Inclusion Complexes of Poly(4-vinylpyridine)−Dodecylbenezenesulfonic Acid Complex and Cyclodextrins

Hua Jiao, S. H. Goh,* and S. Valiyaveettil

Department of Chemistry, National University of Singapore, 3 Science Drive 3, Singapore 117543

Received January 22, 2002

ABSTRACT: P4VPy(DBSA)$_x$ complexes (x = 0.25, 0.50, 0.75, or 1.00 DBSA/P4VPy repeat units) are able to form inclusion complexes with three cyclodextrins (CDs). The complexes were characterized by XRD, XPS, ^{13}C CP/MAS NMR, ^{1}H NMR, DSC, and TGA. A columnar structure with poor order is established in all the inclusion complexes. XPS studies show that the interaction between DBSA and P4VPy is affected by inclusion complexation when the DBSA content is high ($x \geq 0.5$), resulting in the expulsion of some DBSA ions from the polymer chain and reprotonation. TGA shows that the initial decomposition temperatures of the inclusion complexes are lower than those of the CDs and the pristine complexes, a result different from that of the linear chain polymer−cyclodextrin ICs. DSC measurements indicate that the inclusion of the side chains within CDs makes the P4VPy main chain much stiffer, thereby raising the glass transition temperature. ^{1}H NMR measurements also suggest that interactions between CDs and the side chains of P4VPy(DBSA)$_x$ complexes are present even in DMSO solution. However, the mesomorphic layer structures of P4VPy(DBSA)$_x$ complexes are destroyed upon the formation of inclusion complexes with CDs.

Introduction

Supramolecular self-assembly is the spontaneous association of molecules by noncovalent bonds under equilibrium conditions into stable and well-defined structures.[1,2] One example of supramolecular self-assembly is host−guest inclusion complexes made of cyclodextrins and guest molecules. Cyclodextrins (CDs) are cyclic oligosaccharides of six to eight glucose units linked by α-1,4 linkages, which are called α-, β-, and γ-CD, respectively. Since they were discovered a century ago, a large number of inclusion complexes (ICs) based on CDs and small molecules have been studied.[3,4] In recent years, with an increasing interest in macromolecular recognition, inclusion complexes of linear polymers with CDs have been investigated extensively.[5−39] Besides main-chain polymer ICs, side-chain CD-based polyrotaxanes[39,40] have also been studied wherein the CDs bind guest moieties which are covalently attached to a polymer chain.

Complexation between a polymer and an amphiphilic surfactant via specific interaction, such as ionic interactions, affords another type of supramolecular self-assembled polymer material.[41] This type of material may have new properties and phase structures not possessed by either component. In the bulk, polymer−surfactant complexes self-organize into structural patterns through a delicate balance of attractive and repulsive interactions. Mesomorphic phases with liquid crystalline order form in some of these complexes.

Several studies dealt with inclusion complexes based on surfactants and CDs.[42,43] In a polymer−surfactant complex, surfactant molecules are attached along the polymer chain via noncovalent bonds. It is of interest to investigate whether a polymer−surfactant complex, which can be regarded as a "side-chain polymer", can form inclusion complexes with CDs. Dreja et al.[44] reported multilayered supramolecular structures self-assembled from polyelectrolytes and cyclodextrin host−guest complexes, in which two types of self-assembly processes were employed: formation of stable host−guest complexes via hydrophobic interactions and stepwise deposition of multilayered structures via electrostatic interactions.

Poly(4-vinylpyridine) (P4VPy) forms stable complexes with dodecylbenezenesulfonic acid (DBSA) via a neutralization process. The complexes possess mesomorphic phases with ordered structures both in bulk and in xylene solution, when the DBSA content is relatively high.[45] In a previous study,[46] we found that the complexes of P4VPy partially incorporated with DBSA form mesomorphic interpolymer complexes with poly(acrylic acid) (PAA) and miscible blends with poly(*p*-vinylphenol) (PVPh). Here we report our study on inclusion complexation between P4VPy(DBSA)$_x$ (x denotes the number of DBSA molecules per repeat unit of 4-vinylpyridine) complexes and CDs. It will be shown that inclusion complexes can be formed between the three CDs and various P4VPy(DBSA)$_x$ complexes with x values ranging from 0.25 to 1.00.

Experimental Section

Materials. P4VPy (weight-average molecular weight (M_w) = 60 000) was supplied by Aldrich. DBSA (98%, soft type) was obtained from Tokyo Kasei, Tokyo. The preparation of P4VPy-(DBSA)$_x$ complexes was reported previously.[46] α-CD and γ-CD were obtained from Tokyo Kasei, Tokyo; β-CD was supplied by Acros Organics. All CDs were dried at 80 °C in vacuo for at least 12 h before use. DMSO-d_6, the solvent for NMR measurements, was supplied by Aldrich. Poly(ethylene glycol) (PEG) (M_n = 2000) and poly(propylene glycol) (PPG) (M_n = 2000) were supplied by Aldrich.

Preparation of Inclusion Complexes. An appropriate amount of P4VPy(DBSA)$_x$ complex (x = 0.25, 0.50, 0.75, or 1.00) was mixed with a saturated aqueous solution of CD at room temperature, and the mixture was stirred continuously for 2 days, followed by standing overnight at room temperature. A feed ratio of 1:6 (DBSA:CD molar ratio) was used for all systems (see Results and Discussion). The crystalline inclusion complex in a form of precipitate was isolated by

* To whom correspondence should be addressed. E-mail: chmgohsh@nus.edu.sg.

10.1021/ma0201072 CCC: $22.00
Published on Web 04/16/2002

centrifugation and dried in vacuo at 60 °C for at least 2 days. For comparison studies, β-CD/PPG and γ-CD/PEG ICs were also prepared following the procedures reported in the literature.[8,10]

Measurements. The XRD patterns of the complexes were recorded on a Siemens D5005 X-ray powder diffractometer with Cu Kα (1.540 51 Å) radiation (40 kV, 40 mA). Powder samples were mounted on a sample holder and scanned with a step size of $2\theta = 0.01°$ between $2\theta = 1.5°$ and 50°.

Differential scanning calorimetry (DSC) measurements were made on a TA Instruments 2920 differential scanning calorimeter with a heating rate of 20 °C/min. Thermogravimetric analyses (TGA) were made using a TA Instruments SDT 2960 simultaneous DTA−TGA. Samples were heated at 20 °C/min from room temperature to 800 °C in a dynamic nitrogen atmosphere (flow rate = 70 mL/min).

^{1}H NMR spectra of the complexes were recorded at 300 MHz on a Bruker DPX-300 NMR spectrometer. Chemical shifts of the complexes were referenced to $\delta = 2.50$ ppm for DMSO. ^{13}C CP/MAS NMR spectra were acquired on a Bruker DRX-400 NMR spectrometer with a sample spinning rate of 8.0 kHz at room temperature. The spectra were acquired with a 2.75 μs proton 90° pulse, a 3 ms contact time, and a 3 s repetition time.

X-ray photoelectron spectroscopy (XPS) measurements were carried out on a VG Scientific ESCALAB MKII spectrometer equipped with a Mg Kα X-ray source (1235.6 eV photons) and a hemispherical energy analyzer. Detailed information about measurements and data processing has been reported elsewhere.[47−49]

Results and Discussion

The preparation and characterization of P4VPy-(DBSA)$_x$ complexes used in this study were reported earlier.[45,46] Inclusion complexes of P4VPy(DBSA)$_x$ with CDs were prepared by mixing P4VPy(DBSA)$_x$ powder and saturated aqueous solutions of CDs followed by stirring at room temperature for 2 days. All mixtures became gradually turbid, while the component solutions, either the suspended aqueous solution of P4VPy(DBSA)$_x$ or the CD solution, showed no change during the same stirring process. The appearance of turbidity is an indication of the formation of crystalline inclusion complexes between polymers and CDs.[5,7] The inclusion complexes were then separated by centrifugation and dried. XRD measurements show that the peaks belonging to the pristine complexes are absent in the inclusion complexes, indicating that the P4VPy(DBSA)$_x$ complexes were totally complexed with CDs. On the other hand, in some cases, a small peak belonging to the pristine P4VPy(DBSA)$_x$ complex appears after inclusion complex was washed with water (Figure 1b), indicating the destruction of the inclusion complex during washing. Therefore, all the inclusion complexes were analyzed without further purification.

At the beginning, only the pristine complexes with low DBSA contents were studied in view of the lower steric congestion in these complexes. However, it was subsequently found that even the P4VPy(DBSA)$_{1.00}$ complex formed crystalline complexes with the three CDs. Harada et al.[5−18] have studied various kinds of ICs formed between linear chain polymers and CDs. They found a good correlation between the cross-sectional areas of the polymers and the cavity size of the CDs.[12] In the present study, P4VPy(DBSA)$_x$ forms inclusion complexes with all the three CDs. Harada et al.[40] also reported that dodecyl units covalently attached on polymer chains form soluble complexes with three CDs in aqueous solution with association constants in the order of α-CD > β-CD > γ-CD.

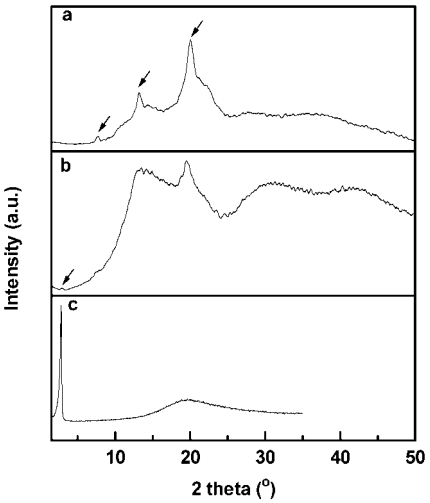


Figure 1. X-ray diffraction patterns for α-CD/P4VPy(DBSA)$_{0.50}$ (unwashed sample) (a), α-CD/P4VPy(DBSA)$_{0.50}$ (washed sample) (b), and P4VPy(DBSA)$_{0.50}$ (c).

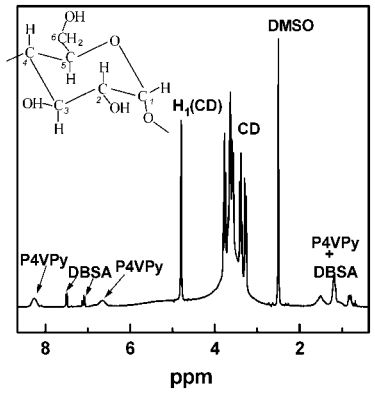


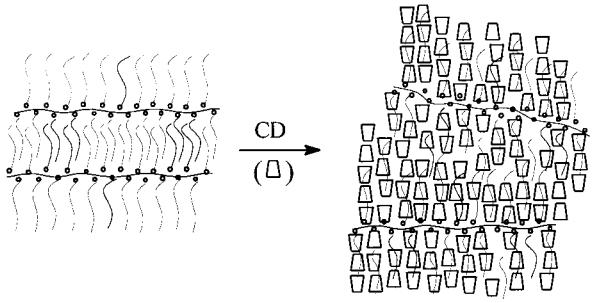
Figure 2. 300 MHz ^{1}H NMR spectrum of the α-CD/P4VPy-(DBSA)$_{0.25}$ complex in DMSO-d_6.

Table 1. Compositions (CD/DBSA Molar Ratios) of Inclusion Complexes

x	α-CD/ P4VPy(DBSA)$_x$	β-CD/ P4VPy(DBSA)$_x$	γ-CD/ P4VPy(DBSA)$_x$
0.25	3.7	3.2	3.5
0.50	2.0	1.9	2.8
0.75	2.7	2.0	2.6
1.00	1.6	1.3	1.5

The compositions of the inclusion complexes were established by ^{1}H NMR measurements. Figure 2 shows the ^{1}H NMR spectrum of an inclusion complex in DMSO. The CD/DBSA molar ratio is calculated by comparing the integration values for H_1 of CD and aromatic C−H of DBSA. Table 1 lists the results for all the CD/P4VPy(DBSA)$_x$ complexes. The extended length of the alkyl tail of DBSA corresponds to the height of two CD molecules. Upon consideration of the additional aromatic ring of DBSA and the pyridine ring, the molar ratio of CD to side chain for a fully included side chain is expected to be about 3. As a feed ratio of 6:1 was used for the preparation of all the inclusion complexes, the pristine complexes are believed to be totally complexed. As shown in Table 1, the CD/DBSA ratios in CD/P4VPy-(DBSA)$_{0.25}$ complexes are larger than 3, suggesting that some CD molecules are free from inclusion. It was found that washing of the inclusion complexes caused a slight decrease of the CD/DBSA ratios (<8% CD was removed). Washing usually led to the destruction of the inclusion complexes to some extent (Figure 1b), indicating that

Scheme 1. Illustration of the Inclusion Complex with a Poorly Ordered Columnar Structure[a]



[a] The layer structure of the pristine complex is destroyed, and some DBSA ions in the pristine complex are expelled from the polymer chain and reprotonated. In the inclusion complex, some DBSA chains are free from inclusion due to high steric hindrance while some CD molecules are not threaded by the DBSA chains.

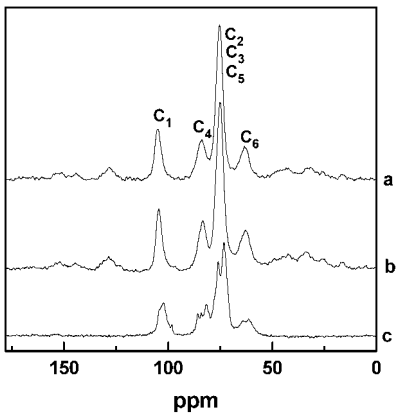


Figure 3. ^{13}C CP/MAS NMR spectra of β-CD/P4VPy(DBSA)$_{0.50}$ (a), α-CD/P4VPy(DBSA)$_{0.50}$ (b), and α-CD (c). The labeled peaks belong to CD and the other signals in the inclusion complex are from the pristine complex.

the unincluded CD molecules are not totally "free" but are trapped in the crystalline structures (see Scheme 1). For the other inclusion complexes, on the other hand, the CD/DBSA ratio decreases with increasing DBSA content, which may indicate that an increasing number of DBSA chains are free from complexation with CDs due to increasing steric congestion.

Figure 3 shows the ^{13}C CP/MAS NMR spectra of α-CD and two typical inclusion complexes. It is known that in free CD crystals the CDs remain in a less symmetrical cyclic conformation, which is characterized by resolved carbon resonances from each of the glucose units. On the other hand, CD molecules in the inclusion complexes have a symmetrical cyclic conformation and are characterized by unresolved carbon resonances.[13,29] In the present study, the spectra of all the inclusion complexes show unresolved carbon resonances, supporting the inclusion complexation between P4VPy(DBSA)$_x$ and CDs.

The crystal structures of the inclusion complexes were established by XRD. Normally a columnar structure is assigned to ICs of linear chain polymers with CDs.[19] Figure 1 shows the XRD patterns of P4VPy(DBSA)$_{0.5}$ and α-CD/P4VPy(DBSA)$_{0.5}$. The pattern of the inclusion complex is similar for all the α-CD/P4VPy(DBSA)$_x$ complexes. Reflections observed at $2\theta = 7.60°$ ($d = 11.6$ Å), 13.0° ($d = 6.80$ Å), and 20.0° ($d = 4.44$ Å) are the same as those reported for α-CD/poly(ϵ-lysine) IC having a hexagonal unit cell with a lateral dimension $a = 13.6$ Å.[29] The peak at 20.0° ($d = 4.44$ Å) is typical for α-CD/polymer ICs.[11,14,19,29] In view of the columnar structure of α-CD/polymer ICs, the present XRD results suggest that α-CD/P4VPy(DBSA)$_x$ complexes possess a columnar structure. It is noted that the reflections of the pristine complexes disappear, indicating the destruction of the layer structure of the pristine complexes during the inclusion complexation with CDs. Figure 4 shows the XRD patterns of β-CD, β-CD/PPG inclusion complex, and β-CD/P4VPy(DBSA)$_{1.00}$ complex. The XRD pattern of the inclusion complex is typical for all the β-CD/P4VPy(DBSA)$_x$ complexes. They are different from that of pure β-CD, which has a cage structure. Two broad peaks in β-CD/P4VPy(DBSA)$_x$ complexes at ca. $2\theta = 11.6°$ and 17.9° are also typical for the β-CD/PPG inclusion complex. The latter complex has been well studied and shown to have a columnar structure.[6,10] Therefore, a columnar structure is also assumed for the β-CD/P4VPy(DBSA)$_x$ complexes. The diffraction patterns of the inclusion complexes of γ-CD are poor. Figure 5 shows the XRD patterns of γ-CD/PEG and γ-CD/P4VPy(DBSA)$_{0.25}$ inclusion complexes. The key feature

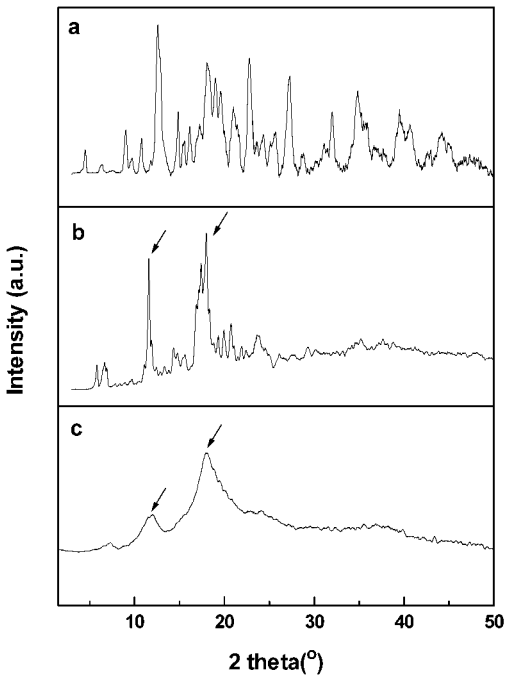


Figure 4. X-ray diffraction patterns for β-CD (a), β-CD/PPG inclusion complex (b), and β-CD/P4VPy(DBSA)$_{1.00}$ (c).

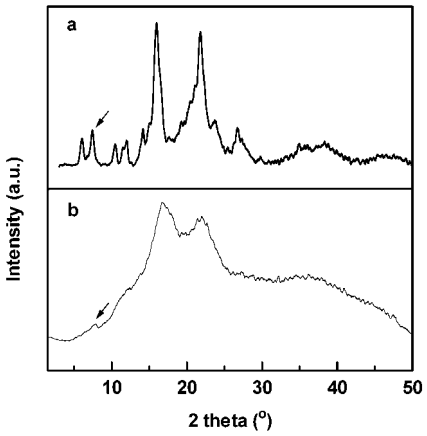


Figure 5. X-ray diffraction patterns for γ-CD/PEG inclusion complex (a) and γ-CD/P4VPy(DBSA)$_{0.25}$ (b).

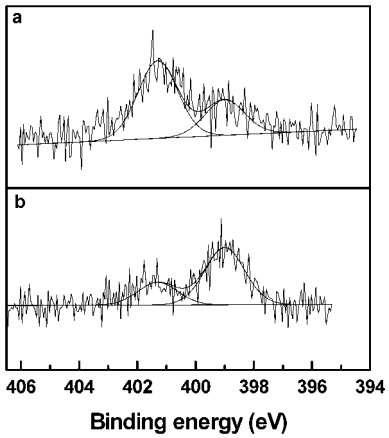


Figure 6. XPS spectra of β-CD/P4VPy(DBSA)$_{1.00}$ (a) and γ-CD/P4VPy(DBSA)$_{0.25}$ (b).

that serves as a fingerprint for the column structure of γ-CD-ICs is the peak at ca. 8.0°.[13,25] Although very weak, this feature is present in the γ-CD/P4VPy-(DBSA)$_{0.25}$ complex. This result indicates that γ-CD/P4VPy(DBSA)$_x$ complexes also possess a columnar structure. Similarly, the layer structures of the pristine complexes are destroyed upon complexation with γ-CD.

The interactions in P4VPy(DBSA)$_x$ complexes have been studied by XPS.[46] It was shown that in the P4VPy-(DBSA)$_x$ ($x < 1.0$) complexes each N 1s peak can be deconvoluted into two component peaks, in which the peak at 399.0 eV is due to neutral pyridine nitrogen and that at 401.3 eV is due to positively charged pyridinium ions. The N^+/N ratio is in agreement with the stoichiometry of the complex. In the present study, the interactions in the inclusion complexes were examined by XPS. Although the signal is noisy due to the low nitrogen content in the complex, the N 1s spectra of the inclusion complexes can still be deconvoluted into two peaks, one at 399.0 eV and the other at 401.3 eV. It is noted that for the three CD/P4VPy(DBSA)$_{0.25}$ complexes the N/N^+ ratios calculated from the area of the deconvoluted N 1s peaks are 2.8, nearly the same as that of 3.0 in the pristine complex. The result indicates that in the three CD/P4VPy(DBSA)$_{0.25}$ complexes the stoichiometric protonation of pyridine is nearly maintained. On the other hand, for the inclusion complexes with higher DBSA contents ($x \geq 0.50$), the N/N^+ ratios are substantially different from those in the pristine complexes. Figure 6 shows the XPS spectra of β-CD/P4VPy-(DBSA)$_{1.00}$ and γ-CD/P4VPy(DBSA)$_{0.25}$. P4VPy(DBSA)$_{1.00}$ show a single peak at 401.3 eV, indicating a complete protonation of pyridine nitrogens by DBSA.[46] However, a minor peak at 399.0 eV can be clearly detected in β-CD/P4VPy(DBSA)$_{1.00}$. The above results indicate that the steric congestion caused by the inclusion complexation rather than the complexation itself induces some changes on interaction in the complexes with high DBSA contents. As the steric congestion in CD/P4VPy-(DBSA)$_{0.25}$ complexes is expected to be the smallest in all the inclusion complexes, the interaction between P4VPy and DBSA is not significantly affected during the inclusion complexation. On the other hand, for the inclusion complexes with high DBSA contents, some DBSA ions are expelled from the P4VPy main chain and reprotonated.

The thermal properties of CD/P4VPy(DBSA)$_x$ complexes were investigated by TGA. Table 2 shows the initial decomposition temperatures of the pristine P4VPy-(DBSA)$_x$ complexes and various CD/P4VPy(DBSA)$_x$ complexes. The P4VPy(DBSA)$_x$ complexes have higher initial decomposition temperatures than pure DBSA (240 °C), which indicates that complexation with P4VPy enhances the thermal stability of DBSA. It is quite interesting that all the CD/P4VPy(DBSA)$_x$ complexes have lower initial decomposition temperatures than both the pristine complexes and CDs (about 298 °C). Typically, the CD/P4VPy(DBSA)$_x$ complexes show a two-stage decomposition (Figure 7), wherein the first stage is dominant and believed to involve the CD-complexed side chains. Normally, the initial decomposition temperatures of inclusion complexes between linear polymers and CDs are higher than those of CDs, and the inclusion complexation is believed to contribute to the better stability of CDs.[29] Thus, the present TGA results are somewhat unusual. At a first glance, the lower decomposition temperatures of CD/P4VPy(DBSA)$_x$ complexes may be due to the weakening of the interaction between P4VPy and DBSA as well as the steric congestion which makes the inclusion complexes unstable. As shown by XPS studies, however, the interaction between P4VPy and DBSA does not change much upon complexation with CDs, especially when $x = 0.25$. On the other hand, as shown in Table 2, for the same CD, the initial decomposition temperature of the CD/P4VPy(DBSA)$_x$ complex decreases with increasing x value. As a higher degree of steric congestion is expected in the complex with a higher DBSA content, steric congestion could affect the thermal behavior of the CD/P4VPy(DBSA)$_x$ complexes.

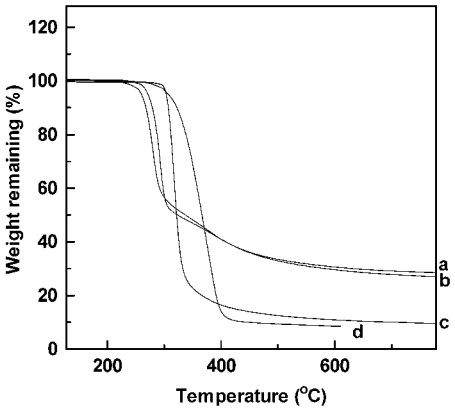


Figure 7. TGA curves of γ-CD/P4VPy(DBSA)$_{0.50}$ (a), α-CD/P4VPy(DBSA)$_{0.75}$ (b), α-CD (c), and P4VPy(DBSA)$_{1.00}$ (d).

Table 2. Initial Decomposition Temperatures (°C) of Pristine and Inclusion Complexes

x	pristine complex	α-CD/P4VP-y(DBSA)$_x$	β-CD/P4VPy-(DBSA)$_x$	γ-CD/P4VPy-(DBSA)$_x$
0.25	273	267	266	267
0.50	278	260	261	263
0.75	285	257	258	258
1.00	310	246	255	244

For the CD/P4VPy(DBSA)$_x$ inclusion complexes, the side chains are included by CD molecules and are expected to affect the mobility of the P4VPy main chain segments. Figure 8 shows the DSC curves of two pristine complexes and two inclusion complexes. The curves were obtained from the second heating scan after quenching the samples from 180 °C in dry ice. As pure CDs have no transitions before 250 °C, the transitions in the two inclusion complexes are the glass transition of the P4VPy main chain in the complexes. Table 3 lists the T_g values of the pristine complexes and two series

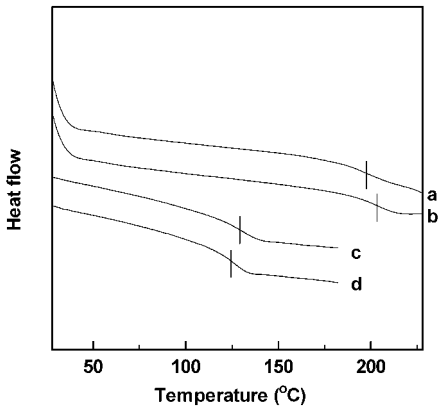


Figure 8. DSC curves of α-CD/P4VPy(DBSA)$_{0.25}$ (a), *β*-CD/P4VPy(DBSA)$_{0.50}$ (b), P4VPy(DBSA)$_{0.50}$ (c), and P4VPy(DBSA)$_{0.25}$ (d).

Table 3. T_g (°C) of Pristine and Inclusion Complexes

x	pristine complex	α-CD/P4VPy-(DBSA)$_x$	*β*-CD/P4VPy-(DBSA)$_x$	*γ*-CD/P4VPy-(DBSA)$_x$
0.25	126	197	185	166
0.50	133	209	203	194
0.75	146			
1.00	127			

of CD/P4VPy(DBSA)$_x$ complexes. Since the pristine complexes with $x = 0.75$ and 1.00 have small heat capacity changes at glass transition, only the inclusion complexes with $x = 0.25$ and 0.50 were studied. As shown in Table 3, the T_g values of the pristine complexes do not change monotropically with *x*, and all T_g values are lower than that of P4VPy (ca. 150 °C). Both the plasticizing effect of the side chains and the stiffening effect of the electrostatic interaction affect the glass transition of the P4VPy main chain in the pristine complexes. On the other hand, the T_g's of the inclusion complexes are much higher than those of the pristine complexes as well as that of pure P4VPy. The results indicate that the inclusion of DBSA side chains by CDs makes the P4VPy main chain much stiffer. It is also noted that for a given CD the T_g value increases with increasing DBSA content in the inclusion complex. This is reasonable as a larger steric congestion in the complex with a high DBSA content will make the main chain much stiffer. Furthermore, as shown in Table 3, the inclusion complexes of *γ*-CD have lower T_g's than the corresponding inclusion complexes of α-CD and *β*-CD with the same DBSA content. This result may be attributed to the larger cavity size of *γ*-CD which allows the included side chains to move more freely.

The ^{1}H NMR spectra of CD/P4VPy(DBSA)$_x$ complexes in DMSO show some peak shifts. Figure 9 shows the ^{1}H NMR spectra of some inclusion and pristine complexes in the aromatic C−H range. The pyridine unit of pure P4VPy in DMSO shows two broad peaks at 6.60 and 8.26 ppm. After complexation with DBSA, both peaks shift to a lower field. Such a shift increases in magnitude with increasing DBSA content. Upon the inclusion complexation of P4VPy(DBSA)$_x$ with CDs, both peaks shift back to higher field. On the other hand, only a slight shift is observed in the aromatic C−H of DBSA in the pristine and inclusion complexes. The above results could be taken to suggest that complexation of CD with the aromatic parts of P4VPy(DBSA)$_x$ side chains is present even in DMSO solutions. Figure 10 shows the ^{1}H NMR spectra of some inclusion and pristine complexes in the aliphatic C−H range. Al-

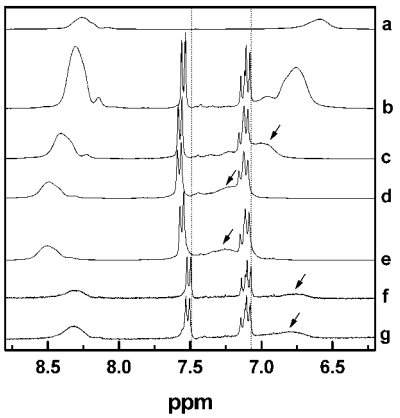


Figure 9. 300 MHz ^{1}H NMR spectra of P4VPy (a), P4VPy-(DBSA)$_{0.25}$ (b), P4VPy(DBSA)$_{0.50}$ (c), P4VPy(DBSA)$_{0.75}$ (d), P4VPy(DBSA)$_{1.00}$ (e), α-CD/P4VPy(DBSA)$_{1.00}$ (f), and α-CD/P4VPy(DBSA)$_{0.75}$ (g).

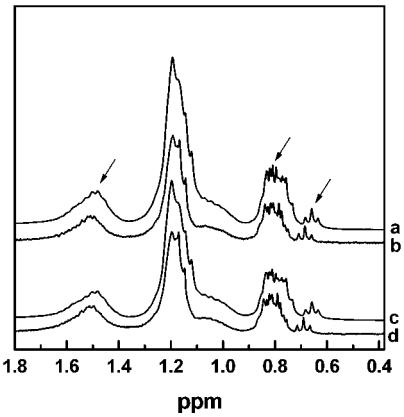


Figure 10. 300 MHz ^{1}H NMR spectra of P4VPy(DBSA)$_{1.00}$ (a), P4VPy(DBSA)$_{0.75}$ (c), α-CD/P4VPy(DBSA)$_{1.00}$ (b), and *γ*-CD/P4VPy(DBSA)$_{0.75}$ (d).

though the peaks are not well resolved, small shifts to lower field are observed in the presence of CD in solution. Harada et al.[40] also observed a shift of the peaks of side chain to a lower field in CD/copolymer aqueous solutions. The shift was taken as an evidence of the interaction of CD with alkyl moieties on the polymer chain. Thus, the present ^{1}H NMR study indicates that there is still some interaction between CD and the alkyl chains of CD/P4VPy(DBSA)$_x$ in DMSO.

The pristine P4VPy(DBSA)$_x$ complexes possess a mesomorphic layer structure in the solid state even when the *x* value is as small as 0.25.[46] DBSA is attached to the P4VPy chain via ionic interaction, with alternating alkyl and ionic sublayers. In the previous study,[46] we found that proton-donating polymers such as PAA or PVPh can be selectively incorporated into the ionic sublayer of the P4VPy(DBSA)$_x$ complexes. The mesomorphic layer structure with nearly unchanged long period is maintained in the interpolymer complexes and miscible blends. In the present study, CD molecules thread through the side chains of the P4VPy(DBSA)$_x$ complexes. Considering the large volumes of CDs,[22] a large steric congestion is expected even when the DBSA content is low. Thus, it is quite surprising that CD can form inclusion complexes even with the P4VPy(DBSA)$_{1.00}$ complex. The XRD patterns of the inclusion complexes indicate that the side chain included CD molecules organize into a crystalline columnar structure. However, the order is quite poor, as indicated by the broadening of the diffraction peaks. The results could be due to the

secondary-bonding nature of the pristine complexes. On one hand, the flexibility of the secondary bond may cancel the steric congestion and thus facilitate the formation of the inclusion complexes. XPS studies suggest that some DBSA ions are reprotonated by the pyridinium groups when the DBSA content is high. On the other hand, the ionic interaction is quite strong so that the CD-included side chains cannot be segregated from the polymer main chain to form well-ordered structures. Scheme 1 gives an illustration of the inclusion complex with a poorly ordered columnar structure, and the layer structure of the pristine complex is thus destroyed.

Conclusion

P4VPy(DBSA)$_x$ complexes (x = 0.25, 0.50, 0.75, 1.00) form inclusion complexes with all three CDs. A columnar structure with poor order is established in all the inclusion complexes. XPS studies indicate that the interaction between DBSA and P4VPy is affected by inclusion complexation when the DBSA content is high ($x \geq 0.5$). TGA shows that the initial decomposition temperatures of the inclusion complexes are lower than those of CDs and the pristine complexes, a result different from those of linear chain polymer ICs. DSC measurements of T_g indicate that the inclusion of DBSA by CDs makes the P4VPy main chain much stiffer. ^{1}H NMR measurements also suggest that interaction between CD and the side chains of the P4VPy(DBSA)$_x$ complexes could be present even in DMSO solution.

Acknowledgment. We thank the National University of Singapore for its financial support of this research and Mr. H. K. Wong for assistance in XPS measurements.

References and Notes

(1) Whitesides, G. M.; Mathias, J. P.; Seto, C. T. *Science* **1991**, *254*, 1312.
(2) Lehn, J.-M. *Science* **1993**, *260*, 1762.
(3) Bender, M. L.; Komiyama, M. *Cyclodextrin Chemistry*; Springer-Verlag: Berlin, 1978.
(4) Szejtli, J. *Cyclodextrins and Their Inclusion Complexes*; Akademiai Kiado: Budapest, Hungary, 1982.
(5) Harada, A.; Kamachi, M. *Macromolecules* **1990**, *23*, 2821.
(6) Harada, A.; Kamachi, M. *J. Chem. Soc., Chem. Commun.* **1990**, 1322.
(7) Harada, A.; Li, J.; Kamachi, M. *Macromolecules* **1993**, *26*, 5698.
(8) Harada, A.; Li, J.; Kamachi, M. *Nature (London)* **1994**, *370*, 126.
(9) Li, J.; Harada, A.; Kamachi, M. *Polym. J.* **1994**, *26*, 1019.
(10) Harada, A.; Okada, M.; Li, J.; Kamachi, M. *Macromolecules* **1995**, *28*, 8406.
(11) Harada, A.; Okada, M.; Kamachi, M. *Acta Polym.* **1995**, *46*, 453.
(12) Harada, A. *Coord. Chem. Rev.* **1996**, *148*, 115.
(13) Harada, A.; Suzuki, S.; Okada, M.; Kamachi, M. *Macromolecules* **1996**, *29*, 5611.
(14) Harada, A.; Kawaguchi, Y.; Nishiyama, T.; Kamachi, M. *Macromol. Rapid Commun.* **1997**, *18*, 535.
(15) Harada, A.; Nishiyama, T.; Kawaguchi, Y.; Okada, M.; Kamachi, M. *Macromolecules* **1997**, *30*, 7115.
(16) Okumura, H.; Okada, M.; Kawaguchi, Y.; Harada, A. *Macromolecules* **2000**, *33*, 4297.
(17) Kawaguchi, Y.; Nishiyama, T.; Okada, M.; Kamachi, M.; Harada, A. *Macromolecules* **2000**, *33*, 4472.
(18) Okumura, H.; Kawaguchi, Y.; Harada, A. *Macromolecules* **2001**, *34*, 6338.
(19) Huang, L.; Allen, E.; Tonelli, A. E. *Polymer* **1998**, *39*, 4857.
(20) Huang, L.; Tonelli, A. E. *J. Macromol. Sci., Rev. Macromol. Chem. Phys.* **1998**, *C38*, 781.
(21) Rusa, C. C.; Tonelli, A. E. *Macromolecules* **2000**, *33*, 5321.
(22) Rusa, C. C.; Luca, C.; Tonelli, A. E. *Macromolecules* **2001**, *34*, 1318.
(23) Lu, J.; Mirau, P. A.; Tonelli, A. E. *Macromolecules* **2001**, *34*, 3276.
(24) Wei, M.; Tonelli, A. E. *Macromolecules* **2001**, *34*, 4061.
(25) Porbeni, F. E.; Edeki, E. M.; Shin, I. D.; Tonelli, A. E. *Polymer* **2001**, *42*, 6907.
(26) Klyamkin, A. A.; Topchieva, I. N.; Zubov, V. P. *Colloid Polym. Sci.* **1995**, *273*, 520.
(27) Fujita, H.; Ooya, T.; Yui, N. *Macromol. Chem. Phys.* **1999**, *200*, 706.
(28) Ikeda, T.; Ooya, T.; Yui, N. *Macromol. Rapid Commun.* **2000**, *21*, 1257.
(29) Huh, K. M.; Ooya, T.; Sasaki, S.; Yui, N. *Macromolecules* **2001**, *34*, 2402.
(30) Huh, K. M.; Ooya, T.; Lee, W. K.; Sasaki, S.; Kwon, I. C.; Jeong, S. Y.; Yui, N. *Macromolecules* **2001**, *34*, 8657.
(31) Wenz, G.; Keller, B. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 197.
(32) Herrmann, W.; Keller, B.; Wenz, G. *Macromolecules* **1997**, *30*, 4966.
(33) Yoshida, K.; Shimomura, T.; Ito, K.; Hayakawa, R. *Langmuir* **1999**, *15*, 910.
(34) Li, J.; Yan, D. *Macromolecules* **2001**, *34*, 1542.
(35) Olson, K.; Chen, Y.; Baker, G. L. *J. Polym. Sci., Part A: Polym. Chem.* **2001**, *39*, 2731.
(36) Li, J.; Li, X.; Zhou, Z.; Ni, X.; Leong, K. W. *Macromolecules* **2001**, *34*, 7236.
(37) Li, J.; Li, X.; Toh, K. C.; Ni, X.; Zhou, Z.; Leong, K. W. *Macromolecules* **2001**, *34*, 8829.
(38) Jiao, H.; Goh, S. H.; Valiyaveettil, S. *Macromolecules* **2001**, *34*, 8138.
(39) Nepogodiev, S. A.; Stoddart, J. F. *Chem. Rev.* **1998**, *98*, 1959.
(40) Harada, A.; Adachi, H.; Kawaguchi, Y.; Kamachi, M. *Macromolecules* **1997**, *30*, 5181.
(41) For recent reviews on polymer/surfactant complexes, see: (a) Ober, C. K.; Wegner, G. *Adv. Mater.* **1997**, *9*, 17. (b) Zhou, S.; Chu, B. *Adv. Mater.* **2000**, *12*, 545. (c) Antonietti, M.; Burger, C.; Thünemann, A. *Trends Polym. Sci.* **1997**, *5*, 262. (d) MacKnight, W. J.; Ponomarenko, E. A.; Tirrell, D. A. *Acc. Chem. Res.* **1998**, *31*, 781.
(42) Palepu, R.; Reinsborough, V. *Can. J. Chem.* **1988**, *66*, 325.
(43) Aman, E. S.; Serve, D. *J. Colloid Interface Sci.* **1990**, *138*, 365.
(44) Dreja, M.; Kim, I. T.; Yin, Y.; Xia, Y. *J. Mater. Chem.* **2000**, *10*, 603.
(45) Ikkala, O.; Ruokolainen, J.; ten Brinke, G.; Torkkeli, M.; Serimaa, R. *Macromolecules* **1995**, *28*, 7088.
(46) Jiao, H.; Goh, S. H.; Valiyaveettil, S. *Macromolecules* **2001**, *34*, 7162.
(47) Zhou, X.; Goh, S. H.; Lee, S. Y.; Tan, K. L. *Polymer* **1998**, *39*, 3631.
(48) Zhou, X.; Goh, S. H.; Lee, S. Y.; Tan, K. L. *Appl. Surf. Sci.* **1997**, *119*, 60.
(49) Zhou, X.; Goh, S. H.; Lee, S. Y.; Tan, K. L. *Appl. Surf. Sci.* **1998**, *126*, 141.

MA0201072