Mobility of Spin Probes in Quaternized Poly(4-vinyl-pyridine) Membranes

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ABSTRACT: The mobility of nonionic and anionic spin probes in water-containing quaternized poly(4-vinylpyridine) membranes was investigated by means of an electron spin resonance (ESR) technique. Poly(4-vinylpyridine) was quaternized and crosslinked by dibromoalkane $Br(CH_2)_nBr$ ($n=4, 6, 8, 10$), and the effects of the side alkyl chain length were studied. Three spin probes, 2,2,4,4-tetramethyl-1,2,3,4-tetrahydro-γ-carboline-3-oxyl (SPII), 2,2,6,6-tetramethyl-1-piperidinyloxy (SPIV), and sodium 2,2,5,5-tetramethyl-1-pyrrolidinyloxy-3-carboxylate (ASPI), were used. In the temperature region examined, the side methylene chain length had no effect on the mobility of SPII and SPIV, but a little effect for ASPI. This suggests that the ASPI can monitor the mobility of the side alkyl chain. In addition, the effects of water on the mobility of the spin probes were investigated. The mobility of the spin probes was much greater in the membrane containing 30 wt% water than in that containing 3 wt% water, and the polarity around the probes was larger in the former than in the latter membrane. From this, as pointed out in our previous papers on nylon 6/spin probe systems, the effects of water are divided into (1) the effects on the mobilities of the polymer chains and probe molecules, and (2) the effects on the microenvironment around the spin probes.

KEY WORDS   Spin Probe / Nitroxide / Poly(4-vinylpyridine) / Molecular Motion / Water / ESR /

In the study of membrane transport phenomena, knowledge on the states of penetrants in membranes gives a clue to the mechanism of the transport involved. From this point of view, we investigated the mobilities of spin probes in nylon films by means of an electron spin resonance (ESR) technique.[1-5] As a results, their mobilities increased with increasing methylene chain length of the nylon, and were strongly affected by water.

In the present study, poly(4-vinylpyridine) (P4VP) membranes were prepared by quaternizing and crosslinking with dibromoalkane $Br(CH_2)_nBr$ ($n=4, 6, 8, 10$), and the mobility of nonionic and anionic spin probes in these membranes was studied by means of ESR

measurements. P4VP has a high chemical reactivity which is due to its nucleophilic and weakly basic ring nitrogens. This reactivity makes it very attractive a material for a number of applications.[6] Recently quaternized P4VP membranes were applied to charged reverse osmosis membranes, and the dependence of the hydrodynamic permeability and the salt rejection on the charge density of the membrane was investigated.[7]
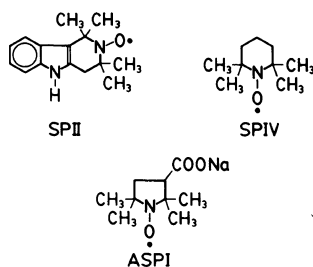
We focus our attention on the effects of the side methylene chain length and water on the mobility of the spin probes in the quaternized P4VP membranes. The effects of the side chain length on the mobility of 4-hydroxy-2,2,6,6-tetramethyl-1-piperidinyloxy in a series of

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acylchitin films[8] and poly(O-acyl-hydroxy-L-proline) films[9] have been reported. In these workes, the mobility of the spin probe increased with an increase in the side chain length. The effects of water on the mobility of nonionic and anionic spin probes in nylon 6 film have been discussed in detail in our previous papers.[2,5] Here, in addition to the above effects, the effects of the spin probe structures are argued, taking into account the interactions of the probe molecules with the membranes.

EXPERIMENTAL

2,2,4,4-Tetramethyl-1,2,3,4-tetrahydro-γ-carboline-3-oxyl (SPII), 2,2,6,6-tetramethyl-1-piperidinyloxy (SPIV), and sodium 2,2,5,5-tetramethyl-1-pyrrolidinyloxy-3-carboxylate (ASPI) were used. SPII was prepared as described in our previous paper.[1] SPIV was pur-

chased from Aldrich Co. and used without further purification. ASPI was prepared by treating 2,2,5,5-tetramethyl-1-pyrrolidinyloxy-3-carboxylic acid (Eastman Kodak Co.) with the molar equivalent of NaOH in water.

Poly(4-vinylpyridine) (P4VP) was purchased from Koei Kagaku Kogyo Co., purified by repeating precipitation from ethanol into diethylether, and dried in vacuo at room temperature. The molecular weight was determined as 1.7×10^5 (the degree of polymerization, 1.6×10^3) by viscosity measurement of its ethanol solution.[10] Four membranes were prepared by quaternizing and crosslinking of P4VP with dibromoalkane $Br(CH_2)_nBr$ ($n=4$,

6, 8, 10) by a method described in the literature.[7] 4.0 g (3.8×10^{-2} base mol) of P4VP were dissolved in 40 ml of ethanol. The prescribed amount (2.9×10^{-3} mol) of dibromoalkane was added in the solution. The solution was cast on a flat poly(ethylene terephthalate) film, and the quaternization and the evaporation of the solvent proceeded at 323—333 K in a nitrogen atmosphere for one day. The degree of quaternization (DQ) of all the membranes was calculated as 0.15—0.17 by an elemental analysis. All the membranes were pretreated in water at 333 K for one day. These membranes are designated as C_nP4VP, where n is the number of methylene groups of dibromoalkane.
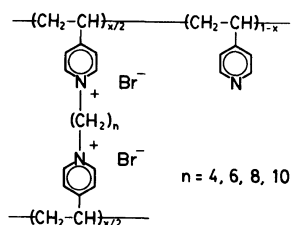
The spin probes were sorbed by the membranes from the aqueous solutions at 333 K for 30—60 min. After sorption, the membranes were rinsed with cold water and blotted with filter paper. The amounts of the spin probes sorbed were determined as 5—8×10^{-7} mol g^{-1} of the membrane by spectrophotometric measurements of the initial and final bath concentrations. The membranes containing 3 and 30 wt% water were used. The membranes immediately after the sorption experiments contained 30 wt% water. The membranes with 3 wt% water were obtained by keeping them in a silica gel desiccator for 2 days. The samples thus prepared were put into ESR quartz tubes and sealed in the presence of air.

ESR spectra were measured by means of a JEOL-FE3X ESR spectrometer in the X band under the same conditions as in our previous studies.[2,3] The temperature was changed from 133 to 343 K by using a JES-VT-3A2 variable

temperature controller together with a JES-UCT-2AX variable temperature adapter. At a temperature higher than 343 K, ESR spectra were not measured since the membrane decomposed. In the temperature region measured, the evaporation of water from the membranes was negligible.

RESULTS AND DISCUSSION

Location of the Spin Probes in the Membranes

The sorption isotherm of ASPI in C_4P4VP at 333 K is shown in Figure 1, which indicates that the probe is sorbed by Langmuir mode (eq 1), i.e., ASPI interacts electrostatically with the positively charged sites of the quaternized poly(4-vinylpyridine).

$$C_p = \frac{nKC_s}{1 + KC_s} \qquad (1)$$

where C_s is the concentration of the aqueous probe solution (mol dm^{-3}), C_p the amounts of the spin probes sorbed by the membrane (mol g^{-1}), K the binding constant of the probe molecules to the membrane (dm^3 mol^{-1}), and n the number of the binding site (mol g^{-1}). Rearrangement of eq 1 leads to eq 2.

$$C_s/C_p = C_s/n + 1/nK \qquad (2)$$
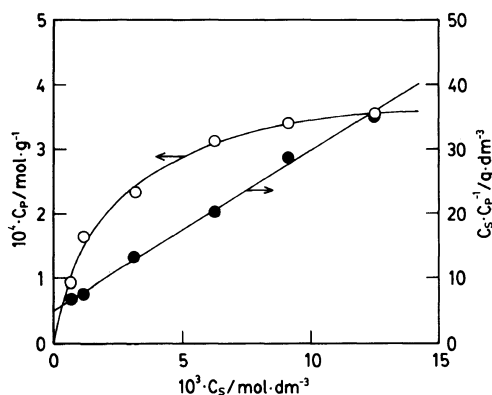
As shown in Figure 1, the plot of C_s/C_p against C_s gave a straight line, supporting the Langmuir type sorption of the anionic probe molecule by the positively charged membrane. From the slope and intercept of the straight line, K and n were determined as 470 dm^3 mol^{-1} and 4×10^{-4} mol g^{-1}, respectively. From the DQ value of the membrane, the number of positively charged groups, i.e., the charge density was estimated as ca. 1×10^{-3} mol g^{-1}, suggesting that 40% of the total positively charged groups is effective. This proportion of the effective charged groups is comparable to that of charged cellulosic membranes.[11,12] On the other hand, the sorption isotherms for SPII and SPIV were linear, suggesting a partition mode. Therefore, it is thought that these nonionic spin probes are located in a hydrophobic region rather than in a hydrophilic region around the positively charged groups.

Extrema Separation

The typical ESR spectra obtained for SPIV in $C_{10}P4VP$ containing 30 wt% water at 173, 263, 283, and 343 K are shown in Figure 2. As the temperature increased, the spectra became narrow and sharp. The extrema separation $2Az'$ is a convenient measure to estimate the mobility of spin probes. Figure 3 shows the change of $2Az'$ with temperature for SPII, SPIV, and ASPI in $C_{10}P4VP$ with 3 wt% water. $2Az'$ for SPIV decreased steeply in the
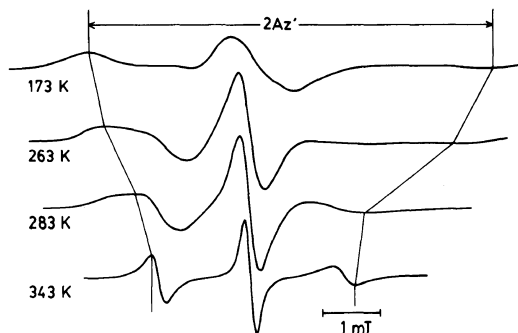

Figure 1. Sorption isotherm of ASPI in C_4P4VP at 333 K.

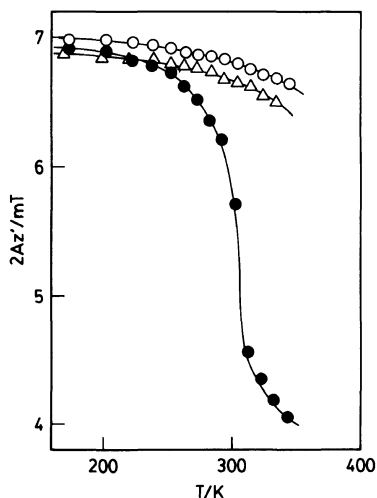**Figure 2.** ESR spectra of SPIV in $C_{10}P4VP$ (water content, 30 wt%).

Figure 3. $2Az'$ vs. temperature. $C_{10}P4VP$ (water content, 3 wt%), ○, SPII; ●, SPIV; △, ASPI.

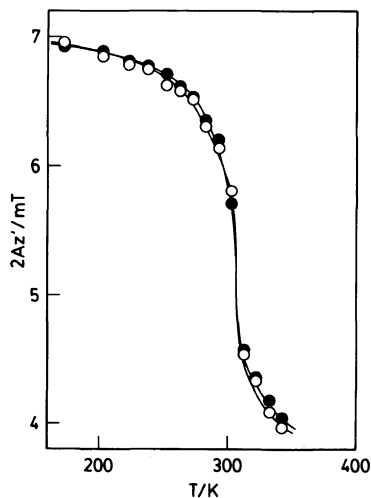**Figure 4.** $2Az'$ vs. temperature. SPIV in the membrane containing 3 wt% water, ○, C_4P4VP; ●, $C_{10}P4VP$.

temperature region observed, while those for SPII and ASPI did not, indicating that SPIV rotates more easily than SPII and ASPI. This can be explained by considering the molar volumes of the spin probes and the interactions between the probe molecules and the polymers.[3] As described in the preceding section, ASPI interacts electrostatically with the positively charged groups of the membranes, and consequently its mobility is greatly restricted. The larger molar volume of SPII makes it more difficult to rotate. It is thus thought that SPIV, which has a smaller molar volume and weakly interacts with the polymer, rotates more easily.

For all the spin probes, $2Az'$ did not vary with the change of the side methylene chain length of the membrane (Figure 4), suggesting that the flexibility of the side chain hardly affects the mobility of the spin probes. The effects of the side alkyl chain length will be discussed in detail using rotational correlation times in the latter section.

The effects of water on the mobility of SPIV and ASPI in $C_{10}P4VP$ were investigated. The plot of $2Az'$ against temperature for SPIV shifted totally to the lower temperature in the
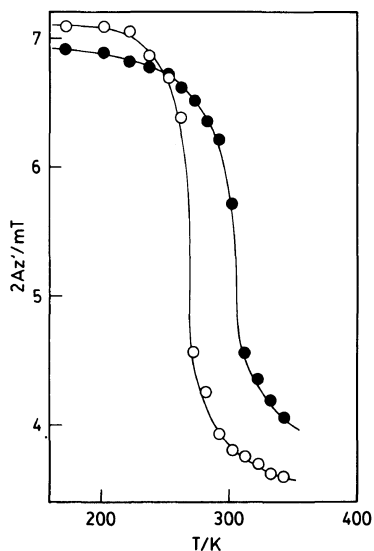

Figure 5. $2Az'$ vs. temperature. SPIV in $C_{10}P4VP$, water content, ○, 30 wt%; ●, 3 wt%.

presence of water (Figure 5). $2Az'$ for ASPI in the membrane containing 30 wt% water was found to decrease steeply in the temperature region measured (Figure 6), and as a result, T_{50G}, the temperature at which $2Az'$ becomes 5 mT (50 Gauss), could be determined as 317 K. T_{50G} can be correlated with the glass
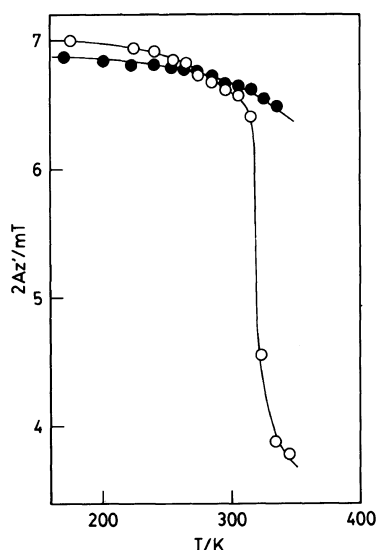
Figure 6. $2Az'$ vs. temperature. ASPI in $C_{10}P4VP$, water content, ○, 30 wt%; ●, 3 wt%.

transition temperature T_g taking into consideration the spin probe structure,[13-15] and is an appropriate measure of the mobility of the spin probes. T_{50G} for ASPI in $C_{10}P4VP$ with 30 wt% water was higher than that for SPIV (270 K). This also indicates that ASPI rotates with more difficulty than SPIV, which is due to the electrostatic interaction of ASPI with the cationic sites of the membrane. The shift of the curve of $2Az'$ against temperature by water is characteristic in the following respect. $2Az'$ decreased with increasing water content above a certain temperature, while it increased with increasing water content below the same temperature as observed in the nylon 6/spin probe systems.[2,5] This phenomenon is explained by two effects of water. One is the effect on the mobility of the spin probe; water acts as a plasticizer, resulting in an increase of the mobility of the polymer chains and hence of the spin probe, or water decreases the local viscosity around the spin probe. This effect shifts the curve to the lower temperature along the abscissa. In addition to this effect, on the other hand, water increases the polarity of the microenvironment around the probe molecule,

resulting in an increase of $2Az'$.[2] This effect shifts the curve vertically along the ordinate. The superposition of these two effects gives the curves shown in Figures 5 and 6.

Rotational Correlation Times

For further discussion, rotational correlation times τ_R were determined from the ESR spectra. As reported in our previous papers,[2,3] the equations derived by Kivelson[16] and Kuznetsov et al.[17] were used for the calculation of τ_R. These equations are based on the assumption of isotropic rotation, and the apparent τ_R thus calculated was used here for the purpose of comparison.

Figure 7 shows Arrhenius plots of the rotational correlation times for SPII, SPIV, and ASPI in $C_{10}P4VP$ containing 3 wt% of water. For SPIV and ASPI, one distinct crossover point was defined in the temperature region observed, while for SPII, it was not. Considering the τ_R values at the crossover points, we may explain the motional change of the spin probes at these crossover points as follows. For SPIV in the nylon films, two crossover points, T_n' and T_n, were found at $\tau_R = 1.4 \times 10^{-8}$ and 4×10^{-9} s, respectively, in the Arrhenius plots of τ_R.[18] T_n' and T_n are assumed to correspond to the temperature at which the full rotation of SPIV occurs without translational diffusion and the temperature at which the rotational motion of the whole probe molecule takes place with translational diffusion. The crossover point for SPIV in the quaternized poly(4-vinylpyridine) appeared when τ_R became 1.4×10^{-8} s. From this, it is thought that the crossover point for SPIV in the quaternized C4VP membranes corresponds to T_n', i.e., the temperature at which the rotation of the whole probe molecule without translational diffusion occurs. On the other hand, for ASPI in the nylon films, three crossover points, T_n', T_n, and T_n'', were observed at $\tau_R = 1.5 \times 10^{-8}$, 6×10^{-9}, and 2×10^{-9} s, respectively.[4] The full rotation around a single bond in the spin probe, or

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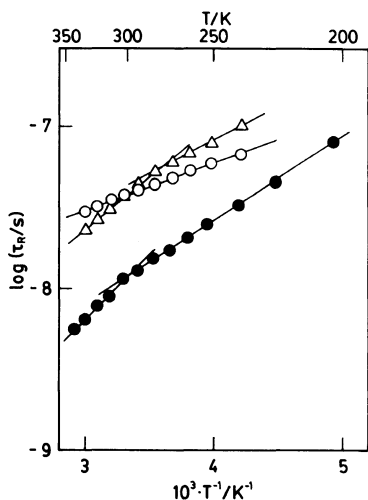
Figure 7. Arrhenius plots of τ_R. $C_{10}P4VP$ (water content, 3 wt%), ○, SPII; ●, SPIV; △, ASPI.

Table I. Crossover points in the Arrhenius plots of τ_R for the membranes containing 3 wt% water

	C_4P4VP	C_6P4VP	C_8P4VP	$C_{10}P4VP$
$T_n*(ASPI)/K$	298	296	291	280
$T_n'(SPIV)/K$	302	—	—	300

Table II. Activation energies for rotation (kJ mol^{-1}). The membranes contain 3 wt% water

	C_4P4VP	C_6P4VP	C_8P4VP	$C_{10}P4VP$
SPII	4.6±0.2	5.6±0.2	6.4±0.3	5.4±0.7
SPIV				
below T_n'	8.2±0.2	—	—	9.79±0.11
above T_n'	14.4±1.2	—	—	15.3±1.0
ASPI				
below T_n*	7.9±0.7	8.7±0.7	7.7±0.4	8.2±0.6
above T_n*	12.0±1.4	12.9±0.6	12.6±0.9	11.4±0.8

around the axis between the negatively charged carboxylate group of ASPI and the positively charged amino end group of the nylon, is thought to start at T_n'. At the same time, the end methylene chains probably start to fluctuate. T_n is assumed to correspond to the temperature at which the rotation of the spin probe becomes coupled with the rotation of the end methylene chains, including the amino groups. At T_n'', the electrostatic interaction between the oppositely charged groups of the spin probe and the nylon may become less directional, and consequently the probe molecule may start to rotate freely. T_n'' was observed only for nylon 11 and nylon 12 film, but T_n' and T_n were found for all the nylon films used in our previous papers.[4] However, the crossover point for ASPI in the quaternized C4VP membranes appeared at $\tau_R = 5 \times 10^{-8}$ s, suggesting that it has a different physical meaning from T_n', T_n, and T_n''. Therefore, that crossover point for ASPI in the quaternized C4VP membranes is designated as T_n*. In the temperature region below T_n', ASPI probably vibrates rotationally.[4] Judging from this, the mode of the rotational vibration of the probe

molecule is thought to change at T_n*.

As shown in Table I, T_n* for ASPI decreased slightly with increasing side methylene chain length, i.e., T_n* reflects the mobility of the side chains. As mentioned repeatedly, ASPI interacts electrostatically with the positively charged nitrogen atom of the pyridine ring which is linked to the side methylene chain, and consequently its mobility may be affected by the flexibility of the side chains. Thus T_n* is assumed to correspond to the temperature at which the mode of the rotational vibration of the probe molecule changes owing to the motional change of the side methylene chains. On the other hand, T_n' for SPIV scarcely changed with increasing side methylene chain length (Table I). SPIV interacts weakly with the polymer membrane. Thus the mobility of the probe is supposed to reflect the change of the relatively large main chain motion rather than that of the local motion. It is thus concluded that the location of the spin probes strongly influences their mobilities.

The activation energies for rotation E_a^R were determined from the Arrhenius plots of τ_R (Table II). E_a^R for all the spin probes did not

change with the side methylene chain length. From this, it is thought that the side chain length does not affect the mode of the spin probe motion. Komai et al. reported the large dependence of the spin probe motion on the side chain length of acylchitin films[8] and poly(O-acyl-hydroxy-L-proline) films.[9] Acyl-chitin and poly(O-acyl-hydroxy-L-proline) used in these reports had approximately two and one side chains per one monomer unit, respectively, whereas C_nP4VP used here had 0.15—0.17 per monomer unit. This difference may affect the dependence of the spin probe motion on the side chain length. In addition, the polymer matrices used here are crosslinked membranes, while the films mentioned above are not; this may also affect the change of the spin probe motion with the side chain length.

In addition, the difference of E_a^R in the spin probes may be interpreted by the motional mode of the spin probes in the different temperature regions. In the temperature region examined here except the temperature region above T_n' for SPIV, the probe molecules probably undergo rotational vibrations. The activation energies for such rotational vibrations are 4—10 kJ mol^{-1} in the nylon films.[3,4,18] The magnitude of E_a^R in this region is probably determined by the restriction of the probe molecules to the polymer membranes and the mode of the rotational vibrations. As ASPI interacts electrostatically with the polymer chains, it has larger activation energies. On the other hand, SPII and SPIV interact weakly with the membranes, and the difference of the vibrational mode between both the nonionic spin probes is thought to determine the E_a^R values. The E_a^R values for SPIV in the temperature region above T_n' are similar to those in the nylon films.[18] This also indicates that the full rotation of SPIV without translational diffusion occurs in this region.

The effects of water on the rotational correlation times τ_R for SPIV and ASPI in $C_{10}P4VP$ are shown in Figures 8 and 9. For both the spin probes, τ_R was found to decrease with increasing water content; water made it easier for the spin probe to rotate. In the case of SPIV, irrespective of water content, one distinct crossover point was defined (Figure 8). The crossover points T_n' for SPIV in the membranes containing 3 and 30 wt% water were 300 and 261 K, respectively, and are comparable to their T_{50G} values (309 and 270 K) discussed in the previous section. On the other hand, the Arrhenius plots for ASPI in the membranes with 3 and 30 wt% water
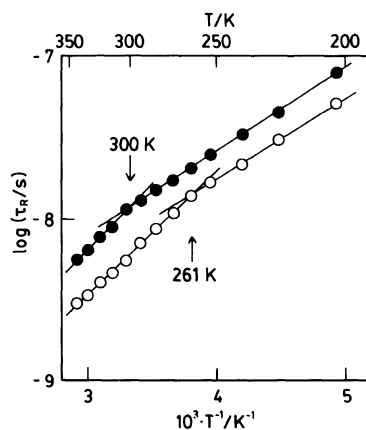

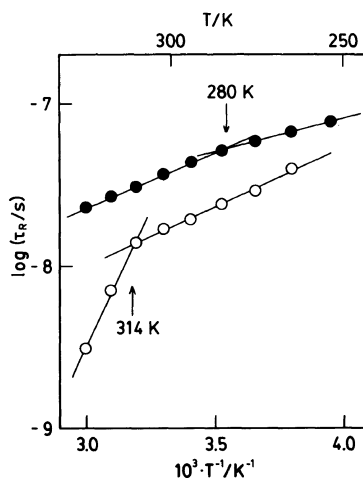**Figure 8.** Arrhenius plots of τ_R. SPIV in $C_{10}P4VP$, water content, ○, 30 wt%; ●, 3 wt%.

Figure 9. Arrhenius plots of τ_R. ASPI in $C_{10}P4VP$, water content, ○, 30 wt%; ●, 3 wt%.

	Water content	
	3 wt%	30 wt%
SPIV		
below T_n'	9.79 ± 0.11	9.6 ± 0.3
above T_n'	15.3 ± 1.0	14.5 ± 0.3
ASPI		
below T_n^*	8.2 ± 0.6	—
between T_n^* and T_n'	11.4 ± 0.8	14.2 ± 0.8
above T_n'	—	65 ± 5

have one distinct crossover point in the temperature region investigated. However, judging from the different τ_R values at these crossover points, it is thought that the crossover point at 280 K for the membrane of low water content has a different physical meaning from that at 314 K for the membrane of high water content. Considering the results of SPIV, we presume that the two crossover points are correlated with the motional change of the side chain and the main chain, and designated as T_n^* and T_n', respectively. T_n' for ASPI (314 K) in $C_{10}P4VP$ with 30 wt% water was much higher than that for SPIV (261 K). Thus T_n' is also as good a measure of the mobility as T_{50G}.

The activation energies for rotation E_a^R were determined from Figures 8 and 9. As given in Table III, E_a^R was hardly affected by water. E_a^R in the temperature region above T_n' was much larger for ASPI than for SPIV. This may be interpreted as follows. At T_n', rotation of the whole probe molecule occurs. SPIV interacts weakly with the polymer membranes and can rotate without restriction. ASPI interacts strongly with the positively charged groups of the membranes and the rotation around a single bond in the spin probe, or around the axis between the oppositely charged groups, takes places. Furthermore, the charged end groups of the nylons can move relatively freely, while the charged groups of the quaternized C4VP are relative-

ly restricted, so that the E_a^R value for ASPI in the quaternized C4VP in the temperature region above T_n' is much larger compared with that in the nylon films (about 25 kJ mol^{-1})[4] and that for SPIV in the quaternized C4VP.

From the above results, we can conclude that water shifts the Arrhenius plot of τ_R to the lower temperature along the abscissa. Accordingly, if T_n' for ASPI in the membrane of low water content appears at 1.35×10^{-8} s of τ_R, at which T_n' exists in the membrane of high water content, it can be estimated as 372 K; the difference between the T_n' values in the membrane containing 3 and 30 wt% water can be calculated as 39 and 58 K for SPIV and ASPI, respectively. If the more hydrophilic probe molecule is more strongly influenced by water, as pointed out in the nylon 6/spin probe systems,[2,5] the results for the quaternized C4VP may be interpreted in a similar manner.

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