

Characteristics of Water in Copoly(methyl methacrylate-*N*-vinylpyrrolidone) Membranes

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ABSTRACT: The characteristics of water in methyl methacrylate-*N*-vinylpyrrolidone (MMA/NVP) copolymer membranes were studied. The sorption and permeation behavior and differential scanning calorimetric behavior of MMA/NVP copolymer-water systems contained two types of water in the copolymer membranes at relative vapor pressures up to *ca.* 0.9: water directly bound to polar NVP residues at low relative vapor pressures, *i.e.*, the "tightly bound" water, and water associated in the vicinity of hydrophobic MMA residues forming multimolecular clusters at higher relative vapor pressures, *i.e.*, "hydrophobic hydration" water. The latter was characterized by a rigid structure resulting in an increase in the shear modulus of the copolymer membrane at relative vapor pressure higher than 0.5. It is concluded that the cluster size or clustering tendency in MMA/NVP membranes, *i.e.*, the amount of hydrophobic hydration water in the copolymer, is enhanced by the presence of the proper amount of NVP residues in the copolymers *via* enhancement of water uptake by the membranes.

KEY WORDS Hydrophobic Hydration Water / Rigid Water Cluster / Sorption / Permeation / Shear Modulus / Copoly(methyl methacrylate-*N*-vinylpyrrolidone) /

Several functional properties of a polymer such as mechanical strength and relaxation behavior, swelling and membrane permeation behavior are directly related to the manner in which the polymer interacts with water. The characteristics of water in polymers have long been the subject of investigation.¹⁻¹¹ Methods for studying polymer-water interactions in solid polymers are numerous and may be classified as thermodynamic (water sorption and desorption,^{1,2} and calorimetric³⁻⁵), kinetics (NMR^{6,7}), spectroscopic (IR⁸), and diffraction (X-ray⁹). These methods suggest that the types of water in solid polymers are generally described in terms of "bound," "bulk," and "hydrophobic hydration" water. Furthermore, two types of bound water have been postulated,¹² *i.e.*, "tightly bound" water and "loosely bound" water. The former is directly associated with polar sites in the poly-

mer and unfreezable. The latter is water in the vicinity of the former and has a reduced freezing point. Such definitions, however, have limited scope of application, since the types and amount of water thus classified are dependent on the experimental techniques employed. It is clear, however, that water molecules in polymers have properties distinctly different from those of bulk water.

Hydrophobic hydration water in the vicinity of polymer hydrophobic residues is believed to have a clathrate-type structure. For various reasons, its properties in solid polymers have been difficult to determine. The main problem is that the amount of this water is generally too small to be directly characterized by certain physical methods. Another problem is interference from the bound or bulk water in the polymer. The real nature of the hydrophobic hydration water in polymers is not yet

clear. Characterization of this water may be important since hydrophobic groups in polymers ought to be in contact with water molecules under the atmosphere. In a previous study,¹³ we showed that water in α -helical polypeptide membranes containing hydrophobic side chains, poly(L-leucine) (PLEu), formed rigid clusters resulting in an increase in the shear modulus of the membrane. This was explained by the fact that a large water cluster could be formed in PLEu by the hydrophobic nature of PLEu side chains and the large space between α -helix molecules. In this paper, we report the application of our results on α -helical PLEu to ordinary hydrophobic linear polymers consist of methyl methacrylate and *N*-vinylpyrrolidone.

EXPERIMENTAL

Materials

Methyl methacrylate (MMA) (Wako Junyaku Co., Ltd.) was distilled under reduced pressure of nitrogen and a fraction of bp 43°C was used. *N*-Vinylpyrrolidone (NVP) (Wako Junyaku Co., Ltd.) was purified in the usual way. After AIBN/benzene was placed in a polymerization tube, given amount of MMA and NVP were added, the tube was degassed and sealed under vacuum in the usual way, and the mixture was copolymerized at 40°C for *ca.* 5 h. The reaction mixture was diluted with a benzene/petroleum ether mixture and poured to a *N,N*-dimethylformamide/water mixture to precipitate the copolymer, which was then washed with water. After filtration, it was dried *in vacuo*. The composition of various copolymers obtained, MMA/NVP in mol%, was 96/4, 90/10, and 73/27. A benzene solution of a copolymer was cast on to a glass plate, and the film was dried *in vacuo*. The thickness of the membrane was about 70 μm .

Sorption and Permeation Measurements

Water vapor sorption experiments were carried out by ordinary gravimetric sorption ap-

paratus.¹⁴ Sorption isotherms were expressed as the amount of water sorbed n (g of water/g of polymer) against the relative vapor pressure of water p/p_0 . For permeation measurements of water vapor through the copolymer membranes, the Rouse-type apparatus¹⁵ was used. From the slope of the steady state straight lines on the permeation curves, the permeability coefficients \bar{P} ($\text{cm}^3 \text{ stp cm}^{-1} \text{ s}^{-1} \text{ cmHg}^{-1}$) were calculated as usual. The sorption and permeation measurements were carried at 25°C.

Dynamic Mechanical Measurements

The free oscillating pendulum equipped in the sorption tube¹³ was used to determine the relative modulus G_r . G_r is defined as the ratio of the modulus under certain water content G_i to that in dry state G_0 at 25°C.

$$G_r = \left(\frac{G_i}{G_0} \right) = \left(\frac{T_0}{T_i} \right)^2 \quad (1)$$

where T_0 and T_i are the periods of oscillation, respectively.

Differential Scanning Calorimetric (DSC) Measurements

A Seiko Co., Ltd. SSC 560 differential scanning calorimeter was used to measure the phase transition of water sorbed on the membranes. DSC curves were obtained by heating the scanning rate of 10 deg min^{-1} from -60 to 60°C . The water content of the membranes was adjusted by sorption equilibrium of water at various vapor pressures lower than *ca.* 0.9 in the sorption tube. The sample was weighed and placed in an aluminum pan which was then rapidly sealed.

RESULTS AND DISCUSSION

The sorption isotherms of MMA/NVP-water systems are shown in Figure 1. The shape of the isotherms changes from a monotonical increasing type to a sigmoid type with increasing NVP content, indicating that

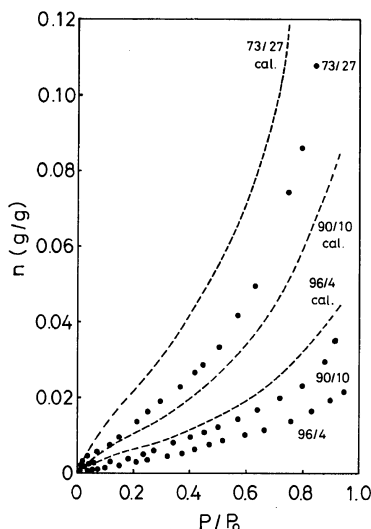


Figure 1. Sorption isotherms of water on 96/4 MMA/NVP, 90/10 MMA/NVP, and 73/27 MMA/NVP membranes at 25°C. Dotted lines show the calculated isotherms of water-copolymer systems obtained from those¹⁷ of the water-PMMA, and PNVP systems.

water sorption occurs at polar NVP sites at low relative vapor pressures. Figure 1 also shows that the amounts of sorbed water increase with increasing NVP content in the membranes. The dotted lines in Figure 1 show the calculated isotherms of copolymer-water systems, obtained from the isotherms of water-poly(methyl methacrylate (PMMA) and poly(*N*-vinylpyrrolidone) (PNVP) systems, assuming additivity of the water holding capacity of both residues in the copolymers. It is clear that the experimental isotherms are lower than the dotted lines. The deviation between the experimental and calculated values of water sorption, n_{dev} , is given by the following relation

$$n_{\text{dev}} = (n_{\text{cal}} - n_{\text{obs}}) / n_{\text{obs}} \quad (2)$$

where n_{cal} and n_{obs} are the calculated and experimental amounts of sorbed water, respectively. Figure 2 shows the relation between n_{dev} at various relative vapor pressures and NVP content of the membranes. The deviation decreases with increasing NVP content, ap-

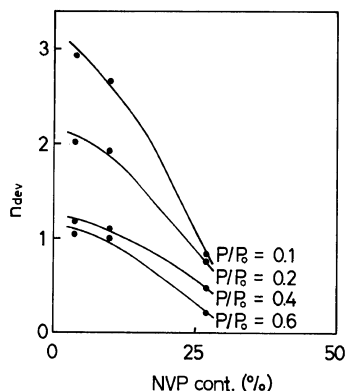


Figure 2. Relation between n_{dev} and NVP copolymer content.

proaching zero at higher NVP content of the copolymers. Thus the phase separation, *i.e.*, the formation of hydrophobic MMA and hydrophilic NVP domains, may occur in copolymers containing more than 30–35 mol% NVP.

The steady state permeability coefficient \bar{P} and diffusion coefficient \bar{D} of water-90/10 MMA/NVP and 73/27 MMA/NVP membranes are shown in Figures 3(a) and (b), respectively. The values of \bar{P} for both systems gradually increase with increasing relative vapor pressure. The values of \bar{D} initially increase with increasing relative vapor pressure and slightly decrease at higher relative vapor pressures. This suggests that polar NVP residues initially sorb water and are plasticized, and at higher vapor pressures, multimolecular water clustering occurs in the vicinity of hydrophobic MMA residues. The clustering tendency of water molecules in polymer matrix is generally characterized by the cluster function, G_{11}/V_1 , or cluster size, $1 + v_1 G_{11}/V_1$.¹⁶

$$v_1 G_{11}/V_1 = v_2 [\partial \ln v_1 / \partial \ln a_1]_{p,T} - 1 \quad (3)$$

where v_1 and v_2 are the volume fractions of the water and polymer, respectively, V_1 , the molecular volume of water, a_1 , the activity of water vapor, and G_{11} is the cluster integral. Applying eq 3 to the results of the sorption isotherms in Figure 1, the cluster size,

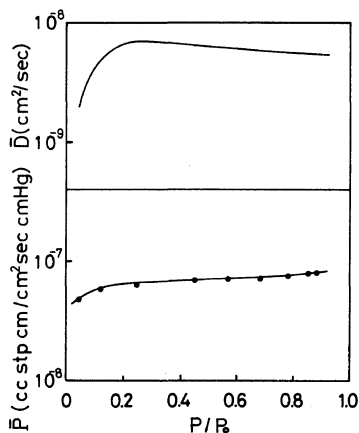


Figure 3(a). Permeability coefficient \bar{P} and diffusion coefficient \bar{D} for the 90/10 MMA/NVP membrane-water systems at 25°C.

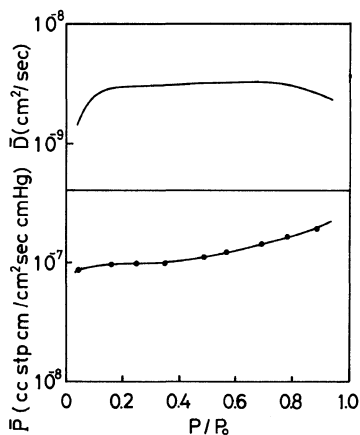


Figure 3(b). Permeability coefficient \bar{P} and diffusion coefficient \bar{D} for the 73/27 MMA/NVP membrane-water system at 25°C.

$1 + v_1 G_{11}/V_1$, was obtained as a function of relative vapor pressure (Figure 4). Figure 4 shows that the cluster size of water in the copolymer membrane is larger than that in both homopolymer membranes, *i.e.*, at low relative vapor pressures, the cluster size in 96/4 MMA/NVP is maximum and the clustering tendency in 73/27 becomes remarkable at relative vapor pressures higher than 0.7. The clustering tendency of water in the copolymers may thus not only depend on the hydrophobicity of the copolymers but on the water

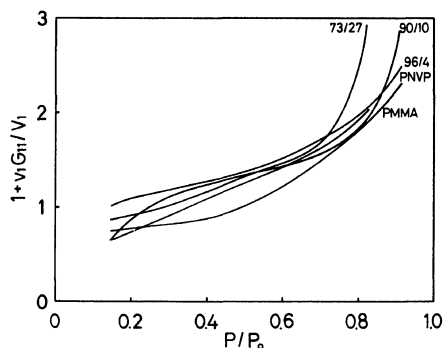


Figure 4. Cluster size of water in PMMA, 96/4 MMA/NVP, 90/10 MMA/NVP, 73/27 MMA/NVP, and PNVP membranes.

content of the copolymer membranes. That is, the clustering tendency of water in MMA/NVP membranes is enhanced by the presence of the proper amount of polar NVP residues in the copolymer *via* enhancement of water uptake by the membrane.

To determine the fraction of freezable or unfreezable water in the copolymers, DSC measurements were made on copolymer membranes containing various amounts of water, prepared by the sorption equilibrium of water at various relative vapor pressures. The DSC curves show no transition peaks from -60 to 60°C , indicating possibly that loosely bound and bulk water do not exist in MMA/NVP copolymers with a NVP content less than 27 mol% at relative vapor pressures lower than *ca.* 0.9. It may thus be concluded that two types of water exist in the copolymers: water directly bound to the polar NVP residues, *i.e.*, tightly bound water, and clustering water in the vicinity of the hydrophobic MMA residues, *i.e.*, hydrophobic hydration water. The latter was also characterized by the dynamic mechanical relaxation behavior of copolymers containing various amounts of water. Figure 5 shows the relation between the relative moduli of 90/10 MMA/NVP, 73/27 MMA/NVP and relative vapor pressure. The relative modulus G_r of 73/27 MMA/NVP membrane decreased at lower relative vapor pressures. However, G_r

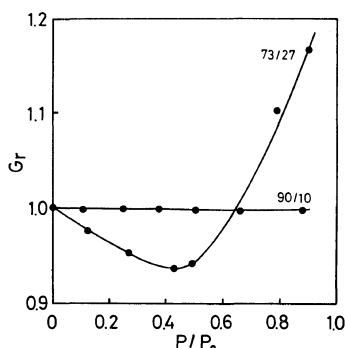


Figure 5. Relation between the relative modulus G_r of water-90/10 MMA/NVP, and 73/27 MMA/NVP membrane systems and relative vapor pressure.

increased at relative vapor pressures higher than 0.5. The initial decrease in G_r of 73/27 MMA/NVP membrane can be explained by plasticizing effect of bound water on the polar NVP residues in the membrane. The increase in G_r at higher relative vapor pressures may be ascribed to the fact that hydrophobic hydration water in the 73/27 MMA/NVP membrane makes a relatively rigid structure similar to that in the α -helical PLeu-water system.¹³ The relative modulus of the 90/10 MMA/NVP membrane was almost independent of the relative vapor pressure, indicating the plasticizing effect to be negligible and the amount of hydrophobic hydration water to be relatively low in the 90/10 MMA/NVP membrane owing to the small amount of polar NVP residues. Figure 5 also suggests that the formation of rigid water clusters exhibiting an anti-plasticizing effect on the shear modulus of the membrane occurs in ordinary linear polymer membrane containing hydrophobic residues and the proper amount of polar residues. It is not specific in α -helical polypeptide containing hydrophobic side chains.

CONCLUSION

Water in MMA/NVP membranes has been classified as tightly bound water on the polar NVP residues and hydrophobic hydration

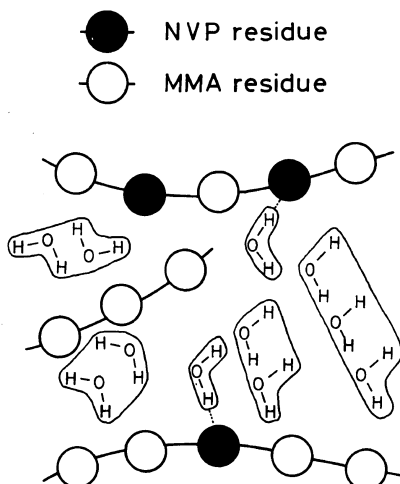


Figure 6. Schematic representation of water in MMA/NVP copolymer membranes at higher relative vapor pressures.

water in the vicinity of MMA residues in the membranes (Figure 6). The tightly bound water has a plasticizing effect on the diffusibility of water-90/10 MMA/NVP, 73/27 MMA/NVP membrane systems and also on the mechanical strength of the 73/27 MMA/NVP membrane at low relative vapor pressures. The hydrophobic hydration water reduces the diffusibility of the water-90/10 MMA/NVP, 73/27 MMA/NVP membrane systems *via* formation of water clusters at higher vapor pressures, and makes a relatively rigid water cluster in the 73/27 MMA/NVP membrane, resulting in increased shear modulus of the membrane. The amount of the hydrophobic hydration water formed in the hydrophobic environment may thus depend on the water content of the copolymer membranes, *i.e.*, this water may increase provided the proper amounts of polar NVP residues are available in the copolymer membranes.

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