

Amphiphilic Graft Copolymer Latex Membranes.

VI. Poly(vinyl Alcohol)-Acrylonitrile-*N*-Hydroxyethyl Acrylamide Graft Copolymer Latex Membranes

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Synopsis

Poly(vinyl alcohol)(PVA)-acrylonitrile(AN)-*N*-hydroxyethyl acrylamide (HEAAm) graft copolymer latex membranes were prepared and properties of the membranes were compared with those of PVA-AN graft latex membranes and Cuprophane PT-150. The physical constants of HEAAm were determined and the tautomerization between hydroxyethyl amide group and aminoethyl ester group upon pH changes was ascertained by infrared spectrum of poly(HEAAm) film. An increase in HEAAm content in the membrane enhanced permeabilities of solute in aqueous solutions in comparison with PVA-AN graft latex membranes, maintaining good mechanical properties in wet state. With pH variation, the permeability of the nonionic solute was unchanged, but that of the anionic solute in acidic condition was superior to that in basic condition, and the permeability of the cationic solute exhibited the opposite trend. The behavior of ionic solute were attributable to the effect of the tautomerization of the functional group in the membrane.

INTRODUCTION

The regenerated cellulosic membranes produced by the cuprammonium process, Cuprophane, has been widely used as dialysis membranes of artificial kidney, but several disadvantages have been pointed out.^{1,2} To improve the permeabilities, several hydrophilic synthetic polymer membranes have been reported, but there is scarcely any promising membrane in the cause of poor mechanical properties in wet state. The synthetic polymer membranes³ practiced in use or being hopeful are polyacrylonitrile membrane (PAN membrane),^{4,5} polycarbonate membrane (PC membrane),⁶ polysulfone membrane (PMD membrane, by Amicon Co. Ltd.), poly(methyl methacrylate) membrane (PMMA membrane),⁷ and ethylene-vinyl alcohol membrane (EVA membrane).⁸ Graft copolymer or block copolymer membranes with hydrophilic and hydrophobic chains have been interested as membrane materials. The microstructure and mechanical properties of the graft copolymer latex membrane consisting of poly(vinyl alcohol)(PVA; hydrophilic polymer chain) and polyacrylonitrile (PAN; hydrophobic polymer chain) were reported by Ohtsuka et al.^{9,10} The stability *in vivo* and permeabilities of PVA-acrylic graft copolymer latex membranes, and PVA-methyl methacrylate (MMA)-methyl acrylate (MA) graft latex membranes were reported by Masuhara et al.¹¹⁻¹³ We also reported the permeabilities of solutes and mechanical properties in wet state of the graft co-

polymer latex membranes prepared from PVA-AN and various monomers, i.e., MA for providing the flexibility to membranes, acrylamide (AAm) for providing the hydrophilic domain,¹⁴ and 2-hydroxyethyl methacrylate (HEMA) for providing good permeabilities of solutes, the blood compatibility, and antitoxity.^{15,16} And in two previous papers, we have performed improvement in poor water permeability of the graft copolymer latex membrane by solvent treatment of the membrane¹⁷ and graft copolymerization in the presence of various kinds of additives.¹⁸

Ogata et al.¹⁹ prepared a membrane containing *N*-hydroxyethylamide group by modifying the corresponding copolymer, and reported the transport phenomena of ionic solutes in this membrane considering the rearrangement²⁰ from *N*-hydroxyethylamide group to aminoethyl ester group under an acidic condition.

In this paper, we examined PVA-AN-*N*-hydroxyethyl acrylamide (HEAAm) graft copolymer latex membranes. HEAAm was synthesized according to Jones,²¹ where its physical constants are not described. The physical constants of HEAAm monomer were determined and the tautomerization of poly(HEAAm) upon pH changes was confirmed. The characteristic permeability of the above latex membrane is also discussed together with the above rearrangement.

EXPERIMENTAL

Chemicals

Poly(vinyl alcohol)(PVA; by Nippon Synthetic Chemicals Co., Ltd.: the average degree of polymerization, 1690; the degree of saponification, 99.2%) was purified by precipitation with methyl alcohol from 5 wt % aqueous solution. Acrylonitrile (AN) was purified by distillation. Ceric ammonium nitrate (Kanto Chemical Co., Inc., Japan) was used after vacuum drying. Acrylic acid, thionyl chloride, cuprous chloride, monoethanolamine, and acetonitrile (Wako Pure Chemical Industries, Ltd., Japan) were used without further purification. All other chemicals of reagent-grade was used without further purification.

Synthesis of *N*-Hydroxyethyl Acrylamide²¹

Acryloyl chloride prepared from acrylic acid and thionyl chloride in the presence of cuprous chloride was added dropwisely to the mixture of monoethanolamine, acetonitrile, and pyrogallol under -5 – -10°C . After filtration, acetonitrile was removed by evaporation under reduced pressure and distilled *in vacuo*. The oily distillate was crystallized below -20°C in the refrigerator, and followed by filtration in order to remove the oily part. Such a solidification process was repeated until thin layer chromatogram was composed of a single spot. The infrared spectra (Hitachi Perkin-Elmer 225 Grating Infrared Spectrophotometer), and the nuclear magnetic resonance spectra (Bruker WM250 Spectrometer) of the resulting product were measured.

Preparation of Graft Copolymer Latexes and Graft Copolymer Latex Membranes

The graft copolymer latexes were prepared from the similar procedure to Ref.

9 as follows: The mixtures of AN and HEAAm were graft-copolymerized onto PVA in 5 wt % aqueous solution using ceric ammonium nitrate (2.6 wt % based on monomers) under a nitrogen atmosphere at 25°C for 2 h. To improve the storage stability of the latexes, the acid and the inorganic salt in the latexes were removed by a treatment with ion-exchange resins (monobed of Amberlite IRA-410 and IR-120B by Rohm and Haas Co., Ltd.). Then, the pH and specific conductivity of the resulting latexes were measured. The latex particles were observed directly by Hitachi transmission electron microscope UH-12AS. The particle size d (cm) was calculated by

$$d = \frac{\sum n_i d_i^3}{\sum n_i d_i^2} \quad (1)$$

where n_i is the number of the particle with a diameter d_i .

The graft copolymer latexes adjusted to pH = 2.0 with 1N hydrochloric acid were spread on PET film (Fujitac by Fuji Photo Film Co., Ltd.) stucked tightly on a glass plate, and followed by evaporation of water under 65% relative humidity at 20°C to give membranes with 11–15 nm thickness. The membranes were extracted with water at 80°C for 48 h to remove water-soluble components and then stored in distilled water until required for use.

Composition of the Membranes

The composition of the membranes was determined from elemental analysis data.

Mechanical Properties in Wet State

Stress-strain curves of the membranes in wet state at 20°C were recorded for specimens with 15 mm width and 40 mm span length by Tensilon UTM-III (Toyo Baldwin Co., Ltd.) at a crosshead speed of 50 mm/min.

Permeabilities of Solutes

Concentration changes of the various solutes as a function of time were measured under 37.0°C at 800 rpm by using a batch dialyzer, and the apparent permeability coefficient P (cm²/s) was calculated by

$$J_s = P\Delta C/L \quad (2)$$

where J_s is solute flux (mol/cm²·s), ΔC is concentration difference (mol/cm³) across the membrane, and L is membrane thickness (cm). The concentration of most of the solutes were determined spectrometrically as follows: *p*-dimethylaminobenzaldehyde method²² for urea (initial concentration 200 mg/L); phenol-sulfuric acid method²³ for glucose (1000 mg/L), sucrose (1000 mg/L), and raffinose (1000 mg/L); and Seligson's method²⁴ for sodium sulfobromophthalein (BSP, 400 mg/L). Vitamin B₁₂ (50 mg/L) was determined by the absorbance at 560 nm, *p*-toluenesulfonic acid (*p*-TSA, 1000 mg/L) at 222 nm and triethylbenzylammonium hydroxyde (TEBA, 1000 mg/L) at 209 nm.

When the dialyses of the ionic solutes were carried out under various pH in the solutions containing acid or base, pH in both compartments of the dialyzer was varied in the course of dialysis. Therefore, the buffer solutions (pH 2.0 and 12.0) should be used to control the pH in the solutions.

Water Permeability

Ultrafiltration apparatus (MC-2 by Bio Engineering Co., Ltd.) was used under the condition at 20°C and pressure difference of 100 mm Hg. The water permeability coefficient K (cm²) was calculated by

$$K = VL\eta/tA\Delta P \quad (3)$$

where V is volume (cm³) of water transported, L is membrane thickness (cm), η is viscosity of water (cP), t is transportation time (s), A is membrane area (cm²), and ΔP is pressure difference (dyn/cm²).

Water Content of the Membrane

The water content H_w (%) of the membrane was defined by

$$H_w = \frac{W - W_0}{W_0} \times 100 \quad (4)$$

where W_0 is the weight (g) after drying at 105°C for 5 h and W is the weight (g) at wet state.

Texture of the Membrane

A field emission scanning electron microscope (FESEM-JFSM30, by JEOL Ltd.) was employed for observation of surface of the membrane which was in contact with air for membrane processing. The specimen was coated with gold-palladium alloy with about 50 Å thickness.

RESULTS AND DISCUSSION

Synthesis of *H*-Hydroxyethyl Acrylamide (HEAAm)

The reaction mixtures should be kept below -5°C in the synthetic reaction because of high reactivity of HEAAm. The total yield of the product was about 10%.

The melting point of the product was -15--16°C, and the refractive index was 1.4919 at 18.0°C.

As shown in Figure 1, HEAAm exhibited characteristic absorptions due to vinyl (1415 cm⁻¹, 1630 cm⁻¹, 3080 cm⁻¹) and amide (1550 cm⁻¹, 1665 cm⁻¹). As shown in Figures 2 and 3, H and ¹³C NMRs also support the chemical structure of HEAAm.

PVA-AN-HEAAm Graft Copolymer Latex Membranes

Ingredients charged, monomer conversions, particle sizes of the latexes, amounts of extract of the membranes with hot water, water contents of the membrane, and weight fractions of each component for PVA-AN-HEAAm graft copolymer latex membranes are listed in Table I. In the case of adding the large amount of HEAAm [PVA-AN-HEAAm = 5-15-7.5 (g)], the gelation of the contents in the flask took place soon after an injection of the initiator. Even in

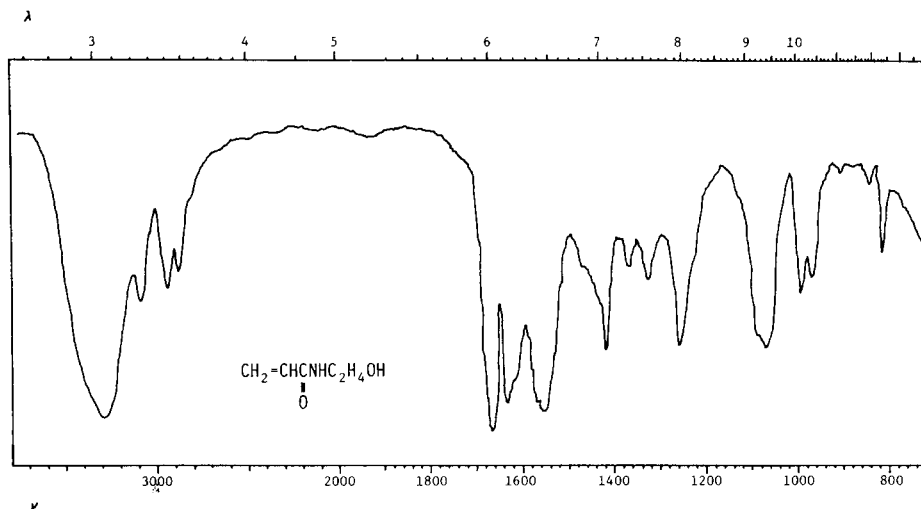


Fig. 1. Infrared spectrum of *N*-hydroxyethyl acrylamide.

the homopolymerization of HEAAm in an aqueous solution, the gelation occurred at the concentration higher than 5 wt %. Therefore, the aqueous concentration of HEAAm was limited below 5 wt %. A particle size of the latex tended to increase with an increase in the amount of HEAAm. An extract of the membrane with hot water was in the range of 2–3%, which was scarcely related with the composition of the membrane. On the other hand, a water content of the

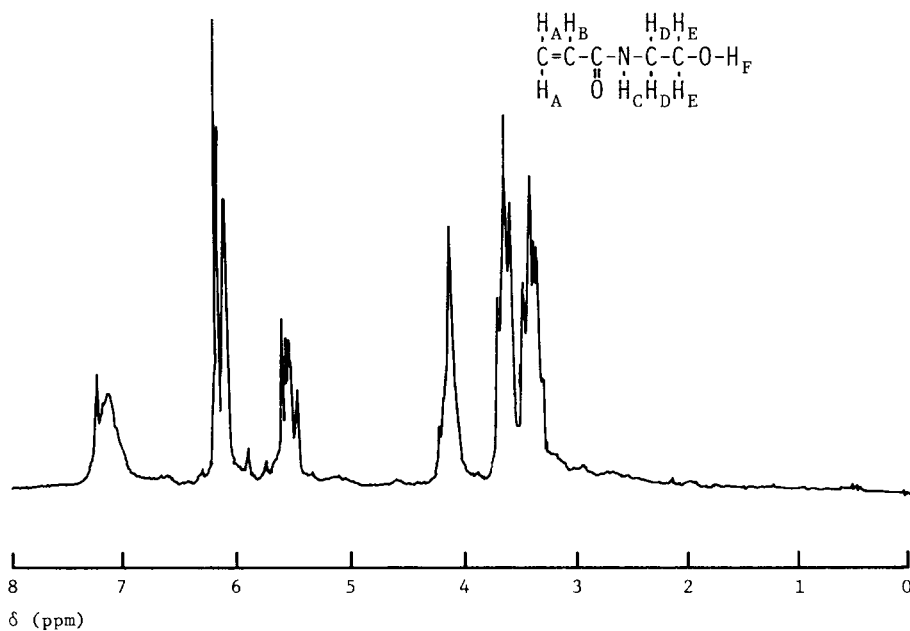


Fig. 2. Proton NMR chart of *N*-hydroxyethyl acrylamide. δ (ppm): (H_A) 6.15; (H_B) 5.55; (H_C) 7.1; (H_D) 3.65; (H_E) 3.41; (H_F) 4.12.

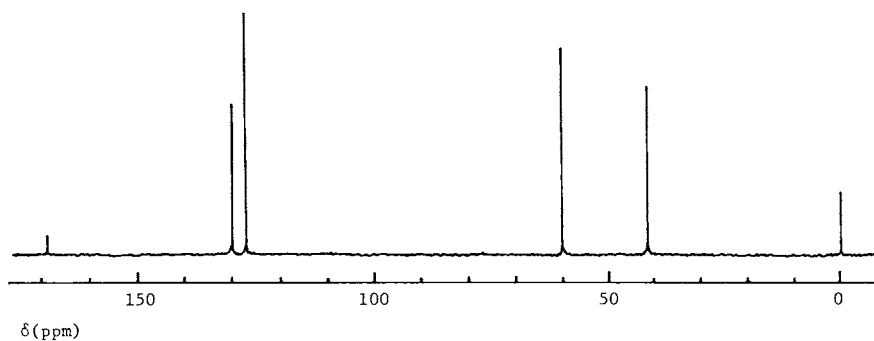
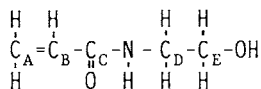


Fig. 3. ^{13}C NMR chart of *N*-hydroxyethyl acrylamide. δ (ppm): (C_A) 127.3; (C_B) 130.0; (C_C) 168.7; (C_D) 41.6; (C_E) 60.0.

membrane increases with an increase in hydrophilic component (PHEAAm+PVA).

As shown in Figure 4, contour of the particle in the membranes became indistinct with an increase in the amount of HEAAm and adherences among particles occurred.

Mechanical properties in wet state of the membranes are listed in Table II. The microstructure of these membranes was quite similar to those of PVA-AN,⁹ PVA-AN-MA,¹⁰ and PVA-AN-HEMA¹⁵ latex membranes. The relations between the mechanical properties and the chemical compositions of the latter membranes had been explained on the basis of a composite membrane structure.

TABLE I
Composition and Properties of PVA-AN-HEAAm Graft Latexes^a and Graft Latex Membranes

No.	HEA-Am(g)	Monomer conversion (%)	Latex particle size (nm)	Extract with hot water (%)	Water content (%)	Composition of membrane ^b		
						PVA	PAN	PHEAAm
1	0	86.3	61.6	2.2	39.3	0.256	0.744	0
2	1.25	97.7	61.8	2.4	43.0	0.238	0.686	0.076
3	2.5	100.0	62.0	3.3	45.7	0.231	0.657	0.112
4	3.75	94.9	66.5	2.7	49.7	0.230	0.631	0.139
5	5.0	92.3	72.9	3.6	53.2	0.199	0.591	0.210

^a PVA 5 g, H₂O 95 g, AN 15 g; $\text{Ce}^{4+} = 0.052 \times (\text{AN} + \text{HEAAm})$.

^b In weight fraction.

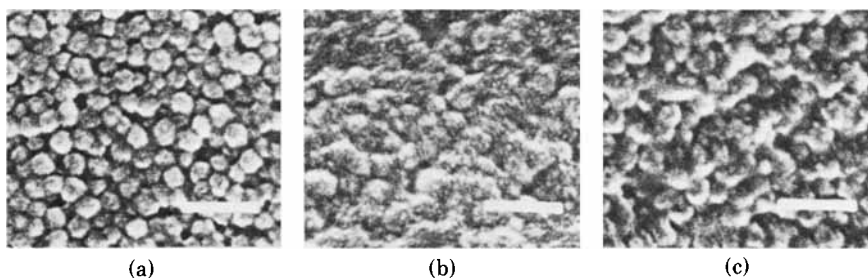


Fig. 4. Scanning electron micrographs of surface texture for graft copolymer latex membranes: (a) no. 1; (b) no. 3; (c) no. 5. The bars represent 100 nm.

Therefore, we attempt to explain the characteristic properties of the membranes containing HEAAm on the line of the above composite structure.

It is assumed that PVA and PAN components are located in the continuous and dispersion regions, respectively, and the PHEAAm component exists in both continuous and dispersion regions. In the case of such the composite structure species, a stress is concentrated at the interface of the two regions. When the dispersion region is soft, deformation of the interface occurs easily in accordance with a stress and a stress concentration at the interface is reduced. Therefore, larger strain is required up to the yield point. Hydrophilic component such as HEAAm component should affect flexibility in both the continuous region and the dispersion region, since HEAAm component is assumed to exist in both regions. Therefore, the Young's modulus of the membrane decreased with an increase in hydrophilic components. An increase in tensile strength with an increase in hydrophilic component to some extent is presumably due to reduction in stress concentration. Further increase in hydrophilic component brought a decrease in tensile strength due to an increase in the water content. Considering that PHEAAm is poorer in affinity to water than PVA, it is conceivable that the change of elongation at break was small with an increase in PHEAAm component. On the whole, the tensile strength and elongation at break of PVA-AN-HEAAm graft copolymer latex membranes were excellent compared with those of Cuprophane PT-150.

Permeabilities of the Membranes

Solute permeability and water permeability of PVA-AN-HEAAm graft copolymer latex membranes are listed in Table II. The relationship between hydrophilic components (PVA + PHEAAm) in the membrane and permeabilities of solutes, and the water content of the membrane are shown in Figures 5 and 6, respectively. A water permeability of the membrane increased with an increase in the hydrophilic components, but was inferior to that of Cuprophane PT-150. Permeabilities of the solutes increased with an increase in hydrophilic components. As described elsewhere,¹⁴⁻¹⁶ permeabilities of nonionic solutes for graft copolymer latex membranes are dependent on the water content of the membrane, and it is clear that an increase in hydrophilic components in the membrane increases the water content of the membrane and consequently the permeabilities of nonionic solutes.

TABLE II
Permeabilities of Solutes, Water Permeability, and Mechanical Properties in Wet State of PVA-AN-HEAAm Graft Latex Membranes

No.	Permeability of solute $\times 10^7$ (cm ² /s)							Mechanical properties				
	Urea	Glu- cose	Su- crose	Raffi- nose	Vita- min B ₁₂	BSP ^a	<i>p</i> - TSA ^b	TEB- A ^c	Water $\times 10^{16}$ (cm ²)	Tensile strength (kg/ cm ²)	Elonga- tion (%)	Young's mod- ulus (kg/ mm ²)
1	5.00	1.57	0.37	0.41	0.037	0.058	3.71	4.53	0.47	179	96	17.0
2	5.56	1.68	0.35	0.28	0.086	0.050	3.44	5.00	0.55	242	100	13.7
3	6.12	1.46	0.43	0.38	0.129	0.048	5.69	5.61	0.59	290	106	10.0
4	7.86	2.48	0.88	0.64	0.241	0.113	7.39	6.19	1.05	182	109	3.65
5	8.76	2.27	1.90	1.26	0.530	0.247	9.87	6.18	0.98	184	93	1.40
Cuprophane												
Pt-150	8.45	3.29	1.56	1.38	0.648	0.0095	5.90	6.72	4.28	160	90	5.33

^a Sodium sulfobromophthalein.

^b *p*-Toluenesulfonic acid.

^c Triethylbenzylammonium hydroxide.

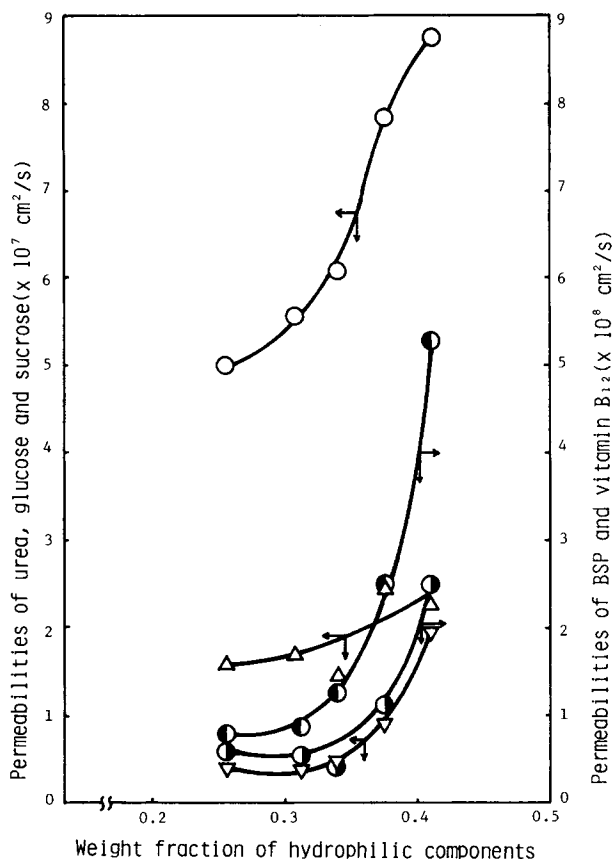


Fig. 5. Relationship between weight fraction of hydrophilic components and permeabilities of solutes for PVA-AN-HEAAm graft latex membrane: (O) urea; (Δ) glucose; (∇) sucrose; (\bullet) sodium sulfobromophthalein (BSP); (\blacklozenge) vitamin B₁₂.

The permeability of the ionic species is now focused. A glucose dialysis, which is nonionic solute and comparable molecular weight with that of *p*-toluenesulfonic acid (*p*-TSA, anionic solute) or triethylbenzylammonium hydroxide (TEBA, cationic solute) was carried out for comparison. The results are shown in Table III. The permeability of glucose was little affected by pH for both the HEAAm-free and the HEAAm-containing membranes. Taking into account a small variant in water content of the HEAAm-containing membrane no. 5 under various pH (53% at pH 2.0 and 59% at pH 12.0), the physical structure of the studied membranes is not varied significantly with pH. On the other hand, introduction of HEAAm unit in the membrane enhanced the permeability of *p*-TSA in acidic condition and that of TEBA in basic condition. It is known that ethanolamide group rearranges to aminoethyl ester group upon pH change in an aqueous solution.²⁰ As shown in Figure 7, the tautomerization of HEAAm homopolymer with pH variation was confirmed by IR spectrum, in which the band due to absorption of ester appeared in the region near 1730 cm⁻¹ and the NH₃⁺ overtone band in the region near 2000 cm⁻¹. In acidic condition, *N*-hydroxyethylamide group in PHEAAm tautomerizes to the aminoethyl ester group having NH₃⁺, and the membranes have positive charge. Consequently, it is ex-

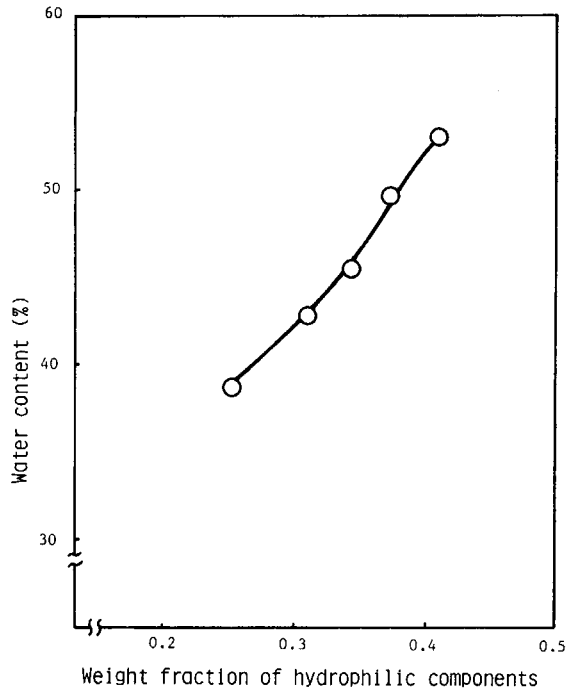


Fig. 6. Relationship between weight fraction of hydrophilic components and water content for PVA-AN-HEAAm graft copolymer latex membrane.

pected that anionic solutes permeate easily and cationic solutes with difficulty in acidic condition. It is clear that the behavior of the permeation of the ionic species is affected by the tautomerizable functional group in the membrane.

In the case of Cuprophane PT-150, the difference of permeability in glucose dialysis upon pH change was small, whereas the basic condition enhanced the permeability of cationic species and depressed that of anionic species. It is known that cellulosic membrane such as Cuprophane contains a small amount of the carboxylic group.¹⁶ The above behavior is attributable to a weak negative charge of Cuprophane membrane under basic condition.

TABLE III
Permeabilities of *p*-Toluenesulfonic Acid, Triethylbenzylammonium Hydroxide, and Glucose for Graft Latex Membranes with pH Variation

No. ^a	1		5		Cuprophane PT-150	
	2.0	12.0	2.0	12.0	2.0	12.0
P of <i>p</i> -TSA ^b × 10 ⁷ (cm ² /s)	2.82	2.68	6.07	4.78	4.85	3.20
P of TEBA ^c × 10 ⁷ (cm ² /s)	3.12	3.79	3.95	8.27	3.33	5.30
P of glucose × 10 ⁷ (cm ² /s)	1.46	1.48	3.11	3.29	2.82	3.04

^a See Table I.

^b Permeability of *p*-toluenesulfonic acid.

^c Permeability of triethylbenzylammonium hydroxide.

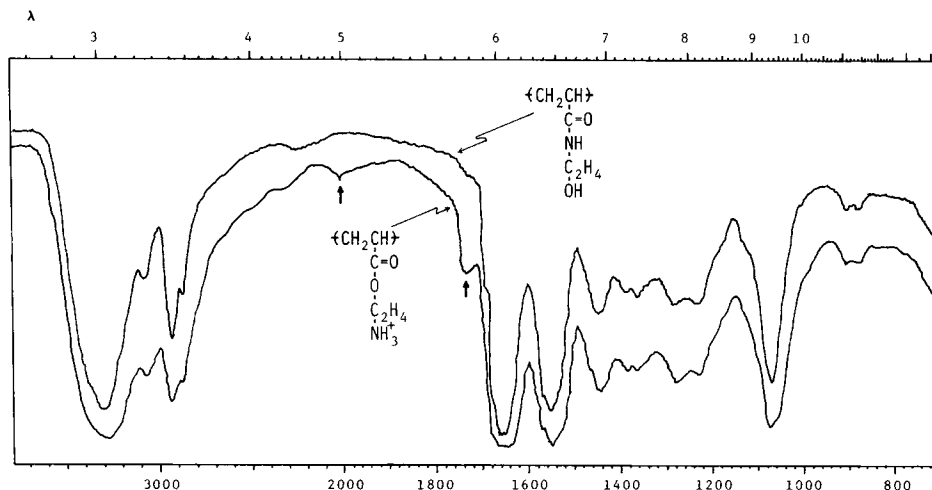


Fig. 7. Infrared spectra of tautomerization for poly(*N*-hydroxyethyl acrylamide).

Permeation Mechanism of the Membranes

Permeability characteristic in the graft copolymer latex membranes was inexplicable on the basis of the free volume theory proposed by Yasuda,²⁵⁻²⁷ because the permeability data were not linear to the reciprocal of volume fraction of water in the membrane.

In the previous papers, the permeation of the graft latex membrane was reported to be explicable on the basis of the microporous capillary model proposed by Lyman,²⁸ combining a hydraulic permeation of water with a diffusional permeation of solutes.¹⁶⁻¹⁸ Here, the microporous capillary model is applied to no. 5 membrane. The true permeability of urea was estimated from Wilson's plots, and the volume fraction of water in the membrane was calculated taking into account of the apparent density (1.030) and the degree of swelling (1.158) of the membrane. The capillary radius r_b (cm), capillary number density n_b (cm⁻²), and tortuosity b were determined by the following equations¹⁶:

$$r_b = \sqrt{8DK/P} \quad (5)$$

$$n_b = P\sqrt{H/8K}/\pi Dr_b \quad (6)$$

$$b = r_b\sqrt{H/8K} \quad (7)$$

where D of urea is 1.81×10^{-5} (cm²/s),²⁹ K is the water permeability (cm²), P is the permeability of urea (cm²/s), and H is the volume fraction of water in the membrane. The results of the calculations are given in Table IV.

Refojo³⁰ reported about the water transport of the hydrogel membranes, i.e., HEMA hydrogel and propylene glycol monomethacrylate (PGMA) hydrogel. In the article, pore radii r calculated from water permeability K and volume fraction of water in the membrane H were 0.40 ± 0.13 nm for HEMA and 0.45 ± 0.10 nm or 0.63 ± 0.21 nm for PGMA, where Refojo indicated that diffusion may contribute greatly to net water transport. Here tortuosity b was unable to be calculated for lack of P values. We attempted a comparison of pore radius

TABLE IV
Parameter Values of Capillary Model for PVA-AN-HEAAm Graft Latex Membrane (No. 5)

Permeability of urea (cm ² /s)	8.76 × 10 ⁻⁷
True permeability of urea (cm ² /s)	1.56 × 10 ⁻⁶
Water permeability (cm ²)	0.98 × 10 ⁻¹⁶
Volume fraction of water in membrane	0.261
Capillary radius (cm)	9.54 × 10 ⁻⁸
Capillary number density (1/cm ²)	5.24 × 10 ¹²
Tortuosity	1.74

and capillary number density for the graft latex membranes with those of the above hydrogels. Expressions r and capillary number density n become $r = (8K/H)^{1/2}$ and $n = H^2/8\pi K$, because the available data should be restricted to H and K . The calculated n for the hydrogels are $4.13 \times 10^{13} \text{ cm}^{-2}$ for HEMA and 3.90×10^{13} or $2.11 \times 10^{13} \text{ cm}^{-2}$ for PGMA. Assuming capillaries existing in the hydrophilic domain surrounded by particles, the r and n for no. 5 membrane are 0.55 nm and $2.77 \times 10^{13} \text{ cm}^{-2}$, respectively. These values are close to that for HEMA and PGMA hydrogels, which means that diffusion may contribute greatly to the hydraulic water transport across the continuous region dispersing the particles in the membrane.

CONCLUSIONS

(1) *N*-hydroxyethyl acrylamide (HEAAm) was synthesized from acryloyl chloride and monoethanolamine. The melting point was -15 – -16°C and the refractive index was 1.4919 at 18.0°C . The tautomerization between hydroxyethylamide group and aminoethyl ester group in poly(HEAAm) upon pH changes was ascertained by the infrared spectrum.

(2) The graft copolymer latex membranes composed of PVA, PAN, and PHEAAm had well-balanced composition of hydrophilic and hydrophobic components, and exhibited good mechanical properties in wet state. An increase in hydrophilic component in PVA-AN-HEAAm graft copolymer latex membrane improved permeabilities of solutes in aqueous solution in comparison with PVA-AN membrane, maintaining good mechanical properties in wet state. Compared with Cuprophane PT-150, the membranes had similar or rather excellent permeabilities of solutes and mechanical properties in wet state. But the water permeability was inferior to that of Cuprophane PT-150.

(3) The permeation of ionic species is affected by tautomerization of the functional group in the membrane. The permeation of cationic solutes decreased in acidic condition. Tautomerization of hydroxyethylamide group into aminoethyl ester group with NH_3^+ in acidic condition brings positive charge to the membrane, and, hence, cationic solutes were rejected. The opposite trend was observed for the anionic species.

(4) The pore size calculated in the microporous capillary model indicates that the hydraulic water transport across the membrane is rather diffusion process than viscous flow.

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