

Crosslinked Polystyrene Beads Modified with Polar Groups for the Separation of Aromatic/Aliphatic Hydrocarbons

Huanyang Yu,^{1,2} Zhenzhen Cai,¹ Xianying Liu,³ Ming Li,¹ Zuosen Shi,¹ Zhanchen Cui¹

¹State Key Laboratory for Supramolecular Structure and Materials, College of Chemistry, Jilin University, Changchun 130012, People's Republic of China

²College of Material Science and Engineering, Jilin Institute of Architecture and Civil Engineering, Changchun 130118, People's Republic of China

³Clinical Skills Training Center, Second Bethune Hospital, Jilin University, Changchun 130041, People's Republic of China

Correspondence to: Z. Cui (E-mail: cuizc@jlu.edu.cn) or Z. Shi (E-mail: shizs@jlu.edu.cn)

ABSTRACT: Crosslinked polystyrene (CPS) beads modified with polar groups for the separation of aromatic/aliphatic hydrocarbons were successfully prepared. The synthesized beads were characterized by Fourier transform infrared spectroscopy, X-ray photoelectron spectroscopy, and thermogravimetric analysis. The effects of the crosslinking agents and polar groups on the swelling and selectivity performances toward *n*-heptane/toluene mixtures were studied. Impressively, the results indicated that the sulfone-modified CPS beads obtained a high toluene selectivity. Further adsorption tests with a variety of aromatic/aliphatic hydrocarbons were carried out at 50°C with initial aromatic concentrations of 13 wt %, and the results showed that the beads had a preferential selectivity for aromatic hydrocarbons, in particular, a higher separation factor of 6.76 for benzene/cyclohexane mixtures. We expect that modified CPS beads will serve as an effective material for the selective separation of aromatic/aliphatic hydrocarbons in chemical and petrochemical fields. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2014**, *131*, 40156.

KEYWORDS: adsorption; crosslinking; polystyrene; separation techniques; swelling

Received 9 May 2013; accepted 27 October 2013

DOI: 10.1002/app.40156

INTRODUCTION

The separation of aromatic/aliphatics has been attracting considerable attention because of its extensive application in the chemical and petrochemical industries.^{1–3} The close boiling points of the C₄–C₁₀ hydrocarbons pose a great challenge and highlight the need for an effective separation method. Many efforts have been made to realize separation,^{4–7} such as liquid extraction and extractive distillation;⁸ these need another high-boiling-point solvent such as *N*-formyl morpholine, sulfolane, *N*-methyl pyrrolidone, or ethylene glycol. This implicates an additional distillation process to remove solvent from the extract and raffinate phase, an additional investment and energy consumption. Another class of solvents, which are considered to be promising as replacements for the aforementioned organic solvents, is ionic liquids.^{9–11} Moreover, for feeds with low aromatic contents, ionic liquids can be superior to conventional extraction solvents. However, the use of ionic liquids also has some disadvantages: the price of ionic liquids is expensive; ionic liquids with [I₃][−], [F][−], and [Cl][−] are extremely corrosive; and the concentration of the ionic liquid present in the raffinate phase is low.

The pervaporation separations of aromatic/aliphatic hydrocarbons by polymeric membranes have been studied for decades because of the potential energy savings. Aromatic polyimides, polybenzoxazoles, and polyacrylonitrile have attracted attention for this application.^{12–14} A relatively high separation factor has been attained with these membranes,^{15–18} but the major roadblocks in pervaporation are the low flux and harsh operating conditions. Therefore, there is still an urgent call for an economic and efficient method for separating aromatic/aliphatic hydrocarbon mixtures with a material with a high selective capacity that possesses chemical and thermal stability.

Crosslinked polystyrene (CPS) beads have excellent mechanical properties and good chemical stability. Their excellent performances provide wide applications as packing materials for liquid chromatography,^{19–22} as ion-exchange resins^{23,24} and as imprinted adsorbents for the selective separation of hazardous organic compounds.²⁵ As a type of adsorbent for the potential separation of aromatic/aliphatics, compared with ionic liquid and pervaporation membranes, CPS beads have a lower raw material cost and simple operation conditions, and they can be directly desorbed by heat-drying and can be used repeatedly. All

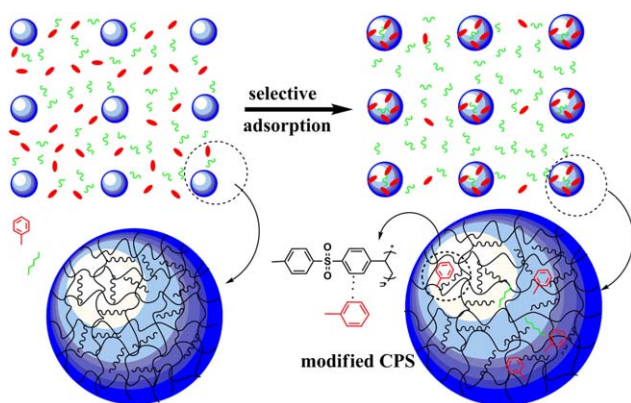


Figure 1. Selective adsorption process for the modified CPS beads. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

of these characteristics make CPS beads a good candidate for the industrial separation of aromatic/aliphatic hydrocarbons in large volumes.

Compared with membrane pervaporation, the separation mechanism of CPS beads is based on the different swelling and adsorption abilities for aromatic/aliphatic hydrocarbons instead of the difference in the diffusion properties.²⁶ Therefore, the swelling ratio and adsorptive selectivity are two important factors in improving the efficiency of separation. The swelling properties are attributed to the presence of physical or chemical crosslinks within polymer chains and can be influenced by a crosslinking agent.²⁷ The adsorptive selectivity mostly depends on the strong π - π interaction between the phenyl group of the polystyrene and aromatics. Another possibility for enhancing the selectivity for aromatic hydrocarbons is the introduction of polar groups to the CPS beads, such as phosphorylate groups, sulfone groups, and acrylate groups. All of these groups have π -electron acceptor properties, so they can produce a higher affinity to aromatic components.²⁸

In this study, we modified the CPS beads to improve the separation of aromatic/aliphatic hydrocarbons by means of introducing acrylic ester and sulfone groups. The swelling properties and selectivity were examined with toluene/*n*-heptane and other aromatic/aliphatic hydrocarbon mixtures. The selective adsorption process of modified CPS beads is schematically shown in Figure 1. The effects of the crosslinking agents, variety and con-

tents of polar groups, and concentration of aromatic hydrocarbons were studied.

EXPERIMENTAL

Materials

Benzoyl peroxide was purchased from Shenyang Xinxi Chemical Reagent Co. and was used after recrystallization. Poly(vinyl alcohol) (PVA) was purchased from Shanxi Sanwei Co., Ltd., and was made into a 3 wt % solution. Styrene (St) was obtained from Shantou Xilong Chemical Co., Ltd. Divinylbenzene (DVB) was obtained from Sigma-Aldrich. Dichloroethane (DCE), dichloromethane, anhydrous AlCl_3 , 4-toluene sulfonyl chloride (TsCl), and methyl methacrylate (MMA) were obtained from Beijing Beihua Fine Chemical Co., Ltd., and were used without any purification.

Measurements

Fourier transform infrared (FTIR) spectra (KBr pellets) in the range 4000 – 400 cm^{-1} were taken on an AVATAR 360 FTIR spectrometer. Elemental analyses were performed on a Vario MICRO elemental analyzer. The chemical composition was analyzed with a DSCALAD MARK II X-ray photoelectron spectrometer (XPS). Thermogravimetric analysis (TGA) scans were obtained in a PerkinElmer TGA-7 thermogravimetric analyzer at a heating rate of $10^\circ\text{C}/\text{min}$ under a nitrogen atmosphere.

Preparation of the CPS Beads

CPS resins were prepared by suspension polymerization; St (or St/MMA mixtures) and different molar fractions of DVB were mixed together in a three-necked flask. Then, water was added as a disperse medium. PVA solution (3 wt %) was added as a stabilizer, and benzoyl peroxide was added as the initiator. The mixture was stirred at 70°C under a nitrogen atmosphere for 1.5 h, then at 85°C for another 4 h, and finally at 90°C for 5 h. The stirring rate was accurately controlled to obtain beads at a size of 0.45–1 mm. After the reaction, polystyrene beads were washed with water and dichloromethane to remove the PVA and the unreacted monomers.

Preparation of the Sulfone-Modified CPS Beads

Polystyrene beads (11 g) were placed into a cleaned three-necked flask; this was followed by the addition of a predetermined amount of DCE. This suspension was stirred at room temperature for 2 h to swell the beads, and this was followed by the addition of anhydrous AlCl_3 under a nitrogen atmosphere. The mixture of TsCl and DCE was added dropwise slowly to

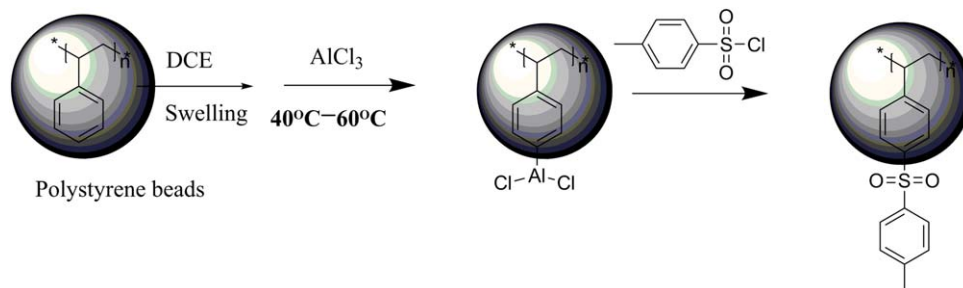


Figure 2. Synthesis of the sulfone-modified CPS beads. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

maintain the reaction temperature of 40–50°C and large amounts of gas overflow. The reaction then proceeded at 60°C under continuous stirring after addition until there was no gas emission. The reaction mixture gradually changed from a red color to a black color. The modified CPS beads were filtered and poured into a mixed solution of ice with HCl; they were then cleaned with water and alcohol until there was no white deposit or oil beads in the solution. The modified CPS beads were dried in an oven until a constant weight was reached.²⁹ The synthesis of the sulfone-modified CPS beads is presented in Figure 2.

Selective Adsorption of the Aromatic Hydrocarbons by CPS Beads

A determined amount of the modified CPS beads were put into a conical flask containing a toluene/*n*-heptane mixed solution (or other aromatic/aliphatic mixtures). Then, the conical flask was placed in an oscillator at a shaking speed of 100 rpm at 50°C. At definite intervals of time, the samples were removed from the mixed solution and tapped with filter paper to remove any excess solution on the surface of the CPS beads and weighed. The composition of the aromatic/aliphatic mixtures after adsorption was determined by gas chromatography (GC-14C). Measurements were carried out three times to increase the accuracy. The deviation in the calibration curves had a maximum of 1%. The averages of the three measurements were used as our results.

The equilibrium swelling ratio of the CPS beads (W) and the separation factor (α) were calculated with the following equations:

$$W = \frac{(G_1 - G_0)}{G_0} \times 100\% \quad (1)$$

$$\alpha = \frac{X_i Y_j}{X_j Y_i} \quad (2)$$

where G_1 is the weight of the swollen CPS beads, G_0 is the weight of the dried CPS beads, X_i is the weight of toluene (or

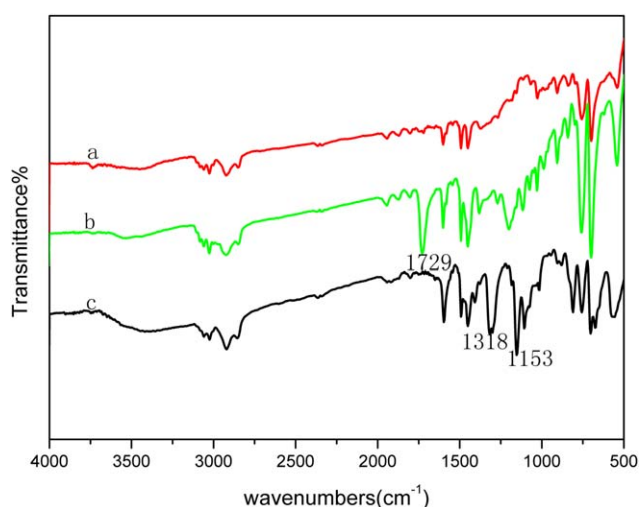


Figure 3. FTIR spectra of the CPS beads and modified CPS beads: (a) CPS, (b) ester-modified CPS, and (c) sulfone-modified CPS. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table I. Elemental Analysis Data for the Modified CPS Beads

Bead composition	N (%)	C (%)	H (%)	S (%)
St/TsCl = 2:1	0.12	81.92	6.652	3.657
St/TsCl = 5:1	0.07	81.92	6.979	2.927
St/TsCl = 10:1	0.06	88.54	7.325	1.263
St/TsCl = 20:1	0.05	88.99	7.294	0.397

other aromatic hydrocarbons) by CPS bead adsorption, X_j is the weight of *n*-heptane (or other aliphatic hydrocarbons) by CPS bead adsorption, Y_i is the weight of toluene (or other aromatic hydrocarbons) in the raffinate phase, and Y_j is the weight of *n*-heptane (or other aliphatic hydrocarbons) in the raffinate phase.

RESULTS AND DISCUSSION

Characterization of the CPS Beads

The FTIR spectra of the CPS beads and modified CPS beads are shown in Figure 3. It was notable that the modified CPS beads showed new peaks at 1318, 1153, and 1729 cm^{-1} ; this corresponded to the sulfone groups of TsCl and carbonyl groups of MMA, respectively, and suggested that the sulfone and ester groups were introduced to the CPS beads successfully.

The content of sulfur in the reagent and in the resultant, determined by the elemental analysis method, was used to evaluate the grafting degrees of TsCl onto the CPS beads. The results, shown in Table I, indicated that the content of sulfur gradually increased with the increasing content of TsCl monomer. This further verified that the sulfone groups were efficiently grafted onto the CPS beads.

The surface and interior composition of the sulfone-modified CPS beads were further researched by XPS. We obtained the interior composition of the modified CPS by cutting a bead in half. The results are shown in Table II. From Table II, we found that the surface atomic ratio of S to C was obviously larger than the interior value for all of the samples; this indicated that the sulfone groups were mainly distributed on the surface of the beads.

Effect of the Crosslinking Agents

The phenyl of polystyrene had strong interactions with aromatics, and this interaction was a main factor in the increase in the selectivity for aromatics. However, the interaction was so strong that line polystyrene beads easily dissolved in the aromatic solvents. So, crosslinking modification is quite necessary. In fact, crosslinking is a simple and efficient method for

Table II. XPS Data for the Modified CPS Beads

Bead composition (St/TsCl)	Surface (S/C $\times 10^{-2}$)	Interior (S/C $\times 10^{-2}$)
2:1	4.47	0.24
5:1	2.88	1.82
10:1	1.72	0.77
20:1	2.62	0.75

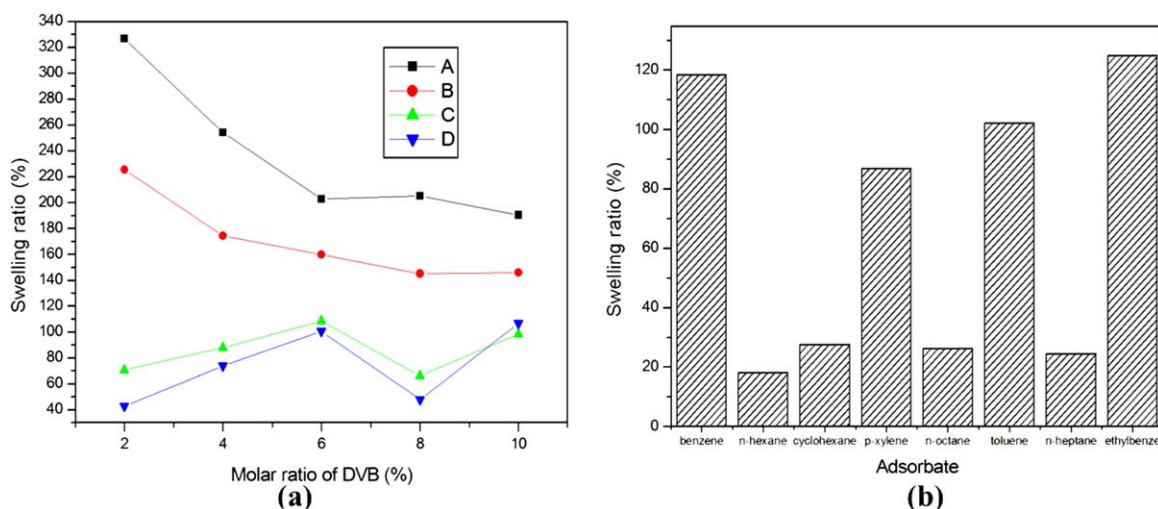


Figure 4. Swelling ratios of the modified CPS beads: (a) various crosslinking agents [(A) toluene, (B) 58 wt % toluene, (C) 13 wt % toluene, and (D) *n*-heptane] at 50°C and (b) various aromatic and aliphatic solvents. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

retaining indispensable properties, such as the swelling behavior, dimensional stability, and chemical stability.³⁰ Matsui and Paul³¹ reported the pervaporation separation of aromatic/aliphatic hydrocarbons by crosslinked poly(methyl acrylate-co-acrylic acid) membranes. Inui et al.³² also reported on pervaporation for the separation of benzene/cyclohexane through acrylate membranes that were ionically crosslinked by iron and cobalt cations. Here, the effect of the crosslinking agents (DVB) on the swelling ratio of the CPS beads was investigated, and the results are shown in Figure 4(a). We observed that with increasing content of DVB, the swelling ratios on pure toluene and 58 wt % toluene strongly decreased. However, the swelling ratios on *n*-heptane and 13 wt % toluene fluctuated in the range from 43 to 109%. This phenomenon revealed that toluene could fully swell the CPS but *n*-heptane could not swell CPS. Samples exposed to pure *n*-heptane showed a very low swelling ratio only because of the adherence of a little *n*-heptane to the CPS beads. Sun and Ruckenstein³³ also showed that the swelling of a pervaporation membrane was mainly due to the absorption of aromatics rather than aliphatics. Furthermore, the swelling ratio on toluene is considerably higher than that on *n*-heptane when the content of crosslinking agents is in a low range between 2 and 6%. Therefore, the higher selectivity for aromatic hydrocarbons might have been obtained with a small portion of crosslinking agents.

Effect of the Polar Groups

According to Semenova,³⁴ some special polar groups, such as sulfone groups, acrylate groups, phosphorylate groups, and phenyl groups, with π -electron acceptor properties can produce a high affinity to aromatic components. Through the introduction of these polar groups into CPS beads, the separation efficiency may be improved. In this study, CPS beads were modified with acrylic ester or sulfone groups at different molar ratios. A comparison of the experiments with two kinds of polar groups led to the conclusion that the sulfone groups were favorable for higher aromatic selectivity. As shown in Table III, the optimum

selectivity was found when the composition of St/TsCl was 5:1 was used and the maximum of separation factor was 3.26. However, the addition of excess polar groups (St/TsCl = 2:1) led to a relative decrease in the proportion of phenyl groups. The impaired π - π interaction caused a decrease in the toluene selectivity. Furthermore, acrylic ester groups also slightly increased the selectivity for aromatic hydrocarbons when the composition of St to MMA was 5:1. However, because of the weaker polar interactions between the ester groups and aromatics, the selectivity of the CPS beads modified with ester groups was low. In addition, the values of the swelling ratio showed, as expected, that the more the CPS beads swelled, the less selective the adsorption was.

Swelling Ratio and Adsorptive Selectivity of the CPS Beads

As mentioned previously, CPS beads modified with sulfone showed preferential selectivity. Furthermore, the swelling ratios of the sulfone-modified CPS beads in various aromatic or aliphatic solvents became attractive. Figure 4(b) shows that the modified CPS beads possessed higher swelling ratios for the aromatic hydrocarbons but lower ratios for the aliphatic

Table III. Influence of Polar Groups on the Swelling Ratio and Separation Factor

Bead composition	Feed concentration (wt % toluene)	Swelling ratio (%)	α
St	13.2	52	1.55
20:1 St/TsCl	13.2	35	2.19
10:1 St/TsCl	13.2	30	2.53
5:1 St/TsCl	13.2	24	3.26
2:1 St/TsCl	13.2	49	1.97
St/MMA	13.2	37	2.08
5:2 St/MMA	13.2	49	1.43
5:3 St/MMA	13.2	42	1.57

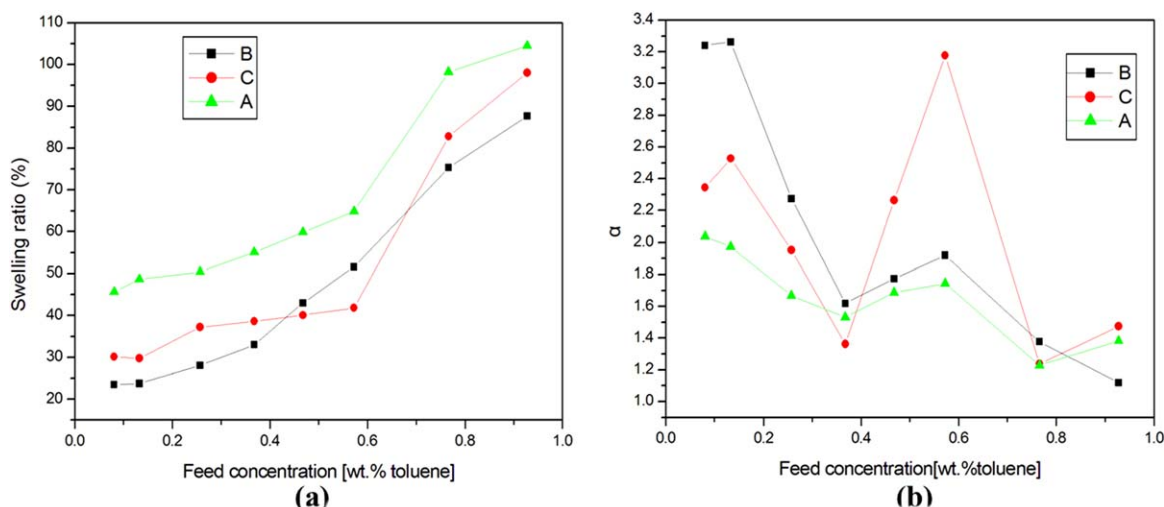


Figure 5. Influence of the feed concentration on the swelling ratio and separation factor at 50°C: (a) swelling ratio and (b) separation factor [$S_t/TsCl = (A) 2:1, (B) 5:1, \text{ and } (C) 10:1$]. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

hydrocarbons. For example, the swelling ratio of the modified CPS was 118% for benzene but only 18% for *n*-hexane. It was shown that the swelling ability was in the order Ethyl benzene > Benzene > Toluene > Xylene > Cyclohexane > Octane > Heptane > Hexane. We expected that the modified CPS beads had an obvious selective adsorption for aromatic hydrocarbons, which suggests great potential for the separation of aromatic/aliphatic hydrocarbons.

Further adsorption tests with toluene/*n*-heptane mixtures were carried out at 50°C, and the concentration of toluene was determined to be in the range from 8 to 93 wt %. The results are summarized in Figure 5. With increasing toluene content in the feed, the swelling ratios increased drastically for three samples, whereas the toluene selectivity achieved its maximum at lower feed concentrations (13 wt % toluene). At a higher toluene concentration, little separation was proven. This was intuitively understood: with increasing toluene content in the feed, a greater quantity of toluene went into the interior of the bead, and at the same time, some *n*-heptane also entered the bead because of the interaction between the aromatic/aliphatic hydro-

carbons. This caused completely different trends in the swelling ratio and selectivity. However, an interesting enhancement in the selectivity occurred at feed compositions of approximately 40 and 60 wt %, especially for sample C. This phenomenon was in agreement with the results of Okeowo and Dorgan³⁵ and was related to changes in the toluene–heptane interaction, toluene–CPS interaction, and heptane–CPS interaction.

For the application of CPS beads in a real technical processes, the performance of CPS for different feed mixtures is particularly attractive and important. Therefore, the aromatic selectivity and swelling ratio of CPS from a variety of aromatic/aliphatic hydrocarbons were evaluated. As shown in Table IV, all of the modified CPS beads displayed aromatic selectivity in these different mixtures. In particular, the separation factor was 6.76 for benzene/cyclohexane, 7.42 for toluene/cyclohexane, and 7.08 for *p*-xylene/cyclohexane. These values were much higher than those of other aromatic/aliphatic hydrocarbon mixtures. This result was similar to that of Yamasaki et al.³⁶ In his study on the pervaporation of benzene/cyclohexane and benzene/*n*-hexane mixtures through PVA membranes, he found that

Table IV. Selective Adsorption in Various Aromatic/Aliphatic Mixtures

Feed mixture	Temperature (°C)	Feed concentration (wt % aromatics)	Swelling ratio (%)	α
Toluene/ <i>n</i> -heptane	50	13.2	24	3.27
Benzene/cyclohexane	50	12.6	30	6.76
<i>p</i> -Xylene/ <i>n</i> -octane	50	12.7	18	3.54
Toluene/cyclohexane	50	13.4	28	7.42
Toluene/ <i>n</i> -octane	50	12.8	26	4.06
Benzene/ <i>n</i> -heptane	50	12.4	29	3.82
Benzene/ <i>n</i> -octane	50	12.5	22	4.12
<i>p</i> -Xylene/ <i>n</i> -heptane	50	13.0	24	3.76
<i>p</i> -Xylene/cyclohexane	50	12.8	30	7.08

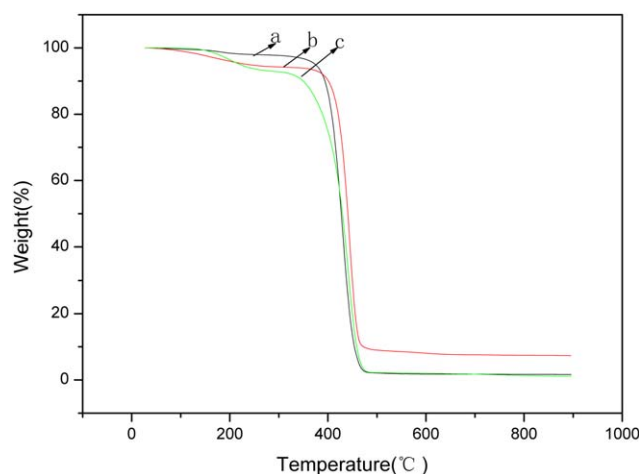


Figure 6. TGA of the CPS beads and modified CPS beads: (a) ester-modified CPS, (b) sulfone-modified CPS, and (c) CPS. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

the selectivity for benzene in a benzene/cyclohexane mixture was larger than that of a benzene/*n*-hexane mixture. This might have been due to the fact that the linear compound was more difficult to separate from benzene than the cyclic one.²⁶

Thermal Stability of the Modified CPS Beads

Despite the importance of the swelling and selective properties of the CPS beads, other factors must also be taken into consideration for the target application. For example, the desorption of aromatics and the regeneration of CPS beads will require high operation temperatures, and therefore, the thermal stability of beads must be considered. Typical TGA results for the CPS beads are shown in Figure 6. We observed that none of the three kinds of CPS beads in this study showed a significant loss of weight below 400°C; this exhibited their excellent thermal stability.

Regeneration of the Modified CPS Beads

In addition to the excellent selective capacity, it was highly desirable that an adsorbent could be regenerated with regard to the cost. The desorption of aromatic hydrocarbons was carried out by the heat-drying of the beads in oven at 120°C for 6 h until the weight of the beads was almost equal to the original value before absorption (uncertainty = 0.1%). The samples after desorption were used in five selective separation cycles (Table V). The separation factor of beads in the fifth cycle was 3.16; this indicated a loss in the selectivity of only 3.4%, compared to the first value. Similarly, the loss in the swelling ratio was only 4.1%. All of the results indicate the very good regeneration capacity of the modified CPS beads.

Table V. Regeneration of the Modified CPS Beads

	Cycle				
	First	Second	Third	Fourth	Fifth
Swelling ratio (%)	24	24	23	23	23
Separation factor	3.27	3.25	3.22	3.22	3.16

CONCLUSIONS

The heterogeneous CPS beads modified with sulfone and acrylic ester groups, respectively, were applied for the selective separation of aromatic/aliphatic hydrocarbon mixtures. The impact of the crosslinking agents and polar groups on the swelling ratio and aromatic selectivity was analyzed with the toluene/*n*-heptane system as feed mixtures. Impressively, the CPS beads modified with sulfone groups showed a higher selectivity for toluene.

In the selective adsorption experiments, CPS modified with sulfone groups beads revealed a preferential selectivity for aromatic hydrocarbons from a variety of aromatic/aliphatic hydrocarbon mixtures. By changing the aromatic concentration in the aromatic/aliphatic hydrocarbon mixtures, we found that beads had better separation effects at low aromatic contents, whereas sometimes a higher separation factor could be achieved at high aromatic contents through the adjustment of the components of the CPS beads. In conclusion, the modified CPS beads displayed a high aromatic selectivity, a large swelling ratio, an excellent thermal stability, and good generation capacities. All of these performances provide a promising approach for reducing the energy consumption and cost for the separation of aromatic/aliphatic mixtures, especially for separation at a low aromatic content.

ACKNOWLEDGMENTS

This work was supported by the National Natural Science Foundation of China (contract grant numbers 21204028, 20921003, and 51173063).

REFERENCES

- Rolling, P.; Lamers, M.; Staudt, C. *J. Membr. Sci.* **2010**, *362*, 154.
- Deng, Z.; Nicolas, C. H.; Guo, Y. *Sep. Purif. Technol.* **2011**, *80*, 323.
- Bai, Y.; Qian, J.; Zhao, Q.; Xu, Y.; Ye, S. *J. Appl. Polym. Sci.* **2006**, *102*, 2832.
- Maji, S.; Banerjee, S.; Pradhan, N. C. *Sep. Purif. Technol.* **2009**, *70*, 128.
- Li, Z. S.; Zhang, B.; Qu, L. X.; Ren, J. Z.; Li, Y. *J. Membr. Sci.* **2011**, *371*, 163.
- Deng, Z.; Nicolas, C. H.; Guo, Y.; Giroir-Fendler, A.; Peratitus, M. *Sep. Purif. Technol.* **2011**, *80*, 323.
- Chen, J.; Li, J.; Lin, Y.; Chen, C. *J. Appl. Polym. Sci.* **2009**, *112*, 2425.
- Hamid, S. H.; Ali, M. A. *Energy Sources* **1996**, *18*, 65.
- Meindersma, G. W.; Podt, A.; Haan, A. B. *Fuel Process. Technol.* **2005**, *87*, 59.
- Zhang, J.; Huang, C. P.; Chen, B. H. *Energy Fuels* **2007**, *21*, 1724.
- Meindersma, G. W.; Haan, A. B. *Chem. Eng. Res. Des.* **2008**, *86*, 745.
- Katarzynski, D.; Staudt, C. *J. Membr. Sci.* **2010**, *348*, 84.
- Ribeiro, C. P.; Fremana, B. D.; Kalikab, D. S.; Kalakkunnath, S. *J. Membr. Sci.* **2012**, *390*, 182.

14. Wang, H.; Ugomori, T.; Tanaka, K.; Kita, H.; Okamoto, K.; Suma, Y. *J. Polym. Sci. Part B: Polym. Phys.* **2000**, *38*, 2954.
15. Ren, J.; Staudt-Bickel, C.; Lichtenthaler, R. N. *Sep. Purif. Technol.* **2001**, *22*, 31.
16. Matsui, S.; Paul, D. R. *J. Membr. Sci.* **2002**, *195*, 229.
17. Suding, M. T. H.; Staudt, C. *J. Appl. Polym. Sci.* **2013**, *127*, 5065.
18. Mandal, M. K.; Bhattacharya, P. K. *Sep. Purif. Technol.* **2008**, *61*, 332.
19. Qin, L.; He, X. W.; Zhang, W.; Li, W. Y.; Zhang, Y. K. *J. Chromatogr. A* **2009**, *1216*, 807.
20. Yu, P. Z.; Li, X. Q.; Li, X. N.; Lu, X. L.; Ma, G. H.; Su, Z. *G. Bioorg. Med. Chem. Lett.* **2007**, *17*, 5605.
21. Mizutani, A.; Nagase, K.; Kikuchi, A.; Kanazawa, H.; Akiyama, Y.; Kobayashi, J.; Annaka, M.; Okano, T. *J. Chromatogr. A* **2010**, *1217*, 522.
22. Zhang, X.; Shen, S.; Fan, L. *J. Mater. Sci.* **2007**, *42*, 7621.
23. Belfer, S.; Glozman, R. *J. Appl. Polym. Sci.* **1979**, *24*, 2147.
24. Jun, B. H.; Byun, J. W.; Kim, J. Y.; Kang, H.; Park, H. J.; Yoon, J.; Lee, Y. S. *J. Mater. Sci.* **2010**, *45*, 3106.
25. Yun, Y. H.; Shon, H. K.; Yoon, S. D. *J. Mater. Sci.* **2009**, *44*, 6206.
26. Frahn, J.; Malsch, G.; Matuschewski, H. *J. Membr. Sci.* **2004**, *234*, 55.
27. Atta, A. M.; El-Ghazawy, R. A.; Farag, R. K.; El-Kafrawy, A. F. *Polym. Int.* **2005**, *54*, 1088.
28. Schwarz, H. H.; Malsch, G. *J. Membr. Sci.* **2005**, *247*, 143.
29. Olah, G. A.; Kobayashi, S.; Nishimura, J. *J. Am. Chem. Soc.* **1973**, *95*, 564.
30. Yu, J.; Dong, C.; Liu, J.; Li, C.; Fang, J.; Guan, R. *J. Mater. Sci.* **2010**, *45*, 1017.
31. Matsui, S.; Paul, D. R. *J. Membr. Sci.* **2002**, *195*, 229.
32. Inui, K.; Noguchi, T.; Miyata, T.; Urugami, T. *J. Appl. Polym. Sci.* **1999**, *71*, 233.
33. Sun, F.; Ruckenstein, E. *J. Membr. Sci.* **1995**, *99*, 273.
34. Semenova, S. I. *J. Membr. Sci.* **2004**, *231*, 189.
35. Okeowo, O.; Dorgan, J. R. *Macromolecules* **2006**, *39*, 8193.
36. Yamasaki, A.; Shinbo, T.; Mizoguchi, K. *J. Appl. Polym. Sci.* **1997**, *64*, 1061.