

## 钠盐对聚丙二醇与 $\beta$ -环糊精超分子聚集体的组成、结构和降解的影响

杨 军<sup>1</sup> 宋乐新<sup>\*,1,2,3</sup> 郭雪晴<sup>1</sup> 杨 晶<sup>2</sup> 陈 杰<sup>2</sup>

(<sup>1</sup> 中国科学技术大学高分子科学与工程系, 中国科学院软物质化学重点实验室, 合肥 230026)

(<sup>2</sup> 中国科学技术大学化学系, 合肥 230026)

(<sup>3</sup> 南京大学国家配位化学重点实验室, 南京 210093)

**摘要:** 本文报道了一系列钠盐在调控聚 1,2-丙二醇(PPG)与  $\beta$ -环糊精( $\beta$ -CD)超分子组装过程中的重要作用。首先,几个从钠盐溶液中沉淀出来的组装体在 PPG 与  $\beta$ -CD 的化学计量比上存在着差异,对于 NaCl 和  $\text{Na}_2\text{CO}_3$  得到的是  $\text{PPG-(}\beta\text{-CD)}_7$ ,对于  $\text{NaAsO}_2$  得到的是  $\text{PPG-(}\beta\text{-CD)}_8$ ,此结果与从水中得到的产物  $\text{PPG-(}\beta\text{-CD)}_5$  以及从锂盐溶液得到的产物  $\text{PPG-(}\beta\text{-CD)}_6$  完全不同;其次,基于 3 个独立的实验(包括黏度、表面张力、摩尔电导率)所得结果的比较可以部分地解释产物组成上的差别;最后,场发射扫描电子显微镜、热重分析表征结果表明:产物即使具有相同的组成,它们的表面结构和物理性质也相当不同,这说明了盐效应在设计、构建超分子聚集体中的重要性和复杂性。

**关键词:** 超分子化学; 盐效应;  $\beta$ -环糊精; 聚丙二醇

中图分类号: O614.112, O636.1<sup>2</sup>, O632.31 文献标识码: A 文章编号: 1001-4861(2011)10-2013-08

## Effect of Sodium Salt on Composition, Structure and Degradation of Supramolecular Assemblies of Polypropylene Glycol with $\beta$ -Cyclodextrin

YANG Jun<sup>1</sup> SONG Le-Xin<sup>\*,1,2,3</sup> GUO Xue-Qing<sup>1</sup> YANG Jing<sup>2</sup> CHEN Jie<sup>2</sup>

(<sup>1</sup>CAS Key Laboratory of Soft Matter Chemistry, Department of Polymer Science and Engineering, University of Science and Technology of China, Hefei 230026, China)

(<sup>2</sup>Department of Chemistry, University of Science and Technology of China, Hefei 230026, China)

(<sup>3</sup>State Key Laboratory of Coordination Chemistry, Nanjing University, Nanjing 210093, China)

**Abstract:** The present work reveals that there is a significant effect of sodium salt in mediating supramolecular assemblies between 1, 2-polypropylene glycol (PPG) and  $\beta$ -cyclodextrin (CD). First, several molecular aggregates precipitated from different sodium salt solutions exhibit different stoichiometric ratios of PPG to  $\beta$ -CD:  $\text{PPG-(}\beta\text{-CD)}_7$  for NaCl and  $\text{Na}_2\text{CO}_3$  and  $\text{PPG-(}\beta\text{-CD)}_8$  for  $\text{NaAsO}_2$ , both of which are completely different from  $\text{PPG-(}\beta\text{-CD)}_5$  for pure water and from  $\text{PPG-(}\beta\text{-CD)}_6$  for lithium salts. Second, the current results obtained from three independent experiments (viscosity, surface tension and molar conductivity) may partially explain the difference in composition of the aggregates. Third, field emission scanning electron microscopy and thermogravimetric analyses indicate that the supramolecular assemblies prepared, even though with the same composition, have rather different surface features and physical properties. These findings emphasize the importance and complexity of salt effect in designing and constructing supramolecular assemblies.

**Key words:** supramolecular chemistry; salt effect;  $\beta$ -cyclodextrins; polypropylene glycol

收稿日期: 2011-03-01。收修改稿日期: 2011-04-21。

国家自然科学基金(No.21071139)资助项目。

\*通讯联系人。E-mail: solexin@ustc.edu.cn

Cyclodextrins (CDs), a group of cyclic oligosaccharides, can interact with many kinds of guests, including inorganic salts, coordination compounds and organic molecules<sup>[1-5]</sup>. In recent ten years, the intermolecular interaction between CDs and polymers has attracted many scientists in the fields of physics, chemistry and materials science<sup>[6-9]</sup>. Numerous efforts have been directed at the development of supramolecular assemblies constructed by CDs and polymers<sup>[10-13]</sup>. Although there are many reports about the effect of inorganic salts on polymer chains, to the best of our knowledge few literatures are available on the relationship between supramolecular assemblies and the salt effect. Very recently, we found that lithium salts played an important role in regulating the intermolecular interaction between 1, 2-polypropylene glycol (PPG) and  $\beta$ -CD in solutions, since the presence of lithium salts led to a fundamental change in composition of supramolecular assemblies from PPG-( $\beta$ -CD)<sub>5</sub> obtained in water medium to PPG-( $\beta$ -CD)<sub>6</sub> under the same reaction conditions<sup>[14]</sup>.

The aim of this work is to understand whether there is a difference of salt effects in mediating the formation of supramolecular assemblies of PPG with  $\beta$ -CD. Several sodium salts, such as sodium chloride (NaCl), sodium carbonate (Na<sub>2</sub>CO<sub>3</sub>) and sodium arsenite (NaAsO<sub>2</sub>), were chosen to compare with lithium salts. Attention is now focused on three issues: (1) how do the sodium salts affect the composition of supramolecular assemblies of PPG with  $\beta$ -CD? (2) what is the relationship between composition and structure of the assemblies? (3) is there a relation between structure of the assemblies and their degradation degree?

Initially, the data from elemental analysis and <sup>1</sup>H nuclear magnetic resonance (<sup>1</sup>H NMR) exhibit different compositions of the assemblies formed by PPG and  $\beta$ -CD in sodium salt solutions. And then, a possible mechanism of the salt effect is proposed based on three independent experiments (viscosity, surface tension and molar conductivity). Finally, a series of measurements was performed to investigate the structure and stability of the assemblies. These analytical results have allowed us to understand the important role of inorganic salts in

regulating the formation and degradation of supramolecular assemblies of a polymer with macrocyclic hosts.

## 1 Experimental

### 1.1 Materials

$\beta$ -CD was purchased from Shanghai Rich-Joint Chemical Reagent Co., Ltd. Liquid PPG (Mn 1000,  $M_w/M_n=1.12$ , C<sub>51</sub>H<sub>104</sub>O<sub>18</sub>) was supplied by The Third Petrochemical Factory, Tianjin Petrochemical Inc. NaCl and Na<sub>2</sub>CO<sub>3</sub> were obtained from Shanghai Chemical Reagent Co., Ltd. NaAsO<sub>2</sub> from Sigma-Aldrich. The inorganic salts were used as received without further purification. DMSO-d<sub>6</sub> used as a solvent in NMR measurements was purchased from Sigma-Aldrich.

### 1.2 Preparation of Solid Supramolecular Assemblies

Three assemblies, PPG-( $\beta$ -CD)<sub>7</sub>-1, PPG-( $\beta$ -CD)<sub>7</sub>-2, and PPG-( $\beta$ -CD)<sub>8</sub>-3, formed by  $\beta$ -CD with PPG in aqueous solutions of NaCl, Na<sub>2</sub>CO<sub>3</sub> and NaAsO<sub>2</sub>, respectively, were precipitated in the light of the following procedure<sup>[14]</sup>. Liquid PPG of 180 mg (0.18 mmol) was added to an aqueous solution (200 mL) of  $\beta$ -CD (1.8 mmol, 2.043 g) and one of the sodium salts (1.8 mmol) at room temperature. Subsequently, this mixed solution was stirred for 1 h at 353 K, and then for 48 h at room temperature. A white precipitate was gradually generated. This coagulative precipitation was washed repeatedly with deionized water until the effluents gave a negative flame test for sodium ions. Before use, all samples were kept in an oven under vacuum at 383 K for 24 h. The dried samples were obtained as a white powder, and weighed at room temperature. Their percentage yields were calculated from the amount of the PPG employed.

PPG-( $\beta$ -CD)<sub>7</sub>-1: yield, 54.4% . The results of elemental analyses: Anal. Calcd. for C<sub>51</sub>H<sub>104</sub>O<sub>18</sub> · 7C<sub>42</sub>H<sub>70</sub>O<sub>35</sub> · 32H<sub>2</sub>O: C, 43.46; H, 6.91. Found: C, 43.42; H, 6.96. <sup>1</sup>H NMR (300 MHz, DMSO-d<sub>6</sub>, 298 K):  $\delta$  5.71 (d, 49 H, O<sub>2</sub>H of  $\beta$ -CD), 5.66 (s, 49 H, O<sub>3</sub>H of  $\beta$ -CD), 4.83 (d, 49 H, C<sub>1</sub>H of  $\beta$ -CD), 4.42 (t, 49 H, O<sub>6</sub>H of  $\beta$ -CD), 3.63 (t, 49 H, C<sub>3</sub>H of  $\beta$ -CD), 3.58 (m, 98 H, C<sub>6</sub>H of  $\beta$ -CD), 3.55 (m, 49 H, C<sub>5</sub>H of  $\beta$ -CD), 3.38 (m, 98 H,

C<sub>2</sub>H and C<sub>4</sub>H of  $\beta$ -CD), 1.03 (m, 51 H, methyl H of PPG).

PPG-( $\beta$ -CD)<sub>7</sub>-2: yield, 52.0% . The results of elemental analyses: Anal. Calcd. for C<sub>51</sub>H<sub>104</sub>O<sub>18</sub> · 7C<sub>42</sub>H<sub>70</sub>O<sub>35</sub> · 32H<sub>2</sub>O: C, 43.46; H, 6.91. Found: C, 43.44; H, 6.96. <sup>1</sup>H NMR (300 MHz, DMSO-d<sub>6</sub>, 298 K):  $\delta$  5.71 (d, 49 H, O<sub>2</sub>H of  $\beta$ -CD), 5.65 (s, 49 H, O<sub>3</sub>H of  $\beta$ -CD), 4.82 (s, 49 H, C<sub>1</sub>H of  $\beta$ -CD), 4.42 (d, 49 H, O<sub>6</sub>H of  $\beta$ -CD), 3.63 (d, 49 H, C<sub>3</sub>H of  $\beta$ -CD), 3.61 (m, 98 H, C<sub>6</sub>H of  $\beta$ -CD), 3.55 (m, 49 H, C<sub>5</sub>H of  $\beta$ -CD), 3.38 (m, 98 H, C<sub>2</sub>H and C<sub>4</sub>H of  $\beta$ -CD), 1.03 (m, 51 H, methyl H of PPG).

PPG-( $\beta$ -CD)<sub>8</sub>-3: yield, 89.2% . The results of elemental analyses: Anal. Calcd. for C<sub>51</sub>H<sub>104</sub>O<sub>18</sub> · 8C<sub>42</sub>H<sub>70</sub>O<sub>35</sub> · 40H<sub>2</sub>O: C, 42.98; H, 6.89. Found: C, 43.09; H, 6.88. <sup>1</sup>H NMR (300 MHz, DMSO-d<sub>6</sub>, 298 K):  $\delta$  5.71 (d, 56 H, O<sub>2</sub>H of  $\beta$ -CD), 5.65 (s, 56 H, O<sub>3</sub>H of  $\beta$ -CD), 4.82 (d, 56 H, C<sub>1</sub>H of  $\beta$ -CD), 4.43 (s, 56 H, O<sub>6</sub>H of  $\beta$ -CD), 3.63 (d, 56 H, C<sub>3</sub>H of  $\beta$ -CD), 3.58 (m, 112 H, C<sub>6</sub>H of  $\beta$ -CD), 3.55 (m, 56 H, C<sub>5</sub>H of  $\beta$ -CD), 3.38 (m, 112 H, C<sub>2</sub>H and C<sub>4</sub>H of  $\beta$ -CD), 1.03 (m, 51 H, methyl H of PPG).

### 1.3 Preparation of Solution Samples

The solution samples of 10.0 mmol · dm<sup>-3</sup> of PPG in the absence and presence of NaCl, Na<sub>2</sub>CO<sub>3</sub> or NaAsO<sub>2</sub> with a concentration from 0.0 to 10.0 mmol · dm<sup>-3</sup> were prepared using a mixed solvent of ethanol and water (volume ratio, 1:6) at 298 K to measure the change in viscosity of the PPG solution under different concentrations of salts. The flow times (*t*) of each solution were determined as an average of three measurements.

Aqueous solutions of 0.400 mmol · dm<sup>-3</sup> of PPG in the absence and presence of NaCl, Na<sub>2</sub>CO<sub>3</sub> or NaAsO<sub>2</sub> with a concentration from 0.0 to 10.0 mmol · dm<sup>-3</sup> were prepared to examine the change in surface tension ( $\sigma$ ) of PPG solutions. The mixed solutions were stirred for five minutes at 298 K before use, and the values of  $\sigma$  were determined as an average of three measurements.

Aqueous solutions of 1.00 mmol · dm<sup>-3</sup> of NaCl, Na<sub>2</sub>CO<sub>3</sub> or NaAsO<sub>2</sub> in the absence and presence of PPG with a concentration from 0.000 to 0.100 mmol · dm<sup>-3</sup> were prepared to estimate the change in molar

conductivity ( $\Lambda_m$ ) of the salt solutions under different concentrations of PPG. Aqueous solutions were stirred at 298 K for ten minutes before test and each value of  $\Lambda_m$  for comparison was obtained as an average of three measurements.

### 1.4 Instruments and Methods

<sup>1</sup>H NMR spectra were recorded on a Bruker AV-300 NMR spectrometer at 300 MHz at room temperature. The chemical shifts ( $\delta$ ) were referred to the solvent peaks ( $\delta$  = 2.5 ppm for DMSO-d<sub>6</sub>) using tetramethylsilane (TMS) as an internal standard. Elemental analyses were performed using a Vario EL III elemental analyzer. The mass percentage of Na<sup>+</sup> in the samples was measured by using a Thermo Jarrell Ash Atomscan Advantage spectrometer (AAS).

The *t* values were measured by an Ubbelohde viscometer in a thermostatically controlled bath at 303 K. The  $\sigma$  values were determined using the Wilhelmy plate method and a JK99B automatic surface tensiometer (Shanghai Zhongchen Co.) at 298 K. The values of  $\Lambda_m$  of solutions were obtained using a DDSJ-308 conductivity meter (Shanghai Leici Instrument Inc.) at 298 K with a conductance cell of 1.083 cm<sup>-1</sup>. The  $\Lambda_m$  values of aqueous solutions of PPG itself at different concentrations served as a standard of reference for all the data concerning PPG.

Surface morphologies of solid samples were characterized using a JEOL-JSM-6700F field emission scanning electron microscope (FE-SEM) operated at 5 kV. X-ray diffraction (XRD) measurements were performed on a Philips X'Pert Pro X-ray diffractometer with a scintillation counter detector using a monochromatized Cu K $\alpha$  radiation source (40 kV, 40 mA) with a wavelength of 0.154 18 nm and analyzed in the range 5° ≤ 2 $\theta$  ≤ 48°. Thermogravimetry (TG) and derivative thermogravimetry (DTG) analyses were recorded on a Shimadzu TGA-50 thermogravimetric analyzer at a constant heating rate of 10.0 K · min<sup>-1</sup> under a nitrogen atmosphere with a gas flow of 25 mL · min<sup>-1</sup>. A gas chromatography-time of flight-mass spectrometry (GC-TOF-MS) was conducted using a Micromass GCT-MS spectrometer. The heating program of samples was the same as that reported in the previous

literatures<sup>[15-16]</sup>.

## 2 Results and discussion

### 2.1 Salt Effects and Probable Explanations

According to elemental analyses and  $^1\text{H}$  NMR data for the products, the compositions of the three supramolecular assemblies formed by PPG and  $\beta$ -CD in aqueous solutions of NaCl,  $\text{Na}_2\text{CO}_3$  and  $\text{NaAsO}_2$  were determined to be 1:7, 1:7 and 1:8, respectively. This result is surprising since it is completely different from those obtained both in pure water (1:5)<sup>[17]</sup> and in lithium salt solution (1:6)<sup>[14]</sup>. It reflects the importance and complexity of salt effects on the formation of supramolecular assemblies in solution. Especially, the fact that the sodium salt has different effects gives us an impression that there are differences in intensity of molecule-ion interactions between PPG chains and inorganic ions. Hence, we attempt to explain the differences by three independent experiments in aqueous solutions.

Initially, Fig.1 illustrates the change ( $\Delta t$ ) of  $t$  in

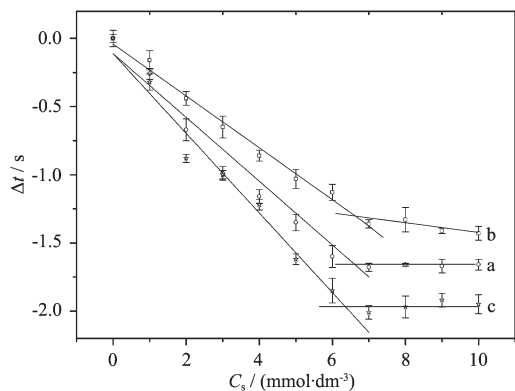


Fig.1 Changes of  $\Delta t$  in viscosity measurements of PPG solutions ( $10.0 \text{ mmol} \cdot \text{dm}^{-3}$ ) with the addition of NaCl (a),  $\text{Na}_2\text{CO}_3$  (b) and  $\text{NaAsO}_2$  (c) in the concentration ( $C_s$ ,  $\text{mmol} \cdot \text{dm}^{-3}$ ) range from 0.00 to  $1.00 \times 10^{-2} \text{ mol} \cdot \text{dm}^{-3}$

viscosity measurements of PPG solutions with the addition of sodium salts. Apparently, the presence of the salts leads to a gradual decrease of  $t$ , clearly reflecting the decrease in viscosity of the PPG solutions. In particular, the degree of the decrease is strongly dependent on the concentration of the salts. This change is explained by an increasing tendency of the

interaction among polymer chains, water molecules and inorganic ions, leading to a decreasing tendency of the interaction between PPG chains<sup>[14,18-21]</sup>. Further, the decrease in viscosities of PPG solutions presents a good linear concentration dependence (correlation coefficient  $r > 0.99$ ) at a lower salt concentration range of 0.00 to  $6.00 \text{ mmol} \cdot \text{dm}^{-3}$ . However, at a higher salt concentration range from 6.00 to  $10.00 \text{ mmol} \cdot \text{dm}^{-3}$ , the viscosities of the solutions exhibit a constant level, indicating that there is a maximum concentration of salt effects that can be accommodated on PPG chains. Importantly, the data presented in Fig.1 also depicts that the salt effects increase in the order:  $\text{NaAsO}_2 > \text{NaCl} > \text{Na}_2\text{CO}_3$ .

Next, Fig.2 shows the changes in  $\sigma$  value of PPG solution ( $0.400 \text{ mmol} \cdot \text{dm}^{-3}$ ) with the addition of a sodium salt. The result of this figure gives a strong indication that the  $\sigma$  value appears to increase nonlinearly with the increase of a salt concentration. And the influence of the salt on the surface tension of PPG solutions obeys the same order:  $\text{NaAsO}_2 > \text{NaCl} > \text{Na}_2\text{CO}_3$  as that seen in the viscosity change of PPG solutions. This phenomenon reveals that the molecule-ion interaction between PPG chains and  $\text{AsO}_2^-$  is much stronger than that between PPG chains and  $\text{Cl}^-$  or  $\text{CO}_3^{2-}$ .

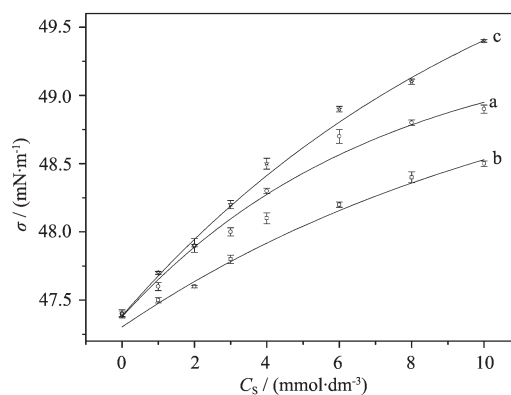


Fig.2 Changes in  $\sigma$  values of PPG solutions ( $0.400 \text{ mmol} \cdot \text{dm}^{-3}$ ) with the addition of NaCl (a),  $\text{Na}_2\text{CO}_3$  (b) and  $\text{NaAsO}_2$  (c) in the concentration range from 0.0 to  $10.0 \text{ mmol} \cdot \text{dm}^{-3}$

Finally, as displayed in Fig.3A, there is a good linear correlation ( $r > 0.99$ ) between the  $\Lambda_m$  values of the sodium salt solutions and the concentrations of PPG.

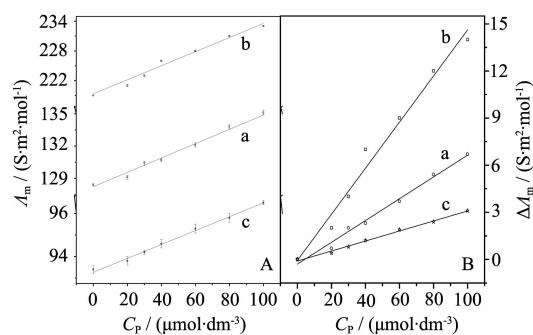


Fig.3 Changes in  $A_m$  (A) and  $\Delta A_m$  (B) values of NaCl (a),  $\text{Na}_2\text{CO}_3$  (b) and  $\text{NaAsO}_2$  (c) solutions ( $1.00 \text{ mmol} \cdot \text{dm}^{-3}$ ) with the addition of PPG in the concentration ( $C_P$ ,  $\mu\text{mol} \cdot \text{dm}^{-3}$ ) range from 0.000 to  $0.100 \text{ mmol} \cdot \text{dm}^{-3}$

This further provides a direct and strong evidence for the presence of a concentration dependence of the molecule-ion interaction between PPG chains and the sodium salt from another point of view. More importantly, the change of the difference ( $\Delta A_m$ ) between the solution without and with the salt, as shown in Fig. 3B, clearly reveals that there is a different tendency of the same concentration of PPG to promote the mobility of ions, and there will be a continuously graded response produced. Undoubtedly, this fact that the values of  $\Delta A_m$  decrease in the order:  $\text{Na}_2\text{CO}_3 > \text{NaCl} > \text{NaAsO}_2$ , gives an implication that different salts have different intensities of molecule-ion interactions with PPG, which is in good agreement with results obtained from measurements in  $\Delta t$  and  $\sigma$  values of PPG solutions.

Overall, based on the three independent experiments above, it is concluded that the mutual effect of the sodium salts and PPG chains in solution is required to comply with the order:  $\text{NaAsO}_2 > \text{NaCl} > \text{Na}_2\text{CO}_3$ . Together with the results reported in a previous literature<sup>[14]</sup>, we consider that there is a double-role of inorganic salts in the formation process of the assemblies: (1) The dehydration of PPG chains is initiated by inorganic ions, and the effect of anions dominates the process<sup>[14]</sup>. Further, the dehydration effect of the anions decreases in the order<sup>[20]</sup>:  $\text{AsO}_2^- > \text{CO}_3^{2-} > \text{Cl}^-$ . (2) The presence of cations might be involved in a protective role against dehydration for PPG chains, as illustrated in Fig.4.

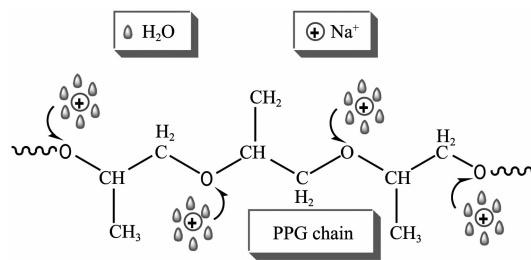


Fig.4 A proposed mechanism depicting the role of  $\text{Na}^+$  ions in favor of hydration of PPG chains

Clearly, the ionic radius of  $\text{Li}^+$  is much smaller than that of  $\text{Na}^+$ , so it is more likely to get close to ether oxygen atoms. That is to say,  $\text{Li}^+$  has a stronger ability in promoting hydration of PPG chains than  $\text{Na}^+$ . The magnitude of such an effect may be comparable to that evoked by the Hofmeister effect<sup>[22-23]</sup>. Different effects of cations and anions on PPG chains may be one reason for different compositions in the assemblies precipitated in inorganic salt solutions.

In short, although the sodium salts are not precipitated in the formation process of the assemblies of PPG and  $\beta$ -CD, the addition of them has caused an interesting change of composition of the assemblies. This leads us to further attempt to determine what the relation is between the composition and microstructure of the supramolecular assemblies.

## 2.2 Microstructures of the Supramolecular Assemblies

Fig.5 depicts XRD patterns of  $\beta$ -CD, NaCl and PPG-( $\beta$ -CD)-1. There is a significant position difference in the three strongest signals between free  $\beta$ -CD ( $9.1^\circ$ ,  $12.6^\circ$  and  $19.3^\circ$ ) and PPG-( $\beta$ -CD)<sub>7-1</sub> ( $5.9^\circ$ ,  $11.8^\circ$  and

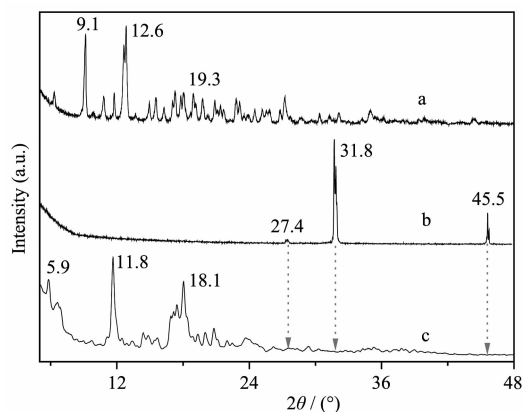


Fig.5 XRD patterns of  $\beta$ -CD (a), NaCl (b) and PPG-( $\beta$ -CD)<sub>7-1</sub> (c)

18.1°). And the characteristic peaks of NaCl at 27.4° (111), 31.8° (200) and 45.5° (220) disappear in the assembly, providing further evidence for the absence of NaCl in this case.

XRD patterns of the other two assemblies show a high similarity to that seen in Fig.5c, as well as those precipitated in lithium salt solutions<sup>[14]</sup>, suggesting that all the PPG- $\beta$ -CD assemblies have a similar stacking behavior dominated by  $\beta$ -CD, regardless of the difference in composition between them. The interlayer spacings are determined to be 7.5 and 15.0 nm based on the two characteristic peaks at  $2\theta$  angles of 11.8° and 5.9°, which correspond approximately to the cavity height of one (7.9 nm) and two (15.8 nm)  $\beta$ -CD molecules, respectively. This finding suggests a channel-type arrangement of the  $\beta$ -CD molecules in the binary assemblies like in the case of PPG-( $\beta$ -CD)<sub>5</sub>, but unlike the cage-type arrangement of free  $\beta$ -CD<sup>[17]</sup>. Such a stacking pattern is characteristic of interactions

between numerous polymers and CD molecules<sup>[24-28]</sup>. As such, here it reflects that the PPG chains have adequate flexibility to enable a threading through the ring-like cavity of  $\beta$ -CD.

Similar stacking structures of the assemblies impel us to examine surface structures emerged in different forms in different assemblies.

Fig.6 illustrates that the surface features of the assemblies are entirely different from the hexagonal prism structure of free  $\beta$ -CD<sup>[29]</sup>, and from one another. Apparently, PPG-( $\beta$ -CD)<sub>7</sub>-1, PPG-( $\beta$ -CD)<sub>7</sub>-2 and PPG-( $\beta$ -CD)<sub>8</sub>-3 are shaped like an irregular stone, a stalagmite and a large stone slab, respectively. The large difference in morphologies gives an impression that the formation process of surface structures of the assemblies in solution is related to the inorganic salt used. In other words, different salts can cause the binary assemblies to generate different shapes, regardless of the consistency in composition.

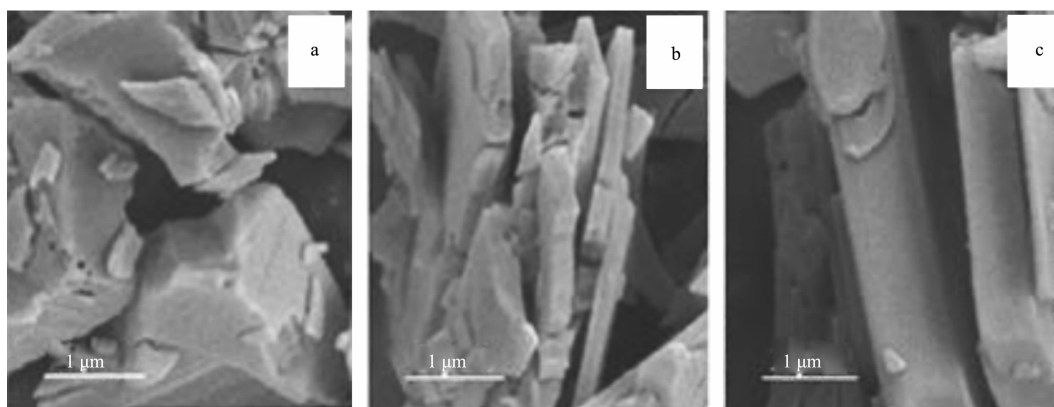


Fig.6 FE-SEM images of PPG-( $\beta$ -CD)<sub>7</sub>-1 (a), PPG-( $\beta$ -CD)<sub>7</sub>-2 (b) and PPG-( $\beta$ -CD)<sub>8</sub>-3 (c)

In brief, the difference in composition of the assemblies cannot be reflected by their stacking structures and surface structures. Such a result encourages further experimental investigation of thermal stabilities of the assemblies.

### 2.3 Thermal degradation of the supramolecular assemblies

Fig.7 shows the degradation temperatures, degradation rates ( $V$ , %·s<sup>-1</sup>) and residual masses (RM, %) of the three assemblies. From Fig.7A, we find two important facts: (1) that there is a large decrease ( $\Delta RM > 7\%$  from 320 to 390 K) in water content in the

assemblies compared to that of free  $\beta$ -CD at the same drying conditions, and (2) that although the degradation onset temperature of  $\beta$ -CD and its assemblies is rather similar at about 543 K, their RM values at higher temperature differ completely for the same temperature.

For instance, the RM values of  $\beta$ -CD, PPG-( $\beta$ -CD)<sub>7</sub>-1, PPG-( $\beta$ -CD)<sub>7</sub>-2 and PPG-( $\beta$ -CD)<sub>8</sub>-3 at 775 K are 16.9, 10.0, 3.9 and 11.3%, respectively. It is apparent that there is a lower RM values in the assemblies in comparison with free  $\beta$ -CD. In consideration of the difference of water content among these samples, the degradation degree ( $\alpha$ , %) of both PPG and  $\beta$ -CD can be

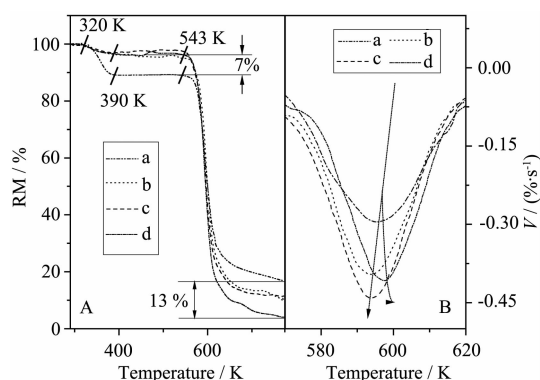


Fig.7 TG (A) and DTG (B) profiles of free  $\beta$ -CD (a), PPG-( $\beta$ -CD)<sub>7</sub>-1 (b), PPG-( $\beta$ -CD)<sub>7</sub>-2 (c) and PPG-( $\beta$ -CD)<sub>8</sub>-3 (d) in nitrogen

calculated based on Equation 1.

$$\alpha = 1 - RM \times (1 - r)^{-1} \quad (1)$$

In this equation,  $r$  expresses the mass fractions of water in the samples as determined by TG analysis. The values of  $\alpha$  were determined to be 95, 81, 89, 96 and 88% in PPG<sup>[31]</sup>,  $\beta$ -CD, PPG-( $\beta$ -CD)<sub>7</sub>-1, PPG-( $\beta$ -CD)<sub>7</sub>-2 and PPG-( $\beta$ -CD)<sub>8</sub>-3, respectively. The result indicates that the interaction between PPG and  $\beta$ -CD in the assemblies stimulates the degradation of  $\beta$ -CD.

Fig.7B shows the DTG curves of the samples in the range of the rapid degradation stage at about 570 to 620 K. As seen in the figure, there is an increase in maximum degradation rates ( $V_{\max}$ ) of the assemblies relative to  $\beta$ -CD and those obtained from lithium salt solutions<sup>[14]</sup>. Also, the maximum degradation temperatures ( $T_{\max}$ ) appear to decrease from  $\beta$ -CD, PPG-( $\beta$ -CD)<sub>7</sub>-1 to PPG-( $\beta$ -CD)<sub>7</sub>-2, but PPG-( $\beta$ -CD)<sub>8</sub>-3 shows a higher value of  $T_{\max}$ , as indicated by the arrows. This implies the relationship between the degradation processes and the compositions of the assemblies. Such a situation also occurs in vacuum.

Fig.8 describes the thermal degradation of the assemblies under GC-TOF-MS conditions, indicating a relation between relative abundances (RA, %) of total ionic current and heating time of the sample. The difference in the degradation processes of  $\beta$ -CD and its assemblies can be clearly seen from the position of main peaks and the number and position of satellite peaks (indicated by asterisks). The earlier degradation (indicated by an arrow) of the assemblies compared to

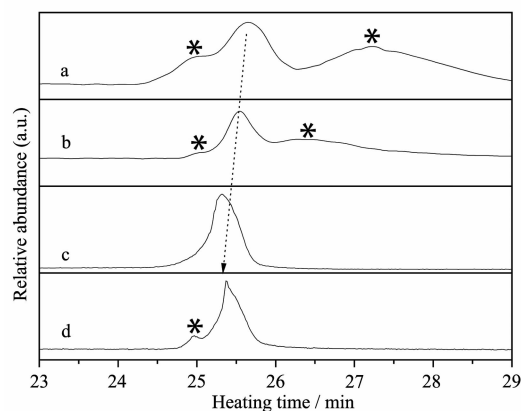


Fig.8 Thermal degradation curves of free  $\beta$ -CD (a), PPG-( $\beta$ -CD)<sub>7</sub>-1 (b), PPG-( $\beta$ -CD)<sub>7</sub>-2 (c) and PPG-( $\beta$ -CD)<sub>8</sub>-3 (d) in vacuum

free  $\beta$ -CD should be a consequence of salt effects.

Fig.9 exhibits a group of mass spectra of the assemblies at the main peak positions of Fig.8. Based on a careful comparison for the spectra, we can see that the assemblies with the same stoichiometries give a different degradation scheme, revealing the complexity of salt effects. For example, two key molecule-ion peaks at  $m/z$  113.024 ( $C_5H_5O_3^+$ ) and 114.031 ( $C_5H_6O_3^+$ ) are observed in different RA values in Fig.9a and b. Both of them are derived from a glucopyranose ring of  $\beta$ -CD.

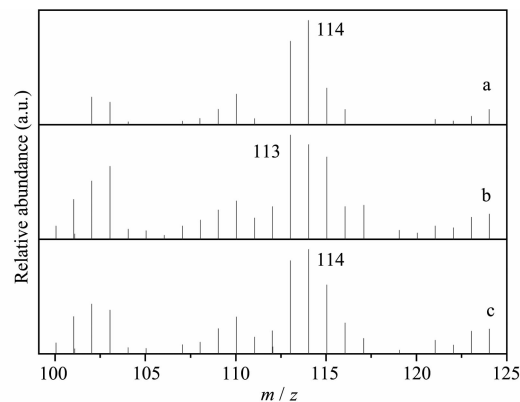


Fig.9 Mass spectra of PPG-( $\beta$ -CD)<sub>7</sub>-1 (a), PPG-( $\beta$ -CD)<sub>7</sub>-2 (b) and PPG-( $\beta$ -CD)<sub>8</sub>-3 (c) corresponding to the main peak positions of Fig.8

A probable formation and transformation mechanism concerning the fragments is illustrated in Fig.10. It is clear that there is a proton exchange between  $C_5H_5O_3^+$  and  $C_5H_6O_3^+$ . As shown in Fig.9, such a proton exchange has different responses in the three assemblies. This should be a reflection of the structural

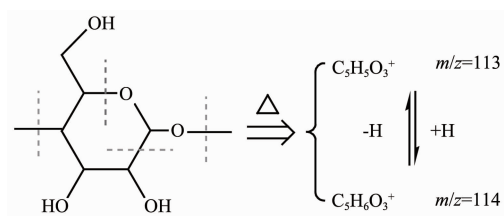


Fig.10 A proposed formation mechanism of the two fragments:  $C_5H_3O_3^+$  and  $C_5H_6O_3^+$

difference of the assemblies.

### 3 Conclusions

This study reveals the important effect of the sodium salt on the composition of supramolecular assemblies of PPG and  $\beta$ -CD. A probable mechanism is proposed to explain the difference in composition of the assemblies. Also, the evaluation of the microstructures and thermal behaviors of the assemblies presents the consequence of salt effects though the salts are not precipitated in the assemblies.

**Acknowledgements:** This project was supported by NSFC (No. 21071139).

**Supporting Information Available:** XRD patterns of PPG-( $\beta$ -CD)<sub>7</sub>-2 and PPG-( $\beta$ -CD)<sub>8</sub>-3 are available: from the corresponding author.

### References:

- [1] LIU Yu(刘育), YOU Chang-Cheng(尤长城), ZHANG Heng-Yi(张衡益). *Supramolecular Chemistry: Molecular Recognition and Assembly of Synthetic Receptor* (超分子化学—合成受体的分子识别与组装). Tianjin: Nankai University Publishers, **2000**:191-239
- [2] Hapiot F, Tilloy S, Monflier E. *Chem. Rev.*, **2006**,**106**:767-781
- [3] WANG Nan-Ping(王南平), YU Xiao-Dong(余晓冬), CHEN Hong-Yuan(陈洪渊). *Chem. Res. Appl. (Huaxue Yanjiu Yu Yingyong)*, **2001**,**13**:27-32
- [4] Song L X, Bai L, Xu X M, et al. *Coord. Chem. Rev.*, **2009**,**253**:1276-1284
- [5] Connors K A. *Chem. Rev.*, **1997**,**97**:1325-1258
- [6] Harada A, Hashidzume A, Yamaguchi H, et al. *Chem. Rev.*, **2009**,**109**:5974-6023
- [7] Yamaguchi I, Osakada K, Yamamoto T. *Macromolecules*, **2000**,**33**:2315-2319
- [8] Harada A, Kamachi M. *Macromolecules*, **1990**,**23**:2821-2823
- [9] Song L X, Guo X Q, Du F Y. *Polym. Degrad. Stabil.*, **2010**,**95**:508-515
- [10] Binkowski C, Lequart V, Hapiot F, et al. *Carbohydr. Res.*, **2005**,**340**:1461-1468
- [11] Liu Y, Li L, Zhang H Y, et al. *Macromolecules*, **2002**,**35**:9934-9938
- [12] Yu Y M, Cai W S, Chipot C, et al. *J. Phys. Chem. B*, **2008**,**112**:5268-5271
- [13] Tu Y F, Chen H Y. *Anal. Biochem.*, **2001**,**299**:71-77
- [14] Guo X Q, Song L X, Du F Y, et al. *J. Phys. Chem. B*, **2011**,**115**:1139-1144
- [15] Song L X, Xu P. *J. Phys. Chem. A*, **2008**,**112**:11341-11348
- [16] Song L X, Yang J, Bai L, et al. *Inorg. Chem.*, **2011**,**50**:1682-1688
- [17] Guo X Q, Song L X, Dang Z, et al. *Bull. Chem. Soc. Jpn.*, **2009**,**82**:1209-1213
- [18] Ferry A. *J. Chem. Phys.*, **1997**,**107**:9168-9175
- [19] Zhang Y J, Cremer P S. *Curr. Opin. Chem. Biol.*, **2006**,**10**:658-663
- [20] Zhang Y J, Furryk S, Bergbreiter D E, et al. *J. Am. Chem. Soc.*, **2005**,**127**:14505-14510
- [21] Rashidi M, Blokhuis A M, Skaug A. *J. Appl. Polym. Sci.*, **2010**,**117**:1551-1557
- [22] Kunz W, Lo N P, Ninham B W. *Curr. Opin. Colloid Interface Sci.*, **2004**,**9**:1-18
- [23] Parsegian V A. *Nature*, **1995**,**378**:335-336
- [24] Rusa C C, Luca C, Tonelli A E. *Macromolecules*, **2001**,**34**:1318-1322
- [25] Liu Y, Zhao Y L, Zhang H Y, et al. *Macromolecules*, **2004**,**37**:6362-6369
- [26] Liu Y, Li L, Zhang H Y, et al. *Macromolecules*, **2002**,**35**:9934-9938
- [27] He L H, Huang J, Chen Y M, et al. *Macromolecules*, **2005**,**38**:3845-3851
- [28] He L H, Huang J, Chen Y M, et al. *Macromolecules*, **2005**,**38**:3351-3355
- [29] Song L X, Wang M, Dang Z, et al. *J. Phys. Chem. B*, **2010**,**114**:3404-3410
- [30] Song L X, Du F Y, Guo X Q, et al. *J. Phys. Chem. B*, **2010**,**114**:1738-1744