

Article

Porous Composite Polymers Composed of Polyethyleneimine and Cyclodextrins: Synthesis and Application as Adsorbents for an Organic Compound

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Abstract: Polyethyleneimine-based porous composites have been prepared by ring-opening polymerization of 2,2-bishydroxymethylbutanol-tris[3-(1-aziridinyl)propionate] (3AZ), a tri-aziridine compound, in water, in the presence of cyclodextrins (CDs), i.e., α -CD, γ -CD, methyl- β -cyclodextrin (Me- β -CD), monoacetyl- β -cyclodextrin (Ac- β -CD), and hydroxypropyl- β -cyclodextrin (HP- β -CD). The corresponding 3AZ-CD porous polymer composites were successfully obtained in most cases under a wide range of CD concentrations, 5–20 wt%, and reaction temperatures, 20–60 °C. The reaction system in the presence of Ac- β -CD preferentially yielded gels. The polymer composites were composed of connected particles with sizes of the order of 10^{-9} m. The particle sizes decreased with an increase in the CD concentration. Young's moduli of the 3AZ-CD porous polymer composites tended to increase with an increase in bulk density. The 3AZ-CD porous polymer composites with Me- β -CD and HP- β -CD effectively adsorbed phenolphthalein in the solution. The adsorption value increased with increasing the CD content and rose to more than 600 mg/g of porous polymer composite.

Keywords: polyethyleneimine; porous; phase separation; cyclodextrin; composite; adsorption

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1. Introduction

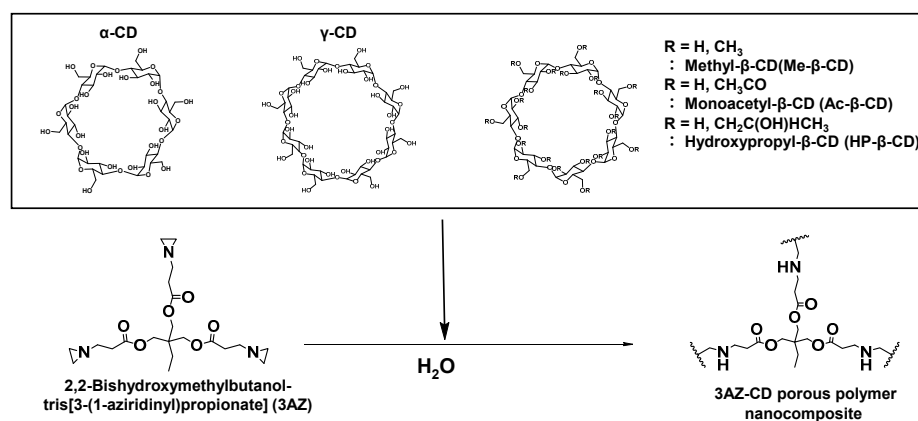
Molecular recognition is one of the most distinctive features of biochemistry. This function is induced by various interactions between molecules, such as hydrogen bonding, coordination bonding, hydrophilic effects, van der Waals forces, π - π stacking, halogen bonding, electrostatic forces, and so on. Host–guest chemistry is a fundamental mechanism for static molecular recognition. Molecular imprinting has been widely studied for molecular recognition in artificial chemical systems and used to fabricate polymers called molecular imprinting polymers (MIPs) that can recognize not only the imprinted molecules but also those with similar structures [1–13]. Clathration, or inclusion, is another mechanism for molecular recognition that is well known for cyclodextrins (CDs). CDs can form non-covalent complexes with organic molecules within their cyclic structure, which features a hydrophobic inner cavity composed of glucose units linked by α -1,4-glycosidic bonds [14–17]. This characteristic molecular structure of CDs makes it possible to clathrate various organic molecules.

Porous polymers are useful materials for separation processes due to their co-continuous structure with a high surface area [18–24]. Various porous polymers have been synthesized by polymerization-induced phase separation (PIPS) and have been used mainly as packing for chromatography (columns, filters, and discs), exhibiting high separation ability based on their co-continuous porous structure [25–30]. The complex conjugation of porous polymers with functional materials is used to improve the separation ability and add new functions. PIPS in the presence of the composite materials should make it possible to prepare composite porous polymers. The following two characteristics would be required for the composite materials. One is homogeneous dispersibility in the reaction system to form the homogeneous porous polymer. The corresponding solution or sol with the solvent used in the PIPS is preferable. Another is that the composite materials do not inhibit phase separation during the polymerization. Additives in the PIPS system sometimes inhibit phase separation, yielding a gel without a porous structure.

Composite polymers with CD derivatives should be a useful method to add characteristic functions derived from CDs to polymer materials. The surface modification of fibers with a reactive CD, monochloro-triazinyl- β -CD (MCT- β -CD) achieved through a chemical reaction successfully produced fabrics with β -CD moieties [31]. The development of a facile method to prepare the porous polymer composites with CDs should increase the separation performance and applicability of the polymer material.

We previously reported a facile synthesis method to prepare a polyethyleneimine-based porous polymer by ring-opening polymerization of a tri-aziridine derivative in water [32]. Dissolution of 2,2-bishydroxymethylbutanol-tris[3-(1-aziridinyl)propionate] (3AZ) in water initiated cationic ring-opening polymerization, induced phase separation and successfully yielded a porous polymer. This reaction should be applicable to prepare porous polymers in the presence of the composite materials that are soluble and/or dispersible in water. As the next step, we came up with the idea of producing 3AZ porous composite polymer with CDs. Among the conventional CDs, α -CD and γ -CD are soluble in water. Although β -CD is almost insoluble in water, water-soluble substituted- β -CD derivatives can be applicable to this reaction system.

In this study, polyethyleneimine-based porous composite polymers were synthesized by the ring-opening polymerization of 3AZ in CD solutions (Scheme 1). Polyethyleneimine-based porous composite polymers with α -CD, γ -CD, and substituted- β -CD derivatives were successfully obtained. The obtained porous composite polymers containing CDs may be useful in the separation and adsorption of organic compounds because CDs can capture molecules in their hydrophobic inner cavities. The porous composite polymers with substituted- β -CD compounds were found to effectively adsorb phenolphthalein, as model organic compounds, via a host–guest mechanism.



Scheme 1. Synthesis of 3AZ-CD porous composites polymers by ring-opening polymerization of 3AZ in the presence of CDs simultaneous phase separation.

2. Materials and Methods

2.1. Materials

2,2-Bishydroxymethylbutanol-tris[3-(1-aziridinyl)propionate] (3AZ) was kindly donated by Nippon Shokubai Co., Ltd., (Osaka, Japan) and used as received. α -CD, γ -CD, and methyl- β -cyclodextrin (Me- β -CD, Fuji-film Wako Pure Chemical Industries, Osaka, Japan), monoacetyl- β -cyclodextrin (Ac- β -CD, Junsei Chemical Co., Ltd., Tokyo, Japan), and hydroxypropyl- β -cyclodextrin (HP- β -CD, Kanto Chemical Co., Inc., Tokyo, Japan) were commercially obtained and used as received. Methanol (MeOH), ethanol (EtOH), phenolphthalein (phph), and sodium carbonate were commercially obtained from Kanto Chemical Co., Inc., and used without further purification.

2.2. Synthesis of Porous Polymer Composites

The reaction of 20 wt% 3AZ in the presence of 5 wt% CD is described as an example. A CD (0.25 g) and distilled water (3.75 g) were added to a 20 mL vial and stirred by a vortex mixer (Mixer N-40M-1, NISSIN, Tokyo, Japan) for a few minutes to make a homogeneous solution. 3AZ (1.0 g) and the CD solution were added to a quadrangular prism polyethylene bottle (1.7 cm $\times$ 1.7 cm $\times$ 3.0 cm), stirred using a vortex mixer, and then stored at the desired temperature in an ESPEC SU-641 constant temperature chamber (ESPEC CORP., Osaka, Japan) for 24 h. The obtained porous polymer composite was washed by immersion in an excess of methanol for 24 h. The porous polymer composite was air-dried at room temperature for 72 h and further dried in vacuo at 40 °C for 4 h. Reactions with different monomer concentrations were conducted by the same procedures.

2.3. Adsorption Test of Phph

Solutions with different concentrations of phph, 10, 20, 42, 62, 82 mg/L in Na₂CO₃ aq. (20.0 g/L) pH: 11.3 were prepared for the adsorption test. A cubic sample of a porous polymer composite (0.7 $\times$ 0.7 cm $\times$ 0.7 cm) was soaked into a 10 mL of phph solution for 24 h at 25 °C. The concentration of phph in the solution after adsorption was determined by a UV-vis spectrum using a calibration curve. The adsorption value (q_e) was calculated using Equation (1) below.

$$q_e \text{ (mg/g)} = \{C_e \text{ [mg/L]} - C_o \text{ [mg/L]}\} \times V \text{ [L]} / m \text{ [g]}$$

C_o : phph concentration before adsorption
 C_e : phph concentration after adsorption
 V : volume of phph solution used (=10 mL)
 m : weight of porous polymer composite used

(1)

2.4. Analytical Procedures

FT-IR spectra of porous composite polymers and CDs were recorded on a FTIR-8400 or an IRAffinity-1S spectrometer (SHIMADZU Corporation, Kyoto, Japan), and 30 scans were accumulated from 4000 to 500 cm⁻¹.

Scanning electron microscopy (SEM) images or SEM/energy dispersive X-ray spectroscopy of 3AZ-CD porous polymer composites were acquired by a JEOL JSM-7610F microscope (Tokyo, Japan) with a LEI detector at an acceleration voltage of 3.0 kV or 20 kV, respectively. The nitrogen (N) content was determined by the atomic number (Z)-absorption (A)-fluorescence (F) (ZAF) correction method. The size of the particles in the SEM images was evaluated by image analysis using an Image-J software package.

The mechanical properties of the porous polymer composites were investigated using the compression test with a Tensilon RTE-1210 apparatus (ORIENTEC Co., Ltd., Tokyo, Japan). The test samples were cut into a 1 cm³ cube and pressed at a rate of 0.5 mm/min

at room temperature. The bulk density of the porous polymer composite, g/cm³, was calculated from the weight of the samples before the test. The porosity of the porous polymer composite was calculated using Equation (2).

$$\begin{aligned} \text{Porosity (\%)} &= \{1.0 - \text{true volume of polymer (V}_p\text{) \& CDs (V}_{cd}\text{) cm}^3/\text{porous polymer composite (cm}^3)\} \times 100 \\ V_p &= \{\text{bulk density (g/cm}^3\text{)} \times 3\text{AZ polymer in composite (wt\%)/100}\} / \{\text{true density of 3AZ polymer (g/cm}^3\text{)}\} \quad (2) \\ V_{cd} &= \{\text{bulk density (g/cm}^3\text{)} \times \text{CD in composite (wt\%)/100}\} / \{\text{true density of CD (g/cm}^3\text{)}\} \end{aligned}$$

UV-vis spectra of phenolphthalein (phph) solutions were recorded on a UV2450 spectrometer (SHIMADZU Corporation, Kyoto, Japan).

3. Results and Discussion

3.1. Synthesis of 3AZ-CD Porous Polymer Composites

Ring-opening polymerizations of 3AZ (20 wt%) were conducted in water in the presence of 5–20 wt% CDs at 20–60 °C. Most of the reaction systems yielded porous polymers over a wide range of temperatures and CD concentrations. The reaction systems with Ac-β-CD preferentially yielded the gel, and a corresponding porous polymer was obtained under the reaction conditions of 5 wt% Ac-β-CD at 60 °C.

These results can be explained by the affinity between the polymer network formed by the ring-opening polymerization of 3AZ and the solvent, based on their solubility parameter (SP) values. Two molecules with small difference in SP values show high affinity and compatibility. The solvent of the reaction system is the CD solution, water + CD. The SP value of water, 47.8 MPa^{1/2}, is much higher than those of CDs, α-CD: 31–34 MPa^{1/2}, β-CD: 29–33 MPa^{1/2}, γ-CD: 27–31 MPa^{1/2}. The addition of CDs to water should decrease the SP value of the solvent, bringing it closer to that of polyethyleneimine backbone, 30–35 MPa^{1/2}, formed by the polymerization of 3AZ. In the case of the reaction with Ac-β-CD, the modification of the OH group of β-CD by the Ac group effectively decreases the SP value of the solvent and increases the affinity between the polymer network and the solvent. As a result, the phase separation rate was drastically decreased, with an increase in the Ac-β-CD concentration. As mentioned above, the porous structure of polyethyleneimine is formed by polymerization-induced phase separation via spinodal decomposition processes. The 3AZ in the Ac-β-CD system should be fixed before the phase separation to yield gel in the end.

3.2. Structure and Properties of 3AZ-CD Porous Polymer Composites

3.2.1. Composition and Morphology

FT-IR spectra of the 3AZ-CD porous polymer showed the profiles overlapping with those of 3AZ and CD, indicating a blend of 3AZ and CD without interaction (Figure S1). However, the spectra were insufficient for quantitative analysis of the compositions. The CD contents in 3AZ-CD porous polymer composites (obtained from reactions with 20 wt% of 3AZ at 20 °C) were quantitatively evaluated by SEM-EDX based on the nitrogen (N) content. A 3AZ porous polymer without CD (entry 0) contains 15.1 wt% of nitrogen. The CD content in the 3AZ-CD porous polymer composite can be calculated using Equation (3) below.

$$\text{CD content (wt\%)} = \{15.1 - \text{N content (wt\%)}\} / 15.1 \times 100 \quad (3)$$

The CD content in the 3AZ-CD porous polymer composite increased with increasing CD feed in the reaction system (Table 1). There was not a significant difference in the contents between the CDs.

Table 1. Composition, structure, and mechanical properties of 3AZ-CD porous polymer composites (3AZ in feed: 20 wt%, reaction temperature: 20 °C).

Entry	CD	CD in Feed wt%	CD in Composite ¹ wt%	Average Diameter μm	Bulk Density g/cm^3	Porosity %	Young's Modulus kPa
0	non		0	4.58	0.267	75.7	1150
1	α -CD	5.0	12.7	3.70	0.329	70.8	1657
2	α -CD	10.0	18.2	3.34	0.330	70.9	1861
3	α -CD	15.0	20.0	n.d. ²	0.359	68.4	1974
4	α -CD	20.0	21.8	n.d. ²	0.432	62.1	3809
5	γ -CD	5.0	9.7	4.26	0.334	70.1	2790
6	γ -CD	10.0	12.0	3.88	0.345	69.2	3284
7	γ -CD	15.0	20.5	3.28	0.366	67.6	5192
8	γ -CD	20.0	30.0	2.88	0.385	66.1	8800
9	Me- β -CD	5.0	9.7	3.80	0.311	72.4	2560
10	Me- β -CD	10.0	15.7	3.43	0.311	72.6	3250
11	Me- β -CD	15.0	23.2	3.24	0.344	70.1	3902
12	HP- β -CD	5.0	11.4	4.00	0.340	70.1	1342
13	HP- β -CD	10.0	14.7	3.71	0.344	70.0	2160
14	HP- β -CD	15.0	19.3	3.10	0.347	70.1	5679
15	HP- β -CD	20.0	26.7	2.81	0.368	68.7	5950

¹ Calculated using Equation (3). ² Not determined (n.d.) due to their distorted structures.

The surface morphology of the 3AZ-CD porous polymer composites was observed by SEM. The SEM images of the 3AZ-CD porous polymer composites prepared at 20 °C with an average particle size (diameter) are shown in Figure 1. The porous polymer composites showed surface morphologies composed of connected particles. The average particle size of the porous polymer composites tended to decrease with an increase in the CD content and increase with increasing reaction temperature (Figures S2–S5). The size ranged from a few micrometers to the order of sub-nanometers, and the polymers may be regarded as nanocomposites.

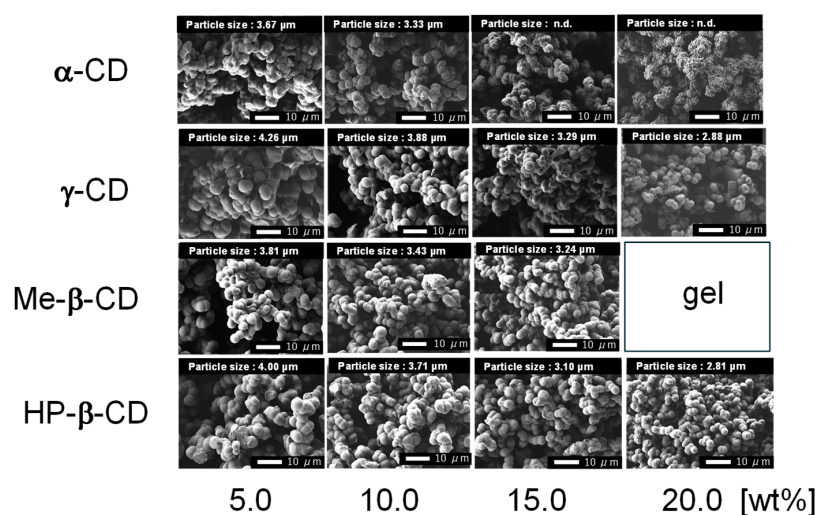


Figure 1. SEM images of 3AZ-CD porous polymer composites (3AZ in feed: 20 wt%, reaction temperature: 20 °C); CD: α -CD, γ -CD, Me- β -CD, or HP- β -CD. The particle size is indicated (average diameter).

The porous structure in the composites should be formed by polymerization-induced phase separation via spinodal decomposition processes. The morphology of the porous polymer depends on the fixation stage of the phase separation, as shown in Figure 2.

When the system is fixed during the first stage of the phase separation (Figure 2b) the co-continuous monolithic structure is formed. This phase-separated structure transforms into connected drops due to the interfacial tension (Figure 2c) and the spheres grow large (Figure 2d) as the phase separation progresses (the second stage). The porous morphology composed by the connected particles should be formed by the fixation of the phase separation structure during these stages. In cases where phase separation proceeds too quickly, the precipitates are obtained at the bottom of the reaction vessel (Figure 2e). The morphologies in most of the 3AZ-CD porous polymer composites should be completed at the phase separation stages, corresponding to Figure 2c,d. The reaction conditions should affect both the network formation (polymerization) rate (R_p) and phase separation rate (R_s). The morphology of the porous polymer prepared by the polymerization-induced phase separation should be affected by the relative ratio of the polymerization to phase separation (R_p/R_s). The increase in the CD contents in the polymerization systems should preferentially accelerate the network formation (increase R_p) and fix the systems at the earlier period of the second stage in the phase separation (Figure 2c). By contrast, the higher reaction temperature should be more effective in increasing the phase separation rate (R_s), which causes the growth of the particles, as observed in the porous polymers fixed at the later second stage, Figure 2d.

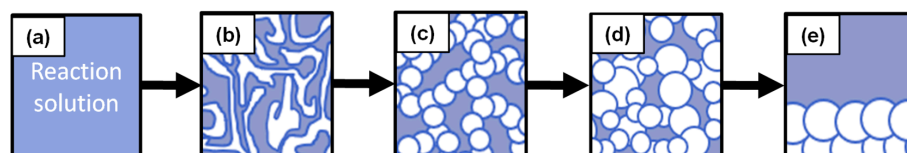


Figure 2. A model of polymerization-induced phase separation via spinodal decomposition processes.

3.2.2. Mechanical Properties

Incompatible complex combinations in polymer nanocomposites sometime induces brittleness in the materials. The mechanical properties of the 3AZ-CD porous polymer composites were evaluated using the compression test to investigate the effect of CD. Figure 3 shows the stress–strain (s-s) curves of 3AZ-HP- β -CD porous polymer composites. Young's moduli, determined from the initial slope of the s-s curves, are summarized in Table 1. All the 3AZ-CD porous polymer composites were unbreakable under the compression of 40 N. The Young's modulus increased with increasing the CD content in the porous polymer composites. The result can be explained by the increase in bulk density caused by the small size of the particles with increasing CD content, as observed in SEM images (Figure 1). The profile with a slope changes (two steps deformation) in the s-s curves indicates consequent deformation derived from the compression of the vacant spaces following the particles.

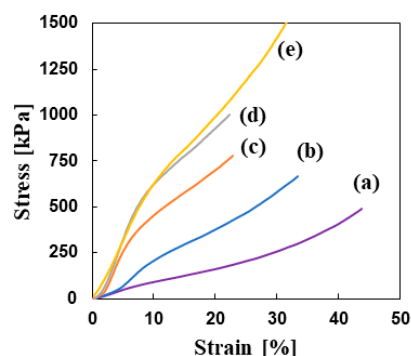


Figure 3. Stress–strain curves of 3AZ-HP- β -CD porous polymer composites. 3AZ in feed: 20 wt%; reaction temperature: 20 °C. CD concentration in feed: (a) 0 wt% (entry 0), (b) 5 wt% (entry 12), (c) 10 wt% (entry 13), (d) 15 wt% (entry 14), (e) 20 wt% (entry 15).

3.3. Adsorption Test of Phph

The macrocyclic structure of CDs can include small organic molecules, especially with hydrophobic features. The CDs are composed by 6–8 glucose units, which have cavity diameters of about 0.45–0.6 nm in α -CD, 0.6–0.8 nm in β -CD, and 0.8–0.95 nm in γ -CD. These structures are suitable for the capture of organic compounds with the corresponding sizes. In the present study, we tested adsorption of some dyes from the solutions by the 3AZ-CD porous polymer composites. In most cases, the adsorption value of the dye was independent of the CDs content in the porous polymer composites. For example, methyl orange was adsorbed by all the 3AZ-CD porous polymer composites, and even the 3AZ porous polymer without CD adsorbed an almost constant amount (about 900 mg/g), indicating direct adsorption onto the 3AZ polymer network. By contrast, phph was not adsorbed by any 3AZ- α -CD and 3AZ- γ -CD porous polymer composites. We found selective adsorption of phph (related to the CD concentration) by the porous polymer composites containing β -CD-based CDs, including Me- β -CD and HP- β -CD. Figure 4i shows UV-vis spectra of the phph original solution and the solutions after immersion of the 3AZ-HP- β -CD porous polymer composites at 25 °C for 24 h. The absorbance peak intensity at 554 nm derived from phph decreased with increasing CD content in the porous polymer composites. The adsorption value of phph per unit weight of the porous polymer composite (q_e : mg/g) increased with an increase in CD content, as summarized in Table 2. By contrast, the immersion of the 3AZ porous polymer without CD (for reference) did not decrease the absorbance peak intensity. These results make it clear that phph was adsorbed by the β -CDs in the porous polymer composites. The adsorption tests were conducted in the phph solutions with different concentrations (10–82 mg/L) to fit Langmuir and Freundlich adsorption isotherm equations, as shown in Figure 4ii. The Freundlich adsorption might be rather appropriate for the adsorption of phph. When the incorporated CDs were homogeneously immobilized on the adsorption surface, the plots tended to fit the Langmuir adsorption isotherm. One explanation of the result is the inhomogeneous composition of β -CD-based CDs in the porous polymer [33–35]. Figure 5 shows a plausible model of phph adsorption by 3AZ-Me- β -CD and HP- β -CD. A phph molecule is adsorbed by one β -CD moiety. The present 3AZ-CD porous polymer composites were prepared from corresponding homogeneous CD solutions. Although the CD should be distributed homogeneously in the porous polymer composites, the random incorporation in the disordered porous structure should cause inactive CD moieties, which cannot adsorb phph molecules, and induce inhomogeneity on the adsorption surface of the 3AZ-Me- β -CD and HP- β -CD porous polymer composites.

Table 2. Adsorption test of phph by 3AZ-Me- β -CD and HP- β -CD porous polymer composites, 3AZ in feed: 20 wt%, reaction temperature: 20 °C.

Run	CD	CD Content wt%	q_e ¹ mg/g
9	Me- β -CD	9.7	104.9
10	Me- β -CD	15.7	483.5
11	Me- β -CD	23.2	624.1
12	HP- β -CD	11.4	247.3
13	HP- β -CD	14.7	542.5
14	HP- β -CD	19.3	624.5
15	HP- β -CD	26.7	579.7

¹ Adsorption value of phph per unit weight of the porous polymer composite calculated using Equation (2).

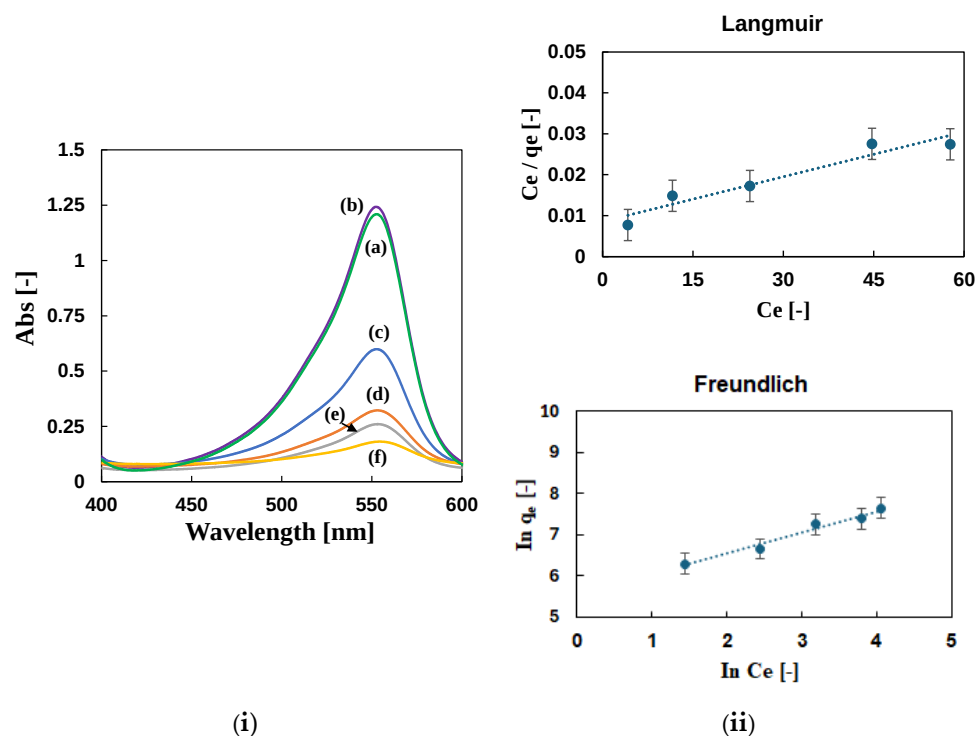


Figure 4. (i) UV-vis spectra of phph solution. (a) Original and after immersion of 3AZ-HP-β-CD porous polymer composites, 3AZ in feed: 20 wt%, reaction temperature: 20 °C; HP-β-CD content: (b) 0 wt% (entry 0, reference), (c) 11.4 wt% (entry 12), (d) 14.7 wt% (entry 13), (e) 19.3 wt% (entry 14), (f) 26.7 wt% (entry 15). (ii) Adsorption isotherms, Langmuir and Freundlich, for phph adsorption by 3AZ-HP-β-CD porous polymer composites (entry 13).

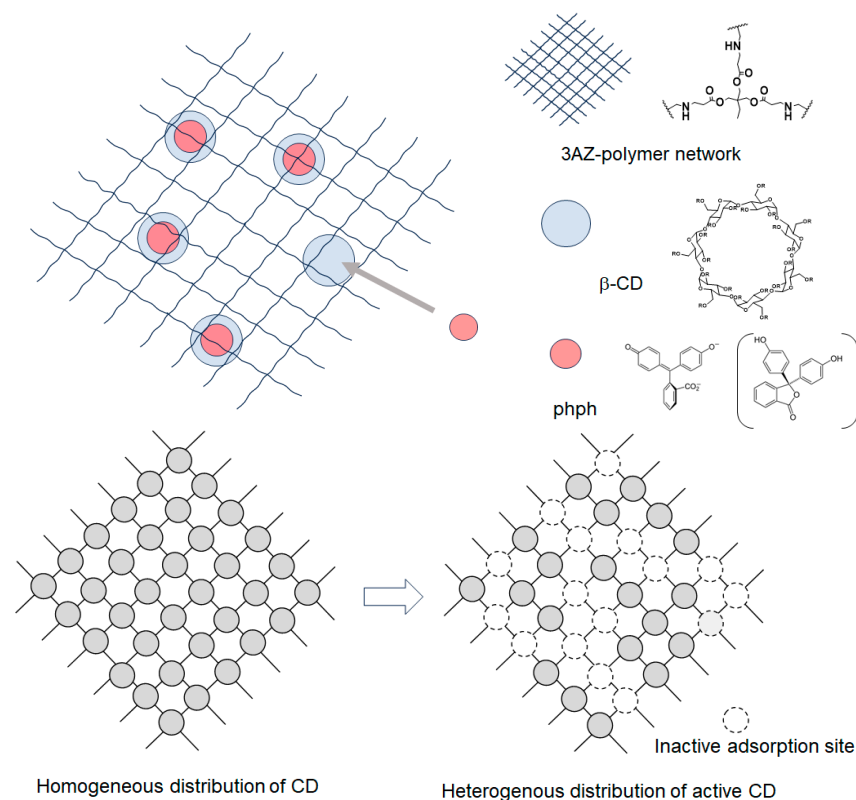


Figure 5. A plausible model of phph adsorption by 3AZ-Me-β-CD and HP-β-CD porous polymer composites.

4. Conclusions

The ring-opening polymerization of a 3AZ in the presence of CD solutions successfully yielded polyethyleneimine-based porous polymer composites. The porous structures were composed of connected particles formed through polymerization-induced phase separation via a spinodal decomposition process, and their size tended to decrease with increasing CD feed in the reaction system. The Young's moduli of the porous polymer composites increased with increasing CD content, accompanied by an increase in their bulk densities. The porous polymer composites containing Me- β -CD and HP- β -CD selectively and effectively adsorbed phph from the solution, with more than 600 mg/g porous polymer composites, which obeyed the Freundlich adsorption isotherm. The Freundlich adsorption isotherm was better obeyed for the adsorption of phph due to the inhomogeneous composition of β -CD-based CDs in the porous polymer. The random incorporation in the disordered porous structure, causing inactive CDs, might be a possible explanation for the results.

The present molecular design of porous polymer composites is usable for producing a separation material for a selective molecule from its solution. The high liquid permeability of the porous structure is a preferable feature for the application in separation columns and filters. Porous polymer composites with selective molecular capture should be usable, as well as MIPs. As the next step, we are preparing porous polymer composites that can separate some molecules using the chiral selective capture function. These investigations are now underway, and the results will be reported elsewhere in due course.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/separations12040094/s1>, Figure S1: FT-IR spectra of (a) 3AZ porous polymer (entry 0), (b) α -CD, and (c) 3AZ- α -CD porous polymer composite. 3AZ in feed: 20 wt%; α -CD in feed: 10 wt% (entry 2). Figure S2: SEM image of 3AZ porous polymer. 3AZ monomer concentration in the reaction solution: 20 wt%, (entry 0). Figure S3: SEM images of 3AZ- α -CD porous polymer composites. 3AZ in feed: 20 wt% Figure S4: SEM images of 3AZ- γ -CD porous polymer composites. 3AZ in feed: 20 wt%. Figure S5: SEM images of 3AZ-Me- β -CD porous polymer composites. 3AZ in feed: 20 wt%. Figure S6: SEM images of 3AZ-HP- β -CD porous polymer composites. 3AZ in feed: 20 wt%. Figure S7: SEM image of 3AZ-Ac- β -CD porous polymer composite. Ac- β -CD concentration: 5.0 wt%; 3AZ monomer concentration: 20 wt% in the reaction solution; reaction temperature: 60 °C.

Author Contributions: Conceptualization, N.N. and T.N.; investigation, Y.M. and N.N.; analysis, Y.M., N.N. and T.N.; writing—original draft preparation, N.N.; writing—review and editing, T.N.; supervision, N.N. and T.N.; project administration, N.N.; funding acquisition, N.N. and T.N. All authors have read and agreed to the published version of the manuscript.

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