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# Studies of Polystyrene-based Ion Exchange Fiber. I. The Preparation and Fundamental Characteristics of Polystyrene-based Ion Exchange Fiber†

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A polystyrene-based ion exchange fiber which has a large ion exchange capacity (*ca.* 2.5 mequiv $g^{-1}$) and a high mechanical strength (*ca.* 1.4 g $d^{-1}$) has first been prepared by using an islands-in-a-sea type composite fiber, the sea ingredient predominantly comprised of polystyrene for ion exchange and the island ingredient comprised of fiber-forming polypropylene for reinforcement, as the starting material; it can be used in an arbitrary form. It was found that the resulting fiber has two fundamental characteristics; the ion exchange rate for metal ions is extremely high, and the capacity of adsorbing the macromolecular ionic substance is exceedingly large, compared with ordinary ion exchange resins. The diffusion equation of ion exchange in the case of a cylindrical, endless fiber was solved by a modification of the method used for a spherical resin in a simple system. The former results are interpreted in terms of their solutions for two limiting cases. The latter results are explained by the fact that the surface-area ratio of the fiber to the resin is about ten.

There have been many investigations regarding the method of preparing ion exchange fiber, which has a large surface area per unit of weight and can be used in an arbitrary form.[1–6] These characteristics, however, have scarcely been studied because it is difficult to prepare ion exchange fiber which satisfies the following indispensable conditions:

(1) The ionic group and the basic polymer should be chemically stable.

(2) The ion exchange capacity should be large enough.

(3) The mechanical strength should be sufficiently high.

We have investigated ion exchange fiber which satisfies the above-mentioned three conditions and studied its characteristics. Polystyrene-based ion exchangers have already been selected from many polymer-based exchangers, as they satisfy the first two conditions, (1) and (2), and used industrially in the form of resin or film. Polystyrene has been well studied because it is suitable to the addition not only of ionic groups, but also of various functional groups. This has, therefore, been chosen as our basic polymer for the introduction of the ionic group. Polystyrene fiber, however, possesses so poor a mechanical strength as to be changed into various forms. It is also liable to break into fine particles when the ionic group is introduced, and thus does not satisfy the (3) condition.

The adoption of an additional fiber-forming polymer for reinforcement has been examined in order to satisfy the (3) condition. As a result, polystyrene-based ion exchange fiber, which satisfies the three conditions, has first been prepared by the introduction of a crosslinking group and an ion exchange group into the polystyrene part by chemically treating an islands-in-a-sea type composite fiber, the sea ingredient predominantly comprised of polystyrene for ion exchange and the island ingredient comprised of fiber-forming polypropylene for reinforcement.[7,8] The present authors would like to report here on this ion exchange fiber (abbrev. IONEX). This fiber was applied to the exchange of metal ions and to the adsorption of a caramel pigment from a sucrose solution. From these results, the fundamental characteristics of the fiber will also be discussed.

## Experimental

Forty parts of polystyrene and 10 parts of polypropylene for the sea ingredient and 50 parts of polypropylene for the island ingredient were melt-spun at 255 °C into composite filaments having an islands-in-a-sea type sectional structure in which the number of islands was sixteen. The composite filaments were drawn five times as long as their original length in a conventional manner. The diameters of the sea and the islands of the resulting filaments were 24 and 4.2 μm respectively.

Ten grams of the filaments were crossinked in 100 ml of a solution consisting of 5 wt% paraformaldehyde, 25 wt% acetic acid, and 70 wt% concentrated sulfuric acid. A strong cation IONEX was obtained by the sulfonation of the crosslinked (90 °C, 4 h) filaments (10 g) in a solution comprised of 200 ml of trichloroethylene and 8 ml of chlorosulfonic acid at 20 °C for 2 h. Ten grams of the crosslinked (80 °C, 2 h) filaments were chloromethylated in a solution comprised of 100 ml of chloromethyl methyl ether and 10 ml of stannic chloride at 30 °C for 4 h. A strong anion IONEX was obtained by the quaternization of the chloromethylated filaments (10 g) in 100 ml of a 30 wt% trimethylamine aqueous solution at 30 °C for 1 h.[7–9]

The concentration of the calcium ion was determined by the EDTA methods. The color value (C.V.) was measured by means of a 1-cm cell at 410 nm both before and after the decoloration treatment. The resulting color values were referred to "*A*" and "*B*" respectively. Then the decoloration ratio was calculated by means of the following equation:

$$\text{Decoloration ratio}(\%) = \frac{A-B}{A} \times 100.$$

## Results and Discussion

*Preparation and Fundamental Properties.* The process of preparing the ion exchange fiber is shown in Fig. 1. Polystyrene (PSt) was used as the basic polymer for the ion exchange, while polypropylene (PP), which exhibits

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† A preliminary report of this work was presented in *Polym. Prepr. Jpn.*, **31**, 2025 (1982).

Table 1. Fundamental properties of IONEX

| No. | Composition of original fiber[a] | Ionic group | Diameter μm | Strength g d$^{-1}$ | Elongation % | Capacity[b] mequiv g$^{-1}$ | Water[c] content |
|---|---|---|---|---|---|---|---|
| — | | — | 24 | 3.0 | 40 | — | — |
| 1 | (40//10)/50 | $-SO_3^-Na^+$ | 30 | 1.3 | 18 | 2.6 | 1.6 |
| 2 | | | 32 | 1.4 | 29 | 2.4 | 1.9 |
| 3 | (30//7.5)/62.5 | $-CH_2N^+(CH_3)_3$ | 32 | 2.0 | 38 | 1.9 | 1.7 |
| 4 | (20//5)/75 | $Cl^-$ | 28 | 3.0 | 28 | 1.3 | 1.0 |

a) Sea(PSt//PP)/Islands(PP). b) Capacity of the strong-acid(base)groups. c) $(W-W_0)/W_0$. $W$: wet weight. $W_0$: dry weight.

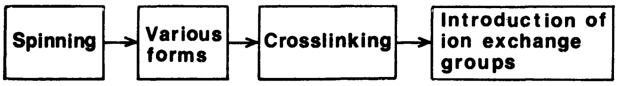

Fig. 1. Process of preparing the polystyrene-based ion exchange fiber (IONEX).

an enhanced resistance to chemicals, was used as the fiber-forming polymer for reinforcement. In the case of using as the starting material a blend fiber made from a uniform blend of PSt and PP, the ion exchange rate and the adsorption capacity of the resulting fiber are lowered when the amount of PP exceeds 50%; the fiber, on the other hand, becomes very poor in mechanical strength when the amount of PP is less than 50%. A sheath-core type composite fiber, which consists of PSt for the sheath ingredient and PP for the core ingredient, is not good as the starting material because of its poor resistance to separation between the two phases. An islands-in-a-sea type composite fiber which consists of PSt for the sea ingredient and PP for the island ingredient could provide a suitable ion exchange fiber, IONEX, which exhibits an enhanced ion exchange rate, adsorption capacity, mechanical strength, and resistance to separation.[7] A schematic cross-sectional drawing of the composite fiber is shown in Fig. 2. A composite fiber which consists of PSt mixed with a small amount of PP for the sea ingredient and PP for the island ingredient was finally used to enhance further the resistance to separation.[8] The methods of chemical reaction to the polystyrene part are shown in Fig. 3.

The strength, elongation, ion exchange capacity, and water content of several filamentary IONEX are summarized in Table 1. The ion exchange capacities of IONEX Nos. 1—4 correspond to 94, 88, 86, and 82% of the theoretically calculated values respectively. When a crosslinking group and an ionic group are introduced, the tensile strength of the resulting filaments becomes lower than the value estimated in consideration of the weight increase from the data on the original filaments; that is, the tensile strength per filament of the original filament was 12.9 g, and those of the crosslinked filament, the chloromethylated filament, and the strong anion exchange filament were 12.0, 11.9, and 10.5 g respectively. No change in the capacity or the water content was recognized, even if the strong cation or anion IONEX was repeatedly used ten times in the following treatment: add to 1 M (1 M=1 mol dm$^{-3}$) hydrochloric acid or sodium hydroxide, wash with deionized water, add to 1 M sodium chloride, and finally wash with deionized water. From these results, it can be presumed that a methylene bond is formed between phenyl rings by the crosslinking reaction and that then the resulting filament is strongly crosslinked and insolubilized.[9] IONEX with an arbitrary water content can be obtained by chosing the conditions of the crosslinking reaction. The acidity or basicity of a strong cation or anion IONEX is almost equal to that of polystyrene-based ion exchange resin. IONEX in an arbitrary form, such as staple fibers, cut fibers, needle punched felts, nonwoven fabrics, woven fabrics, knitted fabrics, braids, and papers, can also be obtained by processing the filaments before the chemical reaction; it can then be prepared so as to have the same capacity and water content as the filamentary form by controlling the processing density. Figure 4 presents a strong cation IONEX in a form of the cut fibers.

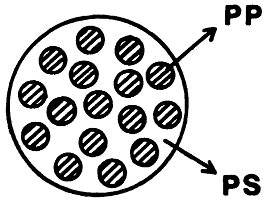

Fig. 2. Schematic cross sectional drawing of the composite fiber.

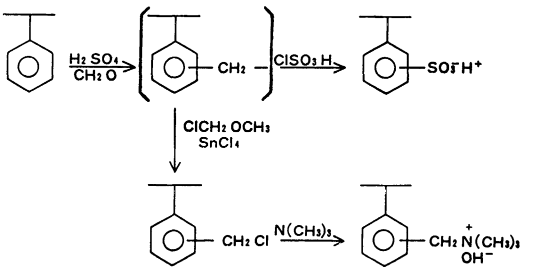

Fig. 3. The methods of chemical reaction to polystyrene part.

*Exchange of Metal Ions.* A strong cation exchanger of 6.6 mequiv in the Na form was added to 250 ml of a 0.008 M $CaCl_2$ aqueous solution containing 50 wt% sucrose; it was then strongly shaken at 20 °C. Similarly, a strong cation exchanger of 5.7 mequiv in the Ca form was added to 250 ml of a 1 M NaCl aqueous solution, and then the mixture was strongly shaken. The fractional attainment of equilibrium was evaluated in those two cases by measuring the calcium-ion concentration in the solution at several intervals. The results are shown in Figs. 5 and 6 respectively. A commercially available strong cation exchange resin and strong cation

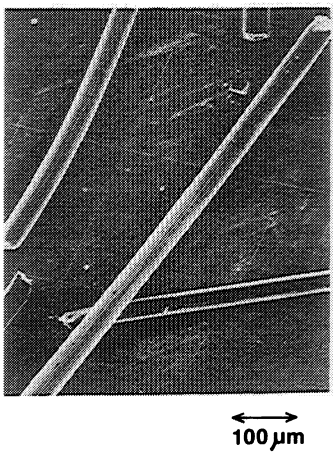

Fig. 4. Strong cation IONEX in a form of cut fibers.

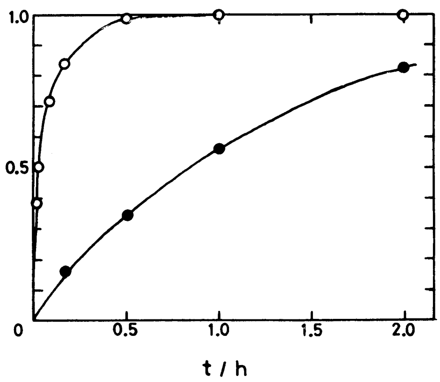

Fig. 5. Fractional attainment of equilibrium as a function of time.
Ion exchange between Na form of cation exchanger (6.6 mequiv) and 0.008 M $CaCl_2$ solution containing 50 wt% sucrose (250 ml). ○: IONEX No. 1 (2.5 g), ●: Amberlite IR-120B (1.5 g).

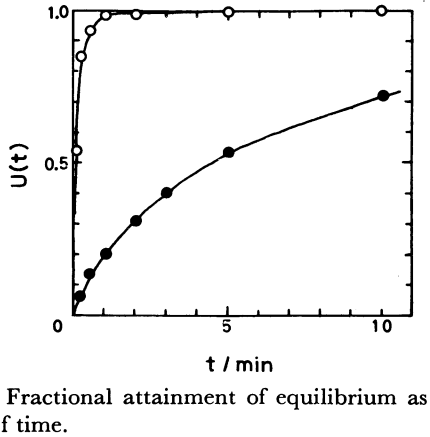

Fig. 6. Fractional attainment of equilibrium as a function of time.
Ion exchange between Ca form of cation exchanger (5.7 mequiv) and 1 M NaCl solution (250 ml). ○: IONEX No. 1 (2.2 g), ●: Amberlite IR-120B (1.3 g).

IONEX No. 1 were used as cation exchangers.

According to the rate laws of ion exchange in a simple system, the fractional attainment of equilibrium $U(t)$ within a spherical resin with a radius of $r_0$ can be described in the two limiting cases of ideal film and ideal particle diffusion control respectively by the following equations:[10]

$$U(t) = 1 - \exp\left(-\frac{3DCt}{r_0\delta\bar{C}}\right), \tag{1}$$

$$U(t) = 1 - \frac{6}{\pi^2}\sum_{n=1}^{\infty}\frac{1}{n^2}\exp\left(-\frac{\bar{D}\pi^2 n^2 t}{r_0^2}\right). \tag{2}$$

The signification of the symbols in the above equations has been described in Ref. 10. The half-times, $t_{1/2}$, of ion exchange are calculated from Eqs. 1 and 2 respectively as follows:[10]

$$t_{1/2} = 0.230\, r_0\delta\bar{C}/DC, \tag{3}$$

$$t_{1/2} = 0.030\, r_0^2/\bar{D}. \tag{4}$$

We could solve the diffusion equation in the case of an endless fiber with a radius of $r_f$ by the modification of the method used for a spherical resin; we could thus obtain the fractional attainment of equilibrium in the two limiting cases as, respectively:

$$U(t) = 1 - \exp\left(-\frac{2DCt}{r_f\delta\bar{C}}\right), \tag{5}$$

$$U(t) = 1 - \sum_{n=1}^{\infty}\frac{4}{x_n^2}\exp\left(-\frac{\bar{D}_f x_n^2 t}{r_f^2}\right). \tag{6}$$

where $\bar{D}_f$ is the interdiffusion coefficient in the ion exchange fiber and where the quantities $x_n$ are the roots of the equation $J_0(x)=0$, in which $J_0(x)$ is the zero-order Bessel function. The half-times of ion exchange were finally derived from Eqs. 5 and 6 as follows:

$$t_{1/2} = 0.345\, r_f\delta\bar{C}/DC, \tag{7}$$

$$t_{1/2} = 0.065\, r_f^2/\bar{D}_f. \tag{8}$$

Although the diffusion equations have been solved under several conditions, the solutions can be applied to our experimental results in the case of a relative comparison between the fiber and the resin. The results in Fig. 5 are considered to correspond to the case of film diffusion control, since the concentration of the solution is sufficiently low: $C \ll 0.1$ M. The ratio of the half-time of the resin to that of the fiber can be calculated to be 11 from Eqs. 3 and 7 when $r_0=250$ μm and $r_f=15$ μm. The ratio obtained from the experimental data is, however, 25, almost twice as high as the calculated ratio. This fact may be interpreted owing to film diffusion control in terms of the increase in the surface area per unit of capacity of IONEX by the amount of the polymer for reinforcement. On the other hand, the results in Fig. 6 are considered to correspond to the case of particle diffusion control, since the concentration of the solution is sufficiently high: $C \gg 0.1$ M; the ratio can similarly be calculated to be 128 from Eqs. 4 and 8 if $\bar{D}=\bar{D}_f$ is assumed. The ratio obtained from the experimental data, however, is in the range of from 50 to 70 and is about half the calculated ratio. The results can be interpreted on the assumption that the polymer for reinforcement disturbs the diffusion of ions because of the particle diffusion control.

*Adsorption of a Caramel Pigment.* Two grams of a strong anion exchanger in the Cl form was added to 200 ml of a 50 wt% sucrose aqueous solution containing a commercially available caramel pigment (C.V. 0.92); the mixture was then stirred at 60 °C. The data of the

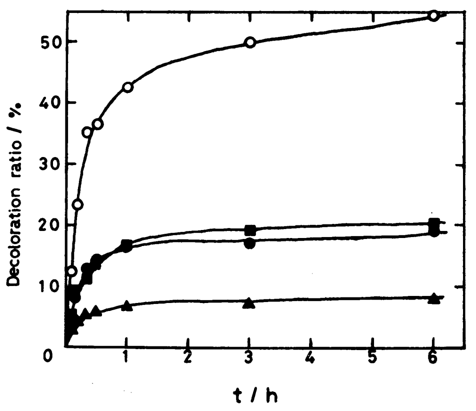

Fig. 7. Decoloration ratio as a function of time. Decoloration of 50 wt% sucrose solution containing caramel pigment (200 ml, C.V. 0.92) by Cl form anion exchanger (2.0 g) at 60 °C.
○: IONEX No. 2, ●: Amberlite IRA-401 (low crosslinked type), ▲: Amberlite IRA-400 (standard crosslinked type), ■: Amberlite IRA-900 (MR type).

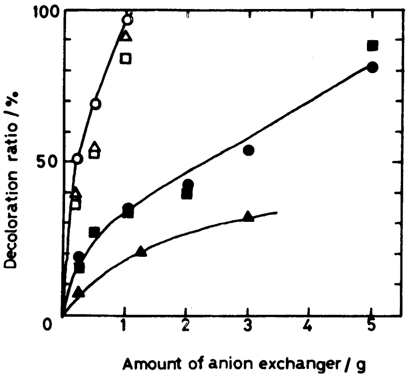

Fig. 8. Decoloration ratio *vs.* amount of anion exchanger. Decoloration of 50 wt% sucrose solution containing caramel pigment (25 ml, C.V. 0.92) by Cl form of anion exchanger (60 °C, 6 h). ○: IONEX No. 2, △: IONEX No. 3, □: IONEX No. 4, ●: IRA-401, ▲: IRA-400, ■: IRA-900.

decoloration ratio as a function of the time are shown in Fig. 7. It is apparent that the decoloration rate by the fiber is much greater than that by the three resins. This indicates that the effective capacity of the fiber to adsorb the caramel pigment is much larger than that of the resins, in spite of the fact that the ion exchange capacity of the fiber is about two thirds that of the resins.

Next, a strong anion exchanger in the Cl form was added to 25 ml of the same sucrose solution, and the mixture was shaken at 60 °C for 6 h. The correlation between the amounts of various anion exchangers and the decoloration ratio is shown in Fig. 8. This shows that the fibers have from seven to ten times as large an effective capacity of adsorbing the pigment as the low-crosslinked-type and the MR-type resins and, further, forty times as large a capacity as the standard-crosslinked-type resin. No large difference in the effective capacity was not observed between the strong anion IONEX Nos. 2—4. These results can be explained by the fact that the surface-area ratio of the fiber to the resin ($2r_0/3r_f$) is about ten, since the caramel pigment of a macromolecular weight cannot diffuse into the exchangers and can be adsorbed only near their surface. The reason why the low-crosslinked-type resin is superior to the standard-crosslinked-type resin is probably the small diffusion of the pigment into the former exchanger. Furthermore, the effective capacity of the MR-type resin is almost equal to that of the low-crosslinked-type resin, although it is said that the former resin has a large inner surface area of 30—100 $m^2\,g^{-1}$. The reason for this is considered to be that the crosslinking degree of the MR-type resin is so high that the pigment cannot diffuse into the gel at all.

## Conclusion

1. An excellent polystyrene-based ion exchange fiber which sufficiently satisfies the three indispensable conditions mentioned above was obtained by using the islands-in-a-sea type composite fiber as the starting material.

2. It was found that the resulting fiber has two fundamental characteristics; the ion exchange rate for metal ions is extremely high, and the capacity of adsorbing the macromolecular ionic substance is exceedingly large, compared with ordinary ion exchange resins.

3. The former results are interpreted in terms of the rate laws of ion exchange for the two limiting cases of ideal film and ideal particle diffusion control in a simple system. The latter results are explained by the fact that the fiber has a very large surface area in comparison with that of the resins.

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