Macromolecules **2006,** *39,* 1577−1584

High Frequency Dielectric Behavior of Polyelectrolytes with Controlled Charge Densities in Aqueous Solution

Kenji Nakamura and Toshiyuki Shikata*

Department of Macromolecular Science, Osaka University, Toyonaka, Osaka 560-0043, Japan

Received November 25, 2005; Revised Manuscript Received December 15, 2005

ABSTRACT: Dielectric relaxation behavior was investigated in the high-frequency range from 1 MHz to 20 GHz, or 6.3×10^6 to 1.3×10^{11} rad s^{-1} in angular frequency (ω), for aqueous solutions of polyelectrolytes, random copolymers of styrene and sodium styrenesulfonate with a controlled degree of sulfonation (X_S), by varying the concentration (c_P) of polyelectrolytes at 25 °C. Besides dielectric measurements, the degree of Na^+ binding (F_{bin}) to benzenesulfonate (BS^-) groups for the polyelectrolytes in aqueous solution was determined as a function of X_s. Pronounced dielectric relaxation processes, which had no established assignments, were observed for $\omega > 10^9$ rad s^{-1}. A dielectric relaxation mode found at a relaxation time of 0.12 ns irrespective of c_P, with relaxation strength proportional to the product c_PX_S, was attributed to the detachment of two to three hydrated water molecules from BS^- groups. Another relaxation at 0.9 ns, with relaxation strength proportional to $c_PX_SF_{bin}$, was assigned to the rotation of $BS^-{-}Na^+$ ion pairs with large dipole moments.

Introduction

Dielectric relaxation measurement (DRM) is a very powerful method for investigating motions of molecules or substituent groups over a broad time range, on the order of 10^0-10^{11} rad s^{-1}. If these molecules or substituent groups bear electric dipole moments, DRM provides useful information on the sizes of dipoles and the time scales of their molecular motions. Thus, the DRM technique has been widely employed for the study of polymer dynamics in the bulk state, in blends, and also in solutions even under dilute conditions.[1] The history of dielectric research on aqueous polyelectrolyte solutions goes back more than 50 years.[1−6] Although DRM is a very useful method to investigate the dynamics of polyelectrolytes in aqueous solution, the high electric conductance and the inevitable strong electrode polarization effects usually encountered in DRMs of such solutions were crucial problems in obtaining precise experimental data, especially at frequencies lower than 10^4 rad s^{-1}.[5] To overcome the electrode polarization effect, a four-electrode method based on time domain measurements and employing a Fourier transform procedure to obtain dielectric spectra as a function of frequency was proposed in the early 1980s.[7] Dielectric spectra over a wide frequency range (up to 10^7 rad s^{-1}) for aqueous solutions of some polyelectrolytes, e.g., DNA,[8] poly(styrenesulfonate) salts,[9,10] and poly(vinylamine) salts,[11] have been reported.

On the other end of the frequency range, efforts to measure the dielectric relaxation behavior of aqueous polymer solutions at frequencies higher than 10^{11} rad s^{-1} succeeded in the mid-1980s. Subsequently, a time domain reflectometry method has been successfully developed, besides the usual frequency domain technique, for measurements at frequencies up to 10^{11} rad s^{-1}, by Mashimo et al.,[1,12−14] who carried out DRM on several kinds of aqueous polymer solutions including those of polyelectrolytes such as DNA,[12] poly(glutamic acid),[13] and poly(acrylic acid).[14]

As a result of such endeavors, it has become clear that counterions dissociated from polyelectrolytes frequently play significant roles in the dielectric behavior of aqueous solutions since the time dependent fluctuation of the spatial distribution of dissociated counterions induces considerable dielectric relaxation at a frequency corresponding to the motion of the counterions. Thus, it has been well-known from experiments and theory that dielectric relaxation spectra for linear polyelectrolytes show at least two major relaxation processes irrespective of the nature of the polymer. Although dielectric relaxation spectra are highly dependent on the concentration (c_P) of a dissolved polyelectrolyte, low (10^2-10^5 rad s^{-1}) and high (10^6-10^8 rad s^{-1}) frequency relaxation processes are clearly recognized at high dilution. The relaxation time and strength of the low frequency relaxation (LFR) process at infinite dilution depend strongly on the molecular weight (M) of the examined polyelectrolyte, whereas those of the high-frequency relaxation (HFR) process do not depend on M.[1−11] These facts indicate that the origin of the LFR process lies in the slowest mode of fluctuation of counterions distributed along the long axis or main chain of the polyelectrolyte,[5,6,8−11] whereas higher order harmonics of the counterion fluctuation along the long axis or fluctuations perpendicular to the long axis of the polyelectrolyte cause the HFR process.[5,6,15−18] Vaughan et al.[19−21] were the first to provide a detailed theoretical analysis of the contribution of Coulomb interactions between counterions on the surface of linear polyelectrolytes to the dielectric behavior of their aqueous solutions, and they concluded that the magnitude of the relaxation strength rose rapidly with increasing number of counterions to a maximum and then decreased, and that the relaxation frequency increased with increasing interactions between counterions.

The dielectric relaxation behavior of aqueous polyelectrolyte systems in the frequency range above 10^9 rad s^{-1}, i.e., the *hyper high-frequency relaxation* (HHFR) process, which includes the relaxation frequency of the solvent, bulk water, ca. 1.3×10^{11} rad s^{-1} at 25 °C, has not been fully discussed so far. Only a small number of experimental studies have been reported because of experimental difficulties.[12−14,22−24] In these reports, HHFR has been assigned to the rotational relaxation modes of water molecules bound to monomer units of polyelectrolytes by hydrogen bonds;[12−14] the rotational modes of polar side groups of polyelectrolytes;[24] or to the fluctuations in the counterion distribution perpendicular to the long axis of the

---

* Corresponding author. E-mail: shikata@chem.sci.osaka-u.ac.jp.

10.1021/ma052522a CCC: $33.50

polyelectrolyte as in the HFR process described above.[22,23] It is naturally expected that HHFR contains important information on the fastest dynamics in aqueous polyelectrolyte solutions on the order of monomer size scales, which has not been investigated in detail so far using DRM techniques.

Recently, significant dielectric relaxation was observed in an aqueous micellar solution of a cationic surfactant, cetyltrimethylammonium bromide (CTAB), at ca. 10^9 rad s^{-1}. This relaxation process was assigned to the rotational relaxation mode of ion pairs formed between a cationic headgroup of CTA$^+$ and an anionic counterion, Br$^-$.[25,26] An aqueous micellar solution of an anionic surfactant, sodium dodecyl sulfate (SDS), also showed a strong dielectric relaxation process, as for aqueous CTAB.[27] Moreover, because aqueous solutions of zwitterionic surfactants such as alkyldimethylammonioacetate, which bears covalently linked ion pairs on its headgroup, also showed marked dielectric relaxation behavior in the same frequency range, $\sim 10^9$ rad s^{-1},[28] it has been confirmed that the presence of any type of ion pair formed between ionic headgroups and counterions on the surface of surfactant micelles will lead to significant dielectric relaxation in aqueous solution. These results suggest that ion pairs formed between ionic side-chain groups such as benzenesulfonate, BS$^-$, or sulfonate, SO_3^-, and counterions like sodium, Na$^+$, in aqueous polyelectrolyte systems possibly account for the HHFR process observed at frequencies higher than 10^9 rad s^{-1}.

In this study, the dielectric relaxation behavior of aqueous solutions of random copolymers of styrene and sodium styrenesulfonate (P(St/NaSS)s) with varying degrees of sulfonation (X_S = 0.45, 0.74, and 1.0) was investigated over a wide frequency range, from 6.3×10^6 to 1.3×10^{11} rad s^{-1}, at 25 °C. The HHFR process observed in these systems was the main focus of this study. Because the polyelectrolytes used, P(St/NaSS)s, bore controlled electric charge densities, the influence of changes in the concentration of ion pairs formed in the system on dielectric behavior could be precisely evaluated. Finally, the essential origin of HHFR for polyelectrolytes in aqueous solution was established.

Experimental Section

Materials. Anionically polymerized polystyrenes used as precursors to P(St/NaSS)s were supplied by Tosoh Corp. Ltd. (Tokyo), and had number-average molecular weights (M_n) of 9.2×10^3 and 3.4×10^5 g/mol and polydispersities of 1.04 and 1.07, respectively. P(St/NaSS)s with $X_S = 0.45$ and 0.74 were prepared by a partial sulfonation procedure described by Makowski,[29] and P(NaSS), namely with $X_S = 1.0$, was obtained by complete sulfonation using sulfuric acid. The resulting sulfonated polymers obtained in the acid form were neutralized with aqueous sodium hydroxide, and were dialyzed against water initially controlled at pH 9.0 with sodium hydroxide for more than 5 days. Finally, the P(St/NaSS)s were obtained in powder form via a freeze-drying technique.

Highly deionized water with specific resistance higher than 16 MΩ cm obtained by a Milli-Q system (Japan Millipore, Tokyo) was used as the solvent for sample preparation. Deuterium oxide (D_2O) and deuterated dimethyl sulfoxide (DMSO-d_6) were purchased from Aldrich Chemical Co., Inc. (Milwaukee, WI) and Isotec Inc. (Cambridge, U.K.), respectively, and were used as solvents for proton nuclear magnetic resonance (^{1}H NMR) measurements. Sodium dodecylbenzenesulfonate (SDBS) was purchased from Wako Pure Chemical Industries, Ltd. (Osaka, Japan) and was used without further purification.

The X_S values for P(St/NaSS)s were determined by two methods, elemental analysis and ^{1}H NMR measurements on DMSO-d_6 solutions of P(St/NaSS)s, and were in good agreement with each other. The concentrations of P(St/NaSS)s in monomer units (c_P) for sample solutions ranged from 1 to 200 mM.

Methods. Dielectric relaxation measurements were carried out using two measuring systems. For the frequency (ω) range from 6.28×10^6 to 1.88×10^{10} rad s^{-1}, a system consisting of an RF LCR meter (4287A, Agilent Technologies, Palo Alto) equipped with a homemade electrode cell with a vacant capacitance (C_0) of ca. 0.23 pF was used. The temperature of sample liquids was maintained at 25 °C. The electrical capacitance (C) and conductance (G) for sample liquids as functions of ω were determined using a parallel coupling equivalent circuit. The real and imaginary parts of the relative electric permittivity, ϵ' and ϵ'', were calculated in the usual way: $\epsilon' = CC_0^{-1}$ and $\epsilon'' = (G - G_{dc})(C_0\omega)^{-1}$, where G_{dc} is the dc conductance owing to the presence of ionic components such as dissociated Na$^+$ ions and other impurities contained in the sample liquids.

A dielectric material probe system (HP85070B, Hewlett-Packard, Palo Alto, CA) including a network analyzer (8720ES, Hewlett-Packard, San Jose, CA), equipped with a coaxial probe cable and controlled by Hewlett-Packard software was used for the ω range from 3.14×10^8 to 1.26×10^{11} rad s^{-1}. The temperature of sample liquids was again kept at 25 °C. In this system, ϵ' and ϵ'' as functions of ω were automatically calculated by the installed program. Detailed measurement procedures have been described elsewhere.[25,26]

The densities of aqueous solutions of P(St/NaSS)s were measured using a digital densitometer (DMA5000, Anton Paar, Graz, Austria) at 25 °C to evaluate the average partial molar volume ($\bar{V}_m$) of P(St/NaSS) monomers in aqueous solution.

Three types of NMR spectrometers, a JEOL (Tokyo) EX-270 and JEOL LA-500 and Varian (Palo Alto, CA) UNITY INOVA 600, with different proton resonance frequencies (270, 500, and 600 MHz, respectively), were used to determine the longitudinal relaxation time (T_1) of the meta-protons of phenyl rings of both styrene and styrenesulfonate moieties in P(St/NaSS)s dissolved in water (D_2O) at 25 °C. A conventional inversion recovery pulse sequence was employed.

The concentration of Na$^+$ ions was determined using an Na$^+$ ion-selective electrode (1512A, Horiba, Kyoto, Japan). A homemade Ag−AgCl electrode, which was inserted into 3.3 M KCl aqueous solution with a salt bridge of 3% agar containing 1.0 M KCl, was used as the reference electrode. A potentiometer (pH-meter F-22, Horiba, Kyoto) was used to measure the potential difference between the electrodes.

Results

Dielectric Relaxation Behavior. Figure 1 shows typical dielectric relaxation spectra, ϵ' and ϵ'' ($= G(C_0\omega)^{-1} - G_{dc}(C_0\omega)^{-1}$) as functions of frequency, ω, for an aqueous solution of a P(NaSS), $M_n = 3.4 \times 10^5$, at $c_P = 50$ mM. $G(C_0\omega)^{-1}$ and $G_{dc}(C_0\omega)^{-1}$ data for the solution were also plotted in the same figure to indicate the contribution of G_{dc} to ϵ''. (The adopted G_{dc} value was determined with care, as $\Delta\epsilon'$ and $\Delta\epsilon''$ showed consistent ω dependence given by eq 3, as will be seen later in Figure 2, and was very slightly smaller than the G value determined at the lowest ω examined.) This figure also contains dielectric relaxation spectra for pure (bulk) water, ϵ_w' and ϵ_w''; it can be seen that the small contribution of ionic impurities was adequately removed. Solid lines in the figure represent calculated curves from published[30] standard functions for ϵ_w' and ϵ_w'' given by simple Debye-type formulas (eq 1) with parameters $\tau_w = 8.3$ ps, $\Delta\epsilon_w = 73.3$, and $\epsilon_\infty = 5.1$, which have been employed as the calibration parameters for the measuring systems in this study. It is obvious that both the solution and bulk water have major relaxation processes observed at the relaxation time (8.3 ps) assigned to the rotational relaxation of bulk water molecules.

$$\epsilon_w' = \frac{\Delta\epsilon_w}{1 + \omega^2\tau_w^2} + \epsilon_\infty \quad \epsilon_w'' = \frac{\Delta\epsilon_w \omega\tau}{1 + \omega^2\tau_w^2} \qquad (1)$$

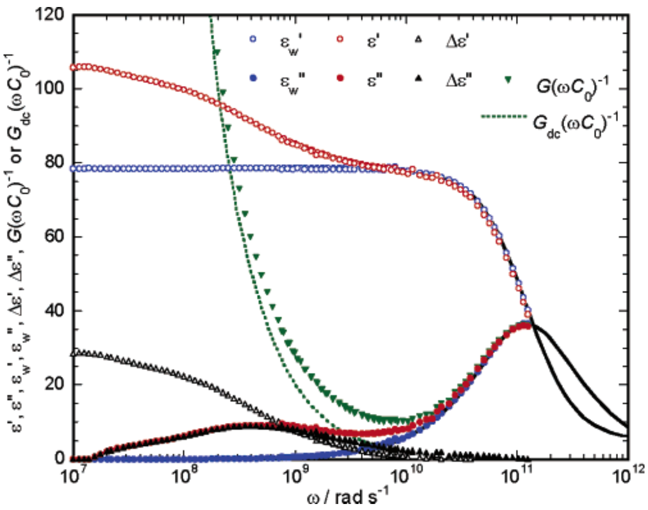


Figure 1. Dependence of real and imaginary parts of electric permittivities, ϵ' and ϵ'', on ω for aqueous solution of P(NaSS), $M_n = 3.4 \times 10^5$ and $X_S = 1.0$, at $c_P = 50$ mM and 25 °C. Permittivities of pure water, ϵ_w', ϵ_w'', at 25 °C are also shown in the same figure together with the standard calibration curves (solid lines) given by eq 1. The contributions of the polyelectrolyte, $\Delta\epsilon'$ and $\Delta\epsilon''$ ($= G(C_0\omega)^{-1} - G_{dc}(C_0\omega)^{-1}$), evaluated via eq 2 assuming $\Phi = 0.984$ are contained in the figure. The data of $G(C_0\omega)^{-1}$ and $G_{dc}(C_0\omega)^{-1}$ for the system are also shown as reference.

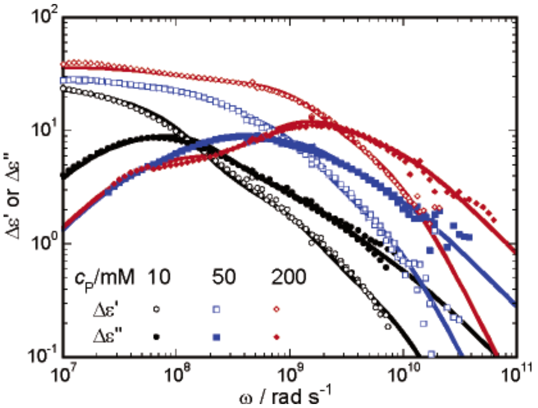


Figure 2. Dependence of $\Delta\epsilon'$ and $\Delta\epsilon''$ on ω for aqueous solutions of P(NaSS), $M_n = 3.4 \times 10^5$ and $X_S = 1.0$, at various c_P in a double-logarithmic scale. Solid lines represent the best fit curves calculated by eq 3 assuming the presence of four Debye type relaxation modes.

The contribution of bulk water, ϵ_w' and ϵ_w'', and of a solute polyelectrolyte to the total dielectric spectra, ϵ' and ϵ'', will be described by the sum of these components. Thus, we simply assume that eq 2 quantitatively expresses the dielectric spectra of solute polyelectrolytes, $\Delta\epsilon'$ and $\Delta\epsilon''$, by introducing an additional parameter Φ (≤ 1), which accounts for the fractional contribution of bulk water; for pure water, $\Delta\epsilon' = \Delta\epsilon'' = 0$ and $\Phi = 1$. The value of Φ is close to 1 in this study because the concentration of solute polyelectrolytes, c_P, is not high.[25,26,31]

$$\epsilon' = \Delta\epsilon' + \Phi\epsilon_w' \quad \epsilon'' = \Delta\epsilon'' + \Phi\epsilon_w'' \tag{2}$$

Figure 1 also contains dielectric spectra, $\Delta\epsilon'$ and $\Delta\epsilon''$, of the P(NaSS) obtained assuming $\Phi = 0.984$ for both the $\Delta\epsilon'$ and the $\Delta\epsilon''$ curves to show smooth diminution to zero around $\omega = 10^{11}$ rad s^{-1}. These spectra manifest the presence of both HFR and HHFR processes in ω ranges lower and higher than 10^9 rad s^{-1} for this aqueous polyelectrolyte.

As shown in Figure 2, the measured $\Delta\epsilon'$ and $\Delta\epsilon''$ curves containing the HFR and HHFR processes for an aqueous solution of P(NaSS), $M_n = 3.4 \times 10^5$ and $X_S = 1.0$, clearly exhibit two major relaxation modes in ω ranges near 10^8 and 3×10^9 rad s^{-1}. The magnitude of the two relaxation strengths changed systematically with increasing c_P. Here, we assumed that $\Delta\epsilon'$ and $\Delta\epsilon''$ could be expressed as the sum of Debye type relaxation modes as given by eq 3. In many reports[1,5,6] of the dielectric behavior of aqueous polyelectrolyte systems, adjustable parameters had to be determined to express the breadth of the dielectric spectra by fitting the data to semiempirical dielectric relaxation functions such as the Cole−Cole,[32] Davidson−Cole,[33] and Havriliak−Negami[34] formulas for a $\Delta\epsilon''$ curve with a single broad peak. However, each $\Delta\epsilon''$ vs ω curve in our experiments clearly possessed a major peak and an additional shoulder as seen in Figure 2. Such an additional shoulder and multipeak type ω dependence in $\Delta\epsilon'$ and $\Delta\epsilon''$ cannot be expressed by using a semiempirical relaxation function with a single relaxation time. Thus, we employed a generalized Debye-type expression for $\Delta\epsilon'$ and $\Delta\epsilon''$ given by eq 3 for detailed analysis.

$$\Delta\epsilon' = \sum_{i=1}^{n} \frac{\delta\epsilon_i}{1 + \omega^2\tau_i^2} + \epsilon_\infty \quad \Delta\epsilon'' = \sum_{i=1}^{n} \frac{\delta\epsilon_i \omega\tau_i}{1 + \omega^2\tau_i^2} \tag{3}$$

The solid lines in Figure 2 represent the best fit curves for $\Delta\epsilon'$ and $\Delta\epsilon''$ for solutions with varying c_P, and it can be seen that the spectra were successfully deconvoluted into two major modes through the curve fit procedure via eq 3. A major fast relaxation mode found around $\omega = 3 \times 10^9$ rad s^{-1}, which could be further decomposed into two relaxations with $\tau_1 = 0.11{-}0.15$ ns and $\tau_2 = 8.0{-}10$ ns, belonged to the HHFR process and their strength increased markedly with increasing c_P. This HHFR will be analyzed in detail in this study. The other major mode consisted of two relaxations at $\tau_3 = 4.5{-}9.5$ ns and $\tau_4 = 25{-}40$ ns, whose relaxation times and strengths decreased slightly with increasing c_P, and this mode was classified as an HFR process. Although the HFR process found in Figure 2 was reasonably described with curve fit procedures using certain conventional semiempirical relaxation functions,[32−34] the presence of the HHFR process in the ω range higher than 10^9 rad s^{-1} was beyond doubt regardless of the relaxation function chosen for the curve fitting.

There exist major dielectric relaxation modes, especially in dilute solutions, at ω ranges lower than those examined in this study, belonging to the low-frequency relaxation, or LFR, process. However, in the c_P range shown in Figure 2, the contribution of the LFR process was negligible.

The concentration normalized real part spectra, $\Delta\epsilon' c_P^{-1}$ vs ω, for aqueous solutions of P(NaSS)s, $M_n = 9.2 \times 10^3$ and 3.4×10^5, are shown in Figure 3, parts a and b, respectively. The shapes of these spectra were strongly dependent on c_P when $\omega < 10^9$ rad s^{-1} (the region of HFR processes for both polyelectrolytes). According to leading studies[18] focusing on the HFR process, the HFR process is directly related to fluctuations in the distribution of counterions electrostatically bound to polyelectrolytes, controlled by a characteristic time constant and amplitude, both highly dependent on the average separation between polymers or constituent segments of polyelectrolytes. This separation is sometimes called the *correlation length*, and is governed by c_P: the lower the value of c_P, the greater the average separation between segments. This led to increases in both relaxation time and strength for HFR with decreasing c_P, as observed when ω was less than 10^9 rad s^{-1} in Figures 3a and 3b.

The overarching trend of the $\Delta\epsilon c_P^{-1}$ spectra (c_P-independent universal curves) observed for $\omega > 10^9$ rad s^{-1} in Figure 3,

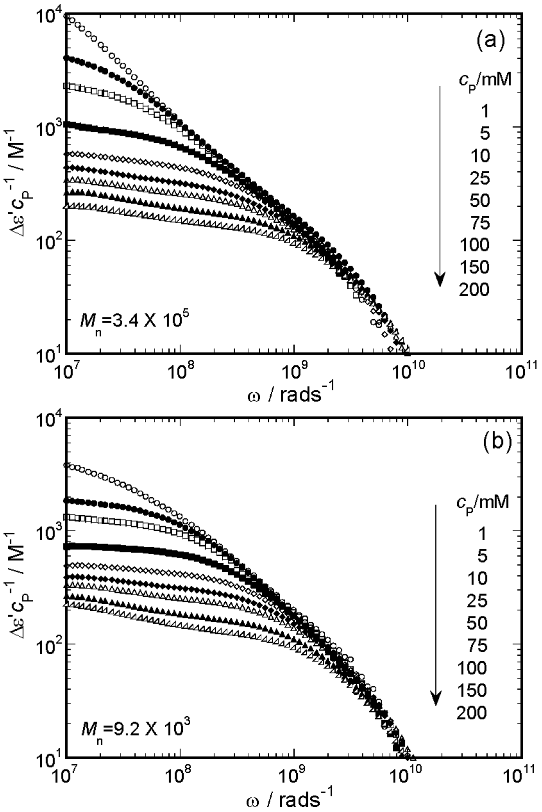


Figure 3. Dependence of the concentration normalized real part, $\Delta\epsilon' c_P^{-1}$, on ω for aqueous solution of P(NaSS)s, $X_S = 1.0$, at various c_P with $M_n = 3.4 \times 10^5$ (a) and 9.2×10^3 (b).

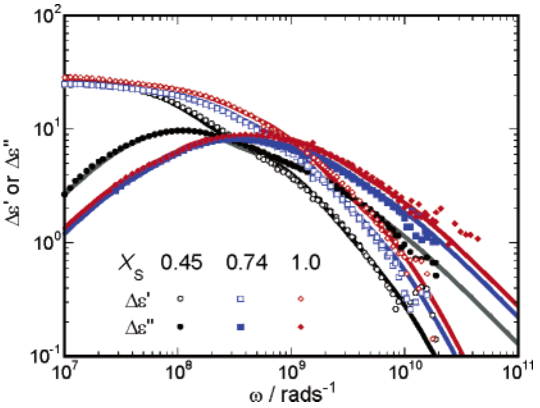


Figure 4. Dependence of $\Delta\epsilon'$ and $\Delta\epsilon''$ on ω for aqueous solutions of P(St/NaSS)s, $M_n = 3.4 \times 10^5$ and various X_S, at $c_P = 50$ mM. Solid lines represent the best fit curves for spectra calculated via eq 3.

parts a and b, strongly suggested that relaxation modes $i = 1$ and 2 relevant to HHFR were independent of the c_P-governed average separation of segments. The fact that $\Delta\epsilon c_P^{-1}$ was independent of c_P in the HHFR process meant that the relaxation strength, $\Delta\epsilon$, specifically, $\delta\epsilon_1$ and $\delta\epsilon_2$, were simply proportional to c_P, in contrast to the behavior of HFR. These findings suggested that the HHFR process originates in dynamic events on the order of monomer units in size.

Figure 4 shows the dependence of $\Delta\epsilon$ on ω for aqueous solutions of P(St/NaSS)s, $M_n = 3.4 \times 10^5$ with varying X_S, at $c_P = 50$ mM. In this case, the concentration of repeat units, c_P, was kept constant at 50 mM, while the concentration of NaSS units changed with X_S. Because increases in $\Delta\epsilon$ relevant to HHFR for $\omega > 10^9$ rad s^{-1} with increasing X_S were clearly seen, it is possible that $\delta\epsilon_1$ and $\delta\epsilon_2$ were not simply proportional to c_P. The changes with X_S in the HFR process observed around $\omega = 10^8$ rad s^{-1} suggested that $\delta\epsilon_3$ decreased markedly with increasing X_S.

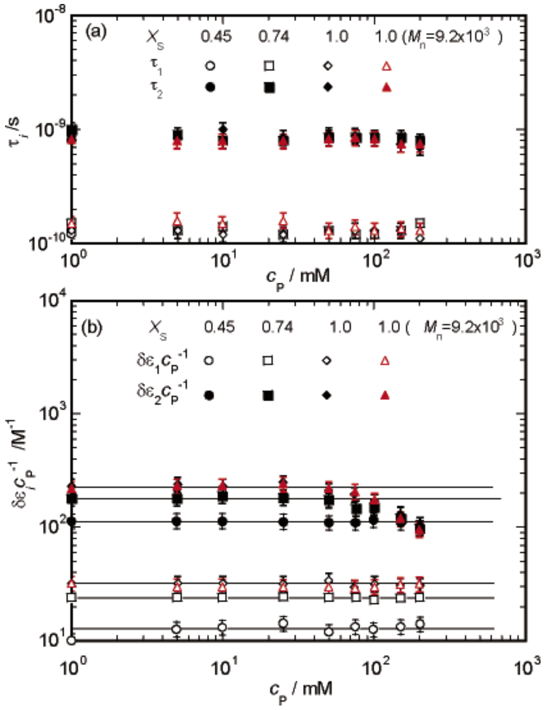


Figure 5. Dependence of τ_i (a) and $\delta\epsilon_i c_P^{-1}$ (b) ($i = 1, 2$) on c_P for aqueous solutions of P(St/NaSS)s, $M_n = 3.4 \times 10^5$ and various X_S and $M_n = 9.2 \times 10^3$ and $X_S = 1.0$.

Table 1. Concentration Normalized Dielectric Strength, $\Delta\epsilon_i c_P^{-1}$, and Relative $\Delta\epsilon_i c_P^{-1}$ Values Compared to Those Obtained at $X_S = 1.0$, $[\Delta\epsilon_i c_P^{-1}]_r$ (i = 1 and 2), for P(St/NaSS)S, $M_n = 3.4 \times 10^5$, in Aqueous Solution

X_S	$\delta\epsilon_1 c_P^{-1}$/M^{-1}	$[\delta\epsilon_1 c_P^{-1}$/M$^{-1}]_r$	$\delta\epsilon_2 c_P^{-1}$/M^{-1}	$[\delta\epsilon_2 c_P^{-1}$/M$^{-1}]_r$
1.0	31.6 ± 4.7	1.0	228 ± 34	1.0
0.74	24.1 ± 3.6	0.76 ± 0.11	176 ± 26	0.77 ± 0.12
0.45	13.1 ± 2.0	0.41 ± 0.06	113 ± 17	0.50 ± 0.08

To quantitate the relationship between relaxation times and strengths vs c_P for the HHFR process, τ_1 and τ_2, and $\delta\epsilon_1 c_P^{-1}$ and $\delta\epsilon_2 c_P^{-1}$, are plotted as functions of c_P (with error bounds owing to uncertainty in the curve fitting procedure using eq 3) in Figures 5a and 5b, respectively. Because the curve fit was carried out by simultaneously fitting both $\Delta\epsilon'$ and $\Delta\epsilon''$ data to calculated curves assuming a set of parameters over the ω range examined, the uncertainty in the fit was estimated to be less than ±15% of determined values. Obviously both τ_1 and τ_2 were independent of c_P and M_n as seen in Figure 5(a). Also, $\delta\epsilon_1 c_P^{-1}$, which was roughly proportional to the value of X_S, was completely independent of c_P and M_n over the whole range examined. Finally, $\delta\epsilon_2 c_P^{-1}$, which seemed to have a slightly weaker X_S dependence than $\delta\epsilon_1 c_P^{-1}$, was also independent of c_P up to 50 mM, beyond which concentration it decreased with increasing c_P irrespective of M_n as seen in Figure 5b. These results strongly suggested that both the relaxation modes $i = 1$ and 2 belonging to the HHFR process resulted from dynamic events associated with the benzenesulfonate, BS$^-$, groups in P(St/NaSS)s. Values of $\delta\epsilon_1 c_P^{-1}$ and $\delta\epsilon_2 c_P^{-1}$ ($c_P \leq 50$ mM) relative to those obtained at $X_S = 1.0$ ($[\delta\epsilon_1 c_P^{-1}]_r$ and $[\delta\epsilon_2 c_P^{-1}]_r$) are summarized in Table 1. Because the overlap concentrations of both the P(NaSS)s were estimated to be much less than 50 mM,[18,35] the decrease in $\delta\epsilon_2 c_P^{-1}$ observed at $c_P > 50$ mM must have been related to contacts between monomer units or ion pairs in the polyelectrolytes.

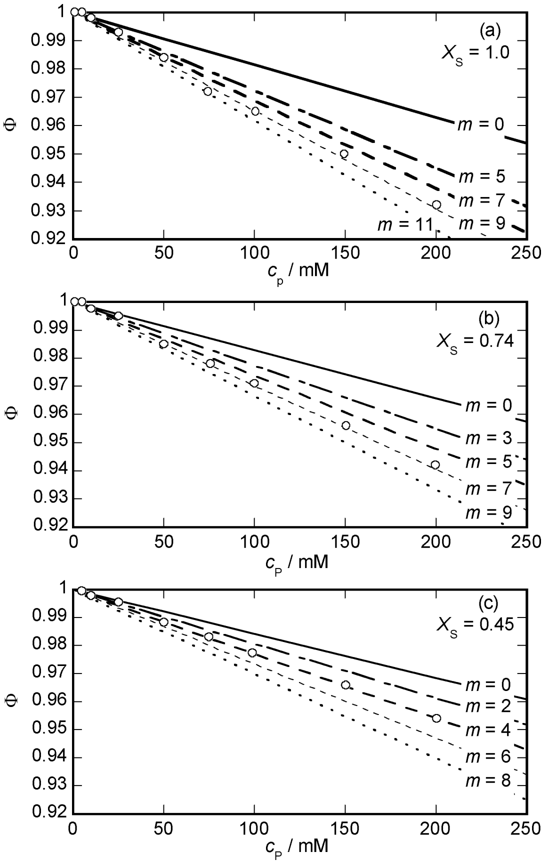


Figure 6. Relationships between Φ and c_P for aqueous solution of P(St/NaSS)s, $M_n = 3.4 \times 10^5$ and various $X_S = 1.0$ (a), 0.74 (b), and 0.45 (c). Lines represent the theoretical prediction via eq 4 with varying *m*.

Parts a−c of Figure 6 show the c_P dependence of the Φ values used to evaluate spectra, $\Delta\epsilon'$ and $\Delta\epsilon''$ vs ω, at each X_S for aqueous P(St/NaSS) solutions. For aqueous solutions, it has been known that the Φ value is well described by eq 4

$$\Phi = \frac{1-\phi}{1+\frac{1}{2}\phi} + \frac{mc}{55.6} \qquad (4)$$

where *c*, *m*, and ϕ represent the molar concentration of solute, the number of water molecules tightly bound to the hydrated solute, and the volume fraction of solute given by $\phi = \bar{V}_m c$, respectively.[31,36] For ionic solutes such as sodium *p*-toluenesulfonate (Na*p*TS), *m* refers to the total hydration number of each constituent ion, Na^+ or pTS^-.[37] In this study, *c* should be replaced by c_P in eq 4 and in the expression for ϕ. The average monomeric partial molar volumes, $\bar{V}_m$, were evaluated from the densities of aqueous P(St/NaSS)s solutions to be $\bar{V}_m = 125.01$ $cm^3\ mol^{-1}$ at $X_S = 1.0$; $\bar{V}_m = 115.72$ $cm^3\ mol^{-1}$ at $X_S = 0.74$; and $\bar{V}_m = 105.92$ $cm^3\ mol^{-1}$ at $X_S = 0.45$. The lines drawn in Figure 6a−c show the calculated curves for various values of *m* in eq 4. The $m = 9$ line for aqueous P(St/NaSS) at $X_S = 1.0$ showed reasonable agreement with the data, as seen in Figure 6a. Similarly, the values of *m* for $X_S = 0.74$ and 0.45 were evaluated to be 7 and 4, respectively, as shown in Figure 6, parts b and c. The fact that *m* was proportional to X_S strongly suggested that all the BS^- groups and Na^+ ions of P(St/NaSS)s were completely hydrated by a fixed number of water molecules irrespective of the degree of dissociation. The value of *m* found for aqueous P(NaSS) at $X_S = 1.0$ was identical to that for aqueous sodium *p*-toluenesulfonate (Na*p*TS).[37] Because the number of water molecules hydrating Na^+ was reported to be 5−6, that of water molecules hydrating each pTS^- anion was calculated to be 2−3 in aqueous Na*p*TS.[37] Consequently, in the case of P(St/NaSS)s in aqueous solution, it was concluded that 2−3 water molecules hydrated each BS^- group, as in aqueous Na*p*TS.

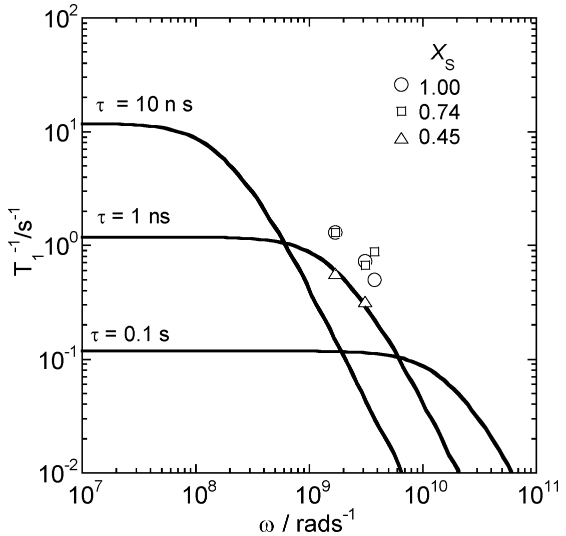


Figure 7. Dependence of T_1^{-1} on ω for the meta proton of NaSS units in D_2O solution of P(St/NaSS)s, $M_n = 3.4 \times 10^5$ and various X_S, at c_P = 100 mM. Solid lines represent the theoretical prediction at some τ values calculated by use of eq 5.

^{1}H NMR Relaxation Behavior. To estimate the time scale for motions of St and SS^- repeat units of P(St/NaSS)s in aqueous solution, the correlation time (τ_c) for NMR relaxation was determined via ^{1}H NMR measurements of T_1. According to the theory proposed by Bloembergen, Purcell, and Pound,[38] if a molecule is in isotropic rotational motion and its chief mechanism of longitudinal relaxation in NMR is the dipole−dipole interaction between two ^{1}H nuclei, T_1 can be related to the correlation time τ_c as shown in eq 5 below:

$$\frac{1}{T_1} = \frac{\gamma^4 h^2 I(I+1)}{10\pi^2 r^6}\left(\frac{\tau_c}{1+\omega^2{\tau_c}^2} + \frac{4\tau_c}{1+4\omega^2{\tau_c}^2}\right) \qquad (5)$$

where γ, *h*, *I*, *r*, and ω are the gyromagnetic ratio, Planck's constant, a spin quantum number ($^1/_2$ for ^{1}H nuclei), the distance between two interacting ^{1}H nuclei, and the resonance frequency, respectively. The rotational relaxation time, τ, which has the same physical meaning as the dielectric relaxation time, is given by $\tau = 3\tau_c$.[39]

The relationship between T_1^{-1} and ω for *meta* protons of the St and SS^- moieties of P(St/NaSS), $M_n = 3.4 \times 10^5$ and various X_S, at $c_P = 100$ mM is shown in Figure 7. The solid lines in the figure represent the calculated T_1^{-1} curves via eq 5 with τ = 10, 1.0, and 0.1 ns, respectively.

The T_1 data of a P(St/NaSS) with $M_n = 3.4 \times 10^5$ and X_S = 0.45 were reproduced reasonably well by eq 5 assuming $\tau = 1$ ns, while similar data for P(St/NaSS)s with $X_S = 0.74$ and 1.0 were not so well expressed by eq 5 with only one τ value. These findings suggested that the rotational motion of the monomer units of the P(St/NaSS)s with $X_S = 0.74$ and 1.0 exhibited more than two relaxation modes. However, considering the uncertainty in T_1 measurements and for simplicity of discussion, we concluded that τ was roughly 1 ns for the monomer units of the P(St/NaSS)s examined in aqueous solution.

Degree of Na^+ Dissociation. The degree of dissociation (F_{dis}) of Na^+ from P(St/NaSS)s in aqueous solution was calculated

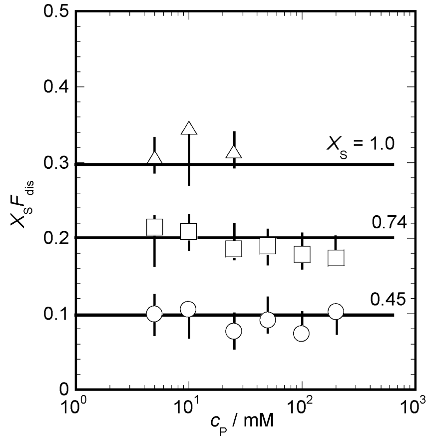


Figure 8. Dependence of, $X_S F_{dis}$, on c_P for aqueous solution of P(St/NaSS)s, $M_n = 3.4 \times 10^5$ and various X_S, determined by using an Na^+ ion selective electrode.

Table 2. Average Fraction of Dissociated SS^- Units Relative to the Total Monomer Units Defined by the Product between X_S and the Degree of Na^+ Dissociation from the Total NaSS Units, F_{dis}, Calculated from the Data of Na^+ Ion Concentration and Conductivity Measurements: $F_{dis}X_S$, Molar Conductivity at 25.0 °C, Λ, Average Charge Fraction Relative to the Total Monomer Units, $F_{bin}X_S$, and Relative $X_S F_{bin}$ Values Compared to Those at $X_S = 1.0$, $[X_S F_{bin}]_r$, for P(St/NaSS)s, $M_n = 3.4 \times 10^5$ and Various X_S, in Aqueous Solution

	$X_S F_{dis}$				
X_S	electrode	conductivity	Λ/Scm^2 mol^{-1}	$X_S F_{bin}$	$[X_S F_{bin}]_r$
1.0	0.30	0.30	35.2	0.70	1.0
0.74	0.20	0.24	27.7	0.54	0.77
0.45	0.10	0.10	11.7	0.35	0.50

from the concentration of Na^+ determined using an Na^+ ion selective electrode. Figure 8 shows the relationship between the average fraction of dissociated SS^- units relative to the total number of monomer units, $X_S F_{dis}$, and c_P for aqueous P(St/NaSS)s solutions with varying X_S. Because of pronounced polyelectrolyte adsorption on the electrode surface, the measured values of $X_S F_{dis}$ showed marked scattering, especially at X_S = 1.0. It is likely that F_{dis} did not depend strongly on c_P. The $X_S F_{dis}$ values obtained from Figure 8 are summarized in Table 2. The $X_S F_{dis}$ values agreed reasonably well with published measurements using different techniques.[40]

It is worth noting that the measured dependence of $X_S F_{dis}$ on X_S was much less than that predicted by Manning–Oosawa theory.[3,41] Such pronounced deviations from the predictions of the Manning–Oosawa theory as found in this study have been also reported for other aqueous P(St/NaSS) systems.[42–44]

It is well-known that the measurement of dc electric conductance, G_{dc}, is another useful method to determine F_{dis}.[6,22] The dependence of the conductivity (κ_{dc}), calculated from G_{dc} determined by dielectric relaxation measurements, on c_P for P(St/NaSS)s with varying X_S in aqueous solution is shown in Figure 9. Because κ_{dc} is clearly proportional to c_P, the slopes of these lines provide the molar conductivities (Λ) of P(St/NaSS)s in aqueous solution. The values of Λ calculated from Figure 9 are summarized in Table 2. For salt-free aqueous polyelectrolyte solutions, Λ is given empirically as[45]

$$\Lambda = X_S F_{dis}(\lambda_p + \lambda_c^{\,0}) \tag{6}$$

where $\lambda_c^{\,0}$ is the ionic equivalent conductivity of counterions in pure solvent and λ_p is that of polyelectrolyte ions in solution. We assumed simply that λ_p was independent of c_P,[46] to obtain the relationship $\Lambda \propto X_S F_{dis}$. Employing the most reliable $X_S F_{dis}$ value from Figure 8, namely $X_S F_{dis} = 0.10$ for P(St/NaSS) with $X_S = 0.45$, the F_{dis} values for different X_S were calculated from eq 6 as tabulated in Table 2. The obtained $X_S F_{dis}$ values at X_S = 0.74 and 1.0 from the molar conductivity, Λ, were identical to those obtained by the Na^+ ion selective electrode measurements. These findings implied that the similar F_{dis} values obtained by the two independent methods were reliable.

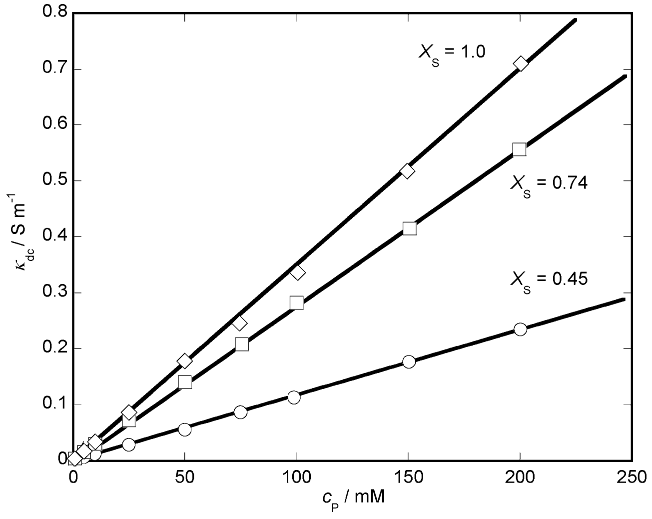


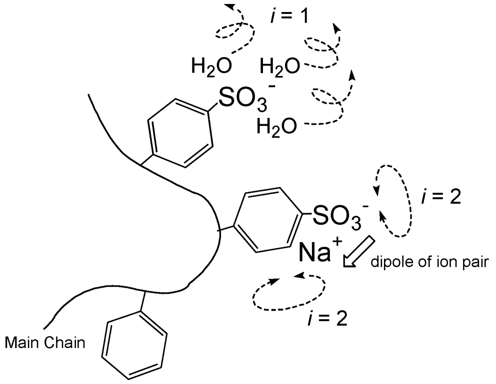
Figure 9. Relationship between the direct current conductivity, κ_{dc}, and c_P for aqueous solution of P(St/NaSS)s, $M_n = 3.4 \times 10^5$ and various X_S.

Discussion

Mechanisms of the HHFR Process. The near-perfect agreement between $[\delta\epsilon_1 c_P^{-1}]_r$ and X_S in Table 1 revealed that the relaxation strength of the $i = 1$ mode was proportional to the total concentration of both dissociated SS^- and undissociated NaSS units of P(St/NaSS)s in aqueous solution. Moreover, because each SS^- unit was tightly hydrated by 2–3 water molecules irrespective of the Na^+ dissociation, the relaxation strength of the $i = 1$ mode was likely proportional to the concentration of water molecules hydrating the SS^- and NaSS units of P(St/NaSS)s. On the other hand, the degree of Na^+ binding to SS^- units of P(St/NaSS)s (F_{bin}) was easily evaluated from the expression $F_{bin} = 1 - F_{dis}$. The average fraction, $X_S F_{bin}$, of undissociated NaSS units relative to the total number of monomer units (both St and NaSS) is tabulated in Table 2, as is the ratio of $X_S F_{bin}$ to that obtained at $X_S = 1.0$ ($[X_S F_{bin}]_r$). A comparison of $[X_S F_{bin}]_r$ and $[\delta\epsilon_i c_P^{-1}]_r$ (for $i = 1$ and 2) showed that $[X_S F_{bin}]_r$ was perfectly identical with $[\delta\epsilon_2 c_P^{-1}]_r$, whereas the value of $[\delta\epsilon_1 c_P^{-1}]_r$ at $X_S = 0.45$ was smaller than that of $[X_S F_{bin}]_r$ even when experimental uncertainty was taken into account. These results suggested that the relaxation strength of the $i = 2$ mode was essentially proportional to the concentration of undissociated NaSS units, namely of ion pairs formed between BS^- and Na^+ of P(St/NaSS)s. Since all the BS^- and Na^+ in aqueous P(St/NaSS)s were completely hydrated as described above, ion pairs formed between them were doubtless hydrated as well.

As stated above, the relaxation time of molecular motions of St and NaSS units of these copolymers was calculated from T_1 measurements to be ca. 1 ns, which agreed fairly well with the value of τ_2 (= 0.9 ns) determined for the $i = 2$ dielectric relaxation mode. These findings strongly suggested that this relaxation mode originated in molecular motions of the NaSS unit. This unit is an ion pair bearing a large dipole moment, and is responsible for the relaxation strength of the $i = 2$ mode

Scheme 1. Schematic Depictions for Molecular Motions in Relaxation Modes $i = 1$ and 2 Belonging to the *Hyper High Frequency Relaxation*, HHFR, Process of P(St/NaSS) in Aqueous Solution



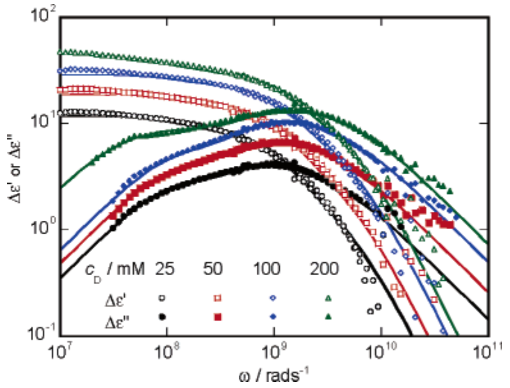


Figure 10. Dependence of $\Delta\epsilon'$ and $\Delta\epsilon''$ on ω for aqueous solution of SDBS at various concentration, c_D. Solid lines represent the best fit curves for the $\Delta\epsilon'$ and $\Delta\epsilon''$ spectra calculated via eq 3 assuming the presence of three Debye type relaxation modes.

involving BS^- and Na^+ in aqueous solution, because the St unit bears a dipole moment too small to be observed. The fact that the relaxation strength of this mode was proportional to the concentration of undissociated NaSS units also supported the assertion that the motion of NaSS units was the essential origin of this mode in aqueous solution.

Poly(glutamate) is a water-soluble polyelectrolyte showing dielectric relaxation at around 10^8 to 10^9 rad s^{-1}, which is assigned to motions of polar side-chain groups.[13,24] Fluorescence anisotropy relaxation measurements revealed that the relaxation time of side-chain groups lay in the range 5−25 ns for aqueous solutions of poly(methacrylic acid) labeled with vinylnaphthalene.[47] These experiments have demonstrated that relaxation times of side-chain groups of other polyelectrolyte also range from 1 to 30 ns in aqueous solution. Thus, the $i = 2$ relaxation mode for aqueous P(St/NaSS)s seemed to occur on a time scale similar to that of side-chain group relaxations of other polyelectrolytes.

In contrast, according to the dielectric study of aqueous Na*p*TS solutions,[37] the concentration normalized relaxation strength of the permanent dipole moment of the dissociated $p\mathrm{TS}^-$ anion has been determined to be ca. 30 M^{-1}. Since the molecular structure of $p\mathrm{TS}^-$ is similar to that of the BS^- group of P(St/NaSS)s, the magnitudes of their dielectric strengths should have been similar. However, the value of 30 M^{-1} is much less than the value of $\delta\epsilon_2 c_P^{-1}(X_S F_{bin})^{-1}$, ca. 325 M^{-1}, calculated from parameters in Tables 1 and 2 for P(St/NaSS)s. Consequently, we concluded that the ion pair formed between BS^- and Na^+ was solely responsible for the $i = 2$ relaxation mode with its very high relaxation strength because of the ion pair's large dipole moment. At present, the lifetime of the ion pair between BS^- and Na^+ has not been known. The conclusion involves that the lifetime should be longer than the τ_2 value, ca. 0.9 ns.

We now focus on the $i = 1$ relaxation mode. Since the relaxation time τ_1 was much shorter than the relaxation time of SS^- units or BS^- groups obtained from the T_1 measurements discussed above, the molecular origin of the $i = 1$ mode was assigned to motions of water molecules hydrating the BS^- groups of P(St/NaSS)s. It is well-known that the rotational motions of water molecules hydrating dissolved polymers are highly restricted, and show relaxation times much longer than that of bulk water, ca. 8.3 ps.[1,12,48] After the elapse of the residence time, hydrated water molecules are detached from their positions on the BS^- groups and pass into the bulk aqueous phase, where they undergo free rotation. Accordingly, the value of τ_1 should be close to that of the residence time of these hydrated water molecules. A schematic depiction of the molecular mechanisms responsible for the relaxation modes $i = 1$ and 2 in aqueous solutions of P(St/NaSS)s are shown in Scheme 1.

Dielectric Behavior of Aqueous SDBS Micellar Solution. It has been known that aqueous micellar solutions of ionic surfactants show dielectric relaxation attributed to the presence of ion pairs formed between a surfactant headgroup's ion and counterion.[25−27] This motivated us to perform an investigation of the dielectric relaxation behavior of aqueous micellar solutions of a surfactant molecule which was a model compound for the monomer units of P(St/NaSS) in order to confirm the importance of ion pairs and water molecules associated with BS^- groups in aqueous P(St/NaSS). Thus, we investigated the dielectric relaxation behavior of sodium dodecylbenzenesulfonate, SDBS, which is a surfactant model of an NaSS unit in P(St/NaSS).

The dependence of $\Delta\epsilon'$ and $\Delta\epsilon''$ on ω for aqueous SDBS at various concentrations (c_D) is shown in Figure 10. The solid lines in this figure represent the best fit curves calculated with eq 3 assuming three Debye-type functions with relaxation times: $\tau_1 = 0.18$ ns, $\tau_2 = 0.80$ ns and $\tau_3 = 10-13$ ns. Because the critical micelle concentration of SDBS is reported to be about 2.5 mM,[49] all solutions examined contained spherical micelles, and definitely formed $BS^- - Na^+$ ion pairs. The relaxation times of the three modes for SDBS had little c_D dependence and the concentration normalized relaxation strengths ($\delta\epsilon_i c_D^{-1}$) of $i =$ 1 and 3 were also independent of c_D. However, $\delta\epsilon_2 c_D^{-1}$ decreased slightly with increasing c_D at $c_D > 100$ mM as was observed for aqueous P(NaSS) (Figure 5b). It is likely that frequent contact between micellar surfaces at high c_D reduced $\delta\epsilon_2 c_D^{-1}$ slightly.

Comparing the dielectric relaxation behavior of aqueous SDBS with that of other surfactant micellar systems,[25−27] it could be ascertained that the $i = 2$ relaxation mode was caused by ion pairs and that the slowest relaxation modes, $i = 3$, were attributed to fluctuations in the counterion distribution around the spherical micelles. However, the fastest relaxation mode ($i = 1$) was not observed in aqueous solutions of a cationic surfactant, CTAB, because of reduced hydration of CTA^+ headgroups.[26] Fernandez et al. investigated the dielectric behavior of aqueous SDS micelles and found that the relaxation attributed to the surfactants' water molecules of hydration occurred at ca. 0.10 ns.[27] Therefore, the $i = 1$ relaxation mode observed in aqueous SDBS in this study was also attributed to water molecules hydrating the BS^- groups. The number of water molecules associated with a BS^- group of SDBS in aqueous solution calculated from the data of m and Φ was 2−3 as for aqueous P(St/NaSS).

In these SDBS solutions, it was determined that $\delta\epsilon_1 c_D^{-1} \approx$ 25 M^{-1} and $\delta\epsilon_2 c_D^{-1} \approx 230$ M^{-1} ($c_D \leq 50$ mM), and the degree of Na^+ dissociation of SDBS was evaluated to be ca. 0.30. These values were similar to those of aqueous P(NaSS) ($X_S = 1.0$), for which $X_S F_{dis} = 0.30$ as listed in Table 1. Furthermore, the relaxation times of the modes of aqueous SDBS were also close to those of aqueous P(St/NaSS). These findings strongly suggested that the origin of the $i = 1$ and 2 relaxation modes in the aqueous SDBS system had the same mechanisms as in the P(St/NaSS) solution. Finally, we concluded again that the $i =$ 1 and 2 relaxation modes involved in the HHFR process for aqueous P(St/NaSS) were attributable to the detachment of water molecules hydrating the BS^- groups of P(St/NaSS), and to the rotation of $BS^{-}-Na^+$ ion pairs, respectively.

Conclusions

The dielectric relaxation behavior at high frequencies (from 6.3×10^6 to 1.3×10^{11} rad s^{-1}) of aqueous solutions of polyelectrolytes with controlled charge density revealed two very fast molecular events, in addition to low and high-frequency relaxation processes, on the order of a monomer unit and solvent in size, and which have not been addressed much hitherto. Irrespective of the polyelectrolyte species studied, low and high-frequency relaxation processes were observed from 10^2 to 10^5 and from 10^6 to 10^8 rad s^{-1}, respectively. The first depended on the molar mass of the polyelectrolyte, whereas the second did not. The polyelectrolytes used in this study were random copolymers of styrene and sodium styrenesulfonate with varying degrees of sulfonation. The newly found ultrafast relaxation modes were classified with hyper high-frequency relaxation processes. These modes had relaxation times of 0.12 and 0.90 ns, irrespective of c_P, and were attributed to the detachment of hydrated water molecules from benzenesulfonate groups and to the rotation of ion pairs with large dipole moments composed of benzenesulfonate and sodium ions, respectively.

Acknowledgment. T.S. wishes to thank Dainippon Ink and Chemicals Inc., Ltd., for their financial support of this study. K.N. wishes to express special thanks to the Center of Excellence (21COE) program “Creation of Integrated Eco-Chemistry of Osaka University”.

References and Notes

(1) Runt, J. P.; Fitzgerald, J. J. *Dielectric Spectroscopy of Polymeric Materials*; American Chemical Society: Washington, DC, 1997.
(2) Hara, M. Ed. *Polyelectrolytes*: *Science and Technologies*; Marcel Dekker: New York, 1993.
(3) Oosawa, F. *Polyelectrolytes*; Marcel Dekker: New York, 1971; Chapter 5.
(4) Schmitz, K. S. *Macroions in solution and colloidal suspensions*; VCH: New York, 1993.
(5) Mandel, M.; Odjik, T. *Annu. Rev. Phys. Chem.* **1984**, *35*, 75.
(6) Bordi, F.; Cametti, C.; Colby, R. H. *J. Phys.: Condens. Matter* **2004**, *16*, 1423.
(7) Nakamura, H.; Husimi, Y.; Wada, A. *J. Appl. Phys.* **1981**, *52*, 3053.
(8) Sakamoto, M.; Kanda, H.; Hayakawa, R.; Wada, Y. *Biopolymers* **1976**, *15*, 879.
(9) Mandel, M. *Biophys. Chem.* **2000**, *85*, 125.
(10) Minakata, A. *Biopolymers* **1972**, *11*, 1567.
(11) Mandel, M.; Jenard, A. *Trans. Faraday Soc.* **1963**, *59*, 2158; 2170.
(12) Mashimo, S.; Umehara, T.; Kuwabara, S.; Yagihara, S. *J. Phys. Chem.* **1989**, *93*, 4963.
(13) Mashimo, S.; Miura, N.; Shinyashiki, N.; Ota, T. *Macromolecules* **1993**, *26*, 6859.
(14) Shinyashiki, N.; Yagihara, S.; Arita, I.; Mashimo, S. *J. Phys. Chem. B* **1998**, *102*, 3249.
(15) Minakata, A. *Ann. N.Y. Acad. Sci.* **1977**, *303*, 107.
(16) Imai, N.; Sasaki, S. *Biophys. Chem.* **1980**, *11*, 361.
(17) Hall, B.; Wennerström, H.; Piculell, L. *J. Phys. Chem.* **1984**, *88*, 2482.
(18) Ito, K.; Yagi, A.; Ookubo, N.; Hayakawa, R. *Macromolecules* **1990**, *23*, 857.
(19) Meyer, P. I.; Vaughan, W. E. *Biophysical Chem.* **1980**, *12*, 329.
(20) Meyer, P. I.; Wesenberg, G. E.; Vaughan, W. E. *Biophysical Chem.* **1981**, *13*, 265.
(21) Wesenberg, G. E.; Vaughan, W. E. *Biophysical Chem.* **1983**, *18*, 381.
(22) Bordi, F.; Cametti, C.; Tan, J. S.; Boris, D. C.; Krause, N.; Plucktaveesak, N.; Colby, R. H. *Macromolecules* **2002**, *35*, 7031.
(23) Bordi, F.; Cametti, C.; Gili, T.; Colby, R. H. *Langmuir* **2002**, *18*, 6404.
(24) Bordi, F.; Cametti, C.; Paradossi, G. *Phys. Chem. Chem. Phys.* **1999**, *1*, 1555.
(25) Shikata, T.; Imai, S. *Langmuir* **1998**, *14*, 6804.
(26) Imai, S.; Shiokawa, M.; Shikata, T. *J. Phys. Chem. B* **2001**, *105*, 4495.
(27) Fernandez, P.; Schrödle, S.; Buchner, R.; Kunz, W. *Chem. Phys. Chem.* **2003**, *4*, 1065.
(28) Ono, Y.; Shikata, T. *J. Phys. Chem. B* **2005**, 109, 7412.
(29) Makowski, H. S.; Lundberg, R. D.; Singhal, G. H. U.S. Patent 3,-870,841, 1975.
(30) Kaatze, U. *J. Chem. Eng. Data* **1989**, *34*, 371.
(31) Shikata, T.; Itatani, S. *J. Sol. Chem.* **2002**, *31*, 823.
(32) Cole, K. S.; Cole, R. H *J. Chem. Phys.* **1941**, *9*, 341.
(33) Davidson, D. W.; Cole, R. H. *J. Chem. Phys.* **1951**, *18*, 1417.
(34) Havriliak, S.; Negami, S. *Polymer* **1967**, *8*, 161.
(35) Kaji, K.; Urakawa, H.; Kanaya, T.; Kitamaru, R. *J. Phys.* (*Paris*) **1988**, *49*, 993.
(36) Pottel, R. *Water*; Franks, F., Ed.; Plenum: New York, 1973; Vol. 3; Chapter 8.
(37) Shikata, T.; Watanabe, S.; Imai, S. *J. Phys. Chem. A* **2002**, *106*, 12405.
(38) Bloembergen, N.; Purcell, P. E. M.; Pound, R. V. *Phys. Rev.* **1948**, *73*, 679.
(39) Wossner, D. E.*J. Phys. Chem.* **1962**, *37*, 647.
(40) Essafi, W. Ph.D. Thesis, Université Paris VI, France, 1996.
(41) Manning, G. S. *J. Chem. Phys.* **1969**, *51*, 924.
(42) Baigl, D.; Sferrazza, M.; Williams, C. E. *Europhys. Lett.* **2003**, *62*, 110.
(43) Lee, M.-J.; Green, M. M.; Mikeš, F.; Morawetz, H. *Macromolecules* **2002**, *35*, 4216.
(44) Qu, D.; Baigl, D.; Williams, C. E.; Möhwald, H.; Fery, A. *Macromolecules* **2003**, *36*, 6878.
(45) Kurucsev, T.; Stell, B. J. *Rev. Pure. Appl. Chem.* **1967**, *17*, 149.
(46) Jordan, D. D.; Kuruscev, T.; Martin, M. L. *Trans. Faraday Soc.* **1969**, *65*, 606.
(47) Soutar, I.; Swanson, L. *Macromolecules* **1994**, *27*, 4304.
(48) Nandi, N.; Bhattacharyya, K.; Bagchi, B. *Chem. Rev.* **2000**, *100*, 2013.
(49) Kumar, S.; Sharma, D.; Khan, Z. A.; Kabir-ud-Din. *Langmuir* **2002**, *18*, 4205.

MA052522A