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Active Transport of Alkali Metal Ion Through a Membrane Composed of Gluconolactone-Containing Polymer

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SUMMARY

The membrane composed of gluconolactone-containing polymer was prepared by the following three steps, (1) the copolymerization between acrylonitrile and a styrene derivative carrying a protected glucose substituent, (2) casting a membrane from the DMF solution of the copolymer, and (3) a sequence of reactions for the membrane. It exhibited active transport of Na^+ ion against the concentration gradient.

INTRODUCTION

Current efforts for development of efficient systems capable of separation and concentration of metal ions have focused considerable interest on liquid and polymer membranes. Active and selective transport of alkali metal ions through a synthetic membrane was realized for the first time by Shimidzu *et al.*(1977, 1980, and 1981) with use of several lactone-containing polymers. In the course of the studies on the polymers endowed with sugar derivatives as pendant groups (KOBAYASHI and SUMITOMO, 1978, 1980, and 1981), the membrane composed of another lactone-containing polymer has been prepared. This paper describes its preparation and application to the transport phenomena.

RESULTS AND DISCUSSION

Preparation of the Membrane Composed of Gluconolactone-Containing Copolymer

The styrene derivative carrying a protected glucose substituent on the benzene ring was copolymerized with acrylonitrile. The resulting copolymer I was cast to a tough and transparent membrane, which was then subjected to a series of the reactions of Scheme 1. As judged by the IR spectroscopy (Fig. 1), each transformation went to completion without change of the acrylonitrile unit.

Removal of the isopropylidene protection converted I to the glucopyranose-containing copolymer II. Instead of the bands due to methyl groups at 2980, 1385, and 1375 cm^{-1}, a hydroxyl absorption appeared at 3400 cm^{-1}. The change from the furanose to the pyranose ring structure was inferred

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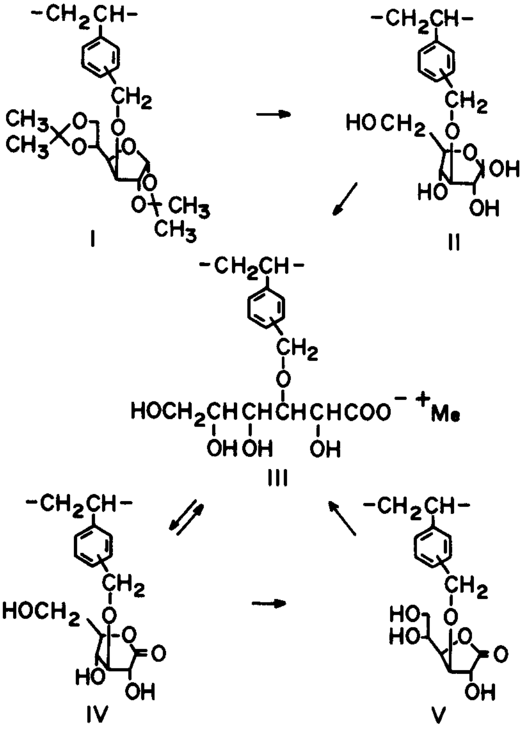
SCHEME I Chemical Transformations of the Copolymer Membranes (Acrylonitrile component is not formulated)



from analogy with the corresponding homopolymer. Subsequent hypoiodite oxidation gave the copolymer containing sodium gluconate moiety (III), which was indicated by the appearance of the absorption at 1600 cm^{-1}.

Lactonization of III was carried out in 0.1 M hydrochloric acid solution. The carbonyl band was shifted to 1740 cm^{-1} after 30 min and to 1780 cm^{-1} after 2 days. The former band was attributable to the kinetically-controlled six-membered glucono-1,5-lactone (IV) and the latter to the thermodynamically-controlled five-membered glucono-1,4-lactone (V). The gluconate absorption (1600 cm^{-1}) was restored by treating IV and V with 0.1 M sodium hydroxide solution overnight. It was possible to repeat the interconversion between the gluconate and the gluconolactone moieties.

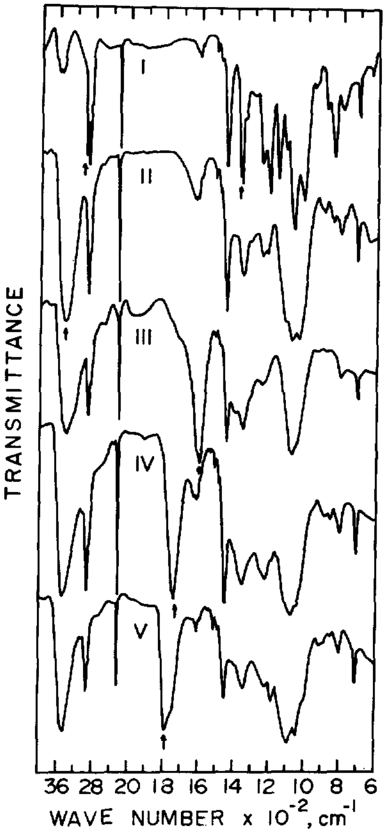


Fig. 1. IR spectra of the copolymer membranes. The numbers correspond to those in Scheme I.

Active Transport

The membrane equilibrated to the glucono-1,4-lactone moiety (V) was used for the transport experiment. Fig. 2 shows the time-course of the Na^+ concentrations of both sides separated by the membrane. Its initial concentration in the left solution was a little higher than that in the right solution. At the beginning of the transport, the former increased with time; in contrast, the latter decreased. Thus Na^+ ion moved from a region of low concentration to a region of high concentration against its concentration gradient. The concentrations reached a maximum in the left side and a minimum in the right side in about 10 hr, and converged to the average in 80 hr.

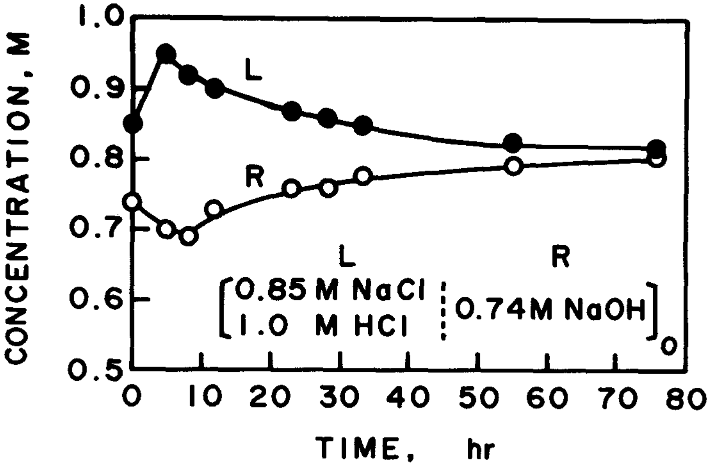


Fig. 2. Active transport of Na^+ ion through the membrane composed of gluconolactone-containing polymer.

The active transport can be explained by the tentative mechanism proposed by Shimidzu *et al.* as follows. On the alkaline (right) side, the lactone moiety exists in the ring-opened carboxylate form. Metal ions were bound to the carboxylate groups, taken into and transferred through the membrane, and released by H^+ on the acid (left) side where the lactone moiety exists in the ring-closed form. That is, metal ions were transported from the alkaline side to the acid side. The driving force of the active transport is the difference of H^+ concentration. The gradual decrease of H^+ concentration in the left side lowered the efficiency of active transport and, in time, resulted in the back-transfer of the concentrated Na^+ ions.

EXPERIMENTAL

Preparation of the Membrane

Radical copolymerization between 1,2:5,6-di-*O*-isopropylidene-3-*O*-vinylbenzyl-α-D-glucofuranose (0.004 mol) and acrylonitrile (0.196 mol) was carried out in DMF (20 ml) at 60 °C with 0.05 mole % azobisisobutyronitrile as initiator for 2 hr. The mole fraction of the sugar residue in the resulting copolymer (yield, 16.8 %) was 0.11 and the intrinsic viscosity ([η]) in DMF at 25 °C was 2.85. A tough and transparent membrane of 0.01 mm thick was cast from a DMF solution (5 %).

Following chemical modifications were carried out by immersing the membrane in aqueous reaction solutions with occasional shaking at room temperature. The membrane was washed with distilled water and dried in a vacuum oven at 50 °C. IR spectra were recorded on a JASCO A-3 infrared spectrophotometer.

The isopropylidene protection was removed by treating the membrane I with a trifluoroacetic acid-water (0.2:0.8 v/v) mixture for 3 hr and then with 12 N sulfuric acid for 1 day. The subsequent oxidation was carried out in 0.1 N iodine solution for 30 min and then in 0.1 N sodium hydroxide solution for 3 hr. The procedure was repeated three times until the relative intensity of the carboxylate band at 1600 cm^{-1} became equal to that of the homopolymer analogue.

Transport

The membrane was mounted tightly between the two 50 ml compartments made of poly(methyl methacrylate), and was aged with 0.1 M hydrochloric acid solution overnight. The effective area of the membrane was 4.52 cm^2. Aqueous 0.74 M sodium hydroxide solution was charged to the right compartment and 0.85 M sodium chloride and 1.0 M hydrochloric acid solution to the left compartment. The transport was carried out at 29 °C under magnetic stirring. At intervals, 0.5 ml of each solution was pipetted, diluted, and analyzed by using a Hitachi 208 atomic absorption spectrophotometer.

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