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Switching the Morphologies of Cylindrical Polycation Brushes by Ionic and Supramolecular Inclusion Complexes

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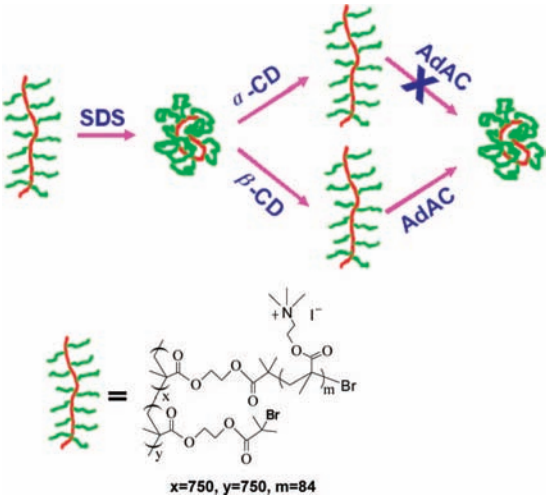
Responsive polymers are sensitive to environmental stimuli, which can greatly change their conformations or macro-/microscopic properties.[1] They have drawn increasing attention due to the potential of building smart sensors or actuators based on these intelligent molecules.[2] Smart single-molecular nanostructured polymers are of particular interest for the possibilities of building nanoscopic devices.[3] Among them, cylindrical polymer brushes (CPBs) are good candidates. They are composed of a long linear backbone and densely grafted side chains.[4] In good solvents, they normally adopt a worm-like conformation owing to the steric hindrance caused by the repelling side chains, which can be directly observed by atomic force microscopy (AFM) on a suitable substrate.[5] The anisotropic nature provides the brushes with peculiar solution and bulk properties. The chemical properties of the brushes are mainly dependent on the side chains. However, when the backbones are flexible, it provides the CPBs one more degree of freedom, and different morphologies could result from the conformational changes of the backbones caused by the interactions between the side chains and external stimuli. Worm-to-sphere[6] and worm-to-helix[7] conformational transitions have been evidenced for CPBs with different side chains and stimuli. These kinds of morphology transitions may give inspirations to creating intelligent nanodevices.[8]

Polyelectrolyte CPBs, mimicking some biological macromolecules in nature, contain linear ionic side chains and show different properties from their neutral counterpart. It is well-known that linear polyelectrolytes can form complexes with oppositely charged surfactants and polymers.[9] Although the polyelectrolyte CPBs behave similarly to their linear analogues when forming complexes with surfactants, their distinctive cylindrical nanostructure makes it possible to detect the morphology changes directly by microscopy such as AFM. Recently, Schmidt et al.[7a] reported helical structures formed by a complex of sodium dodecyl sulfate (SDS) and a cationic polypeptide CPB. When SDS was in excess, a worm-to-sphere transition was observed.

Recently, we reported the synthesis of a new cationic CPB (CCPB) with side chains of poly(*N*,*N*-dimethylaminoethyl methacrylate) (PDMAEMA) and its quaternized analogue (PMETAI) and its responsiveness to mono- and multivalent salts.[7b,10] The initiating efficiency of 50% in the synthesis by ATRP led to the chemical structure of the CCPB in Scheme 1. Here we present its worm-to-sphere transition by forming ionic complexation with negatively charged surfactant SDS. More importantly, we are able to switch back to the worm-like morphology by a supramolecular inclusion complex between SDS and cyclodextrins (CDs). When β-CD is used for the complex with SDS, we could even make the transition process reversible by using a more competitive inclusion agent, 1-adamantylammonium chloride (AdAC). Scheme 1 depicts the transition process.

Scheme 1. Morphological Transitions of CCPB Brushes



Nonpolar compounds,[11] linear polymers,[12] and polymers with nonpolar side groups[13] form stable inclusion complexes with CDs. Figure 1 shows the ^{1}H NMR spectra of SDS and its mixture with α-CD in D_2O. The three peaks for the methyl and methylene groups shift to lower field, and the peak for the methylene groups separates into two peaks, indicating that the alkyl chains form an inclusion complex with α-CD with part of the methylene groups inside the hydrophobic cavity.

At relatively high concentration (1 g/L) of CCPB, when SDS is added at a charge ratio (ratio of charges of SDS and those carried by the CCPB) $Z_{-/+} = 1$, precipitation appears immediately, indicating the instantaneous formation of the complex and aggregates (see Supporting Information, Figure S1). Dynamic light scattering (DLS)

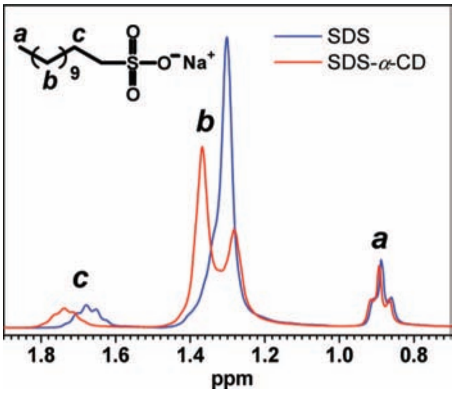


Figure 1. ^{1}H NMR spectra of SDS and its complex with α-CD.

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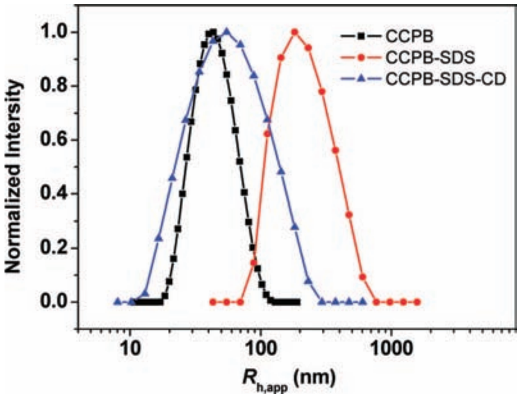

Figure 2. Intensity-weighted hydrodynamic radii distributions of CCPB and its complexes with SDS and with SDS + α-CD in aqueous solution (c_{CCPB} = 0.2 g/L, equimolar amounts).

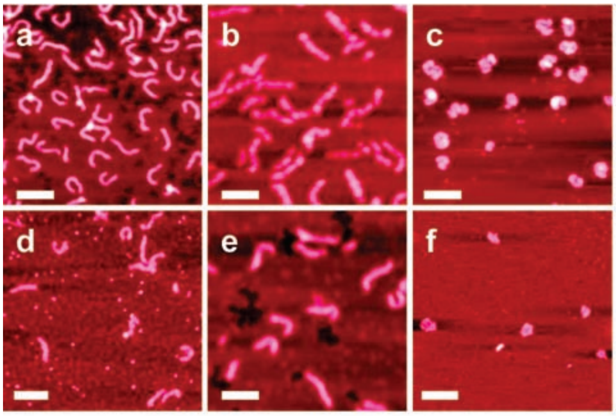

Figure 3. AFM height images of (a) pure CCPB; (b) CCPB with SDS, with $Z_{-/+}$ 0.5; (c) CCPB with SDS, $Z_{-/+} = 1$; (d) CCPB/SDS $Z_{-/+} = 1$ with added α-CD (equimolar with SDS); (e) same, but with added β-CD; (f) sample with β-CD after addition of AdAC (equimolar with α-CD). The scale bars represent 200 nm, and the brush concentration is 0.02 g/L. Samples were spin-coated to a freshly cleaved mica surface. AFM height ranges are 5, 12, 8, 8, 8, and 4 nm, respectively.

measurements (Figure 2) show the change of the brush size at c = 0.2 g/L from the CCCB to its complex with SDS, and then with SDS ($Z_{-/+}$=1) and α-CD (in equal amounts). For the pure CCPB, the apparent z-average hydrodynamic radius, $R_{h,app}$, is 44 nm. When SDS was added, the solution becomes turbid immediately but does not precipitate. $R_{h,app}$ increases to ca. 200 nm, indicating the formation of aggregates at this concentration. When α-CD is added to the mixture, the solution becomes clear again and $R_{h,app}$ returns to 53 nm, somewhat higher and more disperse than that of the original brush. This might indicate that the inclusion complex of SDS and α-CD may still form an ionic complex with CCPB, expanding the size of the brushes (see also Supporting Information, Figure S2).

The DLS results demonstrate that it is not possible to avoid aggregates of the CCPB with SDS at a brush concentration above 0.2 g/L. To observe the single-molecular morphology changes, AFM measurements from a very low concentration (0.02 g/L) were carried out to diminish the intermolecular aggregates.

Figure 3 shows the results of the AFM measurements on mica. The pure CCPB shows typical worm-like structures. When a medium amount of SDS is added, the brush forms pearl-necklace structures, indicating that the SDS forms a complex with cationic side chains and causes the insoluble part around the backbone of the brush (Figure 3b). Simulations show that pearl-necklace structures form when the inner part of a CPB becomes insoluble.[14] Samokhina et al. made a similar observation with spherical polyanion brushes and the cationic surfactant CTAB.[15] The brushes straighten somewhat, probably due to the cross-linking effect of SDS around the backbone. However, when the charge ratio reaches $Z_{-/+}$= 1, most of the worm-like structures are turned into collapsed spheres (Figure 3c). When α- or β-CD is added to the CCPB-SDS complex ($Z_{-/+} = 1$), the collapsed spheres return to their worm-like shape (Figures 3d, e), as a result of the inclusion complexes between the dodecyl groups with CDs, which again solubilize the side chains of the CCPB.

When a more competitive hydrophobe, AdAC, is added to the SDS-β-CD complex, it removes the β-CD from the relatively weak inclusion complex. Then SDS is released and again forms the insoluble polyelectrolyte−surfactant complex with the CCPB, causing the collapse of the brush to spheres again (Figure 3f). Due to the unmatched size of AdAC and the cavity of α-CD, attempts for recollapsing with α-CD are not successful.

In conclusion, we have shown that the anionic surfactant SDS forms an ionic complex with the cationic CPB, leading to the collapse of the brush from worms to spheres, while both α-CD and β-CD form supramolecular inclusion complexes with SDS, liberating the CCPB, thus again enabling the worm-like conformation. AdAC can remove the β-CD from the SDS-β-CD complex, causing the recollapse of the brush. This drastic conformation switching between worms and spheres makes the system a good candidate for sensors or devices on the nanoscale.

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Supporting Information Available: Characterization methods and photographs of solutions. This information is available free of charge via the Internet at http://pubs.acs.org.

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