Supramolecular Gels

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Responsive Supramolecular Gels Constructed by Crown Ether Based Molecular Recognition**

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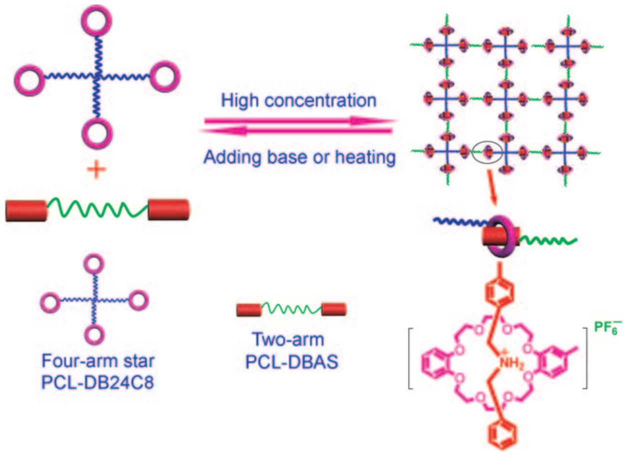
Supramolecular gels can be constructed from small molecules, as well as oligomeric and polymeric species.[1] These building blocks are typically brought together by noncovalent interactions, such as hydrophobic,[2] π–π stacking,[3] multiple hydrogen bonding,[4] and metal–ligand interactions,[5] as well as host–guest recognition.[6] Since supramolecular gels can respond to external stimuli, including temperature, pH, solvent composition, and electric/magnetic fields, owing to the relatively low activation energy required for breaking weak bonds, they can serve as drug-delivery carriers, functional membranes, and smart devices.[7] As the first artificially synthesized host molecules, crown ethers can bind metal and organic ammonium cations, if these guest molecules fit into the macrocyclic cavities.[8] Previously, crown ether-based molecular recognition has facilitated the synthesis of a variety of supramolecular polymers with chain topologies varying from linear (AB, ABA, alternating),[9] star,[10] cross-linked,[11] hyperbranched,[12] and dendronized polymers,[13] as well as dendrimers.[14] Notably, reports concerning crown ether-based supramolecular gels are relatively rare,[15] partially owing to synthetic difficulties encountered in the preparation of well-defined polymer precursors embedded with multiple crown ether hosts at predetermined positions.

Herein we report the fabrication of responsive supramolecular gels on the basis of reversible molecular recognition between dibenzo[24]crown-8 (DB24C8) and dibenzylammonium salt (DBAS) moieties, using biodegradable poly(ε-caprolactone) (PCL) segments as the scaffold (Scheme 1). DB24C8-terminated four-arm star PCL (four-arm star PCL–DB24C8) and DBAS-terminated two-arm PCL (two-arm PCL–DBAS) were synthesized by a combination of ring-opening polymerization (ROP) and click reaction. At relatively high concentrations in organic solvents such as $CHCl_3$, the mixture of four-arm star PCL–DB24C8 and two-arm PCL–DBAS spontaneously form supramolecular gels, exhibiting fully reversible thermo- and pH-induced gel–sol transitions. ^{1}H NMR spectroscopy, viscometry, and differential scanning calorimetry (DSC) were employed to characterize this novel type of crown ether-based supramolecular network.



Scheme 1. Schematic representation for the fabrication of responsive supramolecular networks from four-arm star PCL–DB24C8 and two-arm PCL–DBAS as a result of molecular recognition between dibenzo[24]crown-8 (DB24C8) and dibenzylammonium salt (DBAS) moieties.

Synthetic routes for the preparation of four-arm star PCL–DB24C8 and two-arm PCL–DBAS are shown in Scheme 2. Firstly, to incorporate sites for molecular recognition onto polymer precursors by click chemistry, alkynyl-containing DB24C8 and dibenzylamine (DBA) moieties were synthesized (see the Supporting Information, Scheme S1). Alkynyl–DB24C8 was obtained in approximately 71 % yield from a macrocyclization reaction between propargyl 3,4-dihydroxybenzoate and 1,2-phenylenebis(oxyethylenoxyethylenoxyethylene) ditosylate, catalyzed by LiBr under semi-high dilution conditions (see the Supporting Information, Figure S1). Alkynyl–DBA was synthesized by reacting 4-formylphenyl propargyl ether with benzylamine followed by reduction with $NaBH_4$ (see the Supporting Information, Figure S2). Pentaerythritol and ethylene glycol were used as initiators for the ROP of ε-caprolactone (CL) in the presence of $Sn(Oct)_2$ catalyst, yielding four-arm star PCL and α,ω-dihydroxy-terminated PCL, respectively. Terminal hydroxy groups were then converted into tosylate groups by reacting

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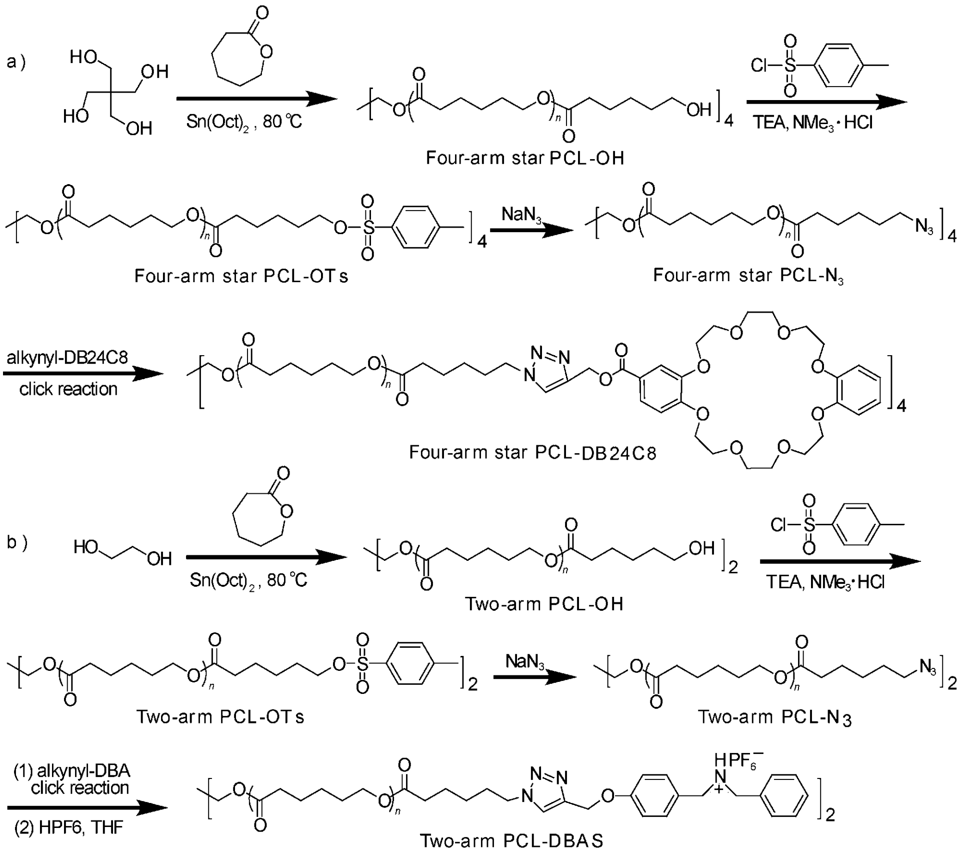

Scheme 2. Synthetic routes for the preparation of a) dibenzo[24]crown-8-terminated PCL (four-arm star PCL–DB24C8) and b) dibenzylammonium-terminated difunctional PCL (two-arm PCL–DBAS) by a combination of ring-opening polymerization and click reactions. TEA = triethylamine.

with tosyl chloride. Quantitative end-group transformation was confirmed by the disappearance of the resonance signal at $\delta = 3.86$ ppm, which is characteristic of methylene protons adjacent to terminal hydroxy groups, in the ^{1}H NMR spectra of four-arm PCL–OTs and two-arm PCL–OTs (see the Supporting Information, Figures S3 and S4).

Next, four-arm star PCL–N$_3$ and two-arm PCL–N$_3$ were obtained by azidation with NaN$_3$. The end group functionality was determined to be quantitative, as evidenced by the complete disappearance of characteristic NMR signals of tosylate and the emergence of a new signal at $\delta = 3.28$ ppm (methylene protons adjacent to azide; see the Supporting Information, Figures S3 and S4). Finally, four-arm star PCL–DB24C8 and two-arm PCL–DBAS were successfully obtained by click reactions of four-arm star PCL–N$_3$ and two-arm PCL–N$_3$ with alkynyl–DB24C8 and alkynyl–DBA, respectively. In both click reactions, alkynyl-containing species were in excess relative to those of azido moieties to ensure quantitative "click" end-group functionalization of polymer precursors, which was again confirmed by ^{1}H NMR and FT-IR spectroscopy (see the Supporting Information, Figures S3–S6).

Four-arm star PCL–DB24C8 and two-arm PCL–DBAS incorporate complementary molecular recognition moieties. Complexation between DB24C8 and DBAS led to the formation of a pseudorotaxane, with a desirably high association constant ($K_a \approx 2.7 \times 10^4\,\text{M}^{-1}$, CDCl$_3$, 25 °C).[16] The supramolecular self-assembly between equivalent amounts (1:1 molar ratio, crown ether/ammonium ion) of four-arm star PCL$_{20}$–DB24C8 and two-arm PCL$_{18}$–DBAS was initially examined by NMR spectroscopy. The ^{1}H NMR spectrum (Figure 1c) was recorded 2 h after mixing four-arm star PCL$_{20}$–DB24C8 and two-arm PCL$_{18}$–DBAS in CDCl$_3$ at a total concentration of 20 g L^{-1}. Compared to that of two-arm PCL$_{18}$–DBAS (Figure 1a), the NMR spectrum of the mixture revealed that characteristic methylene proton signals (H$_a$ and H$_b$) of DBAS, which initially overlapped with signals corresponding to the PCL main chains, shifted downfield to $\delta = 4.5$–4.7 ppm upon complexation (Figure 1c). Moreover, signals characteristic of the crown ether (H$_\beta$ and H$_\gamma$) at $\delta = 3.72$ and 3.82 ppm in four-arm PCL$_{20}$–DB24C8 (Figure 1b) shifted upfield to the range of $\delta = 3.4$–3.8 ppm (Figure 1c). These NMR spectroscopic signal shifts indicated that dibenzylammonium ions at the chain terminals of two-arm PCL$_{18}$–DBAS were encircled by the macrocyclic cavities of the crown ether, forming pseudorotaxane linkages. The percentage of complexation between DB24C8 and DBAS moieties was calculated to be 79 % by comparing the integrals of NMR signals characteristic of uncomplexed and complexed crown ether moieties. Molecular recognition between terminal crown ether and dibenzylammonium moieties, from four-arm star PCL$_{20}$–DB24C8 and two-arm PCL$_{18}$–DBAS, respectively, will lead to the formation of supramolecular networks (Scheme 1).

The reversible formation of noncovalent bonds between four-arm star PCL$_{20}$–DB24C8 and two-arm PCL$_{18}$–DBAS was further investigated by NMR spectroscopy. Treatment by heating or introduction of organic base (triethylamine, TEA) would be expected to disrupt pseudorotaxane formation. Figure 1 also shows ^{1}H NMR spectra for the mixture of four-arm star PCL$_{20}$–DB24C8 and two-arm PCL$_{18}$–DBAS upon addition of TEA and upon heating to 60 °C. In the presence of TEA, the characteristic resonance signals resulting from the pseudorotaxane formation ($\delta = 4.5$–4.7 and 3.4–3.8 ppm, Figure 1c) completely disappeared (Figure 1d). The addition of organic base led to deprotonation of the dibenzylammonium ions and the break-up of the complexation between four-arm star PCL$_{20}$–DB24C8 and two-arm PCL$_{18}$–DBAS.

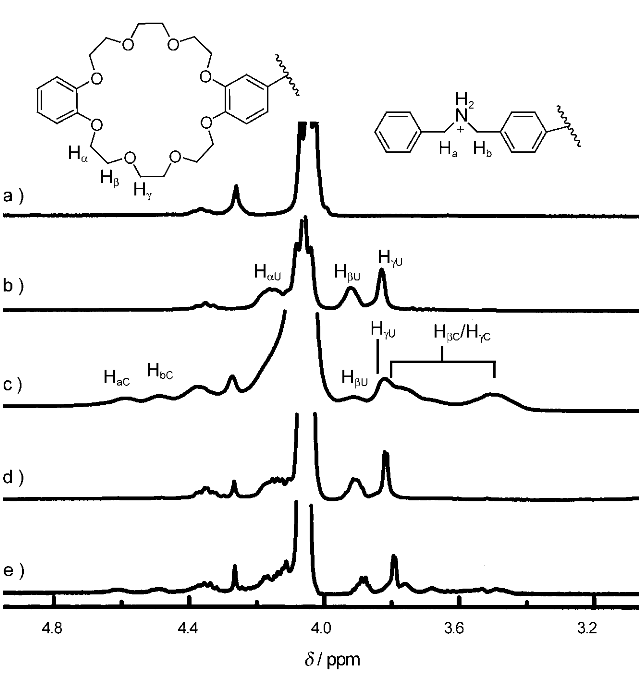

Figure 1. Partial ^{1}H NMR (300 MHz, $CDCl_3$) spectra for a) two-arm PCL_{18}–DBAS; b) four-arm star PCL_{20}–DB24C8; c) molecular recognition complexes of four-arm PCL_{20}–DB24C8 and two-arm PCL_{18}–DBAS (1:1 molar ratio of crown ether/ammonium ion; 20 g L^{-1}, 20 °C); d) complexes after treating with TEA (20 °C); e) complexes at 60 °C (C and U denote complexed and uncomplexed moieties, respectively).

Conversely, at elevated temperatures (60 °C), it was also evident that intensities of signals at $\delta = 4.5$–4.7 and 3.4–3.8 ppm reduced considerably, again confirming the disruption of molecular recognition (Figure 1 e). In the latter case, the percentage of remaining complexation was determined to be roughly 10 % in $CDCl_3$ at 60 °C.

Pseudorotaxane formation between terminal crown ether and dibenzylammonium moieties of four-arm star PCL_{20}–DB24C8 and two-arm PCL_{18}–DBAS will lead to supramolecular networks and a size increase of polymer chains. Viscometry is a convenient and simple technique to characterize the growth of polymer networks with increasing polymer concentrations.[4a,f] The variation of reduced viscosity as a function of polymer concentration for the solution mixture of four-arm star PCL_{20}–DB24C8 and two-arm PCL_{18}–DBAS (1:1 molar ratio, crown ether/ammonium ion) is shown in Figure 2. For comparison, variation of reduced viscosity of the solution mixture of four-arm PCL_{20}–OH and two-arm PCL_{18}–OH was also plotted. In the concentration range 1–30 g L^{-1}, reduced viscosity varied linearly with total polymer concentrations, indicating that no significant physical entanglements or noncovalent interactions occurred between four-arm PCL_{20}–OH and two-arm PCL_{18}–OH in $CHCl_3$. Conversely, for the solution mixture of four-arm star PCL_{20}–DB24C8 and two-arm PCL_{18}–DBAS, the reduced viscosity varied exponentially with total polymer concentrations, indicating the formation of supramolecular networks. The dramatic increase of reduced viscosity also indicates the growth of supramolecular networks with increasing polymer concentrations. A comparison of reduced viscosity/concentration profiles obtained for the two types of solution mixtures tells us that the introduction of complementary host–guest-interaction moieties at the chain terminals of non-interacting polymer precursors can dramatically modify the blend solution rheology.

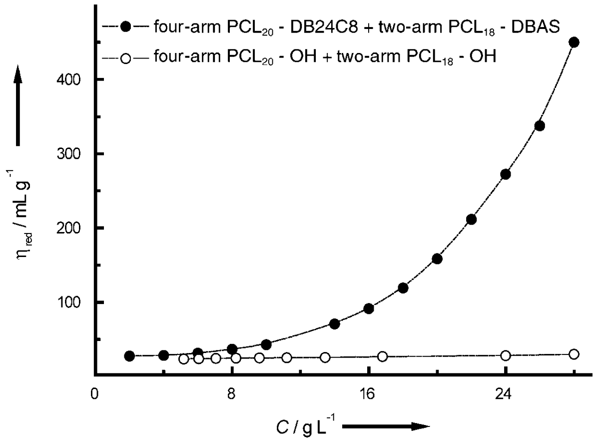

Figure 2. Variation of reduced viscosities ($CHCl_3$, 20 °C) as a function of total polymer concentrations obtained for molecular recognition complexes of four-arm star PCL_{20}–DB24C8 and two-arm PCL_{18}–DBAS (1:1 molar ratio, crown ether/ammonium ion), and the control mixture of four-arm star PCL_{20}–OH and two-arm PCL_{18}–OH at the same molar ratio.

At even higher polymer concentrations, the formation of supramolecular gels and reversible thermo- and pH-induced gel–sol transitions can be visualized macroscopically (Figure 3). After weighing proper amounts of four-arm star PCL_{20}–DB24C8 and two-arm PCL_{18}–DBAS into a vial, the addition of $CHCl_3$ and subsequent heating to 60 °C led to a transparent solution. Upon cooling to 20 °C, nearly transparent supramolecular gels formed. Heating the resultant supramolecular gels resulted in recovery of the fluid solution.

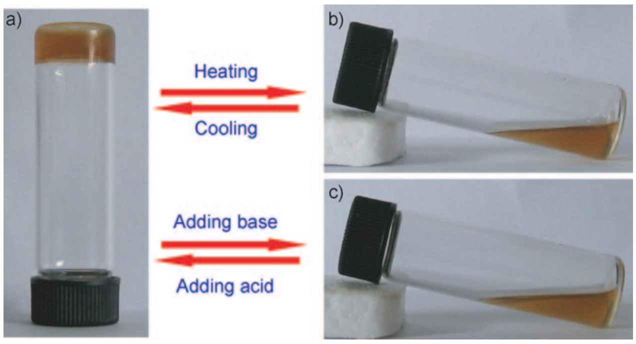

Figure 3. a) Supramolecular gel formed from the mixture of four-arm star PCL_{20}–DB24C8 and two-arm PCL_{18}–DBAS (1:1 molar ratio, crown ether/ammonium ion) in $CHCl_3$ (150 g L^{-1}, 20 °C); b) the same mixture after heating to 60 °C (150 g L^{-1}); c) the same mixture after treating with 1.1 equivalents of TEA relative to DBAS moieties (150 g L^{-1}, 20 °C).

The formation of gels at lower temperatures can be ascribed to the restoration of the complexation between crown ether moieties and dibenzylammonium ions, which was disrupted at elevated temperatures (Figure 1). Moreover, supramolecular gels formed at 20 °C were also converted into fluid solution upon addition of 1.1 equivalents (per crown ether) of TEA, as a result of the deprotonation of dibenzylammonium ions, which again disrupted the supramolecular network. Interestingly, the introduction of roughly 1.2 equivalents (per crown ether) of trifluoroacetic acid (TFA) led to the reformation of supramolecular gels. It should be noted that these thermo- and pH-induced gel–sol transitions are completely reversible, reflecting the dynamic nature of typical supramolecular systems (Scheme 1).

Differential scanning calorimetry (DSC) was further employed to characterize the pseudorotaxane linkage formation in the mixture of four-arm star PCL_{20}–DB24C8 and two-arm PCL_{18}–DBAS (see the Supporting Information, Figure S7). Compared to those of the two separate components, the DSC thermogram of the mixture (1:1 molar ratio of crown ether/ammonium ion) revealed a broad endothermic peak in the temperature range 55–80 °C, which can be attributed to disruption of the host–guest interactions between DB24C8 and DBAS moieties. This result was in agreement with that obtained by ^{1}H NMR spectroscopic studies.

In summary, DB24C8-terminated four-arm star poly(ε-caprolactone) (PCL) and dibenzylammonium-terminated two-arm PCL were synthesized by a combination of ring-opening polymerization and click reaction. Based on these well-defined precursors, responsive supramolecular gels were constructed, taking advantage of the formation of pseudorotaxane linkages between terminal crown ether and ammonium moieties. The resultant supramolecular gels underwent thermo- and pH-induced reversible gel–sol transitions. Moreover, the multiresponsive supramolecular networks contain cavities with sizes which are expected to be facilely adjusted by changes in the arm lengths of four-arm star PCL–DB24C8 and two-arm PCL–DBAS, which augurs well for their application as smart nanocarriers for guest molecules and complicated molecular devices. Further work towards this aspect is currently underway.

Experimental Section

Experimental details, including procedures for the synthesis of alkynyl–DB24C8, alkynyl–DBA, four-arm star PCL–N_3, and two-arm PCL–N_3, characterization methods, and data interpretation are available in the Supporting Information.

Typical procedure for the preparation of four-arm star PCL–DB24C8: A mixture of four-arm star PCL_{20}–N_3 (1.87 g, 0.2 mmol), alkynyl–DB24C8 (0.531 g, 1.0 mmol), PMDETA (0.139 g, 0.8 mmol), and CuBr (0.115 g, 0.8 mmol) in DMF (10 mL) was degassed by three freeze–thaw cycles and sealed under vacuum. After stirring the mixture at 80 °C for 8 h, it was diluted with THF (30 mL) and passed through a basic alumina column. After removal of the solvents under reduced pressure, the residues were dissolved in THF and purified by precipitation (three times) in excess diethyl ether antisolvent. After drying in a vacuum oven overnight at room temperature, four-arm star PCL_{20}--DB24C8 was obtained as a pale yellow solid (2.0 g, 87 %, $M_{n,GPC} = 11.8$ kDa, $M_w/M_n = 1.10$).

Typical procedure for the preparation of two-arm PCL–DBAS: A mixture of two-arm PCL_{18}–N_3 (0.844 g, 0.2 mmol), alkynyl–DBA (0.151 g, 0.6 mmol), PMDETA (69 mg, 0.4 mmol), CuBr (57 mg, 0.8 mmol) in DMF (5 mL) was degassed by three freeze–thaw cycles and sealed under vacuum. After stirring the mixture at 60 °C for 12 h, it was diluted with THF (30 mL) and passed through a basic alumina column. After removal of the solvents under reduced pressure, the residues were dissolved in THF and purified by precipitation (three times) in excess diethyl ether, affording two-arm PCL–DBA as a pale yellow powder (0.88 g, yield: 93 %; $M_{n,GPC} = 5.3$ kDa, $M_w/M_n = 1.14$). The resultant two-arm PCL–DBA (0.472 g, 0.1 mmol) was dissolved in THF (20 mL). After cooling to 0 °C, HPF_6 (60 wt % in water, 0.486 g, 2.0 mmol) was slowly added. After the mixture was stirred for 30 min at room temperature, the reaction was quenched with water. The dispersion was extracted with CH_2Cl_2 (3 × 40 mL). The combined organic fractions were dried ($MgSO_4$) and the solution was concentrated under reduced pressure. The remaining portion was added to excess diethyl ether and the resultant precipitate was removed by filtration and dried in a vacuum oven overnight at room temperature, affording two-arm PCL–DBAS as a pale yellow solid (0.44 g, 88 %; $M_{n,GPC} = 5.1$ kDa, $M_w/M_n = 1.15$).

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