Polymer Bulletin 13, 493–498 (1985)

Polymer Bulletin

Water-Polymer Interactions

Primary Hydration of Poly(Acrylic Acid) Sodium Salts

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SUMMARY

The equilibrium water contents of linear poly(acrylic acid) sodium salts with different degrees of neutralisation were found to be dependent on temperature and relative humidity. An octahedral model for the primary hydration of poly(acrylic acid) sodium salts (HIRAOKA and YOKOYAMA 1980) was critically evaluated in the light of these findings and an anomaly in the water uptake versus neutralisation curve at approximately 33% neutralisation was explained by the counterion condensation theory. (MANNING 1979).

INTRODUCTION

Crosslinked polyacrylates can absorb up to several hundred times their own mass of water to form gels. The structures of these gels and the forces involved in maintaining their rigid structures have not been fully elucidated (WHISTLER 1977). In this study the hydration of linear polyacrylates was investigated under controlled conditions in order to gain an insight into the fundamental nature of the water-polymer interactions responsible for the macroscopic properties of swollen gels.

EXPERIMENTAL

Synthesis

Poly(acrylic acid) (PAA) was prepared by the radical polymerisation of acrylic acid in benzene with 2,2' azo-bis-(2-methylpropionitrile) (AIBN) initiator. Thus 0,229 g ($1,39 \times 10^{-3}$ mol) AIBN was dissolved in 98,2 g (1,36 mol) acrylic acid and added dropwise over one hour to 1000 ml dry distilled benzene purged with nitrogen at 60 °C with stirring. Approximately 1,5 hours after the start of the polymerisation, PAA precipitated to give a thick slurry. This was filtered, washed with dry benzene and vacuum dried at 60 °C. The yield of dry material was approximately 96 g (98%). Samples of this PAA were dissolved in water and neutralised to 32, 50, 67 and 100 mole percent (viz. designated NaPAA 32, NaPAA 50, NaPAA 67 and NaPAA 100 respectively) by dropwise addition of the calculated amount of standard sodium hydroxide solution with stirring.

Molecular Mass Determination

The viscosity average molecular mass values, $\overline{M}_v$, for PAA and NaPAA 100 were determined using the intrinsic relation (NEWMAN et al.1954)

$$[\eta]_\theta = K\overline{M}_v^a$$

where K and a are constants for a particular polymer/solvent system (NEWMAN et al. 1954, NODA et al. 1970) and $[\eta]_\theta$ is the intrinsic viscosity of the system. The calculated molecular mass values for the two polymers correspond to average degree of polymerisation values, Z, of 2700 and 2800 which are well within experimental error limits of each other. (See Table 1).

Table 1: Viscosity data for PAA and NaPAA 100

	PAA	NaPAA 100
Solvent	1,4 Dioxane	0,5 M NaBr
$K/10^{-3}\ dl^{-1}$	0,85	0,506
a	0,50	0,656
$[\eta]_\theta/dl^{-1}$	0,38	1,77
$M_v\ /\ 10^5$	2,0 ± 0,2	2,5 ± 0,2
Z	2800	2700

Rate of Water Uptake

A sample of each of PAA, NaPAA 50 and NaPAA 100 of approximately 100 mg was weighed into a flat-bottomed dish immediately after being dried at 60 °C for 24 hours in a vacuum oven. The dish was placed in a small cell through which air at 75% relative humidity was passed at a rate of approximately 2 ml per second. The humidity of the air was controlled by passing it through a saturated sodium chloride solution. The entire apparatus was immersed in a water bath of which the temperature could be controlled to within 0,5 °C. Relative humidity was assumed to be constant throughout the temperature range employed. (YOUNG 1967).

The dish was removed from the cell at appropriate intervals, rapidly weighed to within 0,1 mg, and immediately returned to the cell. From the mass increase, the molar water uptake per repeat unit of polymer could be determined for each sample over a range of temperatures. (See fig. 1).

Equilibrium Water Uptake

Dry samples of approximately 100 mg of each of the prepared polymers were weighed into shallow flat-bottomed dishes which were then each suspended in a static atmosphere of controlled relative humidity. Atmospheres of controlled relative humidity in the range 10% to 90% were obtained by employing saturated solutions of various salts in closed vessels in a temperature controlled environment of 25,0 ± 0,1 °C. (YOUNG 1967)

The samples were allowed to equilibrate for several days until no increase in the mass of the sample could be detected over a period of 24 hours. Each sample was then removed from the humidity chamber and rapidly weighed to within 0,1 mg. From the mass increase, the equilibrium molar water uptake per repeat unit of polymer could be determined as a function of relative humidity. The results are shown in Fig 2.

RESULTS AND DISCUSSION

The results of the rate of water uptake studies on PAA, NaPAA 50 and NaPAA 100 are presented in fig. 1.

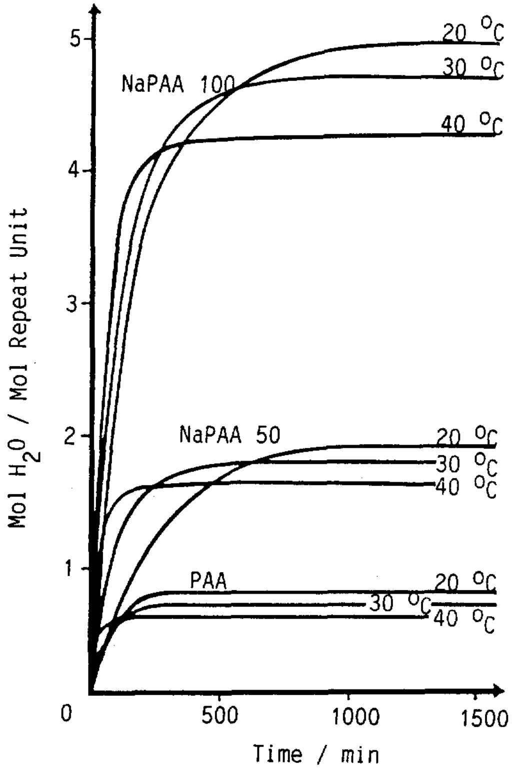

Fig. 1 : Rate of Water Uptake of Linear Polyacrylates at 75% Relative Humidity.

Both the initial rate of sorption and the equilibrium water uptake values were found to increase with increasing degree of neutralisation. For any given degree of neutralisation, the initial rate of water uptake was seen to increase with increasing temperature whereas the equilibrium molar water content decreased.

The decreasing equilibrium water content of each sample with increasing temperature indicates that the sorption process is mildly exothermic. This is to be expected if the sorption process involves a decrease in entropy.

From optical microscopy and screening, particle size appeared to increase with increasing neutralisation. Despite the fact that NaPAA 100 had the largest particle size, it showed the highest rate of water sorption. Attempts were made to crush and screen all samples to within similar particle size limits, but this was unsuccessful due to the sorption of moisture from the atmosphere.

Equilibrium molar water content at 25,0 °C is shown to increase monotonically with relative humidity in fig. 2.

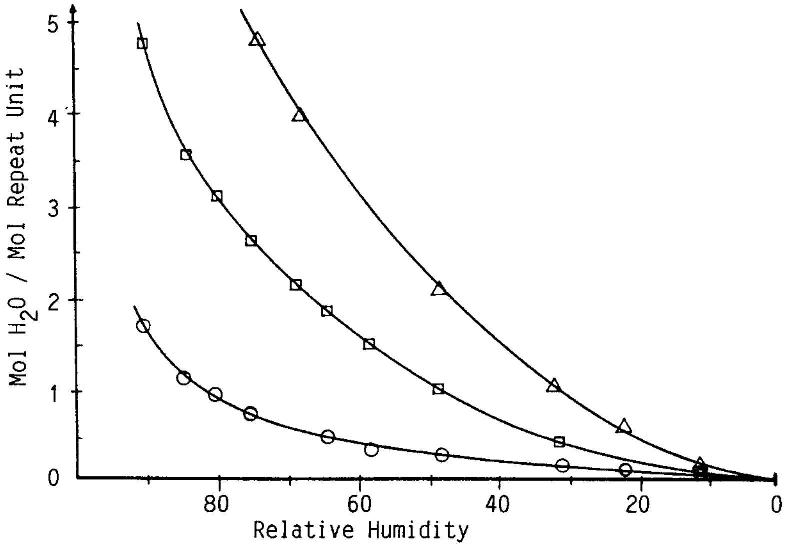

Fig. 2 : Equilibrium Molar Water Content as a Function of Relative Humidity at 25 °C. ▲ = NaPAA 100 ; ■ = NaPAA 67 and ○ = PAA.

Equilibrium molar water content of NaPAA at 25 ^{0}C and 73% relative humidity as a function of neutralisation is shown in fig. 3. The molar water content versus neutralisation curve obtained in this study is in excellent agreement with that obtained by other workers and shows a break at approximately 33% neutralisation. (HIRAOKA and YOKOYAMA 1980).

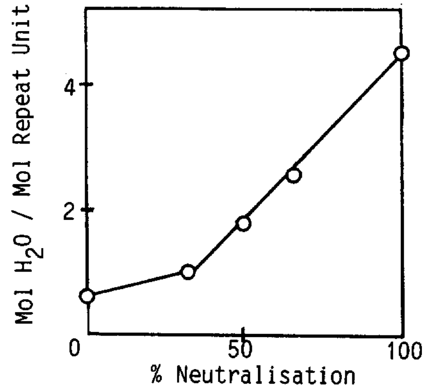

Fig. 3 : Equilibrium Molar Water Contents of Poly(acrylic acid) Sodium Salts with Different Degrees of Neutralisation at 25 °C and 73% Relative Humidity.

In order to account for the observed break in the curve at 33% neutralisation, Hiraoka and Yokoyama proposed an octahedral co-ordination structure model for the sodium ion with the co-ordination sites occupied by polymeric carboxyl oxygen atoms at degrees of neutralisation less than 33%, and by oxygen atoms of water molecules above 33% neutralisation.

The proposed octahedral model does not account for the observed water uptake of the polymer system below 33% neutralisation and Hiraoka and Yokoyama made no attempt to explain how charge neutrality is preserved in the dehydrated system at 33% neutralisation. All of the sodium ions and carboxyl groups present in the system would have to be co-ordinated simultaneously in the manner described at 33% neutralisation for the model to successfully predict the break in the water uptake versus neutralisation curve. This is clearly not the case, as such a system would be 100% crystalline and could have no adsorbed water present. Furthermore, the octahedral structure model is based on hydration studies at 73% relative humidity and 25 ^{0}C which indicate an equilibrium molar water content of four water molecules per repeat unit for fully neutralised poly(sodium acrylate) (NaPAA 100). From this a primary hydration number per repeat unit of four was inferred. However, the present study shows a marked dependence of the equilibrium molar water content on temperature (fig. 1) and relative humidity (fig. 2). This implies that the primary hydration number of four was obtained fortuitously due to the experimental conditions.

Partial molar volume studies cited in support of the octahedral structure model for the Na^+ ion in polyacrylate systems (HIRAOKA et al. 1982) do not appear to be sufficiently precise to unambiguously predict an absolute primary hydration number of four water molecules per repeat unit.

The break in the equilibrium molar water content versus neutralisation curve at 33% neutralisation can be explained by the counterion condensation theory. (MANNING 1979). This theory proposes that as the degree of neutralisation is increased above 33%, the critical charge density for PAA is exceeded, and hydrated conterions "condense" onto the macroion thus affecting the electrostatic forces in the neighbourhood of the polyion chain. There is good evidence to suggest that a change in the electrostatic force between adjacent segments of the flexible PAA molecule with neutralisation can bring about a local conformational change which alters the distance between polymeric charges (KODA et al. 1982) thereby affecting the ability of the polyion to interact with the dipole of surrounding water molecules and enhance the structural properties of the water.

ACKNOWLEDGEMENTS

The authors are indebted to the South African Council for Scientific and Industrial Research and to Johnson and Johnson (Pty.) Limited for their generous financial assistance.

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Accepted June 11, 1985

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