA (PC7) was carried out in two steps. In brief, PVA (1.00 g, 18.21 mmol of OH groups) was dissolved in anhydrous DMSO (100 mL) with a catalytic amount of Et_3N, and then succinic anhydride was added into the PVA solution. PVA with COOH functionalities of 5% (PVA-$COOH_{5\%}$), 10% (PVA-$COOH_{10\%}$), and 15% (PVA-$COOH_{15\%}$) were prepared by adding 91.0 mg (0.91 mmol), 182.0 mg (1.82 mmol), and 273.0 mg (2.73 mmol) of succinic anhydride, respectively. After the overnight reaction, polymers were isolated by dialysis in methanol and precipitation in diethyl ether. The white solid was dissolved in Milli-Q water and freeze-dried. The conjugation of benzo-21-crown-7 units to PVA-COOH was carried out *via* carbodiimide chemistry. A quantitative amount of EDC and NHS was added to the PVA-COOH polymer solution in DMSO. After 30 min, an excessive amount of benzo-21-crown-7 with an amine group was added into the solution. The reaction was then allowed to proceed with overnight stirring at room temperature. The polymers were isolated by dialysis in methanol for 48 h and precipitation in diethyl ether. The white precipitate was dissolved in cold Milli-Q water and freeze-dried to give white solids.



Scheme S1. Synthesis of B21C7-functionized PVA: (i) succinic anhydride, DMSO, Et_3N, room temperature, overnight; (ii) B21C7 with an amine group, EDC, NHS, DMSO, room temperature, 48 h.

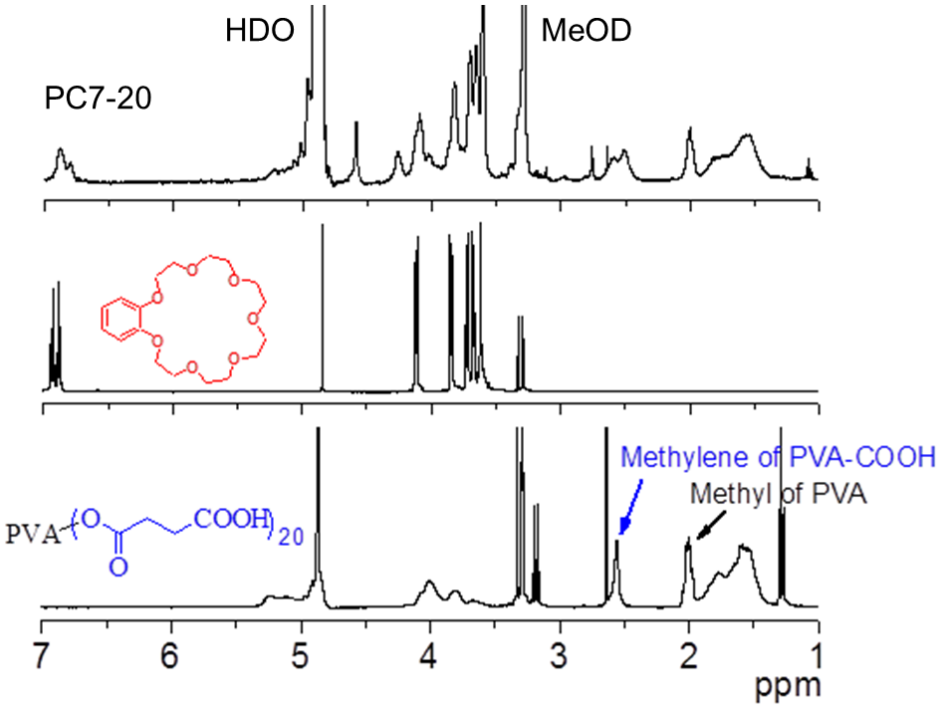


Figure S1. ^{1}H NMR characterization (400 MHz, CD_3OD, 298 K) of carboxyl-functionalized (PVA-COOH) and B21C7-functionalized PVA (PC7-20). The amount of crown ether moiety was calculated according to the integral ratio of the signals at δ 7.00–6.70 and 2.00, which belong to the phenyl groups of crown ether and the methyl groups of unhydrolyzed vinyl acetate (15%) on PVA, respectively.

3. Modeling the phase transition data

To get insight into the K^+-induced LCST phase transition behavior, Stage 2 and 3 were investigated by Eq. 1, which includes a constant, a modified binding isotherm, and a linear term.[S2]

$$T = T_0 + c[M] + (B_{max}[M]e^{-b[M]})/(K_d + e^{-b[M]}) \quad \text{(Eq. 1)}$$

Here, T_0 is the cloud point temperature of PC7 at a KCl concentration of 0.5 mg/mL. Usually the cloud point temperature of salt-free sample is defined as T_0. In this system, we observed three stages and only Stage 2 and 3 fit Eq. 1. Therefore we applied the cloud point at a KCl concentration of 0.5 mg/mL. [M] is the molar concentration of KCl; B_{max} represents the maximum increase in cloud point temperature. b is an electrostatic interaction factor relating to the surface potential of PC7. K_d is the apparent binding constant.

4. ITC data and the calculation of binding percent

The binding capacity between B21C7 and potassium cation was obtained by ITC measurements from our previous work.[S3] In this system, the binding constant (30 M^{-1}) was used to calculate the binding percent of

host-guest complex with the Eq.: K_a = [B21C-K^+]/([$B21C7_{free}$]*[K^+_{free}]). In this Eq., K_a, the concentration of B21C7 and potassium cation are all available.

References

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S2. Zhang, Y.; Cremer, P. S. *Proc. Natl. Acad. Sci.* USA 2009, **106**, 15249.

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