# Water in Hydrogels. 4. Poly(*N*-vinyl-2-pyrrolidinone–methyl methacrylate)/Saline Systems

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ABSTRACT: This paper examines the DSC and $^{23}$Na NMR response of poly(*N*-vinyl-2-pyrrolidinone/methyl methacrylate) copolymer, P(NVP/MMA) hydrated with 2% NaCl solution. The freezing point depression, the enthalpy of fusion, and the amount of nonfreezable water increase with the introduction of sodium ions. Devitrification observed over the DSC heating cycle in an earlier study on hydrated poly(hydroxyethyl methacrylate), P(HEMA), is absent in hydrated P(NVP/MMA). The observed isothermal crystallization behavior was monotonic. $^{23}$Na NMR line shapes recorded as a function of solution content revealed a sensitivity of the $Na^+$ ion to its local environment. The line width and chemical shift increased abruptly as the degree of hydration fell below the nonfreezable water content as determined by DSC in a way that is consistent with current views on the behavior of water in hydrogels.

## Introduction

The complex behavior of water in hydrogel polymers has been examined in a series of papers[1–3] of which this is part 4. Poly(*N*-vinyl-2-pyrrolidinone/methyl methacrylate), P(NVP/MMA), is one such material that finds wide application in the manufacture of soft contact lenses. In part 1, nuclear magnetic resonance (NMR) and differential scanning calorimetric (DSC) measurements expanded upon the substantial extant literature on the subject to unravel the complexities of water in P(NVP/MMA). Five thermal equilibrium states were identified at specific temperatures within the range 160–300 K.

State 1 (<170 K): Below 170 K, rigid polymer coexists with ice and bound, glasslike water below its NMR glass transition temperature $T_g$.

State 2 (170–230 K): Above $T_g$, the 76 ± 10 wt % glasslike water becomes mobile by 230 K.

State 3 (~250 K): At about 250 K there is evidence of polymer plasticization, and two bound or nonfreezable water components with distinguishably different mobilities are resolved in respective amounts of 50 ± 10 and 28 ± 15 wt %.

State 4 (250–276 K): In this temperature range, nearly normal water, nonfreezable water, ice, plasticized polymer, and nonplasticized polymer coexist.

State 5 (>276 K): Both plasticized and unplasticized polymer coexist with normal bulk water and less mobile water, termed associated water, which is exchanging between heterogeneous sites.

In general terms, three water types are identified: loosely bound water (type A), more tightly bound and highly dispersed water (type B), and near-normal water. The NMR estimate of 50 ± 10 wt % for the more mobile of the two resolved bound water components at 250 K agrees reasonably well with the value of $W_o = 47 \pm 7$ wt % for nonfreezable water determined by DSC measurements.

This study is now extended to include an examination of the P(NVP/MMA)/2% NaCl solution system as a preparatory step to the analysis of the hydrogel saturated with a solution which is similar to the pH and osmolality of tears in the eye. $^{23}$Na NMR spectroscopy which sensitively probes the local environment of the $Na^+$ ion complements DSC measurements on P(NVP/MMA) which, for the first time in this series of experiments, include isothermal measurements.

The motivation to understand the complex behavior of water and buffered saline in hydrogels in an ocular environment, which consists essentially of saline solution (tears), is important because of the dryness which results from the dessication of the lens when it is worn for prolonged periods in the eye. This dessication can also be manifested in "dessicative corneal staining" or the slight erosion of the corneal surface[4] which turns out to be a material-dependent phenomenon[5] and, in particular, is sensitive to the amount and type of water in the hydrogel.[6]

## Experimental Section

$^{23}$Na spectra were recorded on a Bruker MSL 300 spectrometer operating at a resonant frequency of 79.38 MHz. Chemical shifts were referenced to the $^{23}$Na peak for 0.1 M NaCl as described earlier.[3] The procedures used to record and analyze the DSC traces are also fully described in foregoing papers.[1,2] In the isothermal experiment, samples of hydrated P(NVP/MMA) were placed in the calorimeter at 323 K and then quenched at 320 K min$^{-1}$ to a specific temperature within the range 254–259 K, at which temperature the isotherm was immediately monitored for 15 min. Hydration levels varied between 300 and 360 wt %. The random P(NVP/MMA) copolymer, known commercially as Lidofilcon, contained 70.66 wt % *N*-vinyl-2-pyrrolidinone, 29.12 wt % methyl methacrylate, 0.026 wt % ethylene glycol dimethacrylate, 0.19 wt % allyl methacrylate, and 0.10 wt % 2,2′-azobis(isobutyronitrile). S(*W*) and SN(*W*) denote, respectively, hydration with *W* wt % of water and of 2% NaCl solution relative to the dry polymer.

## Results and Discussion

Typical DSC endotherms and exotherms for P(NVP/MMA) hydrated with water S(259) and 2% NaCl solution SN(244) are furnished in Figure 1. They are consistent with earlier observations on hydrogels[1–3] in as much as structure on the endotherms signifies a distribution of melting points: the effect is less pronounced for polymer hydrated with salt solution. Supercooling is detected in exotherms, with freezing point depressions, $T_m$, in the respective ranges 14–21 and 14–38 K for S(*W*) and SN(*W*), reflecting, as expected, an increase in $T_m$ with $Na^+$ concentration.

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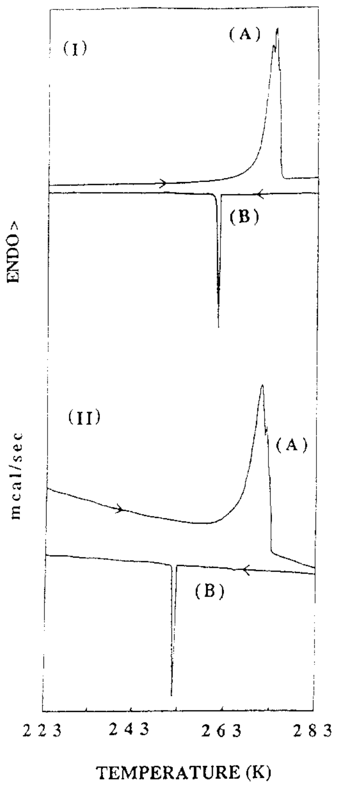

**Figure 1.** Typical DSC endotherms (A) and exotherms (B) for the two hydrated P(NVP/MMA) systems: (I) S(259); (II) SN(244).

The integrated change in enthalpy $\Delta H_f$ (per gram of dry polymer) is shown in Figure 2 as a function of $W$ for both exothermic and endothermic responses. Linear regression fits to the data yield the results summarized in Table I, which show that the nonfreezable water content $W_0$ and $\Delta H_f$ increase with the introduction of $Na^+$ ions into hydrated P(NVP/MMA). All observations are in accord with the view that $Na^+$ is a water-coordinating ion in aqueous solution. That the introduction of NaCl leads to higher values of $\Delta H_f$ (Table I) points to the presence of more bulklike water in P(NVP/MMA)/saline systems. Unlike hydrated poly(hydroxyethyl methacrylate), P(HEMA),[2,3] no broad exotherm is observed over the heating cycle, which ruled out detectable devitrification of part of the glassy or tightly bound water rendered mobile above its $T_g$.

In considering the isothermal behavior, recall the observations of Hatakeyama and co-workers[7] on water–sodium cellulose sulfate systems which showed a two-step transition from a liquid phase to a mesophase at specific temperatures and water concentrations. In contrast, monotonic isothermal crystallization and structureless isotherms are observed for P(NVP/MMA) hydrated with water and with 2% NaCl solution, a typical example of which is shown in Figure 3. On the other hand, a two-step process, in the form of a shoulder on the isotherm and resolution of a bicomponent exotherm, showed up in the P(HEMA)/2% NaCl solution system in the 250–253 K temperature range for a water concentration of 48 ± 1 wt % whereas only monotonic behavior could be detected at a hydration level of 43 ± 1 wt % (Figure 4a). A two-step process was also observed in water-hydrated P(HEMA) at one specific temperature (255 K) and water concentration (57 ± 5 wt %) (Figure 4b). Clearly, the isothermal analysis of hydrated P(NVP/MMA) cannot distinguish between type A and type B water but can resolve different water types in other systems such as hydrated P(HEMA) and sodium cellulose sulfate at specific temperatures and water concentrations. Recall that it was possible to delineate water that devitrified in hydrated P(HEMA).[2]

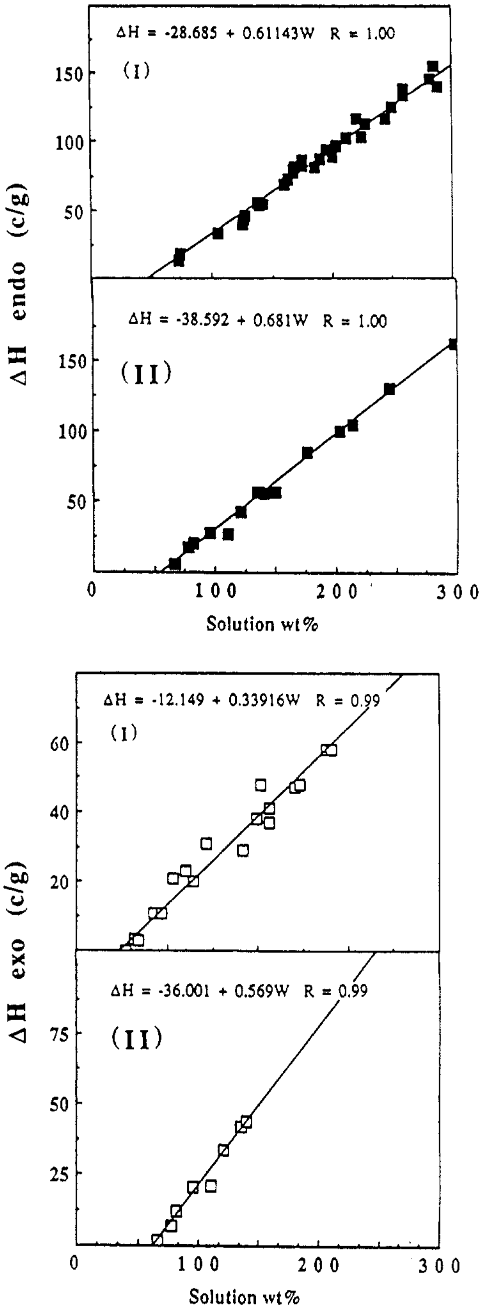

**Figure 2.** Change in enthalpy, $\Delta H$, as a function of water content for endothermic (■) and exothermic (□) hydrated Lidofilcon data. The regression fits to the data are as indicated: (I) S($W$); (II) SN($W$).

**Table I**
**Collated DSC Data for the Hydrated Lidofilcon Systems**

| | heating cycle | | | cooling cycle | | |
|---|---|---|---|---|---|---|
| sample | $W_0$ (wt %) | $\Delta H$ (cal g$^{-1}$) | goodness of fit | $W_0$ (wt %) | $\Delta H$ (cal g$^{-1}$) | goodness of fit |
| water | 47 ± 7 | 61 ± 5 | 1.00 | 37 ± 7 | 34 ± 5 | 0.99 |
| 2% NaCl | 52 ± 5 | 68 ± 4 | 1.00 | 56 ± 6 | 53 ± 4 | 0.99 |
| | 57 ± 5 | 68 ± 4 | 1.00 | 63 ± 7 | 57 ± 5 | 0.99 |

Turning to the $^{23}Na$ NMR results, line widths ($\Delta\nu$, Hz) and chemical shifts ($\sigma$, ppm) were recorded for the P(NVP/MMA)/2% NaCl solution system over a wide range of hydration levels and a modest temperature range (293–313 K). In keeping with earlier studies,[3,8-11] a single symmetric line was observed (Figure 5). As in the comparable study on hydrated P(HEMA),[3] both $\Delta\nu$ and

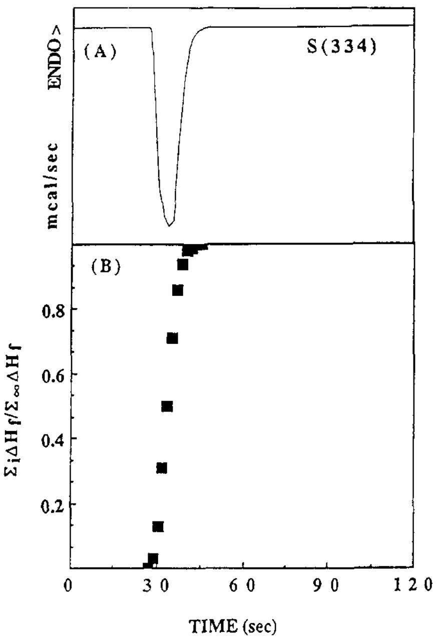

**Figure 3.** Typical exotherm (A) and the corresponding isothermal crystallization curve (B) for water-hydrated P(NVP/MMA), S(334), at 256K.

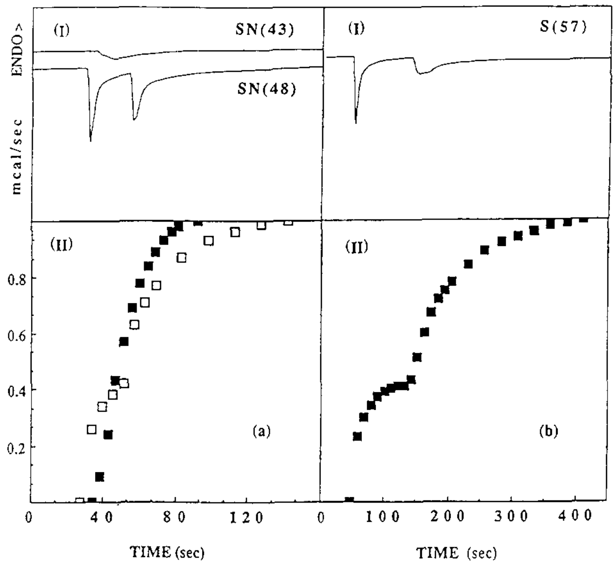

**Figure 4.** Typical isotherms (I) and their corresponding isothermal crystallization curves (II) for (a) 2% NaCl-solution-hydrated PHEMA at 250 K [(□) SN(48); (■) SN(43)] and (b) water-hydrated PHEMA at 255 K [(■) S(57)].

σ begin to increase in the region of $W_o$, in this case, 50 ± 10 wt %. Briefly, it is recalled that $Na^+$ ions can exchange between relatively free and bound states at high levels of hydration via rapid chemical exchange according to

$$\Delta\nu_{obs} = P_b\Delta\nu_b + P_f\Delta\nu_f$$
$$\sigma_{obs} = P_b\sigma_b + P_f\sigma_f \qquad (1)$$

f and b denote free and bound states, and $P$ is the mole fraction in each state. Since $\Delta\nu$ and $\sigma$ are higher in bound states which have longer motional correlation times $\tau_c$, it is clear that both $\Delta\nu_{obs}$ and $\sigma_{obs}$ will increase as $W$ approaches $W_o$. More generally, the asymmetry of the electric field gradient surrounding the $^{23}Na$ nucleus will increase as the hydration sphere around the $^{23}Na$ ions begins to deplete, leading to the observed increase in $\Delta\nu$ and $\sigma$. As noted earlier,[3] $\Delta\nu$ for the highest levels of hydration is still significantly greater than $\Delta\nu$ for aqueous electrolytes of comparable salt concentration, indicating that the $Na^+$ ion still senses the copolymer matrix even at high levels of hydration.

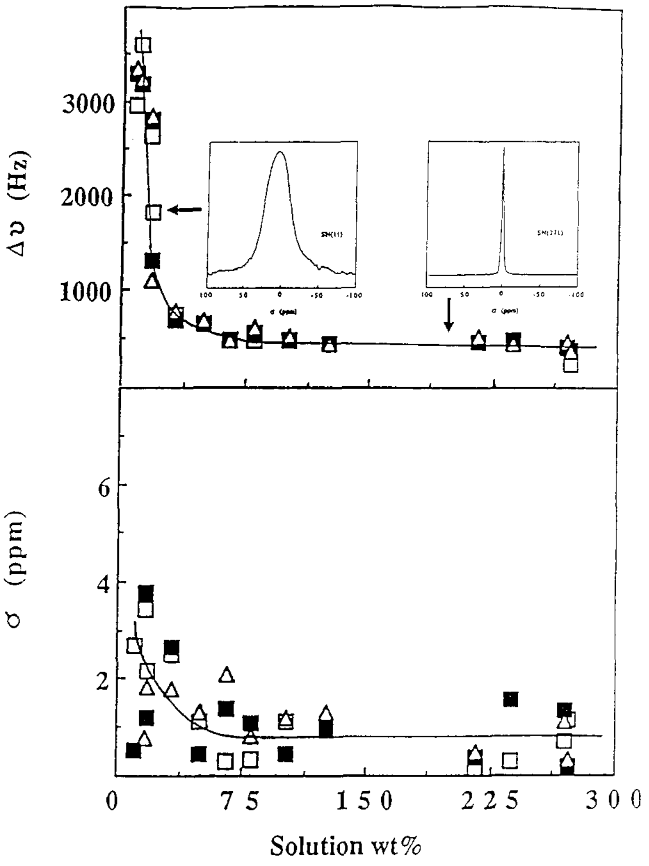

**Figure 5.** Line width ($\Delta\nu$) and chemical shift ($\sigma$) as a function of solution content for SN($W$) at 293 K (□), 303 K (■), and 313 K (△). The symmetric line shapes above and below $W$ = 50 ± 10 wt % are portrayed.

## Summary

The principal conclusions of this study are as follows.

(i) Freezing point depression ($T_m$), the amount of nonfreezable water ($W_o$), and the enthalpy of fusion ($\Delta H_f$) increase with the introduction of sodium ions. One consequence is that water behaves more normally in saline-hydrated P(NVP/MMA) compared to P(NVP/MMA) hydrated with water. Of course, the addition of NaCl will depress the freezing point, which is in keeping with this observation.

(ii) No devitrification is detected over the DSC heating cycle in the P(NVP/MMA)/2% NaCl solution system.

(iii) Monotonic isothermal behavior is observed for a range of temperatures and hydration levels which contrasts with the two-step response of hydrated P(HEMA) and sodium cellulose sulfate.

(iv) $^{23}Na$ NMR spectra are sensitive to the $Na^+$ ion environment. $\Delta\nu$ and $\sigma$ increase when the water content falls below $W_o$, the DSC nonfreezable water estimate. No noticeable dependence on temperature within the, albeit limited, temperature range of 293–313 K was detected.

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**Registry No.** P(NVP/MMA), 25655-01-0; Na, 7440-23-5; water, 7732-18-5.