Ionic Mobility and Contact Ion Pairing Study by ^{23}Na, ^{35}Cl, and ^{39}K Nuclear Magnetic Resonance in a Poly[methacrylic acid-*co*-(*N,N*-dimethylamino)ethyl methacrylate] Hydrogel

Seung Koo Kang and Mu Shik Jhon*

Center for Molecular Science and Department of Chemistry, Korea Advanced Institute of Science and Technology, 373-1 Kusung-Dong, Yusung-Gu, Taejon 305-701, Korea

Received April 2, 1992; Revised Manuscript Received September 11, 1992

ABSTRACT: ^{23}Na, ^{35}Cl, and ^{39}K line widths and chemical shifts were studied for amphoteric copolymer hydrogel systems as a function of water content and 1 N NaCl and 1 N KCl solution contents. A rapid decrease of the ^{23}Na line width and a downfield shift of the resonance appeared in the range between 1 and 6 water molecules per sodium ion. These results show that the counterions in the sodium methacrylate-*co*-(*N,N*-dimethylamino)ethyl methacrylate (MAANa-*co*-DMAMA) hydrogel establish a contact ion pairing with the polyions. The data suggest the presence of 5 or 6 water molecules in the first hydration sphere of sodium and potassium as counterions. The line shape of ^{23}Na and ^{39}K NMR between 6 and 15 water molecules per counterion shows the non-Lorentzian character. Also the chemical shifts move downfield, and the correlation time remains at a constant value. The results in the range show that the relaxation rate and chemical shift of counterions in the MAA-*co*-DMAMA hydrogel mainly depend on the change of electric field gradients occurring at the anisotropic hydrated counterion around the polyion and the hydrogen bonding between the $-COO^-$ groups and the hydrated ion species, respectively. The ^{35}Cl relaxation rate of the systems MAANa-*co*-DMAMA·HCl and MAAK-*co*-DMAMA·HCl in a 1 N NaCl solution is markedly decreased when free water is produced. This result shows that the ^{35}Cl relaxation is strongly affected by the mobility of water molecules in this system.

Introduction

Synthetic amphoteric copolymer hydrogels containing both acidic and basic groups may provide useful analogs to the behavior of biological proteins.[1,2] In copolymers of MAA and DMAMA systems, the interaction between charged macromolecules and their surrounding ionic media is important. The nature of these interactions is a prerequisite for an understanding of the biological functions on a molecular level.[3-6] Various NMR parameters have been shown to offer a detailed investigation of the interactions between ions and amphoteric polyelectrolytes.[7]

Alkali-metal and halide NMR are the sensitive probe of the immediate chemical environment and the mobility of ions and/or water in aqueous solution.[8-11] The pioneering work of the NMR groups in Lund on alkali-metal and halide NMR endeavors to gain a basis for interpreting the fundamental modes of ionic interactions occurring in polyelectrolyte systems.[3,12-14]

We report the ^{23}Na,^{35}Cl, and ^{39}K NMR relaxation rates and chemical shifts of amphoteric copolymer hydrogel systems under a variety of water contents and 1 N NaCl and 1 N KCl solution contents. Attempts were made to determine whether these studies provide information about (1) the direct probe to the contact ion pairing and ionic mobility phenomena at the molecular levels in the first hydration sphere,[15,16] (2) the specific site binding and the hydrogen-bonding effect of the hydrated counterions to MAANa-*co*-DMAMA and MAAK-*co*-DMAMA hydrogels,[17,18] (3) the influence on the conformational restriction as a deswelling agent and/or the competitive binding to the polyion of 1 N NaCl and 1 N KCl solutions,[19,20] and (4) the offer as a direct probe to the water mobility in the hydrogels.[14]

Experimental Section

(1) Polymer Materials. A 1:1 (MAA:DMAMA = 51%:49%) MAA-*co*-DMAMA hydrogel was prepared by solution polymerization in methanol. Azobis(isobutyronitrile) (0.5%) was used as the initiator; *N,N*-methylenebis(acrylamide) (0.2%) was used as the cross-linking agent; the polymerization temperature was 60 °C. A 2:1 (MAA:DMAMA = 65%:35%) MAA-*co*-DMAMA hydrogel was prepared by solution polymerization in 50% aqueous methanol, using potassium persulfate as the initiator. A 1:2 (MAA:DMAMA = 33%:67%) MAA-*co*-DMAMA hydrogel was prepared by polymerization in a 1% aqueous HCl solution, using potassium persulfate as the initiator. Conversions for all systems obtained nearly 100%. The copolymer composition was determined by elemental analysis. The data on the experimental results are presented in Table I.

A copolymer in powder form is converted to Na, K, and Cl salt forms by 1 N NaOH, 1 N KOH, and 1 N HCl solutions, respectively, at 50 °C for approximately 24 h. The samples were then repeatedly washed with distilled water and dried overnight under vacuum at 80 °C. For the variable water content experiments, portions of dried samples were quickly transferred to capped 10-mm NMR tubes and then weighed. Measured amounts of water are then added to the various samples to give predetermined percentages of H_2O. The sealed samples were vigorously mixed, warmed at 60 °C for several days, and allowed to equilibrate.

(2) Methods. The ^{23}Na, ^{35}Cl, and ^{39}K line widths and chemical shifts were determined on a Bruker AM 300 spectrometer operating at 79.4, 29.4, and 13.9 MHz, respectively. As the reference for the chemical shifts, we used 0.1 N NaCl for ^{23}Na NMR, 0.1 N NaCl for ^{35}Cl NMR, and 0.1 N KCl for ^{39}K NMR. D_2O external locking is used to keep the field homogeneous. Spectra were obtained with quadrature detection and spectral widths of 20, 10, and 20 kHZ for ^{23}Na, ^{39}K, and ^{35}Cl NMR. At least 10^3 scans were acquired for each ^{23}Na spectrum, and the ^{39}K and ^{35}Cl spectra were the result of 3×10^4 scans. The first few points of each free induction decay (FID) were distorted by acoustic ringing within the probe. The line widths ($\Delta\nu_{1/2}$) were obtained from the Lorentzian curve fitting. The errors in measuring line widths were estimated to be ±3%. The temperature during all NMR experiments was 25 ± 0.5 °C.

Theory

^{23}Na and ^{39}K NMR Relaxation.[3,19] The quadrupolar relaxation of ^{23}Na and ^{39}K is domonated by the interaction of its quadrupole moment with the electric field gradients brought about by the polymer. The asymmetric charge

0024-9297/93/2226-0171$04.00/0

Table I
Polymer Formulations

MAA, mL	DMAMA, mL	MBAA, mg	AIBN, mg	$K_2S_2O_8$ (2.7 g/100 mL), mL	composition (MAA:DMAMA)
4	7	28	150		51:49
4	3.5	21		7	65:35
2	7	21		7	33:67

distribution between the species together with the perturbation of the hydration symmetry, caused by the polyion field, is the main source of field gradients. The relaxation of ^{23}Na and ^{39}K is biexponential and gives rise to two NMR line components having different line widths. Under conditions of fast exchange and upon the assumption that the relaxation is dominated by isotropic motions, the broad component ($1/T_{2f}$) has a transversal relaxation rate given by

$$1/T_{2f} = P_f(1/T_{20}) + P_b\frac{\pi^2}{5}\chi^2\tau_c\left(1 + \frac{1}{1+\omega^2\tau_c^{\,2}}\right) \quad (1)$$

The slower relaxing, narrow-line component ($1/T_{2s}$) accounting for the remaining intensity relaxes according to

$$1/T_{2s} = P_f(1/T_{20}) + P_b\frac{\pi_2}{5}\chi^2\tau_c\left(\frac{1}{1+\omega^2\tau_c^{\,2}} + \frac{1}{1+4\omega^2\tau_c^{\,2}}\right) \quad (2)$$

Here t_{20} is the relaxation time for free ions, χ^2 denotes the quadrupolar coupling constant, this being proportional to the magnitude of the field gradient, ω is the angular NMR frequency, P_f and P_b are the fractions of free and bound ions, and τ_c is the correlation time for the motion modulating the relaxation of these ions.

If $\omega\tau_c$ is not too small, it is possible to separate the two components, and τ_c can be obtained from the ratio of their widths. By fitting the high-resolution spectrum to two Lorentzians, we can extract $1/T_{2f}$ and $1/T_{2s}$. If $P_f(1/T_{20})$ is known, then by subtracting this quantity from each of the relaxation rates, we can calculate

$$\frac{1/T_{2f} - P_f(1/T_{20})}{1/T_{2s} - P_f(1/T_{20})} = \frac{\left(1 + \frac{1}{1+\omega^2\tau_c^{\,2}}\right)}{\left(\frac{1}{1+\omega^2\tau_c^{\,2}} + \frac{1}{1+4\omega^2\tau_c^{\,2}}\right)} \quad (3)$$

which is a function only of $\omega\tau_c$. Through the obtained correlation time, we can calculate a value for $P_b\chi^2$. If $\omega\tau_c$ becomes smaller, the relaxation approaches an exponential behavior, with T_2 values given by the approximate relation

$$1/T_2 = P_f(1/T_{20}) + P_b\frac{\pi^2}{5}\chi^2\tau_c\left(0.6 + \frac{1}{1+\omega^2\tau_c^{\,2}} + \frac{0.4}{1+4\omega^2\tau_c^{\,2}}\right) \quad (4)$$

The counterion binding to polyions cannot be discussed in terms of simple binding sites. Furthermore, the relaxation rates obtained from this system are 1 or 2 orders of magnitude greater than that for the general solution study. However, these results show phenomena similar to those for ^{23}Na NMR studies in many dilute polyelectrolyte solutions. If the $P_f(1/T_{20})$ values have very small values compared with observed relaxation rates, these values are negligible. Therefore, the $P_f(1/T_{20})$ values is neglected.

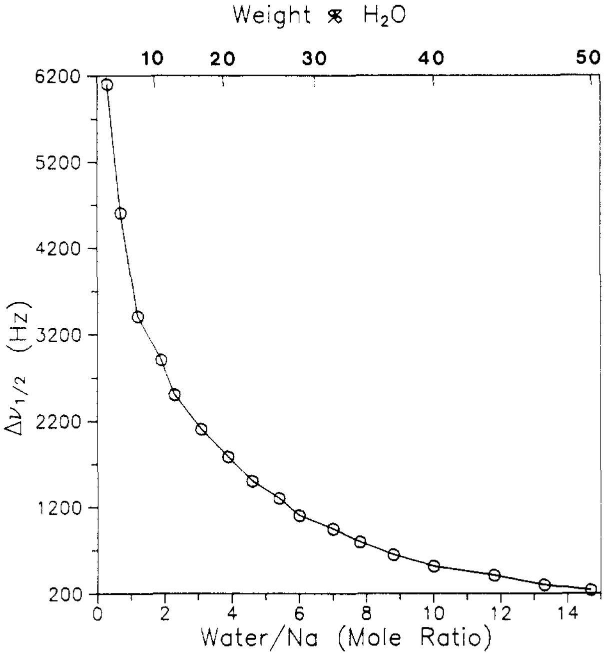

Figure 1. Plot of the ^{23}Na line width of a 1:1 MAANa-*co*-DMAMA hydrogel vs water content and H_2O/Na molar ratio.

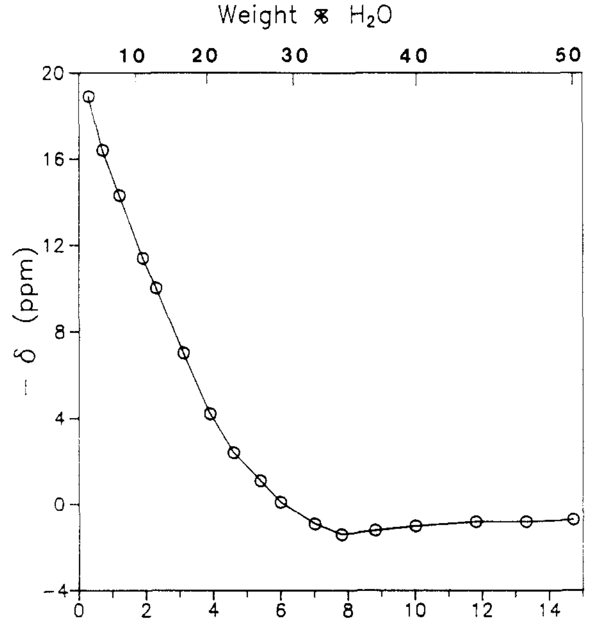

Figure 2. Plot of the ^{23}Na chemical shift of a 1:1 MAANa-*co*-DMAMA hydrogel vs water content and H_2O/Na molar ratio.

Results and Discussion

Figures 1 and 2 are plots of ^{23}Na line widths and chemical shifts at 79.4 MHz, respectively, vs water content and H_2O/Na molar ratio for a 1:1 MAANa-*co*-DMAMA hydrogel. The data of ^{23}Na line widths and chemical shifts for 1:2 and 2:1 MAANa-*co*-DMAMA hydrogels as a function of water content are given as supplementary material. As the amount of water is decreased at a constant temperature, the line widths reached a value of 6 kHz at 2% water content. Simultaneously, the resonance shifts about 20 ppm upfield. Likewise, ^{23}Na line widths and chemical shifts for 1:2 and 2:1 MAANa-*co*-DMAMA hydrogels remarkably depend on the number of water molecules per sodium ion.

^{23}Na line widths and chemical shifts in the range of 1–5 water molecules per sodium ion give rise to the largest change. The magnitude of chemical shifts observed in

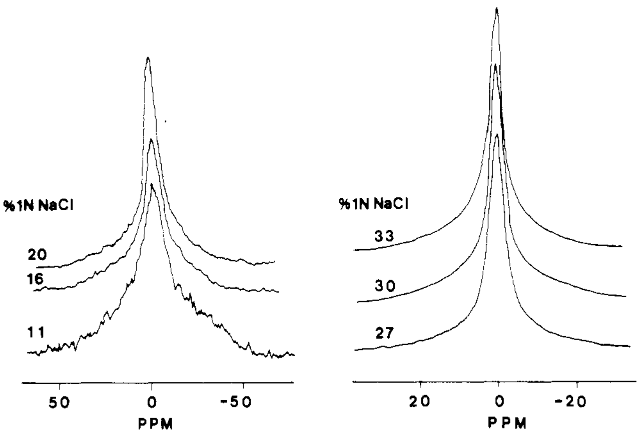

Figure 3. ^{23}Na NMR spectra of a 1:1 MAA-*co*-DMAMA·HCl hydrogel as a function of 1 N NaCl solution content.

Table II
^{23}Na Chemical Shifts (ppm), $\Delta\nu_{1/2}$ (Hz), $\Delta\nu_{1/8}$ (Hz), $\Delta\nu_{1/2s}$ (Hz), $\Delta\nu_{1/2f}$ (Hz), and Correlation Times (ns) of a 1:1 MAANa-*co*-DMAMA Hydrogel as a Function of Water and 1 N NaCl Solution Contents

% H_2O	$\Delta\nu_{1/2}$	$\Delta\nu_{1/8}$	$\Delta\nu_{1/2s}$	$\Delta\nu_{1/2f}$	δ^a	H_2O/Na	τ_c, ns
29	1100	3280	805	1764	0.8	2.1	6
32	943	2770	697	1460	1.53	2.0	7
35	792	2450	572	1391	1.23	2.3	8
38	645	1980	466	1114	1.0	2.3	9
41	513	1540	374	839	1.0	2.2	10
44	409	1270	295	725	0.8	2.2	12
47	299	915	216	514	0.8	2.2	13
50	225	690	163	389	0.7	2.3	15

% 1 N NaCl soln	$\Delta\nu_{1/2}$	$\Delta\nu_{1/8}$	$\Delta\nu_{1/2s}$	$\Delta\nu_{1/2f}$	δ^a	H_2O/Na	τ_c, ns
4	4700				−16.3		0.4
11	2900				−12.4		2
18	2000				−8.9		3
22	1600				−6.5		4
26	1350				−3.2		5
29	1180	3200	975	1411	0.6	1.3	6
33	960	2620	869	1211	1.5	1.4	7
37	807	2290	616	1126	1.4	1.6	8
40	638	1840	540	1040	1.2	1.7	10
45	542	1590	400	834	1.2	2.0	12

[a] A positive δ is a shift to a lower applied field.

Table III
^{23}Na Chemical Shifts (ppm), $\Delta\nu_{1/2}$ (Hz), $\Delta\nu_{1/8}$ (Hz), $\Delta\nu_{1/2s}$ (Hz), $\Delta\nu_{1/2f}$ (Hz), Correlation Times (ns), and $P_b\chi^2$ (Hz^2) of 1:1 MAAK-*co*-DMAMA and 1:1 MAA-*co*-DMAMA·HCl Hydrogel as a Function of 1 N NaCl Solution Content

% 1 N NaCl soln	$\Delta\nu_{1/2}$	$\Delta\nu_{1/8}$	$\Delta\nu_{1/2s}$	$\Delta_{1/2f}$	δ	τ_c, ns	$P_b\chi^2 \times 10^{-11}$
			1:1 MAAK-*co*-DMAMA				
6	4200				−14.2		
11	2800				−9.2		
16	1800				−5.1		
20	1300				0.2		
24	1020	3250	732	1931	2.3	2.5	7.9
27	828	2930	594	1990	1.5	3.2	6.7
30	658	2420	477	1716	1.3	3.3	6.0
33	518	1600	374	909	1.2	2.4	5.5
36	431	1400	310	835	1.2	2.6	5.1
			MAA-*co*-DMAMA·HCl				
5	2100				−4.8		
11	1450	5330	1051	3780	−2.1	3.3	8.8
16	870	3045	625	2132	−0.1	3.2	6.9
20	633	2280	457	1576	1.0	3.2	5.8
27	420	1550	305	1105	0.7	3.3	4.8
30	360	1160	258	844	0.4	3.2	4.4
33	304	1090	218	750	0	3.2	4.0
36	252	945	183	686	0	3.4	3.6

this range is 20 ppm. Also, ^{23}Na line widths rapidly decrease with increasing water content. These results indicate the presence of 5 or 6 water molecules in the first hydration sphere of sodium ion in a MAANa-*co*-DMAMA hydrogel. The upfield shift changes are strong evidence for the formation of contact ion pairs with the polyions. In this range, all of the water molecules are expected to participate in the first hydration sphere of the Na^+ ion or to interact with the $-COO^-$ group.

The 20 ppm shielding difference of MAANa-*co*-DMAMA is a very small value in comparison with the 130 ppm difference of perfluorosulfonate.[15] This difference in shielding between two systems is due to the relative acidity, the charge density, and the mode of interaction between the counterions and the polyions. The hydrogen bonding between the $-COO^-$ group and the water of a hydrated counterion plays an important role in a carboxylate group, whereas this mechanism is not significant for $-SO_3^-$ groups with their low basicity.

On the other hand, ^{23}Na line widths and chemical shifts between 6 and 15 water molecules per sodium ion slowly decrease and shift downfield, respectively. A plausible explanation for this phenomenon would be in terms of hydrogen bonding between the water molecules in Na^+ hydration spheres and the CO_2^- moieties. That is as the water molecule is filled with the first hydration sphere around Na^+ ions, the formation of contact ion pairs is broken and the hydrogen bonding between $-COO^-$ and hydrated Na^+ ions becomes important. Indeed, this phenomenon has been discussed with surfactant systems in previous works.[12,13]

Figure 3 shows ^{23}Na NMR spectra for 1:1 MAA-*co*-DMAMA·HCl hydrogel as a function of 1N NaCl solution content. These spectra show the non-Lorentzian character. To deconvolute the experimental line shapes, the method of Delville et al., based on widths measured at half, $\Delta\nu_{1/2}$, and at one-eighth the height, $\Delta\nu_{1/8}$, was applied.[21] The data obtained from ^{23}Na spectra which have the non-Lorentzian character are listed in Tables II and III. Here, we neglected the $P_f(1/T_{20})$ values because the observed line widths are 1 or 2 orders of magnitude broader than that of free Na^+ ions.

Correlation time (τ_c) values of ^{23}Na nuclei obtained from eq 3 remain at constant values with an increase in the water content for each system. The τ_c values obtained for these systems are 2.2 ns for MAANa-*co*-DMAMA in water, 1.7 ns for MAANa-*co*-DMAMA in a 1 N KCl solution, 2.5 ns for MAAK-*co*-DMAMA in a 1 N NaCl solution, and 3.3 ns for MAA-*co*-DMAMA·HCl in a 1 N NaCl solution. The large τ_c value for 1:1 MAA-*co*-DMAMA·HCl in a 1 N NaCl solution may be ascribed to a chain contraction of the MAA part interacted with a Na^+ ion; i.e., DMAMA residues in 1:1 MAA-*co*-DMAMA·HCl are extended by the chloride salt form, whereas MAA residues are led to the aggregated state.

Although the τ_c values are too ambiguous to assign a particular molecular motion, a few mechanisms are considered. The rate of exchange of a Na^+ ion between a free and a bound state is correlated to τ_c values within nanoseconds. These values indicate that the overall motion of the polymer chains is too slow to affect the correlation time. If ^{23}Na ion motions mainly depend on atmospheric condensation, hydrated ion species will be restricted by the internal motion inside a certain volume surrounding the polyions. Indeed this suggestion may very

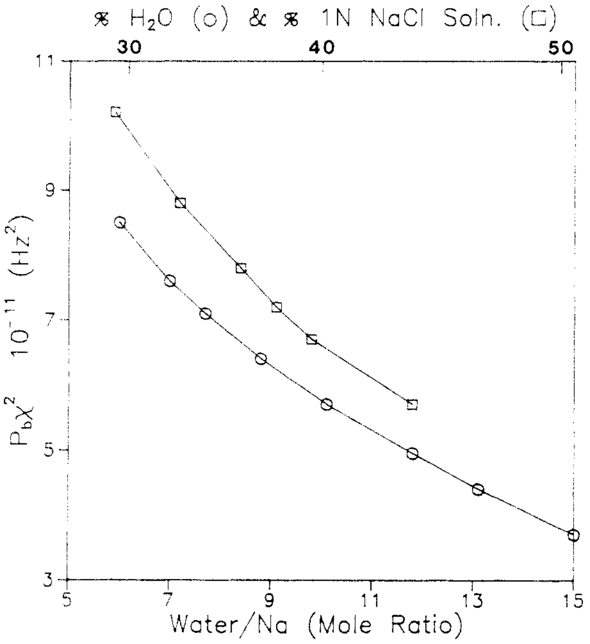

Figure 4. Plot of $P_b\chi^2$ for the bound sodium ions of a 1:1 MAANa-*co*-DMAMA hydrogel as a function of water and 1 N KCl solution content.

Table IV

^{39}K Chemical Shifts (ppm), $\Delta\nu_{1/2}$ (Hz), $\Delta\nu_{1/8}$ (Hz), $\Delta\nu_{1/8}$ (Hz), $\Delta\nu_{1/2s}$ (Hz), $\Delta\nu_{1/2f}$ (Hz), Correlation Time (ns), and $p_b\chi^2$ (Hz^2) of a 1:1 MAAK-*co*-DMAMA Hydrogel as a Function of Water and 1 N NaCl Solution Content

% H_2O	$\Delta\nu_{1/2}$	$\Delta\nu_{1/8}$	$\Delta\nu_{1/2s}$	$\Delta\nu_{1/2f}$	δ^a	τ_c, ns	$P_b\chi^2 \times 10^{-10}$	H_2O/K
29	1360				−5.7			6
31	880				−2.9			7
34	708	2080	524	1091	−0.2	11.2	8.4	8
37	560	1740	404	995	0.4	13.3	6.1	9
42	401	1220	291	676	0.1	12.5	4.5	11
45	303	880	226	454	0.5	10.5	3.7	13
48	216				0.2			15
55	109				0			19

% 1 N NaCl soln	$\Delta\nu_{1/2}$	$\Delta\nu_{1/8}$	$\Delta\nu_{1/2s}$	$\Delta\nu_{1/2f}$	δ^a	τ_c, ns	$P_b\chi^2 \times 10^{-10}$	H_2O/K
33	1010				−2.1			7
36	740	2400	536	1455	0.8	14.8	7.7	8
39	580	1820	417	1055	1.2	13.3	6.2	9
41	460	1480	330	886	3.3	14.7	4.8	10
45	326	1010	235	740	1.9	13.3	3.6	12
48	242	680	187	321	1.4	8.8	3.2	14
52	160				1.2			16

[a] A positive δ is a shift to lower applied field.

well be accorded with the experimental result, provided the hydrating shell volume of Na^+ ions bound to a MAA-*co*-DMAMA hydrogel is unchanged upon an increase of the water content.

The decreasing relaxation rates for increasing water content indicate the change in the environment of bound Na ions. In Table II, ^{23}Na relaxation rates for 1:1 MAANa-*co*-DMAMA in a 1 N KCl solution are larger than those in water. These values indicate that the chain contraction and/or the restriction of water mobility by the addition of a KCl salt solution is more effective than the competitive binding of the potassium ion to the $-COO^-$ group. The values of ^{23}Na shielding for a MAA-*co*-DMAMA hydrogel in 1 N NaCl and 1 N KCl solutions (Tables II and III) are observed in downfield ranges in comparison with those in water. This phenomenon is regarded as repulsion between the same charged ions around the polyions.

^{23}Na relaxation rates and shielding differences for 1:1 MAAK-*co*-DMAMA and 1:1 MAA-*co*-DMAMA·HCl as a function of 1 N NaCl solution content are provided in Table III. The ^{23}Na relaxation rates of a 1:1 MAAK-*co*-DMAMA hydrogel system at low water content are markedly large than those of a 1:1 MAA-*co*-DMAMA·HCl system, and its shielding is an upfield shift as larger as 10 ppm. These values assume that the Na^+ ions in a 1:1 MAA-*co*-DMAMA·HCl hydrogel system lead to the decrease of the bound ion content and/or the weak interaction with the carboxyl group in comparison with those in a 1:1 MAAK-*co*-DMAMA hydrogel system. From this point of view, the results for the shielding phenomena are interpreted such that a 1:1 MAAK-*co*-DMAMA system offers the contact ion pairing sites by the $-COO^-$ groups, whereas a 1:1 MAA-*co*-DMAMA·HCl system does not offer the contact ion pairing sites for the Na^+ ions.

The $P_b\chi^2$ values of ^{23}Na nuclei for a MAANa-*co*-DMAMA hydrogel in water and a 1 N KCl solution are obtained from eq 4 and are presented in Figure 4. The variation of $P_b\chi^2$ corresponds to the change of relaxation rate. The $P_b\chi^2$ and relaxation rates deal with the qualitative relation that indicates the degree of interaction of the bound counterions and the change of electric field gradients brought about by the polyions. Here, the specific-site binding with a $-COO^-$ group cannot be ruled out because the local concentration of counterions around the polyions is fairly high. However, it is somewhat unsatisfactory to expect the real site binding from the value obtained for these systems, considering the dehydration and the shielding of counterions.[22,23] As far as the value is concerned, the $P_b\chi^2$ value of a 1:1 MAANa-*co*-DMAMA hydrogel in a 1 N KCl solution is relatively higher than that of a 1:1 MAANa-*co*-DMAMA in water. This value is different from that of real site binding for the Na^+ ions. If $P_b\chi^2$ value entirely depends on the real site binding, the value for a 1 N KCl solution system, must be lower than that of the water system because it is due to competitive binding of a potassium ion to the polyion binding sites. Hence, the $P_b\chi^2$ values with increasing water content mainly depend on the change of electric field gradients occurring at the anisotropic hydrated sodium ions bound around the polyions.

The line widths and chemical shifts for ^{39}K nuclei in a 1:1 MAAK-*co*-DMAMA hydrogel as a function of water content are presented in Table IV. Unfortunately, at the condition below 30% water content, the ^{39}K signal is lost by the ring-down phenomena. A ^{39}K NMR line shape between 7 and 15 water molecules per potassium ion shows the non-Lorentzian character, and the rate of exchange is greater than the chemical shift difference between the species. ^{39}K NMR behavior can arise from either the fluctuation of electric field gradients occurring at the anisotropic hydrated ion species or the chemical binding localizing the ion at a specific site on the polyions. Chemical binding would be expected to cause large chemical shifts, whereas the nonspecific binding implied by atmospheric condensation would not. It is impossible for us to extract the values for the chemical binding and the population of bound ions from these data. The shielding to the extent of 6 and/or 7 water molecules per potassium ion is upfield. In view of the results so far, these values are surmised by the increase of the capability of the contact ion pairing and/or the hydration number of the potassium ions.

In ^{23}Na and ^{39}K NMR results, in the range between 6 and 15 water molecules per counterion, are found that

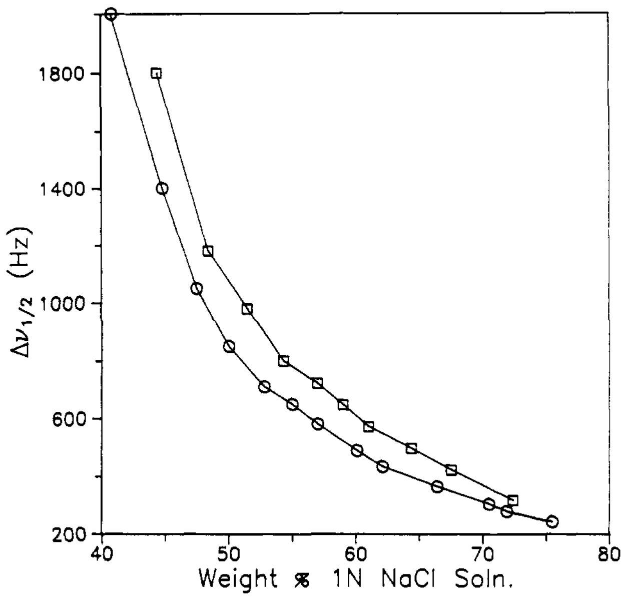

Figure 5. Plot of the ^{35}Cl line width of a 1:1 MAANa-*co*-DMAMA hydrogel (○) and a 1:1 MAAK-*co*-DMAMA hydrogel (□) as a function of 1 N NaCl solution content.

Table V
^{35}Cl Line Widths (Hz) and Chemical Shifts (ppm) of a 1:1 MAA-*co*-DMAMA·HCl Hydrogen as a Function of Water and 1 N NaCl Aqueous Content

% H_2O	$\Delta\nu_{1/2}$	δ^a	% 1 N NaCl soln	$\Delta\nu_{1/2}$	δ
48	2250	−6.1	49	2400	−8.0
50	1900	−2.2	50	2100	−3.0
54	1750	0.5	54	2000	−0.4
58	1600	4.2	59	1850	5.8
62	1500	5.9	63	1700	4.9
67	1440	6.1	66	1560	6.3
71	1390	7.3	71	1450	4.5
76	1350	7.8	76	1340	6.3
80	1300	4.1	81	1280	6.0
			84	1200	4.7

[a] A positive δ is a shift to lower applied field.

each line represents a trend similar to the relaxation rates, the shielding, and the $P_b\chi^2$ values. The interaction mode between the counterion and the polyion which is affected by the acidity and the charge density of the polyion becomes an important clue for the studies of the super-swelling and/or the bioactivity. The interaction modes with counterions of the system MAA-*co*-DMAMA hydrogel in water, in 1 N NaCl, and in 1 N KCl solutions are summarized as follows.

1. Variation of relaxation rates with increasing water content corresponds well with a change in the $P_b\chi^2$ value, and this result is mainly due to the change of electric field gradients brought about by the asymmetric charge distribution around the polyions.

2. The competitive binding effect by K^+ ions, at a 1:1 MAANa-*co*-DMAMA hydrogel in 1 N KCl solutions, is small for the ^{23}Na relaxation rates and $P_b\chi^2$ values, whereas the aggregation and/or the restriction of water mobility by a KCl salt solution is more effective for these values. This result also indicates that the bound ^{23}Na ion is affected not by the real site binding to the polyion but the atmospheric condensation, hydration, and conformational restriction, etc.

3. The shielding phenomena mainly depend on the hydrogen bonding effect between the $-COO^-$ groups and the hydrated ion species.

4. The motions of a hydrated ion species including atmospheric condensation are dominated by the internal motion and/or the polyion conformations.

Figure 5 shows the line widths for ^{35}Cl nuclei in 1:1 MAANa-*co*-DMAMA and 1:1 MAAK-*co*-DMAMA hydrogels as a function of 1N NaCl solution content. Like ^{39}K NMR pointed out in the previous content, the ^{35}Cl NMR signal below 40% water content is lost by the ring-down phenomena. ^{35}Cl relaxation rates are markedly decreased at the vicinity of 43% 1 N NaCl solution content. As differential scanning calorimetry (DSC) results for these systems show, the water melting peak at ca. 0 °C was not represented for the extent of this content.[24] These results probe strongly that the water mobility influences ^{35}Cl relaxation rates critically.

Table V presents the line widths and chemical shifts for ^{35}Cl nuclei in a 1:1 MAA-*co*-DMAMA·HCl hydrogel as a function of water and 1 N NaCl solution content. These results show that ^{35}Cl relaxation rates are more greatly dependent on the ion-pair formation with $-N^+(CH_3)_2H$ groups than on the water mobility. The comparatively small difference in shielding between the two systems indicates that the direct chloride–polyion contact is relatively unimportant and the chloride ions remain in a hydrated state on attachment to the $-N^+(CH_3)_2H$ group. The variation of ^{35}Cl relaxation with the nature of polyions is necessary to consider not only how the counterions interact with the associated $-N^+(CH_3)_2H$ groups but also how the counterions interact with the water molecules.[25,26] The degree of downfield shift on a MAA-*co*-DMAMA hydrogel may be concerned about a modified chloride–water interaction. It is a fact that ^{35}Cl relaxation rate is dominated by the mobility of water molecules in the immediate neighborhood of counterions. The ^{35}Cl relaxation rate is affected by the mobility of water molecules, and it indicates that the counterions are hydrated also when they are attached to the $-N^+(CH_3)_2H$ groups in DMAMA.

Acknowledgment. This research was supported by Korea Science and Engineering Foundation and Korea Research Center for Theoretical Physics and Chemistry.

Supplementary Material Available: Table of the ^{23}Na chemical shifts and line widths for 1:2 and 2:1 MAANa-*co*-DMAMA hydrogels as a function of water content (1 page). Ordering information is given on any current masthead page.

References and Notes

(1) Alfrey, T., Jr.; Fuoss, R. M.; Morawetz, H.; Pinner, H. *J. Am. Chem. Soc.* **1952**, *74*, 438.
(2) Ehrlich, G.; Doty, P. *J. Am. Chem. Soc.* **1954**, *76*, 3764.
(3) Gustavsson, H.; Lindman, B.; Bull, T. *J. Am. Chem. Soc.* **1978**, *100*, 4655.
(4) Detellier, C.; Laszlo, P. *J. Am. Chem. Soc.* **1980**, *102*, 1124.
(5) Kang, S. K.; Sung, Y. K.; Jhon, M. S. *J. Polym. Sci., Polym. Chem. Ed.*, in press.
(6) Kang, S. K.; Jhon, M. S. *J. Polym. Sci., Polym. Chem. Ed.*, in press.
(7) Watterson, A. C.; Olson, C. C.; Salamone, T. C. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1988**, *21*, 164.
(8) Halle, B.; Anderson, T.; Forsén, S.; Lindman, B. *J. Am. Chem. Soc.* **1981**, *103*, 500.
(9) Halle, B.; Piculell, L. *J. Chem. Soc., Faraday Trans. 1*, **1982**, *78*, 255.
(10) Ulmius, J.; Lindman, B.; Lindblom, G.; Drakenberg, T. *J. Colloid Interface Sci.* **1978**, *65*, 88.
(11) Templeman, G. J.; Van Geet, A. L. *J. Am. Chem. Soc.* **1972**, *94*, 5578.
(12) Gustavsson, H.; Lindman, B. *J. Am. Chem. Soc.* **1975**, *97*, 3923.
(13) Gustavsson, H.; Lindman, B. *J. Am. Chem. Soc.* **1978**, *100*, 4647.
(14) Lindblom, G., Lindman, B. *J. Phys. Chem.* **1973**, *77*, 2531.

(15) Komoroski, R. A.; Mauritz, K. A. *J. Am. Chem. Soc.* **1978**, *100*, 7478.
(16) Wong, M.; Thomas, J. K.; Nowak, T. *J. Am. Chem. Soc.* **1977**, *99*, 4730.
(17) Cornelis, A.; Laszlo, P. *Biochemistry* **1979**, *18*, 2004.
(18) Belton, P. S.; Morris V. J.; Tanner, S. F. *Macromolecules* **1986**, *19*, 1618.
(19) Grasdalen, H.; Kvan, B. J. *Macromolecules* **1986**, *19*, 1913.
(20) Qian, C.; Asdjodi, M. R.; Spencer, H. G.; Salvitsky, G. B. *Macromolecules* **1989**, *22*, 995.
(21) Delville, A.; Detellier, C.; Laszlo, P. *J. Magn. Reson.* **1979**, *34*, 301.
(22) Prestegard, J. H.; Chan, S. I. *Biochemistry* **1969**, *8*, 3921.
(23) Herwats, L.; Laszlo, P.; Genard, P. *Nouv. J. Chim.* **1977**, *1*, 173.
(24) Bound water contents for these systems were ca. 42 wt % for the MAANa-*co*-DMAMA system and ca. 45% for the MAAK-*co*-DMAMA system. These values are measured within experimental error. The difference between the MAANa-*co*-DMAMA system and the MAAK-*co*-DMAMA system may be mainly due to the hydrating ability of these ions to water molecules.
(25) Lindman, B.; Forsén, S. In *Chlorine, Bromine and Iodine NMR*; Diehl, P., Fluck, E., Kosfeld, R., Eds.; Springer-Verlag: Berlin, 1976; pp 222–225.
(26) Gutsavsson, H.; Lindman, B. *J. Chem. Soc., Chem. Commun.* **1973**, 93.

Registry No. (DMAMA)(MAA)(MBAA) (copolymer), 90999-18-1; (DMAMA)(MAANa) (copolymer), 129380-60-5; (DMAMA)-(MAAK) (copolymer), 144669-02-3; H_2O, 7732-18-5; NaCl, 7647-14-5; KCl, 7447-40-7.