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Inclusion Interaction of Highly Densely PEO Grafted Polymer Brush and α-Cyclodextrin

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ABSTRACT: Inclusion interaction of highly densely PEO grafted polymer brushes with α-cyclodextrins (α-CDs) has been investigated in this study. The polymers grafted with poly(poly(ethylene oxide) macromonomers) were prepared through the "grafting from" approach by atom transfer radical polymerization (ATRP) of poly(ethylene glycol) methyl ether methacrylate, PEOMA, from a well-defined poly(macroinitiator), poly(2-(2-bromoisobutyryloxy)ethyl methacrylate) (PBIEM, $M_w/M_n = 1.27$; degree of polymerization of backbone $DP_b = 157$). The inclusion complexation of this type of polymer brush with α-CD was studied by X-ray diffraction (XRD), ^{1}H NMR, electron diffraction (ED), scanning electron microscope (SEM), differential scanning calorimetry (DSC), and thermogravimetric analyses (TGA). For polymer brushes from PEOMA of $M_n = 475$, i.e., PBIEM-*g*-P(PEOMA475), hydrogels were formed because of the interaction of inclusion complex columns. The column-type crystalline structures of the hydrogels were confirmed by XRD measurement. The hydrogels showed unique temperature-dependent sol−gel phase transition. The interaction of polymer brush from PEOMA of $M_n = 300$, i.e., PBIEM-*g*-P(PEOMA300), with α-CD resulted a low yield complex of uniform crystals with luster in aqueous solution. The ED analysis combined with optical microscope and XRD showed that these crystals were hexagonal crystals with columnlike structure.

Introduction

Studies of supramolecular interaction between polymer guests and hosts are not only highly interesting to basic research but also very important for the development of smart materials such as stimuli-responsive hydrogels.[1−5] Cyclodextrins (CDs) are cyclic oligosaccharides with D-(+)-glucose as the repeating unit coupled by α-1,4-linkages. α-, *β*-, and *γ*-CDs are commonly available forms which consist of 6, 7, and 8 glucose units, respectively. The most important characteristic of CDs that adopt a truncated cone structure is their ability to include a wide range of guest molecules in water.[6−27] Since Li et al. first discovered poly(ethylene oxide) (PEO) threaded by α-CDs,[6] great effort has been paid to explore the inclusion complexation between polymers and CDs. Besides PEO, the polymers that have been used for complexation studies include poly(propylene oxide),[10] polyalkene,[11,17] polyester,[12] polyaniline,[14] and polysiloxane.[16] In addition to homopolymers, complexation with random and block copolymers has also been studied.[28−33] Furthermore, nonlinear polymers such as star-shaped and hyperbranched PEO polymers were also used for complexation studies with CDs.[34−36] PEOs are commonly used polymers that can be selectively threaded by α-CD. To some extent, α-CDs thread onto PEO chain as much as the chain permits, and for a fully covered IC, the stoichiometry of EO unit to α-CD is 2:1. However, ICs formed from star-shaped polymers with PEO arms and α-CDs have higher stoichiometry than 2:1 (EO:CD) because of spatial hindrance between the backbone and side chains.[34]

When polymers are threaded, the necklace structure tends to further aggregate and results in a solid crystalline product. Another form of material based on the interaction of CDs with a polymer is the hydrogels resulting from noncovalent interactions. These materials have great potentials in biomedical application due to their unique physicochemical characteristics.[2,35,37,38] Li et al. have reported that pluronics (PEO-*b*-PPO-*b*-PEO triblock copolymers) with high molecular weight can form hydrogels with α-CD.[38] Also, Huh et al. have reported the thermal reversible hydrogels formed from poly(ethylene glycol) grafted dextrin and α-CD.[2] Previously, we have found that comblike PEO grafted polymers P(PEOMA) (shown in Scheme 1) and α-CDs form inclusion complex with column-type crystalline structure. When the length of PEO side chains decreases, the complexation becomes more difficult, and it takes longer time to give the precipitates of ICs. The stoichiometry is higher than 2:1 (EO:CD) because of the repulsion between the backbone and side chains and side chains themselves.[39]

The polymer brush is a comblike densely grafted polymer, and its length of backbone is much longer than that of the branches. Single molecular brush shows a wormlike morphology because of the strong repulsion between side chains.[40−43] Herein, we report the inclusion complexation of α-CDs with double-grafted polymer brush, PBIEM-*g*-P(PEOMA); i.e., PEO chains were comblike grafted along the side chains of the molecular brush backbone as shown in Scheme 1. As one can see, the grafted polymer used here has very bulky side chains owing to the side chain structure of poly(macromonomer). We synthesized this highly densely grafted brush polymer through the "grafting from" approach by atom transfer radical polymerization (ATRP) of PEO macromonomers initiated with a well-defined poly(macroinitiator). The experiments were initially

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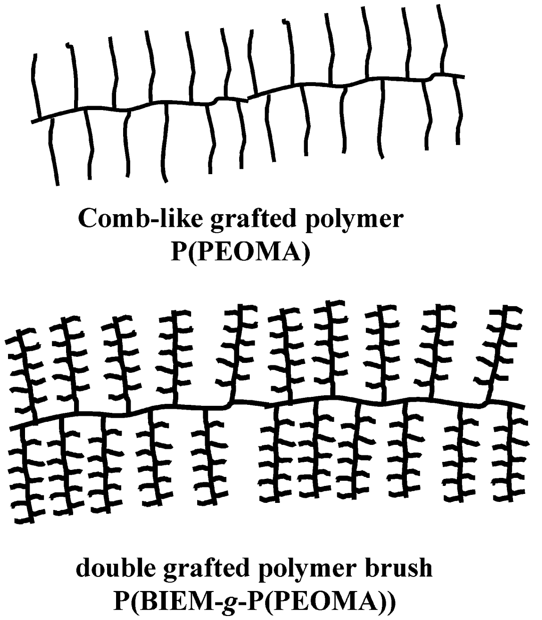
Scheme 1. Schematic Structure of Comblike Grafted Polymer P(PEOMA) and Double-Grafted Polymer Brush PBIEM-*g*-P(PEOMA)



designed to explore how this type of highly densely PEO grafted polymer forms ICs with α-CDs; yet surprisingly, thermal reversible hydrogels or well-defined crystals were obtained depending on the molecular weights of PEO macromonomers.

Experimental Section

Materials. Poly(ethylene glycol) methyl ether methacrylate (PEOMA, M_n = 300 g/mol, DP_{PEO} = 5 and M_n = 475 g/mol, DP_{PEO} = 9) were obtained from Aldrich. Symbols of PEOMA300 and PEOMA475 were used to represent these two macromonomers. The inhibitors were removed from the macromonomers by passing through an alumina column. 2-(Trimethylsilyloxy)ethyl methacrylate (HEMA-TMS) and 4,4′-di(5-nonyl)-2,2′-bipyridyne (dNbpy) were prepared according to the literature.[43,44] Tosyl chloride (TsCl) was purified by recrystallization from ethanol. Potassium fluoride dihydrate ($KF{\cdot}2H_2O$) was dried at 200 °C for 12 h prior to use. Tetra-*n*-butylammonium fluoride was obtained from TCI and used directly. Triethylamine was dried over KOH. CuBr was purified by washing with acetic acid and acetone. Tetrahydrofuran (THF), ether, and toluene were distilled over Na prior to use. Anisole was washed with 10% NaOH aqueous solution, dried by $CaCl_2$, and distilled before use. 2-Bromoisobutyryl bromide (98%), *N,N,N′,N″,N″*-pentamethyldiethylenetriamine (PMDETA, 99%), and α-CD were obtained from Aldrich and used without any treatment. All other reagents were commercial available chemicals and used as received.

Measurement. Gel permeation chromatography (GPC) was performed on a Waters 515 HPLC pump equipped with a Waters 2414 differential refractometer. Three Waters Styragel columns (HT2, HT3, and HT4) were used. THF was used as eluent at a flow rate of 1.0 mL/min at 35 °C. Polystyrene standards were used for calibrations. GPC-LLS was performed on the multiangle laser photometer (DAWN DSP, Wyatt Technology Co.) at 633 nm in an angular range from 26° to 142° at 25 °C, combined with a P100 pump (Thermo Separation Products, San Jose, Japan) and an interferometric refractometer (optilab/903, Wyatt Technology). PSW 6000 and PSW 4000 (TSK) columns were used. ^1H NMR spectra were recorded with a BrukerAV-400 NMR spectrometer operated at 400 MHz in $CDCl_3$ and DMSO-d_6 with tetramethylsilane (TMS) as internal standard at room temperature. Chemical shifts of the complexes were referenced to δ = 7.26 ppm for $CDCl_3$ and δ = 2.50 ppm for DMSO-d_6. XRD patterns of the complexes were recorded on a Rigabu D/max 2500 X-ray powder diffractmeter with Cu Kα (1.541 Å) radiation (40 kV, 40 mA). Powder samples were mounted on a sample holder and scanned with a step size of 0.01° between 2θ = 3° and 50°. Electron diffraction was carried out by JEM 2010. DSC measurements were performed under a nitrogen flow of 30 mL/min on a DSC822^e differential scanning calorimeter. The sample was heated at a rate of 10 °C/min from −20 to 160 °C and scanned for two times to erase thermal history. Thermogravimetric analyses were performed on a Thermal Analyst 2100 (TA Instruments). Samples were heated at 20 °C/min from room temperature to 800 °C in a dynamic nitrogen atmosphere (flow rate = 70 mL/min). The optical microscopy analysis was made on an Olympus BX51 microscope.

Preparation of Poly(HEMA−TMS), P(HEMA−TMS). In a 25 mL Schlenk flask, CuBr (14.4 mg, 0.10 mmol) was added and air was exchanged by N_2 for three times, and deoxygenated PMDETA (21 uL, 0.1 mmol) was then added. Afterward, a mixture of HEMA−TMS (6.06 g, 0.03 mol) and tosyl chloride (TsCl) (20 mg, 0.1 mmol) was transferred to the flask, and the flask was placed in an oil bath at 90 °C with stirring. The reaction mixture was stirred for 0.5 h before cooling to room temperature and exposed to air. The crude product was diluted with THF and filtered through activated (alkali) alumina column to remove the copper catalyst. Finally, the solvent was removed, and the polymer was precipitated in the mixture of methanol and water for two times to remove unreacted monomer. The final product was then dried under vacuum to a constant mass. Yields: 52%. GPC analysis: $M_{n,app}$ = 31 800 and M_w/M_n = 1.27.

Transformation of P(HEMA−TMS) to Poly(2-(2-bromoisobutyryloxy)ethyl methacrylate) (PBIEM).[41,43] P(HEMA−TMS) (3.17 g, 15.7 mmol) was dissolved in dry THF (30 mL) under nitrogen. Potassium fluoride (2.18 g, 37.5 mmol) was added followed by slow addition of tetrabutylammonium fluoride (82 mg, 0.31 mmol) in THF. 2-Bromoisobutyryl bromide (4.74 mL, 37.6 mmol) was added dropwise over the course of 20 min. The reaction mixture was stirred at room temperature for 36 h and afterward precipitated from THF into methanol/ice (50/50 vol %). The isolated polymer was reprecipitated three times in hexanes and dried under vacuum at 30 °C for 24 h.

Synthesis of PBIEM-*g*-P(PEOMA). dNbpy (73 mg, 0.18 mmol) and CuBr (25.7 mg, 0.18 mmol) were added in a flask that had been degassed by three purge−pump−purge cycles. Then, the degassed mixture of PEOMA, M_w = 300 g/mol (32.3 g, 108 mmol), PBIEM (50 mg, 0.18 mmol initiator site), and toluene (20 mL) were added in the flask. After stirring for several minutes, the flask was placed at a thermostated oil bath at 70 °C. The polymerization was stopped by opening the flask to air and cooling to room temperature. GPC was used to determine the molecular weight and polydispersity index. The reaction mixture was diluted with THF and passed through a column of activated alumina to remove the copper catalyst. The unreacted macromonomer PEOMA was removed by precipitation in ether for two times, and the polymer was dried under vacuum to a constant mass.

Preparation of the Inclusion Complexes. The α-CD/PBIEM-*g*-P(PEOMA300) inclusion complexes were prepared as follows: A solution of polymer (155 mg, 7.24×10^{-5} mmol) in 0.5 mL of deionized water was mixed with a saturated solution of α-CD (1.20 g, 1.23 mmol) in 8.6 mL of water at room temperature, and the mixture was sonicated for 10 min, followed by standing overnight at room temperature. A feeding ratio of 2:1 (ethylene glycol unit:α-CD) was used for all three systems. The inclusion complex was isolated by centrifugation, washed with a limited amount of water, and dried in a vacuum at 60 °C for 1 day. The stoichiometry (EO unit:α-CD) was measured by ^1H NMR, and the yields was calculated on the basis of the amount of polymers and α-CD used.

Morphologies of Hydrogels. For α-CD/PBIEM-*g*-P(PEOMA475), samples of hydrogels used for XRD analysis were obtained by drying at 50 °C directly or by freeze-drying treatment. The microstructure and morphologies of the hydrogel samples were visualized by scanning electron micros-

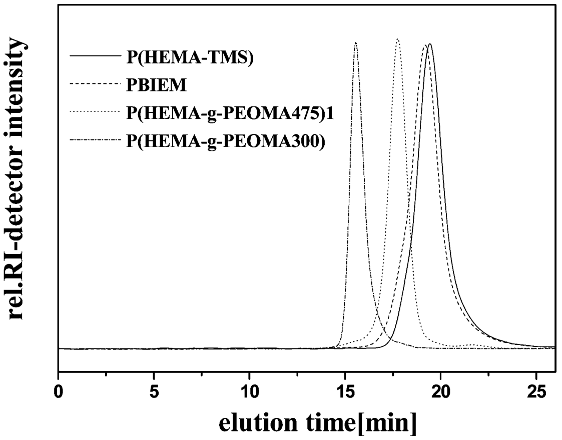
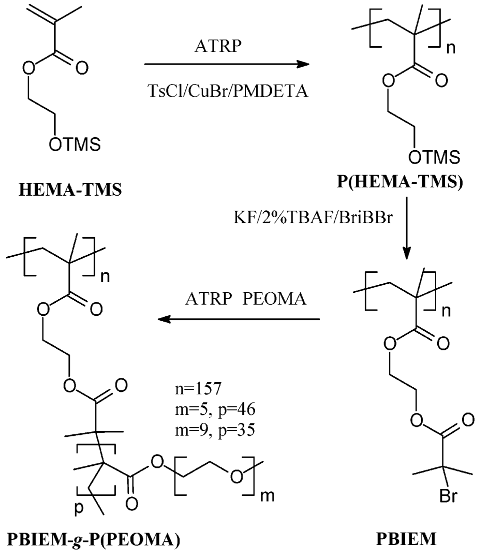


Figure 1. GPC traces of P(HEMA−TMS), PBIEM, PBIEM-*g*-P(PEOMA300), and PBIEM-*g*-P(PEOMA475)1.

Scheme 2. Synthesis of Densely Grafted Polymer Brush PBIEM-*g*-P(PEOMA) by "Grafting from" PBIEM



copy (SEM, Hitachi S4300). The samples were coated with Pt before observation.

Results and Discussion

Synthesis of Double-Grafted Polymer Brushes. Preparation of well-defined double-grafted polymer brushes, PBIEM-*g*-P(PEOMA), were achieved through the "grafting from" approach by ATRP of poly(ethylene glycol) methyl ether methacrylates. The macroinitiator, i.e., the backbone to be, was also prepared by ATRP of HEMA−TMS from monofunctional initiator, followed by functionality transformation.[41,43] Therefore, the composition of the molecular brush can be controlled by two steps of controlled radical polymerization. The synthetic approach is illustrated in Scheme 2. The degree of polymerization (DP) of the main chain P(HEMA−TMS) estimated by monomer conversion was 157, which was close to the value of 163 established by ^{1}H NMR. Figure 1 gives the GPC traces of the macroinitiator, and two polymer brushes, PBIEM-*g*-P(PEOMA475)1 and PBIEM-*g*-P(PEOMA300), were used for the complexation experiments. The curves showed that both the precursors and resultant polymer brushes have a low polydispersity index, and with every subsequent reaction the entire distribution curves move smoothly toward higher molecular weight values. Figure 2 shows the ^{1}H NMR spectra for the polymers of P(HEMA−TMS), PBIEM, and PBIEM-*g*-P(PEOMA). In Figure 2a, peaks a, b, and c were assigned respectively to the two methylenes adjacent to ester group and three methyl groups of TMS. However, peaks a and b in Figure 2b move completely toward peaks d and e of low field due to the formation of the 2-bromoisobutyryl ester group; also, the peak f at 2.0 ppm assigned to methyl groups near the bromide group appeared correspondingly. This indicates the successful esterification of P(HEMA−TMS) with 2-bromoisobutyryl bromide. After grafting the poly(macromonomer) by ATRP of PEOMA monomer initiated by PBIEM, the two peaks d and e disappeared while new peaks g and h appeared, indicating ethylene glycol protons and methyl protons at the side chains end, as shown in Figure 2c. This demonstrated the successful formation of the polymer brush with P(PEOMA) side chains. The preparation condition and some characteristics of PBIEM-*g*-P(PEOMA) used in the experiments are summarized in Table 1. PBIEM-*g*-P(PEOMA475) polymers with two different side chain lengths were obtained by controlling the monomer conversion. Absolute molecular weights of these brushes were determined by GPC with a multiangle light scattering detector.

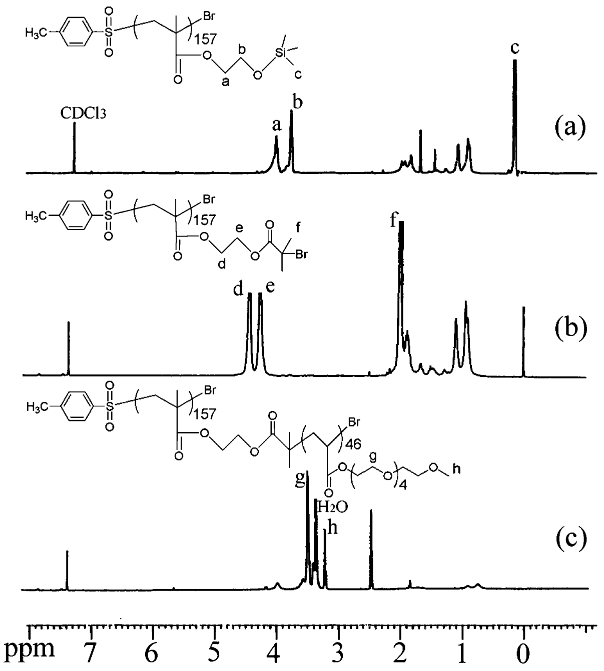


Figure 2. ^{1}H NMR spectra of (a) PBIEM-*g*-P(PEOMA300), (b) PBIEM, and (c) P(HEMA−TMS).

Gel Formation between α-CDs and PBIEM-*g*-P(PEOMA475). The solution of the polymer brush in water became cloudy with light blue tint instantaneously after the addition of a saturated α-CD solution, and the opaque hydrogel formed after standing for about 2 h at room temperature. Figure 3 shows the photograph of the hydrogel formed between PBIEM-*g*-P(PEOMA475)1 and α-CD. Interestingly, when heating to above ca. 40 °C, the hydrogel became nearly transparent liquid with light blue tint; the hydrogel formed again after cooling to room temperature gradually. This reversible process demonstrated that the hydrogel was thermosensitive and the presence of physical cross-linking. Moreover, the time to form hydrogel was greatly

Table 1. Preparation, Characterization of PBIEM-*g*-P(PEOMA)s and Their Complexation with α-CD[a]

polymer brush	condition[b]	time (h)	DP[e] (conv)	$M_w \times 10^6$ [f]	M_w/M_n [f]	yield of ICs (%)	EO/α-CD[g]
PBIEM-*g*-P(PEOMA475)1	300:1:1:1[c]	1.5	6	0.5	1.16		
PBIEM-*g*-P(PEOMA475)2	300:1:1:1[c]	2.5	35	2.9	1.04		
PBIEM-*g*-P(PEOMA300)	600:1:1:1[d]	0.5	46	4.2	1.07	6.4	1.1:1

[a] Initiator: PBIEM (DP_{PBIEM} = 157, obtained from [HEMA−TMS]/[TsCl] × conversion). [b] Feed: [PEOMA]:[PBIEM]:[CuBr]:[dNbpy]. [c] T = 70 °C, toluene/monomer = 1.89/1 (w/w). [d] T = 70 °C, toluene/monomer = 0.58/1 (w/w). [e] Degree of polymerization (DP) given by [PEOMA]/[Br] × conversion. [f] Determined from GPC-LLS. [g] Given by ^{1}H NMR analysis.

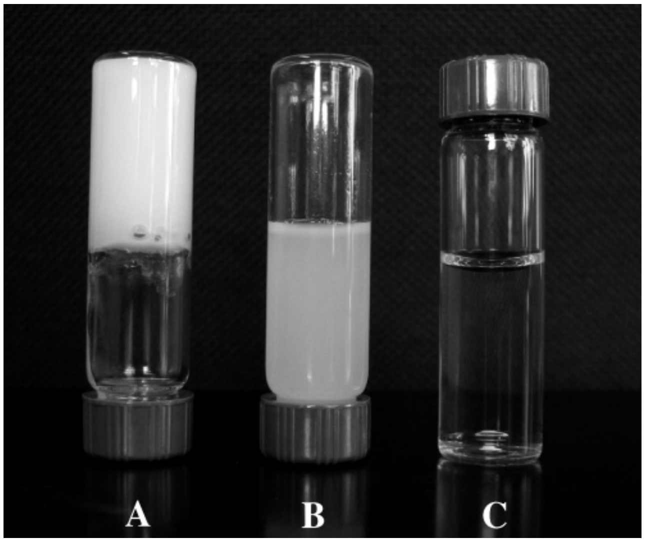


Figure 3. Photograph of hydrogels produced from water solution containing 1.3% of PBIEM-*g*-P(PEOMA475)1 and 11.5% of α-CD at room temperature (A) and after heating (B). Water was used for comparison (C).

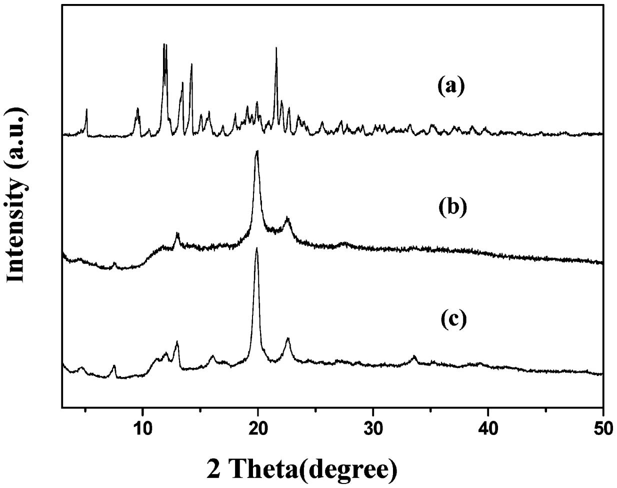


Figure 4. X-ray diffraction patterns of (a) α-CD and hydrogels of (b) α-CD/PBIEM-*g*-P(PEOMA475)1 and (c) α-CD/PBIEM-*g*-P(PEOMA475)2 after dried at 50 °C.

dependent on the side chain length of polymer brushes, for only half an hour was needed to form the hydrogel for PBIEM-*g*-P(PEOMA475)2, while ca. 2 h was needed for PBIEM-*g*-P(PEOMA475)1. In addition, the hydrogel formed within a short time could be partially destroyed under the centrifugation with rotation speed of 3500 rpm.

The hydrogels formed between α-CDs and PBIEM-*g*-P(PEOMA475)1 and PBIEM-*g*-P(PEOMA475)2 were dried by drying at 50 °C directly or by freeze-drying treatment. Figures 4 and 5 show the XRD patterns of dried samples by two different methods. The characteristic peaks at 2θ ca. 20° demonstrated that the hydrogels all had column-type crystalline structure, and

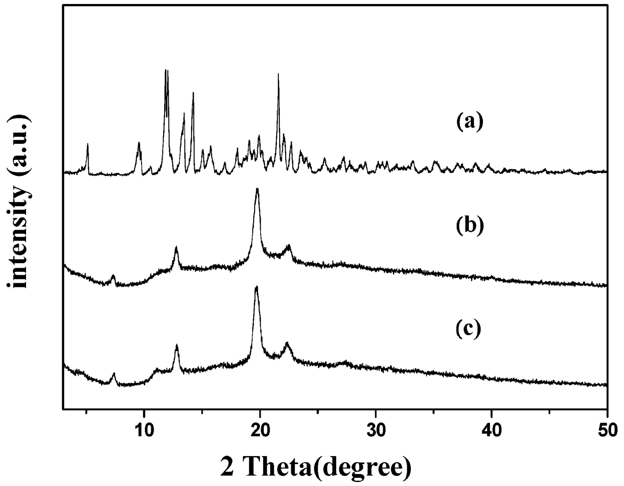


Figure 5. X-ray diffraction patterns of (a) α-CD and hydrogels of (b) α-CD/PBIEM-*g*-P(PEOMA475)1 and (c) α-CD/PBIEM-*g*-P(PEOMA475)2 after freeze-dried treatment.

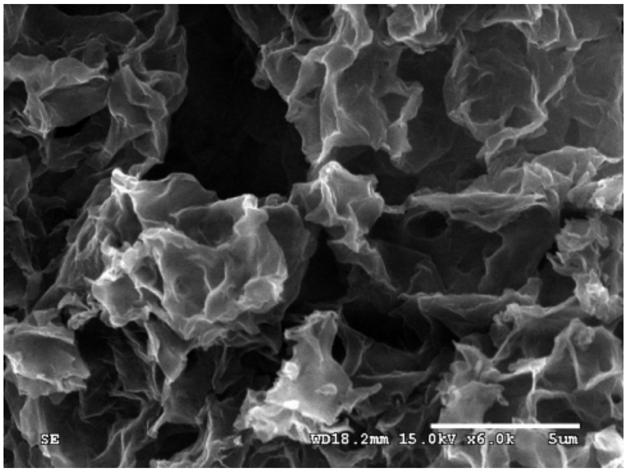
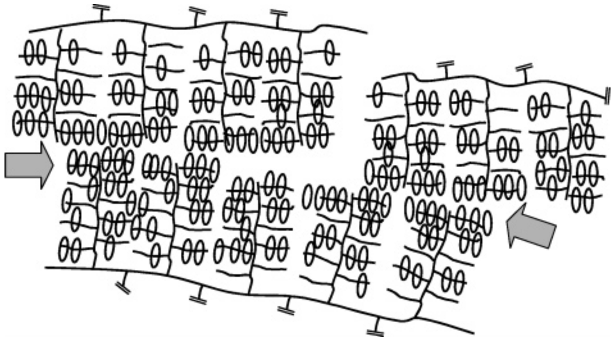


Figure 6. SEM images of hydrogels formed from α-CD/PBIEM-*g*-P(PEOMA475)2 being freeze-dried.

the method of drying had no impact on the microstructure of the ICs. No obvious peaks from pure CD crystals were observed, indicating that the majority of CDs had threaded onto the side chains of polymer brushes. Furthermore, the freeze-dried hydrogels were analyzed by scanning electron microscopy (SEM). The hydrogels from both of α-CD/PBIEM-*g*-P(PEOMA475)1 and α-CD/PBIEM-*g*-P(PEOMA475)2 had porous structures which were resulted from the phase-separated process during the complexation of α-CDs and PEO segments in polymer brushes. Figure 6 showed the SEM results of dried α-CD/PBIEM-*g*-P(PEOMA475)2 hydrogels.

In previous study, the inclusion complexation between PEOMA475 homopolymer comb, P(PEOMA475), and α-CDs formed column-type crystalline complex.[39] In contrast, in this study, the polymer PBIEM-*g*-P(PEOMA475) with even higher densely grafted PEO chains formed hydrogels with α-CDs due to the density of

Scheme 3. Schematic Illustration of Proposed Structure of Hydrogel Formed from Polymer Brush PBIEM-*g*-P(PEOMA475) and α-CD Molecules; Arrows Indicate the Cross-Linking Points



grafted PEO segments. The reason for difference is explained as follows. For the polymer brush, those PEO segments that located at the outer end of the side chains could be threaded relatively easily and formed column ICs aggregates to give a physical cross-linking point. Furthermore, the alignment of the threaded PEO chains is different comparing PBIEM-*g*-P(PEOMA475) brush to P(PEOMA475) comb. For the former, the formed IC columns are parallel to the main chain, while the columns are perpendicular to the main chain for the latter, and the orientation of the IC columns for the polymer brush may promote the physical cross-linking of gelation. On the other hand, owing to the steric hindrance, those PEO segments attached close to the backbone were very crowded and difficult to be threaded by CDs. Therefore, some PEO segments were free of complexation and were swelled by water. The combination of above two factors induced formation supramolecular networks of the hydrogels.[2,38] Scheme 3 represents the proposed hydrogel structure of ICs.

Interaction of α-CDs and PBIEM-*g*-P(PEOMA300). Complexation of brush PBIEM-*g*-P(PEOMA300) with α-CDs was greatly different from that of brush PBIEM-*g*-P(PEOMA475). As described in Experimental Section, a cloudy solution was formed after the two solutions of polymer brush PBIEM-*g*-P(PEOMA300) and α-CD were mixed together, and then white precipitants with luster from the reflection of crystals in the aqueous solution formed after standing for about 12 h. The crystals were collected by centrifugation and characterized. Figure 7 shows the ^{1}H NMR spectra of α-CD, PBIEM-*g*-P(PEOMA300), and α-CD/PBIEM-*g*-P(PEOMA300) complexes. By comparing the area of the protons from PEO segments and α-CD rings, the stoichiometry of EO to CD was estimated, and the data are listed in Tables 1 and 2. Surprisingly, the results indicated that the stoichiometry (EO to CD) in α-CD/PBIEM-*g*-P(PEOMA300) was 1.1:1, and EO was much less than expected. Moreover, the yield of ICs was rather low, and it only increased slightly with the increase of standing time or the concentration of two components (Table 2).

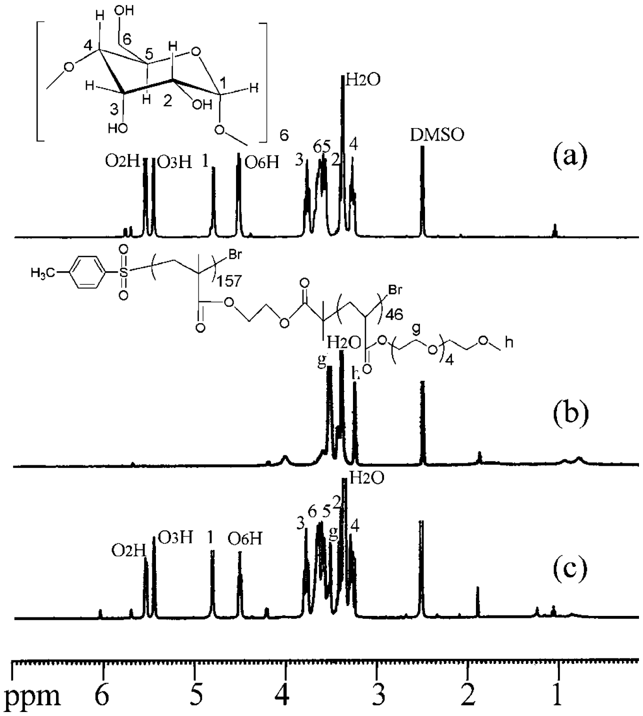


Figure 7. ^{1}H NMR spectra of (a) α-CD, (b) PBIEM-*g*-P(PEOMA300), and (c) α-CD/PBIEM-*g*-P(PEOMA300) in DMSO-d_6.

Normally, the crystals of the α-CD/PEO complex were too small to show regular shapes with facets.[45] But when the inclusion complexes were recrystallized in phosphate buffer or in deionized water, hexagonal fibers with 2 μm in side and more than 5 μm in height formed at room temperature.[46] In the present work the polymers used may have more artifacts during the polymer synthesis. However, the light reflection from the crystal facets of α-CD/PBIEM-*g*-P(PEOMA300) can even be observed by naked eyes. The suspension of the precipitates formed after standing a period of time in the aqueous solution was dropped onto a glass plate, and the morphology of crystals was observed by use of optical microscope directly. As shown in Figure 8a, the crystals have a regular appearance with hexagonal morphology in a size of ca. 10 μm. SEM image of the crystals (Figure 8b) indicates that the crystals of ICs are flake like lamellar structure and have clear contours similar to the image obtained from optical microscope. The solid samples were dispersed in ethanol, and the suspension was dropped onto a carbon-coated copper grid to make electron diffraction (ED) analysis. Figure 9 shows the XRD patterns of α-CD/PBIEM-*g*-P(PEOMA300) complex and an ED pattern corresponding to it. The XRD and ED all showed that the crystalline inclusion complexes are of hexagonal structures, similar to that of ICs from linear PEO and α-CD.[6,45,46] All these characterizations confirmed that α-CD/PBIEM-*g*-P(PEOMA300) ICs were hexagonal form. Therefore, even though the morphologies are different, the crystalline structure of this flake is the same as that of microfiber.[46]

It has been demonstrated in the literature that the yields of the ICs from linear PEO and α-CD increased with the increase of molecular weight of PEO.[7] In the previous work,[39] the comblike densely PEO grafted polymer, poly(PEOMA300), failed to form stable ICs crystals with α-CD due to steric hindrance of interbranches. The double-grafted polymer brush with P(PEOMA300) side chains used in this work formed crystalline product with an unexpected stoichiometry and a large size of uniform morphology. Therefore, formation of inclusion complexes with highly ordered structure should be related with the structural specialty in the present system. However, the stoichiometry of ca. 1:1 is still puzzling since it is well-known that two EO units are needed for one α-CD ring when a linear PEO fully covered by α-CDs. It also needs to point out that the

Table 2. Characteristics of More ICs Formed from α-CD and PBIEM-*g*-P(PEOMA300) in Aqueous Solution

run	$C_{\alpha-CD}$/(w/w %)[a]	$C_{polymer}$ (w/w %)[a]	standing time/h	yields/%	crystal	EO/α-CD[b]
1	11.5	1.5	18	2.2	hexagonal	1.06:1
2	11.5	1.5	24	3.2	hexagonal	1.12:1
3	14.4	1.8	336	6.8	hexagonal	1.04:1

[a] The concentration of α-CD and polymer brushes in mixed solution; [b] Given by ^{1}H NMR analysis.

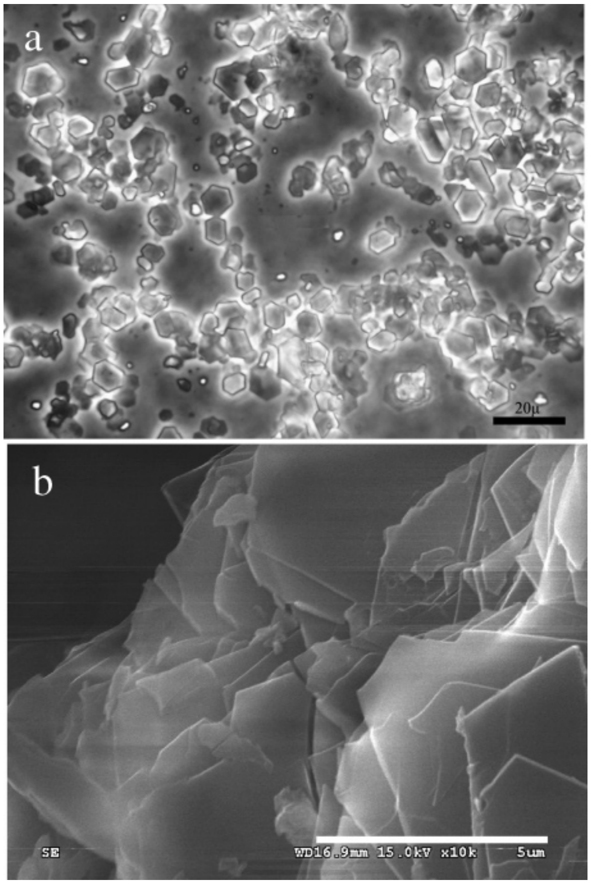


Figure 8. Photographs of crystals from α-CD/PBIEM-*g*-P(PEOMA300) given by (a) optical microscope and (b) SEM. The bar is 5 μm.

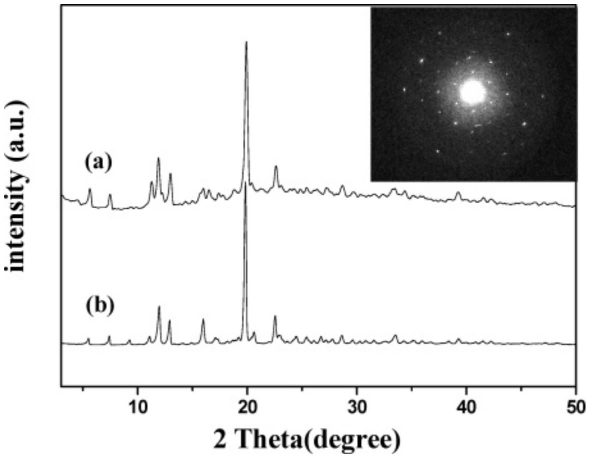


Figure 9. XRD patterns of the complex of (a) α-CD/PBIEM-*g*-P(PEOMA300) and (b) α-CD/PEO750. Inset is electron diffraction of the inclusion complex of (a).

yields of this type of crystals were low (<10%) and the majority of CD and grafted polymers failed to take part in forming the crystals. Hence, there may have some α-CDs that have no PEO segments to thread onto. Considering the well-defined crystals and packed column structure, the free α-CDs were also packed as a column structure; i.e., there were two forms of α-CD stacked columns in this crystal. It has been reported recently that α-CDs adopt columnar structures with only water molecules included by appropriate recrystallization from their aqueous solutions,[47] similar to the cyclodextrin inclusion compounds formed with guest polymers. By applying the silica nanocasting technique, wormlike aggregates were also found through self-assembly of purely α-CDs in water.[48] Minimization of the mutual contact area of hydrophilic and hydrophobic was believed to be driving force to give columnar structure of CDs. Therefore, we speculate that the α-CDs stacked into columns without PEO inside might be induced by the columns with PEO being threaded.

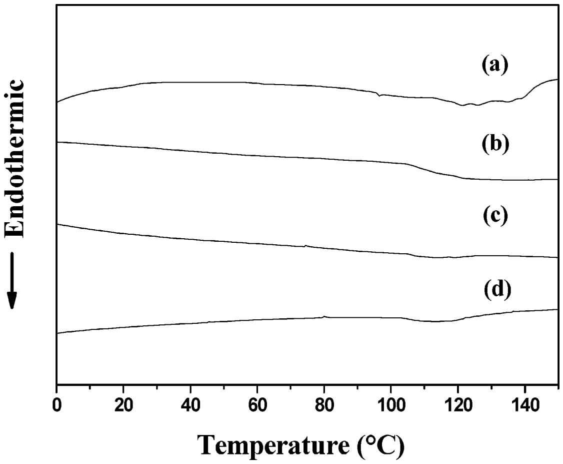


Figure 10. DSC thermograms of (a) α-CD, (b) α-CD/PBIEM-*g*-P(PEOMA300), and hydrogels of (c) α-CD/PBIEM-*g*-P(PEOMA475)1 and (d) α-CD/PBIEM-*g*-P(PEOMA475)2 being freeze-dried.

Thermoproperties of Complexes of α-CD/ PBIEM-*g*-P(PEOMA). Figure 10 showed the DSC thermograms of α-CD and α-CD/PBIEM-*g*-P(PEOMA300) and the freeze-dried hydrogels formed from PBIEM-*g*-P(PEOMA475)1 and PBIEM-*g*-P(PEOMA475)2. The results indicate that there were no melting peaks of PEO for all the ICs, and this was consistent with the corresponding XRD analysis, which means that all the guest polymer brushes participated in the complexation with α-CD molecules. In terms of those PEO segments free of threading, the column-type structures may limit their crystallization.

TGA measurement (Figure 11) indicated that the α-CD/PBIEM-*g*-P(PEOMA300) had similar thermal stability to that of free α-CD, and the initial decomposition temperatures were about 298 °C. But for ICs from the brush PBIEM-*g*-P(PEOMA475)2, the decomposition temperature decreased sharply comparing with that of α-CD. Such difference is related to the forms of the samples. The crystals with highly ordered packing structure were more stable than the samples dried from hydrogels with less ordered structures.

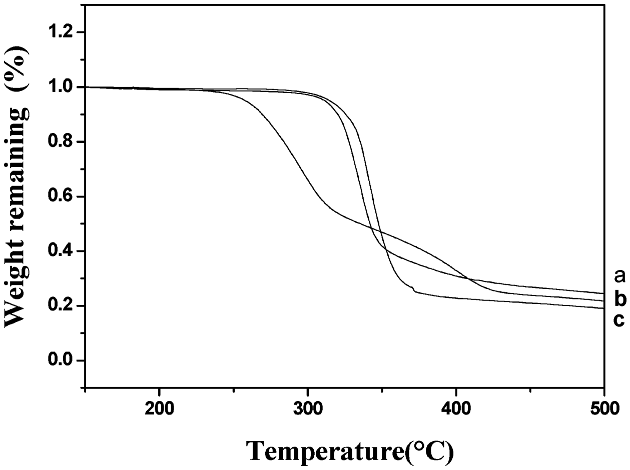


Figure 11. TGA curves of (a) α-CD/PBIEM-*g*-P(PEOMA300) and freeze-dried hydrogel of (b) α-CD/PBIEM-*g*-P(PEOMA475)2 comparing with (c) α-CD.

Conclusion

A series of double-grafted polymer brushes (PBIEM-*g*-P(PEOMA)), i.e., comblike polymers that were densely grafted from a polymer backbone, were synthesized through grafting poly(PEO macromonomer)s from a poly(macroinitiator) by ATRP. The ICs formed between α-CDs and polymer brushes from the macromonomers of different molecular weights, M_n = 300 and 475 Da, were very different. Inclusion interaction of PBIEM-*g*-P(PEOMA475) and α-CD in aqueous formed thermal reversible hydrogels. XRD analysis of dried gels demonstrated a column-type structure. The gelation was resulted from the combination of the IC column-type structure and those swollen unthreaded PEO segments. For α-CD/PBIEM-*g*-P(PEOMA300), fine hexagonal crystals formed as observed by optical microscope and SEM analysis. Electron diffraction and XRD analysis further confirmed the hexagonal crystal lattice structure. Furthermore, the stoichiometry of EO to α-CD was ca. 1:1. To our knowledge, this is the first report on inclusion complexation of α-CD with such highly densely PEO grafted polymer brushes of well-defined structure. In addition, the results have also indicated that the branched polymers are very different from linear polymers in forming ICs with α-CDs.

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