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Electric Field Orientation of Poly(*p*-styrenesulfonate) and Its 9-Aminoacridinium Complex as Studied by Square-pulse Transient Electric Birefringence

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Electric birefringence was measured at 20 °C and at 535 nm for sodium poly(*p*-styrenesulfonate) (NaPSS), with and without added sodium chloride, and the 9-aminoacridinium (AA) complex in aqueous solutions. The field strength dependence of both the steady-state EB ($\Delta n(\infty)$) and the field-free decay time ($\langle\tau\rangle_{EB}$) was examined. Charge suppression by added Na$^+$ ions or neutralization by strongly bound AA decreased both $\Delta n(\infty)$ and $\langle\tau\rangle_{EB}$ considerably, altering not only the optical factor Δg and electric moments, but also the backbone chain length. The weight-average values of chain length (l_w), pseudopermanent dipole moment (μ_w), counterion-induced electric polarizability anisotropy ($\Delta\alpha_w$), and the length-independent values of Δg were estimated by analyzing the experimental data on the basis of the "classical" orientation function which takes into account the continuous distribution of chain length for the polydisperse NaPSS sample. The electric field orientation of NaPSS and the AA-complex could be described by the interaction between an applied field and the electric moment which transforms from counterion-induced type in the extremely low field region (<1.5 kV/cm) to saturated induced permanent type at higher fields.

Among synthetic vinyl polymers, poly(*p*-styrenesulfonate) (NaPSS) has been employed as a model polyelectrolyte in many physicochemical studies.[1–12] These studies indicate that the PSS chain is stiff and may be represented by a rodlike model. A recent electric dichroism study showed that the ionized NaPSS can be oriented by an external electric field, exhibiting a negative dichroism of considerable magnitude, and that the *p*-sulfonatophenyl chromophores are arranged nearly at 60° relative to the PSS backbone chain.[10] Earlier, Yoshioka and his coworkers[2,3,7] extensively studied the electric birefringence of the potassium salt of PSS (KPSS) in aqueous solutions with various additives; they found that the field orientation of KPSS may be described as being due to the permanent dipole moment. Very recently, Tricot and Houssier[11] reported a careful work on the electric birefringence of some NaPSS fractions, finding that the birefringence (Δn) curve fits a pure induced dipole orientation. These two groups are mostly concerned with the field strength dependence of the steady-state data. We believe that the solution property of PSS polyions should also be deduced from the result obtained by transient electrooptical techniques.

The objectives of this work are (1) to show that the field orientation mechanism of the chain of NaPSS in salt-free solution can be described in terms of a transformation of the electric polarizability to a permanent-like moment, by analyzing the field strength dependence of the steady-state Δn; (2) to exemplify that the weight-average chain length (hence, the overall shape) may be estimated from the field strength dependence of the field-free relaxation times with a reasonable model by taking into account the polydispersity of the sample; (3) to demonstrate that the PSS backbone chain can be contracted significantly due to partial neutralization or suppression of the negative charge on the sulfonato group by monovalent cationic additives; (4) to simulate the rise and decay portions of a transient signal in the Kerr-law region, in order to support the notion that the field orientation is due to fast counterion-induced dipole moment.[8,12] These objectives were successfully achieved by the method of fast square-pulse transient electric birefringence.

Experimental

Materials. Sodium poly(*p*-styrenesulfonate) (NaPSS) is the same sample that was used in previous studies.[8,10,13] The original sample (KPSS) was a generous gift of Professor Koshiro Yoshioka of the University of Tokyo. The degree of polymerization was estimated to be 1360.[10] 9-Aminoacridinium chloride (denoted simply as AA), a strongly binding monocationic dye, was described elsewhere.[10,13]

Preparation of Sample Solutions. The salt-free NaPSS solution was prepared by dissolving an anhydrous sample in twice-distilled water. The NaCl-added NaPSS solution was prepared by adding an appropriate amount of NaCl to the stock NaPSS solution, the ratio of the total Na$^+$ ions to the counterion Na$^+$ being 6.00. The AA-added NaPSS solution was prepared in a similar manner. The ratio of the polymer residue to AA finally present in the mixture (denoted as P/D)[10,13] is 6.14. The concentration of NaPSS in the monomer unit is 0.66 mM (1 mM$=1\times10^{-3}$ mol dm^{-3}) in all cases.

Measurements. Square-pulse electric birefringence was measured on an apparatus built in this Laboratory.[10,14] The pulse width was continuously variable up to 5 ms and the pulse amplitude was varied up to 11.3 kV/cm. A 1-cm long H-shaped Kerr cell made of Kel-F was used, the electrode gap being 0.207 cm. Instrumental time constants were less than 0.5 μs for the transient rise and decay signals. The phase retardation, δ, in degrees was measured at 535 nm and at 20 °C, the sign being determined with a quarter-wave plate.

Analysis of Data. The steady-state birefringence Δn and the specific Kerr constant, B/c, are defined as[14]

$$\frac{B}{c}=\lim_{E^2\to 0}\frac{\Delta n}{\lambda c}\left(\frac{1}{E^2}\right)=\lim_{E^2\to 0}\frac{\delta}{2\pi dc}\left(\frac{1}{E^2}\right), \qquad (1)$$

where λ is the wavelength *in vacuo*, c is the mass concentration in g/cm^3, and d is the optical path length ($=1$ cm). Since the theoretical treatments of the field orientation of polyelectrolytes are under development, no complete expression for the transient electric birefringence is available as yet. Under these circumstances, the "classical" theory for nonconducting rodlike macromolecules of axial symmetry should be utilized.[15] This theory is nevertheless known to be an adequate approximation for NaPSS in aqueous solutions.[2,3,7,10,11] For a polydisperse polymer sample, the steady-state birefringence, $\Delta n(\infty)$, at an arbitrary electric field strength E is given as[16-18)]

$$\Delta n(\infty)=\frac{2\pi\bar{C}_{\mathrm{v}}}{n}(g_3-g_1)\langle\Phi(\beta(l),\gamma(l))\rangle_w, \tag{2}$$

where n is the refractive index of the solution ,$\bar{C}_{\mathrm{v}}$ is the volume fraction of the solute, (g_3-g_1) is the optical anisotropy factor, $<\Phi(\beta,\gamma)>_{\mathrm{w}}$ is the weight-average orientation function, $\beta(l)=\mu(l)E/kT$, and $\gamma(l)=\Delta\alpha(l)E^2/2kT$. In the low electric field region where the Kerr law holds, the rise portion of the normalized transient signal is expressed by

$$\frac{\Delta n(\mathrm{t})}{\Delta n(\infty)}=1-\frac{\displaystyle\int_0^{\infty}\Delta n(\infty,l)\left\{\frac{3\beta(l)^2\mathrm{e}^{-2\theta_{11}(l)t}-[\beta(l)^2-4\gamma(l)]\mathrm{e}^{-6\theta_{11}(l)t}}{2[\beta(l)^2+2\gamma(l)]}\right\}\mathrm{d}l}{\displaystyle\int_0^{\infty}\Delta n(\infty,l)\mathrm{d}l}, \tag{3}$$

where θ_{11} is the rotary diffusion coefficient of the undeformable molecule around the transverse axis, $\Delta n(\infty,l)=(2\pi\bar{C}_{\mathrm{v}}/15n)(g_3-g_1)\times\phi(l)[\beta(l)^2+2\gamma(l)]$, $\phi(l)$ is the fraction of solute molecules with the length l, and $\Delta n(0)=\Delta n(\infty)$. The decay portion is expressed by

$$\frac{\Delta n(t)}{\Delta n(0)}=\frac{\displaystyle\int_0^{\infty}\Delta n(0,l)\mathrm{e}^{-6\theta_{11}(l)t}\mathrm{d}l}{\displaystyle\int_0^{\infty}\Delta n(0,l)\mathrm{d}l}. \tag{4}$$

Results and Discussion

Dependence of Steady-state Birefringence on Electric Field. Figure 1 shows the dependence of phase retardation, δ, on electric field strength for NaPSS solutions with and without additives. The charge suppression of the ionized sulfonato group by added Na$^+$ decreases the magnitude of δ. More remarkably, the charge neutralization of the same group (one out of six) by bound AA cations diminishes the values of δ nearly tenfold. In order to ascertain if these decreases in δ are due solely to the change in the optical anisotropy factor in Eq. 2, the δ *vs.* E^2 curves of the NaPSS–AA and NaPSS–NaCl systems were multiplied by factors at an arbitrarily selected field strength ($E^2=10$ (kV/cm)^2). As indicated in Fig. 1, the NaPSS–AA and NaPSS–NaCl curves cross at this point, but otherwise they do not coincide with the salt-free NaPSS curve. This behavior suggests that the electric part in Eq. 2 is also affected; hence, the electric moment of the salt-free NaPSS chain should also be decreased by the addition of NaCl or AA.

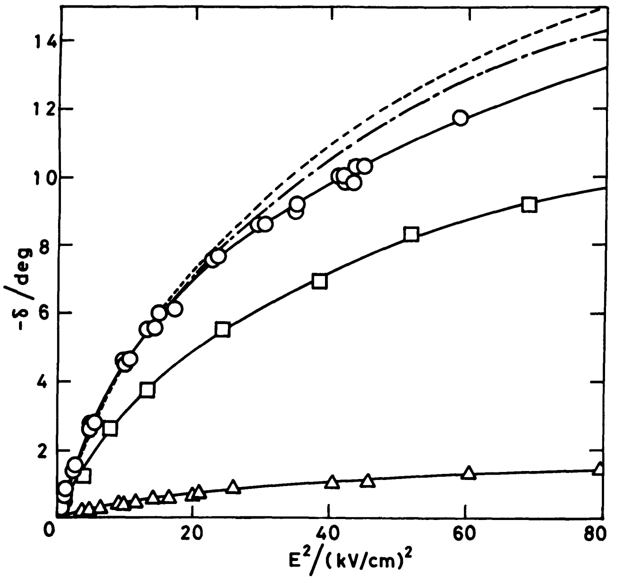

Fig. 1. The dependence of steady-state birefringence, δ, on the square of electric field strength, E^2, for the salt-free NaPSS (○), the NaPSS–NaCl (□), and the NaPSS–AA (△) solutions. The residue concentration of NaPSS is 0.66 mM in these cases. The dashed (- - -) line represents the NaPSS–AA curve which is multiplied by a factor of 10.3 at a field strength ($E^2=10$ (kV/cm)^2), while the dash-dot-dashed (—·—) line is the NaPSS–NaCl curve multiplied by 1.47.

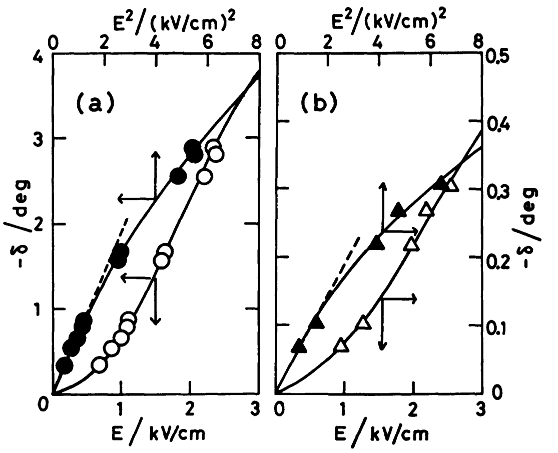

Fig. 2. The linear and quadratic dependence of δ on field strength in the low field region. (○, ●) for NaPSS and (△, ▲) for NaPSS–AA. The dashed lines indicate a linear dependence of δ on E^2 at limiting low fields.

Low Electric Field Behavior and the Kerr Constant. Figure 2 shows the values of δ in the low electric field region for the NaPSS and NaPSS–AA solutions. They

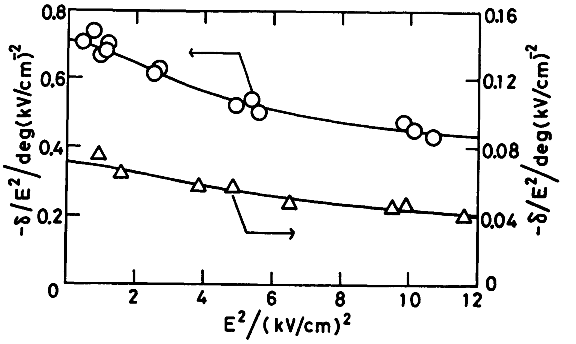

Fig. 3. Plots of the phase retardation per square of field strength, δ/E^2, against the square of field strength for NaPSS (○) and NaPSS–AA (△). The values extrapolated to zero field strength, $(-\delta/E^2)_{E\to0}$, are 0.701 deg(cm/kV)^2 for NaPSS and 0.071 deg(cm/kV)^2 for NaPSS–AA.

TABLE 1. ELECTROOPTICAL AND HYDRODYNAMIC PROPERTIES OF NaPSS WITH AND WITHOUT IONIC ADDITIVES

Samples	$\frac{B/c}{10^{-6}\ \mathrm{cm^4\ V^{-2}\ g^{-1}}}$	$\frac{\langle\tau\rangle_W}{\mu s}$	$\frac{l_W}{Å}$	$\frac{\mu_W}{10^3\ D^{b)}}$	$\frac{\Delta\alpha_W}{10^{-15}\ \mathrm{cm^3}\ ^{c)}}$	$(g_3-g_1)^{a)} \times 10^2$
NaPSS	14.2	35	1210	6.48	1.32	−1.2
NaPSS–NaCl	—	20	980	5.65	—	−0.98
NaPSS–AA	1.44	10	760	5.12	0.99	−0.16

a) A value of 0.565 was used for the partial specific volume of NaPSS in water.[11] b) 1 D=3.336×10^{-30} C m. c) 1 cm^3=1.113×10^{-16} F m^2.

are plotted against E and also against E^2. The linear dependence of δ on the second power of the field strength is clear. It is thus evident that the Kerr law holds for the 0.66 mM NaPSS solutions with and without ionic additives.

Figure 3 shows the procedure for determining the Kerr constant. The observed values of δ/E^2 are plotted against E^2. The values extrapolated to zero field strength yield the Kerr constant B. The specific Kerr constant is given in Table 1. It should be noted that the extrapolation is inevitably associated with a small uncertainty, since the curvature of the δ/E^2 *vs.* E^2 curve depends on the electric property of a particular polymer system (*cf.* Fig. 7).[15]

Dependence of Decay Process on Electric Field. Since the field-free decay curves of the 0.66 mM NaPSS solution indicate that the sample is polydisperse,[12] the relaxation time must be the birefringence-average quantity obtained by area method[19] (*e.g.*, Eq. 6 in Ref. 17), $\langle\tau\rangle_{EB}$, which depends on the field strength of a pulse applied to orient the solute prior to the start of the decay process.[16,19] Figure 4 shows a large field dependence of $\langle\tau\rangle_{EB}$ for the salt-free NaPSS system; a clear indication of the polydispersity of molecular length.[10,16] It should be noted that the addition of NaCl or AA decreases the relaxation time considerably; unfortunately, the values of $\langle\tau\rangle_{EB}$ are scattered or undetermined at low electric fields due to low signal-to-noise ratios. The $\langle\tau\rangle_{EB}$ value at infinitely high electric field reduces to the weight-average relaxation time $\langle\tau\rangle_w$ (Eq. 9 in Ref. 17), which is independent of the electric parameters of the molecules, since the orientation function $\langle\Phi\rangle_w$ approaches unity. The values of $\langle\tau\rangle_w$ for the NaPSS, NaPSS–NaCl, and NaPSS–AA systems are given in Table 1.

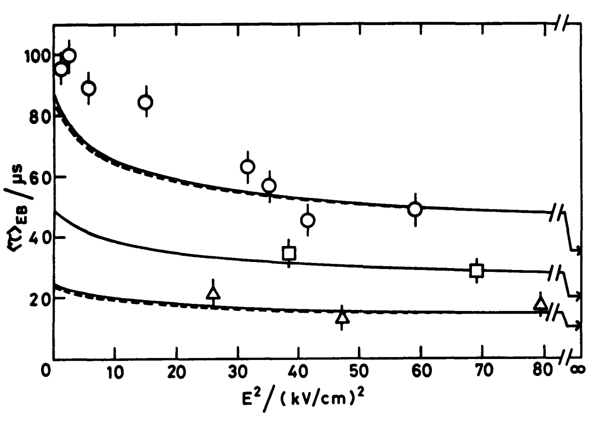

Fig. 4. The dependence of field-free relaxation time, $\langle\tau\rangle_{EB}$, on electric field strength applied prior to the start of decay process. (○) for NaPSS, (□) for NaPSS–NaCl, and (△) for NaPSS–AA. Horizontal arrows indicate the values extrapolated to infinite field strength. Points are experimental and smooth curves are theoretical.

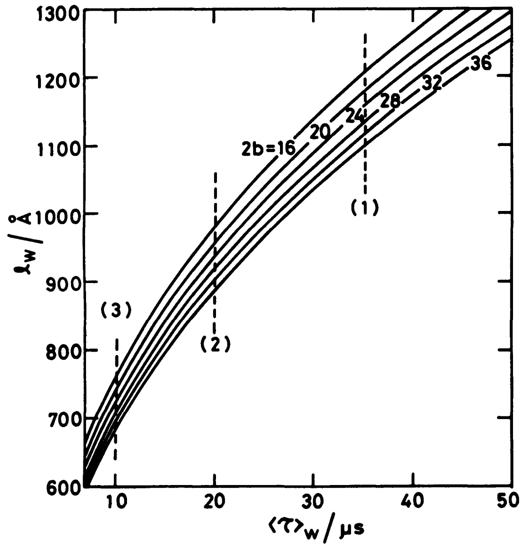

Fig. 5. Relationship between the weight-average length, l_w, and the weight-average relaxation time, $\langle\tau\rangle_w$, calculated for a polydisperse sample. The Schulz-Zimm distribution function was used to describe the polydispersity ($l_w/l_n=1.3$). The diameter of a molecule with length l was changed from 16 Å to 36 Å to calculate the value of $\langle\tau\rangle_w$ by using the Broersma equation. Vertical lines indicate the experimentally obtained values of $\langle\tau\rangle_w$ for salt-free NaPSS (1), NaCl-added NaPSS (2), and AA-added NaPSS (3).

Weight-average Relaxation Time and Chain Length. The overall shape of the PSS backbone chain may be assumed to be an undeformable cylinder in the sense that an applied electric field does not alter the molecular conformation. This is a reasonable approximation, when the field strength is less than 19 kV/cm for NaPSS and NaPSS–AA.[10,20] The rotational relaxation time $\tau(l)$ is related to the length l with the aid of the Broersma equation for a cylindrical model[21] (*e.g.*, Eq. 8 in Ref. 17). The diameter of the cylinder, $2b$, is not known for the present NaPSS system; therefore, it must be varied parametrically. The axial translation per residue of the most elongated PSS backbone is *ca.* 2.5 Å. It shortens to about 2.0 Å without changing the diameter appreciably; hence, the elongated chain length is in the range of 3400—2700 Å. The diameter of this rather stretched backbone is estimated to be at least 16 Å with CPK atomic models, if the *p*-sulfonatophenyl groups wind around the backbone. If a folding of hair-pin type occurs in the backbone chain, the diameter may be widened, from 16 Å to 24 Å (radius times three) and further to 32 Å (radius times four). By varying the diameter $2b$ from 16 Å to 36 Å at intervals of 4 Å, the weight-average length l_w was calculated as a function of $\langle\tau\rangle_w$. The results are shown in Fig. 5, where the vertical dashed lines indicate the experimental values of $\langle\tau\rangle_w$ for the salt-free NaPSS (1), NaPSS–NaCl (2), and NaPSS–AA (3) solutions. The length l_w of the salt-free NaPSS ranges from 1200 Å ($2b=16$ Å) to 1100 Å ($2b=36$ Å), being affected only slightly by these diameters. These lengths are far shorter than the most extended chain length (3400 Å); hence, the folding-back of the vinyl backbone is evident. If a value of 16 Å is assumed for $2b$, the chain length l_w is 1210 Å for the salt-free NaPSS, 980 Å for the NaPSS–NaCl, and 760 Å for the NaPSS–AA. Thus, the binding of AA probably reduces the overall chain length appreciably.

An entirely different approach to the interpretation of the rotary diffusion coefficient $\theta_{11}(=(6\tau)^{-1})$ is possible. By adopting a flexible wormlike model, the persistence length of a polymer chain could be estimated from Hearst's[22] expression, which, however, introduces an additional parameter. This in turn means that to avoid ambiguities the polymer sample should be nearly monodisperse as regards the molecular weight. Thus, the flexibility of the polymer chain is an interesting subject for future studies.

Orientation Mechanism and Electric Moments. The orientation mechanism of the NaPSS in aqueous solution may be deduced from the electric field dependence of steady-state Δn (*cf.* Fig. 1). Yoshioka and his coworkers showed that the dependence can be best fitted by the permanent dipole orientation over a limited range of field strength.[2,3,7] Recently, Tricot and Houssier also studied the field dependence for NaPSS, confirming this permanent dipole orientation.[11] In addition, they believe that the induced dipole moment may also be adequate to describe the field dependence. In an electric dichroism study of NaPSS, Matsuda and Yamaoka have shown that, by taking into account a polydispersity in chain length, the field dependence can be best fitted by a mixed dipole orientation with the ratio $(\beta_w)^2/2\gamma_w$ of 8 over a very wide field strength range.[10] They also pointed out that, if the polydispersity is ignored, the dependence can be described equally well by the permanent dipole (*i.e.*, β-term only) orientation. In either case, Matsuda and Yamaoka have indicated that the fitting between the theoretical orientation function $\Phi(\beta)$ or $\langle\Phi(\beta)\rangle_w$ and the experimental points is poor in the very low field region.

With the above background, we can now analyze the field dependence of Δn. It is unrealistic to consider that the ionized PSS backbone bears a true permanent dipole moment of large magnitude. By now, ample evidence from reversing-pulse electric birefringence (PREB) indicates that the field orientation of NaPSS is not due to the permanent dipole but due to the counterion-induced dipole moment.[8,12] The redistribution of the counterions (Na$^+$) responsible for the induced dipole moment is faster than 10^{-6} s. We now demonstrate that the orientation of NaPSS results from the interaction between an external electric field and the ionic polarizability of the polyion in a limited, very low field region, in analogy to the pure electronic polarizability orientation for a nonconducting polymer, and that the interaction transforms gradually to a type between the field and an apparent permanent dipole moment. Theoretical treatments on this concept of induced dipole-permanent dipole transformation have lately appeared,[23,24] but further refinements are needed to fit experimental data over an entire field range.[10]

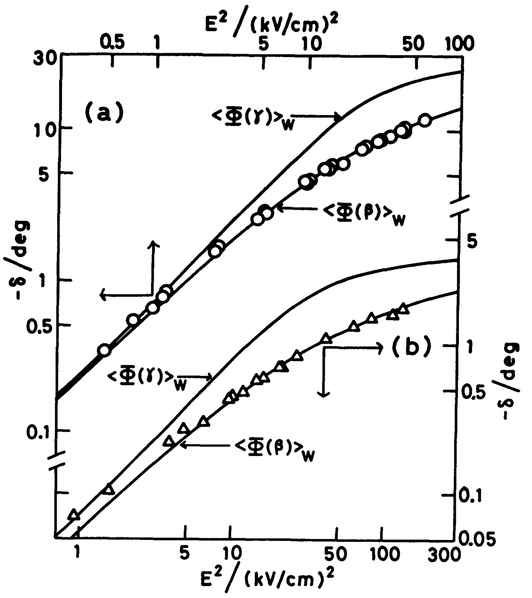

Fig. 6. Double logarithmic plots of the steady-state phase retardation *vs.* electric field strength and the theoretical orientation function, $\langle\Phi\rangle_w$. (a) Salt-free NaPSS (○) for which δ is $-29°$ at limiting high field, $\Delta\alpha_w=1.32\times10^{-15}$ cm^3, and $\mu_w=6480$ D. (b) AA-added NaPSS (△) for which δ is $-3.9°$ at limiting high field, $\Delta\alpha_w=0.99\times10^{-15}$ cm^3, and $\mu_w=5120$ D. $2b=16$ Å.

Experimental values of δ for NaPSS and NaPSS–AA in Fig. 1 have been replotted against E^2 on a double logarithmic scale in Fig. 6. With the parameters l_w, obtained in the preceding section, $l_w/l_n(=1.3)$, and the Schulz-Zimm distribution function[25,26] (*e.g.*, Eq. 3 in Ref. 17), the orientation functions for pure polarizability anisotropy $\langle\Phi(\gamma)\rangle_w$ and for pure permanent dipole moment $\langle\Phi(\beta)\rangle_w$ were calculated. The observed points were fitted to these functions under the assumption that the orientation mechanism transforms from the pure polarizability anisotropy γ_w in the extremely low electric field region to the pure permanent dipole moment β_w over a wide medium-to-high field range. The best-fitted orientation functions are shown with solid-lined curves in Fig. 6. In this matching procedure, both functions are adjusted to yield the same optical anisotropy factor, since this is considered to be independent of field strength.[10,18,27] The values of μ_w, $\Delta\alpha_w$, and (g_3-g_1), all obtained from the fitting, are given in Table 1.

The pure γ_w-orientation is considered to be equivalent to the counterion-induced or ionic polarizability, while the pure β_w-orientation is equivalent to the saturated

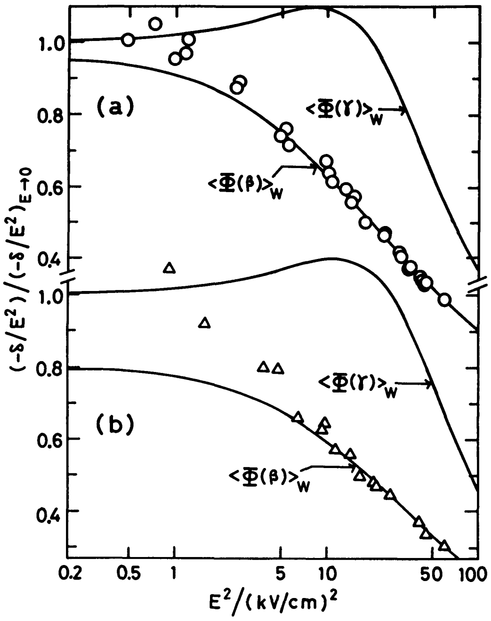

Fig. 7. Semilogarithmic plots of $(-\delta/E^2)/(-\delta/E^2)_{E\to 0}$ *vs.* E^2. Experimental values are given by circles for salt-free NaPSS (a) and by triangles for AA-added NaPSS (b), and theoretical curves by solid lines. Notations, parameters, and other conditions are all the same as those in Fig. 6.

induced-dipole moment. In conformity with classical theory, both the ionic polarizability and the saturated dipole moment are assumed to be proportional to the first power of the length. The dependence of these moments on the chain length remains to be explored more thoroughly in the future. In any case, it is clear that deviation from the pure γ_w-orientation appears at extremely low fields ($E<1.5$ kV/cm) for NaPSS and NaPSS–AA. This explains the previous observations that the pure permanent dipole orientation is the most appropriate one for the ionized NaPSS solution.[7,10,11]

Theoretical calculations have shown that a maximum appears in the birefringence per field strength ($\Delta n/E^2$) *vs.* E^2 curve, if the pure γ_w-orientation is the case.[15] In Fig. 7, the theoretical orientation functions, $\langle\Phi(\beta)\rangle_w$ and $\langle\Phi(\gamma)\rangle_w$, per (field strength)² are plotted by solid-lined curves. The observed points definitely deviate from the pure γ_w-curve, transforming to the pure β_w-curve already in the extremely low field strength region, before they reach the maximum position of the theoretical curve for the pure γ_w-orientation.

Once the values of μ_w and $\Delta\alpha_w$ are obtained from the above matching, the field strength dependence of $\langle\tau\rangle_{EB}$ shown in Fig. 4 may be examined theoretically. In this Figure are shown the theoretical curves which were calculated by assuming the pure permanent dipole moment orientation and the Schulz-Zimm distribution function. The parameters ($2b$, l_w, μ_w) are as follows: (16 Å, 1210 Å, 6480 D (1 D$=3.336\times10^{-30}$ C m)) for solid line and (32 Å, 1120 Å, 6480 D) for dashed line in the case of the salt-free NaPSS, (16 Å, 980 Å, 5650 D) for the NaCl-added NaPSS, (16 Å, 760 Å, 5120 D) for solid line and (32 Å, 700 Å, 5120 D) for dashed line in the case of the AA-added NaPSS; the viscosity of solvent is 1.009×10^{-3} Pa s. These theoretical curves are in fair agreement with experimental points, particularly, in the medium-to-high field region.

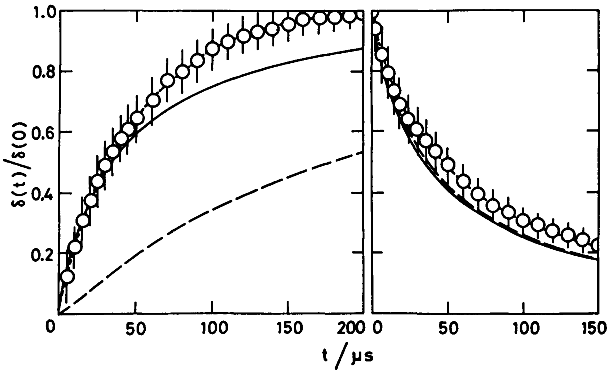

Fig. 8. Comparison of an experimental rise-and-decay signal for salt-free NaPSS with theoretically calculated transient curves. Experimental points are read from an oscillogram taken at a field strength of 1.01 kV/cm. The solid-lined curve is the theoretical one calculated on the basis of the orientation function for pure polarizability with a set of parameters ($l_w/l_n=1.3$, $l_w=1480$ Å, $2b=16$ Å) which yields the z-average relaxation time, $\langle\tau\rangle_z$, of 100 μs. The dash-lined curve is the theoretical one for pure permanent dipole orientation calculated with a set of parameters ($l_w/l_n=1.3$, $l_w=1270$ Å, $2b=16$ Å) which yields the ($z+1$)-average relaxation time, $\langle\tau\rangle_{z+1}$, of 100 μs.

Simulation of the Rise and Decay Processes. In order to confirm the notion that the counterion-induced electric moment is fast as compared with the overall molecular rotation and that this moment can be approximated by the electronic polarizability, two theoretical transient curves for the rise and decay signal are calculated from Eqs. 3 and 4 in Fig. 8: one for the pure γ_w-orientation (solid line) and the other for the pure β_w-orientation (dashed line). In the Figure, the experimental points represent a signal of an NaPSS solution, taken at a low field strength for which the Kerr law holds. The points fit the γ_w-orientation curve better than the β_w-curve in the whole rise and decay process. This may be taken as a strong support for the notion that the orientation of NaPSS results from the fast counterion-induced dipole moment, whose induction is much faster than the overall molecular orientation. At the same time, the result in Fig. 8 indicates the limitation of the use of the classical orientation function derived for nonconducting rodlike macromolecules to an ionized polyion like NaPSS. It is clear from the present work that a further study is desirable to obtain more realistic orientation functions which can describe the electric field orientation of ionized polyelectrolytes.

Conclusion

Although the present NaPSS sample is polydisperse as regards the molecular weight, we could present a unified quantitative treatment of the ionized polyion, which possesses no permanent dipole moment, on the framework of the classical theory for nonconducting polymers. The electric field orientation of NaPSS is due to the ionic polarization which results from the redistribution of counterions on the PSS chain surface. This counterion-induced electric moment saturates at very low electric fields and then behaves as if it was a permanent dipole moment. In conjunction with our previous work on electric dichroism[10] and reversing-pulse electric birefringence,[8,12] we believe that the solution conformation of the NaPSS and NaPSS–AA systems are now established fairly well, and that the dynamic electrooptical techniques are of great assistance in interpreting the electric properties and solution conformation of field-orientable macromolecules.

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