Active and Selective Transports of K$^+$ and Na$^+$ through Poly{3-[3-(4-hydroxyphenyl)phthalidyl]-4-hydroxystyrene-co-4-hydroxystyrene} Membrane

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ABSTRACT: The phenolphthalein analog was introduced into the side chain of poly(4-hydroxystyrene) by a polymer reaction. The blended membrane which was made by means of poly{3-[3-(4-hydroxyphenyl)phthalidyl]-4-hydroxystyrene-co-4-hydroxystyrene} and cellulose acetate showed capability for the active and selective transport of alkali-metal ions at moderately low concentrations.

KEY WORDS   Active Transport / Selective Transport / Phenolphthalein
Analog / Synthetic Polymer Membrane / Poly{3-[3-(4-hydroxy-
phenyl)phthalidyl]-4-hydroxystyrene-co-4-hydroxystyrene} / Lactone-con-
taining Polymer /

The authors have already reported the synthesis of poly(3-vinyl-1,4-butyrolactone-co-acrylonitrile)[1] (5), which has a five-membered lactone moiety as a side chain, and its polymer membrane has the capability of selective transport and the concentration (an active transport) of metal ions against their concentration gradients.[2]

Phenolphthalein is one of the well known acid-base indicators, having a lactone moiety. Its color changes at pH 8.3; that is, the ring-opening and the ring-closing processes of the lactone moiety take place in a weakly basic solution. In the present study, for the purpose of developing a new chemical membrane which can function at a relatively low alkali concentration, a poly(4-hydroxystyrene) carrying a phenolphthalein analog, poly{3-[3-(4-hydroxyphenyl)phthalidyl]-4-hydroxystyrene-co-4-hydroxystyrene} (1), was synthesized by a polymer reaction. The membrane was made by blending the present polymer (1) and cellulose acetate (CA). The membrane showed the capability of active and selective transport of alkali metal ions at moderately low concentrations.

EXPERIMENTAL

Preparation of the Polymer, Poly 3-[3-(4-hydroxyphenyl)phthalidyl]-4-hydroxystyrene-co-4-hydroxystyrene} (1)

By reference to the synthesis of phenolphthalein[3] the phenolphthalein analog was introduced into the side chain of poly(4-hydroxystyrene) (4) by a polymer reaction. The synthetic scheme is shown in Figure 1. A 2.2 cm^3 of concd sulfuric acid (3.9×10^{-2} mol) were added to a mixture of 5.0 g (3.4×10^{-2} mol) of phthalic anhydride (2), 5.0 g (5.3×10^{-2} mol) of phenol (3), and 4.1 g (3.4×10^{-2} unit mol) of poly(4-hydroxystyrene) (4). The mixture was heated for 10 h at 115—120°C. The reaction mixture was precipitated from a methanol–H$_2$O solution. The precipitate was treated with an ethyl acetate–sodium hydroxide aqueous solution, and an appropriate amount of NaCl was added. The polymer, 1, was obtained as a powdery precipitate. The chemical composition of 1 was determined by elemental analysis. No ash was found in the product, 1.

Spectroscopic Measurement

IR spectra were taken on a Hitachi EPI-G2 spectrophotometer. The NMR spectra were obtained by a JNM-FX 100 spectrometer, using dimethyl sulfoxide-d_6 (DMSO-d_6) solution of 1.
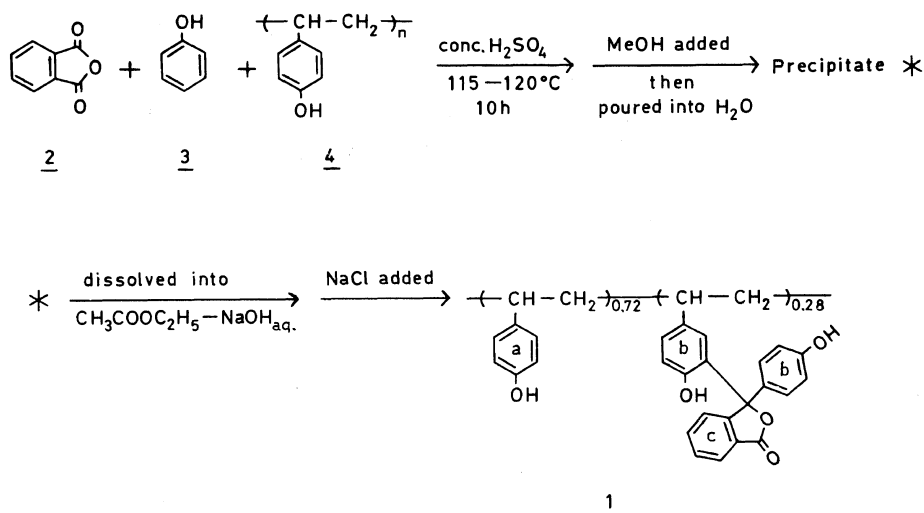
Figure 1. Synthetic scheme of poly{3-[3-(4-hydroxyphenyl)phthalidyl]-4-hydroxystyrene-*co*-4-hydroxystyrene} (1).

Preparation of Membrane

The blended membrane containing **1** and CA (acetyl content, 55%) in the proportions of 30:70 (wt%) was made from an ethyl methyl ketone solution (*ca.* 120 g dm^{-3}). The casting solution was poured onto a glass plate, allowing the solvent to evaporate at 30°C. The content of the phenolphthalein analog in this blended membrane was *ca.* 5 mol%. The thickness of this membrane was 150—170 μm.

Determination of the Acid Dissociation Constant, pK$_a$, of the Lactone Moiety of the Phenolphthalein Analog in the Side Chain of **1**

The acid dissociation constant of the lactone moiety of the phenolphthalein analog in the side chain of **1** was determined by spectrophotometric titration, using a Hitachi EPS-3T Recording Spectrophotometer. 1.55×10^{-3} g of **1** was dissolved in 50 vol% ethanol–aqueous solution which was then measured at various pH's at a wavelength of 260 nm. The degree of dissociation, α, is defined as follows.

$$\alpha = \frac{A_1 - A}{A_1 - A_2}$$

where A, A_1, and A_2 indicate the optical densities at various pH's, the extreme acid region, and the extreme alkali region, respectively. Using these degrees of dissociation, pK_a was estimated, using the Henderson–Hasselbalch equation.

Transport

Transport experiments were carried out in a poly(methyl methacrylate) cell consisting of two chambers, at 40°C under magnetic stirring. The membrane was laid out in the middle of the two chambers of the cell. The effective area of the membrane was 3.0 cm^2. The concentration of K$^+$ and Na$^+$ were measured by atomic absorption spectrophotometers (Jarrel ash AA780 and AA8200). The amount of Cl$^-$ was measured by the mercuric nitrate method.

RESULTS AND DISCUSSION

Characterization of the Polymer, **1**

The IR spectrum of the polymer, **1**, was different from that of the starting material, **4**, and it showed a new band at 1745 cm^{-1}, which is the characteristic stretching vibrations of the carbonyl group of the lactone ring, as is also the case of phenolphthalein.

The ^{1}H NMR spectrum of the DMSO-d_6 solution of **1** with tetramethylsilane as the internal standard showed characteristic signals; δ being 1.17 (backbone), 6.75 and 6.82 (benzene ring a), 7.04 and 7.12 (benzene ring b), 7.64 (benzene ring c), and 9.79 ppm (–OH). From these results, the structure of **1**

was determined as shown in Figure 1. The chemical composition of **1** was also determined by chemical analysis.

In the IR spectrum of **1** treated with 1/10 mol dm^{-3} KOH solution, the characteristic absorption at 1745 cm^{-1} (lactone) disappeared and a new absorption of 1400 cm^{-1} (–COO$^-$) appeared. This result indicates that a ring-opening reaction of the lactone moiety in **1** takes place under this reaction condition.

The pK_a of the lactone in **1** was determined to be about 11.0. That is to say, the ring-opening and the ring-closing processes of the lactone in **1** take place in *ca.* 1/1000 mol dm^{-3} alkali solution. The high liability to ring-opening is reasonable in consideration of the stability of the quinomethine structure which is similar to phenolphthalein,[4] as shown in Figure 2.
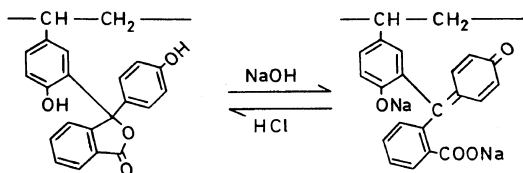

Figure 2. Scheme of the ring-opening and the ring-closing of the phenolphthalein analog.

Active Transport

An example of the time-transport curves of Na$^+$ is shown in Figure 3. Sodium ions were transferred from the R side to the L side across the membrane against its concentration gradient, while Cl$^-$ were scarcely transferred during the experiment. The induction period could hardly be observed during the transport with this membrane.

When the H$^+$ concentration was the same on both sides of the membrane, Na$^+$ was not concentrated to the L side. The rate of the counter-transport of Na$^+$ increased with the H$^+$ concentration. These results suggest that the driving force of the Na$^+$ transport is the counter-flow of the H$^+$ from the L side to the R side.

The mechanism of the active transport is shown as in Figure 4. Metal ions were carried by the ring-opened carboxylates, while H$^+$ was counter-flowed.

Figure 5 shows the time-transport curves of Na$^+$ with the membrane made of **1** and CA, the membrane made of **4** and CA, and the membrane made of CA, where the initial concentration of Na$^+$ was 1.0×10^{-3} mol dm^{-3}. Under this condition,
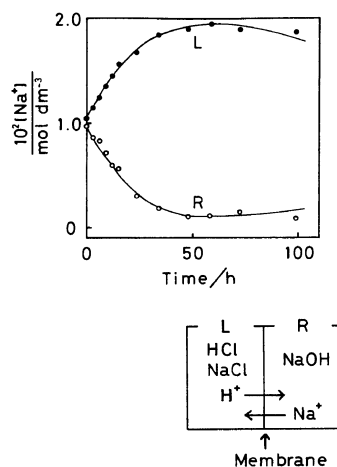

Figure 3. Time transport curves of Na$^+$ with 1+CA membrane:
[HCl]$_0$ = 1.0×10^{-2} mol dm^{-3};
[NaCl]$_0$ = 1.0×10^{-2} mol dm^{-3};
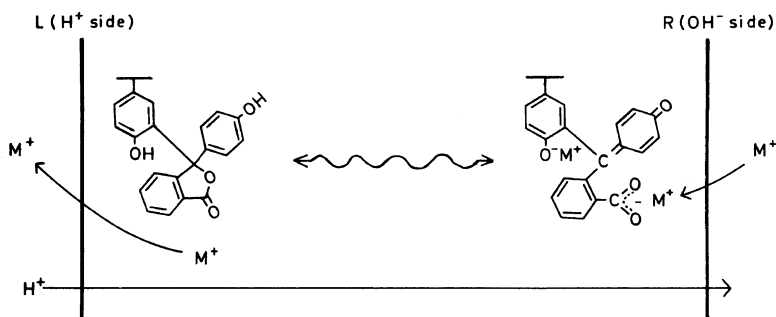[NaOH]$_0$ = 1.0×10^{-2} mol dm^{-3}.
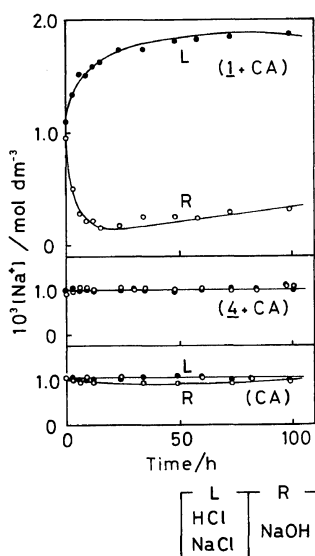

Figure 4. Tentative mechanism of the transport of metal ions.

Figure 5. Time transport curves of Na^+ with various membranes:
$[HCl]_0 = 1.0 \times 10^{-3}$ mol dm^{-3};
$[NaCl]_0 = 1.0 \times 10^{-3}$ mol dm^{-3};
$[NaOH]_0 = 1.0 \times 10^{-3}$ mol dm^{-3}.

was 1.0×10^{-2} mol dm^{-3} (Figure 3), the increase in Na^+ concentration on the L side was almost in accord with the decrease in the Na^+ concentration on the R side. While, under the condition that the initial concentration was 1.0×10^{-3} mol dm^{-3} (Figure 5), the increase on the L side was nõt in accord with the decrease on the R side. When the amount of Na^+ was comparable with the lactone moiety in the membrane, the uptake of Na^+ in the membrane became significant, and this uptake was calculated to be *ca.* 1.2×10^{-5} mol. The amount of the phenolphthalein analog moiety in the membrane was *ca.* 1.1×10^{-5} mol, which is almost the same amount of the uptake. Under this transport condition, since the pH of the alkali solution is 11.0, about a half of the lactone moiety in **1**, whose pK_a is about 11.0, is opened. Accordingly, the number of Na^+ participated in one phenolphthalein analog moiety in the membrane was calculated to be two, as shown in Figure 2. It is speculated that the average boundary zone between the ring-opening and the ring-closing lies in the middle of the membrane.

The initial condition and the maximum values of the concentration of Na^+ by the active transport are summarized in Table I. The present membrane in Exptl. No. 1 and 2, show effective concentrations of Na^+ against their concentration gradients. In addition, Exptl. No. 1 and 2 show that no water was transferred.

The blended membrane consisting of **1** and CA showed high values for the maximum concentration and for the efficiency of the active transport. In

the lactone in **1** was effectively opened, and the effective transport of Na^+ took place. In contrast to this, both the membranes made of **4** and CA, and that made of CA showed no functionality. These results also imply that the polymer-bonded phenolphthalein analog in the membrane played an important role in the active transport of Na^+. Under the condition that the initial concentration

Table I. Active transport of Na^+ with $1+CA$, CA, $4+CA$, and **5** membranes[c]

Exptl. No.	Membrane	$[HCl]_{L,0}$	$[NaCl]_{L,0}$	$[NaOH]_{R,0}$	Maximum concentration
		mol dm^{-3}	mol dm^{-3}	mol dm^{-3}	%
1	$1+CA$	1.0×10^{-2}	1.0×10^{-2}	9.8×10^{-3}	85[a]
2	$1+CA$	1.0×10^{-3}	1.0×10^{-3}	9.6×10^{-4}	69[a]
3	CA	1.0×10^{-3}	1.0×10^{-3}	9.6×10^{-4}	0
4	$4+CA$	1.0×10^{-3}	1.0×10^{-3}	1.0×10^{-3}	0
5	5	2.0	2.1	1.9	28[b]
6	5	1.0	1.0	1.0	14[b]

[a] $\dfrac{[Na^+]_{L,max} - [Na^+]_{L,0}}{[Na^+]_{L,0}}$ [b] $\dfrac{(Na^+)_{L,max} - (Na^+)_{L,0}}{(Na^+)_{L,0}}$

[c] For **1**, **4**, **5**, and CA, see the text.

addition, the present membrane has a high capability to transport of Na^+ even at a low concentration, in contrast to the membrane **5** studied before.

Permselectivity of K^+ and Na^+

The authors investigated the permselectivity of K^+ and Na^+. In all experiments, the concentrations of KOH and NaOH were 5.0×10^{-3} mol dm^{-3}, and the concentrations of HCl varied. The initial flux was almost proportional to the initial proton concentration. This also suggests that the proton plays the role of a driving force in the transport of ions. The permselectivities of K^+ and Na^+ against various initial proton concentrations are summarized in Table II. The permselectivities, K^+/Na^+, were 1.0—1.9. As the H^+ concentration increased, the permselectivity, K^+/Na^+, also increased. This indicates that the hydrophobicity of the membrane controls the permselectivity; the more hydrophobic the membrane, the greater the transport of K^+. This tendency is also found in the

Table II. Influence of H^+ concentration on the selectivities in transport of K^+ and Na^+

LOG[H^+]	K^+/Na^{+a}
-1	1.73
-2	1.86
-3	1.28
-4	1.03

$$^a \ K^+/Na^+ = \frac{[K^+]_{L,t}/[K^+]_{R,0}}{[Na^+]_{L,t}/[Na^+]_{R,0}}$$

membrane of poly(3-vinyl-1,4-butyrolactone-*co*-acrylonitrile).[2]

CONCLUSION

The polymer, poly{3-[3-(4-hydroxyphenyl)-phthalidyl]-4-hydroxystyrene-*co*-4-hydroxystyrene} (**1**), which has the phenolphthalein analog situated in its side chain was obtained. The blended membrane containing **1** and CA has a high capability to function as an active transport of alkali metal ions at relatively low concentrations. In addition, the present membrane shows the permselectivity toward K^+ and Na^+ being 1.0—1.9.

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