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The Electric Birefringence and Dichroism of a Nonlinear Optical Compound, 4-[2-[4-(Dimethylamino)phenyl]ethenyl]-1-ethylpyridinium Iodide, in the Presence of Poly(*p*-styrenesulfonate) and Poly(L-*α*-glutamate) in Solutions

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The pulsed electric birefringence at 633 nm and dichroism at 462 nm of the title cationic compound (DAES) were measured at 20 °C over a wide electric field strength range (0.1—24 kV cm^{-1}) in the presence of poly(*p*-styrenesulfonate) (NaPSS) and poly(L-*α*-glutamate) (PGA) in aqueous solutions at various mixing ratios (*P/D*) of the polymer to the ligand. The steady-state electric birefringence δ of NaPSS–DAES complexes was positive, while that of NaPSS was negative. The optical anisotropy factor of bound DAES was responsible for the sign reversal. The reduced electric dichroism of NaPSS–DAES at a *P/D* of 1.9 was +0.38 at infinitely high fields. A value of ±50° was found for the average angle between the orientation axis of the complex and the direction of the optical transition moment at 462 nm of bound DEAS chromophores. No appreciable permanent dipole moment was present in any of the NaPSS–DAES systems. The field orientation was due mostly to counterion-induced moments. The rotational relaxation time was determined from the decay signals. For PAG–DAES and PGA at pH 6.4 and 4.1, the sign of δ was always positive, the magnitude differing from each other by only 10—20%.

4-[2-[4-(Dimethylamino)phenyl]ethenyl]-1-ethylpyridinium iodide (DAES) is one of the well-known nonlinear optical materials which exhibit a marked second harmonic generation (SHG) phenomenon, due mostly to their large hyperpolarizability in the crystalline state.1) Attempts have been made to observe SHG in some stilbene derivatives in the dissolved state with a strong Nd:YAG laser beam.2) The static electric field-induced SHG of the π-electronic conjugated system is generally weak; therefore, a high external field strength of about 100 kV cm^{-1} or more is required. If nonlinear optical compounds were oriented unidirectionally at much lower electric fields, as in the crystalline state, the SHG measurement could be facilitated with less powerful but easily available laser diodes as the light source; hence, a variety of practical applications would thus become feasible. This idea may be realized if the nonlinear materials are attached either covalently or electrostatically to the appropriate polymeric matrices, which are easily orientable by an external force. The electric field is particularly useful because the field orientation is fast and reversible, which would enable us to develop an on-off switching device.

In order to achieve the above objectives, a series of systematic studies will be necessary to determine the electrooptical properties of polymer-nonlinear optical material complexes. In this work, the field orientation behavior of DAES, a cationic stilbene derivative with a large permanent dipole moment, was studied in the presence of poly(sodium *p*-styrenesulfonate) (NaPPS)3–8) and poly(sodium L-*α*-glutamate) (PGA),9–11) both of which are known to be oriented easily in an aqueous solution by means of an external electric field. The interaction of polymer–ligand complexes is best studied by pulsed electric birefringence and electric dichroism, which measure the anisotropic electric, optical, and hydrodynamic properties.3–14) Since a large change in permanent dipole moments between the ground and excited states of the nonlinear optical ligand effects an SHG phenomenon,1) lower ratios of the polymer site to the ligand are chosen in this work.

Experimental

Materials. The DAES was purchased from Nippon Kankoh Shikiso Kenkyusho (Okayama) and was used without further purification. This compound was insensitive to the irradiation of the 320—450 nm light from a 150-W quartz-iodine lamp. The NaPSS was kindly supplied by the Tosoh Co. and was fractionated by the precipitation method. The weight-average molecular weight was estimated to be 1.63×10^6 from the intrinsic viscosity of 2.61 dl g^{-1} in 0.2 M (1 M=1 mol dm^{-3}) NaCl at 25 °C.15) The PGA was a gift of Dr. Hiroshi Sato of the Mitsubishi Rayon Co. and was fractionated by successive precipitation. The weight-average molecular weight was estimated to be 1.04×10^5 from the intrinsic viscosity of 1.02 dl g^{-1} in 2 M NaCl at 25 °C. The polymer–DAES solution was prepared by adding the DAES solution to the polymer solution at a desired mixing ratio (denoted as *P/D*), which was expressed in terms of the polymer residue-to-DAES concentrations. The polymer concentration was kept constant at all *P/D* values, since the polymer conformation without added salt or at a low ionic strength is concentration-dependent.

Measurements. The absorption spectra in the absence of electric field were measured on a Shimadzu Model UV-250 recording spectrophotometer at 20 °C with quartz cells 0.3 and 1.0 cm in path length. The electric birefringence was measured at 20 °C on a high-speed, high-voltage He-Ne laser (632.8 nm) apparatus constructed in this laboratory. The electric dichroism was determined at 20 °C and at an absorption maximum of 462 nm of DAES on an instrument

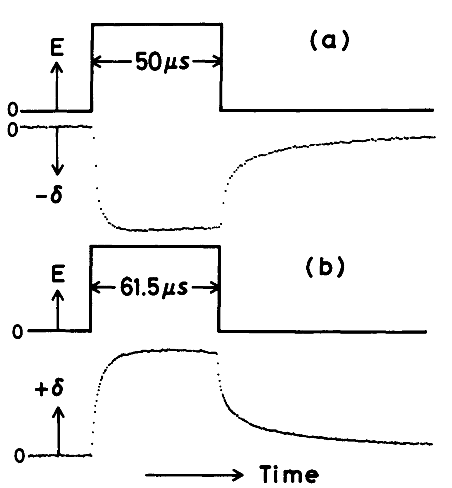

Fig. 1. Transient electric birefringence signals and applied electric square-pulse fields. (a) NaPSS: E=16.83 kV cm^{-1} and δ=−6.19° and (b) NaPSS-DAES at P/D=1.9: E=16.78 kV cm^{-1} and δ= +21.67°. Birefringence signal δ in (a) is an average of four accumulations, while the signal in (b) is the response to a single pulse. The sampling time of the signal detecting system was set at 200 ns. The instrumental time constant was adjusted to 100 ns for the buildup (or the rise) and 300 ns for the decay signal.

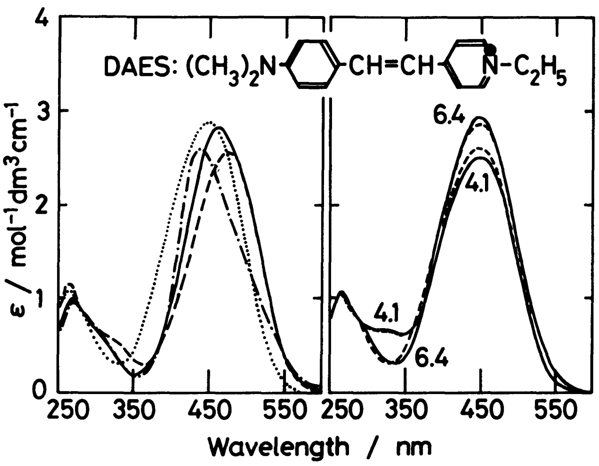

Fig. 2. Isotropic absorption spectra of DAES in the presence and the absence of NaPSS (left) and PGA (right). P/D for NaPSS at pH 6.4: 7.1 (– – –), 1.9 (——), 0.94 (—·—·—), and 0 (·····). P/D for PGA: 9.8 (——) and 0 (-----) at pH 4.1 and 5.4 (——) and 0 (-----) at pH 6.4; the numerals denote pH values. The molar absorption coefficient ε was expressed in terms of the concentration of DAES. The residue concentrations of polymers are constant: [NaPSS]= 0.202 mM containig 0.8 mM NaCl, [PGA]=0.389 mM.

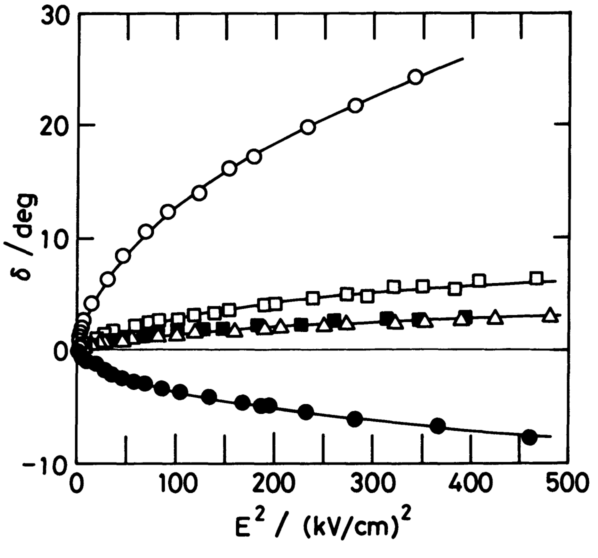

Fig. 3. The steady-state electric birefringence δ of NaPSS-DAES complexes and NaPSS versus the square of applied external electric field strength E^2. P/D: 7.1 (■), 4.7 (□), 1.9 (○), 0.94 (△), and ∞ (●). [NaPSS]=0.202 mM in 0.8 mM NaCl. Solid lines are theoretically calculated SUSID orientation functions (see text).

previously reported.[5,12] The output signals were digitized and processed with the transient wave memory-microcomputer system.[16] Figure 1 shows examples of the transient electric birefringence signals of NaPPS and its DAES complex.

Results and Discussion

Isotropic Absorption Spectra. Figure 2 shows the isotropic absorption spectra of DAES in the presence of NaPSS and PGA, together with those of DAES alone (P/D=0). The spectra of DAES in the presence of NaPSS differ from the reference spectrum of DAES, whose maximum at 450 nm is shifted toward red by 25 nm at higher P/D values, but shifted back to ca. 430 nm at a low P/D of about 1 probably because of the metachromatic effect of bound DEAS.[17] These changes are a strong indication of the formation of a complex by the electrostatic interaction between the anionic sulfonato group and the quarternized ring nitrogen of DAES.[17] The spectra of DAES in PGA differ only slightly from the DAES spectra at two pH's; thus, the binding of DAES to PGA appears to be very weak, regardless of the backbone conformations of PGA (helix at pH 4.1 and random coil at pH 6.4).

Steady-State Electric Birefringence. Figure 3 shows the steady-state birefringence of NaPSS-DAES complexes, expressed in terms of the optical phase retardation δ. Since DAES exhibits no electric birefringence in the absence of NaPSS over a field strength range of $E \leq 22.4$ kV cm^{-1}, the observed signals are all due to the NaPSS-DAES complex. It should be noted that the sign of δ for the complex is reversed to positive, while the sign is negative for NaPSS itself.[3,4,6-8] A large contribution of the bound DAES moiety to the observed δ values is evident. Since more than half of DAES present in solution are unbound at a low P/D ratio of 0.94, the δ values are much less than those of complexes at P/D=7.1—1.9, probably because of the

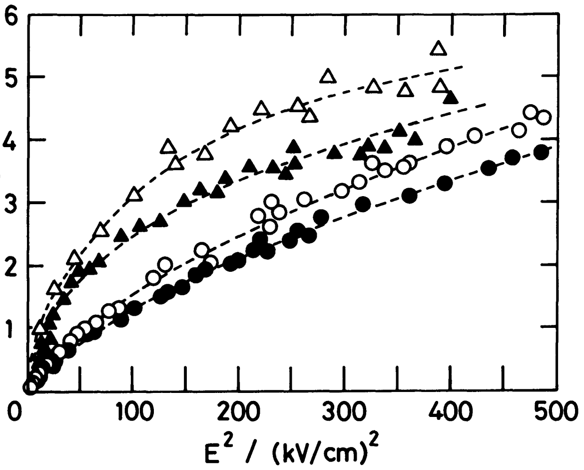

Fig. 4. The steady-state electric birefringence δ of PGA in the presence and the absence of DAES versus the square of field strength E^2. pH at 4.1: P/D=9.8 (○) and ∞ (●). pH at 6.4: P/D=5.4 (△) and ∞ (▲). [PGA]=0.389 mM.

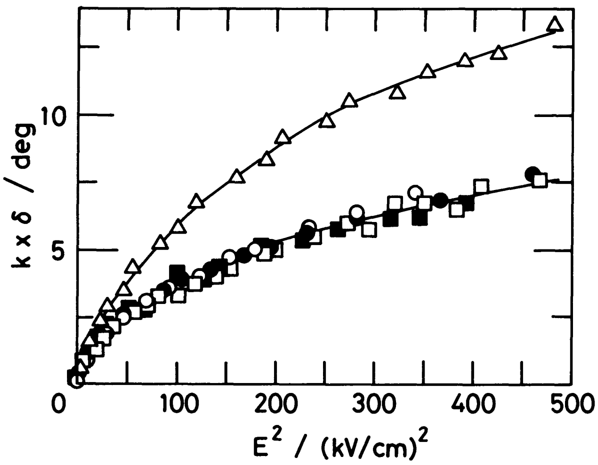

Fig. 5. The field strength dependence of δ multiplied by a normalization factor k for NaPSS-DAES complexes. k=−1.0 (∞), 2.3 (7.1), 1.3 (4.7), 0.29 (1.9), and 4.0 (0.94), P/D values being given in the parentheses. The symbols and other conditions are all the same as in Fig. 3.

presence of unbound DEAS in the solution.

Figure 4 shows the steady-state birefringence of DAES in the presence of PGA at pH 4.1 and 6.4. The magnitude of δ for DAES in the presence of PGA was found to differ from that of PGA by only 10—20% over the 0.1—22.4 kV cm^{-1} range, the sign of δ being positive in all cases. Hence, no appreciable DAES ions are oriented jointly with PGA by an applied field. It is now clear that, though positively charged at those pH's, DAES is not bound tightly to the side-chain carboxylate of PGA, as is also indicated by the spectral changes (cf. Fig. 2).

Electric birefringence is expressed by the product of the optical, $\Delta g/n$, and electric, $\Phi(E)$, terms; it is given as $\delta=(4\pi^2C_vd/\lambda)(\Delta g/n)\Phi(E)$, where C_v is the volume fraction of orientable solutes (i.e., the NaPSS-DAES complex), d is the path length of a Kerr cell (1.0 cm), λ is the wavelength of the incident light (632.8 nm), Δg is the optical anisotropy factor, n is the refractive index of the solution, and $\Phi(E)$ is the orientation function, which describes the dependence of δ on the field strength.[7] If the field orientation of the NaPSS-DAES complexes and NaPSS is described by a common orientation function, the observed δ vs. E^2 plots in Fig. 3 should all be brought to coincide with one another. In such a case, $\delta\times k=\Phi(E)$, where k is a constant, since the optical term is independent of the field strength. Figure 5 shows that all the δ vs. E^2 plots except for P/D=0.94 are now brought into a good coincidence with the appropriate constants, k, evaluated in the low field region. This indicates that a single orientation function is sufficient to describe the field orientation of NaPSS (P/D=∞) and the complexes (P/D=7.1, 4.7, 1.9).

It has been shown that NaPSS is oriented because of its large induced dipole moment.[3,4,8] The results shown in Fig. 5 indicate that NaPPS-DAES complexes also possess practically no net permanent dipole moment μ along the molecular axis of field orientation. If all the DEAS molecules in a solution are bound, the average number of DEAS molecules bound on each NaPSS polyanion would be about 1110(at P/D=7.1)—4150(at P/D=1.9). Because of the permanent dipole moment of ca. 7 Debye units for each DAES molecule, the vectorial sum of μ would be roughly as large as 7000—29000 Debyes if all bound DAES moieties were aligned in parallel fashions like an arrow along a rodlike NaPSS backbone. This case is inconsistent with the present results. Possible explanations are: (1) the bound DAES molecules are so arranged that the individual dipole moments, μ_{DAES}, cancel each other out and/or (2) the overall conformation of the complexes is not rigidly rodlike, but coiled, so that the net moment μ is negligibly small.

In order to analyze the experimentally obtained δ vs. E^2 plots for ionized polymers, which are lacking in the permanent dipole moment and are, therefore, oriented by induced dipole moment(s), a new orientation function is needed. For this purpose, a theoretical function was recently derived on the assumption that an ionized polymer possesses both saturable ($\Delta\sigma E$) and unsaturable ($\Delta\alpha E$) induced dipole (SUSID) moments.[18] These two types of induced dipole moments are responsible for the interaction with the electric field. The former ($\Delta\sigma E$) is induced by the counterion and is saturated at the critical electric field E_0, while the latter ($\Delta\alpha E$) is partly electronic and partly ionic. Here, $\Delta\alpha$ is the electronic polarizability anisotropy, and $\Delta\sigma$ is the ionic polarizability anisotropy (the details are given in Ref. 18). The theoretical curves based on the SUSID mechanism (solid lines) in Fig. 3 reproduce all

Table 1. Optical, Electric, and Hydrodynamic Properties of NaPSS and NaPSS–DAES Complexes at 20 °C

P/D	δ_∞[a)] deg	$\Delta g/n$[b)]	$(\Delta g/n)_{\mathrm{DAES}}$[c)] $\mathrm{mol^{-1}\,dm^3}$	$\Delta\alpha$ $10^{-33}\,\mathrm{F\,m^2}$	$\Delta\sigma$ $10^{-31}\,\mathrm{F\,m^2}$	E_0 $\mathrm{kV\,cm^{-1}}$	τ_w μs	l Å
0.94	5.9	7.01	112	1.8	0.3	2.0	4.1	620
1.9	49.3	58.7	704	1.2	7.1	0.1	15.4	1020
4.7	11.0	13.1	700	1.2	7.1	0.1	18.1	1080
7.1	6.2	7.37	849	1.2	7.1	0.1	18.4	1090
∞	−14.3	−17.0	—	1.2	7.1	0.1	26.7	1250

a) The optical phase retardation at infinitely high fields. b) Values are estimated by curve-fitting. c) The reduced optical anisotropy factor contributed by DAES, defined as $[((\Delta g/n)$ of NaPSS–DAES complex$)-(\Delta g/n)$ of NaPSS$)]/($DAES concentration).

the observed δ vs. E^2 plots quite well. The degree of orientation at a high field of 22.4 kV cm^{-1} is calculated from those theoretical curves to be 0.53 for NaPSS and for NaPSS–DAES at $P/D=7.1$—1.9 and 0.56 for NaPSS–DAES at $P/D=0.94$; these values constitute strong evidence for the ease of the orientation of these polymer systems by external pulse fields. Table 1 shows the optical and electric properties, which were evaluated by means of the curve-fitting.[18] It is interesting to note in Table 1 that the reduced optical anisotropy factor $(\Delta g/n)$ of the NaPSS–DAES complexes varies greatly with the P/D ratio, while the $(\Delta g/n)$ value per DAES molecule, $(\Delta g/n)_{\mathrm{DAES}}$, remains nearly constant in the P/D range of 7.1—1.9, where the DAES molecules in the solution are probably almost all bound to NaPSS.[17]

Relaxation Time from Decay Signal. Figure 6 shows the birefringence-average relaxation time of the NaPSS and NaPSS–DAES complexes, $\langle\tau\rangle_{\mathrm{EB}}$, which was obtained by means of the area method from the decay signal upon the removal of the applied pulse field (cf. Fig. 1).[19] The values of $\langle\tau\rangle_{\mathrm{EB}}$ rapidly decrease in the low field region; however, they reach constant levels at higher pulse fields ($E\geq10$ kV cm^{-1}). This feature is mostly due to the polydispersity of the NaPSS sample.[20] The value of $\langle\tau\rangle_{\mathrm{EB}}$ at infinitely high fields is reduced to the weight-average relaxation time τ_w which is given in Table 1. The τ_w value of 27 μs for NaPSS is the largest, while it is only 4 μs for NaPSS–DAES at $P/D=0.94$. Considering that the weight-average degree of polymerization is 7890, the contour length of NaPSS would be as long as 19700 Å ($=2.5$ Å$\times7890$). For a rigidly rodlike model with this length and a radius of 9 Å, the rotational relaxation time should be ca. 52.6×10^3 μs, as calculated with the aid of the Broersma equation.[7,21] A comparison of this value of 52.6×10^3 μs with the observed value of 27 μs reveals that the backbone chain is probably folded and that the overall shape of NaPSS and its DAES complex may be approximated by an ellipsoid.[7] The apparent length l $(=2a)$ is given in Table 1 for this model, with a probable semi-minor axis b of 32 Å,[7] as calculated with the Perrin equation: $\tau^{-1}=(9kT/4\pi\eta_0a^3)\cdot[\ln(2p)-0.5]$, where η_0 is the viscosity of the solvent, $p=a/b$ (the axial ratio), and a is the semi-major axis.

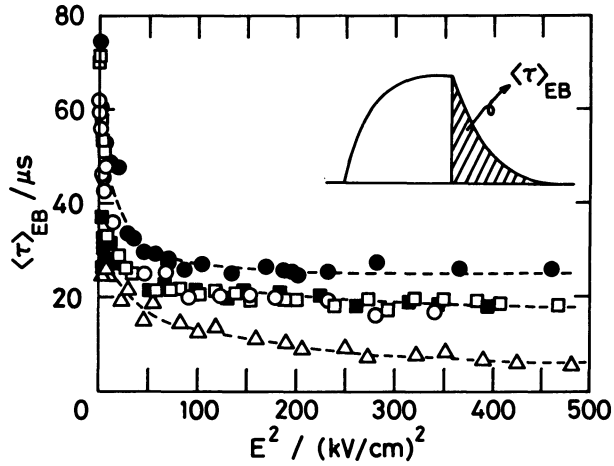

Fig. 6. The birefringence-average relaxation time $\langle\tau\rangle_{\mathrm{EB}}$ of NaPSS and NaPSS–DAES complexes. Symbols are all the same as in Fig. 3.

(In this calculation, the NaPSS sample was assumed to be monodisperse.) The most likely reason for the absence of the net permanent dipole moment μ in the DAES-bound NaPSS is the extensive folding of the polymer chain.[7] The whole shape, approximated by an ellipsoid, apparently becomes more compact with the decrease in the P/D values.

Electric Dichroism of the NaPSS–DAES Complex. Since the value of $\Delta g/n$ was positive for the NaPSS–DAES complexes, in contrast with the case of NaPSS (cf. Table 1), the DAES chromophore is probably bound to the ionized sulfonate group in such a way that the angle θ between the orientation axis of the complex and the optical transition moment direction of the 462-nm absorption band of bound DAES is less than ±54.7°.[5,12] In order to confirm this inference, the steady-state electric dichroism of the NaPSS–DAES complex at $P/D=1.9$ was measured over a wide field-strength range. Figure 7 shows the field-strength dependence of the reduced dichroism $\Delta A/A$ at 462 nm, which is given as $\Delta A/A=(A_{/\!/}-A_{\perp})/A=(3/2)(3\cos^2\theta-1)\times\Phi(E)$, where A is the absorbance at 463 nm of the solution in the absence of an applied field.[12] As in the case of the electric birefringence shown in Fig. 3, the experimental plot was fitted to a SUSID theoretical

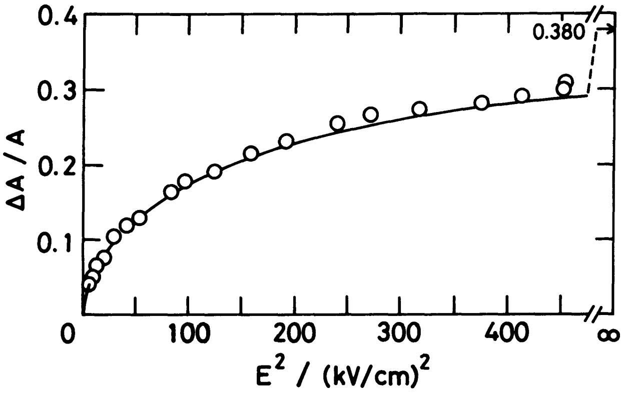

Fig. 7. The field strength dependence of the steady-state reduced electric dichroism $\Delta A/A$ at 462 nm of NaPSS–DAES complex at $P/D=1.9$. [NaPSS]= 0.101 in 0.4 mM NaCl. Circles are experimentally obtained. Solid line is calculated with the SUSID orientation function with the following values: $\Delta\alpha=4.4\times10^{-33}$ F m^2, $\Delta\sigma=4.4\times10^{-31}$ F m^2, $\Delta\sigma E_0=4000$ Debyes, and $E_0=0.3$ kV cm^{-1}.

curve in order to estimate the intrinsic or saturated reduced dichroism, $(\Delta A/A)_s=(3/2)(3\cos^2\theta-1)$, at infinitely high fields. This value was found to be +0.38, from which the angle θ was calculated to be ±50°. The 462-nm transition moment is directed along the long axis of the DAES molecule, which, therefore, makes an angle of ±50° with respect to the orientation axis of the complex. (This angle represents an *average* of all the bound DAES chromophores and should not be construed as meaning that each and every DAES molecule is bound at this fixed angle.)

The positive $\Delta g/n$ value (cf. Fig. 3 and Table 1) is now verified to result from the angle θ, which is less than ±54.7° (where $(\Delta A/A)_s=0$)[12] for all NaPSS–DAES complexes. It is also clear that the angle is nearly constant over P/D values from 7.1 to 1.9, as is indicated by the $(\Delta g/n)_{\mathrm{DAES}}$ values in Table 1. The average angle of ±50° of bound DAES chromophores indicates that the component of the ground-state permanent dipole moment μ_3 along the orientation axis of the NaPSS–DAES complex (the 3-axis)[7] should amount to approximately 4.5 (=7cos 50°) Debyes per bound DAES. Considering the number of DAES on each NaPSS chain, the total moment of μ_3 might be expected to make a large contribution to the field orientation, but the experimental finding is contrary, as has been discussed above. If the conformational deformation of the whole NaPSS–DAES complex backbone or the local motion of the bound DAES moiety should occur as the result of an applied electric field, the $\Delta A_{/\!/}/A=-2\Delta A_{\perp}/A$ relationship generally breaks down between the parallel $\Delta A_{/\!/}$ and prependicular $\Delta A_{\perp}$ dichroism (Eq. 3 of Ref. 12). This relationship was confirmed to hold up to $E\leq22.4$ kV cm^{-1} in the present work; therefore, in this field range no electrochromic effect[22] is expected in NaPSS–DAES complexes.

The steady-state dichroism signal of DAES at 450 nm was very small in the presence of PGA either at pH 4.1 or at 6.4, again indicating that the interaction between DAES and PGA is weak.

Conclusion

In brief summary, NaPSS–DAES complexes can be oriented by external electric fields to exhibit considerable electric birefringence and dichroism signals, but a complete orientation is still difficult to attain at a practical field strength of about 25 kV cm^{-1}. The overall permanent dipole moment of the complex is nearly zero; the cooperative addition of individual moments of DAES did not occur upon binding to NaPSS. A host polymeric matrix with a larger electric moment must be explored to improve the degree of field orientation. The contribution of the first-order hyperpolarizability anisotropy of the NaPSS–DAES complex to the field orientation seems to be of no special significance. The orientation behavior can be described satisfactorily by the interaction between the electric (linear) polarizability anisotropies $\Delta\alpha$ and $\Delta\sigma$ of the NaPSS chain and the applied field E.

PGA is a rigid and rodlike helix in the low pH region, each residue having a permanent dipole moment of 5—4 Debye units;[9—11] thus, it was thought to be very suitable as the host to cationic DAES and other 2-styrylpyridinium derivatives which show optical nonlinearity.[1] Unfortunately, no appreciable binding occurs in these host–ligand systems, probably because of the weak basicity of the quarternary ring nitrogen atom of DAES and also the weak acidity of the carboxylate of the glutamyl residue. In order for bound optically nonlinear materials to show a larges SHG effect, a smaller molecular weight and rigidly rodlike NaPSS, and other host polyelectrolytes may have to be explored. At the same time, the bound ligands may have to be arranged in such a manner that their permanent dipole moments are additive. In this fashion, a large difference in the excited and ground state moments can be expected; this is one of the conditions for the optical SHG phenomenon.[1]

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