-NOTE-

N-벤질화 폴리비닐아민의 합성과 아미노산에스테르 양이온 수송

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Synthesis of N-Benzylated Polyvinylamine and Its Transport Properties of Amino Acid Ester Cations

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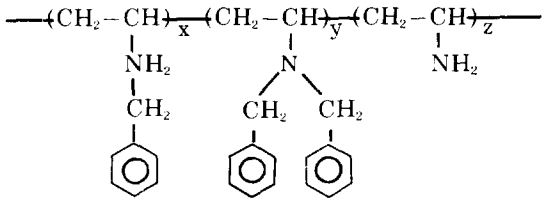
Several naturally occurring polyamine derivatives are recognized to play important roles in biological activity and transportation of anionic and cationic species.[1] As synthetic model compounds, some kinds of polyamine derivatives have been drawing much attention.[2] In particular, polyvinylamine is of interest because it showed unique and strong complexing ability for transition metal cations[3] and also has binding ability for anions. With such interest, the authors prepared N-benzylated polyvinylamine(I)to apply to a lipophilic carrier of liquid membrane and carried out the experiment of transport of amino acid ester cations by using it as a carrier of liquid membrane.



Polyvinylamine as a precursor of I was prepared according to the method of Dawson et al[4]. I was synthesized by the following. Benzylchloride (6.4ml) was dropped into an aqueous solution (25ml) of polyvinylamine hydrobromic acid(5g) and sodium hydroxide(4.3g), and the mixture was stirred overnignt at room temperature. The crude product was extracted with chloroform, and the chloroform solution was washed with water repeatedly, and dried over sodium sulfate. After removal of chloroform, the polymer was freeze-dried by using benzene as a solvent, and the yield was 3.8g.

Its infra-red absorption bands due to C-H bond of phenyl group of I were showed at 740, 700 and 615cm^{-1}, and its band due to C-N bond showed at 1140cm^{-1}. NMR spectrum of I was measured from TMS internal standard with a Varian A-60 analytical spectrometer. It was shown in Fig. 1. The peaks around δ7.2 and δ1.5 were assigned to the hydrogens of benzyl ring and methylene group of main chain, respectively. The peak around δ3.6 was attributable to the hydrogens of -CH- group of main chain and methylene group of benzyl group, respectively. The degree of benzylation was estimated to be about 0.90 from the total peak area of NMR

spectrum. This value was obtained under the assumption that only one benzyl group was substituted on the nitrogen of amino group.

The benzylated polyvinylamine was soluble in chloroform, benzene and trifluoroacetic acid. The inherent viscosity of the polymer was 0.09 at 25°C when chloroform was used as the solvent.

Liquid membrane transport experiments were performed by using an U-tube glass cell[1] as shown in Fig. 2. The concentration of amino acid ester cation for the transport rate was measured with UV spectrophotometer. The transport rates shown in Table 1 were obtained from the rates of appearance of guest cations into A_2. As shown in Table 1, the transport rates in the presence of carrier were much larger than those in the absence of the carrier. Therefore, it was evident that the benzylated polyvinylamine efficiently transported these amino acid ester cations. Also, the rate of phenylalanine ethyl or methyl ester cation was much bigger than that of tyrosine methyl ester cation. This result was similar to that obtained by using lipophilic polyethyleneimine as a carrier of liquid membrane.[2] The difference between the transport rate of phenylalanine ester cation and that of tyrosine ester cation might be due to hydroxyl group of the latter. The rate of tyrosine methyl ester cation was also higher than that of tyramine cation. This result indicates that

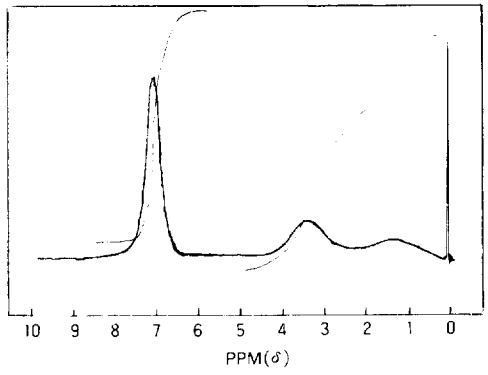


Fig. 1. NMR spectrum of N-benzylated polyvinylamine in $CDCl_3$.

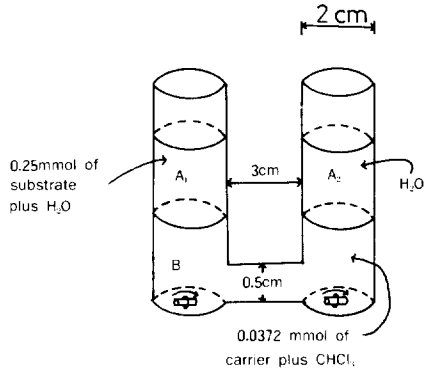


Fig. 2. Experimental setup.

Table 1. Transport Rate of Amino Acid Ester Cation in the Presence of Carrier(A) and in the Absence of Carrier(B) at 30°C[a].

Amino Acid Ester		Transport rate(mole / hr)		A / B
		A	B	
Phenylalanine ethylester hydrochloride	$\langle O \rangle$-CH_2-$CH(NH_2 \cdot HCl)$-$COOCH_2CH_3$	1.37×10^{-4}	1.66×10^{-6}	82.5
Phenylalanine methylester hydrochloride	$\langle O \rangle$-CH_2-$CH(NH_2 \cdot HCl)$-$COOCH_3$	1.26×10^{-4}	–	–
Tyrosine methylester hydrochloride	HO-$\langle O \rangle$-CH_2-$CH(NH_2 \cdot HCl)$-$COOCH_3$	1.59×10^{-5}	2.34×10^{-6}	6.8
Tyramine hydrochloride[b]	HO-$\langle O \rangle$-CH_2-CH_2-$NH_2 \cdot HCl$	8.28×10^{-6}	7.30×10^{-7}	11.3

[a] Initial conditions : 0.25 mmol of substrate and 5 ml of H_2O in A_1 ; 12 ml of chloroform as membrane and 0.0372 mmol(x repeating unit) of carrier in B ; 5 ml of H_2O in A_2.

[b] This compound is not amino acid.

the role of carbonyl group of tyrosine may be important in the transport of the amino acid ester cation by the carrier because tyramine cation has no ester group.

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