A Comparative Study on the Formation and Spectral Properties of the Polypseudorotaxanes of β-Cyclodextrin and Poly(propylene glycol) under Different Conditions

Xue Qing Guo,[1] Le Xin Song,*[1,2] Zheng Dang,[2] and Fang Yun Du[1]

[1]CAS Key Laboratory of Soft Matter Chemistry, Department of Polymer Science and Engineering,
University of Science and Technology of China, Hefei 230026, P. R. China

[2]Department of Chemistry, University of Science and Technology of China, Hefei 230026, P. R. China

Received March 10, 2009; E-mail: solexin@ustc.edu.cn

The results of this paper answer the questions, "Can hydrothermal conditions with higher pressure and higher temperature be used for the preparation of polypseudorotaxanes of cyclodextrins with polymers? If yes, do the prepared polypseudorotaxanes have different stoichiometries and spectral properties from those obtained by the same hosts and guests under nonhydrothermal conditions?" Two polypseudorotaxanes, **1** and **2**, formed by PPG and β-CD, were prepared with magnetic stirring and a hydrothermal method, respectively, in this work. Our results indicate that different host–guest stoichiometries and stacking forms between **1** and **2** significantly change their structural properties and thermal behaviors, implying that a close relationship exists between preparation conditions and spectral properties of the polypseudorotaxanes.

Since the first preparation of polymer–α-cyclodextrin (α-CD) complex composed of multiple α-CD rings threaded onto linear poly(ethylene oxide),[1] more and more attention has focused on the development of new polymer–CD supramolecules,[2–6] including structural demonstration,[7–9] property characterization and practical application in the field of biomaterials and electronics.[10–14] β-CD (Figure 1) comprises seven cyclic oligosaccharides linked by α-1,4-glycosidic bonds, which are arranged in the shape of a hollow truncated cone without hydroxy groups inside cavity.[15] The hydrophobic cavity gives it an ability to include a variety of guest molecules or ions.[16–20] Poly(propylene glycol) (PPG, see Figure 1), a clear light-yellow viscous liquid, is a type of nonionic surfactant,[21] and has been attracting considerable attention owing to its important applications in many industrial fields, for instance, as an emollient in cosmetics and an additive in lubricants, antistatic agents, plasticizers, and the like.[22]

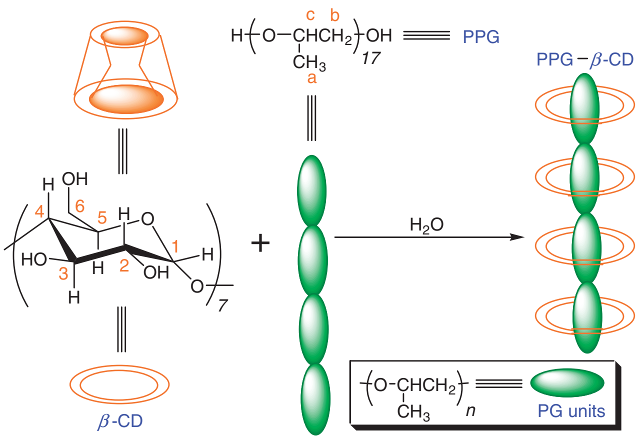

Figure 1. A schematic illustration of the supramolecular formation between β-CD and PPG.

Most CD inclusion complexes of polymers have been prepared by means of ultrasonic vibration or magnetic stirring.[23–27] For example, Harada and his co-workers reported the formation of PPG–β-CD complex in 1995, using ultrasonic agitation.[28] The intermolecular complexation between β-CD and PPG can be roughly illustrated in Figure 1. Whether different preparation conditions such as hydrothermal synthesis and magnetic stirring have an influence on the chemical stoichiometries in a polypseudorotaxane is an important question. If yes, whether and how the host–guest stoichiometries are reflected by spectral properties is of value. As far as we know, less effort has focused on the link among preparation conditions, binding stoichiometries, and physical properties of polypseudorotaxanes.

In view of the facts that hydrothermal methods with higher temperature and higher pressure can provide more favorable contact conditions among reactants,[29,30] and that there have been no reports about the difference in spectral properties and thermal behaviors of polymer–β-CD supramolecules obtained between hydrothermal and nonhydrothermal methods to date, the present work attempts to describe the magnetic stirring preparation and hydrothermal preparation of the supramolecule PPG–β-CD in order to evaluate the effect of reaction conditions on physical properties of PPG–β-CD, including reaction yields, stacking forms, structures, and thermal stabilities.

Two solid inclusion complexes, **1** and **2**, formed by PPG with β-CD were prepared nonhydrothermally and hydrothermally, respectively. ^1H nuclear magnetic resonance (^1H NMR) spectroscopy was applied to determine the chemical stoichio-

Published on the web September 9, 2009; doi:10.1246/bcsj.82.1209

metries of **1** and **2**. Fourier transform infrared (FTIR) spectroscopy, powder X-ray diffraction (PXRD), and derivative thermogravimetric (DTG) analysis were employed to examine the difference in spectral properties and thermal behaviors of β-CD between before and after inclusion.

Experimental

Materials. β-CD was purchased from Shanghai Chemical Reagent Co. and recrystallized twice from deionized water. PPG ($M_n = 1000$) was kindly donated by Miss Wang. DMSO-d_6 used as a solvent in NMR measurements was obtained from Aldrich Chemical Co. All other reagents and chemicals used were of general purpose or analar grade.

Preparation of Polypseudorotaxanes 1 and 2. The polypseudorotaxane **1** was prepared according to the method as follows. Liquid PPG (180 mg, 0.18 mmol) was added into an excess of β-CD aqueous solution (200 mL, 10.2 mg mL^{-1}) in a beaker at room temperature. The mixture was stirred for 1 h at 353 K and then for 48 h at room temperature. During stirring, the mixed solution became turbid, and then a white precipitate was formed, which was filtered off and washed with a little ethanol and deionized water, and dried under vacuum at 383 K. The polypseudorotaxane **2** was prepared by mixing PPG (100 mg, 0.1 mmol) with 1.0 mmol β-CD (1135 mg) in a stainless steel autoclave of 50 mL capacity and by heating at 383 K at a pressure of 276 kPa for 4 h. After the reaction ended, white precipitates were isolated by filtration and washed with a small amount of ethanol and deionized water, and then dried under vacuum at 383 K. The dry synthetic powders were weighed and the percentage yields were calculated from the amount of PPG used.

Instrumentation and Measurement. The ^{1}H NMR spectra were recorded on a Bruker AV-300 NMR spectrometer at 300 MHz at room temperature. Chemical shifts (δ) were referred to the solvent peaks (δ 2.5 for DMSO-d_6) using TMS as an internal standard. PXRD measurements were carried out on a Philips X'Pert Pro X-ray diffractometer using a monochromatized Cu Kα radiation source (40 kV, 40 mA) with a wavelength of 0.1542 nm and analyzed in the range $5° \leq 2\theta \leq 40°$. FTIR spectra and in situ FTIR spectra were obtained with a Bruker Equinox 55 spectrometer in KBr pellets in the range 4000–400 cm^{-1}. DTG analyses were made on a Shimadzu TGA-50 thermogravimetric analyzer at a constant heating rate of 10 K min^{-1} under a nitrogen atmosphere with a gas flow of 25 mL min^{-1}. Elemental analyses were performed using a Vario EL III elemental analyzer.

Results and Discussion

Preparation Analysis. PPG–β-CD polypseudorotaxane **1**. Yield, 92.6%. ^{1}H NMR (300 MHz, DMSO-d_6, 298 K): δ 5.70 (d, 7H, $J = 6.9$ Hz, O$_2$H of β-CD), 5.66 (s, 7H, O$_3$H of β-CD), 4.83 (d, 7H, $J = 3.3$ Hz, C$_1$H of β-CD), 4.43 (t, 7H, $J = 5.4$ Hz, O$_6$H of β-CD), 3.67 (t, 7H, $J = 8.4$ Hz, C$_3$H of β-CD), 3.63 (m, 14H, C$_6$H of β-CD), 3.58 (m, 7H, C$_5$H of β-CD), 3.38 (m, 14H, C$_2$H and C$_4$H of β-CD), 1.03 (m, 3H, methyl H of PPG). The result of elemental analysis: Anal. Calcd for $C_{51}H_{104}O_{18}\cdot 5C_{42}H_{70}O_{35}\cdot 35H_2O$: C, 42.88; H, 7.17%. Found: C, 42.98; H, 7.23%.

PPG–β-CD polypseudorotaxane **2**. Yield, 61.2%. ^{1}H NMR (300 MHz, DMSO-d_6, 298 K): δ 5.69 (d, 7H, $J = 6.9$ Hz, O$_2$H of β-CD), 5.64 (s, 7H, O$_3$H of β-CD), 4.83 (d, 7H, $J = 3.4$ Hz, C$_1$H of β-CD), 4.42 (t, 7H, $J = 5.6$ Hz, O$_6$H of β-CD), 3.67 (t, 7H, $J = 7.7$ Hz, C$_3$H of β-CD), 3.64 (m, 14H, C$_6$H of β-CD), 3.58 (m, 7H, C$_5$H of β-CD), 3.38 (m, 14H, C$_2$H and C$_4$H of β-CD), 1.03 (m, 3H, methyl H of PPG). The result of elemental analysis: Anal. Calcd for $C_{51}H_{104}O_{18}\cdot 7C_{42}H_{70}O_{35}\cdot 28H_2O$: C, 43.88; H, 6.88%. Found: C, 43.90; H, 6.90%.

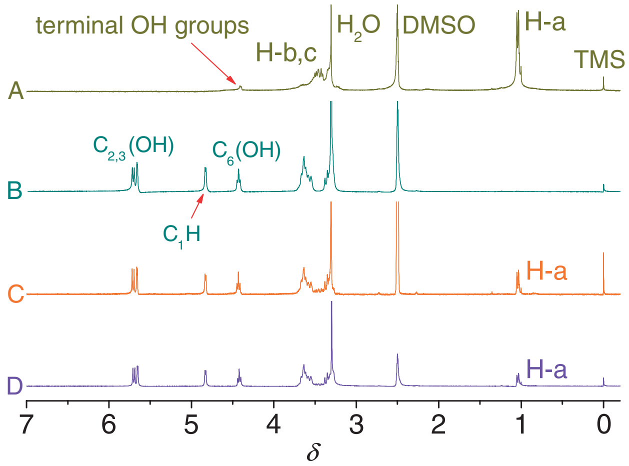

Figure 2. 300-MHz ^{1}H NMR spectra of (A) PPG, (B) β-CD, (C) **1**, and (D) **2** in DMSO-d_6.

A Comparison of ^{1}H NMR Spectra of PPG, β-CD, 1, and 2 in Solution. The compositions of the two polypseudorotaxanes were examined using ^{1}H NMR spectroscopy and elemental analysis. Figure 2 shows the ^{1}H NMR spectra of polypseudorotaxanes **1** and **2**, as well as their precursors. The molecular numbers of β-CD bound in the polypseudorotaxane chains of **1** and **2** are determined to be 5.1 and 7.4, respectively, through a comparison in the integral intensities of the proton signals between β-CD (C$_1$H, see Figures 1 and 2) and PPG (H-a). The binding stoichiometries determined by ^{1}H NMR spectroscopy are in good agreement with the elemental analysis results.

Different preparation conditions of **1** and **2** result in different stoichiometries of them though they have the same initial stoichiometry. Obviously, moderate hydrothermal conditions can be a factor contributing to the positive correlation between the binding stoichiometries and the interaction intensity of β-CD with PPG. It should be noted that PPG and β-CD as well as their polypseudorotaxanes are stable under the moderate hydrothermal conditions in this study according to the ^{1}H NMR data.

Besides, our result shows that magnetic stirring conditions give a much higher yield than hydrothermal conditions, but slightly lower than ultrasonic agitation conditions (yield, 96%).[28] Further, the ratios of linker units (PG units) to β-CD molecules are 3.3 in the complex **1** and 2.3 in the complex **2**, respectively, both of which are higher than 2.0 obtained by ultrasonic agitation.[28] This observation suggests that the magnetic stirring intensity is less effective to stimulate the degree of the inclusion complexation between β-CD and PPG, when compared with either ultrasonic agitation or hydrothermal condition.

Since different preparation methods lead to different host–guest stoichiometries in the polypseudorotaxanes, it is necessary to evaluate whether such differences in binding stoichiometry can result in the differences in spectral properties of polypseudorotaxanes?

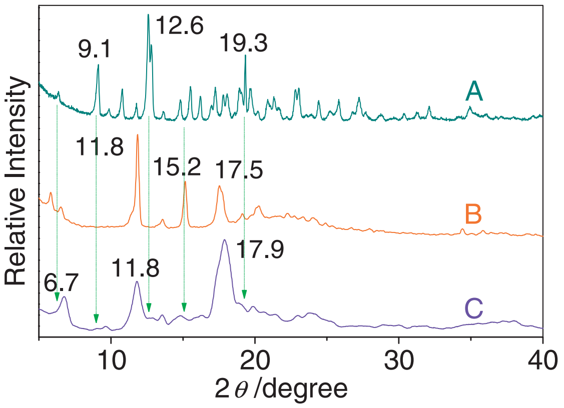

Figure 3. PXRD spectra of (A) β-CD, (B) **1**, and (C) **2**.

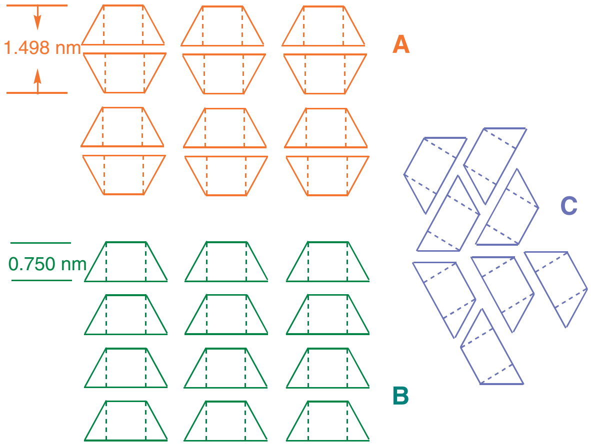

Figure 4. Two kinds of channel arrangements of β-CD: (A) head-to-head/tail-to-tail in **1** and (B) head-to-tail in **2**, and (C) a cage-type arrangement of free β-CD.

A Comparison of PXRD Patterns of β-CD, 1, and 2. PPG is liquid at room temperature, so there is no XRD data available. As shown in Figure 3A, the first (I_1), second (I_2), and third (I_3) strongest peaks of β-CD are 12.6, 19.3, and 9.1° with a typical cage-type arrangement (Figure 4C).[31] In Figures 3B and 3C, the patterns of the polypseudorotaxanes **1** and **2** contain several sharp reflections such as the I_1, I_2, and I_3 at 11.8, 15.2, and 17.5° for **1** and at 17.9, 11.8, and 6.7° for **2**. The 2θ values of these main peaks display a channel-type arrangement.[28,32–36] The channel-type arrangement of **1** and **2** is built from the collaboration between β-CD molecules and PG units as depicted in Figure 1. These channels are likely to be oriented along the chain direction and to be linked through hydrogen bonds between hydroxy groups of neighboring β-CD molecules.

Besides significant differences in positions of I_1, I_2, and I_3 between the PXRD patterns of β-CD and its two polypseudorotaxanes, there are also other important changes.

Initially, after complexation, large numbers of peaks belonging to β-CD, as well as the I_1 and I_3, disappear in the patterns of **1** and **2**, and I_2 is seriously weakened. However, the small peak of β-CD at 11.8° is markedly strengthened as I_1 for **1** and I_2 for **2** upon inclusion. The results indicate that the stacking behavior of β-CD molecules has been changed completely because of the binding interaction with PPG.

Next, polypseudorotaxane **1** has a strong sharp peak (I_2) at 15.2°, and two small peaks at lower 2θ values of 5.8, and 6.6°, but **2** only has a very weak peak at around 15.2°, and one moderate peak (I_3) at lower 2θ values of 6.7°. Moreover, all the half-widths of the peaks at I_1, I_2, and I_3 of **2** are obviously wider than those of **1** and β-CD, revealing that the size of the sample particles prepared using the hydrothermal method is smaller. Additionally, the PXRD pattern of the polypseudorotaxane prepared using ultrasonic agitation is very similar to that of **1**, but significantly different from that of **2**.[28] This phenomenon shows that different preparation methods such as hydrothermal synthesis and magnetic stirring will induce the differences in molecular arrangements of the polypseudorotaxanes formed by the same host and guest.

Furthermore, it is worth noting that the PXRD profiles of **1** and **2** differ largely from those of common complexes formed by small organic molecules and β-CD.[32,36,37] The key difference between them consists in more simplicity of the former patterns.

The differences in the PXRD curves of **1** and **2** are associated with the different stacking forms of β-CD molecules in them. For example, the peak at 2θ value of 5.8° ($d = 1.498$ nm) in the polypseudorotaxane **1** is designable as the average interlaminar of $\{001\}$ faces with a head-to-head structure (Figure 4A), which is two times greater than the cavity height of a β-CD molecule. However, in the polypseudorotaxane **2**, the disappearance of the peak at 2θ value of 5.8° means that the complexed β-CD molecules are most likely to adopt a head-to-tail structure, as shown in Figure 4B. The difference of stacking forms of β-CD molecules in **1** and **2** will produce the difference of intermolecular interactions, such as different hydrogen-bonding interactions in them, which can be detected by FTIR.

A Comparison of FTIR Spectra of PPG, β-CD, 1, and 2. FTIR spectra are usually used to examine intermolecular interactions between CDs and guests, because some characteristic absorption bands of CDs, especially those of guests, will produce slight frequency shifts after complexation. The phase transformation of guest from one to the other should be important evidence of the formation of supramolecules, since PPG is an oily liquid while the inclusion complexes are solid powders at room temperature.

As shown in Figure 5A, the broad absorption band at 3471 cm^{-1} is attributed to the $\nu_{\text{O–H}}$ vibration band of the chain-end hydroxy groups in PPG. Two strong absorption bands centered at 2969 and 2872 cm^{-1} correspond to the symmetric and asymmetric stretching vibration of CH_2 and CH_3, and a team of absorption bands around 1395 cm^{-1} is assignable to the deformation vibration of C–H. The strongest absorption peak due to $\nu_{\text{C–O}}$ appears at 1107 cm^{-1}. The free β-CD (Figure 5B) shows strong absorption bands at 3397 and 1028 cm^{-1}, ascribed to $\nu_{\text{O–H}}$ and $\nu_{\text{C–O}}$ vibrations, respectively. And a series of peaks at 820–1180 cm^{-1} in the fingerprint region are assigned to $\nu_{\text{C–C}}$ vibrations.

The number of bands and the contours of the spectra of **1** and **2** (Figures 5C and 5D) remain essentially the same as that of free β-CD, but slight shifts of some peaks are observed. For instance, the $\nu_{\text{O–H}}$ band is found to exhibit a red shift from 3471 cm^{-1} of PPG, 3397 cm^{-1} of β-CD, 3391 cm^{-1} of **2** to 3376 cm^{-1} of **1**, concomitant with the changes in shape and strength. These changes strongly imply that there exists an

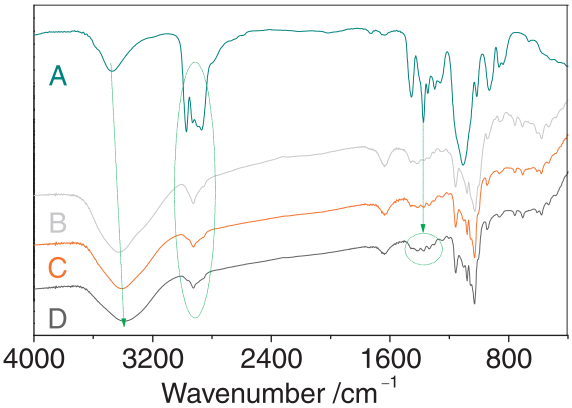

Figure 5. FTIR spectra of (A) PPG, (B) β-CD, (C) **2**, and (D) **1**.

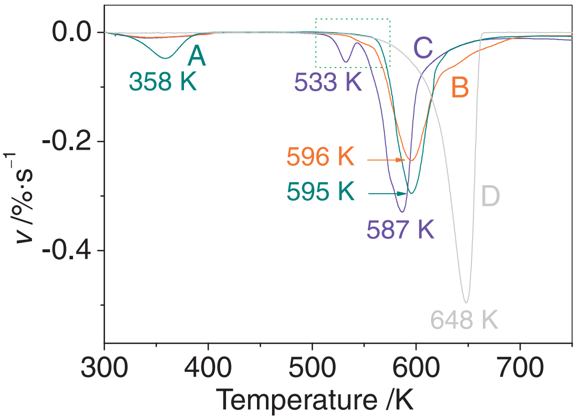

Figure 6. The fractional mass loss per second (v, % s^{-1}) as a function of temperature for (A) free β-CD, (B) **1**, (C) **2**, and (D) free PPG.

Table 1. FTIR Data of β-CD, PPG, **1**, and **2**

	$\nu_{\text{O–H}}$ /cm^{-1}	$\delta_{\text{O–H}}$ /cm^{-1}	$\nu_{\text{asC–O}}$ /cm^{-1}	$\nu_{\text{sC–O–C}}$ /cm^{-1}
PPG	3471	1638	1107	929
β-CD	3397	1638	1157, 1079, 1029	946
2	3391	1640	1157, 1080, 1030	944
1	3376	1638	1156, 1080, 1030	946

intermolecular interaction between PPG and β-CD. Clearly, the presence of PPG seems to strengthen the hydrogen-bonding interaction between β-CD molecules.

The data listed in Table 1 display the frequency shifts of $\nu_{\text{O–H}}$, the bending vibration of O–H ($\delta_{\text{O–H}}$), $\nu_{\text{C–O}}$ and $\nu_{\text{C–O–C}}$ in PPG and β-CD upon inclusion. The stretching vibration band of hydroxy groups in **1** shifts toward a lower wavenumber position than that in **2**, indicating that the hydrogen-bonding interaction in **1** is stronger than that in **2**. To estimate whether or not the presence of PPG can enhance the stability of β-CD, thermal analyses of the complexes are performed.

Analyses DTG Profiles of Free PPG, Free β-CD, 1, and 2. Figure 6 depicts the DTG curves of the four samples. Their maximum observed decomposition rates ($v_{\max}$) and corresponding temperatures differ from one another. There are two peaks (one big and one small) in the curves of β-CD and **2**, but both **1** and free PPG only have one strong peak. The first peak of free β-CD around 358 K is ascribed to the release of water molecules. Nonetheless, for the two complexes **1** and **2**, no peaks are observed below 500 K. The result confirms that the hydration of β-CD has been weakened because of the inclusion complexation with PPG under the same drying conditions.

As we can see from Figure 6, the decomposition or release temperature of the complexed PPG in each complex is much lower than those of free PPG. For instance, the first peak of **2** occurs around 533 K, possibly attributed to the advance release of some of the complexed PPG molecules, because a similar phenomenon was observed in a recent study on the inclusion system of β-CD and short chain aliphatic amines.[38] This finding means that the intermolecular complexation between PPG and β-CD greatly reduce the thermal stability of PPG under the nitrogen atmosphere. We consider that it is the phase change of PPG from a liquid phase in a free state to a solid phase in a complexed state that primarily causes this phenomenon. In other words, the intensity of the intermolecular interaction between PPG molecules in different states will change as a result of phase change: PPG–β-CD < PPG–PPG. The $v_{\max}$ values of the four samples decrease in the order PPG > **2** > β-CD > **1**. According to the calculation, the $v_{\max}$ value of **2** is approximately 1.4 times than that of **1**, and appears at a lower temperature relative to that of pure β-CD. The decomposition temperature point of **1** at 596 K corresponding to the value of $v_{\max}$ is almost the same as that of β-CD (595 K), both of which are higher than that of **2** at 587 K.

The results described above indicate that the thermal stability of the polypseudorotaxane **2** prepared by a powerful strategy (hydrothermal synthesis) is not enhanced by the intermolecular interaction between host and guest. It has been ascertained, and this is surprising, that the effect of the presence of PPG on the thermal performance of β-CD, has a dual nature, both improvement (e.g., in **1**) and deterioration (e.g., in **2**), dependent upon the complexation characteristics between PPG and β-CD. It may be explained that different preparation conditions cause different complexation behaviors between β-CD and PPG, leading to different interactions between β-CD molecules, as well as between PPG molecules.

On the other hand, the different complexation behaviors can also be explained by the different interactions between β-CD molecules before and after inclusion. As we know the interactions between β-CD molecules whether in a free state or in a complexed state are made up by two parts, van der Waals forces and hydrogen bondings, both of which are affected by intermolecular complexation modes and crystal stacking forms. Just as we had found in the FTIR spectra, the hydrogen-bonding interactions in the two samples are enhanced in comparison with those in free β-CD, and the interactions are stronger in **1** than in **2**. Also, PXRD spectra exhibit a channel structure of the two complexes. Therefore, it is reasonable that the van der Waals forces are weakened in the two samples, because the intermolecular distance between β-CDs is usually larger in a channel arrangement (Figures 4A and 4B) than in a cage arrangement (Figure 4C). So in the complex **1**, strong hydrogen-bonding interactions and weak van der Waals forces lead to the strongest intermolecular interactions between β-CDs of the three samples. Free β-CD presents moderate interactions with strong van der Waals forces but weak hydrogen bondings. And in the complex **2**, weak van der Waals forces and moderate hydrogen bondings result in the weakest intermolecular interactions. These descriptions explain the result that the thermal stabilities of them decrease in the order **1** > β-CD > **2**.

An experiment on the hydrothermal treatment of free β-CD sample was performed to estimate the impact of hydrothermal treatment on free CD using the same conditions as the preparation of complex **2**. And the FTIR, DTG, and PXRD spectra of the sample were obtained. It is found that the PXRD profile of the β-CD sample after hydrothermal treatment is simpler than that of untreated β-CD sample. Although the positions of several main peaks are different from each other before and after treatment, for both treated and untreated β-CD, the molecular stacking of them can be regarded as a cage form even with different water molecules in the light of their PXRD data.[39] Also, there are no observable shifts or broadening in the FTIR spectra of free β-CD before and after hydrothermal treatment, indicating little impact of hydrothermal treatment on the vibration bands of free β-CD. Further, the content of water molecules is much lower in the treated β-CD sample than in the untreated β-CD based on the comparison on DTG analyses of them. This observation corresponds to the result of PXRD. In addition, the thermal stability of the treated β-CD sample is slightly better than that of the untreated β-CD sample. However, complex **2**, formed under the same hydrothermal conditions, has a poorer thermal stability than the untreated β-CD based on the result in Figure 6. Therefore, we can declare the effect of inclusion on the thermal stability of β-CD.

Conclusion

In the present work, polypseudorotaxanes **1** and **2** are obtained using magnetic stirring synthesis and hydrothermal conditions, respectively. Our results indicate that the different preparation methods result in different host–guest stoichiometries and molecular stacking forms and thermal stabilities. As far as we know, this is the first example describing the preparation and characterization of polymer–CD inclusion complex formed by a hydrothermal method. The comparative results of the polypseudorotaxanes based on the same host and guest provides an important implication that there is a close relationship between preparation conditions and spectral properties of the polypseudorotaxanes.

References

1 A. Harada, M. Kamachi, *Macromolecules* **1990**, *23*, 2821.

2 G. Wenz, B.-H. Han, A. Müller, *Chem. Rev.* **2006**, *106*, 782.

3 F. Huang, H. W. Gibson, *Prog. Polym. Sci.* **2005**, *30*, 982.

4 A. Harada, J. Li, M. Kamachi, *Nature* **1992**, *356*, 325.

5 Y. Paik, B. Poliks, C. C. Rusa, A. E. Tonelli, J. Schaefer, *J. Polym. Sci., Part B: Polym. Phys.* **2007**, *45*, 1271.

6 K. L. Liu, S. H. Goh, J. Li, *Macromolecules* **2008**, *41*, 6027.

7 S. Kamitori, O. Matsuzaka, S. Kondo, S. Muraoka, K. Okuyama, K. Noguchi, M. Okada, A. Harada, *Macromolecules* **2000**, *33*, 1500.

8 Y. Liu, Y.-L. Zhao, H.-Y. Zhang, H.-B. Song, *Angew. Chem., Int. Ed. Engl.* **2003**, *42*, 3260.

9 H. Shigekawa, K. Miyake, J. Sumaoka, A. Harada, M. Komiyama, *J. Am. Chem. Soc.* **2000**, *122*, 5411.

10 J. Li, C. Yang, H. Li, X. Wang, S. H. Goh, J. L. Ding, D. Y. Wang, K. W. Leong, *Adv. Mater.* **2006**, *18*, 2969.

11 M. Tamura, D. Gao, A. Ueno, *Chem.—Eur. J.* **2001**, *7*, 1390.

12 N. Yui, T. Ooya, *Chem.—Eur. J.* **2006**, *12*, 6730.

13 P. N. Taylor, M. J. O'Connell, L. A. McNeill, M. J. Hall, R. T. Aplin, H. L. Anderson, *Angew. Chem., Int. Ed.* **2000**, *39*, 3456.

14 T. Ooya, H. S. Choi, A. Yamashita, N. Yui, Y. Sugaya, A. Kano, A. Maruyama, H. Akita, R. Ito, K. Kogure, H. Harashima, *J. Am. Chem. Soc.* **2006**, *128*, 3852.

15 J. Szejtli, *Chem. Rev.* **1998**, *98*, 1743.

16 H. M. Wang, L. X. Song, *Chem. Lett.* **2007**, *36*, 596.

17 L. X. Song, H. M. Wang, P. Xu, Z. Q. Zhang, Q. Q. Liu, *Bull. Chem. Soc. Jpn.* **2007**, *80*, 2313.

18 F. Hapiot, S. Tilloy, E. Monflier, *Chem. Rev.* **2006**, *106*, 767.

19 L. X. Song, H. M. Wang, P. Xu, Y. Yang, Z. Q. Zhang, *Chem. Pharm. Bull.* **2008**, *56*, 468.

20 Y. Matsui, M. Ono, S. Tokunaga, *Bull. Chem. Soc. Jpn.* **1997**, *70*, 535.

21 W. Kuran, in *Concise Polymeric Materials Encyclopedia*, ed. by J. C. Salamone, CRS Press, Boca Raton, FL, **1999**.

22 Z. Kulinski, E. Piorkowska, K. Gadzinowska, M. Stasiak, *Biomacromolecules* **2006**, *7*, 2128.

23 H. Jiao, S. H. Goh, S. Valiyaveettil, *Macromolecules* **2002**, *35*, 1399.

24 Y. M. Zhang, X. R. Deng, L. C. Wang, T. B. Wei, *J. Inclusion Phenom. Macrocyclic Chem.* **2008**, *60*, 313.

25 J. Li, X. P. Ni, Z. H. Zhou, K. W. Leong, *J. Am. Chem. Soc.* **2003**, *125*, 1788.

26 K. Olson, Y. Y. Chen, G. L. Baker, *J. Polym. Sci., Part A: Polym. Chem.* **2001**, *39*, 2731.

27 Y. Ni, S. X. Zheng, *J. Polym. Sci., Part A: Polym. Chem.* **2007**, *45*, 1247.

28 A. Harada, M. Okada, J. Li, M. Kamachi, *Macromolecules* **1995**, *28*, 8406.

29 C. Burda, X. B. Chen, R. Narayanan, M. A. El-Sayed, *Chem. Rev.* **2005**, *105*, 1025.

30 B. L. Cushing, V. L. Kolesnichenko, C. J. O'Connor, *Chem. Rev.* **2004**, *104*, 3893.

31 K. Harata, *Chem. Rev.* **1998**, *98*, 1803.

32 L. X. Song, H. M. Wang, X. Q. Guo, L. Bai, *J. Org. Chem.* **2008**, *73*, 8305.

33 Y. Gao, X. Zhao, B. Dong, L. Zheng, N. Li, S. Zhang, *J. Phys. Chem. B* **2006**, *110*, 8576.

34 E.-J. Wang, Z.-X. Lian, J. W. Cai, *Carbohydr. Res.* **2007**, *342*, 767.

35 B. Wang, J. He, D. H. Sun, R. Zhang, B. X. Han, *J. Inclusion Phenom. Macrocyclic Chem.* **2006**, *55*, 37.

36 S. S. Braga, P. Ribeiro-Claro, M. Pillinger, I. S. Gonçalves, A. C. Fernandes, F. Pereira, C. C. Romão, P. B. Correia, J. J. C. Teixeira-Dias, *J. Inclusion Phenom. Macrocyclic Chem.* **2003**, *47*, 47.

37 L. X. Song, H. M. Wang, Y. Yang, P. Xu, *Bull. Chem. Soc. Jpn.* **2007**, *80*, 2185.

38 L. X. Song, C. F. Teng, H. M. Wang, L. Bai, *Chin. J. Chem. Phys.* **2008**, *21*, 174.

39 M. D. Veiga, M. Merino, *J. Pharm. Biomed. Anal.* **2002**, *28*, 973.