Side-Chain Polypseudorotaxanes by Threading Cucurbit[7]uril onto Poly-*N*-*n*-butyl-*N*′-(4-vinylbenzyl)-4,4′-bipyridinium Bromide Chloride: Synthesis, Characterization, and Properties

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ABSTRACT: A novel side-chain polypseudorotaxanes P4VBVBu/CB[7] was synthesized from poly-*N*-*n*-butyl-*N*′-(4-vinylbenzyl)-4,4′-bipyridinium bromide chloride (P4VBVBu) and cucurbit[7]uril (CB[7]) in water by simple stirring at room temperature. CB[7] beads are localized on viologen units in side chains of polypseudorotaxanes as shown by ^{1}H NMR, IR, XRD, and UV–vis studies, and it is considered that the hydrophobic and charge-dipole interactions are the driving forces. TGA data show that thermal stability of the polypseudorotaxanes increases with the adding of CB[7] threaded. DLS data show that P4VBVBu and CB[7] could form polypseudorotaxanes, and the average hydrodynamic radius of the polypseudorotaxanes increases with increasing the concentration of CB[7]. The typical cyclic voltammograms indicate that the oxidation reduction characteristic of P4VBVBu is remarkably affected by the addition of CB[7] because of the formation of polypseudorotaxanes and the shielding effects of CB[7] threaded on the viologen units of polypseudorotaxanes. With the increase of the concentration of KBr or K_2SO_4, the formation of the polypseudorotaxanes was inhibited due to the shielding effects of both Br^- or SO_4^{2-} to viologen ion and K^+ to CB[7] by UV–vis. © 2010 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 48: 2135–2142, 2010

KEYWORDS: cucurbit[7]uril; polyrotaxanes; self-assembly; water-soluble polymers

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INTRODUCTION

Supramolecular chemistry[1,2] has ushered polymer chemistry into a new era. Polypseudorotaxanes, in which many cyclic molecular "beads" are threaded by a long "string," not only have their unique structures but also have their unusual properties different from those of conventional covalent polymers,[1,3–5] such as potential use as a material for molecular devices[6–12] and catalysts.[13–16] Since the earliest example of poly (ethylene glycol) containing α-cyclodextrin threaded in aqueous media,[17] α-, β- and γ-cyclodextrin, crown ether, and cyclophane have been threaded onto a number of different linear polymer backbones.[18–28]

Cucurbit[7]uril(CB[7]), a water soluble, barrel-shaped host, consists of 7 glycoluril groups and 14 methylene bridges at both ends. The two rims are formed by the glycoluril carbonyl oxygens, thereby are negatively charged, and they develop ion-dipole interactions with cationic guests.[29,30] Taking advantage of cucurbit[*n*]uril's structure, various mechanically interlocked molecules including rotaxanes and poly(pseudo)rotaxanes have been synthesized by Kim,[31–39] Buschmann[40–42] and others.[16,43,44] We previously synthesized some side-chain polypseudorotaxanes containing cucurbit[6]uril as a molecular bead that have been also reported.[34,45–48]

These investigations expend our understanding about side-chain polypseudorotaxanes with CB[7] as a molecular bead. Herein, we synthesized a novel water soluble side-chain polypseudorotaxanes with CB[7] threaded on viologen pendants attached to a main polymer chain. The thermal stability of polypseudorotaxanes with CB[7] was investigated by TGA. The average hydrodynamic radius (Rh), the distribution of the hydrodynamic radius, and the oxidation reduction characteristics were studied by DLS and cyclic voltammograms, respectively. The binding constant was obtained and the effects of salt on the formation of polypseudorotaxanes were studied by UV–vis spectra.

EXPERIMENTAL

Materials

CB[7] was prepared according to the literature.[29,30] 4,4′-dipyridyl (98%) and 4-vinybenzyl chlorine (90%) were received from ACRO. Anhydrous acetonitrile (AR) and *n*-butyl bromide (AR) were received from the Sinopharm Chemical Reagent Co., (SCRC).

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Synthesis of *N*-*n*-butyl-4,4′-bipyridinium Bromide (BuV)

4,4′-Dipyridyl (7.8 g, 0.05 mol) was dissolved in anhydrous acetonitrile (40 mL) and stirred for 10 min at room temperature. *N*-butyl bromide (1.71 g, 0.0125 mol) was slowly dripped to the solution of 4,4′-dipyridyl, and the mixture was stirred for 40 h at 85 °C. The reaction solution was concentrated by rotary evaporation method and filtrated, and the yellow precipitate was purified with diethyl ether anhydrous and dried in vacuum to give *N*-*n*-butyl -4,4′-bipyridinium bromide (3.0 g, 81%). mp: 210.0 °C. ^{1}H NMR (400 MHz, D_2O, ppm) δ: 0.87 (t, J = 7.4 Hz, 3H, C$\mathbf{H}_3$), 1.30 (m, J = 7.6 Hz, 2H, C$\mathbf{H}_2$CH$_3$), 1.95 (m, *J* = 7.4 Hz, 2H, CH$_3$CH$_2$C$\mathbf{H}_2$), 4.57 (t, *J* = 7.4Hz, 2H, N$^+$C$\mathbf{H}_2$), 7.82 (d, *J* = 6.2 Hz, 2H, PyH), 8.31 (d, *J* = 6.5 Hz, 2H, PyH), 8.69 (d, *J* = 6.2 Hz, 2H, PyH), 8.87 (d, *J* = 6.8 Hz, 2H, PyH); IR (KBr, cm^{-1}) ν: 1639 (C—N$^+$), 1539 (C=C and C=N from viologen). Anal. calcd for $C_{14}H_{17}N_2Br$: C 57.37, H 5.84, N 9.56, C/N = 7; found C 54.02, H 5.47, N 9.00, C/N = 7.

Synthesis of Monomer *N*-*n*-butyl-*N*′-(4-vinylbenzyl)-4,4′-bipyridinium Bromide Chloride (4VBVBu)

The mixing solution of 4-vinybenzyl chlorine (3.39 g, 0.02 mol) and BuV (1.47 g, 0.005 mol) in anhydrous acetonitrile (40 mL) was stirred for 24 h at 80 °C in the oil bath. The resulting solution was filtrated and then the yellow precipitate was purified with diethyl ether anhydrous and dried in vacuum to give 4VBVBu (2.1 g, 90%). ^{1}H NMR (D_2O, 400 MHz, ppm) δ: 0.91 (t, *J* = 7.4 Hz, 3H, C$\mathbf{H}_3$), 1.35 (m, *J* = 7.6 Hz, 2H, C$\mathbf{H}_2$CH$_3$), 2.0 (m, *J* = 7.5 Hz, 2H, CH$_3$CH$_2$C$\mathbf{H}_2$), 4.70 (the signal of N$^+$CH$_2$ that overlapped with D_2O), 5.35 (d, *J* = 10.9 Hz, 1H, vinyl), 5.82–5.86(m, 3H, vinyl and PhCH$_2$), 6.78 (q, *J* = 6.8 Hz, 1H, vinyl), 7.46 (d, *J* = 8.2 Hz, 2H, Ph), 7.57 (d, *J* = 8.2 Hz, 2H, Ph), 8.46 (t, *J* = 6.6 Hz, 4H, PyH), 9.04 (d, *J* = 6.7 Hz, 2H, PyH), 9.95 (d, *J* = 6.8 Hz, 2H, PyH); IR (KBr, cm^{-1}) ν: 1633 (C—N$^+$), 1539 (C=C and C=N from viologen), 1446 (C=C from phenyl), 924, 725 (C=C from vinyl). Anal. Calcd for $C_{23}H_{26}N_2BrCl \bullet 4H_2O$: C 53.33, H 6.60, N 5.41; found C 53.28, H 6.58, N 5.34.

Synthesis of Poly-*N*-*n*-butyl-*N*′-(4-vinylbenzyl)-4,4′-bipyridinium Bromide Chloride (P4VBVBu)

4VBVBu (3.0 g) was added to a 3-neck flask and stirred with a magnetic stir bar under an inert N_2 atmosphere and heated to 85 °C with an oil bath. After thermal equilibrium reached and the solution had been bubbled for 0.5 h, $K_2S_2O_8$ was added and reacted for 24 h at this temperature to give a crude product (2.58 g, 86%), which was dialyzed through a semipermeable membrane with distilled water for 5 days. The dialyzed aqueous was concentrated and precipitated with acetone and dried in vacuum to give the polymer (1 g, 38.8%). ^{1}H NMR (D_2O, 400 MHz, ppm) δ: 0.92 (br, C$\mathbf{H}_3$), 1.34 (br, C$\mathbf{H}_2$CH$_3$ and C$\mathbf{H}_2$CH from the main chains), 1.99 (br, CH$_3$CH$_2$C$\mathbf{H}_2$ and CH$_2$C$\mathbf{H}$ from the main chains), 4.70 (the signal of N$^+$CH$_2$ that overlapped with D_2O), 5.87 (br, PhCH$_2$), 6.68, 7.40 (br, Ph), 8.53, 8.93, 9.07 (br, PyH); IR (KBr, cm^{-1}) ν: 1633 (C—N$^+$), 1447 (C=C from phenyl), 1539 (C=C and C=N from viologen).

Synthesis of Polypseudorotaxanes P4VBVBu/CB[7]

P4VBVBu (0.5 g) was dissolved in water (200 mL) and CB[7] (0.4 g) was added in the solution of P4VBVBu, and stirred for 24 h at room temperature. The resulting solution was filtrated and the filtrate was concentrated and precipitated by acetone and dried in vacuum to give polypseudorotaxanes P4VBVBu/CB[7] (PC3, 0.85 g, 94%). The solid power of PC1 and PC2 for the measurement of ^{1}H NMR'XRD, TGA, and FTIR were synthesized by the above method as shown in Table 1. ^{1}H NMR (D_2O, 400 MHz, ppm) δ: 0.92 (br, C$\mathbf{H}_3$), 1.35 (br, C$\mathbf{H}_2$CH$_3$ and C$\mathbf{H}_2$CH from the main chains of P4VBVBu), 1.99 (br, CH$_3$CH$_2$C$\mathbf{H}_2$ and CH$_2$C$\mathbf{H}$ from the main chains of P4VBVBu), 4.21 (d, 14H from CB[7]), 4.50 (br, N$^+$CH$_2$), 5.49 (s,14H from CB[7]), 5.66 (d, 14H from CB[7]), 5.88 (br, PhCH$_2$), 6.77, 7.44 (br, Ph), 8.32, 8.49, 8.83, 8.95, 9.13 (br, PyH); IR (KBr, cm^{-1}) ν: 1633 (C—N$^+$of P4VBVBu), 1731 (C=O of CB[7]).

Characterization

All ^{1}H NMR experiments were performed on a Bruker AVANCE400 NMR spectrometer. D_2O was used for field-frequency lock, and the observed ^{1}H chemical shifts were reported in parts per million (ppm) relative to an internal standard (TMS, 0 ppm).

FTIR was carried out on a Tensor 27 spectrometer (Bruker, Switzerland) with sample prepared as KBr pellets. The spectra were acquired in the frequency range 4000–400 cm^{-1} at a resolution of 4 cm^{-1} with a total of 16 scans.

Elemental analyses (C, N, and H) were performed on Elementar Vario E1 III analyzer (German).

Thermal characteristics of samples were determined with Thermogravimetric analyzer (TGA), which was performed with a MettlerToledo SDTA-851 TGA system. The analysis was performed with ~10 mg of dried samples in a dynamic nitrogen atmosphere (flow rate 50 mL/min) at a heating rate of 10 °C/min.

Multiangle laser light scattering (MALLS) measurements were performed by the Wyatt Technology DAWN HELEOS 18 angle (from 15° to 165°) light scattering detector using a Ga-As laser (658 nm, 40 mW). The refractive index increments (dn/dc) of P4VBVBu in aqueous solution were determined at 25 °C by an Optilab Rex interferometeric refractometer (Wyatt Technology) at the wavelength of 658 nm, and the concentrations of P4VBVBu determined in aqueous solution for Zimm plot were 3.3750×10^{-4}, 6.6750×10^{-4}, 1.0013×10^{-3}, 1.3350×10^{-3}, 1.6688×10^{-3}, and 2.0025×10^{-3} g/mL.

DLS was performed on Dawn Heleos, Wyatt QELS and Optilab DSP instrument. The water used for Light Scattering measurements were all filtered through Millipore 0.45 μm hydrophilic membranes before using. The concentrations of P4VBVBu and guest of polypseudorotaxanes for the distribution of the hydrodynamic radius and the average hydrodynamic radius were all 1 mg/mL.

Data of X-ray Powder Diffraction (XRD) were collected on a Max 2200PC power X-ray diffractometer (Rigaku, Japan) with Cu-*K*α (1.54051 Å) radiation (40 kV, 20 mA). Powder

TABLE 1 The Composition and the M_w of Polymer and Polypseudorotaxanes P4VBVBu/CB [7]

Sample	The Molar Ratio of CB[7] to Viologen Units of P4VBVBu at the Time of Synthesis	Elemental Analyses			The Actual Molar Ratio of CB[7] to Viologen Units of P4VBVBu		M_w (g mol^{-1})
		C (wt %)	H (wt %)	N (wt %)			
P4VBVBu	0	53.33	6.60	5.41	0[a]	0[b]	1.14×10^{5}[c]
PC1	0.145	52.69	4.88	10.86	0.11[a]	0.08[b]	1.36×10^{5}[d]
PC2	0.247	51.29	4.65	14.48	0.21[a]	0.18[b]	1.61×10^{5}[d]
PC3	0.347	50.19	4.54	17.11	0.32[a]	0.29[b]	1.90×10^{5}[d]

[a] Determined by elemental analyses.

[b] Determined by ^{1}H NMR spectra.

[c] Determined by static light scattering.

[d] Calculated by the actual molar ratio of CB[7] to viologen units of P4VBVBu determined by ^{1}H NMR spectra.

samples were mounted on a sample holder and scanned with a step size of $2\theta = 0.02°$ between $2\theta = 5°$ and $50°$.

All electrochemical experiments were carried out in a standard three-electrode cell at room temperature (~25 °C) using a CHI 760 dual channel electrochemical workstation (CHI instruments). Mercury/mercurous sulfate electrode (MMSE) as reference electrode, Pt foil as counter electrode, and glassy carbon electrode as working electrode were used in a standard three-electrode cell. All solutions were purged with ultrapure nitrogen for about 20 min before electrochemical measurements.

The UV–vis spectra were measured by UV-4100 (Japan) at 25 °C, and the range of scanning was from 200 to 600 nm.

RESULTS AND DISCUSSION

Preparation of P4VBVBu and Polypseudorotaxanes with CB[7] Threaded

Monomer 4VBVBu was prepared by 4-vinybenzyl chlorine and BuV, which was synthesized by 4,4′-dipyridyl and *n*-butyl bromide, and the polymer P4VBVBu was prepared using $K_2S_2O_8$ as the initiator and 4VBVBu as the polymer monomer in water under the inter N_2 atmosphere by the free radical polymerization as shown in Scheme 1. Side-chain polypseudorotaxanes were easily achieved by self-assembly of P4VBVBu with a certain amount of CB[7] in water at room temperature for 24 h as shown in Scheme 2.

The polypseudorotaxanes with different degree of CB[7] threaded were determined by elemental analyses as shown in Table 1, while the actual mole ratio of CB[7]/P4VBVBu were calculated via the weight percentages of carbon, hydrogen, and nitrogen as listed in Table 1, which was in good agreement with the results of the ^{1}H NMR spectra.

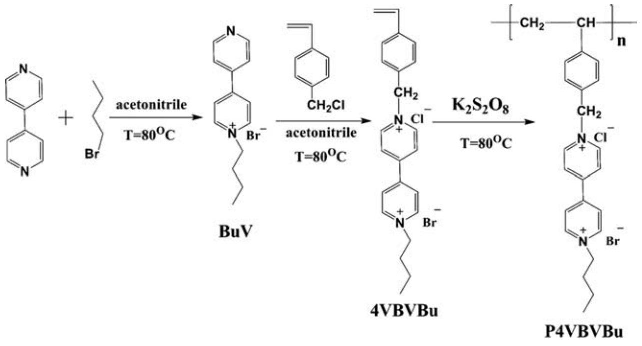
In static light scattering, we are able to obtain the weight-average molar mass M_w, the second-order virial coefficient A_2, and the mean square radius $\langle r_g^2 \rangle$ of polymer chains from the angular dependence of the excess absolute scattering intensity, known as the Rayleigh ratio $R(\theta)$, on the basis of

$$\frac{K^*C}{R(\theta)} = \frac{1}{M_w}\left(1 + \frac{1}{3}\langle r_g^2 \rangle q^2\right) + 2A_2C \tag{1}$$

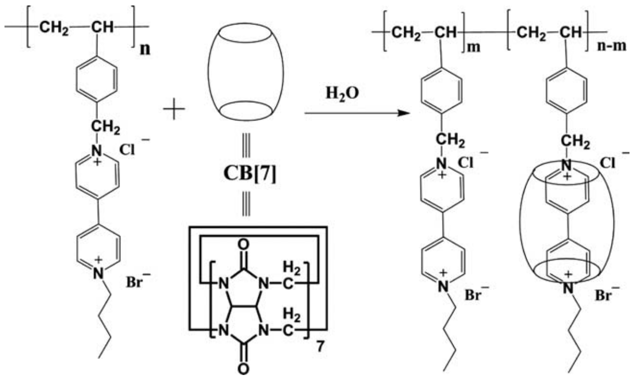
where $K^* = 4\pi(dn/dc)^2\, n_0/(N_A\lambda_0^4)$ and $q = (4\pi n_0/\lambda_0)\sin(\theta/2)$, with n_o, dn/dc, λ_0 and θ being the solvent refractive index, the specific refractive index increment, the wavelength of the incident light in vacuum and the scattering angle, respectively,[49,50]. Figure 1 shows a typical static Zimm plot of P4VBVBu in water solutions, where C ranges from 3.375×10^{-4} to 2.0025×10^{-3} g/mL. The date of static light scattering measurements indicated that the weight-average molar mass Mw of P4VBVBu was 1.03×10^5 g/mol, and Mw of polypseudorotaxanes with CB[7] were calculated by the actual mole ratio of CB[7]/P4VBVBu determined by ^{1}H NMR spectra and the actual Mw of polymer determined by static light scattering.

^{1}H NMR Spectra

The host-guest interaction of P4VBVBu with CB[7] was investigated by ^{1}H NMR spectrum. Figure 2 are the ^{1}H NMR spectra of CB[7] (1 mg/mL), PC1 (2.46 mg/mL), PC2 (2.92 mg/mL), PC3 (3.38 mg/mL), P4VBVBu (2 mg/mL), and monomer 4VBVBu (2 mg/mL). Upon formation of polypseudorotaxanes, new broad signals appear at 4.21, 5.49, and



SCHEME 1 Synthesis of polymer P4VBVBu.



SCHEME 2 Synthesis of the side-chain polypseudorotaxanes.

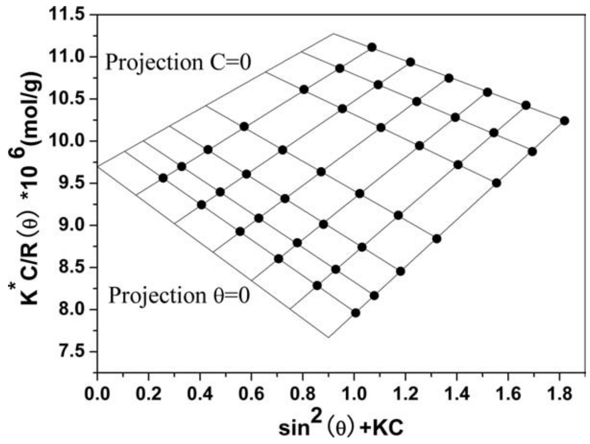


FIGURE 1 Typical Zimm plot for P4VBVBu in water.

5.66 ppm, which correspond to threaded CB[7]. Upon addition of CB[7], a part of the viologen proton signal (peak i and h) of P4VBVBu are upfield shifted from 8.93 to 8.83 (peak i′) and from 8.53 to 8.32 (peak h′) as shown in Figure 2, while the signals (e, f, and g) of the benzyl protons, which are located just outside of the CB[7], are downfield shifted from 5.87, 6.68, 7.40 to 5.88, 6.77, 7.44. The other protons (a, b, c, and d), which are located far from the CB[7], remain unchanged or have a little change. With the adding of CB[7], the areas of the peak i′ and h′ shielded by CB[7] increases as shown with arrows in insert of Figure 2. The ^{1}H NMR data supports that the CB[7] beads threaded in the side chains of P4VBVBu are located on the viologen units, and the amount of CB[7] threaded onto the side chains of the polymer can be estimated by calculating the ratio of the peak area of i′ to peak a (the side-chain methyl peak of P4VBVBu) in the ^{1}H NMR spectra, which indicates that the degree of threading of polypseudorotaxanes P4VBVBu/CB[7] (the molar ratio of CB[7] threaded to the viologen units of P4VBVBu) could be controlled between 0 and 0.3 simply by adding a certain amount of CB[7] into the solution of P4VBVBu.

FTIR Spectra

Figure 3 shows FTIR spectra of CB[7], polypseudorotaxanes PC3 and P4VBVBu. The extreme bands at 1731 cm^{-1} and 1633 cm^{-1} as shown in Figure 3 are the characteristic absorption peaks of C=O of CB[7] and viologen unite of polymer P4VBVBu, respectively. Also, the band at 1731 and 1633 cm^{-1} are observed in polypseudorotaxanes PC3 as shown in Figure 3. The FTIR data are indirect proof for the existence of polypseudorotaxanes P4VBVBu/CB[7].

X-Ray Powder Diffraction (XRD)

Figure 4 shows the XRD patterns of P4VBVBu, CB[7] and polypseudorotaxanes P4VBVBu/CB[7] with different degree of CB[7] threaded. No sharp peaks reflected in the pattern of polymer P4VBVBu show that it is a typical noncrystalline polymer as shown in Figure 4. While comparing with polymer P4VBVBu, CB[7] has crystal composition because there are three sharper peaks ($2\theta = 12.8, 21.1, 27.8$) in the XRD pattern as shown in Figure 4. As the amount of CB[7] threaded increases from 0 to 0.3 as shown in Figure 4, a new set of peaks appear ($2\theta = 12.8, 27.8$). The intensity of the peaks ($2\theta = 12.8, 21.1, 27.8$) increase with increasing amount of CB[7]

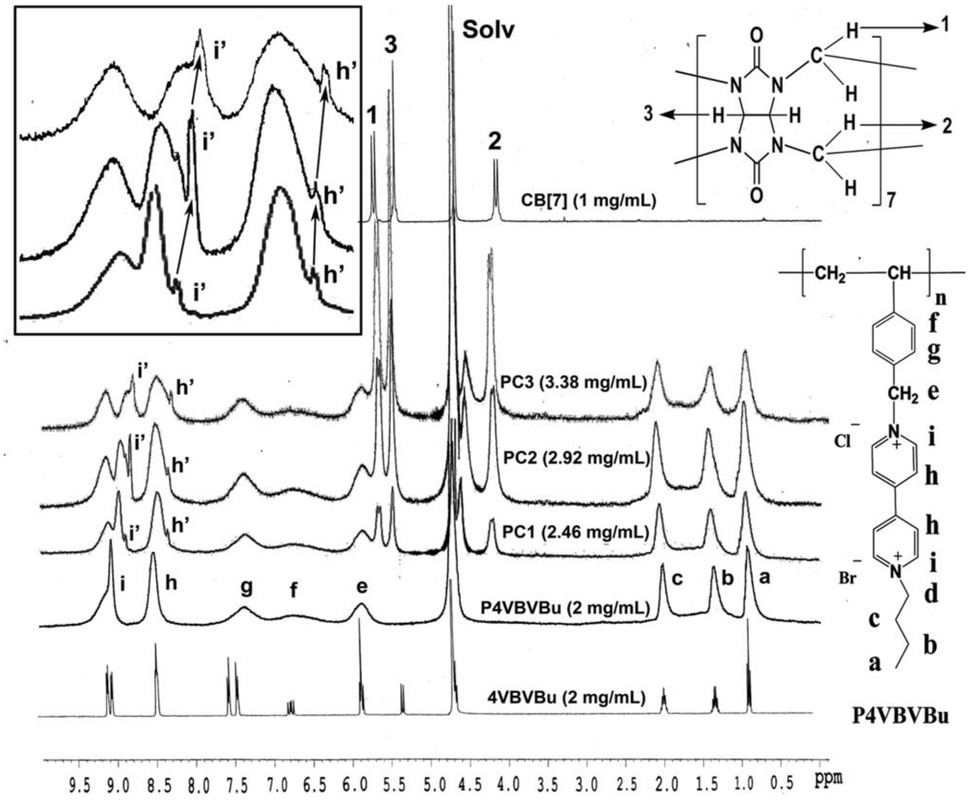


FIGURE 2 ^{1}H NMR spectra of CB[7] (1 mg/mL), PC1 (2.46 mg/mL), PC2 (2.92 mg/mL), PC3 (3.38 mg/mL), P4VBVBu (2 mg/mL), and monomer 4VBVBu (2 mg/mL). Insert image shows a magnified image of the increase of peak i′ and h′.

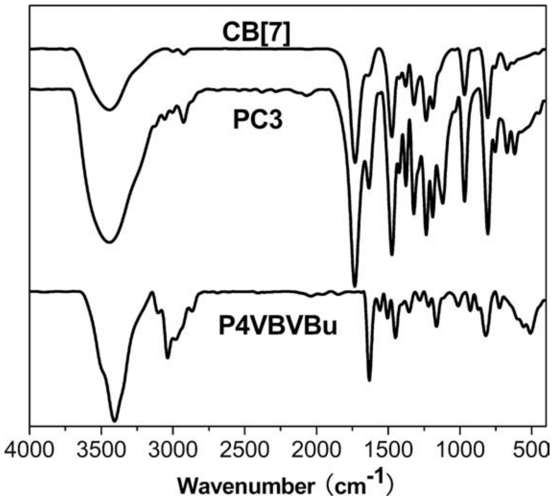


FIGURE 3 FTIR spectra of CB[7], polypseudorotaxanes PC3, and P4VBVBu.

threaded and approach that of pure CB[7] as shown in Figure 4. The increasing intensity suggests that the threading of CB[7] may cause chain conformational changes of the polymer. Compared with the parent polymer, the polypseudorotaxanes have more regular chain conformation because of amount of the threaded CB[7] beads (as shown in Fig. 8), and the regularity of the chain conformation increases with increasing amount of CB[7] threaded.

Thermal Properties

Figure 5 shows the TGA and DTGA curves of P4VBVBu, CB[7] and polypseudorotaxanes with different degree of CB[7] threaded (PC1, PC2, and PC3). The polypseudorotaxanes P4VBVBu/CB[7] show three major mass loss steps under nitrogen atmosphere. The first transition occurs near 325 °C and may be associated with the loss of the side chains of polymer, which are not threaded by CB[7], and this decomposition temperature is somewhat higher than that of P4VBVBu and increases with increasing the mole percentage

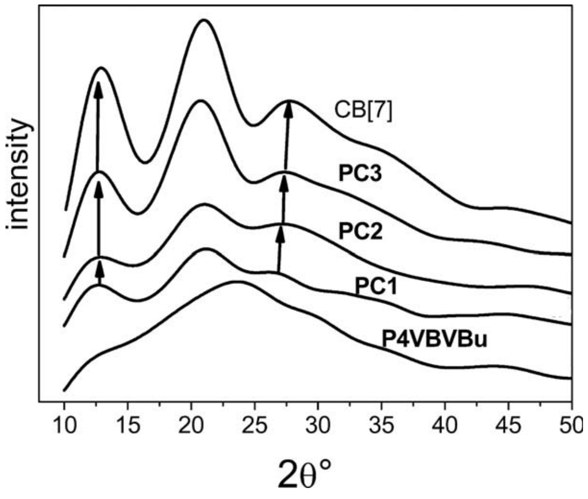


FIGURE 4 XRD patterns of P4VBVBu, polypseudorotaxanes PC1, PC2, PC3, and CB[7].

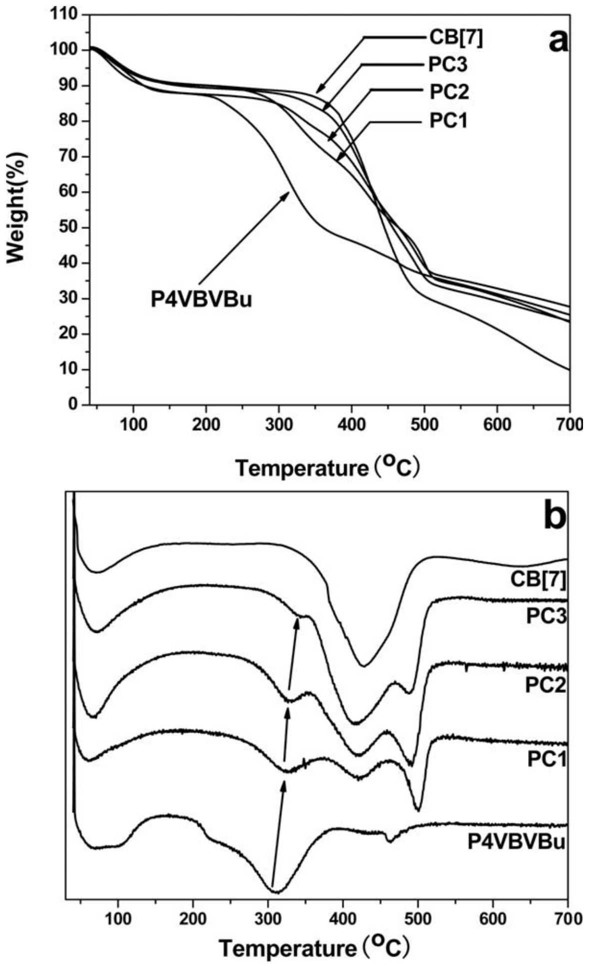


FIGURE 5 (a) TGA curves of polymer P4VBVBu, CB[7], and polypseudorotaxanes with different degree of CB[7] threaded (PC1, PC2, and PC3); (b) DTGA curves of P4VBVBu, CB[7], and polypseudorotaxanes PC1, PC2, and PC3.

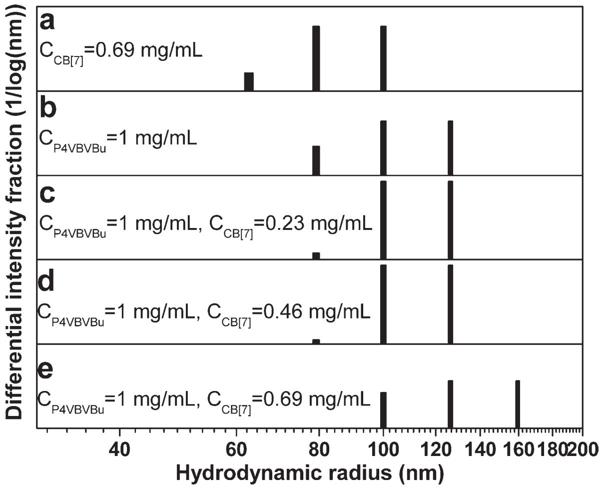


FIGURE 6 The distribution of the hydrodynamic radius of a ($C_{CB[7]} = 0.69$ mg/mL), b ($C_{P4VBVBu} = 1$ mg/mL), c ($C_{P4VBVBu} = 1$ mg/mL, $C_{CB[7]} = 0.23$ mg/mL), d ($C_{P4VBVBu} = 1$ mg/mL, $C_{CB[7]} = 0.46$ mg/mL), and e ($C_{P4VBVBu} = 1$ mg/mL, $C_{CB[7]} = 0.69$ mg/mL) in water.

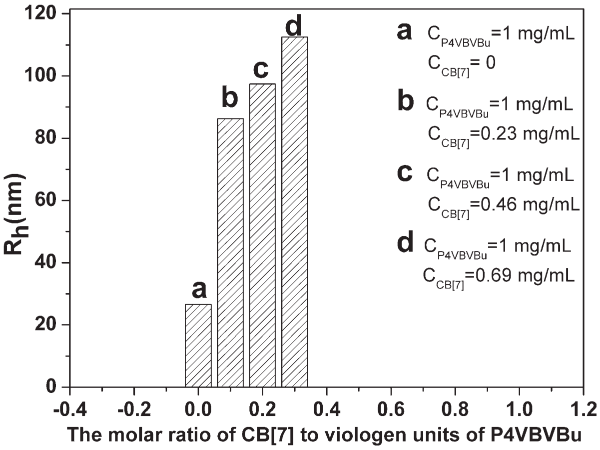


FIGURE 7 The average hydrodynamic radius (R_h) of a ($C_{P4VBVBu}$ = 1 mg/mL), b ($C_{P4VBVBu}$ = 1 mg/mL, $C_{CB[7]}$ = 0.23 mg/mL), c ($C_{P4VBVBu}$ = 1 mg/mL, $C_{CB[7]}$ = 0.46 mg/mL), and d ($C_{P4VBVBu}$ = 1 mg/mL, $C_{CB[7]}$ = 0.69 mg/mL).

of CB[7] (shown with arrows in Figure 5 (b)). This reason may be that the van der Waals interaction of the side chains are enhanced with increasing amount of CB[7] threaded. The second transition occurs at 429 °C and is loss of CB[7] threaded, which is compared with the loss of pure CB[7]. Interestingly, a new peak of the DTGA curve (the third transition of polypseudorotaxanes P4VBVBu/CB[7]) is observed near 492 °C comparing with the curves of pure P4VBVBu and CB[7] and the peak area increases with increasing the mole ratio of CB[7]. It is considered that it is loss of the viologen shielded by CB[7], which enhances the thermal stability of the viologen.

DLS Measurements

The distribution of the hydrodynamic radius and the average hydrodynamic radius of P4VBVBu (1 mg/mL), CB[7] (0.69 mg/mL) and P4VBVBu (1 mg/mL) with different concentrations of CB[7] (0.23, 0.46, 0.69 mg/mL) in water are obtained by DLS as shown in Figure 6 and Figure 7. The sizes of the aggregates in water increase with adding CB[7] as shown in Figure 6, and the average hydrodynamic radius of the aggregates also increases with the adding of CB[7] as shown in Figure 7. These results indicate that P4VBVBu and CB[7] are not simply mixed but form polypseudorotaxanes, and the distribution of R_h and the average R_h of the polypseudorotaxanes increase with the increasing CB[7] threaded because the regularity of the polypseudorotaxanes chain conformation increases with increasing the amount of CB[7] threaded as shown in Figure 8.

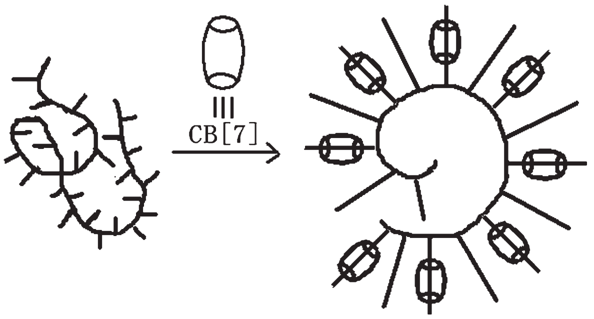


FIGURE 8 The model of conformational changes of the chain with CB[7] threaded.

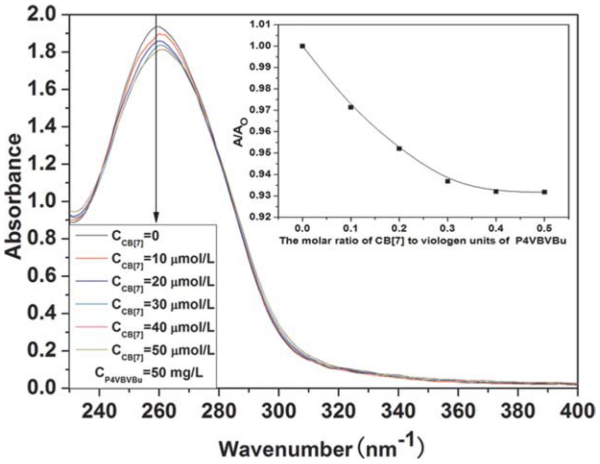


FIGURE 9 UV-vis absorption spectrum of 50 mg/L P4VBVBu in absent and presence of CB[7] (10, 20, 30, 40, 50 μmol/L). Insert shows a plot of the relative absorbance as a function of the ratio of CB[7] to viologen unites of P4VBVBu.

The Binding Constant of the Polypseudorotaxanes by UV–Vis Spectra

Figure 9 shows UV–vis spectra of P4VBVBu (50 mg/L) and P4VBVBu (50 mg/L) with different concentrations of CB[7] (10, 20, 30, 40, 50 μM). The pattern of P4VBVBu exhibits a strong absorption band centered around 260 nm, which is a characteristic absorption peak of polyviologen and the absorption peak of CB[7] around 260 nm is inexistence. The date of the experiment indicate that the intensity of the band decreases with increasing amount of CB[7] threaded. Obviously, both P4VBVBu and CB[7] could form the polypseudorotaxanes by the host-guest interactions, and the viologen chromophore is shielded by the threading of CB[7], which is in accord with the results of ^{1}H NMR and FTIR. The insert of Figure 3 shows a plot of the relative absorbance (A/A_o, where A is the corresponding absorbance intensity at 260 nm in presence of different equiv. of CB[7] and A_o is the absorbance intensity in absent of CB[7]) as a function of the ratio of CB[7] to viologen unites of P4VBVBu. The data show that both CB[7] and P4VBVBu could reach equilibrium and form the polypseudorotaxanes, when the molar ratio of CB[7] to the viologen units of P4VBVBu is 0.4, and the binding constant of CB[7] and the viologen units of P4VBVBu is 2×10^3 L/mol.

Electrochemistry of P4VBVBu and Polypseudorotaxanes with CB[7]

Typical cyclic voltammograms curves of P4VBVBu (50 mg/L) obtained in the absence and presence of CB[7] (10, 20, 30 μM) are shown in Figure 10, and the corresponding peak potentials (E_p) are given in Table 2. The data indicate that P4VBVBu undergoes two reversible one-electron reductions in the absence of CB[7]. However, the addition of CB[7] produces

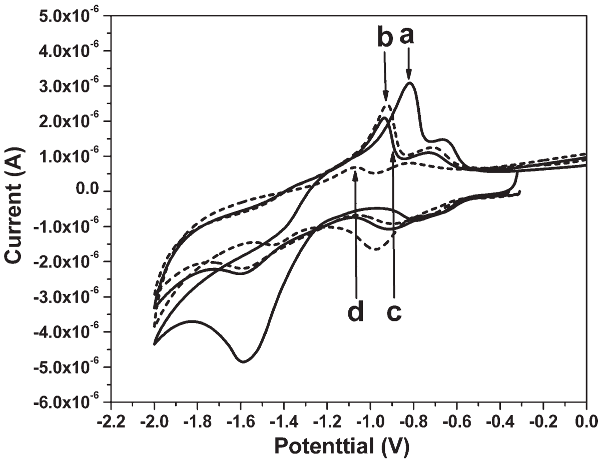


FIGURE 10 Cyclie voltammograms curves (0.05 v/s) of a ($C_{P4VBVBu}$ = 50 mg/L), b ($C_{P4VBVBu}$ = 50 mg/L, $C_{CB[7]}$ = 10 μmol/L), c ($C_{P4VBVBu}$ = 50 mg/L, $C_{CB[7]}$ = 20 μmol/L), and d ($C_{P4VBVBu}$ = 50 mg/L, $C_{CB[7]}$ = 30 μmol/L).

a remarkable effect on the cyclic voltammograms of P4VBVBu, which is that the peak potentials have a noticeable shift and the peak areas have a marked decrease with increasing the concentration of CB[7], because that the viologen units of the polypseudorotaxanes formed P4VBVBu and CB[7] by the host-guest interactions are shielded by CB[7] threaded.

The shift in peak potentials reflects relative binding affinities of the guest of different redox states to the host.[51] The much larger negative shift observed in the peak potential for the first oxidation reveals that the binding affinity of the fully reduced, neutral species to CB[7] is considerably reduced. On the other hand, the small negative shift in the E_p value of the second oxidation of polypseudorotaxanes with CB[7] threaded indicates that the cation radical form interacts slightly less strongly with CB[7] compared with the dication form. Therefore, the voltammeric results clearly demonstrate that CB[7] are threaded in the viologen units of P4VBVBu to form the polypseudorotaxanes and have remarkable effect on the oxidation reduction characteristic of the polypseudorotaxanes.

Effect of Salts on the Formation of Polypseudorotaxanes

Figure 11 shows the molar ratio (1-A_o/A, where A is the corresponding absorbance intensity of P4VBVBu (50 mg/L) and CB[7] (20μmol/L) at 260 nm in presence of different concentrations of KBr or K_2SO_4 and A_o is the absorbance intensity of P4VBVBu (50 mg/L) at 260 nm in absent of CB[7]) of CB[7] threaded to viologen units of P4VBVBu, which indicates the degree of the formation of the polypseudorotaxanes, decreases with increasing the concentration of KBr or K_2SO_4, and the molar ratio effected by the concentration of K_2SO_4 decreases more quickly than KBr. It is considered that the formation of the polypseudorotaxanes was inhibited by the adding of salts because that the host-guest interactions decease by the shielding effects of both Br^- or SO_4^{2-} to viologen ion and K^+ to CB[7], and the more inhibitory effect of K_2SO_4 on the formation of polypseudorotaxanes than KBr may be the result of more shielding effects of SO_4^{2-} than Br^-.

TABLE 2 The Peak Potential for P4VBVBu (50 mg/L) in the Absence and Presence of CB[7] (10, 20, 30 μmol L^{-1})

	E_p^1 (V)[a]	E_p^2 (V)[b]
P4VBVBu (a)	−0.818	−0.656
P4VBVBu/CB[7] (b)	−0.919	−0.693
P4VBVBu/CB[7] (c)	−0.934	−0.712
P4VBVBu/CB[7] (d)	−1.071	−0.792

[a] The peak potential for the first oxidation process expressed in volts vs. saturated calomel electrode.

[b] The peak potential for the second oxidation process.

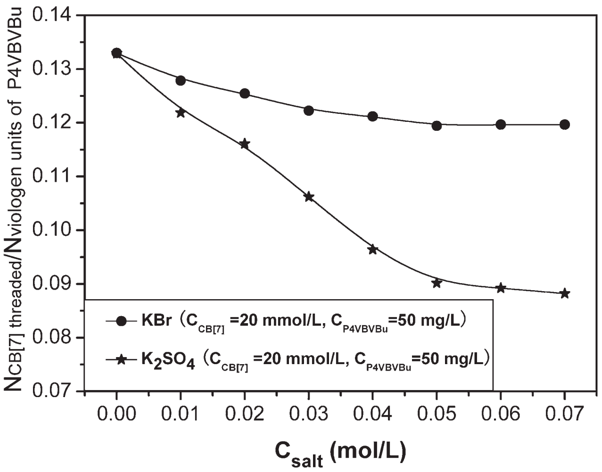


FIGURE 11 The effects of salts on the formation of polypseudorotaxanes between CB[7] and P4VBVBu.

CONCLUSIONS

We synthesized a novel water soluble side-chain polypseudorotaxanes with CB[7], which were localized on the viologen units in side chains of the polymer. The structure of polypseudorotaxanes with CB[7] was characterized by ^{1}H NMR, IR, XRD and UV-vis. DLS results showed that the average size of the aggregates in water increased with the increasing of CB[7] threaded, and TGA data indicated that the regularity of the polypseudorotaxanes chain conformation increased with increasing amount of CB[7] threaded, which led to the increasing of the polypseudorotaxanes thermal stability. The typical cyclic voltammograms showed that the peak potentials had a noticeable shift and the peak areas had a marked decrease with increasing the mole ratio of CB[7] threaded. UV-vis data showed that both CB[7] and P4VBVBu could form the polypseudorotaxanes with the binding constant of 2 × 10^3 L/mol, and the formation of the polypseudorotaxanes was inhibited by increasing the concentration of KBr or K_2SO_4 due to the shielding effects of both Br^- or SO_4^{2-} to viologen ion and K^+ to CB[7].

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