Polymer Communication

Synthesis and cation exchange properties of a new porous cation exchange resin having an open-celled monolith structure

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Abstract

We succeeded in introducing cation exchange groups quantitatively into a porous resin having an open-celled monolith structure. The resulting new cation exchange resin had the following advantages compared with conventional ion exchange resins having a bead structure. First, it was easier to pack it in a column. Second, the ion exchange rate of the new cation exchange resin was much higher than that of the conventional ion exchange resins, and the ion exchange band length of the new resin was smaller than that of the conventional ones. In addition, the electric conductivity was about five times higher than that of the conventional ones, although they had similar ion exchange capacities. These unique properties of the new cation exchange resin were caused by the quantitative introduction of ion exchange groups into the resin having the open-celled monolith structure.
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Keywords: Open-celled monolith; Porous cation-exchange resin monolith; Ion exchange property

1. Introduction

An ion exchange resin having a bead structure was the first commercialized functional polymer produced by Rohm & Haas Co. in 1939. At that time, it was only used for water treatment, but now is applied to many more fields, for example, the separation and purification of medical products and foods, the production of ultra pure water for washing very large scale integrated circuits, an advanced purification of boiler water at power plants, and the production of chemical compounds with solid acid catalysts. However, there are three main drawbacks connected with the conventional ion exchange resins having a bead structure. These are as follows:

1. Although packing the small resin beads uniformly into a column or cell is effective in enhancing the separation ability, it is difficult and requires a great deal of skill especially in the desalination cell of an electrodeionization apparatus [1] because the cell is thin.
2. As the flow rate increases, the ion exchange band length (H) value becomes larger, because the ion exchange rates have distribution: the rates within the beads may be slower than those of the surface. The large H value leads to a reduced performance.
3. The ion mobility between the beads is slow because of the long distance between them. Therefore, the overall conductivity of the resin beads packed in a cell is low in spite of the high charge density of the beads. The low conductivity reduces the performance of electrodeionization apparatuses and so on.

Recently porous resins having an open-celled monolith structure (Fig. 1), which we call 'porous resin monoliths' in this paper, have aroused interest. In the porous resin monoliths, the pores are continuous through the resins that support the open-celled monolith structure. Therefore, the structure of the porous resin monoliths is exactly opposite to the overall structure of the conventional resin beads packed in a column. The porous resin monoliths were prepared by polymerization in unstirred water-in-oil emulsions [2–6].

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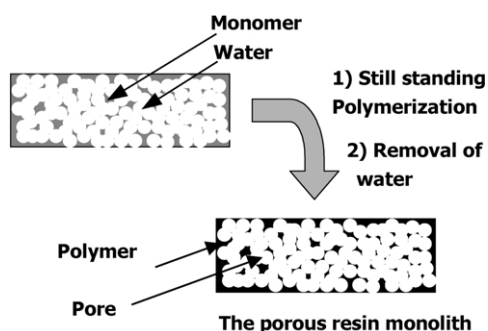
Fig. 1. Schematic structure and formation of the porous resin monolith.

The process of the formation of the open-celled monolith structure is shown in Fig. 1. Since it is possible to prepare the monolith in a shape resembling a column, the above first disadvantage can be removed. If the introduction of ion exchange groups to the monolith is uniform and quantitative, the above problems in the conventional ion-exchange resins will be solved. However, there have been no reports with regard to this issue.

Therefore, we present the synthesis of a new 'porous cation-exchange resin monolith' by the quantitative introduction of cation exchange groups into the porous resin monolith and the measurements of its properties including its electric conductivity. In addition, we compare the properties of the porous cation-exchange resin monolith with those of the conventional ion exchange resins.

2. Experimental

2.1. Synthesis of the porous resin having an open-celled monolith structure (synthesis of the porous cation-exchange resin monolith) [2–6]

Sorbitan monooleate (1.07 g, 2.60 mmol) as an emulsifier, styrene (19.3 g, 186 mmol) as a monomer, divinylbenzene(1.04 g, 6.4 mmol) as a cross-linking agent, and α,α'-azobisisobutyronitrile(0.15 g, 0.90 mmol) as an initiator were mixed homogeneously. The heterogeneous mixture of this solution (21.6 g) and ultra pure water (180 g) in a 500 ml polyethylene container was stirred at 1000 rpm (revolution)/330 rpm (rotation) with a sun-and-planet type mixer (VMX-360®; EME Co.) [7] for 2 min at 100 Torr to form a water-in-oil emulsion. The other conditions and reaction results are listed in Table 1A, Run Nos. 1–3. The mixture was also stirred at 10,000 rpm for 2 min. with a conventional mixer (Creamix®; Organo Co.). The emulsion in the sealed container was heated for 24 h at 60 °C under nitrogen. After the emulsion polymerization, the container was cooled. The crude polymer was purified by Soxhlet extraction using 2-propanol for 18 h to remove unreacted monomers, oligomers, emulsifier, and water. The resulting polymer was dried at 85 °C in a vacuum oven overnight. The results of the polymerizations are listed in Table 1A.

2.2. Introduction of cation exchange groups (sulfonic acid groups) into the porous cation-exchange resin monolith (= synthesis of the porous cation-exchange resin monolith)

The 'porous poly(styrene/divinylbenzene) resin monolith' (4.10 g) obtained above was immersed in 800 ml of 1,2-dichloroethane. To the resulting swelled monolith, chlorosulfuric acid (20.0 g, 172 mmol) was added dropwise slowly at room temperature at 60 °C for 24 h. After the reaction, 30 ml of glacial acetic acid (30.0 ml, 525 mmol) was added in order to inactivate the residual chlorosulfuric acid. The product was washed with ethanol (1.50 l), water (2.00 l), and then 1N NaOH aq (2.00 l, 2.00 mol). The other conditions and results are shown in Table 1B.

To estimate the introduction ratio of the ionic groups, cation exchange capacity (q) was measured. The wetted porous cation-exchange resin monolith (30 g) was cut into many pieces of 3 mm cubes. The q value was determined using many pieces of the cubic monoliths based on the method for conventional resin beads [8] according to Eq. (1).

$$q = (A \times 0.1)/\{W(1 - w)\} \tag{1}$$

where q is the cation exchange capacity of one gram of the dried monolith (mequiv./g), A is the titration value of 0.1N NaOH aq (ml), W is the weight of the wetted monolith at the moisture equilibrium state (g), and w is the ratio of water to the wetted monolith at the moisture equilibrium state.

2.3. Ion exchange properties of porous cation exchange resins having a monolith structure

2.3.1. Measurements of the ion exchange band lengths (H) [8]

Many pieces of the wetted porous cation-exchange resin monolith were packed to a column (the diameter, 8 mm; the length, 180 mm; the volume, 9.04 ml; the ion exchange capacity($q_w = q(1 - w)$), 0.50 mequiv./g). The beads of a conventional cation exchange resin (Amberlite® IR124 from Rohm & Haas Co.) were packed to a similar column (the diameter, 8 mm; the length, 1000 mm; the volume, 12.56 ml; the ion exchange capacity (q_w), 1.90 mequiv./ml). These resins were regenerated by washing with 1N HCl and then washed with pure water until the eluent became neutral (the load solution, 4 mM NaCl; the flow rates (LV), 30–90 m/h). The concentrations of sodium ion in the eluent were detected by a gradient monitor (Nichiri Kogyo Co.) equipped at the end of the column. The breakthrough curve and the breakthrough time (ΔT) were obtained from the plots of the concentration versus the amount of the permeated solution. The ion exchange band length (H) was calculated from Eq. (2).

$$H = (C \times LV \times \Delta T)/(q_w + 0.5 \times C) \tag{2}$$

where H is the ion exchange band length (m), C is the concentration of sodium ion in the eluent (mequiv./g), LV is

Table 1
Synthesis of porous resin monoliths (A) and the introduction of cation exchange groups into the monoliths (B)

Run No.	A						B				q^c (mequiv./g)	Electric conductivity (μ S/cm)
	Feed[a]			Yield (%)	Pore radius[b] (μm)	Pore volume[b] (ml/g)	Sulfonation					
	Styrene (mmol)	DVB[d] (mmol)	AIBN[e] (mmol)				Monolith		CSA[f] (mmol)	Introduction ratio[g]		
							(g)	(St unit mmol)				
1	186	6.4	0.9	84	11	8.7	4.1	37	172	0.91	4.8	–
2	176	12.8	1.1	84	11	8.2	4.5	40	186	0.82	4.4	1000
3	156	26.2	1.5	88	10	8.4	6.9	53	244	0.64	3.4	–
4[h]	–	–	–	–	–	–	–	–	–	0.83	4.4	200

[a] The other components of the emulsion were 1.1 g of sorbitan monooleate and 180 g of pure water.
[b] Measured by mercury intrusion method.
[c] Ion exchange capacity of the dried ion-exchange monolith calculated using Eq. (1).
[d] Divinylbenzene as a crosslinker.
[e] α,α'-azobisisobutyronitrile as an initiator.
[f] Chlorosulfuric acid as a sulfonation reagent.
[g] Introduction ratio of sulfonic acid on benzene ring was calculated from sulfur content determined by ion chromatography.
[h] Amberlite IR124 cation exchange resin (manufactured by Rohm & Haas Co.).

the linear velocity of 4 mM NaCl in the column (m/h), q_w is the cation exchange capacity of the wetted monolith (mequiv./g), $q_w = q(1 - w)$, ΔT is the breakthrough time (h).

2.3.2. Measurements of the electric conductivities

The wetted porous cation-exchange resin monolith were packed in a desalination cell of electrodeionization. Ultra pure water was passed through the cell under constant electric current. After a steady state was reached, the electric conductivity was measured.

2.4. Apparatus

IR spectra were recorded on a Nicoley FT-IR 5DX. The sulfur contents were determined with a Dionex SERIE-S2000i/SP ion chromatograph. A Hitachi S-4000 was used for SEM observation. The pore size distributions and the total pore volumes were measured by the mercury intrusion method using a Micromeritics Auto-Pore III 9420.

3. Results and discussion

3.1. Synthesis of the porous ion-exchange resin having a uniform open-celled monolith structure (Synthesis of the porous cation-exchange resin monolith)

3.1.1. Synthesis of the porous resin having a uniform open-celled monolith structure (Synthesis of the porous resin monolith)

First, the porous resin having a uniform open-celled monolith structure was prepared by emulsion polymeriz-

ation (Table 1A). The formation of the open-celled monolith structure (Fig. 1) was confirmed by SEM observations (Fig. 2A). To evaluate the structures more precisely, the sizes, the distribution, and the total volumes of the pores were measured by the mercury intrusion method (Table 1A). The peak shape in the pore size distribution curve of the porous resin monolith prepared with a sun-and-planet type blender was unimodal and narrow. The half bandwidth of the main peak at 10 μm was 2 μm, a value indicating the formation of a uniform open-celled monolith structure. On the other hand, the pore size distribution of the porous resin monolith prepared with a conventional mixer was broad and the half bandwidth of the main peak at 15 μm was 10 μm. Therefore, it was found that to prepare the emulsion using the sun-and-planet type mixer was very important for the formation of the uniform open-celled structure in the monolith. This may be because the mixer can remove bubbles even in a high viscosity emulsion[1]. The total volume of the pores in the porous resin monolith was much larger (about 8 ml/g) than that of the conventional porous polystyrene beads (0.6–1.7 ml/g) [9].

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[1] The stirring mechanism of the sun-and-planet type mixer is as follows. The motion of the mixer contains both orbital and rotation motion at the same time. These two motions can stir a mixture much effectively. The conventional mixer can stir the limited region only near the impeller blades when the viscosity of an emulsion was high. On the other hand, the sun-and-planet type mixer can stir an emulsion uniformly, because that mixer stir it not with impeller blades but by the composed force generated by orbital and rotation motion. Additionally, the mixer can remove bubbles even in a thick emulsion using centrifugal force generated by the orbital motion, while the conventional mixer cannot.
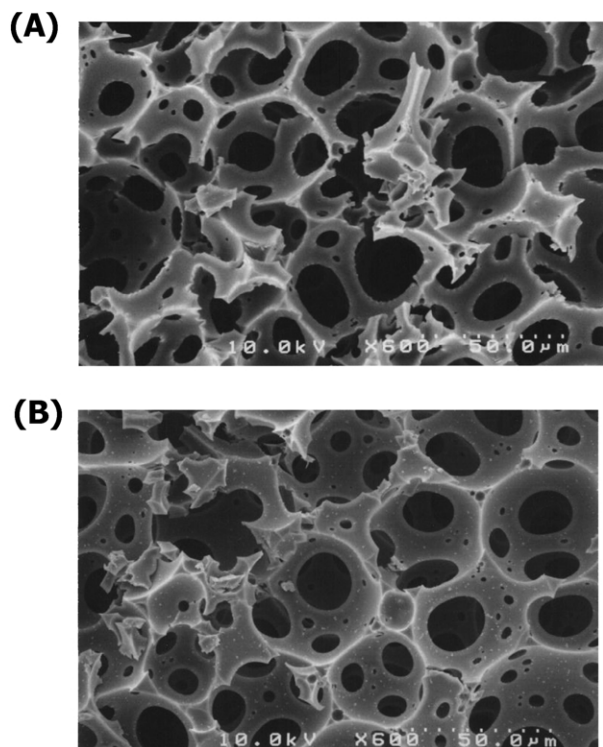
(A)

(B)

Fig. 2. Scanning electron micrographs of the porous resin monolith before (A) and after (B) sulfonation (Table 1, Run No. 2); (A): the porous resin monolith, (B): the porous cation-exchange resin monolith.

3.1.2. Introduction of the cation exchange groups into the porous resin monolith (synthesis of the 'porous ion-exchange resin monolith')

The introduction of sulfonic groups to the porous resin monolith synthesized above was carried out with chlorosulfuric acid in a heterogeneous system. The absorption bands assigned to S=O asymmetric stretching at 1127 and 1180 cm^{-1}, and S=O symmetric stretching at 1039 and 1009 cm^{-1} were observed in the IR spectra of the resulting monolith (Fig. 3B). Therefore, the introduction of sulfonic acid groups into the porous resin monolith was confirmed. To determine the quantity of sulfonic acid groups introduced, the introduction ratios of the sulfonic acid on the benzene ring were calculated from the sulfur contents determined by elemental analysis. When a low cross-linked porous resin monolith was used as a starting resin, the introduction ratio was 0.91 and was higher (Table 1, Run No. 1) than that of conventional resin beads (Table 1, Run No. 4). As the extent of crosslinking in the starting resin increased, the introduction ratios decreased (Table 1, Run Nos. 1–3). This tendency was similar to that of cross-linked polystyrene beads [10].

To reconfirm the high introduction ratio (0.91) of sulfonic acid groups, a measurement of the ion exchange capacities (q) of the porous resin monolith was carried out by titration. The q values of the dried porous monoliths (Table 1B, Run Nos. 1 and 2) were nearly equal to that of the conventional resin beads (Table 1B, Run No. 4). Therefore,

the number of functional groups introduced per benzene ring was found to be similar to that of the resin beads (Table 1B, Run No. 4), a finding indicating the introduction reaction was almost complete.

To confirm that the open-celled monolith structure was kept during the reaction of the introduction of the cation exchange groups, the resulting monoliths were observed with SEM (Fig. 2B). The formation of the porous cation exchange resin having a monolith structure was confirmed, since there were no changes before and after the sulfonation reaction.

3.2. Ion exchange properties of the porous cation exchange resins having a monolith structure (ion exchange properties of the porous cation-exchange resin monoliths)

3.2.1. The ion exchange band length (H) of the porous ion-exchange resin monoliths

To evaluate the dynamic ion exchange properties of theporous cation-exchange resin monoliths, the ion exchange band length (H) was measured. The H value is the length of the part of the resins packed in the column where the ion exchange reaction occurs actively. The H values of the ion-exchange resin monoliths were very small, indicating the possibility of sharp separation. They were approximately three times smaller than those of the resin beads and were constant at 30–90 m/h of the linear velocities (LV) (Fig. 4, solid circles). Such ideal dynamic ion exchange properties of the porous ion-exchange resin monoliths were thought to be caused by the fact that the adsorption and desorption of ions were very fast and uniform, since the resins had a uniform open-celled structure and the skeletons of the monoliths were very
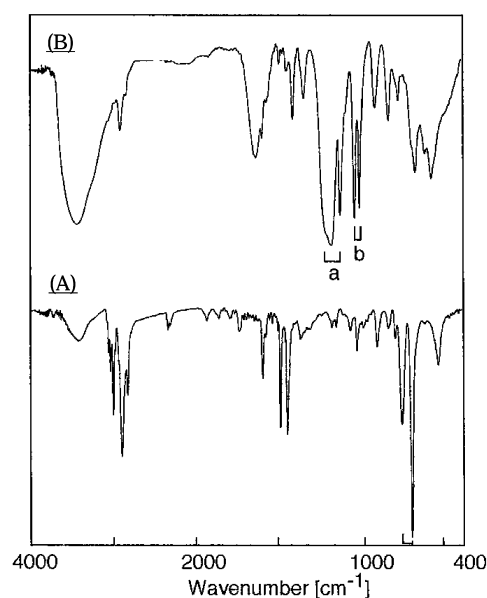

Fig. 3. IR spectra before (A) and after (B) sulfonation of the porous resin monolith (Table 1, Run No. 1); a: S=O asymmetric stretching; b: S=O symmetric stretching.
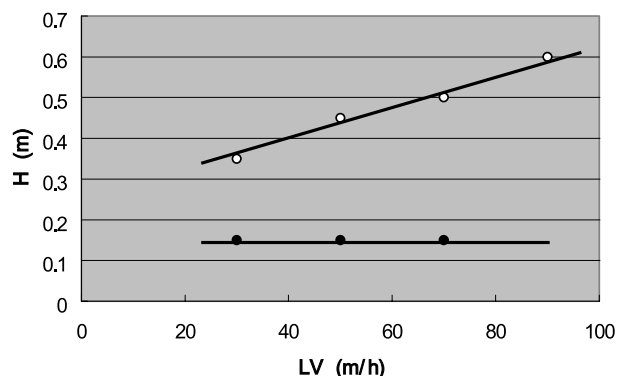
Fig. 4. Dependence of the linear velocities (LV) on the ion exchange band length (H); ●: the porous cation-exchange resin monolith (Table 1, Run No. 1); ○: the conventional cation-exchange resin beads (Table 1, Run No. 4).

thin (1–3 μm). On the other hand, the ion exchange band lengths of the resin beads were influenced by the LV and increased with an increasing LV (Fig. 4, open circles). This phenomenon may exist because the rate of the ion exchange reaction in the interior of the beads was slower than that at the surface of the beads.

3.2.2. Electric conductivity of the porous ion-exchange resin monoliths

In general, the electric conductivity of an ion exchange resin is proportional to its ion exchange capacity. Although the ion exchange capacity of the cation-exchange resin monoliths was similar to that of the conventional resin, the electric conductivity of the resin monolith was five times higher than that of the resin beads (Table 1B, Run Nos. 2 and 4). This finding indicates that the porous cation-exchange resin monoliths can carry ions uniformly throughout the overall packed resins because of its continuous structure. The low electrical conductivity of the ion exchange resin beads may originate in the smaller number of available ion paths in these beads compared to

that of the monolith; this reduced number is due, in turn, to the small contact area between the resin beads.

4. Conclusions

We succeeded in introducing sulfonic acid groups quantitatively into the porous resins having an open-celled monolith structure. The ion exchange band lengths (H) of the ion exchange resin monolith were three times less than those of the resin beads. The electric conductivity of the porous ion exchange resin monolith was five times higher than that of the resin beads. The unique small H value and high electric conductivity of the ion exchange resin monolith were favorable properties that the conventional ion exchange resin beads lacked. The many applications of the resin monoliths may include, for example, the electro-deionization, the production of ultra pure water, and as a column packing for chromatography, catalysts, and adsorbents. Furthermore, we plan to apply this procedure to synthesize anion exchange resin monoliths.

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