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Hydrogels

Crosslinked Poly(Sodium Acrylate) Hydrogels

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SUMMARY

Samples of poly(acrylic acid) (PAA) neutralized to varying degrees with sodium hydroxide were subjected to γ-irradiation to yield insoluble crosslinked polyacrylate hydrogels. The efficiency of crosslinking was found to be dependent on the degree of neutralization of the sample and the concentration of the irradiated polymer solution. The extent of water uptake of the gel was shown to be related to the degree of neutralization by titration of acid groups within the gel subsequent to cross-linking. Lightly crosslinked gels exhibited a maximum degree of swelling at a particular neutralization level. This was ascribed to a maximum in the long-range forces exerted co-operatively by the polymeric charges. The presence of simple electrolyte ions reduces swelling by screening these forces.

INTRODUCTION

Hydrogels consist of hydrophilic polymers which have been cross-linked to varying degrees in order to form insoluble three-dimensional network structures. These three-dimensional matrixes are capable of absorbing up to several hundred times their own mass of water to form rigid gels, the extent of water uptake being governed by factors such as the charge density of the polymer chains, degree of crosslinking and presence of small electrolyte ions. Although it has been possible to construct gels of improved properties or to modify existing natural polymers to improve their gel qualities, the structure of the hydrogel and the mechanism of water immobilisation is still incompletely understood (WHISTLER 1977). The purpose of the present study is to investigate the fundamental water-polymer interactions responsible for the macroscopic properties of swollen acrylate hydrogels.

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EXPERIMENTAL

Preparation of Linear Polyacrylates

Poly(acrylic acid), (PAA) with molar mass 2 x 10^5 was prepared by the radical polymerization of acrylic acid in benzene with 2,2′ azo-bis (2-methylpropionitrile) (AIBN) initiator. The detail of the synthesis and molar mass determination has been previously described (BUCHANAN et al. 1985). Samples of this PAA were dissolved in water and neutralized to 32, 50 and 100 mole percent (viz. designated NaPAA 32, NaPAA 50 and NaPAA 100 respectively) by dropwise addition of the calculated amount of standard sodium hydroxide solution with stirring.

Irradiation Crosslinking

Solutions of each polymer in the concentration range 1% to 15% by mass were made up in glass ampoules such that each ampoule contained approximately 100 mg of polymer. The solutions were then degassed by several freeze-thaw cycles, sealed under vacuum and subjected to γ-irradiation in the dose range 3 KGy to 75 KGy (10 KGy = 1 Mrad). The irradiations were carried out in an Atomic Energy of Canada (Ltd.) ^{60}Co gamma cell with a nominal capacity of 4,1 x 10^{14} Bq (S^{-1}) and a dose rate of 2,5 KGy/hr which was determined by Fricke dosimetry.

Swelling of Crosslinked Hydrogels

After irradiation, the ampoules were carefully opened and the contents swollen in a slight excess of water for several days before being drained on a 100 mesh nylon screen to determine the mass of swollen gel. Selected samples were then stirred for 24 hours in a vast excess of water (approximately 1 ℓ per 100 mg polymer) to remove any uncrosslinked material, drained, dried and weighed. This yielded the mass of crosslinked material in each sample which gave a measure of the crosslinking efficiency. These extracted samples were reswollen in excess water and remaining acid groups in the gel were neutralized in stages by adding calculated amounts of standard sodium hydroxide solution. The saturated equilibrium water uptake of the resulting gel was measured as a function of the extent of neutralization.

Gel De-swelling in the presence of Salt

Relatively small amounts of crosslinked material were prepared by the methods described. As a result, a commercial crosslinked NaPAA hydrogel, Aquakeep SH 4, was used in all gel swelling experiments involving salt solutions. This material was readily available in relatively large quantities and was also selected partly because of it's commercial importance. The degree of neutralization of this material was determined by titration to be 75%. Volumetric solutions of various A.R. grade salts were made up in the concentration range 0,02 to 0,7 normal and a 100 ml aliquot of each solution added to an approximately 100 mg sample of dry Aquakeep SH 4. The mixtures were allowed to stand for 24 hours at room temperature in order to reach equilibrium, then centrifuged at 4500 r.p.m. for 10 min. on a Hattich Universal 1200 Centrifuge with an average radius of 8 cm. Supernatant fluid was decanted and the mass of precipitated gel determined. From the mass of dry material in each sample and the mass of swollen gel, a graph of water uptake versus concentration of the salt solution could be plotted for each of the salts used. These salts are listed in table 1.

TABLE 1 : Salts Used in Gel De-swelling Experiments

Univalent Cationic Salts	Divalent Cationic Salts	Trivalent Cationic Salts
Sodium Fluoride Sodium Chloride Sodium Bromide Sodium Iodide Sodium Salicylate Sodium Formate Potassium Chloride Potassium Bromide Ammonium Chloride Sodium Sulphate Sodium Phosphate	Calcium Chloride Magnesium Chloride Barium Chloride	Aluminum Chloride Chromium III Chloride

RESULTS AND DISCUSSION

Swelling of Crosslinked Hydrogels

The mass of water taken up per gram of polymer present initially in each polymer solution is plotted against the irradiation dose in fig. 1. Although the errors in these data are relatively large, particularly for soft gels, general trends may be observed. The relative rigidities of the gels were estimated by inspection and by stirring with a glass rod.

It has recently been suggested that swollen hydrogels owe their rigidity to internal Donnan osmotic pressure from absorbed water (WHISTLER 1977). However this would imply that the higher the internal pressure, the more rigid the gel would be. This is clearly not the case, the rigidity of any particular hydrogel decreasing with increasing water content.

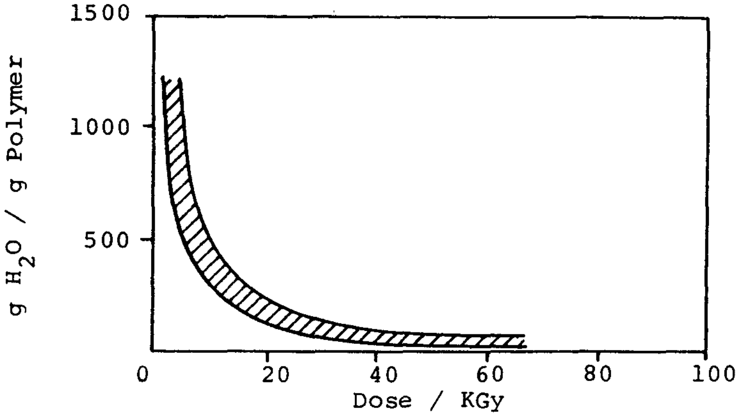

Fig. 1a: Saturated water uptake vs. dose curves for PAA solns. 1% to 15% by mass

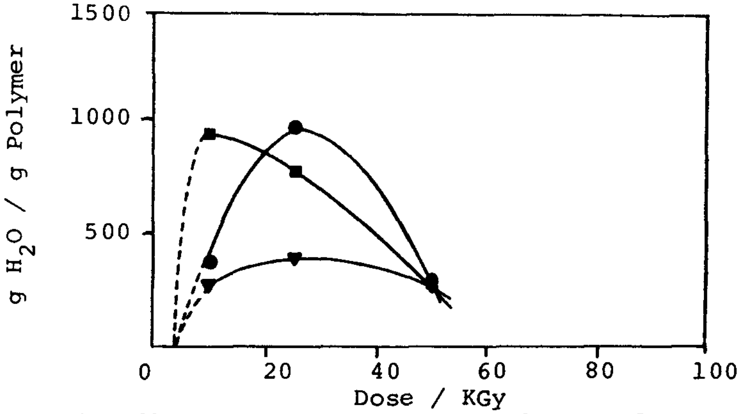

Fig. 1b: Saturated water uptake vs. dose curves for NaPAA 32. ▼ = 2% ; ■ = 5% and ● = 10%

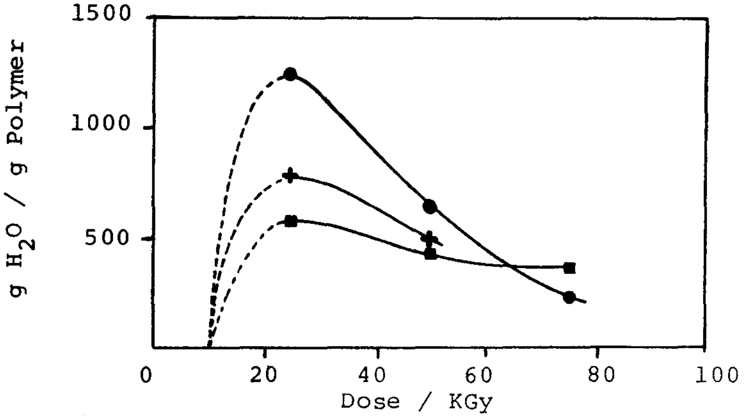

Fig. 1c: Saturated water uptake vs. dose curves for NaPAA 50. ■ = 5% ; ● = 10% & ✚ =15%

For all samples, gel formation only occurred above a certain minimum concentration of the polymer solution and above a critical irradiation dose. The intersection of the dotted lines with the abscissa in figs. 1b and 1c indicates the critical dose below which no gel was formed. Once a gel had formed, further irradiation gave rise to mechanically firmer (more rigid) gels with reduced water uptake. This was ascribed to the formation of more crosslinks which inhibit the swelling of the gel. At even higher irradiation doses, degradation of the polymer caused a reduction in both the rigidity of the gel and it's absorbing capacity.

The minimum dose for gel formation was found to be dependent on the degree of neutralization of the polymer and no gel formation was observed in the NaPAA 100 samples. The viscosity of the fully neutralized samples appeared to decrease with increasing dose suggesting degradation rather than crosslinking. This is in keeping with the findings of other workers that crosslinking is less efficient at increased neutralisation levels. (SAKURADA and IKADA 1963).

Solid samples and very dilute solutions showed little or no gel formation on irradiation. Between these two concentration extremes, there appears to be an optimum concentration for crosslinking efficiency by gamma irradiation, dependent on the degree of neutralization. Concentration effects are clearly seen in NaPAA 32 and NaPAA 50 solutions (figs. 1b and 1c) but are not evident in PAA solutions (fig 1a).

Saturated molar water uptake versus neutralization curves were plotted for extracted crosslinked gel samples (see fig. 2). Maxima were observed in these curves at low levels of crosslinking.

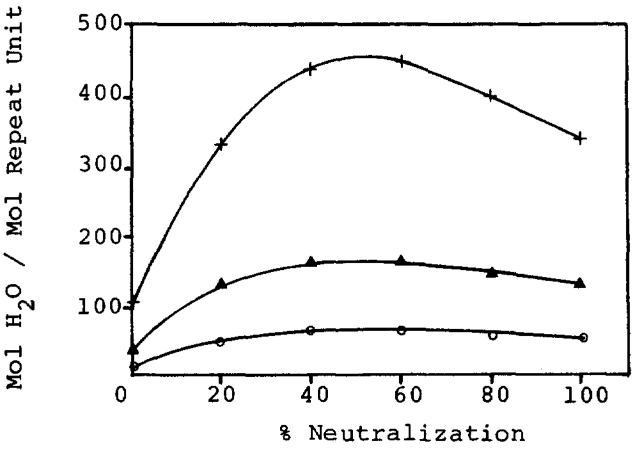

Fig. 2 a : Molar Water Uptake vs. % Neutralization for Gels Obtained From 2% PAA Solutions
+ = 10 KGy ; ▲ = 25 KGy and o = 50 KGy

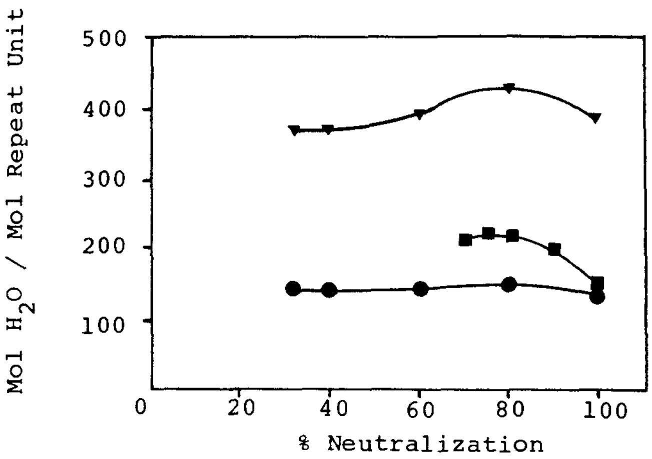

Fig. 2 b : Molar Water Uptake vs. % Neutralization for Gels Obtained From 5% NaPAA 32 Solns.
▼ = 25 KGy ; ● = 50 KGy ; ■ = Aquakeep SH4

Differences between absolute water uptake values for gels obtained from PAA and NaPAA 32 solutions can be attributed to different ratios of crosslinking to main-chain scisson events occurring in each system on irradiation. However, reasons for the observed maxima at low levels of crosslinking are not as obvious.

It has been proposed that the polyion charges act co-operatively to exert long-range electrostatic forces in solution. (LABUZA and BUSK 1979). The existence of such forces can be seen by the fact that an ordered distribution of polyelectrolyte molecules tends to develop even at relatively high dilution (ISE and OKUBO 1980).

Some researchers have postulated that the macroscopic dimensions of the polyion molecules change on neutralization without significant alteration of the local conformation of the polymer segments (SCHAEFER 1971). However, recent Raman spectroscopic studies on PAA exhibited changes in the C-C stretching region of the spectra with degree of neutralization (KODA et al. 1982). This was ascribed to the randomization of the local conformations of segments of the molecular chain as the degree of neutralization increases. Hence it seems feasible that at high levels of neutralization, the macromolecule could expand to such an extent, that the distance between neighbouring charges becomes too great for optimum co-operation effects between the charges. As these co-operative electrostatic effects are thought to play a major role in structuring water within a polyelectrolyte gel, a reduction in these co-operative forces could explain reduced water uptake of the gel at high levels of neutralization.

The dependence of saturated equilibrium water uptake of a partially neutralized sodium polyacrylate hydrogel, Aquakeep SH 4, on salt concentration is shown in fig 3.

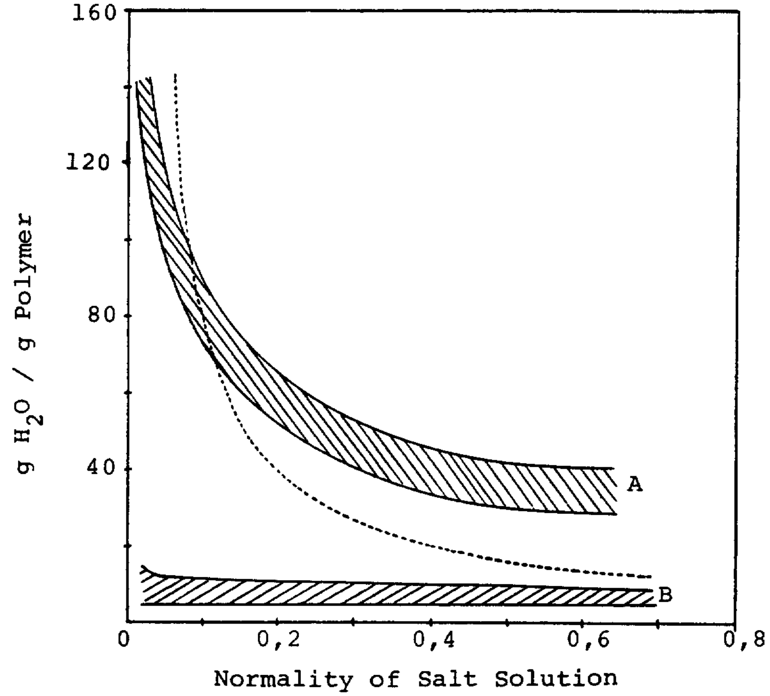

Fig. 3 :

Saturated Water Uptake of Aquakeep SH 4 as a Function of Ionic Strength of Solution. A = monovalent cationic salts B = polyvalent cationic salts. The dotted line indicates the concentration of polyions within the gel.

The saturated equilibrium water content of Aquakeep SH 4 in deionized water is approximately 400 g H_2O/g polymer. The effect of added salt is dependent only on the ionic strength of the solution and the valence of the cation. All univalent cationic species of the same concentration had a similar effect on the water uptake of the gel, independent of the radius of the cation or the nature of the anion. Similarly, all multivalent cations of the same charge concentration (normality) influenced the swelling of the gel to the same extent, having a far greater deleterious effect than univalent cations. This was thought to be due to ionic crosslinking by polyvalent species.

The fact that considerable sorption is observed even when the concentration of monovalent ions in solution exceeds that within the gel, indicated that osmotic pressure is responsible for only part of the swelling. This finding is in keeping with that of other workers (GLASSTONE 1956). Electrostatic effects have been shown to play a major role in the sorption of water by hydrogels. An electric potential applied across a swollen gel causes the gel to collapse above a particular potential, the volume of the collapsed gel being up to several hundred times smaller than that of the swollen gel (TANAKA et al. 1982). Thus it may be concluded that besides osmotic effects, added simple electrolyte screens the co-operative long-range electrostatic forces in the gel, and causes the gel to collapse.

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