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Synthesis, characterization and properties of side-chain pseudopolyrotaxanes consisting of cucurbituril[6] and poly-N^1-(4-vinylbenzyl)-1,4-diaminobutane dihydrochloride

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Abstract

Pseudopolyrotaxanes **3** is synthesized from cucurbituril[6] (CB[6]) and polymer **2** (poly-N^1-(4-vinylbenzyl)-1,4-diaminobutane dihydrochloride) in water by simple stirring at room temperature. The monomer **1**, polymer **2** and pseudopolyrotaxanes **3** are characterized by ^{1}H NMR, ^{13}C NMR, FT-IR and elemental analysis. In **3**, the CB[6] beads are localized on tetramethylene units in side chains of **2**, and combine N^+ by noncovalent bonds. The degree of threading (number of CB[6] beads per repeat unit) can be controlled from 0 to 1.0 by controlling the amount of CB[6] added. The properties of polymer **2** and pseudopolyrotaxanes **3** are researched by TGA, X-ray powder diffraction (XRD), environment scanning electron microscope (ESEM) and potentiometric titrations. The pseudopolyrotaxanes have higher thermal stability and chain regularity than the parent polymer which are attributed to the bulkiness and the rigidity of the CB[6] threaded. The decomposition temperature and chain regularity of the pseudopolyrotaxanes increase with increasing amount of CB[6] threaded. The effects of salts (NaCl, NaBr or NaI) to pseudopolyrotaxanes are studied by the transmittance with UV–vis, and the results show that NaI is the satisfied precipitant to the pseudopolyrotaxanes. The surface morphologies of pseudopolyrotaxanes **3** observed by ESEM shows a series of spherical particle with different diameter. The results of potentiometric titrations show that the pseudopolyrotaxanes **3** have larger pK_{av} and smaller n than polymer **2**.
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1. Introduction

Polymers in which their components are linked through noncovalent bonds have received much attention in recent years not only because of their unique structures but also because of their unusual properties different from those of conventional covalent polymers [1]. Such noncovalent bonds linked polymers include (pseudo)polyrotaxanes in which a number of cyclic units are threaded onto a polymer main chain or side chains. Most (pseudo)polyrotaxanes synthesized so far contain cyclodextrins (CDs) or crown ethers threaded on organic polymers. Harada et al. [2] and Wenz et al. [3] reported main-chain (pseudo)polyrotaxanes containing CDs. Gibson et al. [4] utilized crown ether to synthesize main-chain (pseudo)polyrotaxanes. In addition, side-chain (pseudo)polyrotaxanes have also been synthesized. Ritter et al. [5] synthesized a series of side-chain polyrotaxanes containing CD beads threaded on side chains of various polymer backbones. Takata et al. [6] reported side-chain polyrotaxanes synthesized by polymerization of a semirotaxane monomer containing crown ether threaded on an acrylate derivative. Also, the side-chain polyrotaxanes containing CDs were synthesized by Osakada et al. [7]. However, all of these post-threaded systems in general lack structural regularity as the molecular 'beads' are often not threaded in all the available recognition sites of the polymer chains. It is mainly due to the fact that affinity of the ring components (CDs or crown ethers) towards the recognition sites in the polymers is not high enough to ensure complete threading. The requirement for a molecular 'bead' seems to be met with cucurbituril.

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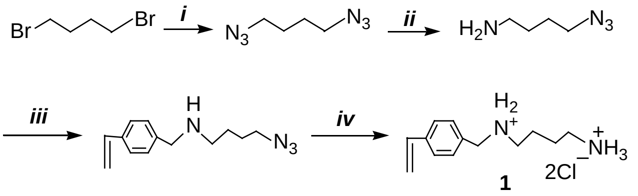
Cucurbituril[6] (CB[6]), which is a macrocycle comprising six glycoluril units interconnected with 12 methylene bridges, has a hydrophobic cavity that is accessible through two identical carbonyl-fringed portals [8]. CB[6] has been attracting much attention not only because of easy synthesis, highly symmetric structure and high chemical and thermal stability, but also because of the polar carbonyl groups at the portals and a hydrophobic cavity allow it to form stable host-guest complexes with small molecules such as protonated aminoalkanes diaminoalkanes ($K > 10^5$) [8] through the formation of (pseudo)rotaxane. Taking advantage of this fact, various mechanically interlocked molecules including rotaxanes and (pseudo)polyrotaxanes have been synthesized by Kim et al. [9], Buschmann et al. [10] and Steinke et al. [11]. But side-chain (pseudo)polyrotaxanes containing CB[6] as a molecular bead have been scarcely reported [9d].

We now synthesized a side-chain pseudopolyrotaxanes in which CB[6] beads were threaded on protonated diaminobutane pendant attached to a main polymer chain. A unique feature of the pseudopolyrotaxanes is that the CB[6] bead can be threaded on every diaminobutane unit of the polymer and the degree of threading (number of CB[6] beads per repeat unit) can be controlled by controlling the mount of CB[6] added. Here, we report the synthesis, characterization and properties of the side-chain pseudopolyrotaxanes.

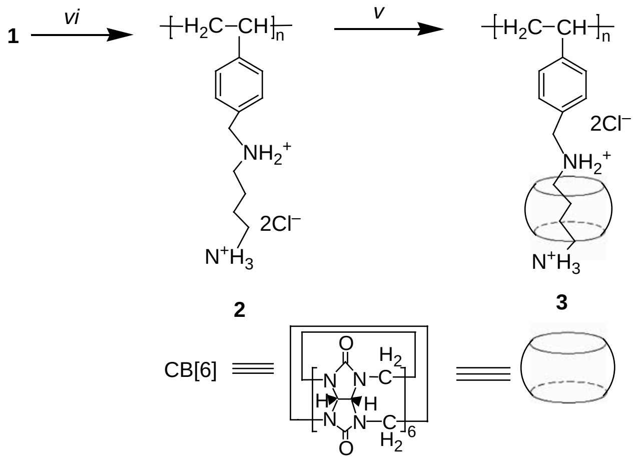
2. Results and discussion

2.1. Preparation of polymer 2 and pseudopolyrotaxanes 3

Monomer **1** (N^1−4-vinylbenzyl-1,4-diaminobutane dihydrochloride) was synthesized according to Scheme 1. Radical polymerization of monomer **1** was carried out in the presence of potassium persulfate (KPS) at 65 °C to give side-chain pendant polymer **2** (poly-N^1-(4-vinylbenzyl)-1,4-diaminobutane dihydrochloride). The intrinsic viscosity [η] of **2** was 0.75 dL/g determined at 25.0 °C in 2.0 mol/L NaCl aqueous solution by Ubblohde viscometer. Side-chain pseudopolyrotaxanes **3** was obtained by mixing **2** and slightly excess CB[6] (∼1.1 equiv per repeating unit of **2**) in water and stirring the mixture at room temperature (rt) (Scheme 2). Pseudopolyrotaxanes with different degree of threading (< 1.0) were prepared by the same procedure as Scheme 2, except that the proper amounts of CB[6] were added to the solution.



Scheme 1. Synthesis of monomer **1** (i) 2.5 equiv NaN_3, DMF, 80 °C, 24 h; (ii) 0.95 equiv PPh_3, Et_2O/Et_2Ac/5%HCl, rt, 24 h; (iii) 0.9 equiv 4-vinylbenzyl chloride, K_2CO_3, CH_3CN, rt, 24 h; (iv) 1.5 equiv PPh_3, THF, rt, 24 h, then concentrated HCl.



Scheme 2. Synthesis of polymer **2** and pseudopolyrotaxanes **3** (vi) 10^{-2} equiv KPS, H_2O, 65 °C, 24 h; (v) 1.1 equiv. CB[6], H_2O, rt, 24 h.

2.2. ^1H NMR spectra

Formations of polymer **2** and pseudopolyrotaxanes **3** were confirmed by ^1H NMR spectra as well as elemental analysis. Fig. 1 shows that no peaks corresponding to $-CH{=}CH_2$ are observed in the ^1H NMR spectrum of **2** (Fig. 1(a)). Upon formation of pseudopolyrotaxanes **3** (Fig. 1(b)), new broad signals appear at 4.42 and 5.77 ppm, which correspond to threaded CB[6]. At the same time, the tetramethylene proton signals (■ and ●) of the pendant diaminobutane unit of **2** are shifted upfield due to the shielding effect of CB[6], while the signals for three protons of the benzylic protons (▲ and ★), which are now located just outside of the CB[6] bead, are shifted downfield. The NMR data support that the CB[6] beads threaded in **3** are localized on the tetramethylene units.

The amount of CB[6] threaded onto the side chains of the polymer can be estimated by comparing the intensities of the CB[6] (5.77 ppm) and polymer side-chain peaks (0.60 or 2.33 ppm) in the ^1H NMR spectrum (Fig. 1(b)). CB[6] bead can be threaded on every side chain containing a protonated diaminobutane unit in **3**. The high threading efficiency is due to the exceptionally strong interaction of CB[6] and the protonated diaminobutane unit ($K > 10^5$) in neutral or acidic media [8]. Because of the multiple noncovalent interactions between the positively charged nitrogen atoms of **2** and the CB[6] portal oxygen atoms, the resulting pseudopolyrotaxanes **3** is quite stable in solution and solid state.

2.3. Control of the degree of threading

The degree of threading (the number of CB[6] threaded per repeat unit of polymer) of pseudopolyrotaxanes **3** can be controlled. Fig. 2 shows a series of ^1H NMR spectra of the pseudopolyrotaxanes taken with different molar of **2** to CB[6]. As the amount of CB[6] added increases from 0 (Fig. 2(b)) equiv to 1.0 (Fig. 2(e)) equiv, the intensity of the signals for CB[6] (4.42 and 5.77 ppm) threaded increases, and a new set of signals for the polymer backbone appear with growing intensities (shown with arrows in Fig. 2). All these data are

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