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Grafting of acrylamide to Nylon-6 by the electron beam preirradiation technique

VI. The state of water in swollen grafted membranes

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Summary

In water swollen nylon grafted acrylamide (NYgAM) membranes, prepared by the electron beam preirradiation technique, water was classified into three categories: bound, free and intermediate states. The partition of water into these states was evaluated by utilizing the data of water sorption capacity and permeability coefficients of water and ionic solutes through the membranes. Reevaluation of the partition was done utilizing the data of water proton relaxation times T_1, measured by pulsed NMR technique. The partition was evaluated as follows: the first 2 moles of water per mole of grafted polyacrylamide (PAM) are bound, the next 4/3 moles are intermediate and the rest of the water is free. It was further found that in highly water swollen membranes, the water beyond 2 moles per mole of PAM can be classified as free water.

Introduction

Synthetic membranes, which display a strong interaction between solvent (typically water) and the membrane matrix that leads to swelling of the membrane, are permeable to both ionic and neutral solutes (1-5). It is generally accepted that there exist in water swollen polymers at least three types of water (6-8), each of which makes a different contribution to the permeability characteristics of a polymer or a membrane: the bound water, the free water and water in an intermediate state (I-water). The bound water is the water which is directly attached onto the polymeric matrix and is an integral part of it. Conversely, as the free water is classified bulk water inside the polymeric membrane or hydrogel, which has physical properties identical to those of pure bulk water. The I-water is water which is neither strongly bound to the polymeric matrix nor free to impart permeability of solutes through a membrane (8).

In previous communications (3) we have discussed the preperative and kinetic aspects of the electron beam induced grafting of acrylamide onto nylon-6 films and the permselectivity features of the water-swollen NYgAM membranes. We have recently shown (5) that the swelling-annealing of the NYgAM membranes with formic acid leads to intense increase in the water sorption capacity of the membranes. This increase was attributed to phase separation between crystalline and amorphous regions of the NYgAM membranes, accompanied by disentanglement of the grafted PAM chains (4). Morphological changes in NYgAM membranes which were modified by crosslinking and swelling-annealing (5), caused a rise in the fluxes of water and small ionic solutes through the membranes, accompanied by a decrease in the selectivity.

In the present study we have focused our attention on the determination of the partition of the water into the three states: bound, intermediate and free water, in a series of swollen NYgAM membranes with graft yields ranging up to 1300%. We also tried to evaluate the effect of the swelling-annealing process on this partition.

Experimental

Detailed procedures for the preparation and modification of the grafted membranes, the determination of their water sorption capacity and the measurements of the permeation rates of water and the ionic solutes through the grafted membranes have been described previously (3-4).

Samples for measurement of the relaxation times of the protons of water in the membranes were prepared as follows: membrane specimens were wetted by soaking in water, wiped thoroughly and placed in 5 mm O.D. teflon NMR ampules, which were used in order to eliminate sorption of water onto the internal surface of the NMR ampules. Equilibration of the membranes with water was attained by introducing the sample ampules into a thermostatted chamber kept at 100% relative humidity (RH) and 37°C for a period of 14 days or longer. The sample ampules were sealed immediately before transferring them into the NMR chamber, which was thermostatted at 37±0.4 °C.

The spin-lattice relaxation times of the water protons T_1 were determined using the BRUKER WH-90-DS-ZV 90 MHz system, according to the procedure described by Andrade (9-10), using the $180^\circ-\tau-90^\circ$ sequence of pulses. The optimal width of the two pulses was found to be 11 and 5.5 μs, respectively. The intensities I of the water protons NMR signals were recorded at several time intervals τ and $\log(I_\tau - I_\infty)$ was plotted against τ (I_∞ was estimated from the intensity I after a very long time interval). The T_1 values were calculated using the relation:

$$T_1 = \log(e) * \Delta\tau \; / \; \Delta\log(I_\tau - I_\infty) \qquad \text{(I)}$$

Results and Discussion

The Bound Water

The water sorption capacity of NYgAM membranes, expressed as percent of water add-on, vs. the PAM content in the membranes is presented in fig. 1.

Extrapolation of the curve to zero PAM concentration provides an estimate of the amount of the first water that can be attached by the PAM units: ca. 50%(w/w), which corresponds to 2 moles of water per mole of PAM. Bearing in mind that at PAM concentrations that are close to zero only very short and diffuse grafted chains of the PAM may exist, clustering of the first water molecules adsorbed onto the PAM chains is most improbable. Therefore, these water molecules may be defined as the bound water. The attachment of two molecules of water onto

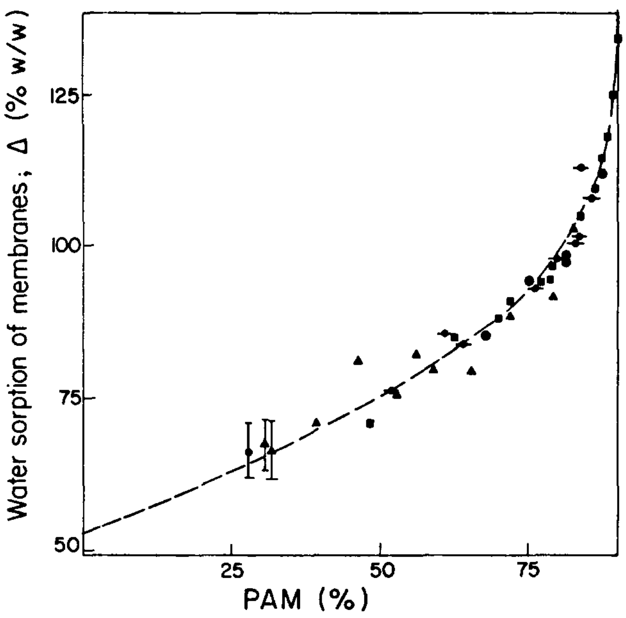

Figure 1: Water sorption at 37°C into PAM in NYgAM membranes prepared under various grafting conditions: Δ = water sorption capacity; Grafting conditions: (■) 12 Mrad, 10% AM; (▲) 12 Mrad, 5% AM; (●) 8.4 Mrad, 10% AM; (-●-) 4.8 Mrad, 10% AM; grafting temp 50°C.

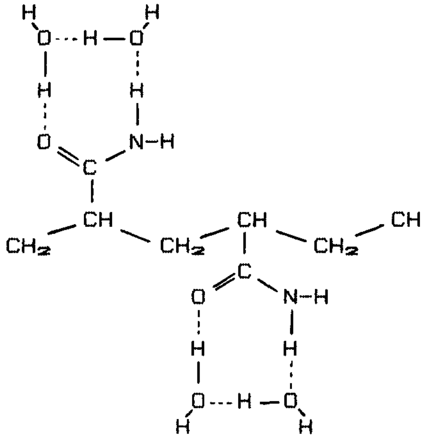

Figure 2: Schematic model description of the water-AM attachment.

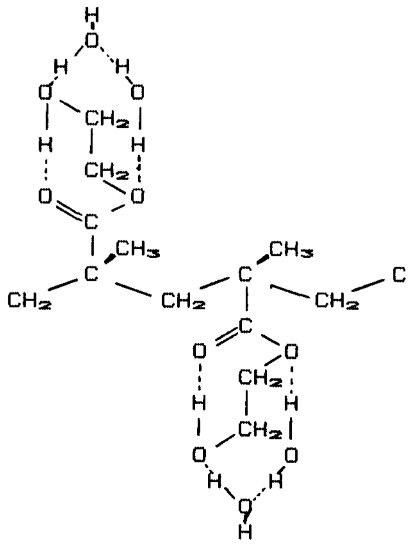

Figure 3: Schematic model description of the water-HEMA attachment.

each acrylamide mer-unit (AM) in the grafted PAM can be described, schematically, by a model displayed in fig. 2.

This type of binding of the water molecules onto the polymer is similar to models suggested by others (11-12). Andrade and coworkers (10) found in non-crosslinked polyHEMA gels a molar ratio of 2 between the bound water and the HEMA mer-units (28% w/w). The attachment of bound water to polyHEMA molecules can be described by a model similar to that of the water-PAM attachment, as shown in fig. 3. This similarity implies that there may exist a general pattern for the attachment of bound water onto hydrophilic acrylic polymers.

The Free Water

Free water in water-swollen polymeric gels exhibits most of the properties of pure water such as dielectric constant and water-ion mobilities (8). This is the water which imparts the high permeabilities to water and aqueous solutes through the highly swollen membranes. The amount of free water in water-swollen membranes can be estimated from the permeability characteristics which they display. Fig. 4 presents the permeabilities of quarternary ammonium salts through a series of NYgAM membranes of various graft yields, vs. the water uptake of the grafted PAM in the membranes, each curve representing a different solute.

The curves of permeability vs. water-uptake drawn for the various solutes converge, upon extrapolating to zero-permeability, at water uptake of ca. 84%. This convergence implies that only above this threshold of water uptake can

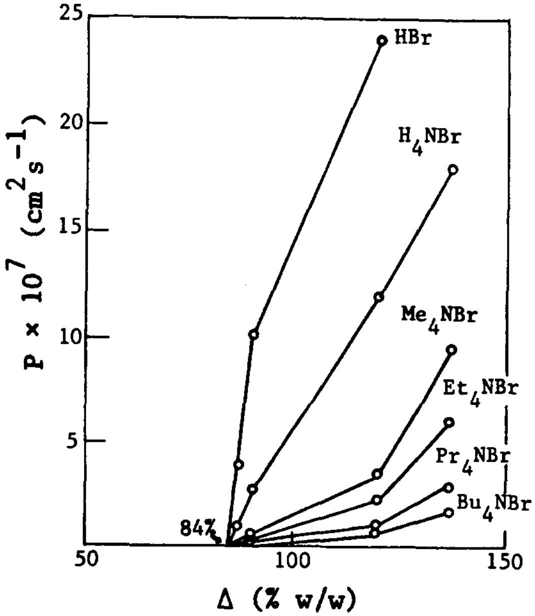

Figure 4: Permeability coefficients P vs. NYgAM water uptake Δ (w/w), at 37°C.

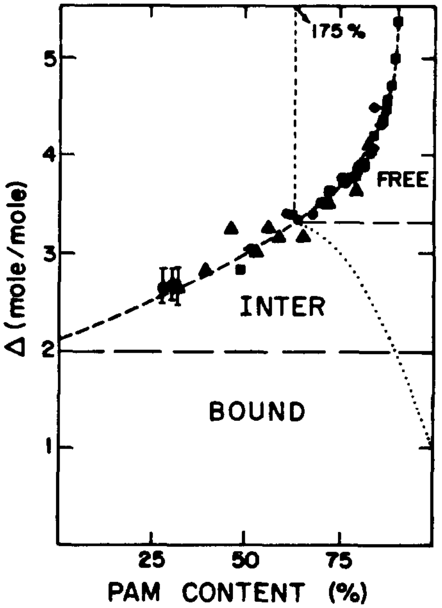

Figure 5: Water partition in NYgAM membranes: ---- 1st evaluation; ···· 2nd evaluation.

significant permeation of aqueous solutes through the membranes take place. This threshold quantity, which corresponds to 10/3 moles of water per mole of PAM may be defined as the "non-free" water. Only absorbed water exceeding this threshold contributes to the permeability of solutes through the membranes and should, therefore, be entitled the free water.

The Water in the Intermediate State

In fig. 5 the conclusions derived in the preceding sections are illustrated, superimposing the partition lines on the curve of water uptake vs. membranes PAM-content (fig. 1).

The water defined as I-water is water which is not directly attached to the polymeric matrix yet is unable to impart to solutes permeability through the membranes. From fig. 5. we can estimate that NYgAM membranes holding up to ca. 175% graft yield, contain only bound and I-water. This inference is consistent with kinetic observations made previously, in the experiments of grafting of AM onto nylon-6 thick films (3). These kinetic observations indicated that during the grafting process, accelerated diffusion of monomer through the grafted layers towards the non-grafted ones took place only after the graft yield of the already grafted layer exceeded ca. 200%, which corresponds to a water uptake of ca. 85% or 3.4 moles water per mole of PAM.

This consistency implies that although only 2 molecules of the water are bound to each mer-unit of PAM, additional water molecules - up to 4/3 per PAM mer-unit are non-free water. This neither bound nor free water falls, therefore, into the category of I-water. This type of water was designated as "bound water II" (8), "intermediate water" (6-7) or "water entrapped in blocked micropores" (13). Another origin of the I-water phenomenon may be the relatively small effective cross-section of the pores in the microporous membranes to the permeation of solutes (14), which is given by equation II:

$$A_{eff} = A \times (r - a)^2 / r^2 \qquad \text{(II)}$$

A, r and a are the pore cross-section, pore radius and permeant radius, respectively. Pores in which a > r are blocked to the transport of permeants having a radius a. In these pores the water can be characterized as "non-free" with regard to the diffusion of that permeant and fall, therefore, into the category of I-water. In pores where r > a the water in adjacency to the pore walls is ineffective for permeability and is, practically, part of the I-water.

The Effect of Swelling-Annealing of the Membranes on the Partition of the Water into the Three Classes

In previous articles (5), we reported that by the swelling-annealing treatment, the swelling capacities of the grafted membranes in water were increased by a factor of 4-5, as compared with those of the non-annealed membranes. This caused a 2-20 times increase in the permeability of ionic solutes through membranes of various graft yields, together with loss of selectivity between small and large solutes.

The extra water sorbed by the swell-annealed membranes as compared with the non-annealed ones, is most probably free water. An increase in the amount of bound water is unreasonable since the amount of grafted PAM, to which the bound water is attached, is not changed by the swelling-annealing treatment. The amount of I-water associated with the bound water is not likely to increase for similar reasons. Part of the additional absorbed water may be in the form of pore-wall I-water, due to an increase in the pore-wall area of the water-filled pores in the annealed membranes.

It is plausible, therefore, that the major portion of the additional absorbed water is in the form of free water. This explains the strong increase in permeability to water and solutes upon swelling-annealing of the grafted membranes. The subsequent significant decrease in selectivity implicates the enlargement of pores as the predominant occurrence of the swelling-annealing process, rather than an increase in the number of pores. This conclusion is in consistency with the suggested mechanism of phase separation following the swelling-annealing process described in a previous article (4).

Pulsed NMR Characterization of the Water Absorbed in the Grafted Membranes

Proton relaxation times T_1 of the absorbed water, measured in membranes of various graft yields, are presented in Table I. In the previous sections, we have reported the following partition of water found in the swollen membranes: the first two moles of water per mole of PAM is bound water, the next 4/3 - I-water and the exceeding amounts is free water, as illustrated in fig. 5. The calculated values of the proton relaxation times according to this partition, postulating the existence of fast exchange between protons of the various classes, were derived using the relation (9):

$$\frac{1}{T_1} = \frac{X_{(B)}}{T_{1(B)}} + \frac{X_{(I)}}{T_{1(I)}} + \frac{X_{(F)}}{T_{1(F)}} \qquad \text{(III)}$$

X and T_1 denote mole fractions and spin lattice relaxation times, respectively, of water in the bound (B), intermediate (I) and free (F) states.

The relaxation times $T_{1(B)}$ and $T_{1(I)}$ presented in col. 5 of Table I were calculated from the T_1 measured values of samples 1 and 2, assuming that these two low-grafted NYgAM membranes do not contain free water (cf. fig. 5). On the basis of these two values and the formerly derived distribution of water in swollen membranes into the three states (col. 4), the T_1 values of the highly grafted membrane samples were calculated and compared with the measured values.

The calculated values of T_1 (col. 6 in Table I) are lower than the measured ones, within the error limits of the technique of the measurement and determination of the Δ values (equation II), of about 10%. This divergence could be vindicated by the existence of a layer of free water adhering onto the surface of the membranes equilibrated with water, thus causing an artificial rise in T_1.

This explanation, however, should be rejected for several reasons. Firstly, when a separate layer of water exists outside the membrane, we should notice two linear sections in the plot

Table I: Distribution of water in NYgAM membranes into Bound, Intermediate and Free water

	Graft yield	Δ[a]	Δ[b] distribution			T_1[c]			T_1[d] average		Δ best-fit distribution		
	%	$\frac{mole}{mole}$	$\frac{mole}{mole}$			ms			ms		$\frac{mole}{mole}$		
			B	I	F	B	I	F	(M)	(C)	B	I	F
1	30	2.49	2	0.49	-	211 (C)	264 (C)	4500 (M)	223 ± 23		2	0.49	-
2	108	3.04	2	1.04	-				230 ± 10		2	1.04	-
3	333	3.75	2	1.31	0.44				351 ± 20	258	2	0.3	1.45
4	386	3.94	2	1.31	0.63				413 ± 13	270	2	-	1.94
5	901	5.64	2	1.31	2.33				490 ± 30	377	2	0.4	1.94
6	1235	7.02	2	1.31	3.71				840 ± 70	460	1.5	-	5.52

[a]– Δ = number of moles of water per mole of PAM.

[b]– B, I and F denote bound, intermediate and free water.

[c]– T_1 values of the water in each state. (M) and (C) denote measured (using pure water) and calculated T_1 values (using the T_1 values of samples 1 and 2), respectively.

[d]– calculated T_1 values were averaged utilizing the data in col. 4 and 5 and equation III.

of $\log(I_\tau - I_\infty)$ vs. τ (cf. experimental), with two slopes, representing two different relaxation times T_1. However, as far as could be detected, all the $\log(I)$ vs. τ plots are composed of a single line. Secondly, equilibration of the samples with water vapor is a very prolonged process (see experimental) and in several cases equilibrium was not reached even after several weeks. Therefore, a surplus amount of water on the surface of the samples is not plausible.

The third reason is the observation that the higher the graft yield and the thickness of the membrane, the more prominent is the difference between the two T_1 values. Conversely, one may anticipate that the relative effect of a surface water layer will be more pronounced on thin membranes rather than on thick, highly water swollen membranes. It is reasonable, therefore, to reject the water-layer explanation and look out for the origin of these differences.

In a former section, we estimated that I-water is accumulated in the membranes upon an increase in the water content from 2 to 10/3 moles of water per mole of PAM. The partition of water presented in col. 4 of table I is based upon the hidden assumption that upon further increase in water content, the amount of I-water does not change. The values of T_1 relaxation times (table I col. 5) were calculated following this argumentation. Andrade and coworkers (10) postulated a similar fixed distriution of water in polyHEMA hydrogels.

However, introduction of additional (free) water into the membranes, above the 10/3 mole/mole I-water threshold, is accompanied by enlargement of pore volume and pore cross-section and a decrease in the fraction of blocked pores. In other words, the additional volume of water introduced into blocked or narrow pores may "open" the pores and change the transport characteristics of the whole amount of the water in the pores, thus converting part of the I-water into free water. Thus, when all three states of water in the swollen membrane are occupied, an increase in the water content of the membrane is followed by an enhanced increase in the amount of free water and a decrease in the amount of I-water. The steep rise in the slopes of the curves of P vs. water uptake (cf. fig. 4) lends support to this conclusion.

Consequently, in col. 7 in table I are presented the calculated corrected values of the amounts of water in the three states, which yield the best agreement with the T_1 values. For most membranes, we adopt the amount of bound water of 2 moles/mole PAM. However, for the 1235% grafted membrane, the calculations performed using this value yield poor agreement between the calculated and measured values of T_1. The best compatability is attained if we assume that in this highly grafted membrane, there are only 1.5 moles of bound water per each mole of AM. The rationale for this estimation is that at very high graft yields, the long PAM chains are probably highly entangled and behave like a crosslinked hydrogel (5). The findings of Andrade (10) that in crosslinked polyHEMA hydrogels the bound water are only 1.6 moles of water per mole of polyHEMA (22% w/w), lend support to our estimation.

Finally, consequent to the above discussion, the corrected distribution of the sorbed water into the classes, at varying levels of water uptake, is presented by the dashed curve in fig. 5, which shows the gradual disappearance of the I-water upon increase in the amount of free water, followed at very high graft yields, by a decrease in the amount of bound water.

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