Studies on the Fabrication of Strong-acid/Weak-base Amphoteric Ion Exchange Fibers and Their Adsorption Property for Amino Acids

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ABSTRACT: The strong acid/weak base amphoteric ion exchange fibers with different ratios of acidic and basic groups and different grafting percentages were prepared by grafting styrene and 4-vinylpyridine onto polypropylene fiber and then sulfonating with chlorosulphonic acid, under various reaction conditions, such as the feed ratio of styrene and 4-vinylpyridine, monomers concentration, sulfonation temperature, and sulfonation time, swelling time, etc. The produced strong acidic and basic groups are the sulfonic group and the pyridyl group, respectively. Only one sulfonic group is induced into an aromatic ring in most of PP-g-St-4VP and it is located in the *para*-position of styrene. The contents of the strong-acid group and the weak-base group of the PP-g-SO$_3$H-Py fibers produced in this work are in the range of 1.98 to 4.22 and 2.33 to 4.24 mmol/g, respectively. The strong acid/weak based amphoteric fibers obtained possess good static adsorption property for basic and acidic amino acids, and they also have a good dynamic adsorption and elution property for amino acids like related strong acid ion exchange fibers. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 92: 418–425, 2004

Key words: Amphoteric ion exchange fiber, strong-acid/weak-base, fabrication, structures, adsorption for amino acids

INTRODUCTION

Among the ion exchangers, ion exchange fibers are the attractive materials for adsorption and separation. Compared with generally used granular ion exchange resins, ion exchange fibers exhibit high efficiency in the adsorption from liquid and gaseous media, because that they have a high specific surface area, a large amount of ion exchange capacity, and a high exchange speed.[1–5] Moreover, they can be produced in the form of filaments, yarns, cloths, and nonwoven fabrics to satisfy the needs of various exchange adsorption processes. There also have been some investigations regarding the adsorption and separation of amino acids by ion exchange fibers, which showed that fibrous ion exchangers possess higher adsorption capacity and higher separation efficiency for amino acids than the granular ones.[5,6]

Amphoteric ion exchange fibers have been prepared and their exchange property for the metal ions in liquid media have been studied in recent years.[7,8] As we know, many biosubstances, such as amino acids, nucleic acids, and proteins, also contain amphoteric structures. We guesstimate that amphoteric ion exchange fibers may possess high adsorption and separation ability for these biosubstances, if the chemical structures, quantity, and space distribution of the acidic and basic groups of amphoteric fibers were appropriately designed and controlled to match the natural structures of biosubstances. Though many works have reported the adsorption and separation of amino aicds mixtures and biosubstances by various technologies, such as precipitation, liquid membrane extraction, electrophoresis, high-performance liquid chromatography, ion exchange, etc.,[9–16] the study of the adsorption and separation of amino acids by amphoteric ion exchange fibers may lead to significant benefits for life science and biotechnology applications.

In this paper, a series of strong acid/weak base amphoteric ion exchange fibers with different ratios of acidic and basic groups were designed and synthesized by grafting of styrene (St) and 4-vinylpyridine (4VP) onto polypropylene (PP) fiber and then sulfonating with chlorosulphonic acid. The structures of the obtained amphoteric fibers were characterized, and the effects of the feed ratio of St/4VP and the

TABLE I
Grafting of St and 4VP onto PP fibers[a]

Feed Ratio of St to 4VP	2 : 8	4 : 6	6 : 4	8 : 2	8.5 : 1.5	9 : 1	9.5 : 0.5	9.8 : 0.2
Total grafting percentage (monomers concentration, 7.5%) (%)	—	/	/	426	402	/	348	287
Total grafting percentage (monomers concentration, 15%) (%)	496	742	711	658	444	471	378	279

[a] PP amount: 0.3 g; irradiation dose: 1.8×10^5 J/kg; grafting temperature: 65°C; grafting time: 4 h; ratio of fiber weight to solution volume: 1 : 100; DVB: 7%; Mohr's salt: 0.1 %; emulsifying reagent content: 0.8%.

sulfonation conditions on the structures of amphoteric fibers obtained were investigated by using XPS, FTIR, elemental analyzer, SEM, etc. Their adsorption property for amino acids was primarily evaluated and compared with other ion exchangers.

EXPERIMENTAL

Synthesis of strong acid/weak base amphoteric fibers

PP fibers (length: ~1 cm, Guangzhou Textile Industry Institute, China) were extracted with acetone and dried under vacuum. They were then preirradiated with Co^{60}–γ-ray in the air to 1.8×10^5 J/kg of irradiation dose. After irradiation, the fibers were sealed in a plastic bag and stored in a refrigerator (below 0°C).

Certain amounts of distilled water, monomers (St, Yonghua Special Chemical Factory, China; 4VP, Acros Organics, USA), divinylbenzene (DVB, Shanghai Liqun Chemical Factory, China), and dodecanesulfonic acid sodium salt (Shanghai Chemical Central Factory, China) were added into a three-necked flask. The air in the flask was exhausted with pure N_2 and the system was heated to a predetermined reaction temperature. Aout 0.3 g preirradiated PP fibers were then put into the flask and subsequently certain amounts of Mohr's salt (Guangzhou Chemical Factory, China) were added. The graft copolymerization was carried out by stirring with a magnetic stirrer under nitrogen conditions for a certain time. After reaction, the graft copolymer was immersed in dilute HCl solution overnight and then washed with distilled water to neutrality. The wet sample was dried at 70°C under vacuum conditions. Finally, the copolymer obtained was extracted with benzene in a Soxhlet extractor for 24 h

and then dried at 70°C under vacuum conditions. The graft percentage was calculated as follows:

$$\text{Graft percentage (\%)} = ((W_2 - W_0)/W_0) \times 100$$

where W_2 is the weight of produced sample after extraction with benzene and W_0 is the weight of the preirradiated PP fiber used. Thus obtained grafted fibers were denoted by PP-g-St-4VP.

Certain amounts of the obtained PP-g-St-4VP were added into a flask and swelled with 1,2-dichloroethane (Wuxi Dongfeng Chemical Factory, China) and then sulfonated with chlorosulphonic acid (Guangzhou Chemical Factory, China). After sulfonation the sample was washed with distilled water to neutrality and finally dried at 70°C under vacuum conditions. The obtained sulfonated fibers were denoted by PP-g-SO_3H-Py. The sulfonation degree of the PP-g-St-4VP copolymers was calculated by the weight increment after sulfonation as follows:

$$\text{Sulphonation degree (\%)} = [\Delta W_{\text{real}}/\Delta W_{\text{theoretical}}] \times 100$$

where ΔW_{real} is the real weight increment after sulfonation and $\Delta W_{\text{theoretical}}$ is the theoretical weight increment calculated by supposing that all of the St grafted on fiber are sulfonated and each St produces one sulfonic group.

The related strong-acid ion exchange fiber was synthesized following the above procedures and denoted by PP-g-SO_3H. The strong-acid ion exchange resin (OOIX7(732#)) was obtained from Gangzhou Golden East Resin Chemical Company.

TABLE II
Ratio of St and 4VP on the grafted copolymers[a]

Feed ratio of St to 4VP	2 : 8	4 : 6	6 : 4	8 : 2	9 : 1
Content of St on the grafted fiber (%)	14.9	33.9	57.1	41.3	30.6
Content of 4VP on the grafted fiber (%)	89.1	66.1	42.9	58.7	69.4

[a] Monomers concentration, 15%.

Figure 1 Sulfonation of PP-g-St-4VP (6 : 4) at different temperatures.

Figure 3 Effect of swelling time on the sulfonation of PP-g-St-4VP (6 : 4)
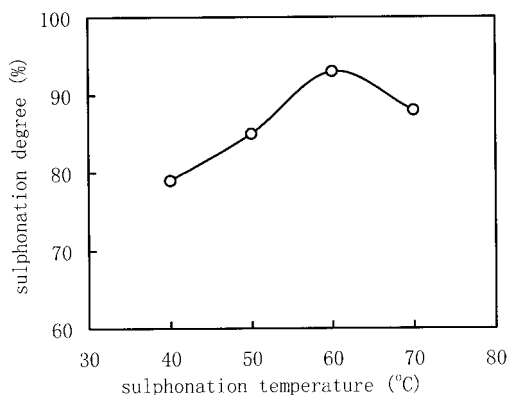
Characterization of the structures of the produced amphoteric fibers

XPS characterization of the produced amphoteric fibers was carried out on a Vacuum Generators Escalab MK II Spectrometer, using Al K_α radiation (energy 1,486.6 eV) in a vacuum of 1×10^{-6} Pa. The FTIR spectra of the samples were recorded by a Nicolet FFIR5DX spectrometer. The carbon, nitrogen, and hydrogen contents of the samples were detected by a Perkin–Elmer 240C Elemental Analyzer, and the sulfur content of the samples was detected by using CHNOS Elementanalyter made in Germany. The samples were mounted on a sample holder, coated with Au/Pd alloy, and then observed using a JSM-6330F Electronic Scanning Microscopy.

Adsorption and elution of amino acids on ion exchangers

The static adsorption of the amino acids mixture was carried out as follows: About 0.23 g of ion exchangers were put into a conical flask and then a certain amount of amino acids mixture was added into the flask. The
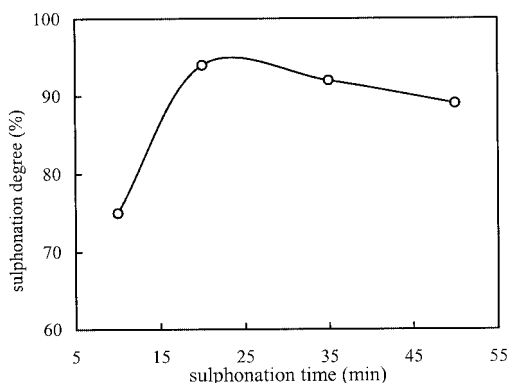
solution was stirred for 24 h and the exchangers were separated from the solution. The concentrations of various amino acids before and after adsorption were measured by a Hitachi 835–50 Automatic Analyzer.

The dynamic adsorption for histidine was carried out as follows: About 0.7 g of ion exchangers were fixed in a glass column with a diameter of 0.5 cm and a length of 12 cm. The histidine solution (4 mg/L) was flowed through the fixed bed with a flow rate of 1 mL/min. Effluent solutions (5 mL) were collected as a separated grade and the concentration of each grade was measured by a Hitachi 835–50 Automatic Analyzer.

The elution experiment was carried out as follows: About 0.7 g of ion exchangers were fixed in a glass column with a diameter of 0.5 cm and a length of 12 cm. Glumatic acid (1.5 mL; pH 2.0; concentration, 20 mg/mL) were loaded into the top of the column with a flow rate of 0.3 mL/min. The loaded column was washed by the pH 3.26 buffer of 0.1 mol/L citric acid/sodium citric acid with a flow rate of 1 mL/min. Every 5 mL of elution solution were collected as a separated grade and the concentration of each grade was measured by a Hitachi 835–50 Automatic Analyzer.

Figure 2 Sulfonation of PP-g-St-4VP (6 : 4) with different times.

TABLE III
Sulphonation of the PP-g-St-4VP Prepared with Different Feed Ratios of St to 4VP[a]

Feed ratio of St to 4VP	2 : 8	4 : 6	6 : 4	9 : 1	10 : 0
Total grafting percentage (%)	496	742	712	236	75
Sulphonation degree (%)	63.8	77.7	90.1	92.5	102.1

[a] Sulphonation temperature: 60°C; sulphonation time: 30 min; sulphonation reagent: 5% chlorosulfonic acid; swelling: 1,2-dichloroethane for 3 h; ratio of fiber weight to solution volume: 1 : 50.
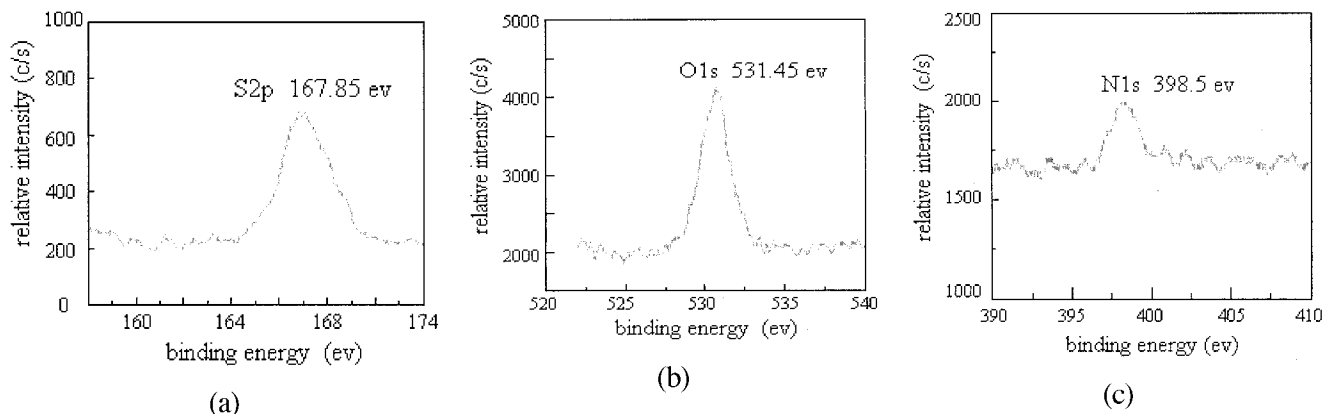
Figure 4 XPS spectra of PP-g-SO$_3$H-Py (6 : 4). (a) S$_{2p}$; (b) O$_{1S}$; (c) N$_{1S}$.

RESULTS AND DISCUSSION

Fabrication of the strong-acid/weak-base amphoteric fibers

We have reported the effects of normal grafting conditions, such as irradiation dose, emulsifying reagent content, grafting temperature, grafting time, etc. on the graft of St and 4VP onto PP fiber initiated by preirradiation of Co^{60}.[7] Based on the optimum grafting condition obtained from previous studies,[7] we further synthesized the graft copolymers with different ratios of St and 4VP and mainly studied the sulfonation conditions to fabricate appropriate strong-acid/weak-base amphoteric fibers. Table I shows that we can obtain PP-g-St-4VP copolymers with a total grafting percentage in the range of 279 to 742% under the grafting conditions used in our experiments. The total grafting percentage of the PP-g-St-4VP copolymers obtained increases at first with the increase of 4VP content used because the monomer of 4VP is more active than St. But, the total grafting percentage

reaches a maximum when the feed ratio of St to 4VP is at 4 : 6, indicating that there is enhanced grafting between acidic and basic monomers. Referenced to the literature,[17] the reactivity ratios of St (r_1) and 4VP (r_2) are 0.54 and 0.70, respectively. This pair of monomers will be mainly polymerized to obtain random copolymers.

According to the nitrogen content of the copolymers detected by the elemental analyzer, the ratios of St and 4VP on the grafted fibers were calculated and listed in Table II. It is concluded from Tables I and II that we can control the grafting percentage and amphoteric structure of the PP-g-St-4VP copolymers by changing the ratio of St to 4VP.

We can also change the total grafting percentage of the copolymers by changing the monomers concentration used. When the monomers concentration increased, the total grafting percentage increased, except for at very high feed ratio of St to 4VP (such as 9.8 : 0.2).

Acidic groups were introduced onto the PP-g-St-4VP fibers by sulfonating with chlorosulphonic acid. Figure 1 shows that the sulfonation degree of the PP-g-St-4VP fibers increases with the increase of sulfonation temperature at the initial stage and reaches a maximum at 60°C. When the sulfonation temperature increases to 70°C, the sulfonation degree conversely decreases because the side
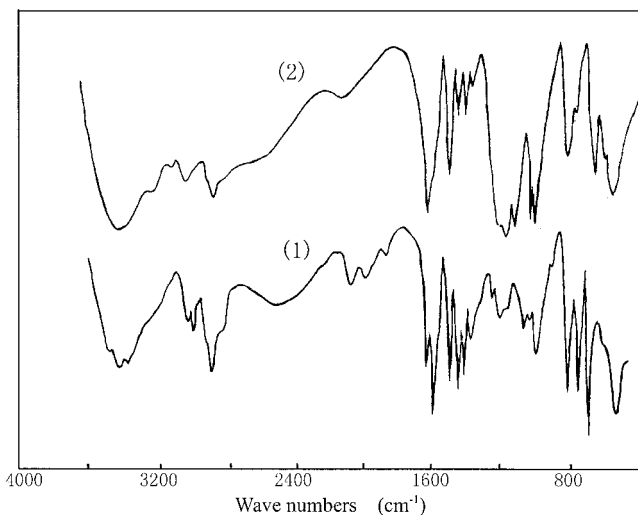

Figure 5 FTIR spectra of PP-g-St-4VP (6 : 4). (1) Before sulfonation; (2) after sulfonation.

TABLE IV
Amounts of Sulphonic and Pyridic Groups on the PP-g-SO$_3$H-Py Fibers

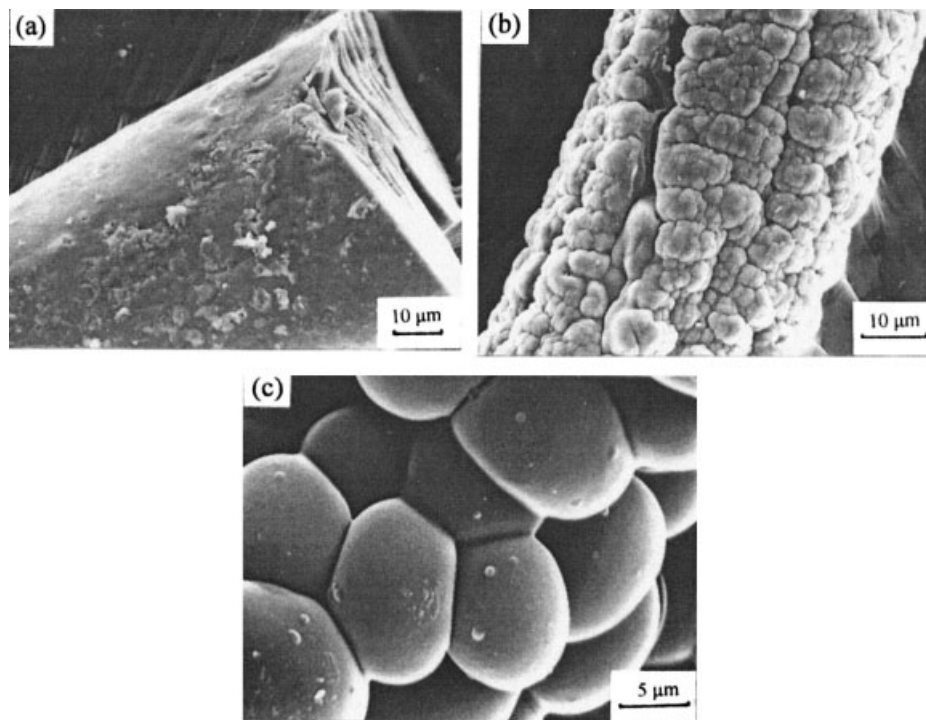| Feed ratio of St to 4VP	2 : 8	4 : 6	6 : 4	8 : 2
Sulphonic group content (mmol/g)	1.98	3.56	4.22	4.12
Pyridic group content (mmol/g)	3.60	2.77	4.24	2.33
Total amount of groups (mmol/g)	5.58	6.33	8.46	6.45

Figure 6   SEM photographs of ion exchange fibers. (a) PP-g-SO$_3$H; (b) PP-g-SO$_3$H-Py (5 : 5); (c) PP-4VP.

crosslinking reaction of SO$_2$ bridges between two benzene rings of styrene units and the dissolution of some grafting chains may decrease the weight increment of sulfonated fiber.

Generally, it will take several hours to complete the sulfonation for granular St-divinylbenaene copolymer resin.[18] However, the sulfonation speed of the PP-g-St-4VP fibers is quite rapid, reaching a maximum in 20 to 35 min (see Fig. 2). Two reasons may cause the high-speed sulfonation of PP-g-St-4VP fibers. One reason is that the fibrous copolymers substantially have a large surface area. Another reason is that the existence of small amounts of polar monomers (such as 4VP) on PP-g-St-4VP fiber enhances the dispersion of sulfonation reagent into the fiber and, at the same time, decreases the activation energy of sulfonation by the neighboring-group effect.[18]

When the sulfonation time is greater than 35 min, the sulfonation degree decreases due to the side crosslinking reaction of SO$_2$ bridges and the loss of some grafting chains on fiber. Therefore, 60°C and 30 min are recommended for the sulfonation of the PP-g-St-4VP fibers.

Generally, the St-containing copolymer should be swelled with swelling reagent before sulfonation to increase the sulfonation speed. Figure 3 shows the effect of swelling on the sulfonation of PP-g-St-4VP fibers. The experimental results indicated that the PP-g-St-4VP fibers prepared are easy to swell, and the sulfonation degree apparently does not change when the swelling time is greater than 3 h.

Table III shows the sulfonation results of the PP-g-St-4VP fibers prepared with different feed ratios of St to 4-VP. It can be seen that, when the feed ratio of 4-VP increases, the sulfonation degree decreases. We explain this phenomenon in that some of St components on the grafted fibers may be embedded by 4VP. It can also be found from the SEM observation (see Fig. 6) that the PP-g-St-4VP copolymer grafted with about 6 : 4 feed ratio of St to 4VP presents a loose morphology that is advantageous to the dispersion of sulfonation reagent.

TABLE V
Adsorption Capacity of Amino Acids Mixture on the PP-g-SO$_3$H-Py (8 : 2)

Amino acid	Asn	Glu	Ala	Ser	His	Total
Initial concentration (mg/ml)	0.104	0.100	0.101	0.099	0.102	0.506
Residual concentration (mg/ml)	0.0043	0.0024	0.0443	0.0491	0.0039	0.1040
Adsorption capacity (mg/g)	12.79	12.52	7.27	6.40	12.58	51.56

TABLE VI
Adsorption Capacity of Amino Acids Mixture on the PP-g-SO$_3$H Fiber

Amino acid	Asn	Glu	Ala	Ser	His	Total
Initial concentration (mg/ml)	0.104	0.104	0.099	0.100	0.099	0.506
Residual concentration (mg/ml)	0.0464	0.0348	0.0202	0.0353	0.0001	0.1367
Adsorption capacity (mg/g)	10.52	12.64	14.39	11.82	18.08	64.44

Structures of the strong-acid/weak-base amphoteric fibers

Figure 4(a–c) shows the XPS spectra of S$_{2p}$, O$_{1s}$, and N$_{1s}$ of the sulfonated PP-g-St-4VP (PP-g-SO$_3$H-Py), respectively. The binding energy of S$_{2p}$ in Figure 4(a) is 167.85 eV. According to the literature,[19] this peak is assigned to the sulfonic group (the binding energy of S$_{2p}$ of the standard PhSO$_3$Na in literature[19] is 168.0 eV). The binding energy of O$_{1s}$ in Figure 4(b) is 534.45 eV, which is almost the same as that of the standard H$_2$NC$_6$H$_4$SO$_3$H (531.5eV) found in the literature.[19] The binding energy of N$_{1s}$ in Figure 4(c) is 398.5 eV, showing that the N in sulfonated PP-g-St-4VP keeps the chemical state of pyridine, in accordance with 398.6 eV of N$_{1s}$ of the standard pyridine in the literature.[19]

Figure 5 shows the FTIR spectra of the PP-g-St-4VP and the related PP-g-SO$_3$H-Py fibers. According to the literature,[20] the peaks at 1,630 and 1,500 cm^{-1} in the pattern of the PP-g-St-4VP fiber are assigned to the absorption band of the pyridic group. The peaks at 1,600 and 1,450 cm^{-1} are assigned to the absorption band of benzene. The peaks at 758 and 695 cm^{-1} are assigned to the bending vibration of C–H in the aromatic ring with only one substituent. As expected, these results indicate that the PP-g-St-4VP possesses pyridine and an aromatic ring. After sulfonation, the produced PP-g-SO$_3$H-Py fiber still contains the pyridic group, judging from the existence of the absorption peaks of 1,630 and 1,500 cm^{-1} (see pattern 2 in Fig. 5). In addition, three strong absorption bands appear at 1,117, 1,173, and 1,223 cm^{-1} on the pattern of the PP-g-SO$_3$H-Py fiber, which are assigned to the absorption of the sulfonic group by referencing to the literature.[20] Furthermore, it is found from pattern 2 in Figure 5 that, after sulfonation, the peaks at 758 and 695 cm^{-1} almost disappear, while a peak at 821 cm^{-1} appears, which is assigned to the absorption band of the aromatic ring with two *para*-substituents. These results indicate that only one sulfonic group is in-duced into an aromatic ring in most of the PP-g-St-4VP and it is located in the *para*-position of St.

It can be concluded from the above results that a strong-acid/weak-base amphoteric ion exchange fiber with sulfonic and pyridyl groups has been successfully fabricated by grafting St and 4VP onto PP fiber and then sulfonating with chlorosulfonic acid.

We detected the nitrogen, sulfur, and oxygen contents of PP-g-SO$_3$H-Py fibers by using an elemental analyzer, and then calculated the amounts of sulfonic and pyridic groups on the fibers. The results (see Table IV) indicate that the contents of strong-acid group of the PP-g-SO$_3$H-Py fibers are in the range of 1.98 to 4.22 mmol/g and the contents of weak-base group are in the range of 2.33 to 4.24 mmol/g.

The SEM photographs of strong-acid/weak-base amphoteric fibers are shown in Figure 6 and compared with that of related strong-acid (PP-SO$_3$H) and weak-base (PP-4VP) ion exchange fibers. It can be seen that the grafted St and related sulfonated products on the PP-SO$_3$H are in the form of tiny particles that aggregate together into a film and coat on the surface of the PP fiber. On the PP-4VP, many separated large grafted particles can be seen, while the morphology of the PP-SO$_3$H-4VP combines both the structures of PP-SO$_3$H and PP-4VP. We can find that the grafted product consists of many big congeries, which consist of many small particles. The grafted congeries closely aggregate and uniformly cover the fiber.

Adsorption of the amphoteric fibers obtained for amino acids

The adsorption properties of PP-g-SO$_3$H-Py fibers for metal ions from liquid media have been reported in previous work.[21] Here, we mainly focus on their adsorption and separation properties for amino acids. Tables V to VII show the static adsorption results of the amino acids mixture on various exchangers. Sim-

TABLE VII
Adsorption Capacity of Amino Acids Mixture on the OOIX7(732#) Strong-Acid Resin

Amino acid	Asn	Glu	Ala	Ser	His	Total
Initial concentration (mg/ml)	0.104	0.104	0.099	0.100	0.099	0.506
Residual concentration (mg/ml)	0.0482	0.0263	0.0137	0.0254	0.0001	0.1136
Adsorption capacity (mg/g)	6.15	8.56	9.40	8.22	10.91	43.23

ilar to the related strong-acid ion exchange fiber PP-g-SO₃H and strong-acid ion exchange resin OOIX7(732#), the PP-g-SO₃H-Py fiber prepared possesses good adsorption ability for amino acids from the mixture solution. The adsorption capacities of the three exchangers for the amino acids mixture are in following order: PP-g-SO₃H > PP-g-SO₃H-Py > OOIX7(732#). It can be seen from the comparison of Tables V, VI, and 7 that the PP-g-SO₃H and the OOIX7(732#) have a strong ability to adsorb basic amino acids so that that the adsorption capacities of various amino acids on them are in following order: basic amino acid > neutral amino acid > acidic amino acid. Amphoteric PP-g-SO₃H-Py fiber possesses high adsorption abilities for both basic and acidic amino acids, but has a low adsorption ability for neutral amino acids, indicating that amphoteric fiber has different adsorption selectivity for the amino acids mixture from simple strong-acid ion exchange fiber or resin.

The dynamic adsorption behaviors of histidine in the columns of various exchangers are shown in Figure 7. It can be seen that the mass transfer zone of histidine in the PP-g-SO₃H-Py column is quite precipitous like that in the PP-g-SO₃H column or OOIX7(732#) strong-acid resin column that has been widely used in the separation of biosubstances in industry. The dynamic saturation adsorption capacity of the PP-g-SO₃H-Py is larger than that of the OOIX7(732#) strong-acid resin but smaller than that of the PP-g- SO₃H fiber.

Figure 8 shows the elution curves of glumatic acid for various exchanger columns. Comparing the times (elution volumes) and the widths of the elution peaks for different columns, it is found that the time (volume) of elution peak for the PP-g-SO₃H-Py sample is smaller than that for the PP-g-SO₃H sample, which is
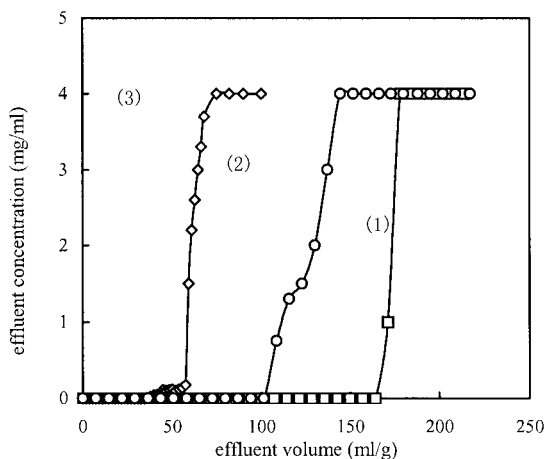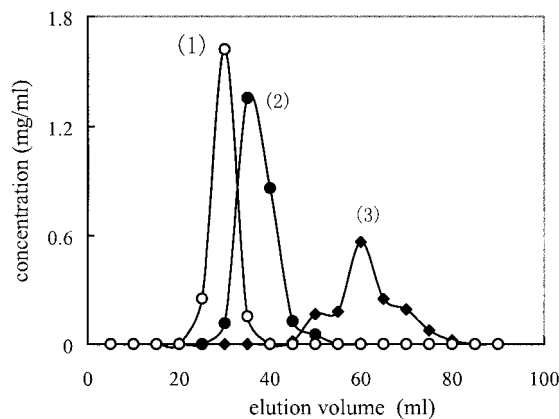

Figure 8 Elution curves of glumatic acid on different exchangers. (1) PP-g-SO₃H-Py (8 : 2); (2) PP-g-SO₃H; (3) strong-acid resin.

smaller than that for OOIX7(732#) strong-acid resin. At the same time, the widths of elution peaks for these columns are in the same order as the times of elution peaks, that is: PP-g-SO₃H-Py < PP-g-SO₃H < OOIX7(732#) resin. These results indicate that adsorbed amino acid on the PP-g-SO₃H-Py is easy to be desorbed and washed out.

CONCLUSION

The graft copolymers with different ratios of St and 4VP and total grafting percentage in the range of 279 to 742% can be fabricated by mainly controlling the feed ratio of St and 4VP, monomer concentrations used, and other polymerization conditions. There is an enhanced grafting between acidic and basic monomers so that the total grafting percentage reaches a maximum when the feed ratio of St to 4VP is about 4 : 6. When the grafted PP-g-St-4VP fibers were sulfonated with chlorosulphonic acid, the sulfonation degree was affected with the sulfonation temperature, the sulfonation time, and the ratio of St on the copolymers: 60°C and 30 min are recommended for the sulfonation of the PP-g-St-4VP fibers. The XPS results indicate that the produced acidic and basic groups are a sulfonic group and a pyridyl group, respectively. The FTIR results show that only one sulfonic group is induced into an aromatic ring in most of the PP-g-St-4VP fibers and it is located in the *para*-position of St. Based on the feed ratio of St and 4VP used, the contents of the strong-acid group of the PP-g-SO₃H-Py fibers are in the range of 1.98 to 4.22 mmol/g and the contents of the weak-base group are in the range of 2.33 to 4.24 mmol/g. The strong-acid/weak-base amphoteric fibers obtained possess a high adsorption ability for both basic and acidic amino acids, but have a low adsorption ability for neutral amino acids. They also have high adsorption speed and good elution

Figure 7 Breakthrough curves of His solution on various exchangers. (1)PP-g-SO₃H; (2) PP-g-SO₃H-Py (8 : 2); (3) strong-acid resin.

properties for amino acids like related strong acid ion exchange fibers.

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