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Preparation of Novel Side-chain *Pseudo*polyrotaxanes Consisting of Cucurbituril[6] and Polyamine Salts

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Abstract: *Pseudo*rotaxane monomer (VBCB) containing cucurbitutil[6] (CB[6]) and N^1-(4-vinylbenzyl)-1,4-diaminobutane dihydrochloride (VBDADC) is obtained by self-assembly of cucurbituril[6] with VBDADC in water and then polymerized using potassium persulfate (KPS) as initiator to give novel water-soluble side-chain cucurbituril[6]-based *pseudo*polyrotaxane (PVBCB). The chemical structures of PVBCB, VBCB and VBDADC are confirmed by ^{1}H NMR, ^{13}C NMR spectra and elemental analysis. In VBCB, CB[6] is localized aliphatic group of the side chain and the molar ratio of CB[6] to VBDAC is 1:1 .

Keywords: *Pseudo*polyrotaxanes, cucurbituril[6], preparation, self-assembly.

Cucurbituril (CB[6]) is a large-cage compound composed of six glycoluril units interconnected with twelve methylene bridges and has a hydrophobic cavity that is accessible through two identical carbonyl-fringed portals[1]. CB[6] has been attracting much attention not only because of easy synthesis, highly symmetric structure and high chemical and thermal stability, but also 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 ($K>10^5$) through the formation of (*pseudo*)rotaxane. While (*pseudo*)polyrotaxanes containing cyclodextrin (CD) or crown ether threaded on side chains have been prepared by Ritter[2], Osakada[3] and Takata[4] *et al.*, but the side-chain *(pseudo*)polyrotaxanes containing CB[6] have been scarcely reported other than Kim[5]. Here, we report the synthesis of a novel water-soluble side-chain *pseudo*polyrotaxanes in which CB[6] is threaded on protonated diaminobutane pendants attached to the main polymer chain. This approach is the first involved formation of a *pseudo*rotaxane monomer by threading CB[6] on olefinic protonated diaminoalkanes, followed by polymerization of the *pseudo*rotaxane monomer to produce CB[6]-based side-chain *pseudo*polyrotaxanes.

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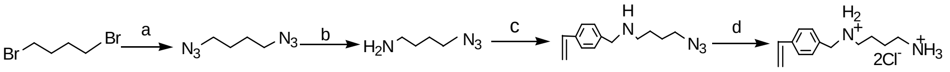
Preparation of the compounds 5, 6, 7

Monomer **5** was prepared according to **Scheme 1**. **1** was reacted with NaN_3 in DMF at 80℃ for 24 h to give **2** in 95% yield. One azido group of **2** was reduced by triphenylphosphine (PPh_3) in Et_2O/EtOAc/5%HCl at room temperature for 24 h to give **3** in 94 % yield. **3** was reacted with 4-vinylbenzyl chloride in anhydrous CH_3CN at r.t. for 24 h. The product was purified by column chromatography using CH_2Cl_2 : MeOH = 1:2 as an eluate to give **4** in 70 % yield. The monomer **5** (N^1-4-vinylbenzyl-1,4-diaminobutane dihydrochloride, VBDAC) was obtained in 73 % yield by reducing the secondary azido group of **4** with PPh_3 in THF at r.t. for 24 h, then concentrated HCl was

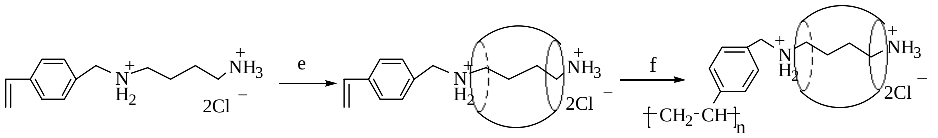
Scheme 1



1 **2** **3** **4** **5**

a) NaN_3, DMF, 80℃, 24 h; b) PPh_3, Et_2O/Et_2Ac/5%HCl, rt, 24 h; c) 4-vinylbenzyl chloride, K_2CO_3, CH_3CN, rt, 24 h; d) PPh_3, THF, r.t., 24 h, then concentrated HCl

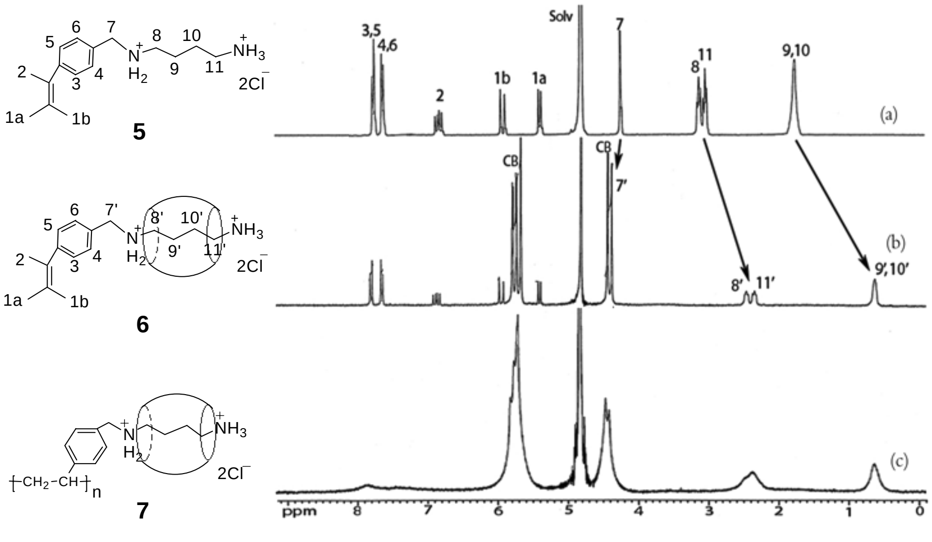
Scheme 2



5 **6** **7**

e) CB[6], H_2O, rt, 24 h; f) KPS, H_2O, 60℃, 24 h

Figure 1 ^1H NMR (600MHz) spectra of **5** (a), **6** (b) and *pseudo*polyrataxanes **7** (c) in D_2O



added slowly on ice cooling to precipitate as the HCl salt of **5**. *Pseudo*rotaxane monomer **6** (VBCB) and *pseudo*polyrotaxanes **7** were prepared according to **Scheme 2**. Construction of *pseudo*rotaxane monomer **6** was carried out by mixing **5** and CB[6] in slight excess in water, and stirring the mixture at r.t. for 10 h, then the product was purified by precipitation with H_2O-EtOH. The yield was high. Although CB[6] itself was sparingly soluble water, it slowly dissolved into the solution as the threading proceeds. The monomer **5** and *pseudo*rotaxane monomer **6** were characterized by ^{1}H NMR, ^{13}C NMR and elemental analysis[6]. ^{1}H NMR spectrum of **6** not only indicated the proton signals for CB[6] at 4.74 and 5.74 ppm, but also signals of three protons for the $-CH=CH_2$ at 5.80, 6.23 and 6.30 ppm, respectively. After threading CB[6], the methylene proton signals (8:3.16 ppm; 11:3.05 ppm; 9-10:1.78 ppm) in the diaminobutane unit of **5** were shifted upfield (8′: 2.45 ppm; 11′: 2.33 ppm; 9′-10′: 0.61 ppm) in **6** due to the shielding effect of CB[6]. While the other methylene (7: 4.25 ppm) of **5**, which was located just outside of the CB[6], was shifted down-field (7′: 4.37 ppm) (**Figure 1a, b**). The NMR data supported that the CB[6] threaded in **6** was localized on the diaminobutane unit and combine N^+ by non-covalent bonds. Peak integrals of ^{1}H NMR spectrum of **6** indicated CB[6] with **5** formed 1:1 complexion. The result was similar to that of other small molecular diaminoalkanes with CB[6][7].

Radical polymerization of *pseudo*rotaxane monomer **6** was carried out by heating **6** at 65℃ in water in the presence of KPS. The polymeric product **7** (PVBCB) was precipitated with ethanol and purified with EtOH : H_2O = 9 : 1 in 81% yield. The ^{1}H NMR spectrum of the polymer clearly indicated the formation of *pseudo*polyrotaxanes **7** which was consisted of not only *pseudo*rotaxane but also diaminobutane ions. The proton signals of vinyl group (5.41, 5.96, 6.84 ppm) disappeared (**Figure 1b, c**). Attempts to determine the molecular weight of *pseudo*polyrotaxanes **7** by GPC had been hampered by the fact that the **7** was only soluble in water and the suitable analytical equipment had not been available.

Acknowledgment

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References and Notes

1. W. L. Mock, *Top. Curr. Chem.*, **1995**, *175*, 1.
2. J. Jeromin, H. Ritter, *Macromolecules*, **1999**, *32*, 5236.
3. I. Yamaguchi, K. Osakada, T. Yamamoto, *Macromolecules*, **2000**, *33*, 2315.
4. T. Takata, H. Kawasaki, N. Kihara, Y. Furusho, *Macromolecules*, **2001**, *34*, 5449.
5. Y. Tan, S. W. Choi, J. W. Lee, Y. H. Ko, K. Kim, *Macromolecules*, **2002**, *35*, 7161.
6. Data of analogues**:** Compound **2**: ^{1}H NMR(600MHz, $CDCl_3$, δ ppm), 3.32 (t, 4H, J=5.8 Hz, $\mathrm{C}H_2\mathrm{N}_3$), 1.68 (m, 4H, J=12.4 Hz, $\mathrm{C}H_2\mathrm{C}H_2$); Compound **3**: ^{1}H-NMR(600MHz, $CDCl_3$, δ ppm), 5.3 (s, 2H, $\mathrm{N}H_2$), 3.31 (t, 2H, J=13.5 Hz, $\mathrm{C}H_2\mathrm{N}_3$), 2.74 (m, 2H, J=13.7 Hz, $\mathrm{C}H_2\mathrm{NH}_2$), 1.67 (m, 2H, J=13.5Hz, $\mathrm{N_3CH_2C}H_2$), 1.56 (m, 2H, J=22.9 Hz, $\mathrm{NH_2CH_2C}H_2$); ^{13}C NMR (600MHz, $CDCl_3$, δ ppm), 51.6 ($C\mathrm{H_2N_3}$), 42.0 ($C\mathrm{H_2NH_2}$), 31.2 ($C\mathrm{H_2CH_2NH_2}$), 26.6 ($C\mathrm{H_2CH_2N_3}$); Compound **4**: ^{1}H NMR (600MHz, $CDCl_3$, δ ppm), 7.26-7.37 (m, 4H, Ph), 6.68

(dd, 1H, J=28.4 Hz, vinyl), 5.72 (d, 1H, J=17.6 Hz, vinyl), 5.18 (d, 1H, J=10.9 Hz, vinyl), 3.74 (d, 2H, J=3.4 Hz, $C\mathit{H_2}$-Ph), 3.23 (t, 2H, J=11.8 Hz, $C\mathit{H_2}N_3$), 2.61 (q, 2H, J=13.3 Hz, $CH_2C\mathit{H_2}NH$), 1.93 (s, br, 1H, $N\mathit{H}$), 1.62 (m, 4H, $CH_2C\mathit{H_2}C\mathit{H_2}CH_2$); ^{13}C NMR (600MHz, $CDCl_3$, δ ppm), 140.4, 137.0, 128.6, 126.7 (Ph), 136.7 (=$\mathit{C}H$-), 113.8 ($\mathit{C}H_2$=), 54.1 (Ph-$\mathit{C}H_2$), 51.7 ($CH_2\mathit{C}H_2NH$), 49.1 ($\mathit{C}H_2N_3$), 27.6 ($\mathit{C}H_2CH_2NH$), 27.1 ($\mathit{C}H_2CH_2N_3$); Compound **5**: ^1H NMR (600MHz, D_2O, δ ppm), 7.61 (d, 2H, J=6.8 Hz, Ph), 7.46 (d, 2H, J=8.1 Hz, Ph), 6.89 (dd, 1H, J=28.6 Hz, vinyl), 5.96 (d, 1H, J=17.7 Hz, vinyl), 5.42 (d, 1H, J=17.9 Hz, vinyl), 4.25 (s, 2H, $C\mathit{H_2}$-Ph), 3.16 (t, 2H, J=13.5 Hz, $CH_2C\mathit{H_2}NH_2^+$), 3.05 (t, 2H, J=13.2 Hz, $C\mathit{H_2}NH_3^+$), 1.78 (s, br, 4H, $CH_2C\mathit{H_2}C\mathit{H_2}CH_2$); ^{13}C NMR (600MHz, D_2O, δ ppm), 139.0, 130.6, 130.4, 127.2 (Ph), 136.2 (=$\mathit{C}H$-), 115.9 ($\mathit{C}H_2$=), 51.1 ($CH_2\mathit{C}H_2N^+H_2$) 46.7 ($Ph\mathit{C}H_2$), 39.2 ($\mathit{C}H_2NH_3^+$), 24.3 ($\mathit{C}H_2CH_2NH_3^+$), 23.1 ($\mathit{C}H_2CH_2NH_2^+$); Anal. Calcd. for $C_{13}H_{22}N_2Cl_2$ (%): C, 56.32; H, 7.94; N, 10.11. Found: C, 56.28; H, 8.01; N, 9.93; Compound **6**: ^1H NMR (600MHz, D_2O, δ ppm): 7.77 (d, 2H, J=8.1 Hz, Ph), 7.65 (d, 2H, J=8.2 Hz, Ph), 6.84 (dd, 1H, J=28.1 Hz, vinyl), 5.96 (d, 1H, J=17.6 Hz, vinyl), 5.41 (d, 1H, J=10.9 Hz, vinyl), 5.78 (d, 12H, J=15.2 Hz, $C\mathit{H_2}$ of CB[6]), 5.66 (s, 12H, $C\mathit{H}$ of CB[6]), 4.42 (s, 12H, $C\mathit{H_2}$ of CB[6]), 4.37 (s, 2H, $C\mathit{H_2}Ph$), 2.45 (s, br, 2H, $CH_2C\mathit{H_2}NH_2^+$), 2.33 (s, br, 2H, $C\mathit{H_2}NH_3^+$), 0.61 (s, br, 4H, $CH_2C\mathit{H_2}C\mathit{H_2}CH_2$); Anal. Calcd. for $C_{49}H_{58}N_{26}O_{12}Cl_2\cdot H_2O$ (%): C, 45.56; H, 4.65; N,28.20. Found: C, 45.94; H, 4.81; N, 28.43.

7 Y. M. Jeon, D. Whang, J. Kim, K. Kim, *Chem. Lett.*, **1996**, 503.

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