

Macroporous Crosslinked Hydrophobic/Hydrophilic Polystyrene/Polyamide Interpenetrating Polymer Network: Synthesis, Characterization, and Adsorption Behaviors for Quercetin from Aqueous Solution

Wenwen Liao, Shuqin Gao, Xianglin Xie, Mancai Xu

College of Chemistry and Chemical Engineering, Hunan Normal University, Changsha, Hunan 410081, People's Republic of China

Received 1 December 2009; accepted 16 February 2010

DOI 10.1002/app.32479

Published online 15 July 2010 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: In the present study, a novel hydrophobic/hydrophilic polystyrene/polyamide interpenetrating polymer network (PS/PAM IPN) was synthesized and its molecular structure was characterized by Fourier transform infrared ray (FT-IR) spectrum, chemical analysis, swelling test, and N₂ adsorption-desorption experiment. The obtained PS/PAM IPN was employed as a polymeric adsorbent to adsorb quercetin from aqueous solution, and the adsorption thermodynamics were calculated according to thermodynamic equations. It was found that no chemical bond was formed between PS and PAM and PS/PAM IPN held characters of amphiphilic polymer network

(APN). The adsorption isotherms could be well fitted by Freundlich isotherm, and the adsorption was shown to be an exothermic, spontaneous, and more ordered process. The total adsorption capacity from the column adsorption experiment was measured to be 8.6 mg/mL wet resin, and the adsorbed quercetin on PS/PAM IPN could be easily desorbed by 10% of hydrochloric acid-ethanol. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 118: 3643–3648, 2010

Key words: interpenetrating polymer network; amphiphilic polymer network; hydrophobic/hydrophilic; adsorption; quercetin

INTRODUCTION

Adsorption was shown to be an effective method to extract or separate one special solute or one family of solutes with similar chemical structure from a complex system. Synthetic polymeric adsorbent has been increasingly proven to be an efficient adsorbent due to its high adsorption selectivity. They can adsorb one single solute or a small number of solutes capable of interacting with the adsorbent through a certain mechanism, while for the others which can not interact with the adsorbent can not be adsorbed on the adsorbent.

Interpenetrating polymer network (IPN) is a kind of polymer network composed of two or more cross-linked polymers through physical entanglement.¹ The cross-linked polymers entangled in IPN are

interpenetrating; hence their microcosmic phase separation behavior is decreased. Generally, the cross-linked polymers employed to synthesize IPN are hydrophobic.^{2–4} In recent years, there are some reports focusing on synthesis of novel IPN from hydrophilic polymers such as polyacrylic acid, polyacryl amide, polyvinyl alcohol, polyvinyl pyrrolidone, and chitosan,^{5–8} and the obtained IPN exhibits some new properties.⁹

Amphiphilic polymer network (APN) is another kind of cross-linked polymer made up of hydrophobic macromolecule chains as well as hydrophilic macromolecule chains via covalent bonding.¹⁰ It can be swollen very well in water as well as in non-polar solvent. However, the sole hydrophobic or hydrophilic macromolecule chains in APN will be self-congregated. As a result, microcosmic phase separation structure will be formed between the hydrophobic macromolecule chains and hydrophilic ones. In particular, the hydrophobic/hydrophilic macromolecule chains remain their own physical and chemical character respectively, which induces its potential application in medicine controlling and releasing, intelligent macromolecule, and adsorption and separation.^{11,12}

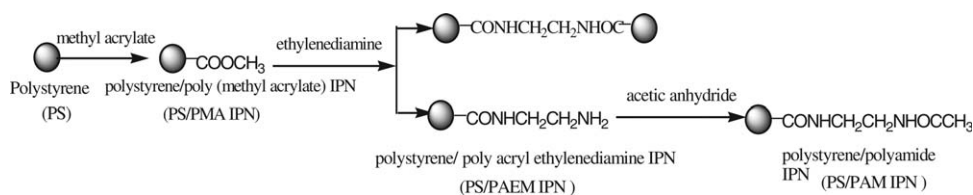
Therefore, hydrophobic/hydrophilic IPN will possess the advantages of IPN and APN. Due to its hydrophobic and hydrophilic macromolecule chains,

Additional Supporting Information may be found in the online version of this article.

Correspondence to: M. Xu (xu_mc@yahoo.com.cn).

Contract grant sponsor: National Natural Science Foundation of China; contract grant number: 20474015.

Contract grant sponsor: Scientific Research Fund of Hunan Provincial Education Department; contract grant number: 04A 029.



Scheme 1 The preparation procedure of PS/PAM IPN.

the hydrophobic/hydrophilic IPN will exhibit strong microcosmic phase separation behavior like APN. In addition, the hydrophobic part will restrain the swelling behavior of the hydrophilic part in water and vice versa in non-polar solvent, which differentiates it from APN. To the best of our knowledge, there are few literatures reporting the hydrophobic/hydrophilic IPN.

In this study, a novel hydrophobic/hydrophilic macroporous crosslinked polystyrene/polyamide interpenetrating polymer network (PS/PAM IPN) was prepared. The chemical structure, pore structure, and swelling behavior of the PS/PAM IPN were characterized by Fourier transform infrared ray (FT-IR) spectrum, chemical analysis, N_2 adsorption-desorption experiment, and swelling test. Its adsorption isotherms, adsorption thermodynamics, and the column adsorption were then investigated in aqueous solution to test its potential application in adsorption and separation, and quercetin was selected as the adsorbate in the adsorption study.

MATERIALS AND METHODS

Materials

Polystyrene resin was obtained from Nankai University Chemical Plant (Tianjin, China). Triallylisocyanurate (TAIC, 98%, purified before use) was purchased from Liuyang Chemical Co. (Hunan, China). Benzoperoxide (BPO) was recrystallized before use. Methacrylate (MA), 2,2'-azobisisobutyronitrile (AIBN), polyvinyl alcohol (PVA), and quercetin (its molecular structure was shown in Supporting Information Scheme s1) were also used in this study and all these chemicals were of analytical grades.

Synthesis of the adsorbent

The preparation procedure of PS/PAM IPN was displayed in Scheme 1. PS was firstly swollen by a mixture of MA, TAIC, AIBN, butyl acetate, and *n*-heptane at room temperature for 24 h. MA and TAIC were used as the reacting monomer and the crosslinking reagent, respectively. AIBN was applied as the inducing reagent, and butyl acetate and *n*-heptane were employed as porogens. The swollen PS beads were then separated and added into 3% of so-

dium chloride aqueous solution (w/w) with 1% of PVA (w/w). The PS/PMA IPN was achieved after polymerizing at 368 K for about 4 h. Then the PS/PMA IPN was refluxed in superfluous ethylenediamine for about 12 h,¹³ and the resultant PS/PAEM IPN was acetylated in a mixture of toluene and acetic anhydride for about 12 h,¹⁴ and the PS/PAM IPN was obtained.

Characterization of the resin

Specific surface area, pore volume, and pore diameter distribution of the resin were measured by Micromeritics Tristar 3000 surface area and porosity analyzer. The weak basic exchange capacity and water retention were measured according to the method in Ref. 15. FT-IR of the samples was obtained on a 510 P Nicolet FT-IR spectrophotometer in the range of 4000–500 cm^{-1} with a resolution of 1 cm^{-1} . The swelling behavior of the resins in different solvents was studied as follows. The resin was snapped after swelling in a certain solvent for 24 h at room temperature, and then the diameters of the resin were measured according to the snapped pictures in dry and swollen states, respectively, and the swelling ratio, R_v , was calculated as:

$$R_v = (D_t/D_0)^3 \quad (1)$$

here D_0 and D_t were the diameters of the resin in the dry and swollen states, respectively.

Adsorption of quercetin onto PS/PAM IPN in aqueous solution

Equilibrium adsorption of quercetin onto PS/PAM IPN in aqueous solution was performed at four temperatures, 293 K, 298 K, 303 K, and 308 K, respectively. PS/PAM IPN (about 0.100 g) was weighed accurately and introduced into a conical flask directly. 50 mL quercetin aqueous solution with known concentration, C_0 (mg/L), ranging from 40 to 120 mg/L was then added to the conical flask and shaken in a thermostatic oscillator for 24 h until adsorption equilibrium was reached. The residual concentration of quercetin, C_e (mg/L), was determined by UV analysis performed on a PE-Lambda

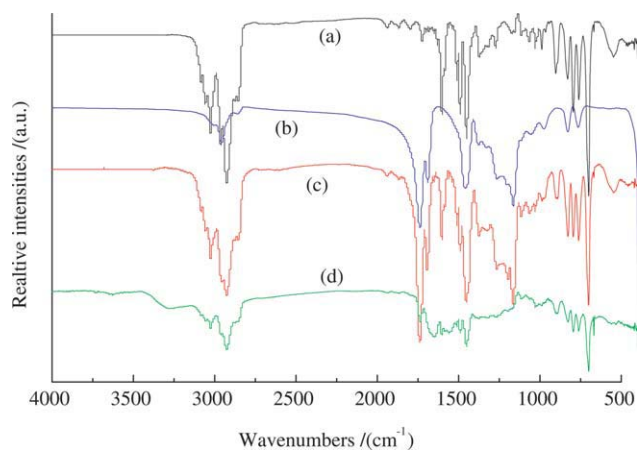


Figure 1 FT-IR spectra of PS (a), PMA (b), PS/PMA IPN (c), and PS/PAEM IPN (d). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

17 UV spectrophotometer. The adsorption capacity was calculated as:

$$q_e = (C_0 - C_e)V/W \quad (2)$$

where q_e was the equilibrium adsorption capacity (mg/g), V was the volume of quercetin aqueous solution, and W was the weight of the dry adsorbent (g).

Dynamic adsorption and desorption

The dynamic adsorption was conducted using a glass column (10 mm in diameter) at room temperature and 10 mL of wet PS/PAM IPN was packed in the glass column. 116 mg/L of quercetin aqueous solution was passed through the column at a flow rate of 2.4 BV/h (1BV = 10 mL), and the solvent (10% of hydrochloric acid-ethanol) was applied for desorbing at a flow rate of 1.0 BV/h.

RESULTS AND DISCUSSIONS

Characterization of the resin

As shown in Supporting Information Table s1, the specific surface area of PS, PS/PAEM IPN, and PS/PAM IPN are 440, 246, and 73 m²/g, respectively, revealing that chemical modification induces the specific surface area to sharply decrease.^{16,17} In addition, the water retentions of PS/PAEM IPN and PS/PAM IPN are much greater than that of PS, implying that PS/PAEM IPN and PS/PAM IPN are much more hydrophilic than PS.

Figure 1 displays the FT-IR spectra of PS, PMA, PS/PMA IPN, and PS/PAEM IPN. PS/PMA IPN keeps the representative vibrations of benzene ring at 1613 cm⁻¹ and 699 cm⁻¹ (which are related to the vibrational bands of PS), it also shows the characteristic band of

C=O stretching at 1738 cm⁻¹ (which is the characteristic peak of PMA).¹⁸ Moreover, the FT-IR spectrum of PS/PMA IPN is superposition of the corresponding ones of PS and PMA, revealing no new chemical bond formation between the chains of PS and PMA.

As for PS/PAEM IPN, there appears a band in the range of 3100–3500 cm⁻¹, and which can be assigned to N–H stretching of the NH₂ (one mole of PS/PMA is reacted with one molar of ethylenediamine) and NH (two mole of PS/PMA is reacted with one molar of ethylenediamine) groups. In addition, the weak basic exchange capacity of PS/PAEM IPN is measured to be 1.717 mmol/g, implying a successful amination reaction (see Supporting Information Table s1). The weak basic exchange capacity of PS/PAM IPN is 0, suggesting that the uploaded ethylenediamine groups on the skeleton are completely acetylated by acetic anhydride, and the PS/PAM IPN is synthesized successfully.

As displayed in Figure 2, the pore diameter distribution of PS is in the range of 2–135 nm, whereas PS/PAEM IPN possesses its pore diameter distribution from 8.9 nm to 60 nm, indicating that the pores of PS ranged 2–8.9 nm are entirely filled after amination reaction, and the pore diameter distribution of PS/PAEM IPN is strait and symmetrical as compared with that of PS. In addition, many changes occur for the pore diameter distribution after preparation of PS/PAM IPN, when the pore diameter is 32.0 nm, the pore volume of PS/PAM IPN decreases to 50% compared with PS/PAEM IPN, which may be from that the –COCH₃ groups fill the pores of PS/PAEM IPN.

Swelling behavior of the resins in different solvents

Supporting Information Table s2 lists the swelling ratio of PS/PAEM IPN and PS/PAM IPN in water,

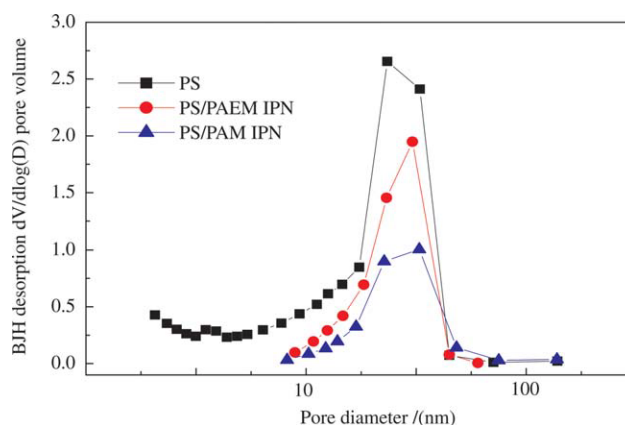


Figure 2 Pore diameter distribution of PS, PS/PAEM IPN, and PS/PMA IPN. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

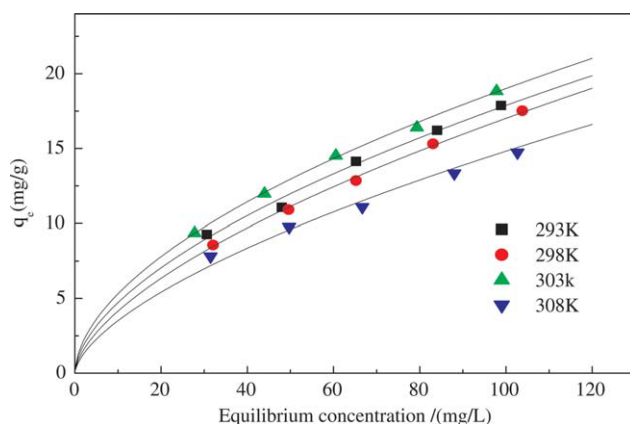


Figure 3 Adsorption isotherms of quercetin on PS/PAM IPN in aqueous solution at 293 K, 298 K, 303 K, and 308 K, respectively. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

ethanol, benzyl alcohol, and toluene. It is clear that the swelling ratio of PS/PAM IPN in water is close to that in toluene. This may be from the fact that the hydrophobic benzene ring of it restrains water molecules to enter its pores when PS/PAM IPN is immersed in water, whereas the hydrophilic acetamide groups limits toluene molecules to enter the pores as toluene is applied as the swelling reagent.

In addition, Supporting Information Table s2 indicates the swelling ratio of PS/PAM IPN in ethanol and benzyl alcohol is greater than that in water and toluene. As PS/PAM IPN is swollen in ethanol, hydrophobic interaction (which is concerned with the interaction between the ethyl group of ethanol and the benzene ring of PS/PAM IPN resin), and hydrogen bonding (which is involved in the interaction between the hydroxyl group of ethanol and acetamide groups of the PS/PAM IPN) will promote ethanol molecules to enter the pores.^{19,20} Moreover, the swelling ratio of PS/PAM IPN in benzyl alcohol is especially great. As PS/PAM IPN is swollen in benzyl alcohol, besides hydrophobic interaction and hydrogen bonding, π - π stacking resulted from the benzene ring of the absorbed benzyl alcohol, and the pendant benzene ring of PS/PAM IPN should also be taken into account.²¹ So the swelling ratio in benzyl alcohol is the greatest.

Adsorption isotherms

The adsorption isotherms of quercetin onto PS/PAM IPN in aqueous solution are depicted in Figure 3. All of the isotherms are Type-I isotherms, and the adsorption capacity decreases with the increasing of the temperature, indicating an exothermic process.¹⁵

Langmuir and Freundlich isotherm models are adopted to describe the adsorption process. Langmuir isotherm can be given as^{19,20}:

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{q_m K_L} \quad (3)$$

here q_m is the maximum adsorption capacity (mg/g), and K_L is a constant (L/mg).

The Freundlich isotherm can be rearranged as²²:

$$\ln Q_e = \ln K_F + \frac{1}{n} \ln C_e \quad (4)$$

Where K_F [(mg/g)(L/mg)^{1/n}] and n (dimensionless) are the characteristic constants.

The regression equations, parameters K_L , K_F , n , and the correlation coefficients by Langmuir and Freundlich isotherms are summarized in Supporting Information Table s3. The experimental data can be well fitted by Freundlich isotherm since the correlation coefficients are all higher than 0.99, suggesting the adsorption is a multilayer adsorption process, and the adsorbents possess heterogeneous adsorption sites.²²

Adsorption thermodynamics

Following the Clapeyron-Clausius equilibrium equation^{19,20}:

$$\ln C_e = \frac{\Delta H}{RT} + K \quad (5)$$

Where ΔH is the adsorption enthalpy as q_e is a fixed value (kJ/mol), R is the ideal gas constant, and K is a constant. By plotting $\ln C_e$ versus $1/T$ (see Supporting Information Fig. S1), the straight lines will be gained, and the ΔH can be calculated from the slopes of the straight lines.

Adsorption Gibbs free energy can be calculated using an expression derived from the Gibbs adsorption isotherm, and the following equation is obtained at a low solute concentration²³:

$$\Delta G = -RT \int_0^x q \frac{dx}{x} \quad (6)$$

Where ΔG is the adsorption Gibbs free energy (kJ/mol), q is the adsorption capacity onto the adsorbent (mg/g), and x is the mole fraction of the adsorbed solute in the solution. As the adsorption can be characterized by Freundlich isotherm equation, incorporating the Freundlich isotherm into eq. (6) will yield:

$$\Delta G = -nRT \quad (7)$$

here n is the characteristic constant in Freundlich isotherm.

Adsorption entropy can be calculated by Gibbs-Helmholtz equation:

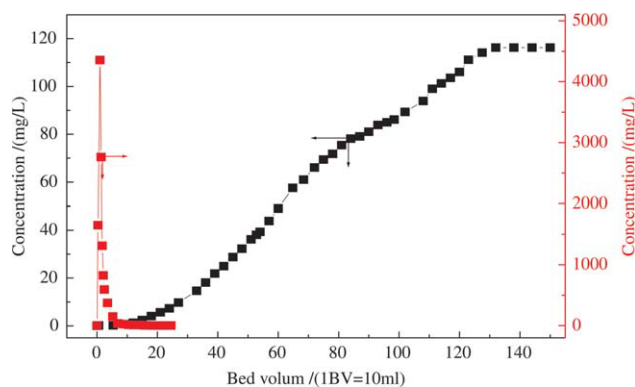


Figure 4 Adsorption curve and desorption curve for quercetin (the initial concentration of quercetin was 116 mg/L, the desorption solvent was 10% of HCl-ethanol solution, at room temperature). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

$$\Delta S = \frac{\Delta H - \Delta G}{T} \quad (8)$$

The ΔH , ΔG , and ΔS of quercetin adsorbed onto PS/PAM IPN are shown in Supporting Information Table S4. The ΔH is negative, indicating an exothermic process.¹⁵ The ΔH decreases with the increasing of quercetin uploading on the adsorbent, which is resulted from the surface energetic heterogeneity.²⁴ Initially, quercetin molecules adsorb onto PS/PAM IPN surface with high-energy site, and the adsorption enthalpy is more negative. With the increasing of adsorption capacity, the PS/PAM IPN surface with high-energy site is occupied, and the subsequent quercetin molecules have to be adsorbed onto the PS/PAM IPN surface with relatively low-energy site, and the adsorption enthalpy is less negative.¹⁶ The ΔG is also negative, illuminating the adsorption process is a spontaneous process.¹⁸ The ΔS is negative, revealing that a more ordered arrangement of quercetin molecules is shaped on the surface of PS/PAM IPN.¹⁹

Dynamic adsorption and desorption process

It is noted from Figure 4 that PS/PAM IPN adsorbs quercetin efficiently in aqueous solution. The concentration of quercetin can not be detected until its effluent is up to 14 BV and reaches its initial concentration as its effluent arrives at 130 BV. The total adsorption capacity of quercetin can be calculated to be 8.6 mg/mL wet resin at room temperature. As for the regeneration of PS/PAM IPN, different solvents are employed, and the results are depicted in Supporting Information Table S5. It is seen that the desorption efficiency increases with increasing of the concentration of ethanol. As the concentration of

ethanol arrives at 100%, the desorption efficiency is still 22%. In particular, as 10% of hydrochloric acid (HCl)-ethanol is used as the desorption solvent, the desorption efficiency is up to 79%. In acidic medium, the independent acidic proton will interact with the active sites on the PS/PAM IPN surface, which weakens the interaction between PS/PAM IPN and quercetin.²⁵ So 10% of HCl-ethanol is selected as the desorption solvent to desorb quercetin. As shown in Figure 4, 10 BV of 10% of HCl-ethanol can desorb the adsorbed quercetin on PS/PAM IPN completely.

SUMMARY

In this study, a novel hydrophobic/hydrophilic PS/PAM IPN is prepared, and it can be swollen in water as well as in organic solvents such as ethanol, toluene, and benzyl alcohol. Its pore diameter distribution is strait and symmetrical in the range of 8.9 nm–60 nm. Freundlich isotherm model gives a good fitting for the adsorption isotherms, suggesting that the surface energy of PS/PAM IPN is heterogeneous. The adsorption is proposed to be an exothermic, spontaneous, and more ordered arrangement process. PS/PAM IPN can adsorb quercetin effectively and the adsorbed quercetin can be desorbed completely. In conclusion, it is promising that the hydrophobic/hydrophilic PS/PAM IPN can be applied for the extraction and purification of ginkgo flavonol glycosides.

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