

Permeability through Cellulose Membranes Grafted with Vinyl Monomers in a Homogeneous System. VIII. *N*-Vinylpyrrolidone-Grafted Cellulose Membranes

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SYNOPSIS

The homogeneous grafting of *N*-vinylpyrrolidone (NVP) onto cellulose was carried out in a dimethyl sulfoxide/paraformaldehyde (DMSO/PF) solvent system. The diffusive permeabilities of solutes through the NVP-grafted cellulose membranes, apparent activation energy for solute permeation through them, states of water in them, and their microphase-separated structures were investigated. The solute permeability through the grafted membranes was superior to that through the cellulose membrane cast from the DMSO/PF solution of cellulose. The total water and nonfreezing water contents of the grafted membranes were larger than those of the cellulose membrane. The difference in permeability through the membranes was not correlated quantitatively with the amount of each state of water in them. Activation energies for permeation of solutes through the grafted membranes were similar to those through the cellulose membrane. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

The diffusive permeation of solutes through water-swollen membranes is considered to occur through water phases in them.¹⁻⁹ However, different states of water are present in the membranes.¹⁰⁻²⁴ Characterization and quantification of each state of water are important for clarifying the mechanism of solute permselectivity through the membranes. The amount of each state of water in the membranes varies with the affinity of membrane substrates for water. In a series of studies,²⁵⁻³¹ cellulose grafted with vinyl monomers in a homogeneous solution system has been used as membrane substrates. The kind of monomer and composition of copolymers were varied to prepare membranes with different affinity for water. The modified cellulose membranes indicated an interesting specificity of solute permeability depending on the monomers grafted.

In this article, a hydrophilic vinyl monomer, *N*-vinylpyrrolidone (NVP), was used. It is expected

that the affinity of the membranes for water would increase to improve the solute permeability through them. The diffusive permeabilities of solutes through the NVP-grafted cellulose membranes were investigated in relation to the composition of graft copolymers, microphase-separated structures of the membranes, and states of water in them.

EXPERIMENTAL

Grafting and Membrane Preparation

The homogeneous grafting of NVP onto cellulose in a dimethyl sulfoxide/paraformaldehyde (DMSO/PF) solvent system and characterization of the grafted products were performed by the method described in our previous articles.³²⁻³⁵ In homogeneous grafting, the molecular weight of the graft polymer is presumed to be equal to that of the attendant homopolymer.³⁶⁻³⁸ We have already confirmed^{33,35} that, in this homogeneous grafting system, both molecular weights are consistent with each other within experimental error. The viscosity-average molecular weight, M_v , of the extracted homopolymer

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was used as that of the graft polymer. The values of M_v of poly(*N*-vinylpyrrolidone) (PNVP) were estimated from the intrinsic viscosity, $[\eta]$, obtained with water at 25°C.³⁹

The crude grafted mixtures were cast at room temperature on glass plates and dried at about 60°C under reduced pressure for 24 h. After being immersed in water for several days, the membranes were easily peeled off. All membranes were stored in distilled water until use.

Diffusive Permeability

The diffusive permeabilities of solutes, P , were measured at given temperatures from 20.0 to 50.0°C by the method described in a previous article.²⁵ Nine solutes of different molecular weights were used. The values of M_v of three commercial poly(ethylene glycol) (PEG) samples were estimated from $[\eta]$ obtained with benzene at 25.0°C.⁴⁰ The PEG samples were abbreviated as PEG-IV, PEG-VI, and PEG-XX in the order of increasing molecular weight.

Transmission Electron Microscopy (TEM)

The microphase-separated structures of the membranes were observed with a Hitachi HU-11A transmission electron microscope. The membranes were stained with osmic acid vapor for 1 day.

Differential Scanning Calorimetry (DSC)

The states of water in the membranes were investigated with a Seiko SSC/560 DSC. The membranes were immersed in pure water and aqueous solutions of NaCl, raffinose, and PEG-VI for several days, surface water was wiped off with paper, and the membranes were placed in aluminum pans. The weight of each sample was about 10–20 mg. The samples were cooled with liquid nitrogen at a rate of 5°C/min to –80°C and then heated at the same rate to 80–90°C. The sample pans were allowed to stand in the DSC cell at a given temperature for a given period to evaporate water. The measurements were repeated several times to investigate the states of water in the membranes with different water contents. The water content was expressed as the ratio of the weight of water in the membrane to that of the dry membrane.

RESULTS AND DISCUSSION

The membranes are characterized in Table I. Two kinds of radical initiators, i.e., ammonium persulfate (APS) and azobisisobutyronitrile (AIBN), were

Table I Characterization of NVP-grafted Cellulose Membranes

Membrane	PNVP Content (%)	$M_v \times 10^{-3}$ of Grafts ^a	No. Grafts ^b
APS membrane			
<i>g</i> -PNVP 1	2.4	5	0.80
<i>g</i> -PNVP 2	15.2	15	1.5
<i>g</i> -PNVP 3	21.9	21	1.5
AIBN membrane			
<i>g</i> -PNVP 11	7.1	12	0.86
<i>g</i> -PNVP 12	9.7	17	0.83

^a Estimated from $[\eta]$ obtained with water at 25.0°C.

^b M_v of cellulose is 146×10^3 .

used to synthesize graft copolymers of different molecular architectures. The membranes thus were classified into two groups: APS membrane and AIBN membrane. It is known³⁸ that the use of AIBN makes the number of grafts small because of the resonance stabilization of its radical fragments. This can be seen from Table I, but the difference in molecular architectures is not remarkable.

The TEM micrographs of the APS and AIBN membranes are shown in Figures 1 and 2, respectively. The dark domains indicate the cellulose phases stained with osmic acid. The PNVP phases are dispersed finely in the cellulose matrix and the interfaces between them are not clear. In contrast with hydrophobic monomer-grafted cellulose membranes,^{25,27,28} the microphase-separated structures of the NVP-grafted cellulose membranes hardly depend on the kind of initiators. This will be because of the absence of attendant homopolymer and the small difference in molecular architectures.

Figure 3 demonstrates the solute molecular weight dependence of permeability through various membranes. The results for the commercial regenerated cellulose membrane, cuprophan,²⁵ and the membrane cast from the DMSO/PF solution of cellulose, named as the cellulose membrane,²⁵ and hydrophilic acrylamide (AAm)-grafted cellulose membrane, *g*-PAAm 2,³¹ are also indicated. The permeability through the *g*-PNVP 3 membrane is superior to that through the cellulose membrane but inferior to that through the cuprophan membrane. The solute molecular weight dependence of permeability through the *g*-PNVP 3 membrane is similar to that through the cellulosic membranes, being different from our previous results.^{25,27–31} The solute molecular weight dependence of permeability through the *g*-PAAm 2 membrane was representative of that through the grafted cellulose membranes.

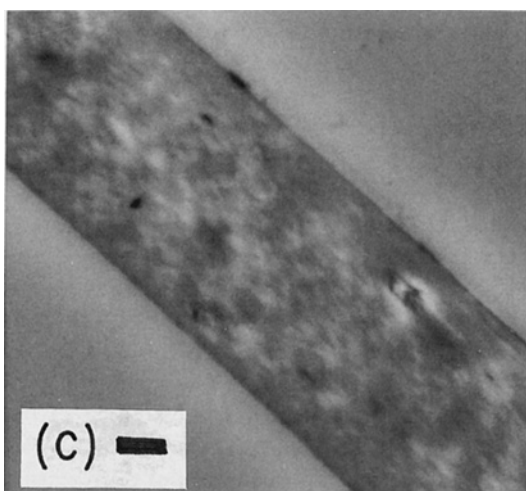
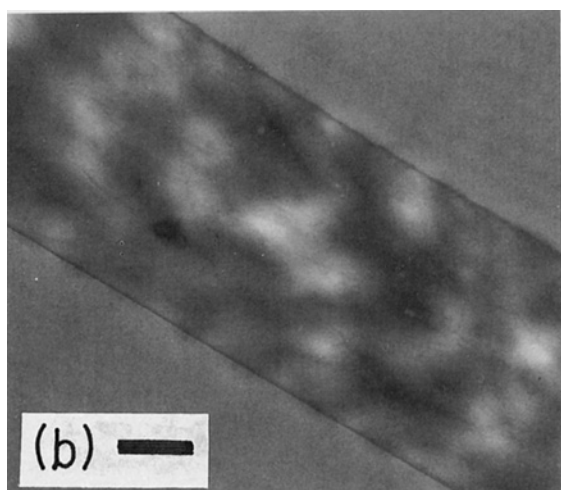
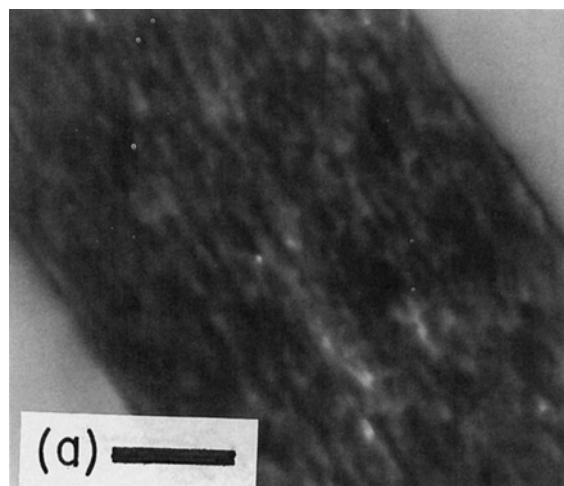


Figure 1 TEM micrographs of the APS membranes stained with osmic acid: (a) *g*-PNVP 1; (b) *g*-PNVP 2; (c) *g*-PNVP 3. A scale bar represents 5 microns.

Figure 4 reveals the relationship between the permeabilities of various solutes and PNVP content. The data for the cellulosic membranes are also in-

cluded.^{25,28,29,31} The permeabilities, except for those of higher molecular weight solutes through the *g*-PNVP 1 membrane, hardly depend on the PNVP content. The permeabilities of solutes through the APS and AIBN membranes are almost on the same level, being also different from the previous results.^{25,27,28,31} The permeability through the APS membranes was superior to that through the AIBN membranes. The difference in permeability depending on the kind of membranes was correlated to that in their microphase-separated structures.^{25,27,28,31} The results in Figure 4 thus are consistent with the TEM micrographs of Figures 1 and 2.

Freezing and melting thermograms of the membranes swollen in water are drawn in Figure 5. The result for the cellulose membrane is also drawn.²⁶ Several peaks are found in each thermogram, indicating the presence of different states of freezing water.^{10-24,26} The exothermic peak at around -20°C

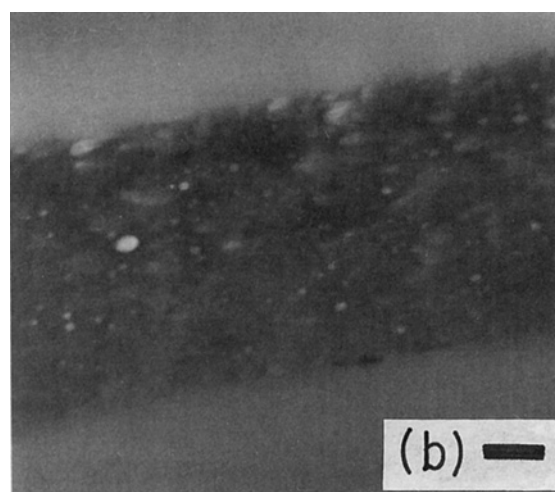
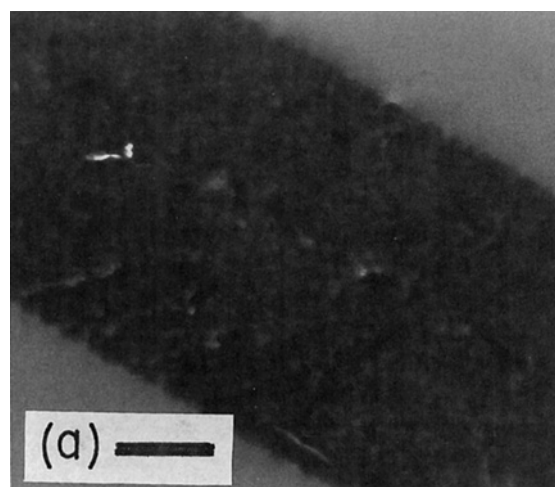


Figure 2 TEM micrographs of the AIBN membranes: (a) *g*-PNVP 11; (b) *g*-PNVP 12.

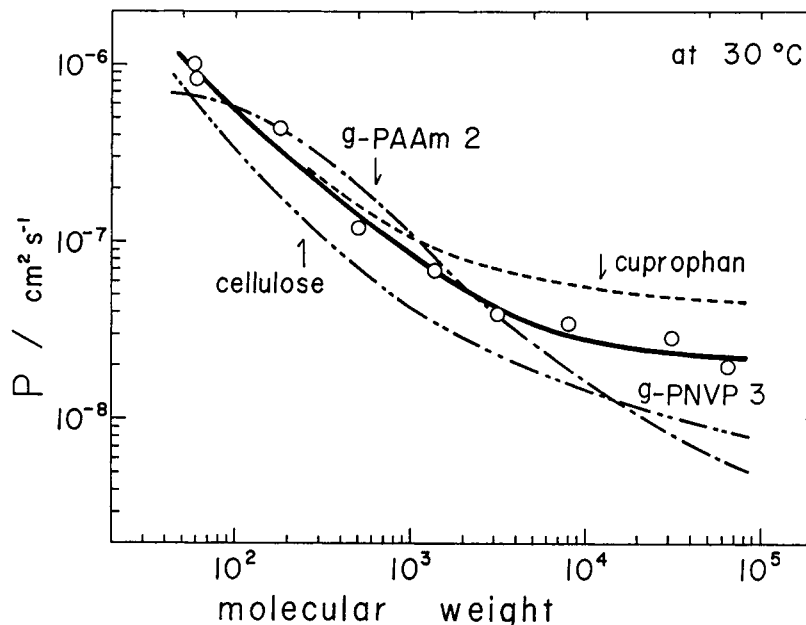


Figure 3 Solute molecular weight dependence of diffusive permeability at 30°C for various membranes: (O) *g*-PNVP 3 membrane; (-----) cuprophan membrane; (-·-·-) cellulose membrane; (---) *g*-PAAm 2 membrane. The solutes are, in the order of increasing molecular weight, NaCl, urea, glucose, raffinose, vitamin B₁₂, PEG-IV, PEG-VI, PEG-XX, and hemoglobin.

and the endothermic peak at around 0°C are assigned to free water. The other peak at lower temperatures is assigned to intermediate water interacting weakly with membrane substrate. The non-freezing water, which does not freeze even when cooled far below the freezing point, is regarded as bound water. The intermediate water peak disappears in the freezing thermogram of the *g*-PNVP 2 membrane, an APS membrane, but appears weakly in the melting thermogram. Similar thermograms were also obtained for other APS membranes. On the other hand, the thermograms of the *g*-PNVP 12 membrane, an AIBN membrane, resemble those of the cellulose membrane. Such a difference in the states of water depending on the kind of membranes has been also found for other monomer-grafted cellulose membranes.^{26-29,31} As can be seen from Figures 1 and 2, no difference in the microphase-separated structures for both kinds of membranes is found. Moreover, no difference in the dependence of permeability on the PNVP content is also found in Figure 4. It is of interest to note that the states of water in the membranes depend on the kind of membranes.

The states of water in the *g*-PNVP 11 membrane with different water contents are depicted in Figure 6. The free water peak decreases remarkably with decreasing water content and almost disappears at about 0.41 water content, whereas the intermediate water peak decreases gradually. Moreover, the free

water peak shifts toward lower temperatures with decreasing water content, but the intermediate water peak hardly shifts at all. The shift of peak temperature is shown in Figure 7. The peak temperatures, except for the exothermic intermediate water peak, shift gradually and remarkably at certain water contents toward lower temperatures with decreasing water content. These results imply that the water molecules interacting more weakly with membrane substrate decrease faster with decreasing water content than those interacting more strongly.^{10,15,19,20,26-31}

Figure 8 shows the relationship between the water content and heat of fusion of freezing water, ΔH , determined from the endothermic peak area. The data points for each membrane do not follow a straight line at lower water contents. The slope of the straight part of each curve is equal to the specific heat of fusion of pure water. The amount of freezing water at each water content is calculated from ΔH on the assumption that the specific heat of fusion of freezing water is equal to that of pure water. The amount of nonfreezing water is determined from the difference in the amounts of total water and freezing water. The deviation from the straight line in Figure 8 thus reveals that the amount of nonfreezing water decreases at lower water contents. A similar result has also been reported for other membranes.^{10,12,23,26-31} The equilibrium nonfreezing water content, W_{non} ,

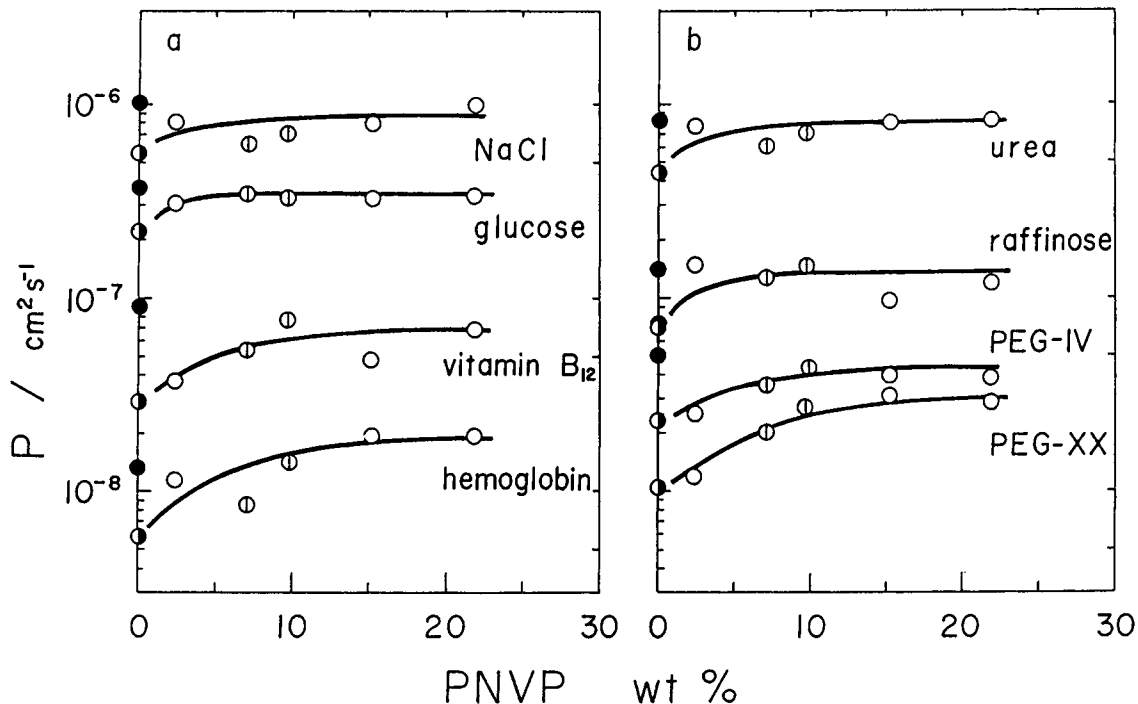


Figure 4 PNVP content dependence of diffusive permeability at 30°C for various solutes: (○) APS membrane; (⊙) AIBN membrane; (●) cuprophan membrane; (●) cellulose membrane.

was estimated by extrapolation of the straight part to $\Delta H = 0$.

Good correlation was also found among the water content determined by blotting water on the membrane surfaces, the water content where the peak temperature changes sharply in Figure 7, and the water content where the curve deviates from a straight line in Figure 8.²⁶⁻³¹ Their average value

thus was used as the equilibrium water content estimated by the DSC method, W_{DSC} . The equilibrium freezing water content was taken as the difference between W_{non} and W_{DSC} . The results are summarized in Table II. The data for cellulosic membranes are also listed.²⁶ The values of both W_{DSC} and W_{non} of the grafted membranes are larger than those of the cellulose membrane, indicating the influence of hydrophilic NVP. The amounts of the freezing water

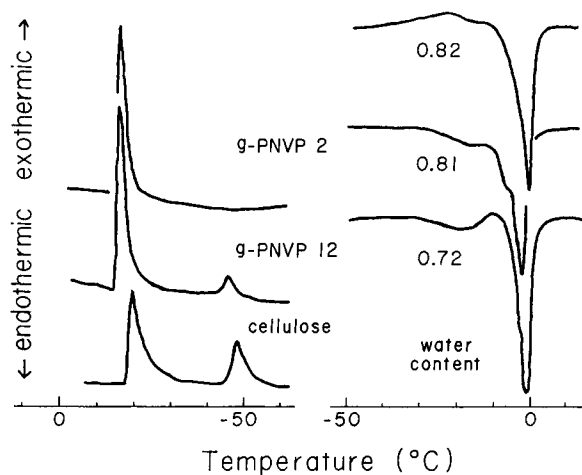


Figure 5 DSC freezing and melting thermograms for various membranes swollen in water. Numbers on curves indicate water content.

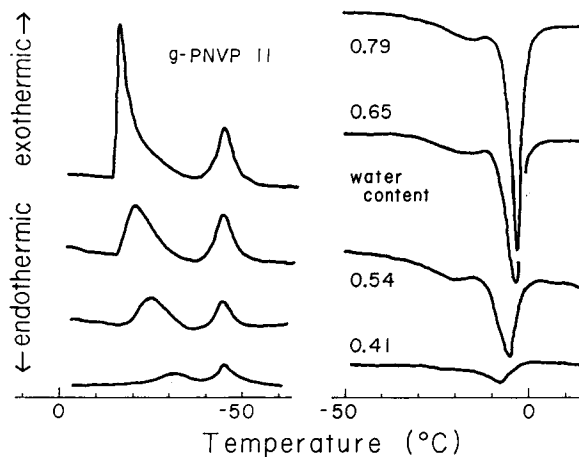


Figure 6 DSC freezing and melting thermograms for the g-PNVP 11 membrane with different water contents.

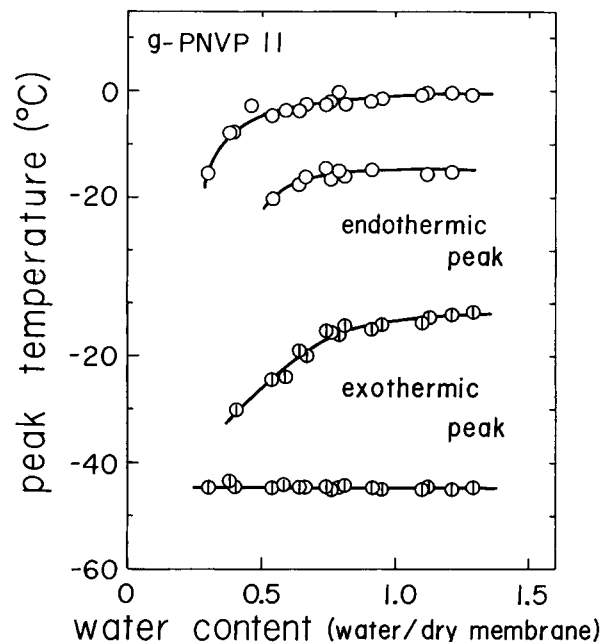


Figure 7 Effect of water content on the (○) endothermic and (⊕) exothermic peak temperatures of the *g*-PNVP 11 membrane.

of the grafted membranes are larger than that of the cellulose membrane but smaller than that of the cuprophane membrane. The amount of freezing water hardly depends on the kind of membranes, being consistent with the results in Figures 3 and 4.

As can be seen from Figures 5 and 6, the endothermic curves can be resolved roughly into each state of water. The results are also summarized in Table II. It has been reported^{10,14,17,41-43} that the solute-permeable water regions depend on the solutes. If a certain solute can permeate only through the

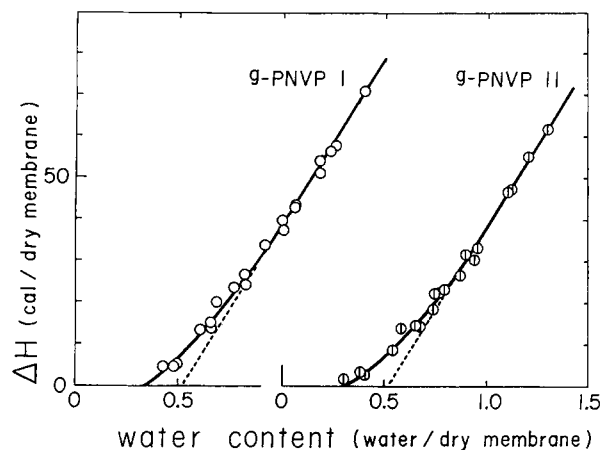


Figure 8 Total water content dependence of the heat of fusion of freezing water for various membranes: (○) *g*-PNVP 1; (⊕) *g*-PNVP 11.

free water regions in membranes, the order of its permeability through membranes would correspond to that of the free water content of membranes. The free water contents of the grafted membranes are larger than that of the cuprophane membranes, disagreeing with the result in Figure 3. It has been reported^{1,2,5} that the amounts of total water and bound water vary with the permeating solutes. Furthermore, we have reported³⁰ that the amount of free water is influenced by the presence of solutes. The states of water in the NVP-grafted membranes swollen in solutions were also investigated in this study. The amount of each state of water in the solution-swollen membranes was almost equal to that in the water-swollen membranes. The results thus were not listed in Table II. A similar result has been obtained for the AAm-grafted cellulose mem-

Table II Amounts of Water in Cellulosic and NVP-grafted Cellulose Membranes Swollen in Pure Water

Membrane	Weight of Water in Membrane/Weight of Dry Membrane				
	Equilibrium Water Content W_{DSC}	Equilibrium Nonfreezing Water Content W_{non}	Equilibrium Freezing Water Content		
			Overall	Free Water	Intermediate Water
Cellulosic membrane					
Cuprophane	1.00	0.49	0.51	0.24 (47%)	0.27 (53%)
Cellulose	0.70	0.45	0.25	0.22 (88%)	0.03 (12%)
APS membrane					
<i>g</i> -PNVP 1	0.82	0.51	0.31	0.30 (96%)	0.01 (4%)
<i>g</i> -PNVP 2	0.77	0.47	0.30	0.28 (94%)	0.02 (6%)
<i>g</i> -PNVP 3	0.80	0.51	0.29	0.28 (97%)	0.01 (3%)
AIBN membrane					
<i>g</i> -PNVP 11	0.82	0.52	0.30	0.24 (80%)	0.06 (20%)
<i>g</i> -PNVP 12	0.80	0.49	0.31	0.25 (82%)	0.06 (18%)

Table III Apparent Activation Energies for Permeation of Solutes

Membrane	Activation Energy (kcal/mol)						
	NaCl	Urea	Glucose	Raffinose	Vitamin B ₁₂	PEG-VI	Hemoglobin
Cellulosic membrane							
Cuprophane	4.3	3.8	4.6	4.6	4.4	3.2	5.3
Cellulose	4.2	4.3	4.9	5.1	5.0	3.2	5.6
APS membrane							
<i>g</i> -PNVP 1	4.2	3.9	4.7	4.9	4.7	3.4	5.2
<i>g</i> -PNVP 2	4.6	4.3	4.4	5.2	4.8	3.5	5.5
<i>g</i> -PNVP 3	4.3	4.2	4.4	4.3	4.6	3.2	5.4
AIBN membrane							
<i>g</i> -PNVP 11	4.4	4.3	4.8	5.0	4.9	3.2	5.8
<i>g</i> -PNVP 12	4.4	4.0	4.5	5.0	4.9	3.4	5.3
AAM-grafted membrane							
<i>g</i> -PAAm 2	4.5	4.5	4.5	4.9	4.7	4.1	5.7

branes.³¹ Comparison of Figures 3 and 4 with Table II indicates that the order of solute permeability through the grafted membranes does not correspond to that of the amount of any state of water. It is difficult to explain the difference in permeability through the grafted membranes in relation to the amount of each state of water.

Apparent activation energies for permeation of solutes through the grafted membranes are listed in Table III. The data for the cellulosic and *g*-PAAm 2 membranes are also shown.^{28,31} The activation energy is thought to be a measure indicating the extent of an interaction between a solute and membrane substrate. It has been reported²⁸⁻³¹ that solutes which are difficult to permeate through the grafted membranes show higher activation energies. As can be seen from Table III, the activation energy for PEG-VI through the *g*-PAAm 2 membrane is larger than those through the cellulosic membranes. Activation energies through the NVP-grafted membranes are similar to those through the cellulosic membranes, explaining the solute molecular weight dependence of permeability in Figure 3.

In conclusion, we used hydrophilic NVP as a monomer to improve solute permeability through the cellulose membrane. The solute permeability through the NVP-grafted cellulose membranes was superior to that through the cellulose membrane. The total water and nonfreezing water contents of the grafted membranes were larger than those of the cellulose membrane, indicating the influence of hydrophilic NVP. However, the difference in permeability through the membranes was not correlated quantitatively to that in the amount of each state of water in them. Further investigation for each state of water in the membranes would be necessary to

clarify the mechanism of solute permselectivity through them. Activation energies for permeation of solutes through the grafted membranes were similar to those through the cellulosic membranes, explaining the dependence of permeability on the solute molecular weight.

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