January, 1982] © *1982 The Chemical Society of Japan* *Bull. Chem. Soc. Jpn.*, **55**, *69—76 (1982)* 69

Electric Linear Dichroism Study of Sodium Poly(*p*-styrenesulfonate) and Its 9-Aminoacridinium Complex in Aqueous Solutions

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(Received May 25, 1981)

Electric linear dichroism (ELD) of sodium poly(*p*-styrenesulfonate) (NaPSS) and its 9-aminoacridinium (AA) complex at a mixing ratio of polymer residue-to-dye of 6.14 was studied in aqueous solutions at 20 °C. ELD signals were measured in the electric field strength range 0—*ca.* 19 kV/cm at the absorption peak wavelengths; they showed a saturating trend at extremely high fields. The average angles between the orientation axis of NaPSS and the transition moments of chromophores were estimated to be 60° at 224.5 nm and 57° at 262 nm for the side chain phenyl group and 50° at 404 nm for the bound AA by using theoretical orientation functions derived for mono- and polydisperse systems. The ELD spectra were measured at fixed field strengths; 275—215 nm for NaPSS and 440—282 nm for NaPSS–AA. The reduced dichroism of NaPSS remained nearly constant throughout the 262 nm band but steadily changed below 224 nm in the 224.5 nm band, indicating that another band exists in the far UV region. The ELD spectrum of the NaPSS–AA complex revealed that the two electronic ^1L_a and ^1L_b transition moments of the bound AA are tilted at different angles to the orientation axis of the NaPSS backbone.

The mechanism of electric field orientation of polyelectrolytes in aqueous solution is an interesting problem. Many studies on electric dipole moments of the synthetic polyelectrolytes in aqueous solutions have been carried out by the electric birefringence method.[1–11] A number of stiff or semi-flexible charged polyions are now known to be orientable by external electric fields. For example, Yamaoka and Ueda[11] recently reported reversing-pulse electric birefringence of poly(*p*-styrenesulfonate) (PSS) with various cationic counterions in aqueous solutions, attributing the orientation of PSS to the translational mobility of the counterions on the polymer surface. The electric linear dichroism (ELD) method is another powerful electrooptical technique for obtaining information on the relative disposition of the intrinsic and/or extrinsic chromophore in polyelectrolytes. However, few studies have been reported on the ELD of synthetic polyelectrolytes and their complexes with small chromophoric ligands in aqueous solutions. Soda and Yoshioka[12] investigated the ELD of Crystal Violet and Malachite Green bound to KPSS in aqueous solution, in order to clarify the metachromatic behavior of these dyes. Recently, Tricot *et al.*[13] reported the ELD of poly(*N*-alkyl-4-vinylpyridinium bromide) in aqueous solution, determining the angle between the orientation axis of the polymer backbone and the pyridinium ring.

In order to determine the conformation of polyelectrolytes and the dye complexes, the effects of the polydispersity of polymer length, the flexibility of backbone, and the transition moment direction of chromophore must be considered. In this work, the wavelength dependence of the reduced dichroism of the sodium salt of PSS (NaPSS) and its 9-aminoacridinium (AA) complex in aqueous solution was examined at 20 °C in the UV and visible absorption regions. The electric field dependence of the reduced dichroism was examined at the absorption peak wavelengths. The aims of this work are to clarify the conformations of both the phenyl ring and the bound AA relative to the molecular orientation axis of NaPSS. The limiting reduced dichroism $(\Delta A/A)_s$ was estimated by comparing the field strength dependence of reduced dichroism with theoretical orientation functions of two different types under due consideration of the polydispersity of polymer length. From this result, the angles for the transition moments of the phenyl ring and the bound AA relative to the orientation axis were obtained.

Experimental

Materials. Sodium poly(*p*-styrenesulfonate) (NaPSS) was the same sample that was used previously.[11,14,15] The original sample in the potassium salt was kindly given by Professor Koshiro Yoshioka of the University of Tokyo. The intrinsic viscosity of NaPSS in 0.1 M NaCl (1 M=1 mol dm^{-3}) was 0.9 cm^3 g^{-1}. From this value, the weight-average molecular weight (M_w) was determined to be 2.8×10^5.[16] The cationic dye, 9-aminoacridinium chloride (AA), was described in previous papers.[11,17–19]

Preparation of Sample Solutions. The freeze-dried NaPSS sample was dried under reduced pressure at 78 °C for 10 h. It was then dissolved in redistilled water. The residue concentration of NaPSS was determined by weighing the dried sample as anhydride. The concentration of AA was determined by using the molar absorption coefficient, ε, of 1.03×10^4 M^{-1} cm^{-1} at 401 nm.[18] The NaPSS–AA solution, which contained neither extra neutral salt nor buffer salt, was prepared by adding the dye solution to the NaPSS solution at a molar mixing ratio of polymer residue-to-dye (P/D) of 6.14. The final concentration of AA was 108 μM.

Absorption Measurements. The UV and visible absorption spectra were measured on a Hitachi EPS-3T spectrophotometer at 20 °C with 2 cm- and 1 cm-long quartz cells.

Measurements of Electric Linear Dichroism. The electric linear dichroism apparatus was constructed in our laboratory. Its design construction, and performance were described in detail elsewhere.[20] The measuring cell unit consists of a Kel-F "Kerr" cell and a water-jacketed cell holder. The optical path lengths of the cell were 2 cm (electrode gap 0.33 cm) and 1 cm (electrode gap 0.207 cm). An R106UH photomultiplier (Hamamatsu TV Co.) was used, and the linear response of the tube was confirmed.[20] The half-intensity band width was kept narrower than 1.5 nm throughout. Both the parallel dichroism ($\Delta A_{//}/A$) and the perpendicular dichroism ($\Delta A_{\perp}/A$) were separately measured at 20 °C. The steady-state dichroism signal was obtained by varying both the voltage of a single square-wave pulse between 0.37 and 3.88 kV and the pulse duration between *ca.* 80 and 350 μs. External electric pulses were always applied to the NaPSS and NaPSS-AA solutions at least twice, but no degradation or irreversible change of dichroism signal was detected.

Data Analysis. The procedure for the dichroism data acquisition has been described in detail elsewhere.[20-22] The reduced dichroism ($\Delta A/A$) was calculated from $\Delta A_{//}/A$ and $\Delta A_{\perp}/A$ with the following expressions:

$$\frac{\Delta A_{//}}{A} = \frac{A^{E}_{//}-A}{A} = -\frac{1}{A}\log\left(1+\frac{\Delta I_{//}}{I_{//,0}}\right), \qquad (1)$$

$$\frac{\Delta A_{\perp}}{A} = \frac{A^{E}_{\perp}-A}{A} = -\frac{1}{A}\log\left(1+\frac{\Delta I_{\perp}}{I_{\perp,0}}\right), \qquad (2)$$

$$\frac{\Delta A}{A} = \frac{A^{E}_{//}-A^{E}_{\perp}}{A} = \frac{\Delta A_{//}-\Delta A_{\perp}}{A}, \qquad (3)$$

where $\Delta A_{//}$ is the change in absorbances of the monochromatic light polarized parallel to the electric field direction in the presence ($A^{E}_{//}$) and the absence (A) of the externally applied pulse field, $\Delta A_{\perp}$ is the corresponding change for the perpendicularly polarized light, $\Delta I_{//}(=I_{//,E}-I_{//,0})$ is the change in transmitted intensities of light polarized parallel to the field direction in the presence ($I_{//,E}$) and the absence ($I_{//,0}$) of the pulse field, and $\Delta I_{\perp}$ is the corresponding change for the perpendicularly polarized light. If there is no electrochromism involved, the following relation should hold:[23]

$$\frac{\Delta A_{//}}{A} = -2\frac{\Delta A_{\perp}}{A} \quad \text{or} \quad A = \frac{1}{3}(A^{E}_{//}+2A^{E}_{\perp}). \qquad (4)$$

In this work, the validity of Eq. 4 was confirmed for NaPSS (the residue concentration of polymer, C_p=3.31 mM) below *ca.* 19 kV/cm, and both for NaPSS (C_p=0.133 mM) and for NaPSS-AA (P/D=6.14) below *ca.* 14 kV/cm.

Results

Electric Field Dependence of NaPSS and NaPSS-AA Complex. Figure 1 shows typical ELD signals of NaPSS (left) and NaPSS-AA complex (right) and applied electric pulse signals. The sign of dichroism (ΔA in Eq. 3) is negative for NaPSS in the 275—215 nm region, but it is positive for NaPSS-AA in the 440—282 nm region. Figure 2 shows the field strength dependence of the reduced dichroism ($\Delta A/A$) of NaPSS and NaPSS-AA. Values of $\Delta A/A$ were measured at the respective absorption band maxima over a wide field strength range (0—*ca.* 19 kV/cm). The similarities and differences between NaPSS at 224.5 nm (C_p=0.133 mM), NaPSS at 262 nm (C_p=3.31 mM), and NaPSS-AA at 404 nm (C_p=0.663 mM) may be summarized as follows: (1) The sign of $\Delta A/A$ is *negative* for the two NaPSS systems, but it is *positive* for NaPSS-AA system throughout the respective absorption regions, (2) the electric field dependence of $\Delta A/A$ shows a saturating trend at high fields in all cases, and (3) no electrochromic effect was observed; Eq. 4 holds for all three systems, unless the applied electric field strength is extremely large. The Kerr-law behavior was not directly observed in this work because of low signal-to-noise ratios at weak field strengths, but the Kerr law had been confirmed to hold for the same NaPSS and NaPSS-AA systems

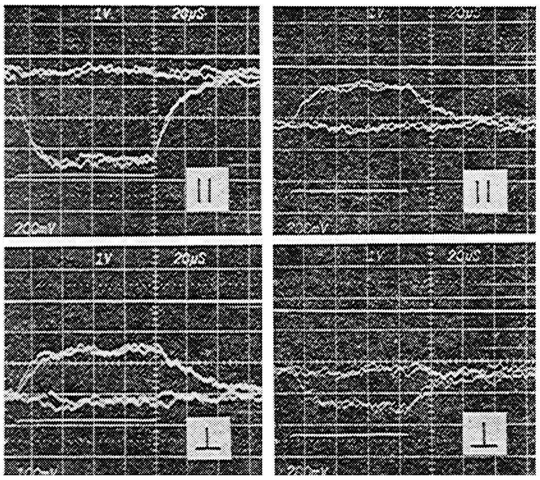

Fig. 1. Photographs of dichroism signals of NaPSS (left) and NaPSS-AA (right) and of applied pulsed electric fields at 20 °C and at 224.5 nm (left) and 404 nm (right). The parallel dichroism (//) is in the upper half and the perpendicular dichroism (⊥) is in the lower half. Electric field strengths in kV/cm are 18.8 (left) and 11.8 (right). Sweep time is 20 μs/division in all cases. Each photograph was a superposition of two displays.

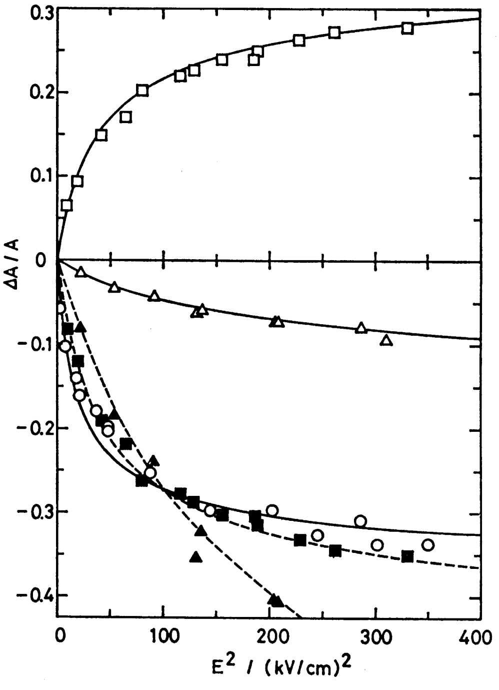

Fig. 2. Dependence of the reduced dichroism ($\Delta A/A$) of NaPSS at 224.5 nm (○) and 262 nm (△) and of NaPSS-AA at 404 nm (□) on the square of electric field strength, E^2. Open symbols were experimentally determined and solid curves were calculated by using the theoretical orientation function $\Phi(\beta,\gamma=0)$. Values of reduced dichroism of NaPSS at 262 nm were multiplied by 5.64 (--▲--▲--), and those of NaPSS-AA at 404 nm were multiplied by −1.26 (--■--■--).

TABLE 1. THE TRANSITION MOMENTS, THE MOLAR ABSORPTION COEFFICIENTS, $\varepsilon_{\max}$ IN mol^{-1} dm^3 cm^{-1}, AND THE PEAK POSITIONS, $\lambda_{\max}$ IN nm, OF BENZENE, SODIUM *p*-TOLUENESULFONATE, NaPSS, AND NaPSS-AA

Benzene[a)			Sodium *p*-toluenesulfonate[b)		NaPSS		NaPSS-AA		
$\lambda_{\max}$	$\varepsilon_{\max}$	Transition moment	$\lambda_{\max}$	$\varepsilon_{\max}$	$\lambda_{\max}$	$\varepsilon_{\max}$	$\lambda_{\max}$	$\varepsilon_{\max}$	Transition moment
203	7.4×10^3	$^1B_{1u}$	220	1.01×10^4	224.5	9.54×10^3	315	1.63×10^3	^1L_b
255	2.2×10^2	$^1B_{2u}$	261.5	3.71×10^2	262	4.68×10^2	404	6.64×10^3	^1L_a

a) Ref. 30. b) Values measured in water at 20 °C.

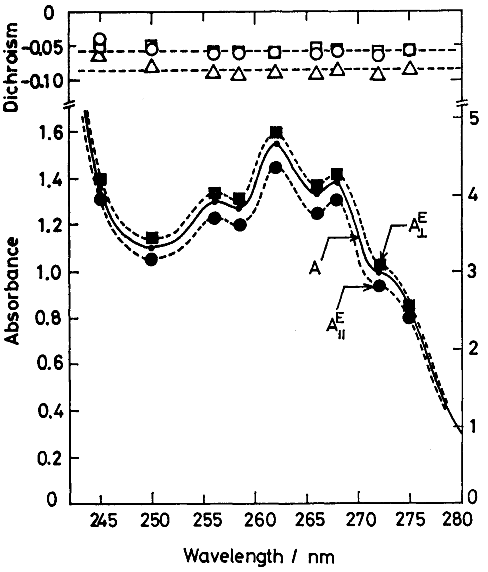

Fig. 3. Linear dichroic spectra of NaPSS in aqueous solution (C_p=3.31 mM) at 20 °C. Electric field strength=17.1 kV/cm. The lower half: Solid curve is the isotropic spectrum A in the absence of external electric field. The spectrum A_{calcd} (—•—) was calculated from the relation $A_{\text{calcd}}=(A_{/\!/}^E+2A_\perp^E)/3$. $A_{/\!/}^E$ (●) and $A_\perp^E$(■) were calculated from Eq. 1 and Eq. 2, respectively. The upper half: The specific parallel dichroism is $\Delta A_{/\!/}/A$ (○) and the reduced dichroism is $\Delta A/A$ (△), together with the specific perpendicular dichroism $\Delta A_\perp/A$ multiplied by -2 (□), in order to indicate that the relation $\Delta A_{/\!/}/A=-2\Delta A_\perp/A$ holds in this case.

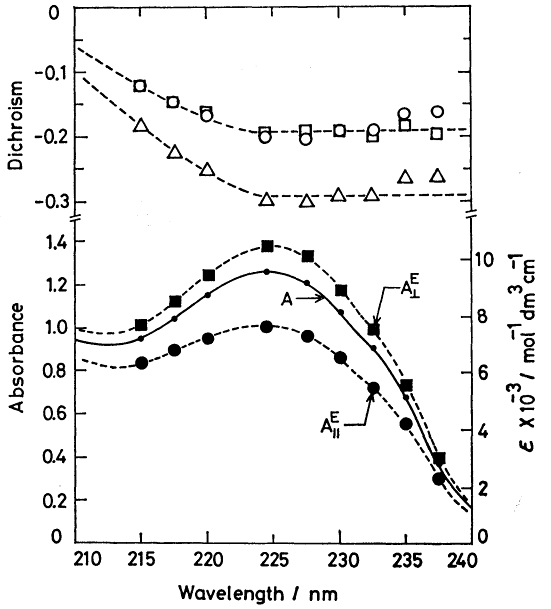

Fig. 4. Linear dichroic spectra of NaPSS in aqueous solution (C_p=0.133 mM) at 20 °C. Electric field strength=12.0 kV/cm. All notations and symbols are the same as in Fig. 3.

below *ca.* 1.2 kV/cm by an electric birefringence study.[11)]

The reduced dichroism at a given electric field strength and given wavelength is the product of the orientation factor and the optical factor, which is, for example, equal to $3(3\cos^2\theta-1)/2$ for an axially symmetric molecule (*cf.* Eq. 5). If differences of the $\Delta A/A$ *vs.* E^2 curves for three systems in Fig. 2 are merely due to the optical factor, these curves should be superimposed upon one another by multiplying the observed $\Delta A/A$ by appropriate constants. In order to verify this possibility, the normalization of the three curves was attempted by multiplying the curve of NaPSS (open triangles) by 5.64 and the curve of NaPSS-AA (open squares) by -1.26 at a selected field strength (E^2=100 (kV/cm)^2). In Fig. 2, these normalized curves are represented by dashed lines with closed symbols; they do not coincide with the solid curve (open circles) of NaPSS at 224.5 nm, to which the normalization was tried. This discrepancy should be ascribed not only to the difference of the optical factor but also to the difference of the orientation factor between the above three systems. Thus, the average degree of molecular orientation by a given externally applied field differs for each, suggesting a difference in the electric moments for the three polymer systems.

Wavelength Dependence of Dichroic Spectra of NaPSS in the 275—215 nm Region. Figures 3 and 4 show absorption spectra of two NaPSS solutions in the presence ($A_{/\!/}^E$ and $A_\perp^E$) and in the absence (A) of applied electric field in the lower half, and the parallel dichroism (circles), the perpendicular dichroism multiplied by -2 (squares), and the reduced dichroism (triangles) in the upper half, respectively. The isotropic spectrum of NaPSS (C_p=3.31 mM) in Fig. 3 was characterized by peaks at 268 nm (ε=418), 262 nm (468), and 256 nm (394), and by a shoulder near 272 nm (300). These values are consistent within 3.8% with those of Soda and Yoshioka,[12)] but they are slightly larger than the data of Boyd.[24)] The reduced dichroism is negative and constant in the 275—255 nm. Both $\Delta A_{/\!/}/A$ and $-2\Delta A_\perp/A$ agree with each other within experimental uncertainty. By using values of $A_{/\!/}^E$ and $A_\perp^E$, the isotropic absorbance

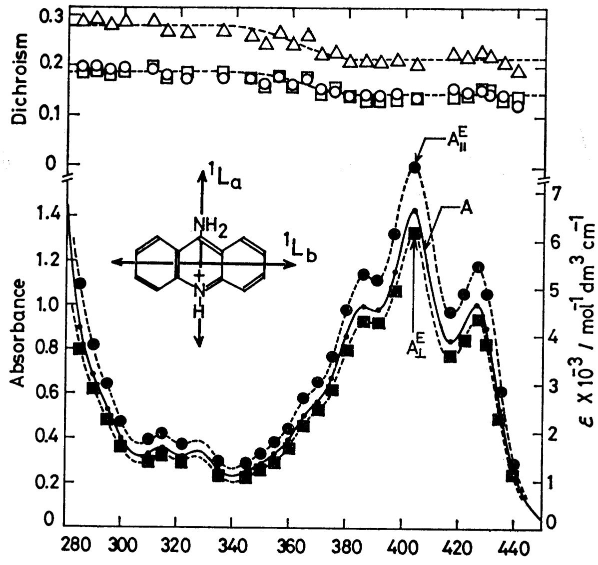

Fig. 5. Linear dichroic spectra of NaPSS–AA in aqueous solutions at a P/D value of 6.14 and at a constant field strength of 11.6 kV/cm. Symbols are all the same as in Fig. 3.

was calculated (A_{calcd}, dots) with Eq. 4. The agreement of A_{calcd} with the observed spectrum (solid curve) indicates that no detectable electrochromism is involved for the NaPSS (C_p=3.31 mM) solution.

Because of a large difference in ε between the 262 nm and 224.5 nm bands, the NaPSS solution was diluted about 25-fold (*cf.* Table 1). The isotropic spectrum of NaPSS (C_p=0.133 mM) in Fig. 4 was characterized by a peak at 224.5 nm ($\varepsilon=9.54\times10^3$) and a weak shoulder near 233 nm (6.58×10^3). The peak value was lower than Boyd's value by 10% at 224.0 nm and at 25 °C.[24] The reduced dichroism was negative throughout the 240—215 nm region. Both $\Delta A_{/\!/}/A$ and $-2\Delta A_{\perp}/A$ agree with each other, indicating no electrochromism. The dichroic spectrum is constant only in the 240—224 nm region, increasing gradually below 224 nm, which is probably due to the influence of some higher-energy absorption bands of NaPSS in the far UV region.[25]

Wavelength Dependence of Dichroic Spectrum of NaPSS–AA Complex in the 440—280 *nm Region.* Figure 5 shows absorption spectra of an NaPSS–AA solution in the presence ($A^E_{/\!/}$ and $A^E_{\perp}$) and in the absence (A) of applied electric field in the lower half, and the parallel dichroism (circles), the perpendicular dichroism multiplied by -2 (squares), and the reduced dichroism (triangles) in the upper half. The isotropic spectrum is characterized by the ^1L_a band [three peaks at 426 nm ($\varepsilon=4.68\times10^3$), 404 nm ($6.64\times10^3$), 386 nm ($4.62\times10^3$), and a weak shoulder near 370 nm (2.55×10^3)], the ^1L_b band [two weak peaks at 328 nm ($\varepsilon=1.61\times10^3$) and 315 nm ($1.63\times10^3$)], and a shoulder near 290 nm (3.16×10^3).[15] The reduced dichroism indicates that (1) its sign is always positive in the visible and near UV regions, (2) two different transitions are present (one with $\Delta A/A$ of 0.22 ± 0.02 in the 440—370 nm region and the other with $\Delta A/A$ of 0.27 ± 0.02 in the 335—282 nm region), (3) no electrochromism is involved, *i.e.*, $\Delta A_{/\!/}/A=-2\Delta A_{\perp}/A$ within experimental uncertainty.

Discussion

Theoretical Orientation Functions for Monodisperse and Polydisperse Systems. The synthetic polyelectrolyte may be in a very extended form in salt-free aqueous solution at a low polymer-concentration, as a result of electrostatic repulsion between the charged side groups.[6,13] Under these conditions, the electro-optical properties of such a polyelectrolyte may be estimated, to a good approximation, with the aid of theoretical expressions for rod-like molecules (*vide post*). In order to know the highest possible reduced dichroism at infinitely high field, $(\Delta A/A)_s$, and the orientation behavior of NaPSS and NaPSS–AA complex, the field strength dependence of steady-state dichroism signals should be compared with a suitable theoretical orientation function. If the polyelectrolyte with identical chromophores in a solution can be regarded as a relatively stiff chain of axial symmetry, the reduced dichroism $\Delta A/A$ for a monodisperse system may be given as[23]

$$\frac{\Delta A}{A}=\frac{3}{2}(3\cos^2\theta-1)\Phi, \tag{5}$$

where A is the absorbance of the same solution in the absence of external electric field, ($3\cos^2\theta$—1) is the optical term as stated before, and Φ is the orientation function.

The "classical" orientation function, $\Phi(\beta,\gamma)$, for a dipolar molecule with the permanent dipole moment (μ) and/or the polarizability anisotropy ($\Delta\alpha$) has been derived by O'Konski *et al.* (Eq. 14 of Ref. 1). The variables, β and γ, are the interaction energy terms and are given as $\beta=\mu E/kT$ and $\gamma=\Delta\alpha E^2/2kT$ (≥0), where k is the Boltzmann constant and T is the absolute temperature. In the strict sense, the O'Konski-Yoshioka-Orttung or the classical function, $\Phi(\beta,\gamma)$, was derived for the nonionic polymer in solution. Nevertheless, it has been used successfully in many cases, which include aqueous solutions of polyelectrolyte.[1,6,8,11,22] Hence, we also use $\Phi(\beta,\gamma)$ for interpreting the data of NaPSS and NaPSS–AA systems on a qualified, empirical basis. For the ionized polymer system, an orientation function, $\Phi(\kappa)$, was derived by Kikuchi and Yoshioka under consideration of ion-atmosphere polarization (Eq. 8 of Ref. 26).[26] The variable κ is given as $\kappa=ZelE/2kT$, where n is the number of condensed counterions per polyion, Z is the valence of counterion, e is the elementary charge, and l is the contour length of polyion. As Kikuchi and Yoshioka have pointed out,[6] the field strength dependence of the molecular orientation of synthetic polyelectrolyte may be related not only to the flexibility of the polyelectrolyte chain but also to the polydispersity of molecular weights. In order to explain the field strength dependence of a poly(N-butyl-4-vinylpridinium bromide) solution, Tricot *et al.*[8] used an orientation function with three different electric polarizabilities. Any synthetic polyelectrolyte sample should not be the sum of a few discrete species of different molecular weights, but it should have an almost continuous molecular weight distribution. Therefore, we extend both $\Phi(\beta,\gamma)$ and $\Phi(\kappa)$ at first in such a way as to include this distribution.

Since the Schulz-Zimm function,[27,28] $f_w(M)$, has been used often for the molecular weight distribution of synthetic polymer samples, we also utilize it to describe a polydisperse NaPSS sample:

$$f_w(M) = y^{k+1}M^k e^{-yM}/\Gamma(k+1) \tag{6}$$

$$M_n = \frac{k}{y},\ M_w = \frac{k+1}{y},\ \text{and}\ \frac{M_w}{M_n} = \frac{k+1}{k}, \tag{7}$$

where M is the molecular weight of a polymer species, M_w and M_n are the weight- and the number-average molecular weights, respectively. The conformation of polyionic NaPSS is probably in a very extended form in a dilute solution,[6,11] the molecular weight M of a particular NaPSS molecule may be equated to m_0l, where l is the length of the NaPSS molecule and m_0 is the molecular weight per unit length. In this case, the ratio M_w/M_n may be equated to the ratio of weight-average length to number-average length l_w/l_n. The relation between $f_w(l)$ and $f_n(l)$, the latter of which is the distribution function for the number of molecules with the contour length l, is given as follows:

$$f_n(l) = \frac{k}{m_0ly}f_w(l). \tag{8}$$

In the insert of Fig. 6, $f_n(l)$ is plotted against l with a value of 340 nm for l_w, which corresponds to the M_w of 2.8×10^5 daltons for NaPSS, as determined from the viscosity data, and with a value of 1.3 for l_w/l_n ($=M_w/M_n$), which was estimated for the present sample from the data of Nagasawa *et al.*[16,29] For the polydisperse system in which the limiting reduced dichroism, $3(3\cos^2\theta-1)/2$, is independent of molecular species (this is the reasonable assumption for a polymer molecule in which the number of identical chromophores is proportional to its length), Eq. 5 may be expressed in terms of the sum of the individual dichroism of the component species for which the length distribution function is defined by $f_n(l)$:

$$\begin{aligned}\frac{\Delta A}{A} &= \frac{3}{2}(3\cos^2\theta-1)\int_{L_1}^{L_2} lf_n(l)\Phi \mathrm{d}l \Big/ \int_{L_1}^{L_2} lf_n(l)\mathrm{d}l \\ &\equiv \frac{3}{2}(3\cos^2\theta-1)\langle\Phi\rangle_w = \left(\frac{\Delta A}{A}\right)_s\langle\Phi\rangle_w,\end{aligned} \tag{9}$$

where $\langle\Phi\rangle_w$ is the weight-average orientation function, Φ corresponds to $\Phi(\beta,\gamma)$ or $\Phi(\kappa)$ for a monodisperse system, and $(\Delta A/A)_s$ is the limiting reduced dichroism. Both L_1 and L_2 are the lower and upper limits of l. At limiting high field strength, $\langle\Phi\rangle_w$ approaches unity; hence, $(\Delta A/A)_s=3(3\cos^2\theta-1)/2$.

In Fig. 6(a), the field strength dependence of the weight-averaged Kikuchi-Yoshioka orientation function $\langle\Phi(\kappa)\rangle_w$ is plotted against $n\kappa_w^2/3$, where κ_w is the weight-average value equal to $Zel_wE/2kT$. The parameter n (1, 5, 10, and 50) is the number of condensed counterions on the polyion surface. Dashed curves represent $\Phi(\kappa)$ for the corresponding monodisperse system. In Fig. 6(b), the field strength dependence of the weight-average classical orientation function $\langle\Phi(\beta,\gamma)\rangle_w$ is plotted against $\beta_w^2+2\gamma_w$, where β_w and γ_w are values of μ_0l_wE/kT and of $\Delta\alpha_0l_wE^2/2kT$. Here, μ_0 and $\Delta\alpha_0$ are the permanent dipole moment and the polarizability anisotropy per unit length, respectively. Values of $\beta_w^2/2\gamma_w$ are a measure of relative contributions of those electric moments to field orientation, corresponding to the pure induced moment (0), the mixed dipole moment (2 and 8), and the permanent dipole moment (∞) orientation. Dashed curves represent $\Phi(\beta,\gamma)$ for the corresponding monodisperse system. In Fig. 6, the orientation factor (the average degree of orientation of polyions in solution) for the monodisperse system is larger than for the polydisperse system at a given field strength, except in the low field strength region.

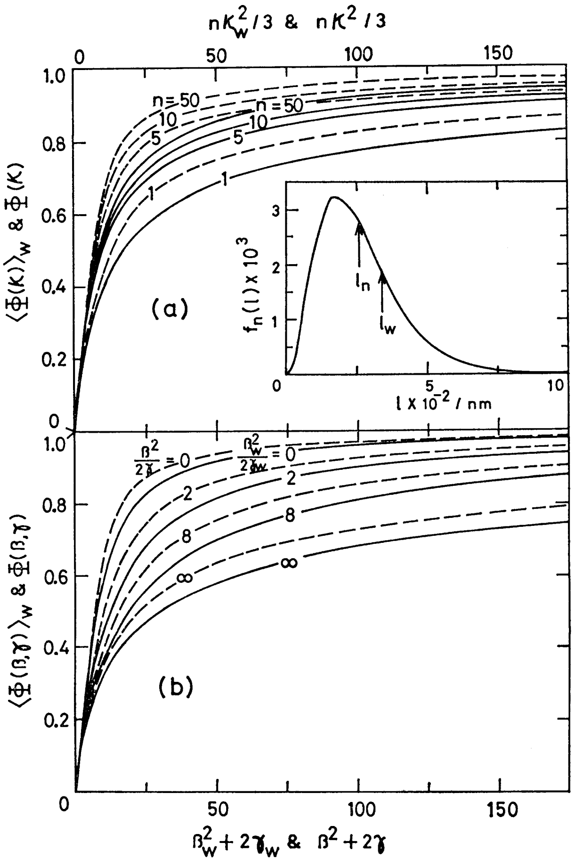

Fig. 6. The Kikuchi-Yoshioka orientation function $\Phi(\kappa)$ and the "classical" orientation function $\Phi(\beta,\gamma)$ for monodisperse and polydisperse systems. In (a), $\langle\Phi(\kappa)\rangle_w$ (——) is plotted against $n\kappa_w^2/3$ for $n=1$, 5, 10, and 50. In (b), $\langle\Phi(\beta,\gamma)\rangle_w$ (——) is plotted against $\beta_w^2+2\gamma_w$ for $\beta_w^2/2\gamma_w=0$, 2, 8, and ∞. The insert shows the Schulz-Zimm length distribution function $f_n(l)$ with the parameter l_w/l_n of 1.3, which was used for calculating both $\langle\Phi(\kappa)\rangle_w$ and $\langle\Phi(\beta,\gamma)\rangle_w$. In (a) and (b), dashed curves (----) are the respective orientation functions $\Phi(\kappa)$ and $\Phi(\beta,\gamma)$ calculated for a monodisperse system ($l_w/l_n=1.0$). The integal limits L_1 and L_2 are set at 12 and 1200 nm.

Curve-fitting Method. Several curve fitting methods[1,6,8,22] have been used to obtain values of the intrinsic optical factor and the electric dipole moment. As shown in Fig. 7(a), the field strength dependence

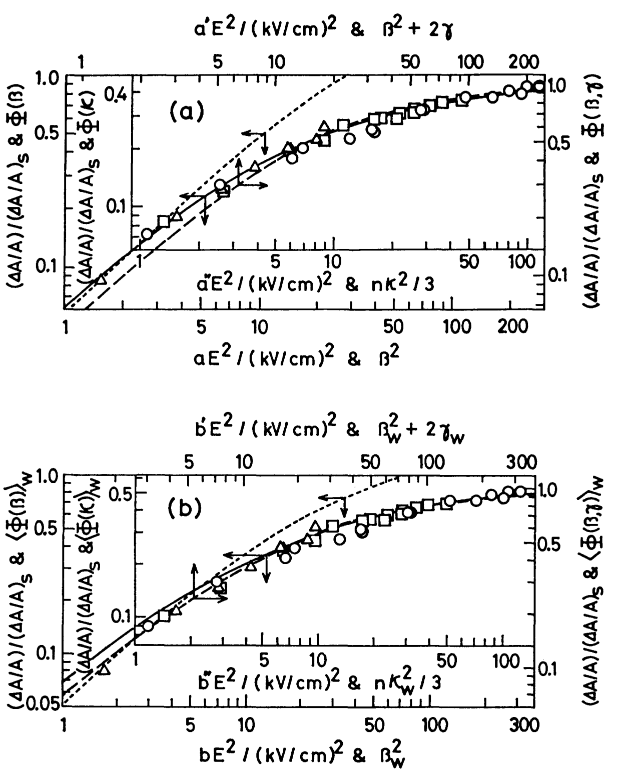

Fig. 7. Comparison of experimental values of reduced dichroism for NaPSS at 224.5 nm (○) and at 262 nm (△) and for NaPSS–AA at 404 nm (□) with theoretical orientation functions (a) for the monodisperse system and (b) for the polydisperse system. In (a), three sets of the double logarithmic plots are shown: $(\Delta A/A)/(\Delta A/A)_s$ against aE^2, $a'E^2$, $a''E^2$; $\Phi(\beta)$ against β^2 (——); $\Phi(\beta,\gamma)$ against $\beta^2+2\gamma$ (----); $\Phi(\kappa)$ against $n\kappa^2/3$ (······). The observed dichroism $\Delta A/A$ for each of NaPSS and NaPSS–AA was normalized by dividing it by the limiting value $(\Delta A/A)_s$ given in Table 2, in order to compare three sets of experimental points (○, △, and □) with a given theoretical orientation function $\Phi(\beta)$, $\Phi(\beta,\gamma)$, or $\Phi(\kappa)$ on each of three coordinates. The factors a, a', and a'' are: $a=0.806$ (○), 0.0704 (△), and 0.339 (□); $a'=0.661$ (○), 0.0577 (△), and 0.278 (□); $a''=0.140$ (□). In (b); three sets of the double logarithmic plots are shown: $(\Delta A/A)/(\Delta A/A)_s$ against bE^2, $b'E^2$, and $b''E^2$; $\langle\Phi(\beta)\rangle_w$ against $\beta_w{}^2$ (——); $\langle\Phi(\beta,\gamma)\rangle_w$ against $\beta_w{}^2+2\gamma_w$ (----); $\langle\Phi(\kappa)\rangle_w$ against $n\kappa_w{}^2/3$ (······). $b=0.799$ (○), 0.0610 (△), and 0.384 (□); $b'=0.769$ (○), 0.0588 (△), and 0.370 (□); $b''=0.151$ (□). Both $\Phi(\kappa)$ and $\langle\Phi(\kappa)\rangle_w$ with the n value of 1 are applicable only to the case of NaPSS–AA (□). Symblos and experimental conditions in (a) and (b) are the same as in Fig. 2.

of observed reduced dichroism of NaPSS at 224.5 and 262 nm and NaPSS–AA at 404 nm was compared with theoretical orientation functions by assuming a monodisperse system. The experimental points fit the permanent dipole moment orientation $\Phi(\beta)$ (solid curve) over a wide range of field strength. A mixed-dipole moment orientation function $\Phi(\beta,\gamma)$ with $\beta^2/2\gamma$ of 8 (dashed curve) is also plotted, but it disagrees with the experimental points except for the high field region. Although the orientation function $\Phi(\kappa)$, in which ion-atmosphere polarization is considered, seems to be the most reasonable one for the salt-free NaPSS and NaPSS–AA solutions, it fits the experimental points only in the low field strength region (dotted curve). This discrepancy may be partly due to the neglect of the effect of counterion repulsion and partly due to the polydispersity of polymer length.

In order to test the effect of polymer lengths, the field strength dependence of reduced dichroism for NaPSS and NaPSS–AA systems is compared, in Fig. 7(b), with the orientation functions which take into account the polydispersity with the length distribution function $f_n(l)$ (Fig. 6). Experimental points fit a mixed-dipole moment orientation function $\langle\Phi(\beta,\gamma)\rangle_w$ with a $\beta_w{}^2/2\gamma_w$ of 8 rather than the pure permanent dipole moment orientation function $\langle\Phi(\beta)\rangle_w$. On the other hand, the experimental points fit $\langle\Phi(\kappa)\rangle_w$ only in the low field strength region; $\langle\Phi(\kappa)\rangle_w$ is definitely closer to the experimental points than $\Phi(\kappa)$. At present, the best (but not necessarily unique) values of $\beta^2/2\gamma$ and $\beta_w{}^2/2\gamma_w$ together with those of $(\Delta A/A)_s$ were obtained by this curve fitting method and are given in Table 2. It is difficult to select either of them as the more reasonable. In order to obtain the exact value of $\beta_w{}^2/2\gamma_w$, the form of the length distribution function for the NaPSS sample must be known. It should be noted that the values of the limiting reduced dichroism $(\Delta A/A)_s$ are not appreciably different when they are obtained from the two best fitted orientation functions, $\Phi(\beta)$ and $\langle\Phi(\beta,\gamma)\rangle_w$. This is because both of the two functions approach unity at the limiting high field strength.

Wavelength Dependence of Reduced Dichroism of NaPSS and NaPSS–AA Complex. By comparing values of ε in Table 1 between NaPSS, sodium *p*-toluenesulfonate, and benzene,[30] the longest-wavelength band of NaPSS in the 280—245 nm region is reasonably assigned to the transition polarized in the direction bisecting the 1- and 4-carbon atoms of a phenyl plane (the ${}^1B_{2u}$ band), while the short-wavelength band in the 245—215 nm region is the transition polarized perpendicular to the long axis in the phenyl plane (the ${}^1B_{1u}$ band). The reduced dichroic spectra could not be determined at a single polymer concentration for these two bands (Figs. 3 and 4), because the ${}^1B_{1u}$ band absorbs light much more strongly than the ${}^1B_{2u}$ band. If the effect of dilution is negligibly small, the difference in $(\Delta A/A)_s$ values for these bands is interpreted as being due to the different tilt angles of the mutually perpendicular transition moments in the phenyl ring relative to the orientation axis of the NaPSS backbone. These angles are given in Table 2. The increase in $\Delta A/A$ values below 224 nm is not explained by the ${}^1B_{1u}$ transition moment alone, because a single transition moment should give rise to a constant reduced dichroism inside an absorption band. This result probably indicates the presence of another transition moment in the far UV region.[25]

The absorption bands of NaPSS–AA arise from the electronic transition moments of the AA molecule (${}^1L_a$- and ${}^1L_b$-bands), the directions of which are shown in Fig. 5.[15,31,32] They are mutually perpen-

TABLE 2. ELECTROOPTICAL PARAMETERS OF NaPSS AND NaPSS-AA IN AQUEOUS SOLUTIONS AT 20 °C

	$\frac{\lambda}{\text{nm}}$	$\left(\frac{\Delta A}{A}\right)_s$	$\lvert\theta\rvert$	$\frac{l_w}{l_n}$	$\frac{\beta_w^2}{2\gamma_w}$	$\frac{E^{2\,\text{a)}}}{(\text{kV/cm})^2}$	$\frac{\langle\mu\rangle_w^{\text{b)}}}{\text{D}^{\text{c)}}}$	$\frac{\langle\Delta\alpha\rangle_w^{\text{b)}}}{\text{cm}^{3\ \text{c)}}}$
NaPSS	224.5	−0.39	60°	1.0	∞	12.4	1.1×10^4	—
(C_p=0.133 mM)		−0.36	60°	1.3	8	13.0	1.0×10^4	3.1×10^{-16}
NaPSS	262	−0.17	57°	1.0	∞	142	3.2×10^3	—
(C_p=3.31 mM)		−0.18	57°	1.3	8	170	2.8×10^3	2.3×10^{-17}
NaPSS-AA	404	0.38	50°	1.0	∞	29.5	7.1×10^3	—
(C_p=0.663 mM)	315	0.49	48°					
	404	0.34	50°	1.3	8	27.0	7.0×10^3	1.5×10^{-16}
	315	0.44	49°					

a) The square of field strength at $\beta^2+2\gamma=10$ or $\beta_w^2+2\gamma_w=10$. b) When polydispersity is taken into account, the weight-average quantities become $\langle\mu\rangle_w$ and $\langle\Delta\alpha\rangle_w$, which are equated to $\mu_0 l_w$ and $\Delta\alpha_0 l_w$, respectively. c) 1 D=3.336×10^{-30} C m and 1 cm^3=1.113×10^{-16} F m^2.

dicular in the dye plane and are widely separated. Since the bound fraction of AA has been estimated to be more than 99% in the NaPSS–AA solution at a *P*/*D* of 6.14,[15] the amount of unbound AA in the present solution should be negligibly small. Therefore, the observed dichroic spectra in Fig. 5 can be considered to be the dichroic spectra of the bound AA. If the flexibility of the NaPSS chain is neglected at a low polymer concentration (C_p=0.663 mM), the average angle θ between the transition moment ^1L_a and the orientation axis of the NaPSS–AA complex is *ca.* 50°. The average angle for the ^1L_b band at 315 nm was calculated to be *ca.* 48°. Although the difference of the angles for the ^1L_a and ^1L_b bands is very small, it is definitely beyond the experimental error. The fact that the reduced dichroism of 0.22±0.02 in the 440—370 nm region differs from that of 0.27±0.02 in the 335—282 nm region may be interpreted as follows: the angles of these transition moments of the bound AA differ from each other relative to the orientation axis of NaPSS–AA (provided that the number and the direction of the transition moments remain unaltered when the dye is bound to the NaPSS site). It should be noted that these angles are still only apparent, since more than one bound AA species may be present on the NaPSS surface.[15,18]

Apparent Dipole Moments of NaPSS and NaPSS–AA Complex. In the preceding section, the experimental points fit $\Phi(\beta,\gamma=0)$ and $\langle\Phi(\beta,\gamma)\rangle_w$ (with a $\beta_w^2/2\gamma_w$ of 8) curves better than $\Phi(\kappa)$ and $\langle\Phi(\kappa)\rangle_w$, over a wide range of field strength. On the other hand, it has been shown by reversing-pulse electric birefringence that both NaPSS and NaPSS–AA possess no appreciable intrinsic permanent dipole moment.[11] Hence, we term μ the pseudo-permanent dipole moment and retain it, until a more complete orientation function is derived for conducting polyelectrolytes. These values are given in Table 2. With an increase in concentrations of NaPSS, the pseudo-permanent dipole moment decreases in the order: NaPSS (C_p=0.133 mM) > NaPSS–AA (C_p=0.663 mM) > NaPSS (C_p=3.31 mM). This result is qualitatively consistent with the concentration dependence of the specific Kerr constant, as observed by Kikuchi and Yoshioka for KPSS.[6] Thus, the dipole moment of NaPSS depends strongly on the concentration, indicating that, as the ionized sulfonate groups increase, the chain stiffness and, hence, the persistence length also increase.

Conclusion

The field strength dependence of reduced dichroism signals of NaPSS and NaPSS–AA in aqueous solutions can be described by the "classical" permanent dipole orientation function $\Phi(\beta)$ for the monodisperse system and also by the mixed-dipole orientation function $\langle\Phi(\beta,\gamma)\rangle_w$ for the polydisperse system. However, the seemingly more realistic orientation functions $\Phi(\kappa)$ and $\langle\Phi(\kappa)\rangle_w$, based on ion-atmosphere polarization, fit the dichroism data of NaPSS and NaPSS–AA only in the low field range. The necessity for an improved expression for the orientation function of charged, flexible polyelectrolytes is apparent. Such an orientation function must contain the effects of counterion repulsion, the flexibility, and the polydispersity of polymer chain. The reduced dichroism at limiting high field, estimated with different theoretical orientation functions, is almost identical. The wavelength dependence of reduced dichroism of NaPSS indicates that the UV band is composed not only of the $^1B_{1u}$ and $^1B_{2u}$ transitions but also of another higher-energy transition in the far UV region. The absorption spectrum of NaPSS–AA is composed of both the ^1L_a and ^1L_b in-plane transitions, whose average angles are slightly, but definitely, different from each other relative to the orientation axis of the NaPSS backbone.

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