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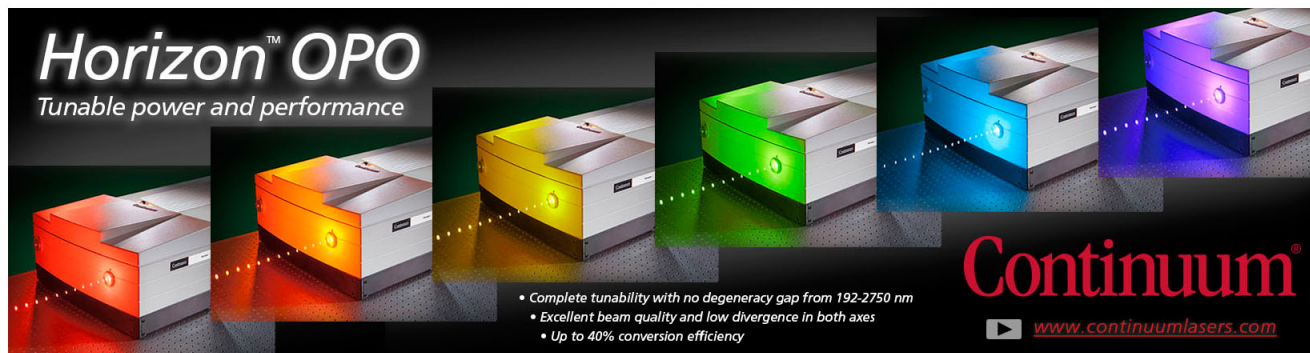
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Evidence of formation of site-selective inclusion complexation between β -cyclodextrin and poly(ethylene oxide)-*block*-poly(propylene oxide)-*block*-poly(ethylene oxide) copolymers

Chi-Chun Tsai,¹ Wen-Bin Zhang,¹ Chien-Lung Wang,¹ Ryan M. Van Horn,¹ Matthew J. Graham,¹ Jing Huang,² Yongming Chen,^{3,a),b)} Mingming Guo,^{1,a),c)} and Stephen Z. D. Cheng^{1,a),d)}

¹Department of Polymer Science, College of Polymer Science and Polymer Engineering, University of Akron, Akron, Ohio 44325-3909, USA

²College of Chemical Engineering, Wuhan University of Technology, Wuhan 430070, China

³State Key Laboratory of Polymer Physics and Chemistry, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China

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A series of inclusion complexes of poly(ethylene oxide)-*block*-poly(propylene oxide)-*block*-poly(ethylene oxide) (PEO-*b*-PPO-*b*-PEO) with β -cyclodextrin (β -CD) was prepared. Their formation, structure, and dynamics were investigated by solution two-dimensional rotating-frame Overhauser effect spectroscopy (2D ROESY) and one-dimensional (1D) and 2D solid-state ^{13}C NMR. The inclusion complexes between the PEO-*b*-PPO-*b*-PEO copolymers and the β -CDs were formed in aqueous solution and detected by 2D ROESY. The high efficiency of cross polarization and spin diffusion experiments in ^{13}C solid-state NMR showed that the mobility of the PPO blocks dramatically decreases after β -CD complexation, indicating that they are selectively incorporated onto the PPO blocks. The hydrophobic cavities of β -CD restrict the PPO block mobility, which is evidence of the formation of inclusion complexes in the solid state. The 2D wide-line separation NMR experiments suggested that β -CDs only thread onto the PPO blocks while forming the inclusion complexes. The stoichiometry of inclusion complexes was studied using ^1H NMR, and a 3:1 (PO unit to β -CD) was found for all inclusion complexes, which indicated that the number of threaded β -CDs was only dependent on the molecular weight of the PPO blocks. 1D wide angle x-ray diffraction studies demonstrated that the β -CD in the inclusion complex formed a channel-like structure that is different from the pure β -CD crystal structure. © 2010 American Institute of Physics. [doi:10.1063/1.3428769]

I. INTRODUCTION

Supramolecular chemistry as a field has evolved and developed significantly in the past two decades. Research has focused on the systems which are capable of self-organizing, namely, spontaneous self-assembly of constituent parts, into supramolecular structures. The assembly of such structures relies on molecular recognition and results from the cooperation of various noncovalent interactions such as van der Waals, electrostatic, hydrophobic, or hydrogen bonding.^{1,2} The principle of molecular recognition can be exemplified in the formation of complexes of the “host-guest” type. Cyclodextrin (CD), one of the promising hosts for macromolecular recognition, has been focused on constructing supramolecular structures due to its good water solubility and ability to include a wide range of guest molecules.^{3–6}

CDs are a series of cyclic oligosaccharides containing six, seven, or eight glucose units connected through

α -1,4-glycosidic linkages. They are abbreviated as α -, β -, and γ -CDs, respectively. The shape of CDs is similar to a shallow, truncated cone that possesses a hydrophilic outer surface. At the primary (narrower-diameter end) and secondary (wider-diameter end) rims of the molecule, there are hydroxyl groups. The central cavity consists of alkyl groups and glycosidic oxygen atoms and is hydrophobic. These CD cavities can thus act as a host for a variety of hydrophobic molecular guests.^{7,8} Harada *et al.* were the first to report the inclusion complexation behavior of various polymers with CDs. They found that polymers are highly selective in forming inclusion complexes with certain CDs. It was suggested that a good accommodation between the cross-sectional area of the polymer chain and the minimum diameter size of the CD cavity is the key to the formation of a stable inclusion complex.^{5,6} The possibility of selective geometrical accommodation opens an interesting prospect when considering the complexation behavior of block copolymers with CDs. Recent studies have demonstrated that in inclusion complexes of CDs with block copolymers, CDs can perform “site-selective complexation” on a specific segment of the block copolymer due to steric fitting, hydrophobic (or van der Waals) interaction, and/or other interactions between the cav-

^{a)}Authors to whom correspondence should be addressed.

^{b)}Electronic mail: ymchen@iccas.ac.cn. Tel.: +86-10-6265-9906.

^{c)}Electronic mail: mguo@uakron.edu. Tel.: 330-972-5204. FAX: 330-972-5290.

^{d)}Electronic mail: scheng@uakron.edu. Tel.: 330-972-6931. FAX: 330-972-8626.

ity of CDs and the polymer, which can generate and/or enhance amphiphilicity of block copolymers.^{9–17}

In this work, we focus on the complexation behavior between copolymers of poly(ethylene oxide)-*block*-poly(propylene oxide)-*block*-poly(ethylene oxide) (PEO-*b*-PPO-*b*-PEO) and β -CD. Amphiphilic PEO-*b*-PPO-*b*-PEO, also known by the trade name, Pluronic, consists of hydrophilic PEO blocks, which maintain the copolymer's solubility in water and hydrophobic PPO blocks, which provide the associative behavior in water. Varying the block compositions (PEO/PPO ratios) and the molecular weights allows us to tailor the final properties of these systems to meet the specific application needs.^{18,19} Due to complex aggregation behavior and widespread utility, PEO-*b*-PPO-*b*-PEO has attracted great interest and has been extensively studied, which provides a good framework for our study of the complexation behavior between PEO-*b*-PPO-*b*-PEO and β -CD. So far, there have been a few papers on the complexation behavior of β -CD and PEO-*b*-PPO-*b*-PEO, and they suggested that β -CD formed a site-selective complex onto the PPO blocks to form inclusion complexes in an aqueous system and did not complex with the PEO blocks.^{20–26} However, the question remains whether all the β -CDs exclusively interact with the PPO blocks or only part of them stay with the PPO blocks and the rest with the PEO blocks. The existing studies only concentrated on the formation of inclusion complexes between β -CDs and PEO-*b*-PPO-*b*-PEO copolymer in the solution. The interaction between β -CDs and the PPO blocks can be detected using the nuclear Overhauser effect technique in solution. However, if part of the β -CDs stayed with the PEO blocks, the interaction between the β -CDs and the PEO blocks in the solution is too weak to be detected due to longer intermolecular distances. Moreover, using NMR techniques to detect the dynamics and molecular motion of the PPO block inside the cavity of β -CDs as well as the β -CDs themselves in the inclusion complexes in the solid state has not been examined.

In order to elucidate the dynamics and inclusion complexation behavior between β -CDs and PEO-*b*-PPO-*b*-PEO, we have utilized high resolution solid-state ¹³C NMR to measure the rates of magnetization exchange between the β -CDs and the copolymer employing the proton T₁ relaxation to observe the length scale of inclusion complexes. ¹H-to-¹³C cross polarization (CP), magic angle spinning (MAS) NMR, and two-dimensional (2D) wide-line separation (WISE) NMR experiments have also been used to investigate the dynamics and molecular motion of the PPO blocks and β -CDs in the inclusion complexes. These results have also been compared with those in the uncomplexed states.

II. EXPERIMENTAL

A. Materials

Three samples of PEO-*b*-PPO-*b*-PEO copolymers with different molecular weights were purchased from Aldrich, St. Louis, MO, USA, and were supplied as commercially available samples from BASF. β -cyclodextrin (β -CD) was pur-

TABLE I. Molecular characteristics of the PEO-*b*-PPO-*b*-PEO triblock copolymers and β -CD.

Sample	Composition ^a	\bar{M}_n^b (g/mol)	\bar{M}_w/\bar{M}_n^b	PPO content ^a (wt %)
EPE46	EO ₂₇ PO ₃₉ EO ₂₇	4600	~1.6	48
EPE77	EO ₆₄ PO ₃₇ EO ₆₄	7700	~1.2	27
EPE146	EO ₁₃₇ PO ₄₄ EO ₁₃₇	14 600	~1.2	17
β -CD	C ₄₂ H ₇₀ O ₃₅	1134		

^aDetermined by ¹H NMR.

^bDetermined by GPC.

chased from Acros, Morris Plains, NJ, USA. All samples were used as received, and the molecular characteristics of PEO-*b*-PPO-*b*-PEO copolymers and β -CD determined using gel permeation chromatography (GPC) and ¹H NMR are listed in Table I.

An aqueous solution of β -CDs was mixed with an aqueous solution of copolymers in a molar ratio of β -CD/PO = 1:1 at room temperature. The temperature and concentration of the triblock copolymer solutions were below the critical micellization concentration.²⁷ After mixing with the β -CD solution, the copolymer solution gradually became turbid and finally produced white precipitates, apparently indicating the formation of hydrophobic inclusion complexes. The samples were vacuum-filtered with 0.4 μ m filter paper and washed with a limited amount of distilled water. The filtered samples were dried in a vacuum oven at room temperature for three days. For one-dimensional (1D) wide angle x-ray diffraction (WAXD) experiments, the powder samples were prepared from the precipitated inclusion complex on the filter paper and dried in a vacuum oven at room temperature again for 3 days. The abbreviations of the inclusion complexes between β -CD and three copolymers are β -CD/EPE46, β -CD/EPE77, and β -CD/EPE146, respectively. The numerical digits represent the overall weight-average molecular weights of the triblock copolymers.

B. Equipment and experiments

The 2D ¹H-¹H rotating-frame Overhauser effect spectroscopy (ROESY) spectrum was obtained on a Varian VNMR-S 500 MHz instrument equipped with Varian One probe with a 2 s relaxation delay, a 6.1 kHz spectral window, a 0.4 s mixing time, and a 0.168 s acquisition time; eight transients were averaged for each of 2 \times 200 increments using the States method of phase sensitive detection in the f1 dimension. Processing was done with sinebell and shifted sinebell weighting functions and zero filling to a 2048 \times 1024 data matrix before Fourier transformation.

High resolution 1D and 2D solid-state ¹³C NMR spectra were obtained on a Varian VNMR-S 500 MHz (¹H frequency) spectrometer. Samples were spun in a Varian 4 mm HXY triple resonance MAS probe at a spinning speed of 10 kHz. ¹³C chemical shifts were referenced to hexamethylbenzene (δ_{CH_3} = 17.3 ppm). Samples were packed into 4 mm silicon nitride rotors with kel-f end caps. Solid-state ¹³C CP/MAS NMR spectra were acquired using a ramped CP pulse sequence with a 4 s relaxation delay, a 3.5 μ s, 90° pulse

width, and a 71.4 kHz decoupling field. ^{13}C Bloch decay MAS NMR spectra were acquired using a 5 s relaxation delay, a $3.5\ \mu\text{s}$, 90° pulse width, a 71.4 kHz decoupling field, and 1000 transients. For the variable contact time ^{13}C CP/MAS NMR spectra of the complexes, 12 spectra were obtained with contact times ranging from 0.02 to 10 ms, which were acquired using a ramped CP pulse sequence with a MAS speed of 10 kHz, a 4 s relaxation delay, a $3.5\ \mu\text{s}$, 90° pulse width, and a 71.4 kHz decoupling field; while for the triblock copolymer, 16 spectra were obtained with contact times ranging from 0.02 to 40 ms. Proton relaxations were measured via CP/MAS model using inversion recovery pulse in the proton channel before contact with carbon. The carbon signals were observed with high power proton decoupling. The proton T_1 and the variable contact time data were processed using Varian VNMRJ software. The 2D WISE spectra were measured using a 1000 kHz spectral width in the proton dimension and a 50 kHz spectral width in the carbon dimension.²⁸ Rapid signal decay was observed in the proton dimension, and the maximum evolution time was 128 μs .

Solution ^1H NMR spectra were recorded on a Varian VNMR 500 MHz instrument at room temperature. The ^1H NMR measurements were carried out with an acquisition time of 2.049 s, a pulse repetition time of 1 s, a 45° pulse width, 8012.8 Hz spectral width, and 32 000 data points. Chemical shifts were referred to the solvent peaks ($\delta=2.50$ ppm for $\text{DMSO-}d_6$). ^1H NMR (500 MHz, $\text{DMSO-}d_6$, ppm): $\delta 5.71$ ($7\text{H} \times 12$, O-2H of β -CD), $\delta 4.81$ ($7\text{H} \times 12$, C-2H of β -CD), $\delta 4.45$ ($7\text{H} \times 12$, O-6H of β -CD), $\delta 3.27$ – 3.63 ($42\text{H} \times 12$, C-3H, C-6H, C-5H, C-2H, C-4H of β -CD, $7\text{H} \times 165$, $-\text{CH}_2\text{CH}_2\text{O}-$ of PEO, and $-\text{CH}_2-\text{CHO}-$ of PPO), and $\delta 1.03$ ($3\text{H} \times 37$, CH_3 of PPO).

1D WAXD patterns were obtained with a Rigaku Multiflex 2 kW automated diffractometer using $\text{Cu } K\alpha$ radiation ($1.542\ \text{\AA}$). The samples were scanned across a 2θ range of 3° – 35° at a $1^\circ/\text{min}$ scanning rate. The peak positions were calibrated using silicon powder in the high-angle region ($>15^\circ$) and silver behenate in the low-angle region ($<15^\circ$). For thin layer samples, the WAXD was recorded with the x-ray beam incident with the plane of the thin layer samples; therefore, the samples were lying down on the sample holder.

III. RESULTS

A. Observation of the threading process of β -CD onto PEO-*b*-PPO-*b*-PEO in the solution

The inclusion complexes of β -CDs with PEO-*b*-PPO-*b*-PEO copolymers were prepared via aqueous media. Precipitates of the inclusion complexes always formed when the β -CDs were saturated onto the PPO blocks. As a result, it was difficult to observe the formation of inclusion complexes in the aqueous state. By decreasing the amount of β -CD to a ratio of β -CD:PO=1:5, only a few β -CDs threaded onto the PPO blocks, which minimized the intermolecular hydrogen bonding between β -CDs, and the inclusion complexes maintained their solubility in the aqueous solution. Figure 1 shows a 2D ROESY NMR spectrum for β -CD/EPE77. The dashed circles in the ROESY spectrum show the antiphase real intermolecular ROE cross

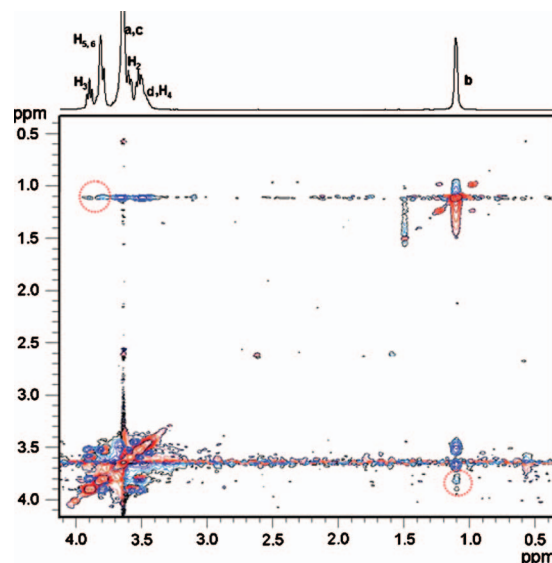


FIG. 1. 2D ROESY NMR spectrum of β -CD/EPE77 inclusion complex in D_2O .

peaks between the inner cavity H_5 and H_3 protons of β -CD (see Fig. 8, schematic) and the methyl protons of the PPO blocks. This observation reveals that β -CDs are threaded onto the PPO blocks in the solution. However, the cross peaks between PEO blocks and β -CDs are difficult to observe or distinguish in the 2D ROESY experiment. Since the interaction between PEO blocks and β -CDs are probably too weak to detect due to longer intermolecular distance, the upper limits for the observed distances between protons are separated by about $4\ \text{\AA}$. Besides, the cross peaks between methylene protons of the PEO blocks and β -CDs as well as CH_2 of the PPO blocks and β -CDs are overlapped and indistinguishable. Therefore, the 2D ROESY results cannot be stand-alone substantial evidence to support the selective complexation behavior of β -CDs. However, the cross peaks between the β -CD and the methyl protons of the PPO blocks in 2D ROESY NMR showed that β -CDs can thread onto PEO-*b*-PPO-*b*-PEO copolymers and form inclusion complexes.

B. Identification of inclusion complex formation in the solid state

Figure 2 shows the solid-state ^{13}C CP/MAS NMR spectra of dehydrated β -CD [Fig. 2(a)], the copolymer EPE146 [Fig. 2(c)], and the β -CD/EPE146 inclusion complexes [Fig. 2(b)]. β -CD assumes a less symmetrical conformation in the crystal when it does not include a guest in the cavity to form the complex. In this case, the spectrum shows resolved carbon resonances from each of the carbon atoms in the glucose residues. The fine structure with several narrow lines appeared, as indicated in Fig. 2(a). On the other hand, in the spectrum of the β -CD/EPE146 complex in Fig. 2(b), each carbon of glucose is merged into a single broad peak. These results indicate that β -CD adopts a more symmetrical conformation, and each glucose unit of the β -CD is in a similar environment. This is an indication that the PEO-*b*-PPO-*b*-PEO copolymer is included inside the cavity

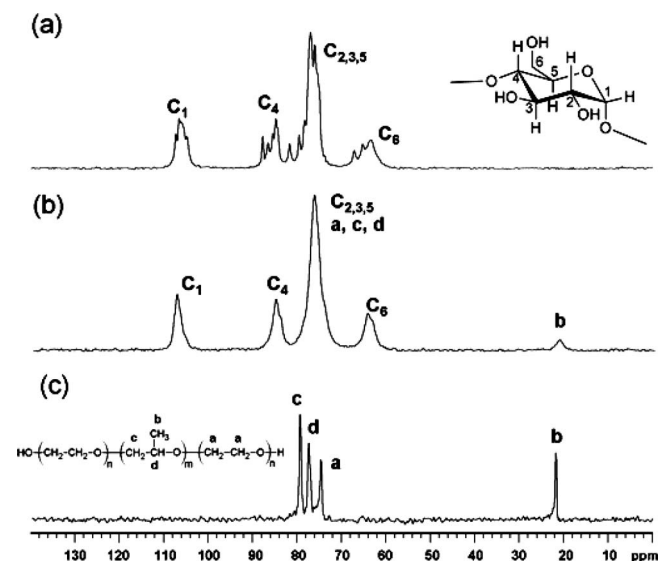


FIG. 2. The solid-state ^{13}C CP/MAS NMR spectra of dehydrated β -CD (a), β -CD/EPE146 inclusion complexes (b), and EPE146 (c).

of the β -CD. Although the main chain resonance of both the PEO and PPO blocks are overlapped with the resonance of $\text{C}_{2,3,5}$ of β -CD (see Fig. 2), the resonance of the methyl carbon atom at 21.7 ppm provides evidence of the formation of the inclusion complex [Fig. 2(b)]. The linewidth at half-height in the pure copolymer was 49.18 Hz [Fig. 2(c)] and changed to 194.42 Hz in the complex [Fig. 2(b)]. This increase is evidence of the restricted mobility of the PPO methyl group in the complex.

Figure 3 shows the solid-state ^{13}C CP/MAS NMR spectra of uncomplexed EPE77 [Fig. 3(a)] and dehydrated β -CD [Fig. 3(d)] as well as the β -CD/EPE77 inclusion complexes [Fig. 3(c)]. In this figure, the solid-state Bloch decay ^{13}C MAS NMR spectrum of β -CD/EPE77 inclusion complexes is also included [Fig. 3(b)]. As reported in literature,^{29,30} the CP process discriminates against the mobile species. The intensity of the mobile carbon resonance is thus drastically decreased due to the inefficient proton-carbon CP process.

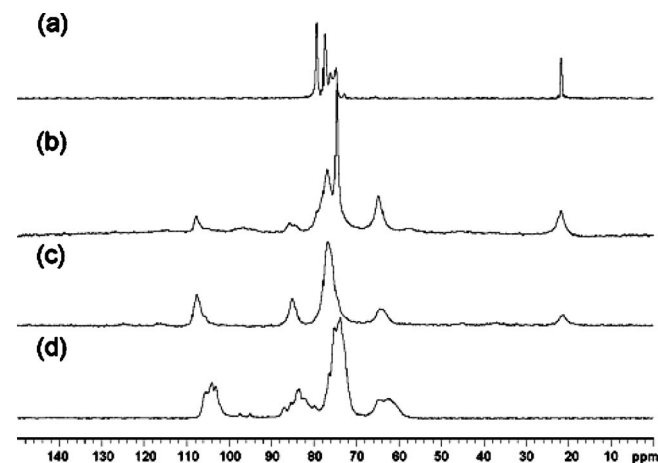


FIG. 3. The solid-state ^{13}C CP/MAS NMR spectra of EPE77 (a), Bloch decay MAS NMR spectra of β -CD/EPE77 inclusion complexes (b), solid-state ^{13}C CP/MAS NMR spectra of β -CD/EPE77 inclusion complexes (c), and dehydrated β -CD (d).

TABLE II. Values of $^1\text{H}T_1$ (ms) determined from curve fitting of the spectra acquired with inversion recovery pulse sequence.

Sample	PEO- <i>b</i> -PPO- <i>b</i> -PEO		β -CD
	<i>c</i> (79.3 ppm)	<i>b</i> (21.7 ppm)	C_1 (107.7 ppm)
EPE77	1.32		
β -CD/EPE77		0.97	1.05
β -CD			0.68

On the other hand, the Bloch decay ^{13}C MAS NMR spectra are more sensitive toward the mobile species. Combining both these solid-state NMR methods on the same sample is a useful method to identify the different species based on the mobility and the order difference in this type of heterogeneous inclusion complex system.

Figure 3(b) shows the solid-state Bloch decay ^{13}C MAS NMR spectra of β -CD/EPE77 inclusion complexes, in which stronger signals of relatively mobile carbons from the sample were found. This spectrum can be compared with that of ^{13}C CP/MAS NMR, as shown in Fig. 3(c). The relative intensities of the peaks of the methyl carbon of the PPO blocks to those of β -CD in Fig. 3(b) are much stronger than those in Fig. 3(c), indicating that the included PPO blocks were not as rigid as the β -CD in the complex. These results are consistent with the view that β -CD molecules are in a channel configuration, forming a tube-shaped frame of the complexes.^{14,25,31} Figure 3(b) also exhibits a new resonance at 74.4 ppm that is missing in Fig. 3(c). This resonance is assigned to the mobile species of the PEO block of the triblock copolymer. The linewidth at half-height of the resonance is 60.44 Hz, which is close to the linewidth at half-height of the PEO resonance from the uncomplexed PEO-*b*-PPO-*b*-PEO copolymer [Fig. 3(a)].

Measurements of proton spin-lattice relaxation times were conducted using an inversion recovery pulse sequence. The carbon signal intensity decay was fitted into a standard first order kinetic expression curve to determine the proton spin-lattice relaxation times for the block copolymers and the inclusion complexes by monitoring the changes in carbon signal intensity as a function of proton delay times. For this particular fit, the C_1 peak at approximately 107.7 ppm is chosen for the β -CD because it is highly resolved in the spectra. However, the same conclusions were obtained for all of the other peaks since they all decay following the same proton spin-lattice relaxation times with the same rate constant due to the effective proton spin diffusion process. We measured the proton relaxation behavior of different carbon atom resonances for the β -CD, EPE copolymers, and β -CD/EPE inclusion complexes. First, the relaxation times were independent of the peak chosen for the calculation. For the copolymers, the CHO carbon atom peak at 79.3 ppm was chosen because the methyl group is too mobile. For the inclusion complexes, the methyl group resonance at 21.7 ppm was chosen because it becomes rigid after the complexation. Furthermore, it was highly resolved in all the spectra.

The proton T_1 values of the β -CD, copolymer EPE77, and β -CD/EPE77 inclusion complex are listed in Table II. A single component decay behavior of the proton T_1 for the

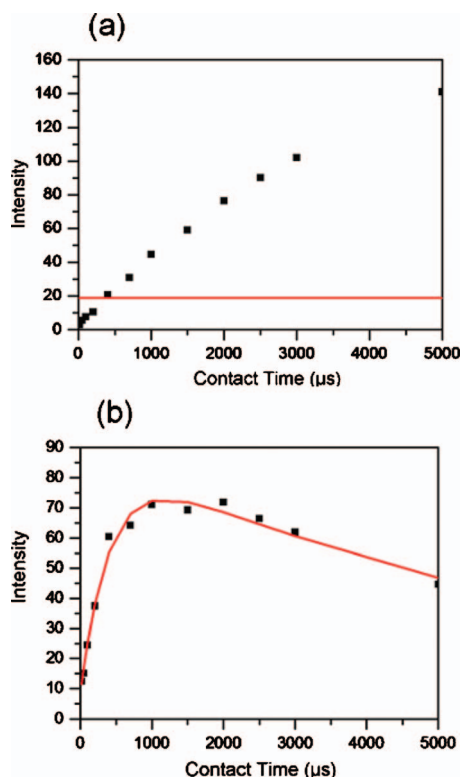


FIG. 4. Plots of $M(t)$ of ^{13}C CP/MAS spectra of the methyl resonance of the PPO blocks versus the contact time for the EPE77 (a) as well as the inclusion complexes with $\beta\text{-CD}$ (b), in which the symbols represent experimental data and the solid lines represent the best fit results based on Eq. (2).

complexes was observed. The proton T_1 value of the inclusion complexes was between the relaxation time values of $\beta\text{-CD}$ and the pure copolymers. This indicated that the spin diffusion occurred quickly among the chemically different constituents, which equilibrated the magnetization; therefore, the chains must be intimately and homogeneously mixed. We are also interested in the morphology of the complex system on a smaller scale. That is, whether or not the intermolecular interaction of the complex system is on the molecular level. In order to further investigate this characteristic of the system, CP kinetics and 2D WISE experiments must be performed.

Quantitatively, the dependence of the magnetization M as a function of the contact time (t) may be written as^{29,30}

$$M(t) = M_0[1 - \exp(-\lambda t/T_{\text{CH}})]\exp(-t/T_{1\rho\text{H}}), \quad (1)$$

where $\lambda = 1 + (T_{\text{CH}}/T_{1\rho\text{C}}) - (T_{\text{CH}}/T_{1\rho\text{H}})$. $M(t)$ denotes the magnetization at contact time t , which is proportional to the peak intensity of particular resonance in the ^{13}C CP/MAS spectra. M_0 denotes the initial equilibrium magnetization, T_{CH} is the CP time, $T_{1\rho\text{C}}$ is the carbon spin-lattice relaxation time in the rotating frame, and $T_{1\rho\text{H}}$ is the proton spin-lattice relaxation time in the rotating frame. Very often, in rigid polymeric materials, $T_{\text{CH}} \ll T_{1\rho\text{C}}$ and $T_{1\rho\text{H}}$, and Eq. (1) can be simplified to

$$M(t) = M_0[1 - \exp(-t/T_{\text{CH}})]\exp(-t/T_{1\rho\text{H}}). \quad (2)$$

Note that for the resonances caused by the mobile PPO blocks, Eq. (2) is not valid to treat the data. Figure 4 shows

TABLE III. Values of T_{CH} (μs) determined from curve fitting the variable contact time.

Sample	b	C_1	C_4	C_6	$C_{2,3,5}$
$\beta\text{-CD/EPE77}$	702	256	258	171	286
$\beta\text{-CD}$		333	294	172	335

the intensity profiles of the methyl group of the PPO blocks before and after complexation with the $\beta\text{-CD}$. While it is impossible to fit the data for $\text{PEO-}b\text{-PPO-}b\text{-PEO}$ due to the mobility of the methyl group, the intensity of the methyl group of the PPO blocks after complexation can be fitted using Eq. (2). T_{CH} values based on the fitting results for $\beta\text{-CD}$ and $\beta\text{-CD/EPE77}$ inclusion complex are listed in Table III.

C. 2D WISE NMR of the inclusion complexes

Information about the molecular dynamics of polymers can also be obtained based on the NMR proton line shapes, which are broadened by the combination of chemical shift anisotropy and homo- and heteronuclear dipolar couplings.^{29,32} Broad lines are commonly observed in the proton spectra, mostly because of the strong proton-proton dipolar couplings (60 kHz). The proton chemical shift range is about 10 ppm (5 kHz using 500 NMR spectrometer), so the individual lines are not resolved. They can, however, be observed indirectly in 2D NMR experiments using WISE NMR.²⁸ A major advantage of the solid-state 2D WISE experiments over the direct measurement of the proton line shapes is that the proton linewidths are correlated with the carbon chemical shifts. It is thus possible to measure the proton line shapes for each resolved carbon resonance in the spectrum.

Figure 5 shows the contour plot of the 2D WISE spectrum for EPE77 (2D WISE spectra for EPE46 and EPE146 are available in the supporting information³³). The proton line shapes obtained from cross sections through the 2D WISE spectra are similar for the different carbon sites and different samples. The linewidth at half-height was in the range from 2.3 to 2.7 kHz, which is more than ten times

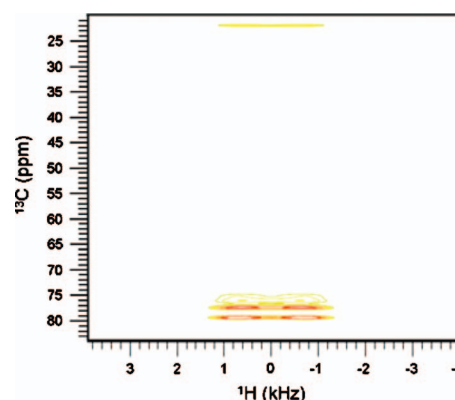


FIG. 5. The contour plot of the 2D WISE spectrum for the triblock copolymer.

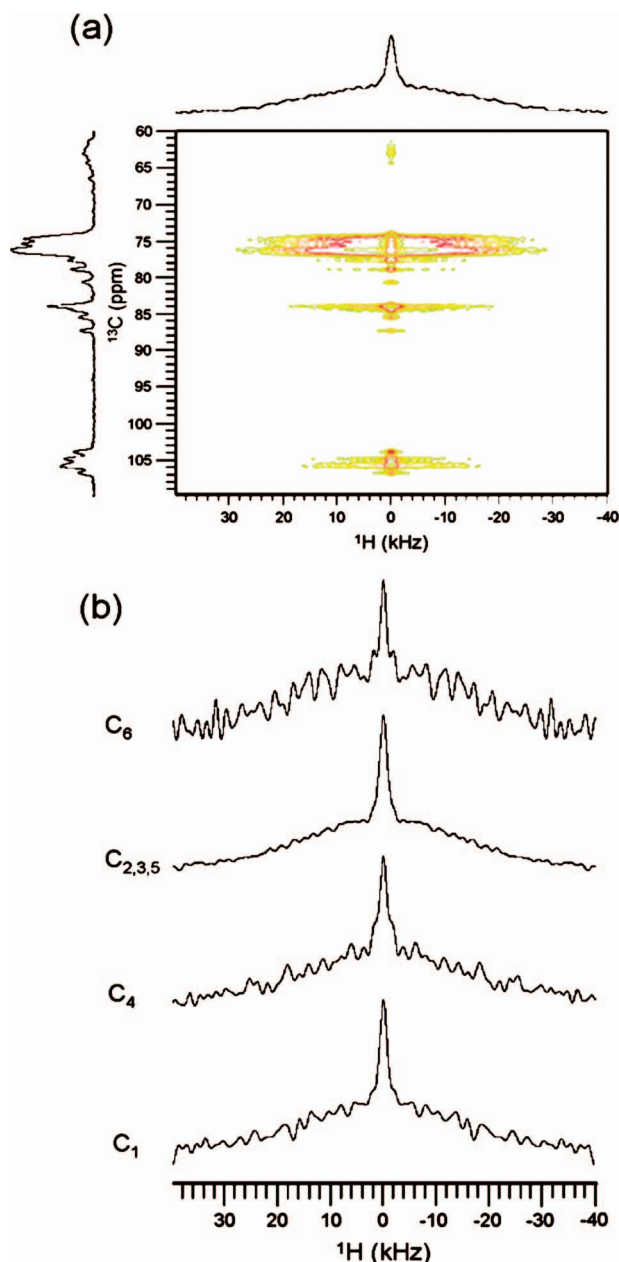


FIG. 6. 2D WISE spectrum of the hydrated β -CD, the contour plot and projections (a), cross sections at the frequency of the 107.7 ppm of C_1 , 85.1 ppm of C_4 , 76.8 ppm of $C_{2,3,5}$, and 64.4 ppm of C_6 (b).

narrower than the linewidth of PCL (Ref. 34) and PCL-*b*-PEO-*b*-PCL (Ref. 35) block copolymer reported in literature.

Figure 6(a) shows the contour plot and projections of the 2D WISE spectrum of the hydrated β -CD, the as-received sample. Notice here that the spectral widths were 80 kHz for the proton dimension, which is ten times wider than in the case of the copolymers in Fig. 5. Figure 6(b) shows the cross sections of the 2D WISE spectrum of the hydrated β -CD for 107.7 ppm (C_1), 85.1 ppm (C_4), 76.8 ppm ($C_{2,3,5}$), and 64.4 ppm (C_6). The results in Fig. 6 reveal that a narrow line with its full-width at half-height of about 1.6–1.7 kHz was on top of the wide line with its full-width at half-height of about 36–38 kHz for both the proton projection and the cross sections of the 2D WISE spectrum in the proton dimension. The

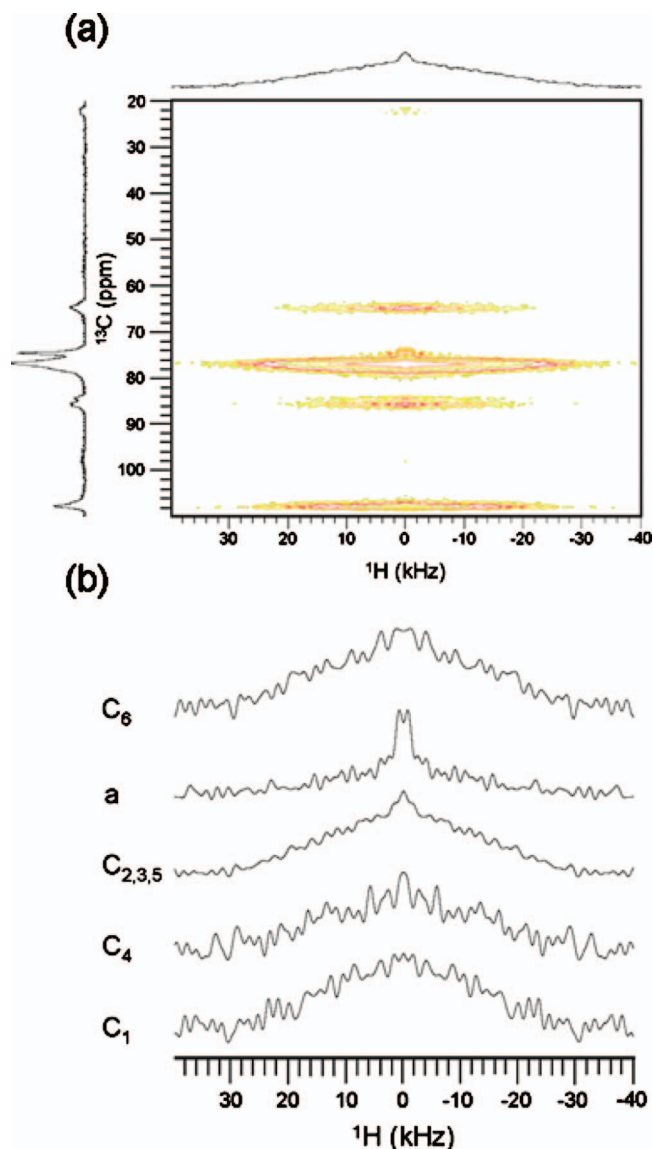


FIG. 7. 2D WISE spectrum of the inclusion complex of β -CD/EPE77, the contour plot and projections (a), cross sections at the frequency of the 107.7 ppm of C_1 , 85.1 ppm of C_4 , 76.8 ppm of $C_{2,3,5}$, 74.4 ppm of a CH_2 from the PEO block, and 64.4 ppm of C_6 (b).

narrow line resulted from the hydration water, and the wide lines were from the rigid β -CD. After deconvolution of the proton 1D spectrum, the water content was about 15% of the total sample weight, which matches the thermogravimetric analysis result (about 15 wt % is lost at 100 °C, as shown in the supporting information³³). Furthermore, the proton full-width at half-height is about 36–38 kHz for β -CDs, which is more than ten times broader than the linewidth value of the PEO-*b*-PPO-*b*-PEO copolymers. Finally, the same proton linewidths for all of the carbons of β -CD were observed. This was consistent with similar results reported for α -CD and γ -CD by Mirau and Tonelli.^{34,35}

Figure 7(a) shows the contour plot and projections of the 2D WISE spectrum of the inclusion complex of β -CD/EPE77. Note that the spectral widths were 80 kHz for the proton dimension, which is ten times broader than the PEO-*b*-PPO-*b*-PEO copolymer in Fig. 5. Figure 7(b) shows the 1H cross sections of the 2D WISE spectrum of the inclu-

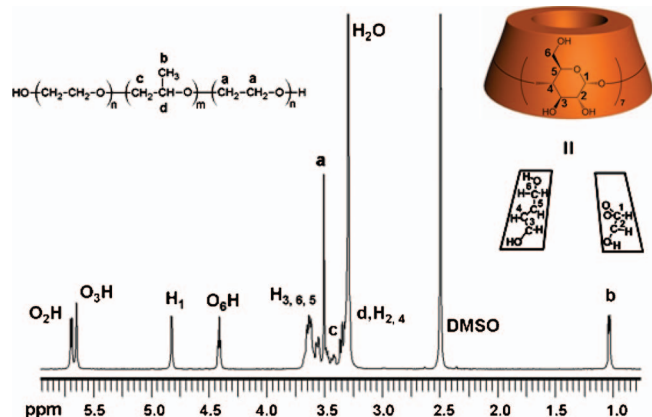


FIG. 8. The 500 MHz ^1H NMR spectrum of β -CD/EPE46 inclusion complex in DMSO-d_6 .

sion complex. These 2D spectra indicate that the resolution of the ^{13}C projection of the 2D WISE spectrum is higher than the 1D ^{13}C CP/MAS spectrum, as shown in Fig. 3(c). The carbon resonance from the PEO block at 74.4 ppm can be unambiguously observed in the ^{13}C projection of the 2D WISE spectrum. This higher resolution of the 2D spectra allows us to observe the proton linewidth of the PEO block separately. Moreover, unlike the cross sections of the 2D WISE spectrum of the hydrated β -CD that showed both the narrow and broad lines, the cross sections of the 2D WISE spectrum of the β -CD in the complex show only one broad line. In other words, after the complexation, the crystal water is replaced by the copolymer chain, and the proton linewidth at different carbon sites of the β -CD is not sensitive to the crystalline structure (pure β -CD) or channel structure (inclusion complexes of β -CD with PEO-*b*-PPO-*b*-PEO). This is consistent with similar results reported by Mirau and Tonelli.³⁶

D. Stoichiometry of inclusion complexes

The average number of threaded β -CDs in the inclusion complexes was determined via ^1H NMR spectroscopy in DMSO-d_6 since the inclusion complexes were completely dissociated into their components in polar solvents.¹⁴ As shown in Fig. 8 for β -CD/EPE46, a comparison between the integral intensities of the H_1 proton peak of β -CDs and the methyl protons of the PPO blocks shows that the molar ratio of PO units to β -CD was identified to be about 3:1. This ratio was maintained in all three inclusion complex samples. Based on the molar ratio, the average number of β -CDs threaded onto the PPO block was about 13, and it was only dependent on the molecular weight of the PPO blocks. Theoretically, it is assumed that based on size matching, two PO repeat units can accommodate one threaded β -CD, whereas Harada *et al.* observed that the ratio of monomer unit to CD increased with an increase in the PPO molecular weight.^{14,25,26} Their observations differ because the inclusion complexes start to precipitate out from the aqueous solution since they become more hydrophobic with increasing intermolecular hydrogen bonding after threading more and more β -CDs. The precipitation occurs before the β -CDs can completely cover the PPO blocks.

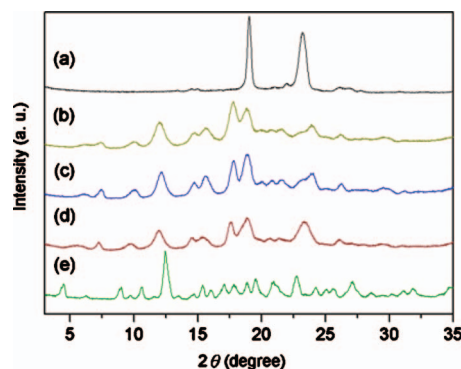


FIG. 9. WAXD powder diffraction patterns for the EPE77 (a), the β -CD/EPE46 inclusion complexes (b), the β -CD/EPE77 inclusion complexes (c), the β -CD/EPE146 inclusion complexes (d), and the hydrated β -CD (e).

E. 1D WAXD of inclusion complexes

Figure 9 exhibits a set of WAXD powder patterns observed for the inclusion complexes, pure EPE77, and hydrated β -CD at room temperature in a 2θ range from 3° to 35° . PEO crystallizes to form a monoclinic structure with $a = 0.805$ nm, $b = 1.304$ nm, $c = 1.948$ nm, and $\beta = 125.4^\circ$.³⁷ Therefore, in the WAXD of EPE77 [Fig. 9(a)], there are two prominent reflection peaks at $2\theta = 19^\circ$, assigned to be the (120) reflection, and at $2\theta = 23^\circ$, which is attributed to several overlapped reflections.³⁸ The hydrated β -CD [Fig. 9(e)] was reported to have a herring-bone packing structure when it is complexed with water.³⁹ The diffraction patterns of the three β -CD/EPE inclusion complexes shown in Figs. 9(b)–9(d) are quite different from the WAXD of the hydrated β -CD and pure copolymer. These differences indicate that the inclusion complexes form a different crystal structure. We have carried out detailed structural characterization of the inclusion complexes and found that their supramolecular crystal structures are distinct from hydrated β -CD. Detailed analyses are outside the scope of this manuscript and will be published elsewhere. However, experiments proving the existence of a different structure were carried out using a thin layer of the inclusion complex. Within the thin layer, the β -CDs are stacked on top of one another and oriented along the normal direction of the thin layer due to drying. Figure 10 shows the WAXD of a thin layer sample of inclusion complexes. Two sharp reflection peaks at $2\theta = 5.8^\circ$ and 11.8° were observed. The other reflections observed in Figs. 9(b)–9(d) did not appear in Fig. 10. This observation indicates that these two reflections represent the spacing along the layer normal direction, and the other reflections observed in Figs. 9(b)–9(d) are attributed to the reflections which are away from the reciprocal vector direction of these two reflections shown in Fig. 10. The reflection peak at $2\theta = 5.8^\circ$ is attributed to the height of a pair of β -CDs (1.52 nm),¹⁵ and the reflection peak at $2\theta = 11.8^\circ$ is the height of a single β -CD (0.75 nm).¹⁵ The appearance of only these two reflections indicates that the β -CDs in the inclusion complex are aligned in a channel-like structure that is parallel to the normal direction of the thin layer of the sample. Furthermore,

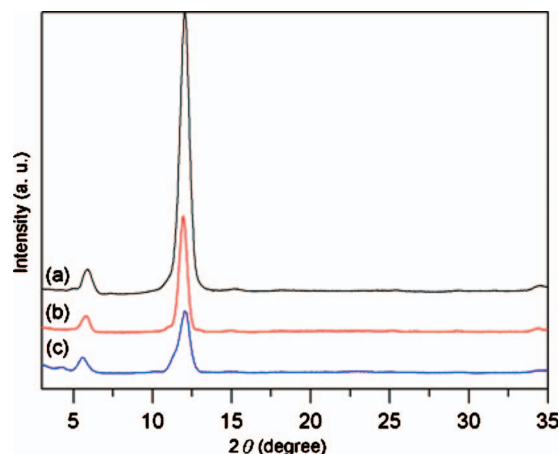


FIG. 10. WAXD diffraction patterns for the β -CD/EPE46 inclusion complexes (a), the β -CD/EPE77 inclusion complexes (b), the β -CD/EPE146 inclusion complexes (c).

the other reflections observed in Figs. 9(b)–9(d) reveal that the inclusion complex is in a three dimensionally ordered crystal in the solid state.

IV. DISCUSSION

The use of solid-state ^{13}C NMR has shown a change in the resonance for the PPO blocks from a variety of analytical techniques. For pure copolymer, the PPO blocks are amorphous, therefore resulting in a mobile methyl group. In the CP/MAS NMR spectra, the carbon resonance for the methyl group was narrow, and the linewidth at half-height was 49.18 Hz, as indicated in Fig. 2(c). However, after forming complexes with β -CD, the carbon resonance became broad [see Fig. 2(b)]. The linewidth at half-height changed to 194.42 Hz, which is about four times broader than the linewidth of methyl carbon resonance before complexation. Similar phenomena were observed for the inclusion complexes of β -CD/EPE77 and β -CD/EPE46. These solid-state NMR results revealed that the methyl groups of the PPO blocks have a more restricted mobility compared to the pure sample. This restricted mobility can only occur when the PPO is included inside the cavity of the β -CDs and thus forms the complexed state.

This same argument can be made for why the β -CDs selectively complex with the PPO. The solid-state CP/MAS and Bloch decay NMR results on the β -CD/EPE77 inclusion complex also demonstrate that while the PPO blocks of the triblock copolymer were included into the cavity of the β -CDs due to reduce mobility, the PEO blocks did not interact with β -CDs. This supports the fact that the PEO blocks were not included within the β -CD. The linewidth of the uncomplexed PEO blocks is narrower than the included PPO blocks, revealing that the mobility of the included PPO blocks was more restricted than the PEO blocks due to the formation of inclusion complexes. Therefore, the β -CDs do possess selectivity in their location of complexation.

The CP time T_{CH} is very sensitive to the short-range proton-carbon intermolecular interaction and the rigidity of the environment of the observed carbon atoms. While it is impossible to fit the data for the PPO blocks of the pure

block copolymer due to the mobility of the methyl groups, fitting using Eq. (2) was achieved for the complexed systems. This result indicates that the PPO blocks are included in the cavity of the β -CD. The rigidity of the methyl group of the PPO blocks increased after complexation. Therefore, the fitting of the intensity profiles of the resonance with variable contact time is only valid for the rigid resonance. This observation is consistent with the results of the linewidth investigation of the spectra, as shown in Fig. 3. Finally, the CP time T_{CH} of all of the resonances of the β -CD decreased after complexation with the PEO-*b*-PPO-*b*-PEO copolymers. This is strong evidence of the formation of the inclusion complexes between the β -CD and PEO-*b*-PPO-*b*-PEO copolymer.

2D WISE analysis allowed us to view the proton linewidths correlated with the carbon chemical shifts for each resolved carbon. As a useful tool, 2D WISE NMR technique is frequently used to semiquantitatively characterize the heterogeneity and the domain structure of block copolymer and polymer blend systems. The definitive use of this experiment is to perform Lee-Goldberg CP to obtain the intrinsic proton linewidth at different carbon sites from different domains. Further experimentation is performed using a mixing time from 10 to 200 ms before the CP to semiquantitatively detect the proton spin diffusion between the domains. Domain size from 50 to 500 nm can be extracted from these 2D WISE experiments of the multiphase polymer systems. For the β -CD block copolymer inclusion complex samples investigated here, the intermolecular distance between the included polymer segment and the β -CD is less than 1 nm. The WISE experiments were thus designed using standard CP rather than Lee-Goldberg CP. We are interested in the information of selective interaction, here, the spin diffusion, of β -CD with different blocks, either PEO or PPO, of the block copolymer. During the 1 ms CP time, while spin diffusion between CD and PEO was not observed, significant spin diffusion between CD and PPO was observed, and the proton linewidth of the PPO block increased from 8 to 80 kHz.

The resonance at 76.8 ppm was attributed to the $\text{C}_{2,3,5}$ carbons of the β -CD and the PPO block. The cross sections of the 2D WISE spectrum at this frequency did not show both the narrow and broad lines. This was strong evidence that the PPO block does reside inside the cavity of the β -CD, and its linewidth changes from 2.5 kHz in the pure copolymer shown in Fig. 5 to 37 kHz after the PPO block is complexed with β -CD. This was because there is no narrow ^1H line from the uncomplexed PPO block observed here on top of the broad CD ^1H line.

Finally, based on the higher resolution of the ^{13}C projection of the 2D spectra shown in Fig. 7(a), the proton linewidth of the PEO block in the complexes can be observed directly from the cross sections of the 2D WISE spectrum at the chemical shift of carbon resonance of this block at 74.4 ppm. Figure 7(b) shows that the proton full-width at half-height of the PEO block in the complexes was 3.3 kHz, which is very similar to the value of the PEO block in the pure EPE77 copolymer (at 2.8 kHz). This value was more than ten times smaller compared to the proton full-width at half-height of the PPO block in the complexes (at 37 kHz). Therefore, this technique provided direct experimental

evidence for the complexation of β -CD with PEO-*b*-PPO-*b*-PEO that the PPO block was placed inside of the cavity of the β -CD and that the PEO block was not involved in this inclusion process within the cavity of the β -CD. The molecular motion behavior of the PEO block in the complexes is similar to pure PEO-*b*-PPO-*b*-PEO copolymer. This is also supported by the observation of a higher level of assembly as seen in the x-ray experiments.

V. CONCLUSION

In summary, we have used 1D and 2D solid-state NMR to elucidate the formation, dynamics, and structure of inclusion complexes of PEO-*b*-PPO-*b*-PEO with β -CD. The cross peaks between protons H_3 and H_5 in the cavity of β -CDs and the methyl protons of the PPO blocks indicate that the β -CDs can thread onto PEO-*b*-PPO-*b*-PEO copolymers and form inclusion complexes in the aqueous solution. ^1H -to- ^{13}C CP experiments showed high CP efficiency of the included PPO blocks and confirmed the formation of the inclusion complexes. WISE NMR experiments provided clear evidence that broad lines appeared for the PPO blocks after forming inclusion complexes, whereas the PEO blocks maintained the narrow line results, indicating that β -CDs only thread onto the PPO blocks. The stoichiometry of inclusion complexes was studied using ^1H NMR. The molar ratio of PO units to β -CD was about 3:1 for three inclusion complexes, and it indicated that the total number of threaded β -CDs was only dependent on the molecular weight of the PPO blocks. The WAXD results indicated that the β -CDs formed a channel-like structure when they thread onto the PPO blocks to form inclusion complexes in the solid state.

ACKNOWLEDGMENTS

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