Active and Selective Transports of Anions through Poly(*N*-propenoyl-9-acridinylamine-*co*-acrylonitrile) Membrane

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ABSTRACT: An acridine unit was incorporated into poly(propenoyl chloride-*co*-acrylonitrile) by a polymer reaction to cause the basic acridine to function as a fixed carrier for halogen ions. The membrane made of poly(*N*-propenoyl-9-acridinylamine-*co*-acrylonitrile) led to the active and selective transport of halogen ions. The selectivity of halogen ions was found to depend on the affinity between a fixed carrier and halogen ion.
     KEY WORDS   Active Transport / Selective Transport / Acridine Unit / Fixed Carrier / Polymer Reaction /

It is important to develop an artificial membrane capable of selectively and specifically transporting substrates or ions and establish a separation method of using an artificial membrane. Synthetic copolymer membranes having functional groups as a fixed carriers have been studied extensively since the active transport of alkali metal ions[1] was reported.

It is known[2-6] that synthetic polymer membranes having basic groups as fixed carriers lead the active transport of halogen ions. In particular, bromide ions are selectively transported by the poly(4-vinylpyridine-*co*-styrene) membrane, while chloride ions by the poly(2-vinylpyridine-*co*-styrene) membrane.[6] Since the basic pyridine moiety causes the selective separation of halogen ions, other basic heterocyclic groups are expected to have the same effect as pyridine. This paper is concerned with the synthesis of a new polymer having an acridine unit, poly(*N*-propenoyl-9-acridinylamine-*co*-acrylonitrile) (5), as a fixed carrier and the active and selective transport of halogen ions through the 5 membrane is described.
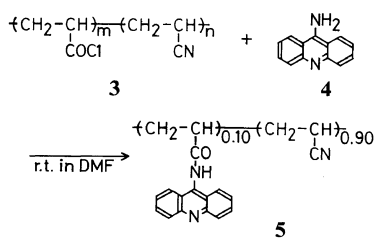
EXPERIMENTAL

Materials

Propenoyl chloride (1) was synthesized from propenoic acid and benzoyl chloride,[7] bp 75—80°C. Crude 9-acridinylamine (4) was obtained by the neutralization of 9-acridinylamine hydrochloride with aqueous sodium hydroxide. Recrystallization of 4 from acetone was carried out before use. Acrylonitrile (2), 2,2′-azobisisobutyronitrile (AIBN), *N,N*-dimethylformamide (DMF), and benzene were purified by conventional methods.

Preparation of Poly(N-propenoyl-9-acridinylamine-co-acrylonitrile) (5)

The acridine unit was incorporated into the side chain of poly(propenoyl chloride-*co*-acrylonitrile) (3) by the polymer reaction shown in Scheme I. Poly(propenyl chloride-*co*-acrylonitrile) (3) was synthesized as follows: $0.7\,\mathrm{cm^3}$ (8.62×10^{-3} mol) of 1, $4.15\,\mathrm{g}$ (7.82×10^{-2} mol) of 2, $0.07\,\mathrm{g}$ (4.26×10^{-4} mol) of AIBN, and $20\,\mathrm{cm^3}$ of DMF were placed in an ampule and sealed under nitrogen atmosphere. The polymerization was carried out at 55°C over a period of 65 h.

To the DMF solution containing $5.03\,\mathrm{g}$ ($2.59 \times$

Scheme I.

Figure 1. Sketch of the glass cell used for the transport experiment. Volume, 100 cm³; membrane area, 4.15 cm².

10^{-2} mol) of **4** was added the obtained polymer **3** solution without isolation of **3**. The mixture was stirred at an ambient temperature for 24 h. After removing the resulting 9-acridinylamine hydrochloride, the mixture was poured into methanol and filtered. The resulting precipitate, **5**, was then collected. The incorporation of **4** into **5** did not exceed more than 0.2 mol/mol because of the difficulty in making the copolymer membrane. Therefore, the content of **4** in **5** was limited to less than 0.1 mol/mol.

Polyacrylonitrile (**6**) was prepared by the usual radical polymerization of **2** initiated by AIBN.

Characterization of 5

An IR spectrum was taken by a Hitachi 260-50 infrared spectrophotometer.

Solution viscosity was measured with a 10 g dm^{-3} DMF solution at 30°C.

Preparation of Membrane

5 was dissolved in DMF (200 g dm^{-3}), and **6** containing **5** in the proportion of 57.7 : 42.3 (wt.%) was dissolved also in DMF (65 g dm^{-3}). These two solutions were poured onto a glass plate with an applicator, allowing the solvent to evaporate at around 40°C. The thickness of these membranes was *ca.* 40 μm. The **6** membrane was made in similar manner.

Transport of Halogen Ions

A sketch of a glass cell for transport experiment is shown in Figure 1. The membrane was placed in the middle of the two chambers of the cell. The transport experiments were carried out at 30°C. To detect the active transport of chloride ions Cl$^-$, the Cl$^-$ concentrations of the both the right (R side) and left (L side) chambers were made the same. The R side contained NaOH, while the L side contained
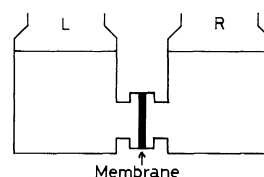
HCl. A mixture of Cl$^-$ and Br$^-$ was placed in the cell whose concentration of Cl$^-$ and Br$^-$ were the same in both the R and L sides so as to determine anion selectivity. Various concentrations of Cl$^-$ and Br$^-$ with various molar fractions were applied to adjust the total concentration of Cl$^-$ and Br$^-$ to 0.2 mol dm^{-3}.

Analysis

Cl$^-$ and Br$^-$ were separated by the ion-exchange method,[8] and their concentrations were determined by Mohr's method.

RESULTS AND DISCUSSION

Characterization of the Polymer 5

The IR spectrum of **5** indicated the following specific absorption bands: 2230 cm^{-1} (stretching vibration of $-C \equiv N$); 1635 cm^{-1} (amide I band); 1555 cm^{-1} (amide II band). The characteristic absorption at around 1720 cm^{-1} assigned to the stretching vibration of $-\overset{\overset{\displaystyle O}{\|}}{C}-$ in poly(propeonic acid-co-acrylonitrile), could hardly be observed. Thus, the propenoyl chloride unit in the polymer **3** reacted nearly quantitatively with **4**.

Elemental analysis of **5** is as follows: C, 65.09%; H, 5.45%; N, 19.35%; 0.10 mol of the **5** unit was in the polymer. From these results, the structure of **5** was identified as that shown in Scheme I. The reduced viscosity of **5** was 0.068 dm³ g^{-1}.

Active Transport

Figure 2 shows the time transport curves of Cl$^-$, it can be seen that chloride ions were transferred from the L side to the R side across the membrane against its concentration gradient. There was hardly any induction period during the transport.

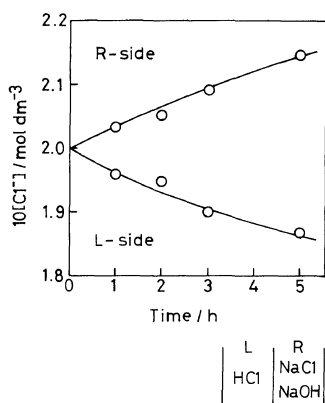From the IR spectrum of the membrane, it was

Figure 2. Time–transport curve of Cl^- through the **5** membrane. Fraction of acridine unit, 0.1; $[HCl]_{L,0} = [NaCl]_{R,0} = [NaOH]_{R,0} = 0.2$ mol dm^{-3}.

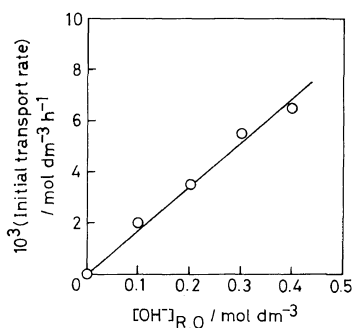**Figure 3.** Effect of OH^- concentration on the initial transport rate of Cl^- through the membrane. Fraction of acridine unit, 0.1.

Figure 4. Effect of the acridine unit fraction on the initial transport rate through the **5** membrane. $[HCl]_{L,0} = [NaCl]_{R,0} = [NaOH]_{R,0} = 0.2$ mol dm^{-3}.

Figure 5. Effect of feed fraction on the selectivity of anion transport through the **5** membrane. $[HCl]_{L,0} + [HBr]_{L,0} = [NaCl]_{R,0} + [NaBr]_{R,0} = [NaOH]_{R,0} = 0.2$ mol dm^{-3}; $[Cl^-]_{L,0} = [Cl^-]_{R,0}$; $[Br^-]_{L,0} = [Br^-]_{R,0}$.

concluded that the amide group in the polymer was not hydrolyzed under the experimental conditions. The transport rate was scarcely influenced by back-transfer of transported Cl^- from the R side to the L side.

The initial transport rate of Cl^- through the **5** membrane, whose acridine unit was 0.10, is plotted against the initial NaOH concentration on the R side in Figure 3. The initial transport rate was proportional to the initial NaOH concentration. Accordingly, the driving force of the transport was considered to be the OH^- concentration gradient across the membrane, and the active transport of Cl^- was achieved by the OH^- transfer.

In Figure 4, the initial transport rate is plotted as a function of the mol fraction of the acridine unit in the **5** membrane. The active transport through the **6**
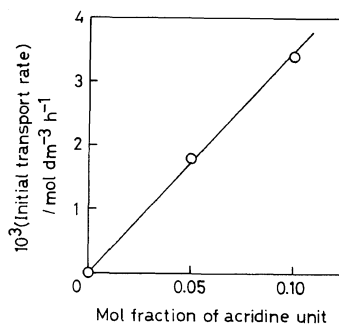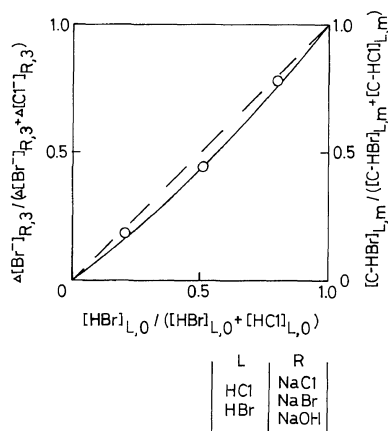
membrane having no acridine unit did not take place at all. But the membrane having the acridine unit led to the active transport of Cl^- and the initial transport rate was proportional to the mol fraction of the acridine unit. This suggests that the acridine unit incorporated into the membrane played an important role as a fixed carrier for the active transport of Cl^-.

Selective Transport

The relationship between the mol fraction of HBr on the R side and that of the transported Br^- fraction after 3 h to the R side is shown in Figure 5.

Fraction of transported Br^- =

$$\Delta[Br^-]_{R,3}/(\Delta[Br^-]_{R,3} + \Delta[Cl^-]_{R,3}) \quad (1)$$

It can be seen from Figure 5 that Cl^- was transported at a rate slightly faster than that of Br^-. Following three steps are considered to control the selectivity of halogen ions.[6]

1) Incorporation of halogen ions into the membrane.

2) Diffusion of halogen ions among the fixed carriers.

3) Release of halogen ions from the membrane to the outside.

Since both Cl^- and Br^- have the same hydrated radius,[9] it seems reasonable to assume that their diffusion rates among fixed carriers may be nearly the same. Also, the exchange reaction rate between OH^- and halogen ion at the R side of the membrane takes place randomly because of the fast ionic reaction. Therefore, the selective transport of $Cl^- - Br^-$ mixed system seems to depend on the incorporation of halogen ions into the membrane (Step 1), *i.e.*, the affinity between the fixed carrier and halogen ion.

The formation rate of acridine units with hydrogen halide on the L side of the membrane is thought to be comparable to the exchange reaction rate between OH^- and halogen ions on the R side of the membrane, and so equilibrium is apparently established on the L side of the membrane. The salt formation constant between the fixed carrier and HBr and HCl is defined by

$$C + HBr \xrightleftharpoons{K} C-HBr \qquad (2)$$

$$C + HCl \xrightleftharpoons{K'} C-HCl \qquad (3)$$
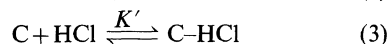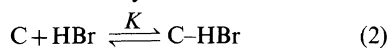
The concentration of each salt, $[C-HBr]_{L,m}$ or $[C-HCl]_{L,m}$, on the L side of the membrane is represented as

$$[C-HBr]_{L,m} = \frac{K[HBr]_{L,0}[C]_0}{1 + K[HBr]_{L,0} + K'[HCl]_{L,0}} \qquad (4)$$

$$[C-HCl]_{L,m} = \frac{K'[HCl]_{L,0}[C]_0}{1 + K[HBr]_{L,0} + K'[HCl]_{L,0}} \qquad (5)$$

where $[HBr]_{L,0}$ and $[HCl]_{L,0}$ are the initial concentrations of HBr and HCl on the L side; $[C]_0$ is the total concentration of the fixed carrier in the membrane ($[C]_0 = [C] + [C-HBr] + [C-HCl]$). The fraction of C–HBr on the L side of the membrane can be represented using the fraction of HBr on the L side as follows.

$$\frac{[C-HBr]_{L,m}}{[C-HBr]_{L,m} + [C-HCl]_{L,m}} = \frac{f_{Br}}{(1-k)f_{Br} + k} \qquad (6)$$

where f_{Br} and k are $[HBr]_{L,0}/([HBr]_{L,0} + [HCl]_{L,0})$ and K'/K, respectively. If the assumption that the present membrane depends on the affinity between the fixed carrier and halogen ion is valid, the composition of the transported halogen ions to the R side should be equal to the composition of the salt on the L side of the membrane as determined by eq 6. Trial and error methods were applied to eq 6, using various values of k. The solid line in Figure 5 was calculated by assuming the value $k = K'/K = 1.2$; the calculated line was in close agreement with that determined by experimental values. Thus, the selectivity of halogen ions was presumably caused by the affinity between the fixed carrier and halogen ions. Accordingly, the salt formation constant between the carrier and HCl was 1.2 times higher than that between the carrier and HBr.

CONCLUSION

Poly(*N*-propenoyl-9-acridinylamine-*co*-acrylonitrile) (5), having the basic acridine unit in its side chain, was obtained. The 5 membrane caused the active and selective transport of halogen ions. The explanation for this is that the selectivity of the active transport of halogen ions depends on the affinity between the fixed carrier (acridine unit) and halogen ions.

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