

Cyclodextrin-functionalized Ordered Porous Block Copolymer Films: Preparation and Property

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Electronic Supplementary Information

Abstract Ordered porous block copolymer films (PBCFs) have attracted much attention because of their potential applications in several fields. In this paper, we first reported a non-destructive, controllable, and efficient approach for preparation of β -cyclodextrin (β -CD)-functionalized PBCFs (β -CD-PBCFs). The key point of the approach is to incorporate β -CD units into the hydrophilic segment of amphiphilic block copolymers before the preparation of films. β -CD-PBCFs with structural integrity and controllable pore parameters were fabricated through combining of self-assembly and breath figure methods. And then, the effective adsorption capacity of β -CD-PBCFs toward Congo red was confirmed through UV-Vis spectroscopy and was found to be affected by β -CD content and solution pH values. Adsorption kinetic results showed that the adsorption behavior of β -CD-PBCFs was consistent with the pseudo-second-order kinetic model and the chemisorption mechanism.

Keywords Porous block copolymer film; β -Cyclodextrin; Breath figure; Self-assembly

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INTRODUCTION

Ordered porous films are important because of their wide range of applications, such as in catalysis^[1, 2], sensors^[3, 4], purification^[5], templates^[6], drug delivery^[7, 8], and biomedical applications^[9, 10]. Generally, porous films can be divided into organic, inorganic, and organic/inorganic composite materials. Compared with porous inorganic films, organic films (e.g., polymer-based films) present enhanced chemical tenability and mechanical flexibility^[11–13]. Ordered porous block copolymer films (PBCFs) have considerably developed since their introduction in 1988^[14]. Block copolymers, which are composed of macromolecules with long covalently connected segments of two or more distinct repeating units, can self-assemble into well-ordered structures with nano/microscopic domains and narrow pore size distribution. PBCFs are potential materials for water purification^[15], gas separation^[16], nanowires^[17], and controlled drug delivery^[18] because of their tunable pore size, narrow pore size distribution, and selective functionalization capacity.

PBCFs should exhibit functionality and controllable structure, in addition to their inherent excellent properties, to be suitable for applications in various fields^[19–21]. These

functionalized films can be prepared through modification of pore walls or surface *via* etching^[22], grafting^[23], and deposition^[24]. However, these functionalization methods present the following limitations. (1) Etching can only be applied to specific block copolymers with easily decomposable segments, and pores are formed by sacrificing a block or additive, which can reduce the mechanical strength and quality of the films. (2) The use of grafting to attach functional groups to pore walls may damage the pore structure, and the graft ratio may be low. In this case, well-controlled pores with uniform sizes cannot be achieved. (3) Deposition-based fabrication techniques are ineffective because the block copolymer films must be post-functionalized, thereby limiting their applications. Thus, a non-destructive, controllable, and efficient approach for preparation of functionalized porous films from block copolymers must be developed.

Herein, we intend to first incorporate the functional monomer into the hydrophilic segment of amphiphilic block copolymers before the preparation of films. And then, the functionalized polymers can be used to prepare the corresponding porous films through a combination of self-assembly and breath figure (BF) methods. As an alternative technique, BF method provides a simple, robust and efficient strategy to fabricate ordered two-dimensional films with a pore size in the range of micrometer and submicrometer. In this process, the foggy array of water droplets induced by solvent evaporative cooling acts as sacrificial templates for

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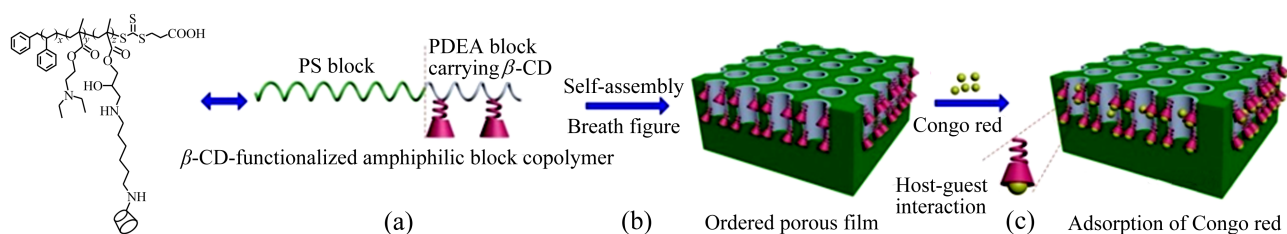
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spherical pores and leaves a honeycomb-patterned porous film after further evaporation^[25–29]. This combined approach can resolve above-mentioned problems, including incomplete pore structure, low graft ratio, and non-controllability of films. First, introduction of a functional monomer into the polymer backbone may avoid damages to the pore structure caused by subsequently direct pore-wall modification. Second, the pore parameters of the fabricated porous film may be effectively controlled by adjusting the content of the functional monomer in the entire block polymer. Finally, porous films can be easily and efficiently fabricated through a conventional controlled self-assembly technique and BF to obtain highly uniform pore size on the film surface.

Several functional monomers, including methacrylic acid^[30], 2-hydroxyethyl methacrylate^[31], *N*-vinyl-2-pyrrolidone^[32], and gallic acid^[33], can be used to prepare functionalized porous films from block copolymers. In particular, β -cyclodextrin (β -CD), a cyclic oligosaccharide containing seven glucopyranose units, has attracted much interest in the field of functional membrane production due to its host-guest inclusion function. Chu *et al.*^[34–36] prepared a series of thermo-responsive and molecule-recognizable films by grafting poly(*N*-isopropylacrylamide-*co*-glycidyl methacrylate/ β -CD) chains into the pores of porous nylon-6 substrate films through plasma-induced pore-filling grafting polymerization and chemical reaction. Schofield *et al.*^[37] developed β -CD-functionalized hierarchical porous structures. Although the presence of β -CD enhances the functionality of the films, it needs to be grafted into the pore walls through methods mentioned in the preceding paragraph. As such, the corresponding limitations persist and a perfect

and controllable pore structure in this kind of β -CD-functionalized porous film remains difficult to achieve.

In this work, we propose a non-destructive, controllable, and efficient approach for preparation of functionalized PBCFs. This approach was developed by introducing monovinyl β -CD monomer (GMA-HDA- β -CD) into the pH-responsive p[2-(diethylamino)ethyl methacrylate] (PDEA)^[38] segment before the preparation of PBCFs. Polystyrene-*b*-p[2-(diethylamino)ethyl methacrylate-*co*-monovinyl- β -cyclodextrin] [PS-*b*-P(DEA-*co*-GMA-HDA- β -CD)] block copolymer was obtained (Scheme 1a) *via* two-step reversible addition-fragmentation chain transfer (RAFT) polymerizations. A series of PS-*b*-P(DEA-*co*-GMA-HDA- β -CD)s were then used to prepare functionalized β -CD-PBCFs through combining of self-assembly and BF methods (Schemes 1a and 1b). Based on the self-assembly of PS-*b*-P(DEA-*co*-GMA-HDA- β -CD), the hydrophilic PDEA segment containing β -CD units served as pore walls during the formation of β -CD-PBCFs. In this case, the pore structure was not damaged and pore parameters, including size, morphology, and specific surface area, can be effectively adjusted by changing the ratios of β -CD to DEA monomers in the hydrophilic segments. Furthermore, β -CD-PBCFs were utilized to adsorb organic dye (Congo red, CR) (Schemes 1b and 1c) because the hydrophobic cavity of β -CD can encapsulate guest molecules^[37, 39]. β -CD content and solution pH were found to have a pronounced influence on the adsorption capacity of β -CD-PBCFs. Meanwhile, adsorption kinetics showed that the adsorption behavior of β -CD-PBCFs toward CR is consistent with the pseudo-second-order kinetic model, thereby indicating a chemisorption process.



Scheme 1 Preparation and adsorption property of β -CD-PBCFs: (a) Chemical structure of β -CD-functionalized block copolymers; (b) Preparation of ordered porous films through self-assembly and breath figure method; (c) Adsorption of Congo red by using the ordered porous films

EXPERIMENTAL

Materials

Styrene was commercially obtained from Guangdong Guang Hua Science and Technology Co., Ltd. and was distilled under reduced pressure before use. DEA was purchased from Alfa Aesar Co., Ltd. The initiator of 2,2'-azobis(2-methylpropionitrile) (> 99%, Tianjin Chemical Company) was purified using ethanol through recrystallization. The RAFT agent of 3-(benzylthiocarbonothioylthio)propanoic acid and GMA-HDA- β -CD were synthesized using previously described methods in Refs. [40] and [41], respectively. All the other reagents were of analytical grade and used without further purification. Poly(ethylene terephthalate) (PET) film was provided by LASPEF Plastic

Co. Ltd. and cleaned with acetone for 2 h before use. Deionized water was used in all experiments after being ultra-filtrated to 18.0 M Ω . CR was obtained from Shanghai Chemical Technology Co., Ltd.

Synthesis of β -CD-functionalized Amphiphilic Block Copolymers

Synthesis of PS-*macroCTA*

We synthesized a series of functionalized amphiphilic block copolymers, namely, polystyrene-block-poly(2-(diethylamino)ethyl methacrylate-*co*-monovinyl β -CD) [PS-*b*-P(DEA-*co*-GMA-HAD- β -CD)], with different β -CD contents through two-step RAFT polymerization. In the first step, 3-(benzylthiocarbonothioylthio)propanoic acid (13.6 mg, 0.05 mmol) and styrene (3165 mg, 30.4 mmol) were

dissolved in 6 mL of 1,4-dioxane in a 25 mL round-bottom flask. The mixture was deoxygenated three times through freeze-pump-thaw cycles, and the flask was sealed and stored in an oil bath at 120 °C with constant stirring. After 22.5 h, the polymer was exposed to air and cooled to room temperature. The viscous mixture was precipitated in excess amount of methanol. The precipitate PS was purified twice by dissolving in THF and then reprecipitated in methanol. Yield: ~78%. FTIR (KBr, cm^{-1}): 1064 (ν , $-\text{C}=\text{S}$); 1705 (ν , $\text{C}=\text{O}$); 3025 (ν , $-\text{C}-\text{H}$ in benzene). ^1H -NMR (CDCl_3 , δ , ppm): 6.41–7.32 (5H, Ph), 2.17 (2H, $-\text{CH}_2-\text{COOH}$), 1.42 ($-\text{CH}_2-$), 1.83 ($-\text{CH}-$).

Synthesis of PS-*b*-P(DEA-co-GMA-HDA- β -CD)

DEA (27.9 mg, 0.015 mmol), GMA-HDA- β -CD (103.05 mg, 0.015 mmol), and PS-macroCTA (494 mg, 0.015 mmol) were dissolved in 3 mL of *N,N*-dimethylformamide (DMF) in a 25 mL round-bottom flask. The mixture was deoxygenated three times by freeze-pump-thaw cycles, and the flask was sealed and stored in an oil bath at 90 °C with constant stirring. After 48 h, polymerization was terminated by exposing the sample to air and then dialyzed (molecular weight cut off: 3500) against DMF for 7 days. Subsequently, the product was dried overnight in a vacuum oven. Yield: ~68.61%. Other samples were synthesized using the similar procedure. ^1H -NMR ($\text{DMSO}-d_6$, δ , ppm): 5.88 (2,3-OH of β -CD), 4.97 (1-H of β -CD), 4.69 (6-OH of β -CD); 6.41–7.32 (5H, Ph-); 4.02 (2H, $\text{O}-\text{CH}_2-$), 0.8 (6H, $-(\text{CH}_2-\text{CH}_3)_2-$).

Fabrication of Ordered Porous Films

A series of PS-*b*-P(DEA-co-GMA-HDA- β -CD) polymers were dissolved in carbon disulfide to form a 3 mg/mL homogeneous solution. An aliquot of 50 μL for each polymer solution was drop-cast onto a PET film placed under a humid airflow (25 °C and > 80% RH). The humid air flow was produced by bubbling nitrogen through deionized water. The nitrogen flow rate was maintained at 1.5 L/min because the increase of flow rate of nitrogen through water would decrease the relative humidity. The effective area of the flow was about 5 cm^2 . The transparent solution turned turbid because of the condensation of water vapor on the solution surface during carbon disulfide evaporation.

Characterization

FTIR spectra were recorded on a NICOLET iS10 IR spectrophotometer, whereas ^1H -NMR spectra were determined on a Bruker Avance 300 spectrometer (Bruker Bio-Spin, Switzerland) operated at 300 MHz (^1H) in $\text{DMSO}-d_6$ or CDCl_3 . The molecular structures of the resulting polymers were determined through SEC/MALLS (DAWN EOS). HPLC-grade DMF containing LiCl (0.01 mol/L, at 40 °C) was used as eluent at a flow rate of 0.5 mL/min. The relative humidity and temperature of the air were measured using an exact hygro-thermograph. A field-emission scanning electron microscope (FESEM, JSM-6700F) was also used to observe the surface morphology of the films after gold sputtering. The water contact angles of the films were measured using the sessile drop method with the OCA15EC contact angle system (Data Physics

Instruments GmbH) at room temperature. Each value was reported as the average of at least five independent measurements.

Adsorption Experiments

Batch mode adsorption was performed to study the adsorption kinetics and adsorption capacities for CR. Dye concentration was determined at the maximum UV absorbance ($\lambda_{\text{max}} = 497 \text{ nm}$ for CR). The calibration curves were plotted between absorbance and CR concentration to obtain the absorbance-concentration profile based on Beer-Lambert's law. Experimental concentrations were obtained through successive dilution. The desired solution pH was obtained by adding the NaOH or HCl solution. Adsorption experiments were performed in a 20 mL flask by using 6 mL of CR solution and the required amount of the porous film adsorbent at $(25 \pm 1)^\circ\text{C}$ until equilibrium was attained. Briefly, 3 mL of the sample was drawn at regular intervals for residual concentration testing. All adsorption experiments were conducted twice, and only the mean values were reported. The adsorption percentage R (%) and the adsorption capacity for $t \text{ min}$ q_t (mg/g) were calculated with Eqs. (1) and (2), respectively.

$$R = (c_0 - c_e) / c_0 \times 100\% \quad (1)$$

$$q_t = (c_0 - c_t) \cdot V / m \quad (2)$$

where c_0 (mg/L) is the initial concentration, c_e (mg/L) is the equilibrium concentration after adsorption, and c_t (mg/L) is the concentration of CR in the aqueous solution after adsorption for $t \text{ min}$, respectively. V (L) is the volume of the solution, and m (mg) is the mass of the adsorbent.

RESULTS AND DISCUSSION

Preparation of Cyclodextrin-functionalized Ordered Porous Block Copolymer Films

A series of PS-*b*-P(DEA-co-GMA-HAD- β -CD)s were first synthesized through two-step RAFT polymerizations to prepare the final β -CD-PBCFs. In the first step, PS macromolecular chain transfer agent (PS-macroCTA) was synthesized via a typical RAFT process using 3-(benzylthiocarbonothioylthio)propanoic acid as CTA^[40] and styrene as monomer (Scheme S1, in electronic supplementary information, ESI). PS-*b*-P(DEA-co-GMA-HAD- β -CD)s with different β -CD contents were synthesized through PS-macroCTA-based RAFT copolymerization using GMA-HAD- β -CD^[41] and DEA as monomers (Scheme S2, in ESI). All the polymers were characterized through Fourier transform infrared (FTIR) spectroscopy, proton nuclear magnetic resonance (^1H -NMR) spectroscopy, and size exclusion chromatography/multi-angle laser light scattering (SEC/MALLS) analysis. Figures S1–S4 (in ESI) present the corresponding spectra. Table 1 summarizes the polymerization results of PS-*b*-P(DEA-co-GMA-HAD- β -CD)s. The $M_{n,\text{NMR}}$ of the polymers increased from 3.63×10^4 to 4.78×10^4 , which is close to the theoretical value in Table 1. The results of SEC/MALLS analysis illustrated that molecular weight distribution (MWD) remained narrow (Fig. S3, in ESI). However, the values of weight-average

Table 1 Polymerization results of PS-*b*-P(DEA-*co*-GMA-HDA- β -CD)s

Sample	Conv. (%)	$M_{n,theory}$ $\times 10^{-4}$ (g/mol)	$M_{n,NMR}$ $\times 10^{-4}$ ^a (g/mol)	$M_{w,SEC}$ $\times 10^{-4}$ ^b (g/mol)	MWD ^b	DP _{hydrophobic} /DP _{hydrophilic} ^c		β -CD content ^d (mol%)	
						Theory ^{c1}	Actual ^{c2}	Theory ^{d1}	Actual ^{d2}
PS ₃₁₈ - <i>b</i> -PDEA ₁₆	74.2	3.62	3.63	3.70	1.07	21	20	0	0
PS ₃₁₈ - <i>b</i> -P(DEA ₁₀ - <i>co</i> -GMA-HDA- β -CD ₈)	68.6	4.21	4.61	3.34	1.03	21	18	33	44
PS ₃₁₈ - <i>b</i> -P(DEA ₇ - <i>co</i> -GMA-HDA- β -CD ₉)	68.8	4.43	4.69	3.38	1.08	21	19	47	56
PS ₃₁₈ - <i>b</i> -P(DEA ₄ - <i>co</i> -GMA-HDA- β -CD ₁₀)	66.5	4.81	4.78	3.47	1.04	21	22	67	71

^a Molecular weight determined by ¹H-NMR; ^b Weight-average molecular weight (M_w) and molecular weight distribution (MWD) determined by SEC/MALLS;

^c The ratio of degree of polymerization (DP) of the hydrophobic and hydrophilic segments was calculated using the following formula: (DP of PS)/(DP of P(DEA-*co*-GMA-HDA- β -CD)), ^{c1} the ratio of the theoretical DP of the hydrophobic and hydrophilic segments is 318/15 = 21, ^{c2} the ratio of the actual DP of the hydrophobic and hydrophilic segments was calculated using the following formula: (DP of PS)/(actual DP of P(DEA-*co*-GMA-HDA- β -CD) calculated by NMR); ^d β -CD content in the hydrophilic segment was calculated using the following formula: (DP of P(GMA-HDA- β -CD))/(DP of P(DEA-*co*-GMA-HDA- β -CD)), ^{d1} the theoretical β -CD content in the hydrophilic segment was calculated using the following formula: (theoretical DP of P(GMA-HDA- β -CD))/15, ^{d2} the actual β -CD content in the hydrophilic segment was calculated using the following formula: (actual DP of P(GMA-HDA- β -CD))/(actual DP of P(DEA-*co*-GMA-HDA- β -CD)) by NMR.

molecular weight determined by SEC/MALLS ($M_{w,SEC}$) deviated from the theoretical value to some degree because of the adsorption of β -CD on the column. Therefore, we used $M_{n,NMR}$ to calculate the degree of polymerization (DP) of the resulted polymers. The actual ratios of the hydrophobic and hydrophilic segments (PS/P(DEA-*co*-GMA-HAD- β -CD)) in PS-*b*-P(DEA-*co*-GMA-HAD- β -CD) were consistent with the theoretical values. The β -CD content in the resulting polymers increased with increasing DP of P(GMA-HAD- β -CD). These results indicated that a series of PS-*b*-P(DEA-*co*-GMA-HAD- β -CD)s with a tunable structure were successfully synthesized.

A series of β -CD-PBCFs were prepared using PS-*b*-P(DEA-*co*-GMA-HAD- β -CD)s through self-assembly of the amphiphilic polymer and BF method. In the BF process, the foggy array of water droplets induced by solvent evaporative cooling functions as sacrificial templates for spherical pores and leaves β -CD-function after further evaporation. Figure 1 depicts the SEM images of the surfaces of β -CD-PBCFs prepared using samples with different β -CD contents. Compared with the porous film without β -CD (Figs. 1a and 1a'), the pores in the β -CD-PBCFs surfaces were more uniform and ordered (Figs. 1b–1d and 1b'–1d'). Figures 1(d) and 1(d') show that the pore was nearly circular at high β -CD contents; hence, β -CD content affected the final pore morphology. Table 2 lists the pore parameters of β -CD-PBCFs drawn from Fig. 1, such as pore size and specific surface area. The increase in β -CD content from 44% to 71% directly increased the pore size from 1.19 μ m to 1.77 μ m and the specific surface area from 34 m²/g to 60 m²/g. Figure S5 (in ESI) shows the cross-sectional view of β -CD-PBCFs. Cylindrical pore structure was observed on the surfaces of β -CD-PBCFs. These results confirmed the successful fabrication of β -CD-PBCFs with pore parameters that can be tuned by adjusting β -CD content in hydrophilic blocks.

Surface Property of Ordered Porous Films

The hydrophilic-hydrophobic property of the β -CD-PBCF surfaces was investigated by measuring the dynamic contact angle (CA). The hydrophilicity of porous films is an important factor that affects the adsorption property of the films^[42, 43]. Table 3 shows the snapshots of the results of CA measurement obtained by adding 0.25 μ L of water droplets

on the surfaces of β -CD-PBCFs at 22 °C. The water CA values of the film surfaces with different β -CD contents became 0° after 240 s, whereas those without β -CD remained at 91° under similar condition. In general, high surface hydrophilicity is associated with low CA values on the film surface. This result indicated that the presence of β -CD with

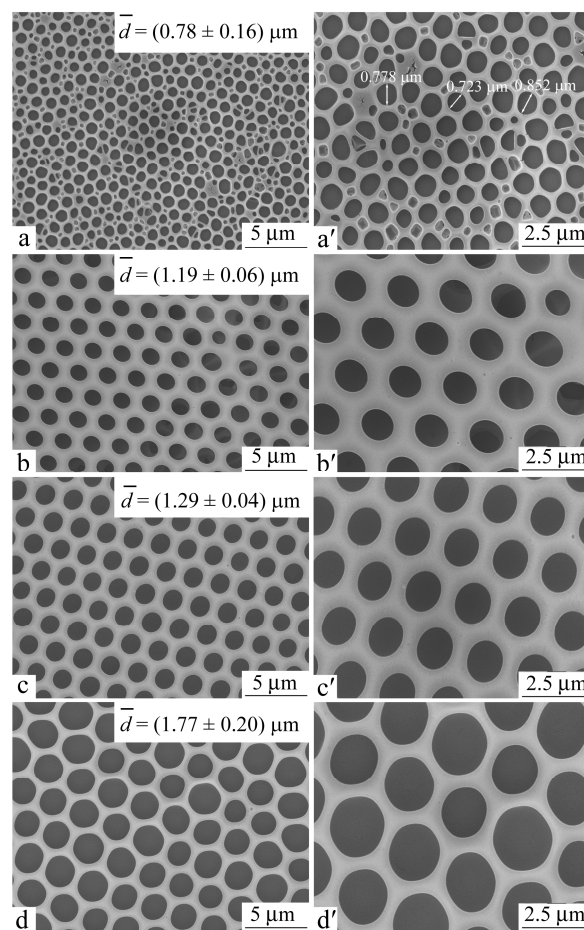


Fig. 1 SEM images of β -CD-PBCFs: (a) porous film prepared using PS₃₁₈-*b*-PDEA₁₆; (b) porous film prepared using PS₃₁₈-*b*-P(DEA₁₀-*co*-GMA-HDA- β -CD₈); (c) porous film prepared using PS₃₁₈-*b*-P(DEA₇-*co*-GMA-HDA- β -CD₉); (d) porous film prepared using PS₃₁₈-*b*-P(DEA₄-*co*-GMA-HDA- β -CD₁₀); (a'–d') typical magnification images of a–d

Table 2 Pore parameters of β -CD-BCOPFs

Sample ^a	β -CD content ^b (%)	Pore size ^c (μm)	Specific surface area ^d (m^2/g)
a	0	0.78 ± 0.16	51
b	44	1.19 ± 0.06	34
c	56	1.29 ± 0.04	41
d	71	1.77 ± 0.20	60

^a Corresponding to the samples a–d in Fig. 1; ^b Listed in Table 1; ^c Determined with the Screen Calipers software. All the samples were measured 10 times, and only mean values were reported; ^d Determined with the Image-Pro 6.0 software. Specific surface area was measured by analyzing the different surface colors of the samples.

a large number of hydroxyl groups effectively enhanced the hydrophilicity of the porous film surfaces. Figure 2 further displays the trend of CA changes in β -CD-PBCFs, and Table S1 (in ESI) shows the linear fitting results of data presented in Fig. 2. Here, it was found that the increase in β -CD content accelerated CA reduction rate to some degree. This result could be mainly attributed to the increased pore size as a result of increased β -CD content, thereby enhancing the adsorption capacity of the porous film toward water droplets.

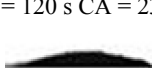
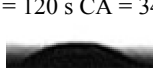
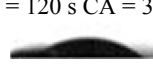
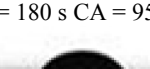
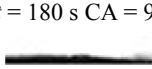
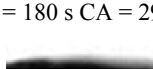
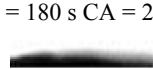
Adsorption Property of Ordered Porous Films

To confirm the contribution of β -CD to the functionality of β -CD-PBCFs, we performed batch model adsorption experiments on CR under different conditions. CR is a benzidine-based anionic dye and considered carcinogenic to humans because it can metabolize into benzidine^[44]. As the initial solution concentration can greatly influence the adsorption performance, selecting the appropriate concentration is thus important. Generally, the equilibrium adsorption capacity (q_e , mg/g) and the removal ratio (R , %) are important parameters for the adsorption capacity^[45]. Thus, a suitable CR concentration was first determined by measuring R and q_e (Figs. S6 and S7, in ESI). On the basis of the above results, we selected 20 mg/L as the initial CR

concentration for subsequent studies. Figure 3 presents the effect of β -CD content on the adsorption property of β -CD-PBCFs. The adsorption curves of β -CD-PBCFs for CR (Fig. 3a) revealed that the adsorption capacity of the films was significantly enhanced as the β -CD content increased from 0% to 71%. Correspondingly, the q_e and R values increased from 45 mg/g to 106 mg/g and from 23% to 53% (Fig. 3b). When the β -CD content increased from 0% to 44%, the q_e and R increased due to the host-guest interaction of β -CD with CR, despite the reduction of specific surface area can decrease the q_e and R ^[39]. As the β -CD content increased to 56% and the specific surface area increased slightly, the role of host-guest interaction was enhanced with the increase of the β -CD content, leading to the obvious increase of q_e and R values^[37].

The effect of pH-responsive PDEA segment on the adsorption capacity of β -CD-PBCFs was studied within the pH range of 5.0–10.0. Figure 4 shows the adsorption curves for CR of β -CD-PBCFs with different β -CD contents. The maximum q_e value for all samples was observed at pH 7.0, which indicated that the adsorption behavior is pH-controlled. This result could be attributed to the PDEA segment that functions as pore walls. As PDEA was a pH-sensitive polymer ($\text{p}K_a = 7.3$)^[46], the charges in the polymer chains repelled each other at $\text{pH} < 7$, which resulted in stretched hydrophilic segments and decreased pore size, along with the reduction of specific surface area; consequently, the adsorption capacity of β -CD-PBCFs for CR decreased. At $\text{pH} = 7$, the hydrophobic chain segment curled up, thereby increasing the pore size, which benefits CR adsorption. Further increase in pH increased the amount of negative charges on the surface of β -CD-PBCFs; however, these ions were repelled by negative ions $-\text{SO}_3^-$ released by CR, thus decreasing the rate of absorption. Additionally, competition for the active adsorption site between OH^- and CR negative ions at $\text{pH} = 10$ may have reduced the adsorption capacity of β -CD-PBCFs^[47].

Table 3 Snapshots of contact angle measurements on the β -CD-BCOPF surfaces

(a) PS ₃₁₈ - <i>b</i> -PDEA ₁₆	(b) PS ₃₁₈ - <i>b</i> -P(DEA ₁₀ - <i>co</i> -GMA-HDA- β -CD ₈)	(c) PS ₃₁₈ - <i>b</i> -P(DEA ₇ - <i>co</i> -GMA-HDA- β -CD ₉)	(d) PS ₃₁₈ - <i>b</i> -P(DEA ₄ - <i>co</i> -GMA-HDA- β -CD ₁₀)
 $t = 0 \text{ s CA} = 104^\circ$	 $t = 0 \text{ s CA} = 47^\circ$	 $t = 0 \text{ s CA} = 55^\circ$	 $t = 0 \text{ s CA} = 57^\circ$
 $t = 60 \text{ s CA} = 101^\circ$	 $t = 60 \text{ s CA} = 32^\circ$	 $t = 60 \text{ s CA} = 43^\circ$	 $t = 60 \text{ s CA} = 44^\circ$
 $t = 120 \text{ s CA} = 98^\circ$	 $t = 120 \text{ s CA} = 23^\circ$	 $t = 120 \text{ s CA} = 34^\circ$	 $t = 120 \text{ s CA} = 35^\circ$
 $t = 180 \text{ s CA} = 95^\circ$	 $t = 180 \text{ s CA} = 9^\circ$	 $t = 180 \text{ s CA} = 29^\circ$	 $t = 180 \text{ s CA} = 26^\circ$
 $t = 240 \text{ s CA} = 91^\circ$	 $t = 240 \text{ s CA} = 0^\circ$	 $t = 240 \text{ s CA} = 0^\circ$	 $t = 240 \text{ s CA} = 0^\circ$

Snapshots of CA measurement of water droplets (0.25 μL) dropped onto different membrane porous surfaces at 22 $^\circ\text{C}$. (a) Porous film prepared using PS₃₁₈-*b*-PDEA₁₆; (b) Porous film prepared using PS₃₁₈-*b*-P(DEA₁₀-*co*-GMA-HDA- β -CD₈); (c) Porous film prepared using PS₃₁₈-*b*-P(DEA₇-*co*-GMA-HDA- β -CD₉); (d) Porous film prepared using PS₃₁₈-*b*-P(DEA₄-*co*-GMA-HDA- β -CD₁₀)

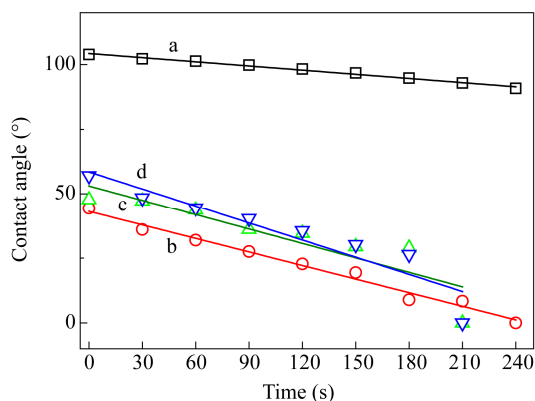


Fig. 2 Trend of CA changes on the different β -CD-PBCFs surfaces: (a) the film from PS₃₁₈-*b*-PDEA₁₆, (b) the film from PS₃₁₈-*b*-P(DEA₁₀-*co*-GMA-HDA- β -CD₈), (c) the film from PS₃₁₈-*b*-P(DEA₇-*co*-GMA-HDA- β -CD₉), (d) the film from PS₃₁₈-*b*-P(DEA₄-*co*-GMA-HDA- β -CD₁₀)

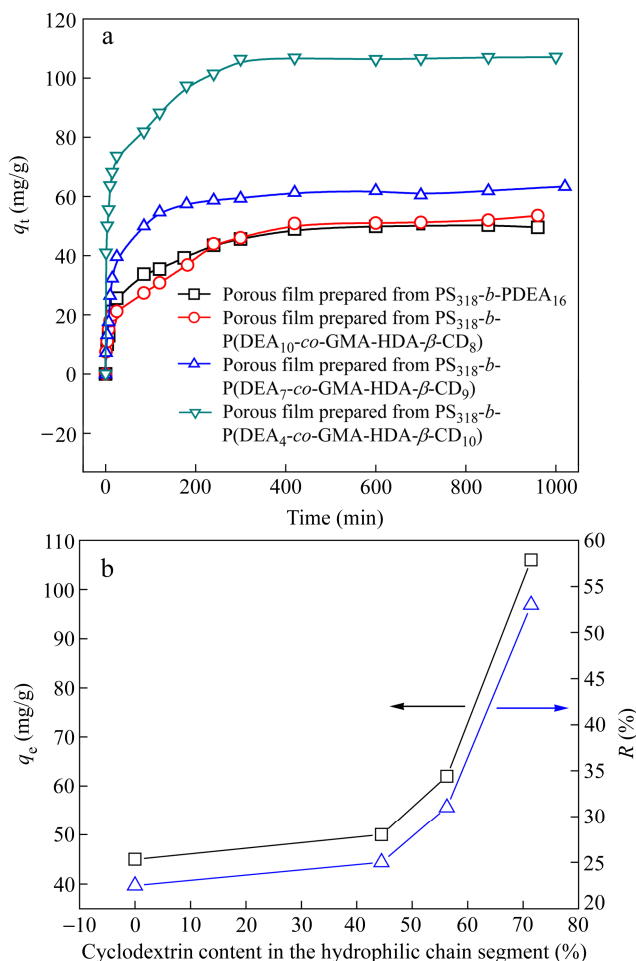


Fig. 3 Influence of β -CD content on the adsorption capacity of β -CD-BCOPFs ($c_0 = 20$ mg/L, pH = 7.0): (a) adsorption curve of β -CD-BCOPFs with different β -CD contents; (b) influence of β -CD content on equilibrium adsorption capacity (q_e) and removal ratio (R)

To further investigate the adsorption mechanism of β -CD-PBCFs for CR, we adopted the pseudo-first-order and pseudo-second-order models, which could be expressed as Eqs. (3) and (4), respectively^[48, 49].

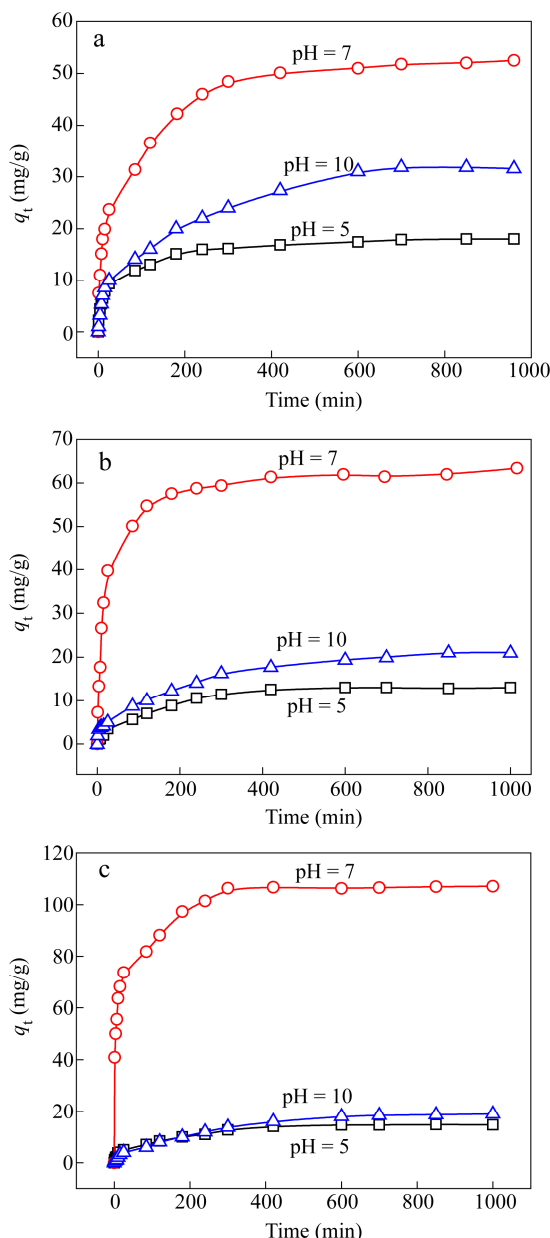


Fig. 4 Influence of pH on the adsorption capacity of a series of β -CD-BCOPFs ($c_0 = 20$ mg/L): adsorption curves of porous films prepared using (a) PS₃₁₈-*b*-P(DEA₁₀-*co*-GMA-HDA- β -CD₈), (b) PS₃₁₈-*b*-P(DEA₇-*co*-GMA-HDA- β -CD₉) and (c) PS₃₁₈-*b*-P(DEA₄-*co*-GMA-HDA- β -CD₁₀) under different pH conditions

(1) Lagergren pseudo-first-order kinetic model:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (3)$$

(2) Pseudo-second-order kinetic model:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (4)$$

where k_1 (mg/(g·min)) and k_2 (mg/(g·min)) are the adsorption rate constants of the pseudo-first-order and pseudo-second-order kinetics, respectively. q_t (mg/g) and q_e (mg/g) represent the adsorption capacity at any time t (min) and at equilibrium, respectively. t (min) is the contact time. The pseudo-first-

order and pseudo-second-order kinetic curves are shown in Fig. 5, and the kinetic parameters are given in Table 4. The correlation coefficient (R^2) value of the pseudo-first-order kinetic curve reaches 0.95, whereas the experimental q_e values do not agree with the calculated ones (Table 4); hence, the adsorption of CR on β -CD-PBCFs did not conform to the pseudo-first-order model. The R^2 value of the pseudo-second-order kinetic curve is higher than 0.99 (Table 4), and the

calculated q_e values are found to be closer to the experimental q_e values. Therefore, the pseudo-second-order model accurately describes the adsorption process, thereby indicating that the adsorption mechanism of β -CD-PBCFs is possibly chemisorption^[50, 51]. This result could be attributed to the presence of β -CD on the pore walls. CR may be encapsulated into the cavities of β -CD because of their host-guest interaction (Scheme 1c).

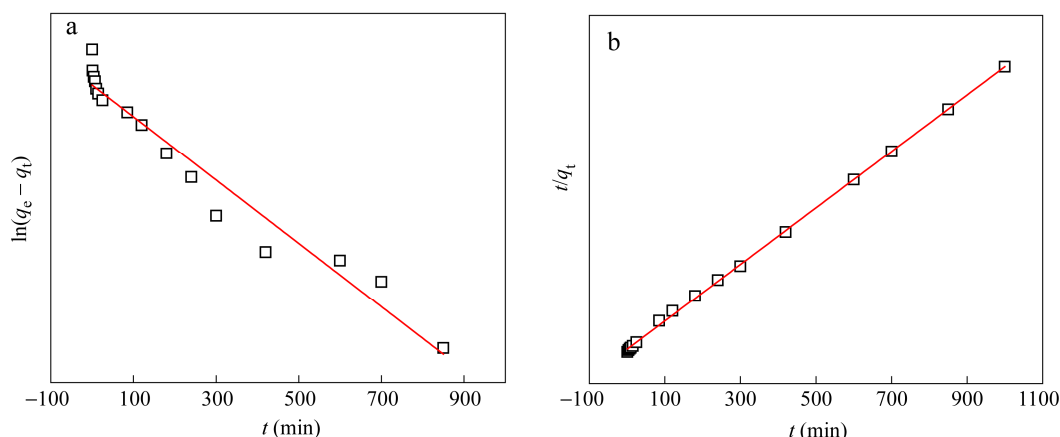


Fig. 5 Adsorption kinetics of CR: (a) pseudo-first-order plot and (b) pseudo-second-order plot ($T = 25\text{ }^{\circ}\text{C}$, $c_0 = 20\text{ mg/L}$)

Table 4 Model parameters of the adsorption kinetics

$q_{e,\text{exp}}$ (mg/g)	Pseudo-first-order kinetic model			Pseudo-second-order kinetic model		
	q_e (mg/g)	k_1 (mg/(g·min))	R^2	q_e (mg/g)	k_2 (mg/(g·min))	R^2
107.11	51	0.007	0.95	108	0.00077	0.99

CONCLUSIONS

We propose a non-destructive, controllable, and efficient approach for preparation of functionalized ordered porous films by introducing β -cyclodextrin (β -CD) units into the hydrophilic block of amphiphilic block copolymer (β -CD-PBCFs) before the preparation of films. β -CD content could be tuned in the hydrophilic block by adjusting the ratio of β -CD to other hydrophilic monomer prior to subsequent non-destructive preparation of the porous film. β -CD-PBCFs with controllable pore parameters could be prepared *via* a combination of self-assembly and BF methods. β -CD-PBCFs exhibited an efficient adsorption capacity toward Congo red (CR). The adsorption capacity of β -CD-PBCFs was evidently enhanced when the β -CD content was increased or solution pH value was adjusted to 7. The adsorption kinetics of β -CD-PBCFs toward CR can be accurately fitted with the pseudo-second-order kinetic model, implying that chemisorption is the possible adsorption mechanism. Our findings introduced new insights into preparation of functionalized ordered porous films from polymers for further applications.

Electronic Supplementary Information

Electronic supplementary information (ESI) is available free of charge in the online version of this article at <http://dx.doi.org/10.1007/s10118-018-2005-2>.

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