

## Hydration of Sulfonated Polyimide Membranes. II. Water Uptake and Hydration Mechanisms of Protonated Homopolymer and Block Copolymers

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Received: November 29, 2004

The hydration of sulfonated polyimide membranes in their protonated form is probed by infrared spectrometry using a recently described method. The membranes considered are the homopolymer, made of identical sulfonated repeat units, and two block copolymers composed of these units plus similar ones with no sulfonic groups in two different proportions. The experiments consist of registering series of spectra of these membranes at various hygrometries of the surrounding atmosphere. The quantitative analysis of the evolution of these spectra allows one to measure precisely the water uptake and to define in terms of chemical reactions the various hydration mechanisms that are active at a definite value of the hygrometry. It shows how the dried homopolymer significantly differs from the two dried block copolymers: in the homopolymer, a good proportion of SO<sub>3</sub>H groups that represent 83% of sulfonate groups, cannot establish H-bonds on C=O groups that are in a relatively small number. As a consequence, all coexisting SO<sub>3</sub><sup>−</sup> groups are H-bonded to single H<sub>3</sub>O<sup>+</sup> cations with no extra H<sub>2</sub>O molecules. In both dried block copolymers, each SO<sub>3</sub>H group (60% of the sulfonate groups) establishes H-bonds on C=O groups that are in a sufficiently great number. These H-bonds stabilize these SO<sub>3</sub>H groups, and coexisting SO<sub>3</sub><sup>−</sup> groups are H-bonded to cations that are found in the form of H<sub>5</sub>O<sub>2</sub><sup>+</sup> or H<sub>7</sub>O<sub>3</sub><sup>+</sup> that contain several H<sub>2</sub>O molecules. When the hygrometry increases, these differences get less marked but can be precisely defined.

### Introduction

In this article, we study the hydration of polyimide sulfonated membranes by infrared (IR) spectrometry, that is, quantitative IR spectroscopy. More precisely, we study “protonated” membranes, where the cation is H<sub>3</sub>O<sup>+</sup>. These polyimide membranes are candidates to be used in fuel cells as proton transferring membranes,<sup>1</sup> and it is consequently of interest to know how water molecules are embedded in these membranes. These protonated membranes represent a somewhat more complex case than the homopolymers we described in a preceding article,<sup>2</sup> where the cations were either Na<sup>+</sup> or triethylammonium HN<sup>+</sup>-(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>. All hydration steps consisted then of the addition of H<sub>2</sub>O molecules, which established hydrogen bonds (H-bonds in the following) on various hydrophilic sites of the membranes that have been found to be, at low hydration level, the carbonyl C=O groups and the negatively charged O<sup>−</sup> atom of the sulfonic SO<sub>3</sub><sup>−</sup> groups. At high hydration levels, the already embedded H<sub>2</sub>O molecules, which had developed a consequent H-bond network, offered new hydrophilic sites. In the protonated membranes we consider in this article, one more step occurs at low hydration level, which is ionization of the SO<sub>3</sub>H groups present in the dried sample. Furthermore, the measurements of the number of H<sub>2</sub>O molecules seem to be more difficult when the actual cations are H<sub>3</sub>O<sup>+</sup>, as the bands due to H<sub>3</sub>O<sup>+</sup> cannot be so easily separated from those due to H<sub>2</sub>O and may have

completely different molar intensities (intensity for 1 mol of either H<sub>2</sub>O or H<sub>3</sub>O<sup>+</sup>). The analysis of the spectra will consequently prove to be more delicate. In this article, we take advantage of this preceding study, relying on the assignments of various vibrations that were then performed and that we recall in Table 2 of this article, as bands of the skeleton, of C=O, and sulfonate groups are the same, and also using well-defined bands due to H<sub>2</sub>O molecules embedded in these polymers that could be then precisely defined.

In this study, we face the same positive points and the same inconveniences as in I. The positive points are found with the stretching  $\nu_s(\text{O}-\text{H} \cdots)$  bands due to H<sub>2</sub>O and the stretching  $\nu_{\text{C=O}}$  bands of the carbonyl groups, which exhibit such good signal-to-noise ratios that a precise quantitative analysis can be performed on them. It allows the proposal of a precise hydration mechanism of these membranes. The inconveniences are concentrated on bands of the SO<sub>3</sub><sup>−</sup> groups, which are not so well defined, being partly overlapped by more intense bands due to the skeleton, and are only slightly modified by the inclusion of H<sub>2</sub>O molecules. As a consequence, no quantitative analysis can be performed on these SO<sub>3</sub><sup>−</sup> groups; that is, we cannot precisely determine the number of these groups that is hydrated by *N* H<sub>2</sub>O molecules. On the basis of the assignments of the bands of these groups proposed in I, which relied on reasonable arguments, we could nevertheless establish that the neutral O atoms that are doubly bonded to the central S atom of this group are not hydrated; that is, they do not act as H-bond receptors for embedded H<sub>2</sub>O molecules.

In this article, we not only consider the homopolymer but extend the study to block copolymers that consist of a block of *x* sulfonated elementary units followed by a block of *y*

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**TABLE 1: Density,  $d$ , Molar Mass,  $M$ , of a Repeat Unit, Thickness,  $e_s$ , of the Sample, for Various Films of Protonated Polymers Described in This Article**

composition		$d$ (g cm <sup>-3</sup> )	$M$ (g mol <sup>-1</sup> )	$e_s$ ( $\mu$ m)
$x$	$y$			
1	0	0.89	576.5	10
5	5	0.87	5045	6.2
5	11.6	0.87	7900	6.3

**TABLE 2: Assignments of Bands of Interest for the Protonated Homopolymer<sup>a</sup>**

wavenumber	assignment
598	$\nu(\text{C}-\text{SO}_3\text{H})$ in $\text{SO}_3\text{H}$
630	$\nu(\text{C}-\text{SO}_3^-)$ in $\text{SO}_3^-$
771	
893	
919	$\nu(\text{S}-\text{OH})$ in $\text{SO}_3\text{H}$
985	
997	$\nu_s(\text{O}=\text{S}=\text{O})$ in $\text{SO}_3^-$
1004	
1032	$\nu_s(\text{O}=\text{S}=\text{O})$ in $\text{SO}_3^-$
1100	$\nu_{\text{as}}(\text{O}=\text{S}=\text{O})$ in $\text{SO}_3^-$
1131	$\nu_{\text{as}}(\text{O}=\text{S}=\text{O})$ in $\text{SO}_3^-$
1186	$\nu_s(\text{O}=\text{S}=\text{O})$ in $\text{SO}_3\text{H}$
1186	
1250 (a doublet?)	$\nu(\text{S}-\text{O}^-)$ in $\text{SO}_3^-$
<i><math>\approx 1347</math></i>	$\nu(\text{C}=\text{C}) + \nu_{\text{C}-\text{N}-\text{C}}$
<i><math>\approx 1350</math></i>	$\nu_{\text{as}}(\text{O}=\text{S}=\text{O})$ in $\text{SO}_3\text{H}$
<i><math>\sim 1450</math></i>	$\nu(\text{C}=\text{C})$
1470	$\nu(\text{C}=\text{C})$
1583	$\nu(\text{C}=\text{C})$
1681	$\nu_{\text{as}}(\text{C}=\text{O})$
1720	$\nu_s(\text{C}=\text{O})$

<sup>a</sup> Bands of the skeleton are indicated by wavenumbers in italic.  $\nu(\text{S}-\text{OH})$  stands for the S—O stretching band of  $\text{SO}_3\text{H}$ , while  $\nu(\text{S}-\text{O}^-)$  stands for the S—O stretching band of  $\text{SO}_3^-$ .  $\nu_s(\text{O}=\text{S}=\text{O})$  and  $\nu_{\text{as}}(\text{O}=\text{S}=\text{O})$  stand for symmetric and antisymmetric stretching vibrations in the  $\text{O}=\text{S}=\text{O}$  groups of  $\text{SO}_3\text{H}$  or  $\text{SO}_3^-$ .  $\nu_s(\text{C}=\text{O})$  and  $\nu_{\text{as}}(\text{C}=\text{O})$  stand for symmetric and antisymmetric stretching vibrations in pairs of interacting  $\text{C}=\text{O}$  groups drawn in the lower part of Figure 1.

elementary units with no sulfonic groups. Their structure is drawn in Figure 1.<sup>1,3</sup> The homopolymer is a particular case of these block copolymers, with  $y = 0$ . The molecular and macroscopic parameters of the various samples we used in this study are displayed in Table 1. This article is organized as follows: In the first section, we describe the spectra of the homopolymer at various hygrometries of the surrounding atmosphere and decompose them on elementary hydration spectra that can be defined from experimental spectra. In the second section, we perform the same operations for the block copolymers. The third section is then devoted to the measurements of the water uptake in all three polymers and is followed in the next section by the determination of hydration mechanisms in terms of chemical reactions.

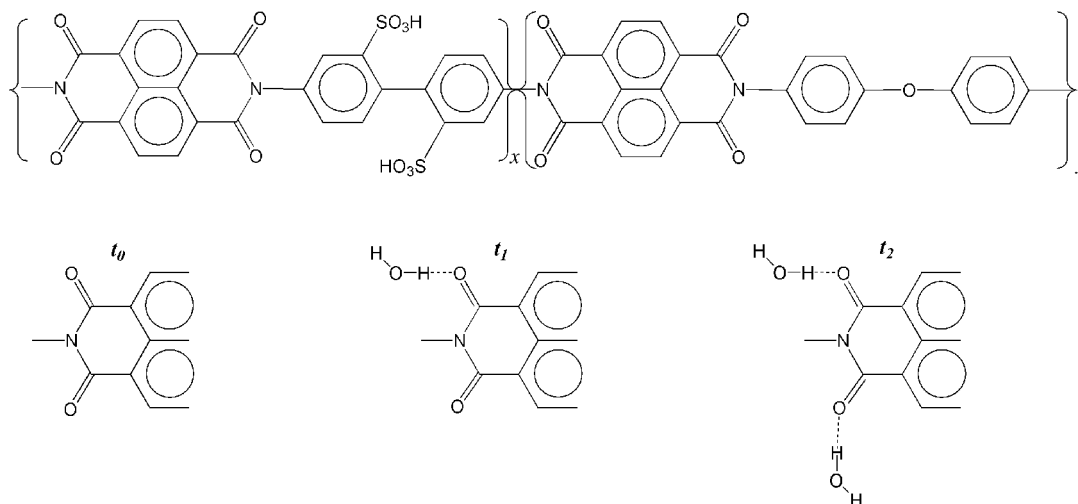
## Homopolymer

We begin with the examination of the spectra of the (protonated) homopolymer, where  $y = 0$  (Figure 1), that is, only the sulfonated elementary units are present. This polymer is, except for the cations, identical to the homopolymer presented in I. It offers a good starting point because we benefit from our previous experience and because this homopolymer exhibits spectral bands due to the sulfonic groups, in both the  $\text{SO}_3\text{H}$  and  $\text{SO}_3^-$  forms, which can be clearly distinguished. They do not appear so clearly in the copolymers with  $y \neq 0$ , where they have smaller intensities as compared to more intense bands of the skeleton. These bands in the copolymers will consequently

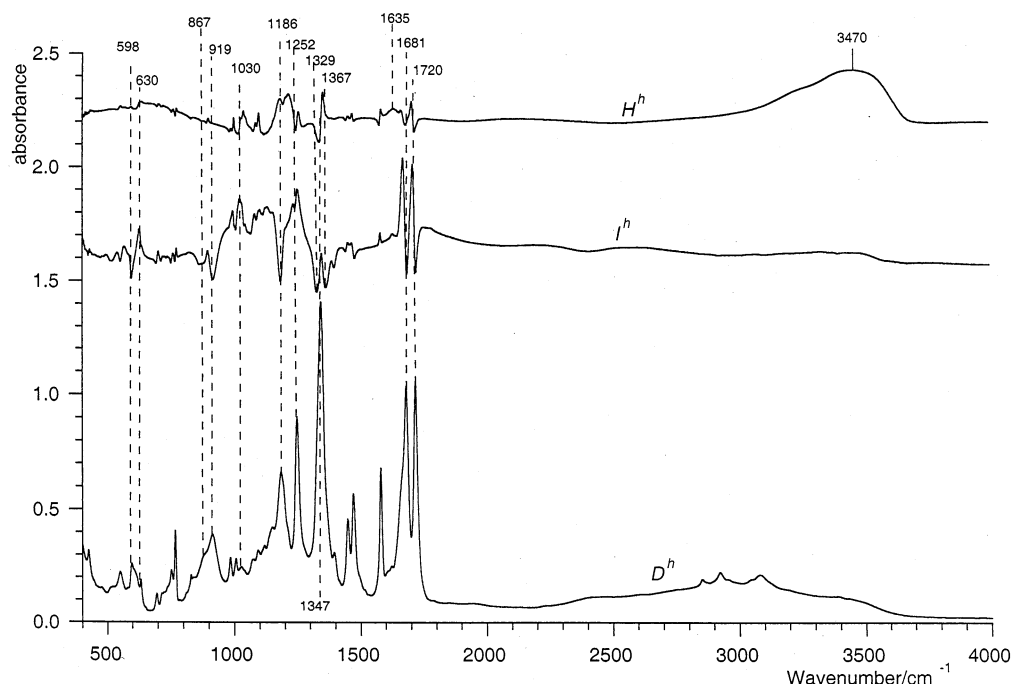
be later analyzed in a subsequent section, referring to the homopolymer we analyze in this section, where they are better defined.

The method used to obtain and analyze hydration spectra has been described previously in more detail.<sup>4</sup> Let us summarize it. A thin sample, some 5–10  $\mu\text{m}$  thick, of a dried polyimide membrane is positioned in a special hydration cell, inside which the hygrometry and the temperature of the atmosphere are controlled and can be varied. A set of 10–12 spectra of the film in equilibrium with its surrounding atmosphere at various values of its hygrometry is registered. This set spans the whole range of hygrometry from 0 to 1. Subtraction of the easily identified bands due to water vapor gives the value of the water vapor pressure,  $p$ , and, consequently, the hygrometry,  $p/p_0$ , where  $p_0$  is the (tabulated) value of the saturating water vapor at the same temperature. In the second step, subtraction of the spectrum of the dried ( $p/p_0 = 0$ ) film from the recorded spectra gives a set of “hydration spectra”,  $S(p/p_0, \tilde{\nu})$ , which are analyzed by decomposing them onto a limited number of “elementary hydration spectra”,  $I^h(\tilde{\nu})$  and  $H^h(\tilde{\nu})$ , where the index  $h$  stands for “homopolymer”. We display them in Figure 2, together with spectrum  $D^h(\tilde{\nu})$  of the dried membrane. The presence of only two elementary hydration spectra, on which all  $S(p/p_0, \tilde{\nu})$  can be decomposed, implies that hydration of this homopolymer is a two-step process.

In spectrum  $D^h$ , bands at 598 and 919  $\text{cm}^{-1}$  that are due to  $\text{SO}_3\text{H}$  (Table 2) clearly appear. The other bands that are due to  $\text{SO}_3\text{H}$  are masked by more intense bands of the skeleton. They nevertheless clearly appear in spectrum  $I^h$  as two negative bands at 1186 and 1329–1367  $\text{cm}^{-1}$ , in addition to the above-mentioned bands at 598 and 919  $\text{cm}^{-1}$ . The structure of the band at 1329–1367  $\text{cm}^{-1}$  is complicated by the simultaneous presence of a more intense band of the skeleton, which culminates at 1347  $\text{cm}^{-1}$  in spectrum  $D^h$ . This band is slightly sensitive to hydration, as it appears in  $H^h$  in the form of a difference band with a minimum/maximum at 1340/1354  $\text{cm}^{-1}$ . It also appeared in spectra B and B' in Figure 3 in I and was then assigned to  $\nu_{\text{C}=\text{C}}$  of ring carbons. As it may have an important  $\nu_{\text{C}-\text{N}-\text{C}}$  component, we label it  $\nu_{\text{C}=\text{C}} + \nu_{\text{C}-\text{N}-\text{C}}$  in Table 2. The complicated shape of this band in  $I^h$  hinders us from assigning with precision this third band of  $\text{SO}_3\text{H}$ . We consequently do not use it in the following. The bands due to  $\text{SO}_3^-$ , which are formed after ionization of  $\text{SO}_3\text{H}$ , appear as positive bands in  $I^h$ . We give their assignments in Table 2. We see that, with the exception of two doublets around 1681 and 1720  $\text{cm}^{-1}$ , which are due to changes in the  $\nu_{\text{C}=\text{O}}$  bands upon the embedding of water molecules, all main bands of  $I^h$  are a signature of the ionizations of the  $\text{SO}_3\text{H}$  groups into  $\text{SO}_3^-$  groups. The hydration step which has  $I^h$  as its spectral signature is thus the ionization process of  $\text{SO}_3\text{H}$  into  $\text{SO}_3^-$ . Let us note that the bands due to  $\text{SO}_3^-$  that appear in  $I^h$  and Table 2 are all doublets, as was also found for the homopolymers of I, where the cations were  $\text{Na}^+$  and  $\text{NH}^+(\text{C}_2\text{H}_5)_3$ . We have attributed this doubling to the interactions of the two  $\text{SO}_3^-$  groups on the adjacent phenyl units (Figure 1). In opposition, the bands of the  $\text{SO}_3\text{H}$  groups are single bands. The reason for this difference is not clear. Let us also note that the bands in the region above 1800  $\text{cm}^{-1}$ , which are due to  $\nu_s(\text{O}-\text{H} \cdots \text{O})$  of  $\text{SO}_3\text{H}$  and  $\text{H}_3\text{O}^+$ , are remarkably weak in  $I^h$ . This is because these bands are so broad that even if their integrated intensities are great, their maxima remain low. Furthermore, these two bands appear with opposite signs, making them partly cancel. They are consequently almost useless for studying the  $\text{SO}_3\text{H}/\text{SO}_3^-$  ionization.



**Figure 1.** Repeat unit of a chain of the protonated polyimide block copolymer membrane in its dried state (upper drawing). Sulfonic groups are drawn in their neutral form SO<sub>3</sub>H. The three drawings in the lower part represent the three hydrogen bond configurations of pairs of carbonyl C=O groups that appear in the spectra.



**Figure 2.** Spectrum of a 10 μm thick dry protonated homopolyimide film,  $D^h$ .  $I^h$  is the corresponding ionization spectrum and  $H^h$  the hydration spectrum of the film with all sulfonic groups ionized. The spectra are off-set for clarity.

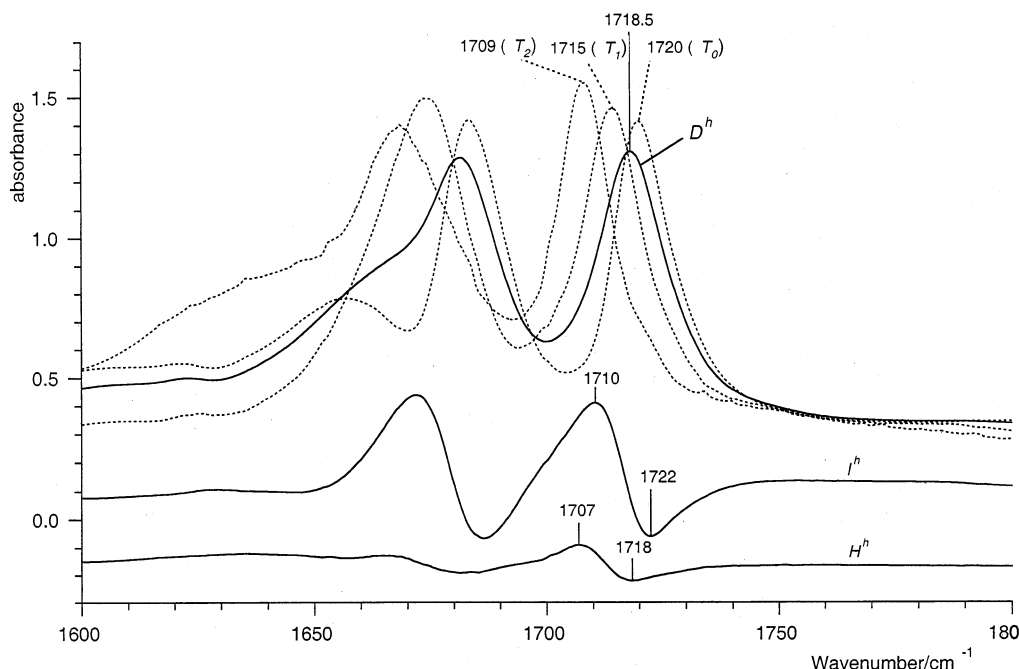
The next step in the quantitative analysis of hydration consists of measuring both the numbers  $N_{\text{H}_2\text{O}}$  of H<sub>2</sub>O molecules that appear in all three spectra of Figure 2 and the proportions of the various hydrophilic groups that are modified by the arrival of these  $N_{\text{H}_2\text{O}}$  molecules, that is, the proportions of these groups that accept H-bonds. We start with these latter groups.

**Sulfonic and Carbonyl Groups.** These are the two hydrophilic groups that give intense bands in spectra  $I^h$  and  $H^h$  in Figure 2. The measurement of the relative proportion of the SO<sub>3</sub>H groups that are ionized into SO<sub>3</sub><sup>-</sup> (spectrum  $I^h$ ) is made using the clearly defined difference bands with minima/maxima at 598/630 and 919/1030 cm<sup>-1</sup>. Other bands of SO<sub>3</sub>H might have been used, but other bands of SO<sub>3</sub><sup>-</sup> are less apparent, in particular, in spectrum  $D^h$ . After establishing that the bands at 598 and 919 cm<sup>-1</sup> disappear in a spectrum equal to  $D^h + 1.32I^h$  and that the bands at 630 and 1030 cm<sup>-1</sup> disappear in  $D^h + 0.27I^h$ , we may write the equations that satisfy these conditions as

$$\frac{D^h(\tilde{\nu})}{N^h} = 2\{0.17S_{\text{O}^-}(\tilde{\nu}) + 0.83S_{\text{OH}}(\tilde{\nu})\} + 0.34W_+(\tilde{\nu}) + \dots \quad (1)$$

$$\frac{I^h(\tilde{\nu})}{N^h} = 2 \times 0.63\{S_{\text{O}^-}(\tilde{\nu}) - S_{\text{OH}}(\tilde{\nu})\} + 1.26W_+(\tilde{\nu}) + \dots \quad (2)$$

where  $N^h$  is the number of repeat units in the sample of thickness  $e_s = 10 \mu\text{m}$  (Table 1),  $S_{\text{O}^-}(\tilde{\nu})$  is the set of bands due to one SO<sub>3</sub><sup>-</sup> group,  $S_{\text{OH}}(\tilde{\nu})$  is that due to one SO<sub>3</sub>H group,  $W_+(\tilde{\nu})$  is that due to one H<sub>3</sub>O<sup>+</sup> (the number of H<sub>3</sub>O<sup>+</sup> is implicitly supposed equal to the number of SO<sub>3</sub><sup>-</sup> groups), and the presence of dots (...) at the end of these equations means that only these sulfonic groups are the objects of eqs 1 and 2, the other groups being the objects of subsequent equations. These equations indicate that the total number of sulfonated groups that contribute to the spectrum of the dried sample  $D^h$  is  $2N^h$ , in agreement with the structure of the homopolymer ( $y = 0$ )



**Figure 3.** Same spectra (full lines)  $D^h$  (dried film),  $I^h$  (ionization), and  $H^h$  (hydration of fully ionized film) as in Figure 2 but in the  $\nu(\text{C}=\text{O})$  region. The three components  $T_0$ ,  $T_1$ , and  $T_2$  of the symmetric  $\nu_s(\text{C}=\text{O})$  are drawn with dashed lines. The spectra are off-set for clarity.

displayed in Figure 1, and that in the ionization spectrum  $I^h$  one  $\text{SO}_3\text{H}$  group is replaced by one  $\text{SO}_3^-$  group and one  $\text{H}_3\text{O}^+$ . The coefficients 0.63 and 0.17 are those that allow the above established conditions to be fulfilled, while  $0.83 = 1 - 0.17$ .

In Figure 3, we display the same three spectra as those displayed in Figure 2 but enlarged in the restricted  $\nu_{\text{C}=\text{O}}$  region. Combining the three spectra  $D^h$ ,  $I^h$ , and  $H^h$  that are derived from experiments, we succeeded in isolating the three well-defined bands  $T_0$ ,  $T_1$ , and  $T_2$  that are also drawn in Figure 3. It means that inversely the  $\nu_{\text{C}=\text{O}}$  bands of these  $D^h$ ,  $I^h$ , and  $H^h$  spectra can be decomposed on these  $T_0$ ,  $T_1$ , and  $T_2$ . These three  $T_n$  exhibit an exceptionally good signal-to-noise ratio and have shapes most similar to the symmetric  $\nu_{\text{C}=\text{O}}$  band of  $D_h$  that displays its maximum at  $1718.5 \text{ cm}^{-1}$ . They are the bands that correspond to the three configurations of pairs of carbonyl  $\text{C}=\text{O}$  groups drawn in the lower part of Figure 1 that differ in their hydration (or H-bond) configurations, as discussed in I. If we denote  $t_0$ ,  $t_1$ , and  $t_2$  as the corresponding bands of a single pair drawn in this Figure 1, we have  $T_n = 2N^h t_n$  ( $n = 0, 1$ , or  $2$ ), and the decomposition of the three spectra of Figure 3 in this  $\nu_{\text{C}=\text{O}}$  region writes then

$$\frac{D^h(\tilde{\nu})}{N^h} = 2\{0.587t_0(\tilde{\nu}) + 0.371t_1(\tilde{\nu}) + 0.042t_2(\tilde{\nu})\} + \dots \quad (3)$$

$$\frac{I^h(\tilde{\nu})}{N^h} = 2\{0.406[t_1(\tilde{\nu}) - t_0(\tilde{\nu})] + 0.09[t_2(\tilde{\nu}) - t_1(\tilde{\nu})]\} + \dots \quad (4)$$

$$\frac{H^h(\tilde{\nu})}{N^h} = 2\{0.034[t_1(\tilde{\nu}) - t_0(\tilde{\nu})] + 0.108[t_2(\tilde{\nu}) - t_1(\tilde{\nu})]\} + \dots \quad (5)$$

Let us note that we only consider the symmetric  $\nu_{\text{C}=\text{O}}$  band, since the antisymmetric one, which appears in the region  $1650\text{--}1700 \text{ cm}^{-1}$  in Figure 3, displays a similar behavior upon hydration but is overlapped by the bending band  $\delta_{\text{H}-\text{O}-\text{H}}$  of  $\text{H}_2\text{O}$ . These eqs 3–5 establish a linear relation between the three experimental bands of  $D^h$ ,  $I^h$ , and  $H^h$  in this region and the three  $T_n$  ( $=2N^h t_n$ ) that are drawn in Figure 3. Inverting this linear

relation gives the decomposition of these three  $T_n$  on experimental spectra, that is, the way these three bands have been defined from the experimental spectra.

**Water Molecules.** Figure 2 clearly shows that only  $H^h$  displays a significant broad libration band,  $\delta_L$ , centered around  $630 \text{ cm}^{-1}$  as well as a significant  $\nu_s(\text{O}-\text{H} \cdots \text{O})$  band around  $3470 \text{ cm}^{-1}$ , in other words, the features that can unambiguously be attributed to the presence of  $\text{H}_2\text{O}$  molecules. These two bands are clearly absent in  $I^h$ . We deduce that during ionization described by  $I^h$  all added  $\text{H}_2\text{O}$  molecules are found in the form of  $\text{H}_3\text{O}^+$  entities, with no extra detectable  $\text{H}_2\text{O}$  molecules, that is, no  $\text{H}_5\text{O}_2^+$ ,  $\text{H}_7\text{O}_3^+$ , and so forth. Said differently, each  $\text{SO}_3\text{H}$  group is ionized by a single  $\text{H}_2\text{O}$  molecule. The resulting  $\text{H}_3\text{O}^+$  ions are responsible for the weak positive features of  $I^h$  that appear in the region  $2300\text{--}3400 \text{ cm}^{-1}$ . In this region, hydrogen bonded  $\text{SO}_3\text{H} \cdots \text{O}$  groups, which disappear upon ionization, are at the origin of negative features, and we have no way to separate these two antagonistic contributions. The case of  $D^h$  is less immediate. However, in spectrum  $D^h - 0.27I^h$ , where the bands due to  $\text{H}_3\text{O}^+$  cations are no longer present, as already mentioned to establish eqs 1 and 2 (no  $\text{SO}_3^-$  in this spectrum), we cannot detect any significant amount of water: subtracting any spectrum due to water, be it that of liquid water or that of  $\text{H}_2\text{O}$  molecules embedded in the  $\text{Na}^+$  polyimide membranes (spectrum B or C of Figure 3 in I), multiplied by any significant coefficients, gives negative bands. We deduce that the number of remaining neutral  $\text{H}_2\text{O}$  molecules is negligibly small in  $D^h$ .

The measurement of the quantity of water in spectrum  $H^h$  is performed using spectra A and B of Figure 3 in I, where bands  $w_A(\tilde{\nu})$  and  $w_B(\tilde{\nu})$  due to water are particularly well defined. We have seen them (eqs 5 and 6 in I) to be precisely equal to

$$w_A(\tilde{\nu}) = N_w^B \times 0.11\{w_0(\tilde{\nu}) - w_1(\tilde{\nu})\} \quad (6)$$

$$w_B(\tilde{\nu}) = N_w^B\{0.39 \times 2w_1(\tilde{\nu}) + 0.61[w_0(\tilde{\nu}) + w_1(\tilde{\nu})]\} \quad (7)$$

where  $N_w^B$  is the number of water molecules in the  $\text{Na}^+$  membrane, which appear in spectrum B of Figure 3 in I,  $w_0$  is the  $\text{O}-\text{H}$  stretching band ( $\nu_s$ ) due to one free (not H-bonded)



**TABLE 3: Decompositions of Spectra  $D^x/(N_{\text{SO}_3}^x N^x)$  ( $D^x$  = Spectra of Dried Samples,  $N_{\text{SO}_3}^x$  = Numbers of Sulfonic Groups per Repeat Unit in the Polymer  $x$ , and  $N^x$  = Number of Repeat Units in This Polymer) of Ionization Spectra  $I^x/(N_{\text{SO}_3}^x N^x)$ , of Hydration of Ionized Samples Spectra  $H^x/(N_{\text{SO}_3}^x N^x)$ , and of Spectra  $W^x/(N_{\text{SO}_3}^x N^x)$  (Insertion of  $\text{H}_2\text{O}$  in the Already Developed H-Bond Network) on Main Bands of Hydrophilic Groups, as Defined in the Text**

	$D^h(\tilde{\nu})/2N^h$	$I^h(\tilde{\nu})/2N^h$	$H^h(\tilde{\nu})/2N^h$	$D^{5+5}(\tilde{\nu})/10N^{5+5}$	$I^{5+5}(\tilde{\nu})/10N^{5+5}$	$H^{5+5}(\tilde{\nu})/10N^{5+5}$	$W^{5+5}(\tilde{\nu})/10N^{5+5}$	$D^{5+11.6}(\tilde{\nu})/10N^{5+11.6}$	$I^{5+11.6}(\tilde{\nu})/10N^{5+11.6}$	$H^{5+11.6}(\tilde{\nu})/10N^{5+11.6}$	$W^{5+11.6}(\tilde{\nu})/10N^{5+11.6}$
$\text{SO}^-(\tilde{\nu})$	0.17	0.63	0	0.42	0.4	0	0	0.37	0.45	0	0
$\text{SOH}^-(\tilde{\nu})$	0.83	-0.63	0	0.58	-0.4	0	0	0.63	-0.45	0	0
$t_0(\tilde{\nu})$	0.587	-0.406	-0.034	0.78	-0.492	0.142	0	1.96	-0.59	0.01	0
$t_1(\tilde{\nu})$	0.371	0.316	-0.074	1.22	0.392	-1.56	0	1.22	0.58	-0.57	0
$t_2(\tilde{\nu})$	0.042	0.09	0.108	0	0.1	1.42	0	0.14	0.01	0.56	0
$t_1(\tilde{\nu}) - t_0(\tilde{\nu})$		0.406	0.034		0.492	-0.142	0		0.59	-0.01	0
$t_2(\tilde{\nu}) - t_0(\tilde{\nu})$		0.09	0.108		0.1	1.42	0		0.01	0.56	0
$W_+(\tilde{\nu})$	0.17	0.63	0	0.42	0.4	0	0	0.37	0.45	0	0
$2w_1(\tilde{\nu})$	0	0	0.656	0.24	0.123	1.04	0.36	0.1	0.077	0.03	0.6
$w_0(\tilde{\nu}) + w_1(\tilde{\nu})$	0	0	0.944	0.13	0.437	4.56	0.84	0.42	0.50	1.895	0.56

O—H group of an  $\text{H}_2\text{O}$  molecule, and  $w_1$  is the  $\nu_s$  band due to one H-bonded O—H  $\cdots$  group of  $\text{H}_2\text{O}$ . The term  $2w_1$  in eq 7 is consequently for  $\text{H}_2\text{O}$  molecules that establish two H-bonds, while the term  $w_0 + w_1$  is for  $\text{H}_2\text{O}$  molecules establishing one H-bond only with their two O—H groups. We find that in spectrum  $H^h + 0.06w_A(\tilde{\nu}) - 0.37w_B(\tilde{\nu})$  intensities are zero at wavenumbers greater than  $3400\text{ cm}^{-1}$ , which means that we annihilate most of the  $\nu_s$  band due to  $\text{H}_2\text{O}$ , keeping only a small broad hump which culminates around  $3200\text{ cm}^{-1}$  and is typical of an HO—H  $\cdots$  O=C H-bond. With the equation

$$\frac{N_w^B}{N^h} = \frac{M^h e_s^B}{d e_s 18} \quad (8)$$

where  $M^h$ ,  $d$ , and  $e_s$  are respectively the mass of one repeat unit in the protonated homopolymer, the density of this homopolymer, and its thickness, all quantities which are given in Table 1,  $e_w^B = 2.4\text{ }\mu\text{m}$  (eq 1 in I), the thickness of a sample of liquid water which contains  $N_w^B$  water molecules on the same surface as this homopolymer sample, and  $18\text{ g mol}^{-1}$ , the mass of 1 mol of water, we deduce

$$\frac{H^h(\tilde{\nu})}{N^h} = 3.2\{0.41 \cdot 2w_1(\tilde{\nu}) + 0.59[w_0(\tilde{\nu}) + w_1(\tilde{\nu})]\} + \dots \quad (9)$$

which means that in  $H^h$  3.2  $\text{H}_2\text{O}$  molecules hydrate one repeat unit, 41% of them by establishing two H-bonds and 59%, only one H-bond.

We display all the former eqs 1–5 and 9 in a condensed form in Table 3. They summarize our spectral measurements on the homopolymer.

### Block Copolymers

In this section, we perform for the block copolymers the same analysis as in the preceding section. We use the same method for the C=O carbonyl bands and for the water uptake but a different method for the sulfonic groups, because these bands of the copolymers display relatively small intensities and are more masked, in the spectra of dried samples, by skeleton bands than in the case of the homopolymer. This is illustrated in Figure 4, where the spectrum of the dried 5 + 5 ( $x = 5$ ,  $y = 5$ ) block copolymer  $D^{5+5}$ , together with elementary hydration spectra  $I^{5+5}$ ,  $H^{5+5}$ , and  $W^{5+5}$  are exhibited. We have there one more elementary hydration spectrum than for the homopolymer,  $W^{5+5}$ . With its difference bands, which are relatively much smaller than those in spectra  $I^{5+5}$  and  $H^{5+5}$  when compared to the  $\nu_s$  band ( $3000\text{--}3600\text{ cm}^{-1}$ ), this spectrum,  $W^{5+5}$ , may already be seen as being due to  $\text{H}_2\text{O}$  molecules which insert themselves

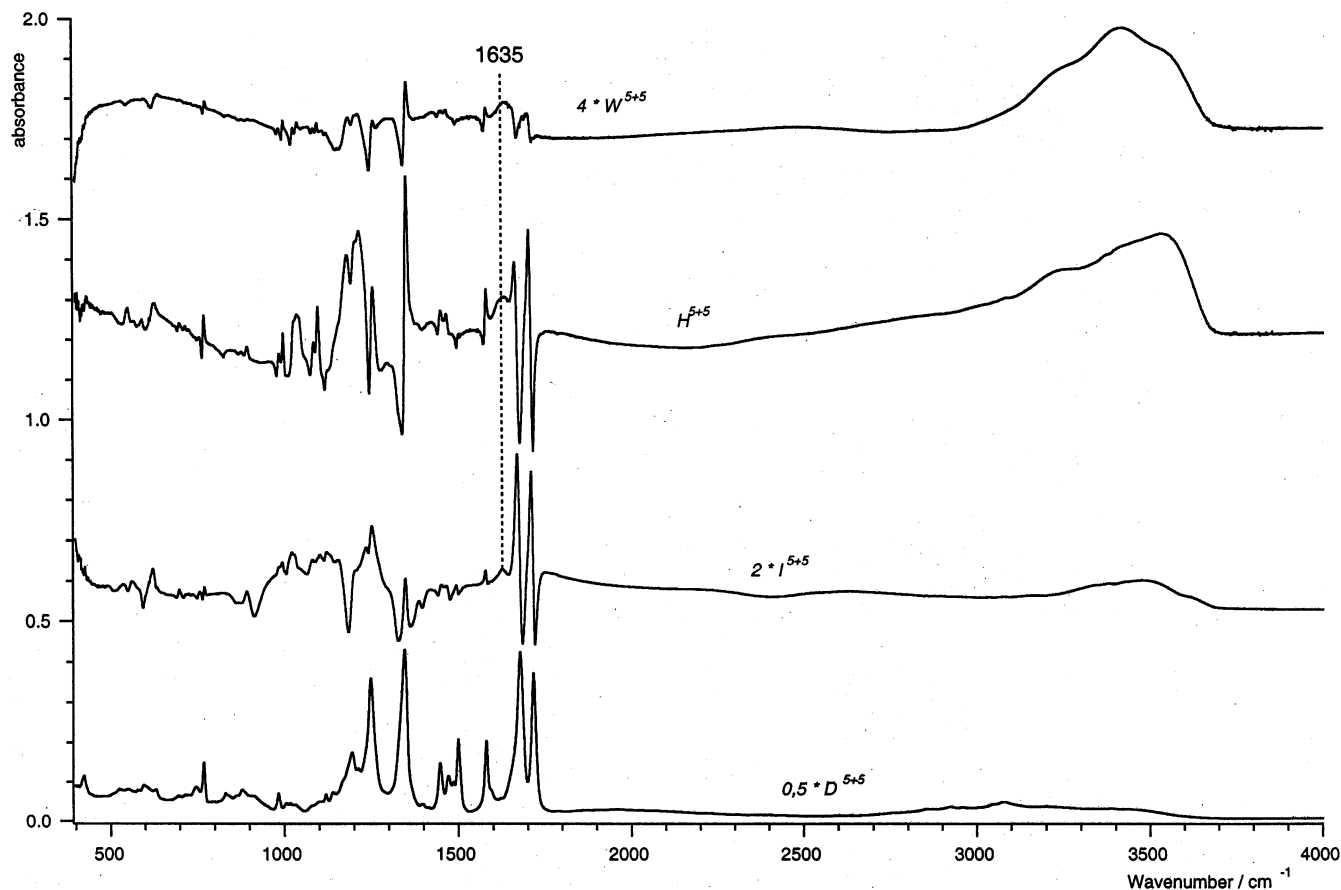
into the H-bond network developed by already present  $\text{H}_2\text{O}$  molecules. We may also note that the ionization spectrum,  $I^{5+5}$ , displays small but nevertheless visible bands due to water, particularly the  $\nu_s$  band in the region  $3200\text{--}3600\text{ cm}^{-1}$  and the  $\delta_{\text{H-O-H}}$  band centered at  $1635\text{ cm}^{-1}$ , which are absent in  $I^h$  (Figure 2) but visible in  $H^h$ . We do not show the corresponding spectra for the other block copolymer with  $x = 5$  and  $y = 11.6$ , which we also analyze in this article, as they display strong similarities with the spectra in Figure 4.

**Carbonyl Groups.** The bands due to the carbonyl groups of our two block copolymers are as well defined as those in the homopolymer. We consequently analyze them by the same method, which consists of isolating in the symmetric  $\nu_{\text{C=O}}$  band three carefully determined bands,  $T_n$  ( $n = 0\text{--}2$ ), which correspond to the three H-bond configurations of the C=O pairs, as drawn in Figure 1. We do not write the decompositions of the  $\nu_{\text{C=O}}$  bands of the four spectra of Figure 4 on the three  $t_n$ 's, as we have done for the homopolymer, but we display them in Table 3, together with the same decompositions related to the 5 + 11.6 copolymer. Let us note that the  $t_n$ 's of the 5 + 5 block copolymer are not exactly the same as those of the homopolymer:  $t_0$  appears at same wavenumber but  $t_1$  and  $t_2$  fall at a wavenumber higher by 1 and  $2\text{ cm}^{-1}$ , respectively, than the corresponding bands of the homopolymer. We should therefore have given them an index to distinguish them. For clarity, we omit this supplementary index, as these shifts are detectable but remain small and at the limit of the resolution of the spectra, but we keep in mind this writing when we have to compare the  $t_n$ 's of the different polymers. For the 5 + 11.6 block copolymer, the shifts of  $t_0$ ,  $t_1$ , and  $t_2$ , as compared to  $t_0$ ,  $t_1$ , and  $t_2$  of the homopolymer, are now respectively of  $-1$  (toward lower wavenumbers), 1, and  $3\text{ cm}^{-1}$ , which remain also small quantities.

**Sulfonic Groups.** These groups are at the origin of weak features in the spectrum of Figure 4, as compared to the equivalent spectra of the homopolymer in Figure 2. We consequently determine the decompositions of  $I^{5+5}$  and of  $I^{5+11.6}$  on  $\text{SO}^-$  and  $\text{SOH}^-$  by establishing that features of these sulfonic groups clearly disappear in spectra  $I^{5+5} - 0.22I^h$  and  $I^{5+11.6} - 0.16I^h$ . Using eq 2 that relates the decomposition of  $I^h$  on this basis and using also the following equations:

$$\frac{N^h}{N^{5+5}} = \frac{d^h e_s^h}{d^{5+5} e_s^{5+5}} \frac{M^{5+5}}{M^h} = 14.4 \quad (10)$$

$$\frac{N^h}{N^{5+11.6}} = \frac{d^h e_s^h}{d^{5+11.6} e_s^{5+11.6}} \frac{M^{5+11.6}}{M^h} = 22.3 \quad (11)$$



**Figure 4.** Spectrum  $D^{5+5}$  of a  $6.2\ \mu\text{m}$  thick dry protonated  $5 + 5$  copolymer film.  $I^{5+5}$  is the corresponding ionization spectrum,  $H^{5+5}$  the hydration spectrum of the film with all sulfonic groups ionized, and  $W^{5+5}$  the spectrum active at high hygrometry. For a fair representation, spectra are multiplied by various coefficients and off-set.

where  $d^x$  ( $x = h, 5+5$ , or  $5+11.6$ ) are the densities of either the homopolymer or the block copolymers,  $M^x$  are the molar masses of their repeat units, and  $e_s^x$  are the corresponding thicknesses of the samples (all of these quantities are displayed in Table 1), we may calculate the coefficients of the decompositions of  $I^{5+5}$  and of  $I^{5+11.6}$  on  $S_{O^-}$  and  $S_{OH}$ . They are displayed in Table 3, together with the coefficients of the decompositions on  $W_+$ , equal, as already stated, to those on  $S_{O^-}$ .

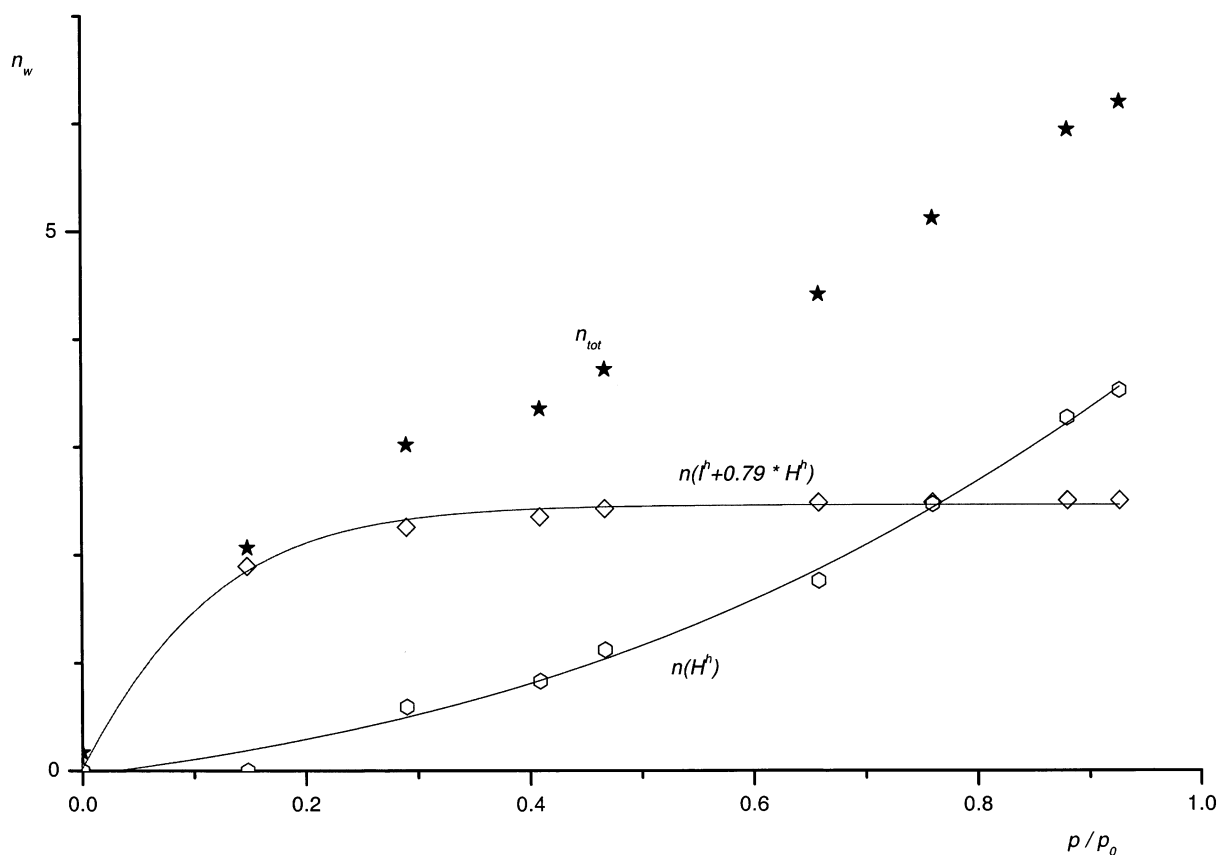
Furthermore, we find that the coefficients of decomposition of the hydration spectra on  $I^{5+5}(\tilde{\nu})$  increase at low hygrometries but reach a plateau for  $p/p_0 > 0.4$ , keeping then a constant value of 1.45 for higher values of  $p/p_0$ . This plateau clearly appears in Figure 6, but the value displayed there is not 1.45, as it is in this figure equal to the number of  $H_2O$  molecules per sulfonated group we calculate below, which is proportional but not equal to this coefficient. Similarly, this coefficient for the  $5 + 11.6$  copolymer reaches a constant value of 1.4 at hygrometries higher than 0.4–0.5. We conclude then that in spectra  $D^{5+5}(\tilde{\nu}) + 1.45I^{5+5}(\tilde{\nu})$  and  $D^{5+11.6}(\tilde{\nu}) + 1.4I^{5+11.6}(\tilde{\nu})$  the ionization is complete. We deduce the decompositions of  $D^{5+5}$  and of  $D^{5+11.6}$  on  $S_{O^-}$ ,  $S_{OH}$ , and  $W_+$  that are displayed in Table 3, using the decompositions of  $I^{5+5}$  and of  $I^{5+11.6}$  on  $S_{O^-}$  and  $S_{OH}$  that we have calculated above.

**Water Molecules.** In this subsection, we calculate the number of  $H_2O$  molecules that are at the origin of bands in the spectra of Figure 4 and in the corresponding spectra of the  $5 + 11.6$  copolymer, which are not exhibited. To do it, we first have to eliminate, as we have done above for the homopolymer, the contribution due to  $H_3O^+$ , which overlaps that due to  $H_2O$ . Using the decompositions of  $D^{5+5}$  and of  $I^h$  already entered in

Table 3 and with the help of eq 10, we may realize that all features due to  $SO_3^-$  and  $H_3O^+$  are zero in  $D^{5+5} - 0.23I^h$ . In this spectrum, we estimate that the remaining water bands are equal to  $0.03w_B(\tilde{\nu}) - 0.07w_A(\tilde{\nu})$ , where these water bands are defined in eqs 6 and 7. Let us note that spectrum  $I^h$  does not display any feature due to water and that adding or subtracting it does not consequently modify the number of water molecules. We have also seen above that all features due to  $SO_3^-$  and  $H_3O^+$  become zero in  $I^{5+5} - 0.22I^h$ , where we estimate that the remaining  $\nu_s$  water bands are equal to  $0.045w_B(\tilde{\nu}) + 0.07w_A(\tilde{\nu})$ . They are also found to be equal to  $0.449w_B(\tilde{\nu}) + 0.834w_A(\tilde{\nu})$  in  $H^{5+5}$ , where no  $H_3O^+$  appears (no feature due to any  $SO_3^-/SO_3H$  transform is visible), and are equal to  $0.095w_B(\tilde{\nu}) + 0.08w_A(\tilde{\nu})$  in  $W^{5+5}$ , where also no  $H_3O^+$  is present. With the help of eqs 6–8 and 11, we can write the decompositions of all spectra— $D^{5+5}$ ,  $I^{5+5}$ ,  $H^{5+5}$ , and  $W^{5+5}$ —on  $2w_1$  and  $w_0 + w_1$  that are displayed in Table 3.

In the same way, all features due to  $SO_3^-$  and  $H_3O^+$  are zero in  $D^{5+11.6} - 0.115I^h$ , where the remaining water bands are estimated to be equal to  $0.027w_B(\tilde{\nu}) + 0.05w_A(\tilde{\nu})$ . We have also seen that all features due to  $SO_3^-$  and  $H_3O^+$  are zero in  $I^{5+11.6} - 0.16I^h$  where we estimate the remaining  $\nu_s$  water bands to be equal to  $0.03w_B(\tilde{\nu}) + 0.07w_A(\tilde{\nu})$ . They are also equal to  $0.1w_B(\tilde{\nu}) + 0.34w_A(\tilde{\nu})$  in  $H^{5+11.6}$  and to  $0.06w_B(\tilde{\nu}) - 0.07w_A(\tilde{\nu})$  in  $W^{5+11.6}$ . It allows us to write the decompositions of spectra  $D^{5+11.6}$ ,  $I^{5+11.6}$ ,  $H^{5+11.6}$ , and  $W^{5+11.6}$  on  $2w_1$  and  $w_0 + w_1$  that are displayed in Table 3.

Let us note that these measurements of the amounts of water molecules are not easy, because of the presence of  $H_3O^+$  ions that should be eliminated. This is indeed a recurrent problem,



**Figure 5.** Numbers,  $n_w$ , of water molecules per sulfonic group in the protonated homopolymer as a function of the hygrometry,  $p/p_0$ .  $n_{tot}$  is for the total number of water molecules, while  $n(I^h)$  is for the number of water molecules that appear in spectrum  $S^h$ . The lines are guides for the eyes only.

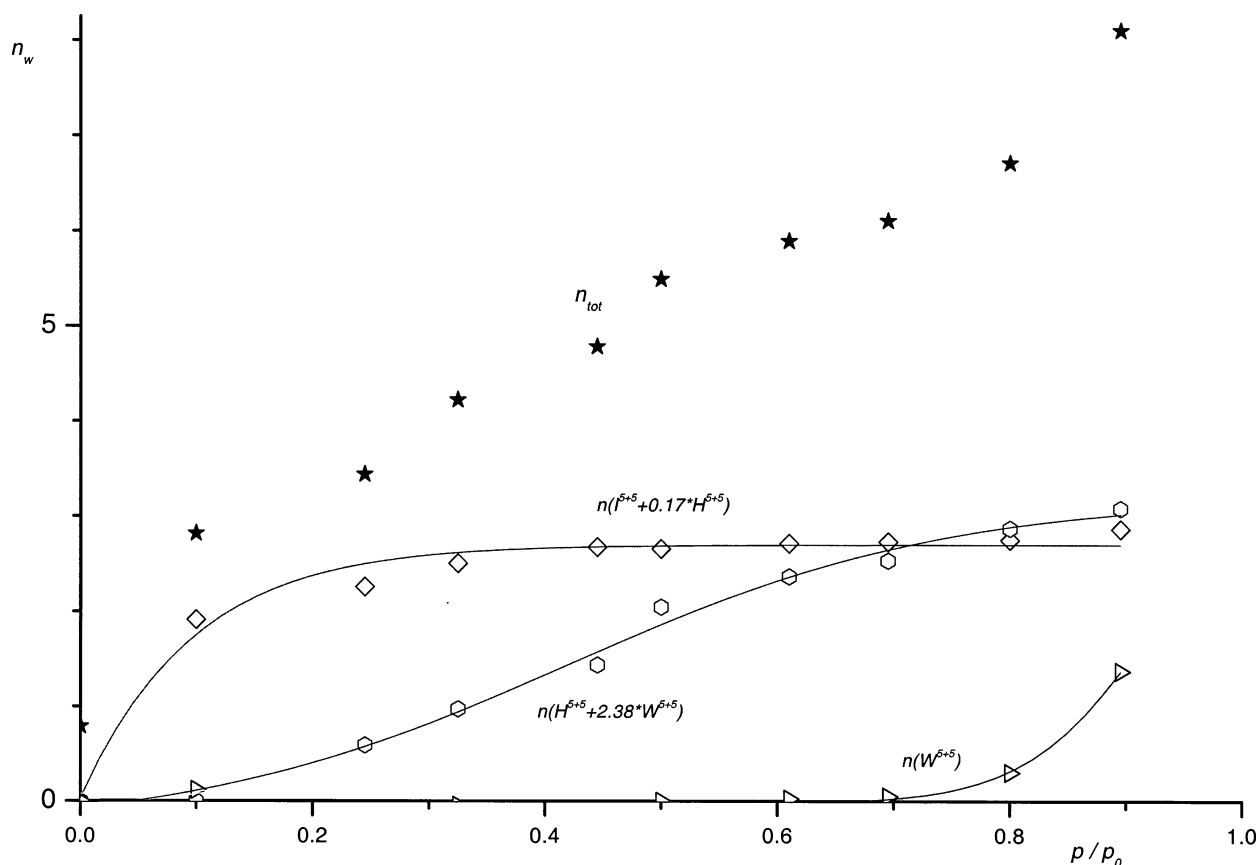
also encountered in the study of the ionization of carboxylic acids,<sup>5</sup> where the “absorption continuum” between 1800 and 3000  $\text{cm}^{-1}$  still exists when  $\text{COOH}$  groups are not ionized. It is consequently due to both  $\text{H}_3\text{O}^+$  and  $\text{H}_2\text{O}$ . Presently, we disentangle the intricate bands of this region by isolating spectra with no  $\text{SO}_3^-$ , that is, no  $\text{H}_3\text{O}^+$ . In other words, we indirectly eliminate  $\text{H}_3\text{O}^+$ , taking advantage of the more precisely defined bands due to  $\text{SO}_3^-$ .

### Water Uptake

**Number of Embedded Water Molecules.** We use the values of the decompositions displayed in Table 3 to calculate the numbers of water molecules per repeat unit we find embedded in the various protonated polymers at hygrometry  $p/p_0$  of the surrounding atmosphere. The elementary hydration spectra  $I^x$ ,  $H^x$ , and  $W^x$  ( $x = h, 5+5$ , or  $5+11.6$ ; some of these spectra are displayed in Figures 2 and 4) we have isolated are the most appropriate spectra to measure these numbers of  $\text{H}_2\text{O}$  molecules and also to measure the proportions of hydrophilic groups that are H-bonded. We have to remember,<sup>4</sup> however, that taking as a basis any three linear combinations of these spectra would have fit with the same statistical precision the decompositions of the experimental spectra. We have therefore to determine now such linear combinations of the elementary hydration spectra that are chemically acceptable, that is, that correspond to a well-defined hydration mechanism. We shall disclose these mechanisms in the next section. To do this, we first calculate the numbers  $n(I^x)$ ,  $n(H^x)$ , and  $n(W^x)$  of water molecules that have been embedded in the polymer at a definite hygrometry by the hydration mechanism corresponding, respectively, to spectra  $I^x$ ,  $H^x$ , and  $W^x$ . Each of these numbers is equal<sup>4</sup> to the coefficient

that multiplies  $I^x$  ( $H^x$ ,  $W^x$ ) in the decomposition of the hydration spectrum at hygrometry  $p/p_0$ , multiplied by the coefficients of the decompositions of  $I^x$ ,  $H^x$ , and  $W^x$  on  $2w_1$  and  $w_0 + w_1$  that are displayed in Table 3. The value  $n(I^x)$  must be augmented with the number of  $\text{H}_3\text{O}^+$  molecules. The total number,  $n_{tot}$ , of embedded water molecules is equal to the sum  $n(I^x) + n(H^x) + n(W^x)$ , plus the numbers of  $\text{H}_2\text{O}$  and  $\text{H}_3\text{O}^+$  molecules that remain in the dried sample,  $D^x$ , also displayed in Table 3.

For all of the polymers, we could find combinations of  $I^x$ ,  $H^x$ , and  $W^x$ , which partition hydration into successive steps that can be easily interpreted. Had we chosen to take the individual  $I^x$ ,  $H^x$ , and  $W^x$  spectra instead of these combinations, we would have lost this successive character, as  $I^x$  and  $H^x$  would have for instance appeared simultaneously at hygrometry 0. We display in Figures 5 and 6 the numbers,  $n_w$ , of  $\text{H}_2\text{O}$  molecules per sulfonic group, which are the usually considered quantities in the case of ionomers, for the homopolymer and for one block copolymer using such combinations which illustrate the successive character of the various hydration mechanisms. Note that these  $n_w$   $\text{H}_2\text{O}$  molecules are not all attached to a sulfonic group. The number of embedded water molecules,  $n(I^x + \lambda H^x)$  in spectrum  $I^x + \lambda H^x$  is equal, for any value of  $\lambda$ , to  $n(I^x) + \lambda n(H^x)$ . Figures 5 and 6 clearly show that for the three considered polymers (we do not display these numbers for the  $5 + 11.6$  block copolymer, as they do not differ significantly from those of the  $5 + 5$  polymer in Figure 6) the hydration starts with ionization of the  $\text{SO}_3\text{H}$  groups, represented by spectrum  $I^h + 0.79H^h$  for the homopolymer,  $I^{5+5} + 0.17H^{5+5}$  for the  $5 + 5$  block copolymer, and  $I^{5+11.6} + 0.68H^{5+11.6}$  for the  $5 + 11.6$  block copolymer. As can be seen in these spectra (see also the next section), this ionization goes along with



**Figure 6.** Numbers,  $n_w$ , of water molecules per sulfonic group in the protonated 5 + 5 block copolymer as a function of the hygrometry,  $p/p_0$ .  $n_{\text{tot}}$  is for the total number of molecules, while  $n(S^{5+5})$  is for the number of molecules that appear in spectrum  $S^{5+5}$ . The lines are guides for the eyes only.

hydration of the C=O groups. These mechanisms reach a plateau at a hygrometry around 0.3–0.4, which means that ionization is complete at these hygometries and is no longer active for hygometries greater than these values. Once this ionization has started and before it is complete, hydration of  $\text{SO}_3^-$  groups proceeds, also accompanied by hydration of C=O groups and represented by  $H^h$ ,  $H^{5+5} + 2.38W^{5+5}$ , and  $H^{5+11.6}$  for these three polymers. In the case of the homopolymer (Figure 5), this latter mechanism seems to still be active when the hygrometry approaches 1, whereas it displays an inflection for both block copolymers (Figure 6), suggesting that it may also reach a plateau at hygometries approaching 1. Ionization of the  $\text{SO}_3\text{H}$  groups and hydration of the C=O groups are the only mechanisms for the homopolymer. For both block copolymers, a third mechanism appears at hygometries around 0.6–0.7, represented by  $W^{5+5}$  and  $W^{5+11.6}$ . We have seen these spectra  $W^{5+5}$  and  $W^{5+11.6}$  resemble the spectrum of liquid water. The corresponding mechanism is therefore embedding of water molecules in the already strongly developed H-bond network of  $\text{H}_2\text{O}$  molecules in the membrane. Almost no C=O or sulfonic groups are hydrated in this latter mechanism. Referring to previous studies of hydration mechanisms,<sup>6,7</sup> we strongly suspect this mechanism becomes predominant when the hygrometry approaches 1 and is at the origin of embedding of a large amount of water molecules. It would make the total number,  $n_{\text{tot}}$ , of embedded water molecules display a sigmoidal shape, as has been found in the case of many proteins<sup>8</sup> and polymers<sup>9–12</sup> of the same family as those presently studied.

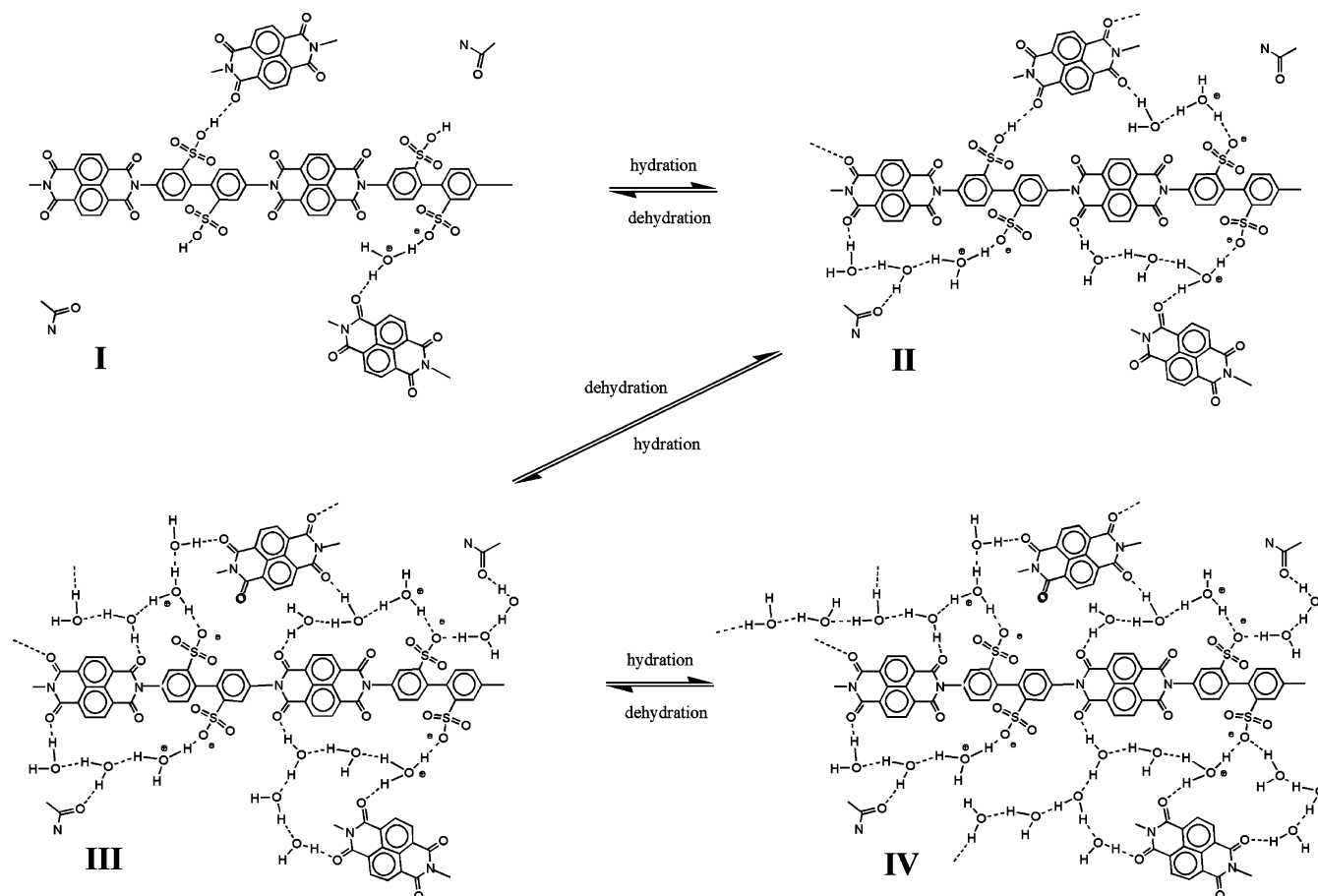
Let us note significant differences between the homopolymer and both block copolymers in their dried state: in the dried homopolymer, the number of  $\text{H}_2\text{O}$  molecules amounts to 0.17

per one sulfonic group, whereas it amounts to 0.85 in both block copolymers. In the case of the copolymers, this corresponds roughly to one  $\text{H}_3\text{O}^+$  cation plus one neutral  $\text{H}_2\text{O}$  molecule per one  $\text{SO}_3^-$  anion, but in the homopolymer, this gives a single  $\text{H}_3\text{O}^+$  cation per one  $\text{SO}_3^-$ . In this latter polymer, 17% only of the sulfonic groups are ionized (eq 1), a proportion which we find in the vicinity of 40% for the block copolymers (Table 3). Differences also appear at hygometries close to 0.9: the number of water molecules slightly varies from 6 per sulfonic group in the homopolymer to 10 in the 5 + 11.6 copolymer, taking on an intermediate value of 8 for the 5 + 5 copolymer. We should however remember that in the protonated homopolymer all units are sulfonated, whereas half of them are sulfonated in the 5 + 5 block copolymer, a proportion that goes down to 30% in the 5 + 11.6 polymer (Figure 1 and Table 1). The average spatial density of  $\text{H}_2\text{O}$  and  $\text{H}_3\text{O}^+$  molecules at a hygrometry of 0.9 is consequently somewhat greater in the homopolymer than in the 5 + 5 block copolymer, and even more so than in the 5 + 11.6 one.

### Hydration Mechanisms

In this section, we establish the hydration mechanisms of the three membranes, relying on the values displayed in Table 3, to which we refer all along this section. We illustrate these hydration mechanisms in Figures 7 and 8, which display the structures of the homopolymer and of the 5 + 5 block copolymer at various stages of hydration. These stages are those found at hygometries of 0, 0.15, 0.65, and 0.9, which, as seen in Figures 5 and 6, correspond to zones where one of the various hydration mechanisms—ionization, hydration of  $\text{SO}_3^-$  groups, and forma-





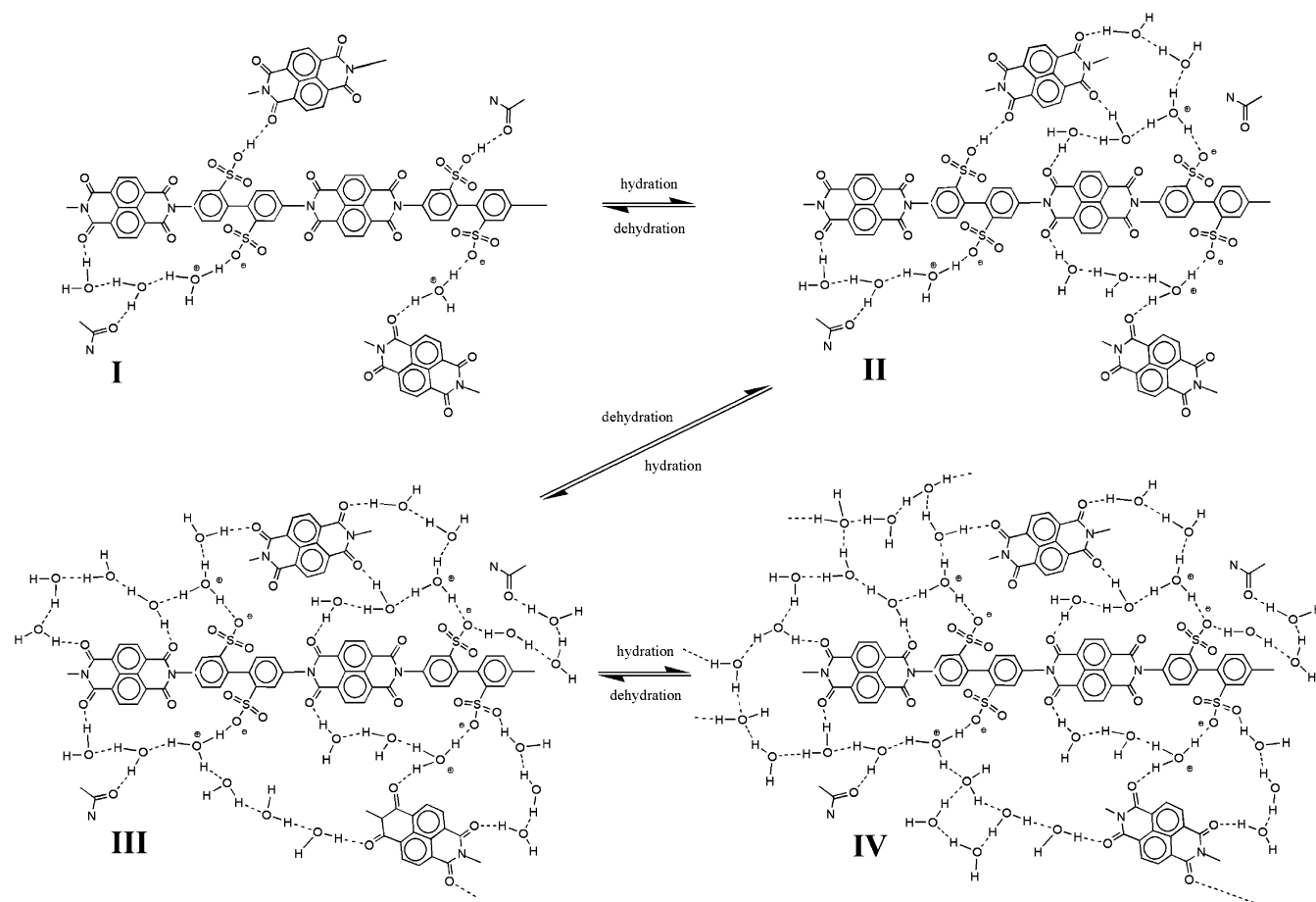
**Figure 7.** Hydration mechanism of the protonated homopolymer: (I) structure of the dried membrane; (II, III, and IV) structures of this membrane at hygrometries of 0.15, 0.65, and 0.9, respectively.

tion of water nanodroplets in the block copolymers—is preponderant. When these values of the hygrometry do not exactly match an experimental measurement, the decomposition of the corresponding spectrum is interpolated between experimental values. With this procedure, we may easily compare the hydration mechanisms of the three polymers. Again, we do not exhibit the structure of the 5 + 11.6 copolymer, as it is qualitatively the same as that of the 5 + 5 copolymer represented in Figure 8. We will nevertheless comment on the small quantitative differences between these two polymers in the following.

**Dried Polymers.** The dried polymers (structure I in Figures 7 and 8) differ in their ionization stage: only 17% of the sulfonic groups are found in their ionized form  $\text{SO}_3^-$  in the homopolymer, whereas this proportion amounts to some 40% (i.e., 4  $\text{SO}_3^-$  per repeat unit that contains 10 sulfonated groups) in both block copolymers. In the homopolymer, each  $\text{SO}_3^-$  group is ionized by a single water molecule, which appears in the form of  $\text{H}_3\text{O}^+$ . In the 5 + 5 block copolymer, each  $\text{H}_3\text{O}^+$  is bound to an average number of 0.88  $\text{H}_2\text{O}$  molecules, which amounts to 1.4 in the 5 + 11.6 copolymer. In other words, the cation found in the dried homopolymer is  $\text{H}_3\text{O}^+$ , but more  $\text{H}_5\text{O}_2^+$  is found in the 5 + 5 copolymer, and a mixture of  $\text{H}_5\text{O}_2^+$  and  $\text{H}_7\text{O}_3^+$  is found in the 5 + 11.6 copolymer. In the dried homopolymer, 23% of the  $\text{C}=\text{O}$  groups accept one H-bond. As all  $\text{H}_2\text{O}$  molecules are found in the form of  $\text{H}_3\text{O}^+$  ions, we deduce that some of the  $\text{SO}_3\text{H}$  groups, which represent 83% of all the sulfonic groups, must establish one H-bond on a  $\text{C}=\text{O}$  group. How many of them? We can calculate this amount in two extreme cases. The first one is that where each  $\text{H}_3\text{O}^+$  is H-bonded to one  $\text{C}=\text{O}$

group. We find then that 35% only of the  $\text{SO}_3\text{H}$  groups establish H-bonds of the type  $\text{SO}_3\text{H} \cdots \text{O}=\text{C}$  on carbonyl groups. The 65% remaining  $\text{SO}_3\text{H}$  establish no H-bonds on carbonyl groups. The other extreme case is that where no  $\text{H}_3\text{O}^+$  establishes any H-bond on a  $\text{C}=\text{O}$  group. We find then that 54% of the  $\text{SO}_3\text{H}$  establish one H-bond of the type  $\text{SO}_3\text{H} \cdots \text{O}=\text{C}$  and that consequently 46% of them establish no H-bond. The real proportion of  $\text{SO}_3\text{H}$  groups that establish H-bonds on  $\text{C}=\text{O}$  groups consequently lies between 35 and 54%. Let us note that we discarded the possibility that one  $\text{H}_3\text{O}^+$  establishes H-bonds on two  $\text{C}=\text{O}$  groups, as it requires stringent sterical conditions that can only be exceptionally fulfilled. In all cases, there remains an appreciable proportion of  $\text{SO}_3\text{H}$  groups which establish no H-bonds. It is certainly possible because no  $\text{H}_2\text{O}$  molecules, other than  $\text{H}_3\text{O}^+$  ions strongly bound to  $\text{SO}_3^-$  groups, remain embedded in the polymer.

In the 5 + 5 block copolymer, 30% of the  $\text{C}=\text{O}$  groups (i.e., 12 groups per repeat unit) accept one H-bond, a proportion which amounts to 22% (14.6 groups per repeat unit) in the 5 + 11.6 polymer, where the number of  $\text{C}=\text{O}$  groups per repeat unit is larger. It allows all  $\text{SO}_3\text{H}$  groups to establish H-bonds on  $\text{C}=\text{O}$  groups, thus allowing neutral forms of these strongly acidic groups to coexist with  $\text{H}_2\text{O}$  molecules bound to  $\text{H}_3\text{O}^+$  ions, forming  $\text{H}_{2n+1}\text{O}_n^+$  ions. We thus see that the homopolymer somewhat differs from the block copolymers in their dried states, with a strong predominance, in the homopolymer, of neutral  $\text{SO}_3\text{H}$  groups which are for the majority of them free (not H-bonded to  $\text{C}=\text{O}$  groups), and the absence of water molecules other than  $\text{H}_3\text{O}^+$  bound to  $\text{SO}_3^-$  groups. In both block copolymers, the ionized  $\text{SO}_3^-$  groups represent some 40% of



**Figure 8.** Hydration mechanism of the protonated 5 + 5 block copolymer: (I) structure of the dried membrane; (II, III, and IV) structures of the membrane at hygrometries of 0.15, 0.65, and 0.9, respectively.

sulfonic groups and the 60% neutral  $\text{SO}_3\text{H}$  are all H-bonded to  $\text{C}=\text{O}$  groups. It allows for the presence of  $\text{H}_2\text{O}$  molecules bounded to  $\text{H}_3\text{O}^+$  which hydrate a greater number of  $\text{C}=\text{O}$  groups.

$p/p_0 = 0.15$ . Ionization accompanied by the hydration of  $\text{SO}_3^-$  groups, a mechanism represented by  $n(I^h + 0.79H^h)$  in Figure 5 and by  $n(I^{5+5} + 0.17H^{5+5})$  in Figure 6, is not far from being accomplished at this hygrometry value, as  $\text{SO}_3^-$  groups represent 80% of the sulfonic groups in the homopolymer, a proportion which amounts to some 83% for both block copolymers. The decompositions on the elementary spectra show that the experimental spectra are then equal to  $D^h + I^h + 0.79H^h$  for the homopolymer, to  $D^{5+5} + 1.06I^{5+5} + 0.2H^{5+5}$  for the 5 + 5 copolymer, and to  $D^{5+11.6} + 1.02I^{5+11.6} + 0.71H^{5+11.6}$  for the 5 + 11.6 copolymer. As a result, we find that the numbers of embedded  $\text{H}_2\text{O}$  molecules per sulfonic group are greater in both block copolymers, where they amount to 2.1 in the 5 + 5 copolymer (2.5 in the 5 + 11.6 one), which is to be compared to 1.3 in the homopolymer. If we refer to the numbers of embedded  $\text{H}_2\text{O}$  molecules per unit drawn between brackets in Figure 1 and which is sulfonated or not, the inverse is then true, as we have 2 sulfonic groups per such unit in the homopolymer, but only 1 (=10/10) in the 5 + 5 block copolymer, and 0.6 (=10/(5 + 11.6)) for the 5 + 11.6 block copolymer. The proportion of the  $\text{C}=\text{O}$  groups which accept H-bonds, most of them established by  $\text{H}_2\text{O}$  molecules, amounts to 52% in both the homopolymer and the 5 + 5 copolymer and to 38% in the 5 + 11.6 copolymer.

$p/p_0 = 0.65$  and  $p/p_0 = 0.9$ . At these hygrometry values, ionization is complete and hydration of the  $\text{SO}_3^-$  groups has

for long been effective. For both block copolymers, a new hydration mechanism appears at hygrometries slightly greater than 0.7, which is the arrival of  $\text{H}_2\text{O}$  molecules, which insert themselves into the H-bond network well developed by already present  $\text{H}_2\text{O}$  molecules (Figures 5 and 6). At  $p/p_0 = 0.65$ , the decomposition of the experimental spectra writes  $D^h + 1.3I^h + 2.05H^h$  for the homopolymer,  $D^{5+5} + 1.42I^{5+5} + 0.53H^{5+5} + 0.73W^{5+5}$  for the 5 + 5 copolymer, and  $D^{5+11.6} + 1.39I^{5+11.6} + 2.28H^{5+11.6} + 0.23W^{5+11.6}$  for the 5 + 11.6 copolymer. In the homopolymer, the proportion of hydrated  $\text{C}=\text{O}$ , that is,  $\text{C}=\text{O}$  groups which accept one H-bond, amounts to 70%. This value is not so much different in the 5 + 5 copolymer (68%) but smaller (54%) in the 5 + 11.6 copolymer. We should however take into account that the numbers of  $\text{C}=\text{O}$  groups are greater in copolymers. The number of  $\text{H}_2\text{O}$  molecules per one  $\text{SO}_3^-$  group differs between the homopolymer, where it is found to be equal to 3.3, and both copolymers, where it is found to be equal to 5 and 6, respectively, with 1  $\text{H}_3\text{O}^+$  that should be added to these numbers. Referred to 1 unit drawn between brackets in Figure 1, it amounts to 6.6  $\text{H}_2\text{O}$  in the homopolymer (+2  $\text{H}_3\text{O}^+$ ), 5 in the 5 + 5 block copolymer (+1  $\text{H}_3\text{O}^+$ ), and 3.6 in the 5 + 11.6 block copolymer (+0.6  $\text{H}_3\text{O}^+$ ).

At  $p/p_0 = 0.9$ , where the decomposition of the experimental spectra then writes  $D^h + 1.32I^h + 3.15H^h$ ,  $D^{5+5} + 1.5I^{5+5} + 0.62H^{5+5} + 2.01W^{5+5}$ , and  $D^{5+11.6} + 1.4I^{5+11.6} + 2.95H^{5+11.6} + 1.38W^{5+11.6}$ , the proportion of hydrated  $\text{C}=\text{O}$  groups amounts to 74% for both the homopolymer and the 5 + 5 copolymer and to 60% for the 5 + 11.6 copolymer. This hydration of the  $\text{C}=\text{O}$  groups seems to become ineffective on approaching the hygrometry 1 for both copolymers (Figure 6), whereas it seems

to remain effective for the homopolymer (Figure 5). In both copolymers, we start having an important embedding of water molecules which insert themselves into the H-bond network in the polymer, no longer hydrating C=O or SO<sub>3</sub><sup>-</sup> groups, a mechanism which we did not detect for the homopolymer. At this hygrometry value, we have 5 H<sub>2</sub>O molecules per sulfonic group (+1 H<sub>3</sub>O<sup>+</sup>) for the homopolymer, 7 (+1 H<sub>3</sub>O<sup>+</sup>) for the 5 + 5 copolymer, and 8.6 (+1 H<sub>3</sub>O<sup>+</sup>) for the 5 + 11.6 copolymer, which means 10 H<sub>2</sub>O per unit drawn between brackets in Figure 1 in the homopolymer (+2 H<sub>3</sub>O<sup>+</sup>), 7 in the 5 + 5 block copolymer (+1 H<sub>3</sub>O<sup>+</sup>), and 5.2 in the 5 + 11.6 block copolymer (+0.6 H<sub>3</sub>O<sup>+</sup>). We see that the number of H<sub>2</sub>O molecules per one SO<sub>3</sub><sup>-</sup>, together with the number of hydrated C=O groups, increases with the number of nonsulfonated elementary units, but reported to one unit drawn between brackets in Figure 1, which reflects the average spatial density of these molecules, this number of H<sub>2</sub>O molecules decreases.

## Conclusion

In the presented study, we recorded series of IR spectra of membranes made of sulfonated polyimides in their protonated form. The polyimides considered were a homopolymer ( $y = 0$  in Figure 1) and two block copolymers, one with  $x = 5$  and  $y = 5$  and the other one with  $x = 5$  and  $y = 11.6$ . In each series, we varied the hygrometry of the atmosphere surrounding these membranes and analyzed the corresponding variations of the spectra, which we could interpret in terms of water uptake and hydration mechanisms. This, we could do because we benefited from a very good signal-to-noise ratio, a property which is usual for IR spectra and is especially true for the  $\nu_{\text{C=O}}$  bands of carbonyl groups. It allowed relatively precise measurements of the proportions of these groups that accept H-bonds from either water molecules or the SO<sub>3</sub>H groups in the dried membrane. It allowed us to put into evidence the important role these C=O groups play in the hydration mechanisms of these membranes, which makes them the main source of the differences between the three polymers. These differences are particularly marked between the dried homopolymer and the dried block copolymers. In the dried homopolymer (Figure 7, I) most of the sulfonated groups are found in their nonionized form SO<sub>3</sub>H. An appreciable proportion of these SO<sub>3</sub>H groups, between 35 and 54%, establish H-bonds on C=O groups, but the rest of them are free; that is, they do not establish H-bonds on C=O groups that are not sufficiently numerous. As a consequence, ionization, the first hydration mechanism to appear at low hygometries, occurs with a single H<sub>2</sub>O molecule per SO<sub>3</sub>H group. This is because the few water molecules that enter the polymer are immediately spread on the maximum number of these extremely hydrophilic groups. In the block copolymers, the number of C=O groups is sufficiently high that all SO<sub>3</sub>H groups can establish in the dried state H-bonds on them (Figure 8, I). They are consequently stabilized, that is, somehow less hydrophilic. As a consequence, H<sub>2</sub>O molecules can bind on H<sub>3</sub>O<sup>+</sup> cations linked to SO<sub>3</sub><sup>-</sup> anions, thus coexisting with SO<sub>3</sub>H groups that ionize only with the arrival of supplementary H<sub>2</sub>O molecules. In these block copolymers, the proportion of ionized sulfonated groups, thus found in the form of SO<sub>3</sub><sup>-</sup> ions linked to H<sub>3</sub>O<sub>2</sub><sup>+</sup> or H<sub>7</sub>O<sub>3</sub><sup>+</sup> cations, is greater (Table 3) than in the homopolymer (40% versus 17%).

The measurements of the quantities of H<sub>2</sub>O molecules, which are also at the origin of well-defined bands displaying a very good signal-to-noise ratio but which are overlapped by bands due to H<sub>3</sub>O<sup>+</sup>, were less precise. These measurements were carried out on the  $\nu_s(\text{O}-\text{H}\cdots)$  and  $\nu_s(\text{O}-\text{H})$  bands which

appeared in spectra where no H<sub>3</sub>O<sup>+</sup> bands were present. More precisely, we used the  $\nu_s$  bands of the Na<sup>+</sup> homopolymer described in our preceding article I<sup>1</sup> to calibrate the quantities of H<sub>2</sub>O molecules in the spectra. This is the first time we could use such an exceptional procedure, the quantities of H<sub>2</sub>O molecules having most of the time been previously measured on their libration bands around 650 cm<sup>-1</sup> or also exceptionally on their bending band around 1640 cm<sup>-1</sup>.<sup>13</sup> Finally, the sulfonic groups, which appeared in both the SO<sub>3</sub>H and SO<sub>3</sub><sup>-</sup> forms, were at the origin of bands, which in the homopolymer are defined sufficiently well to enable direct measurements on these bands. This was not the case in the two block copolymers, where the concentration of these groups is small and consequently the corresponding bands are less intense. We could, however, indirectly measure the amounts of ionized SO<sub>3</sub><sup>-</sup> and neutral SO<sub>3</sub>H forms by comparing their bands with their homologues in the homopolymer. An interesting point to note is that the negatively charged O<sup>-</sup> atoms of SO<sub>3</sub><sup>-</sup> sulfonic groups are the only ones that establish H-bonds with H<sub>2</sub>O molecules, a property we have already encountered with Na<sup>+</sup> and NH<sup>+</sup>Et<sub>3</sub> homopolymers (I).

The water uptakes (Figures 5 and 6) suggest the existence of sigmoidal curves for the total number of embedded H<sub>2</sub>O molecules, in agreement with preceding studies<sup>9-12</sup> that have revealed comparable values. The molecular analysis that we could perform in this study showed relatively small differences between the three polymers. Besides the number of embedded H<sub>2</sub>O molecules per sulfonic group, which slightly increases when passing from the homopolymer to the 5 + 11.6 copolymer (but slightly decreases if reported to one elementary unit), and the difference of the proportion of ionized and nonionized sulfonated groups we have already mentioned, the main difference in hydration lies in the existence for both block copolymers of a mechanism defined by spectra W<sup>x</sup> ( $x = 5+5$  or  $5+11.6$ ), which appear at relatively high hygometries (Figure 6) and which correspond to H<sub>2</sub>O molecules which insert themselves in the H-bond network, which has been developed by already embedded H<sub>2</sub>O molecules. Such a mechanism does not appear in the case of the homopolymer.

Let us finally note that another spectroscopic method could have been used to follow the hydration of these polymers presented in this article. This is 2d-IR correlation spectroscopy.<sup>14</sup> Using it would have enabled us to put into evidence the various bands of the polymers that are simultaneously affected by the arrival of H<sub>2</sub>O molecules. In our opinion, it could not have given the detailed information on the structure and interactions the water molecules establish when entering the polymers (Figures 7 and 8) that we could extract from the analysis of elementary hydration spectra. Isolation of these spectra, which represents a good part of the work, leads to more precise information at the molecular level than correlations provided by this 2d-IR analysis.

**Acknowledgment.** We thank Doctor G. Gebel and Doctor O. Diat for helpful discussions. Contribution to this study of the Commissariat à l'Energie Atomique in the form of a grant for one of us (D.J.) is also greatly acknowledged

## References and Notes

- (1) Cornet, N.; Diat, O.; Gebel, G.; Jousse, F.; Marsacq, D.; Mercier, R.; Pinéri, M. *J. New Mater. Electrochem. Syst.* **2000**, *3*, 33.
- (2) Jamróz, D.; Maréchal, Y. *J. Mol. Struct.* **2004**, *693*, 35.
- (3) Blachot, J. F.; Diat, O.; Putaux, J.-L.; Rollet, A.-L.; Rubat, L.; Vallois, C.; Müller, M.; Gebel, G. *J. Membr. Sci.* **2003**, *214*, 31.
- (4) Maréchal, Y. *J. Mol. Struct.* **2003**, *648*, 27.
- (5) Max, J. J.; Chapados, C. *J. Phys. Chem. A* **2004**, *108*, 3324.

- (6) Grdadolnik, J.; Maréchal, Y. *Biopolymers* **2001**, 62, 54.
- (7) Haxaire, K.; Maréchal, Y.; Milas, M.; Rinaudo, M. *Biopolymers* **2003**, 72, 149.
- (8) Rupley, J. A.; Careri, G. In *Advances in Protein Chemistry*; Anfinsen, C. B., Edsall, J. T., Richards, F. M., Eds.; Academic Press: 1991; Vol. 41.
- (9) Detallante, V.; Langevin, D.; Chappey, C.; Métayer, M.; Mercier, R.; Pinéri, M. *J. Membr. Sci.* **2001**, 190, 227.
- (10) Watari, T.; Fang, J.; Tanaka, K.; Kita, H.; Okamoto, K.; Hirano, T. *J. Membr. Sci.* **2004**, 230, 111.
- (11) Yin, Y.; Fang, J.; Watari, T.; Tanaka, K.; Kita, H.; Okamoto, K. *J. Mater. Chem.* **2004**, 14, 1062.
- (12) Guo, X.; Fang, J.; Tanaka, K.; Kita, H.; Okamoto, K. *J. Polym. Sci., Part A* **2004**, 42, 1432.
- (13) Liltorp, K.; Maréchal, Y. *Biopolymers*, in press.
- (14) Noda, I. *Appl. Spectrosc.* **1993**, 47, 1329.