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Electrooptical Studies on Sodium Poly(styrenesulfonate). 1. Electric Polarizability and Orientation Function from Electric Birefringence Measurements

Michel Tricot* and Claude Houssier

Laboratoire de Chimie Physique, Université de Liège, Sart-Tilman B-4000 Liège, Belgium.

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ABSTRACT: Electric birefringence observations on sodium poly(styrenesulfonate) samples of narrow molecular weight distribution have been used to investigate the influence of concentration and molecular weight on their polyelectrolyte properties. The shape of the orientation function was found to approach that of an induced dipole mechanism at low molecular weight but tended toward that of a permanent dipole mechanism at high molecular weight. Although we found that the orientation function of Kikuchi and Yoshioka for a saturating induced dipole could account for this behavior, we showed that the residual polydispersity of the samples was sufficient to justify the fitting of the birefringence curves with the orientation function for a pure induced dipole using two or three polarizability terms. This analysis reinforced our opinion that the shape of the orientation function is not an adequate criterion to distinguish between various orientation mechanisms. The electric polarizability determined either from the Kerr constant or from the fittings of the whole birefringence curves was found to increase with the 2.6 power of the molecular weight M for M smaller than 200 000. This is in fairly good agreement with the predictions of the Manning and Fixman theories. The calculated polarizability values were, however, 1.5–2 times smaller than the experimental values. Possible origins for this discrepancy are discussed.

Introduction

Progress in the understanding of the electrooptical and dielectric properties of polyelectrolyte macromolecules has been greatly hampered by the complexity of the behavior when polydispersity and flexibility effects are concomitantly present. In the case of DNA, both difficulties can now be overcome since homogeneous short and rigid fragments are available from restriction enzyme treatment. For most synthetic polyelectrolytes, there is little hope to obtain perfectly rigid chains, but samples of very low polydispersity have been prepared for calibration of gel permeation chromatography. Such samples thus appear particularly suitable for investigating the applicability of the various electric polarization theories developed during the past 15 years and of the theories proposed for the electric field orientation of these molecules.

This work is aimed at making an experimental approach to these problems using sodium poly(styrenesulfonate) (NaPSS) samples. Previous electrooptical studies on potassium poly(styrenesulfonate) (KPSS) have been performed by Yoshioka and co-workers;[1,2] those studies will be considered in the discussion of our results. A summary of the basic theory on which the analysis of our experimental data is based is first presented.

Theory

1. Orientation Function in Optical Anisotropy Effects. Any optical anisotropy effect resulting from the orientation of particles in an electric field may be expressed by the general equation

$$\mathrm{An} = (\mathrm{An})_s \Phi \tag{1}$$

where An is the steady-state anisotropy (birefringence or dichroism) for a given amplitude E of the applied electric field, $(\mathrm{An})_s$ is the anisotropy at saturation (infinite field), and Φ is an orientation function ($0 < \Phi < 1$) reflecting the degree of orientation of the particle at field E. In this paper, we will be concerned only with birefringence data ($\mathrm{An} = \Delta n$) and we will not discuss the interpretation of this optical term on the basis of structural parameters. Our attention will be mainly focused on the orientation function and on the electric parameters involved. We will only consider here particles with cylindrical symmetry and coincidence of the symmetry axes for the optical and electric parameters.

The general expression for the orientation function at arbitrary fields may be written as[3-5]

$$\Phi = \frac{3}{2}\,\frac{\int_{-1}^{+1} u^2 \exp(-U/kT)\,du}{\int_{-1}^{+1} \exp(-U/kT)\,du} - \frac{1}{2} \tag{2}$$

where kT is the Boltzmann energy term and $u = \cos\theta$, with θ the angle of the particle symmetry axis with the field. U is the interaction energy with the electric field dependent on the orientation mechanism. When simple permanent and induced dipole moments along the symmetry axis are being considered, the interaction energy term is

$$-\frac{U}{kT} = \frac{\mu_P E B}{kT}\cos\theta + \frac{\Delta\alpha E^2}{2kT}\cos^2\theta = \beta u + \gamma u^2 \tag{3}$$

with $\beta = \mu_P EB/kT$ and $\gamma = \Delta\alpha E^2/2kT$. μ_P, B, and $\Delta\alpha$ define, respectively, the permanent dipole, the ratio between the effective field acting on the polyion and the applied electric field, and the excess of electric polarizability with respect to the long and transverse axes of the particle. Note that B has an unknown value and is generally set to unity for long thin particles. Insertion in eq 2 yields the expression for $\Phi(\beta,\gamma)$, which is relatively complex and cannot be presented in analytical form[5]

$$\Phi(\beta,\gamma) = \frac{3}{2}\,\frac{\int_{-1}^{+1} u^2 \exp(\beta u + \gamma u^2)\,du}{\int_{-1}^{+1} \exp(\beta u + \gamma u^2)\,du} - \frac{1}{2} \tag{4}$$

In the case of a pure permanent dipole orientation mechanism, integration of eq 4 is straightforward and yields

$$\Phi(\beta) = 1 - \frac{3}{\beta}\left(\coth\beta - \frac{1}{\beta}\right) \tag{5}$$

For a pure induced dipole moment, the nonanalytical form of $\Phi(\gamma)$ reads

$$\Phi(\gamma) = \frac{3}{4}\left[\frac{\exp(\gamma)/\gamma^{1/2}}{\int_0^{\gamma^{1/2}} \exp(x^2)\, dx} - \frac{1}{\gamma}\right] - \frac{1}{2} \tag{6}$$

Here the integration of eq 4 can be limited to 0 to +1 boundaries since $\exp(\gamma u^2)$ is an even function of u; this is equivalent to saying that "the electrostatic energies for the two orientations at θ and $\pi - \theta$ are equal".[6,7] All the above equations yield at low fields the limiting Kerr law behavior (E^2 dependence):

$$\lim_{E\to 0} \Phi(\beta,\gamma) = (\beta^2 + 2\gamma)/15 \tag{7}$$

At high fields, the limiting form

$$\lim_{E\to\infty} \Phi(\beta,\gamma) = 1 - \frac{3}{\beta + 2\gamma} \tag{8}$$

shows that $1/E$ and $1/E^2$ linear dependences should be observed for permanent and induced dipoles, respectively. When the approach to saturation is not very pronounced, it is always difficult to appreciate from experimental data at which field the extrapolation to infinite field strength may be considered as linear. This is why the results of such extrapolations are often not very reliable.

It has been frequently noticed that the field strength dependence of the anisotropy of polyelectrolytes is not satisfactorily accounted for by the $\Phi(\gamma)$ function, even though bipolar pulse experiments and the ratio of the rise and decay areas in the Kerr law region revealed the dominance of an induced polarization mechanism. To reach a satisfactory fitting of the electrooptical data, we have used in our previous studies a weighted sum of two or three $\Phi(\gamma)$ functions with different electric polarizability terms, a procedure which has been criticized.[7] In the analysis of our results below, we will present some arguments justifying this procedure.

Kikuchi and Yoshioka[2,8] have considered that the above discrepancy between theory and experimental observations could have its origin in the progessive saturation of the ionic polarization as the field strength increases, so that the shape of the field strength dependence would resemble that of a permanent dipole moment at high fields. The general expression for a saturating induced dipole has been given by Neumann and Katchalsky[9] for a polyion with a number N of regularly distributed charged sites surrounded by n mobile but bound counterions:

$$m = \frac{nzeL}{2}\left[\coth\frac{zeLE}{2kT} - \frac{1}{N}\coth\frac{zeLE}{2NkT}\right] \tag{9}$$

where z is the valency of the counterion, e the elementary electric charge, and L the polyion total length. If ϕ defines the fraction of bound counterions, it ensues that $n = N\phi$. In the limit of low fields, eq 9 reduces to the well-known Mandel expression[10] for a nonsaturating induced dipole or induced polarizability:

$$\Delta\alpha = \lim_{E\to 0} m = \frac{N\phi z^2 e^2 L^2}{12kT} \tag{10}$$

At high fields, the saturated induced dipole is obtained:

$$\mu_{\text{sat}} = \lim_{E\to\infty} m = nzeL/2 \tag{11}$$

The orientation function corresponding to the saturating induced dipole has been derived by Kikuchi and Yoshioka[8] and reads for large N values

$$\Phi(\chi) = \frac{3}{2}\,\frac{\int_0^{+1} u^2(\sinh(\chi u)/\chi u)^n\, du}{\int_0^{+1} (\sinh(\chi u)/\chi u)^n\, du} - \frac{1}{2} \tag{12}$$

with $\chi = zeLE/2kT$.

The integration can be limited to the 0 to +1 boundaries for the same reasons as for eq 6. At low fields, the Kerr law behavior for a nonsaturating induced dipole is obtained:

$$\lim_{E\to 0} \Phi(\chi) = \frac{n\chi^2}{45} = \frac{\Delta\alpha E^2}{15kT} \tag{13}$$

The shape of the orientation function derived by Kikuchi and Yoshioka resembles that of a permanent dipole when $n = 1$ but approaches that of an induced dipole when n tends to an infinite value. The fittings of the experimental data with the $\Phi(\chi)$ function are very slow since numerical integration is required unless the n value is fixed, which enables the function to be introduced in the form of a table, as for $\Phi(\gamma)$. In most of the analyses of electrooptical data using the $\Phi(\chi)$ function published so far,[2,7,11] satisfactory fittings have only been reached with very low n values close to unity. In fact, the shape of the $\Phi(\chi)$ function markedly differs from $\Phi(\gamma)$ only if n is smaller than 10.[8] If n really represents the number of bound counterions, low values of n might seem unrealistic since the number of charged sites is of the order of a few hundreds to a few thousands for such polyelectrolytes.

2. Electric Polarizability of Polyelectrolytes. Several attempts have been made to quantitatively correlate the electric polarizability with molecular characteristics of polyelectrolytes. The large induced dipole moment arises from the perturbation of the counterionic atmosphere under the action of the external electric field. Till now, it has been assumed that only the bound counterions are delocalized from the equilibrium position and hence responsible for the electric polarization. Mandel developed a model based on the distortion of the counterion layer bound to a rodlike polyion, resulting in eq 10 mentioned above. Later on, MacTague and Gibbs[12] and Oosawa[13] introduced the concept of the electrostatic repulsion between counterions as one of the factors determining the value of the electric polarizability. The relation of Oosawa, which affects the Mandel expression by a corrective term taking into account this repulsion effect, was successfully applied by Hornick and Weill[14] to the case of sonicated fragments of DNA. In the Oosawa relation

$$\Delta\alpha = \frac{N\phi z^2 e^2 L^2 B}{12kT}\left[\frac{1}{1 + 2\lambda\phi \ln(R/A)}\right] \tag{14}$$

the difficulty is to estimate the value of A which represents the radius of the cylindrical layer of the bound counterions surrounding the polyion, whereas R is the cylindrical volume containing a single polyelectrolyte molecule. The linear density charge (SI units)

$$\lambda = z^2 e^2/4\pi\epsilon\epsilon_0 bkT \tag{15}$$

involved in the various polyelectrolyte theories results from an extension of the Debye–Hückel–Bjerrum treatment for simple electrolytes and contains the bulk dielectric constant of the medium ϵ (78.5 for water), the permittivity of a vacuum $\epsilon_0 = 8.85 \times 10^{-12}$ F·m^{-1}, and the distance between the charged sites projected on the axis of the polyion, b.

In a previous study of poly(vinylpyridinium) salts in water, we showed that the conformation of these polyions at infinite dilution can be modeled as a semirigid chain.[11,15] In these experiments, only high molecular weight samples

($M > 2 \times 10^5$) were investigated; the electric polarizability appeared to be molecular weight independent, whereas the average relaxation time of the electric birefringence increased with molecular weight. The only explanation we could find to explain this peculiar behavior was to relate the electric polarizability derived from the birefringence experiments to the dielectric increment in the high-frequency dispersion region, which also remains molecular weight independent.[16] In a further development of the earlier Mandel theory, van der Touw and Mandel[17] proposed the following explanation to justify the two dielectric dispersions experimentally observed on polyelectrolyte solutions. They described the polyion as a broken chain including rigid subunits separated by potential barriers. The bound counterions could move along the whole polyion, giving rise to the static dielectric increment at low frequency, but can also fluctuate along short rigid subunits causing the high-frequency dispersion. Such a model is in fairly good agreement with the semirigid chain models, i.e., weakly bending rod or wormlike chain, which have been shown to describe the hydrodynamic behavior of polyions at very high dilution.[11] Minakata et al.[18,19] objected that the separation between the dispersion regions could lie in different rates of fluctuation for the association–dissociation processes between the counterions and the polyion. However, such an assumption does not explain why the high-frequency dispersion disappears in the case of rigid polyions or very low molecular weight polyelectrolytes. The dielectric behavior of polyelectrolytes remains the subject of much controversy[20] and will not be discussed here.

New approaches to the interpretation of the electric polarizability of linear polyions have been recently presented by Manning[21,22] and Fixman.[23,24] Starting with a two-state model which can be formulated as a chemical reaction between free and bound (or condensed) counterions, Manning[22] derived the following expression for the electric polarizability:

$$\Delta\alpha_{\text{Manning}} = \frac{nz^2e^2L^2}{12kT}\left[\frac{1}{1 - 2(|z|\lambda - 1)\ln \kappa b}\right] \tag{16}$$

The Debye–Hückel screening parameter κ is an explicit function of the ionic strength (I) in mol·L^{-1}:

$$\kappa = (8\pi \times 10^3 N_A Q I)^{1/2} \tag{17}$$

N_A is Avogadro's number and Q is the Bjerrum length

$$Q = e^2/4\pi\epsilon\epsilon_0 kT = \lambda b \tag{18}$$

equal to 7.1 Å for water at 25 °C.

Relation 16 allows prediction of the change of $\Delta\alpha$ with ionic strength and accounts for the counterion repulsion through the Debye–Hückel parameter. With respect to the relation of Oosawa, the Manning relation has the major advantage of requiring only the knowledge of easily obtainable parameters directly related to the characteristics of the polyion and of the medium. The treatment of Manning was recently applied to the interpretation of the electric dichroism of sonicated DNA as a function of ionic strength.[25] Charney et al.[25,26] showed that the Manning relation predicts similar values of the orientation degree for DNA in the presence of monovalent and divalent counterions at the same ionic strength, as experimentally observed. It must be pointed out that, on the basis of relation 16, the polarizability of the bound counterions is expected to decrease with decreasing ionic strength, in contrast to various experimental results.[22] Note that Charney and Lee[27] could satisfactorily account, on the basis of Manning's treatment, for the effect of the dielectric constant on the degree of orientation of DNA in water–ethanol mixtures. The dielectric constant appears in the density charge and Debye–Hückel parameters and also influences the magnitude of the orienting electric field.

Recently, Fixman reconsidered the theory of the response of rigid polyions to external electric fields. In the first of a series of investigations,[23] he studied the perturbations induced in the distribution of small ions by steady or oscillating electric fields in the case of spherical polyelectrolytes. An expression allowing estimation of the frequency dependences of the real and imaginary parts of the dielectric increment was derived. In a second investigation,[24] Fixman calculated the induced dipole moment of a cylindrical polyion in the case of a steady electric field, leaving the discussion of oscillating fields for a further development. The cylinder is assumed to be smooth and charged to a uniform surface density. The calculations are restricted to weak external electric fields, which should correspond to the experiments performed in the Kerr region. The Fixman relationship for the electric polarizability may be written as (in SI units)

$$\Delta\alpha_{\text{Fixman}} = \frac{4\pi\epsilon\epsilon_0 LK}{\gamma_a^2}\left(\frac{z_1}{z_1 - z_2}\right)\left[1 - \frac{2\tanh(\gamma_a L/2)}{\gamma_a L}\right] \tag{19}$$

in which L is the length of the cylinder of radius a. z_1 and z_2 refer to the electric charges of the counterion and the coion, respectively. γ_a^2 (molecules·m^{-2}) is a surface density charge parameter given by

$$\gamma_a^2 = 4\pi\bar{c}_1 K/\sigma = 4\pi \times 10^3 N_A c_1 K/\sigma \tag{20}$$

where $\bar{c}_1$ represents the bulk concentration of the counterions and c_1 the concentration of the counterions expressed in mol·L^{-1} and σ is the number of bound counterions per unit length. K is a proportionality constant connected to the axial ratio L/a:

$$K = \left(2\ln\frac{2L}{a} - \frac{14}{3}\right)^{-1} \tag{21}$$

In the derivation of this expression, it was assumed that the double layer of counterions is thin compared to the radius of the cylinder, which can be regarded as a crude approximation in the experimental conditions of low salt concentration considered here. Nevertheless, the theory of Fixman predicts at very low monovalent salt concentration a value of $\Delta\alpha$ in satisfactory agreement with Hornick and Weill's data for sonicated DNA.[24]

Experimental Section

1. **Materials.** The sodium poly(styrenesulfonate) samples were purchased from Pressure Chemical Co.; they were specifically designed for GPC calibration in aqueous media because of their narrow molecular weight distribution. The samples have been prepared by monosulfonation of polystyrene standards, following a modification of the procedure of Carrol and Eisenberg,[28] which involves a reaction of polystyrene with 100% sulfuric acid in the presence of silver sulfate as catalyst. Under these conditions, no degradation or cross-linking occurs.

The molecular weight characterization of the samples was performed by Pressure Chemical Co. with osmotic pressure experiments using a Knauer instrument (0.1 M Na_2SO_4 at 37 °C). The degree of sulfonation, δ, estimated on the basis of sulfur analysis by X-ray fluorescence, ranges from 90% to 70% for increasing molecular weights. The knowledge of this parameter allows another estimation of the number-average molecular weight of NaPSS from the $\bar{M}_n$ values of the parent polystyrene samples. Good agreement was obtained with the osmometry results, except for the highest molecular weight sample F. Table I collects the $\bar{M}_n$ and δ values for the different NaPSS samples, as well as the

Table I
Values of the Degree of Sulfonation δ and of the Average Molecular Weights for the Sodium Poly(styrenesulfonates) and the Parent Polystyrenes

	parent polystyrenes			sodium poly(styrenesulfonates)			
sample	$\bar{M}_w$	$\bar{M}_n$	$\bar{M}_w/\bar{M}_n$	δ	$\bar{M}_n$(calcd)	$\bar{M}_n$(measd)	$\bar{M}_n \times 10^{-3}$
O	9 200	9168		0.90	17 340	15 800	16.1 ± 0.8
A	20 400	15 100	1.35	0.88	31 400[a]	28 260	31.5 ± 3.5
B	32 600	36 300		0.89	68 300	66 100	67.2 ± 1.1
C	53 700	51 150	1.05	0.89	96 200	104 000	100.0 ± 4.0
D	111 000	111 000	1.00	0.81	200 400	207 000	204.0 ± 3.0
E	200 000[c]	200 000[c]		0.80[b]	400 000	400 000	400.0 ± 5.0
F	391 000	350 000	1.12	0.70	593 000	760 000	765.0 ± 25

[a] $\bar{M}_n$ = 34 900 in NaCl 0.1 M. [b] Data not given by Pressure Chemical Co.; δ is assumed to be of the order of 0.8. [c] ±5%.

various molecular weight averages and the polydispersity indexes of the parent polystyrenes mentioned in the data sheets supplied by Pressure Chemical Co. The intrinsic viscosities in 0.1 M Na_2SO_4 at 25 °C are also given.[29] Although no light scattering data are yet available for these samples, we can consider that the polydispersity indexes are lower than 1.1.

Owing to the discrepancy in the molecular weight values observed for the NaPSS sample F, we performed viscosity and sedimentation experiments for this sample. The viscosity–molecular weight relationship of Takahashi et al.[30] cannot be applied to the present case. It was indeed established for fully sulfonated NaPSS samples, but our degree of sulfonation does not exceed 90% and is equal to 70% in the particular case of sample F. The viscometric relationship determined for these samples[29] in 0.1 M Na_2SO_4 is

$$[\eta] = 3.24 \times 10^{-5} M^{0.802} \tag{22}$$

so that intrinsic viscosity of sample F (1.66 $dL \cdot g^{-1}$) yields a molecular weight of 7.4×10^5. Another molecular weight determination is based on the sedimentation coefficient at zero concentration ($s_0 = 11.0 \times 10^{-13} s_v$), intrinsic viscosity ($[\eta] = 1.69$ $dL \cdot g^{-1}$), and partial specific volume ($\bar{v} = 0.58$ $cm^3 \cdot g^{-1}$) in 0.2 M NaCl. By applying the Flory–Mandelkern relationship[31,32]

$$\bar{M}_{s-\eta} = \left[\frac{N_A}{\Phi_F{}^{1/3} p^{-1}}\right]^{3/2} \left[\frac{s_0 \eta_0}{1 - \bar{v}\rho_0}\right]^{3/2} [\eta]^{1/2} \tag{23}$$

in which the viscosity η_0 and the density ρ_0 of water at 25 °C are, respectively, equal to 0.90693×10^{-2} P and 1.00528 $g \cdot cm^{-3}$,[33] we found $\bar{M}_{s-\eta} = 7.9 \times 10^5$.

Nagasawa and Eguchi[34] noticed a pronounced effect of molecular weight and ionic strength on the Flory–Mandelkern coefficient $\Phi_F{}^{1/3} p^{-1}$ in the case of NaPSS in NaCl solutions. In the limit of high molecular weight and high ionic strength, $\Phi_F{}^{1/3} p^{-1}$ tends to a value of the order of 2.0×10^6, which was used in our calculation of $\bar{M}_{s-\eta}$ (a smaller value than that (2.5×10^6) usually accepted for nonionic polymers). Table I shows the average $\bar{M}_n$ values retained below, which are the averages between the measured and calculated $\bar{M}_n$ values; for sample F, a molecular weight of $(7.65 \pm 0.25) \times 10^5$ will be used.

All Pressure Chemical Co. NaPSS samples have been dialyzed in order to remove possible salt contaminants. However, even after drying for several days at 40 °C under vacuum, the dialyzed samples still contained residual amounts of water (1–7% on the basis of elemental analysis), also detected by Mandel et al.[35] This water content was taken into account in the calculation of the polyelectrolyte concentration.

2. Method. Electric birefringence and birefringence relaxation experiments have been performed at 20 °C at a wavelength of 550 nm with a previously described instrument which involves a fast transient recorder and a minicomputer for the storage and the treatment of the signals.[3,5,36] The pulse generator (Cober Electronics) is able to deliver single rectangular pulses at 2.5 kV, which for our Kerr cell (electrode separation of 1.5 mm) corresponds to an applied electric field of the order of 16 kV/cm. For the reversing pulse method, the association of two such generators yields two consecutive pulses, at 2.5 kV, of reversed polarity with a transition time lower than 1 μs.

The fittings of sets containing 20–40 data points of the birefringence vs. field strength were made by using a general multiparametric curve-fitting program.[5,37] The deviation between the calculated and experimental curves was characterized by the sum of the squares of the relative deviations

$$Y = \sum_i \frac{(Y_{i,\text{measd}} - Y_{i,\text{calcd}})^2}{Y_{i,\text{measd}} Y_{i,\text{calcd}}} \tag{24}$$

Results and Discussion

It is worth noting that we did not observe in aqueous media any change of birefringence sign similar to those described for NaPSS in formamide:[38] Δn remains always negative. We verified that the electric dichroism corresponding to the electronic transitions at 225 and 261 nm is also negative; this distinguishes NaPSS from the poly(4-vinylpyridinium) salts, for which a small positive dichroism appeared around 285 nm as discussed in ref 39 and 40.

1. Orientation Mechanism. The nature of the orientation mechanism of synthetic and natural polyelectrolytes is still controversial: many workers have found an experimental orientation function which closely resembles the shape of that theoretically computed for a pure permanent dipole moment. For various polyions, in particular those which possess a vinylic chain as the main backbone [poly(ethylenesulfonic acid) salts, poly(styrenesulfonic acid) salts, and poly(vinylpyridinium)halides], the molecular structure of the repeating unit precludes the existence of a permanent dipole contribution. It is thus inferred that the orientation of these polyions under an external electric field arises essentially from the polarization of the counterionic atmosphere. As discussed more extensively below, the shape of the orientation function cannot be taken as a criterion for deducing the nature of the orientation mechanism. One of the best ways to evidence this mechanism is the bipolar pulse method.[41] In agreement with the recent results of Yamaoka and Ueda,[42] we did not detect for the NaPSS solutions any transient at the reversal of the electric field, whatever the conditions of concentration, molecular weight, and electric field strength (1–10 kV/cm). This also excludes the presence of any slow-induced dipole moment, so the orientation mechanism retained is the fast-induced dipole moment, as also previously concluded for poly(*N*-alkyl-4-vinylpyridinium bromide) in water.[15]

2. Orientation Function. Figure 1 shows typical Δn vs. E^2 curves observed as a function of sample concentration in water. The approach of saturation at high fields (for the lowest concentrations) allows the optical anisotropy term Δn_s to be obtained with very good accuracy from a plot of Δn vs. E^{-2} (Figure 2a). For the low molecular weight sample A, the Kerr law ($\Delta n = K_B E^2$) is obeyed over the entire field strength range investigated (Figure 3) so only the value of the Kerr constant K_B can be derived from these experiments. The measurements performed at very low electric fields ($E \sim 0.4$–2 kV/cm) also allow the de-

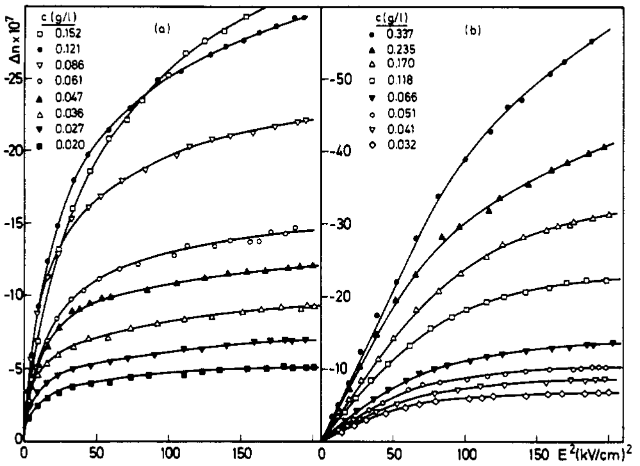

Figure 1. Field strength dependences of the electric birefringence for the NaPSS samples F (a) and B (b) at various concentrations in water.

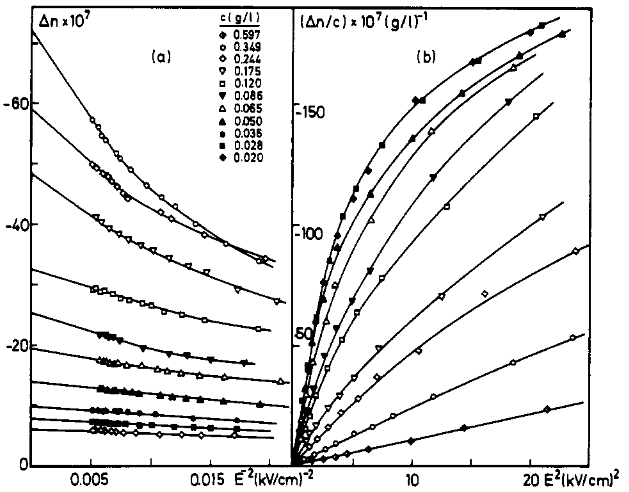

Figure 2. Extrapolation of the birefringence to infinite electric field strength (a) and variation of the specific birefringence with E^2 at low electric field (sample D) (b).

termination of the Kerr constant even if the saturation of the birefringence is reached at relatively low fields (Figure 2b).

The analysis of these data has been made in several steps. First, an estimation of Δn_s and $\Delta\alpha = 15kTK_B/\Delta n_s$ was made by a graphical procedure. For the low molecular weight sample A, $\Delta\alpha$ is estimated by using the optical anisotropy extrapolated to $M \sim 31500$. Hence, we must keep in mind that the $\Delta\alpha$ values for this sample can be affected by a somewhat larger uncertainty than the other ones. A second procedure is based on the fitting of the entire Δn vs. E^2 curve as indicated in the Experimental Section, using the orientation function for an induced dipole $\Phi(\gamma)$ (eq 6). This implies that Δn_s and a set of two or three electric polarizability terms $\Delta\alpha_i$ affected by their respective contributions ω_i, should be kept as adjustable parameters, i.e., four to six adjustable parameters, with the mean electric polarizability given by $\Delta\alpha = \sum_i \omega_i \Delta\alpha_i$. The quality of the fitting is given by the value of Y (sum of the squares of the relative deviations) previously defined (eq 24). For a given sample at x different concentrations, we can also define an average value $\bar{Y} = \sum Y/x$. We consider that a very satisfactory fitting is achieved when Y is equal to or lower than 0.01 (values down to 0.002 are observed in some favorable situations). For sample B, the fittings with $\Phi(\gamma)$ involving two $\Delta\alpha_i$ contributions are very good, but for the higher molecular weight samples C–F, three $\Delta\alpha_i$ contributions were required. Table II presents a comparison of the different Δn_s and $\Delta\alpha$ values calculated for sample C. It should be noted that the respective contributions ω_i of the three polarizability terms are rather similar for all the fittings: 12 ± 2, 48 ± 5, and 40 ± 5% for the higher, intermediate and lower $\Delta\alpha_i$ terms, respectively. As shown previously,[11] the Δn_s values derived from the graphical extrapolation and from the fitting with $\Phi(\gamma)$ are in fairly good agreement, within 0.7–1.4%, whereas the $\Delta\alpha$ values calculated by the two procedures differ by 1.8–3.6%, the electric polarizability derived from the Kerr constant often being somewhat larger. Only the mean $\overline{\Delta n_s}$, and $\overline{\Delta\alpha}$, values given by the two procedures will be retained for further discussion.

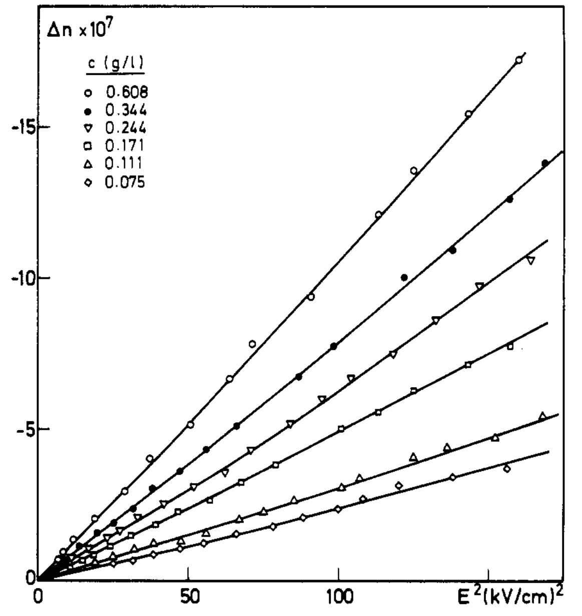

Figure 3. Kerr behavior of the birefringence for low molecular weight sample A at various concentrations.

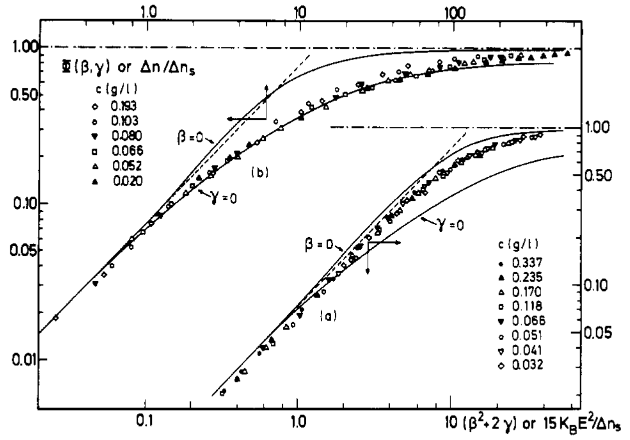

Figure 4. Comparison of the experimental orientation functions for the samples B (a) and E (b) with the theoretical orientation functions $\Phi(\gamma)$ and $\Phi(\beta)$.

With the aid of a bilogarithmic plot analogous to that used by Kikuchi and Yoshioka,[2] it is possible to clearly display the change of the shape of the experimental orientation function with the molecular weight (Figure 4). When Φ or $\Delta n/\overline{\Delta n_s}$ is plotted vs. $\beta^2 + 2\gamma$ or $15K_BE^2/\overline{\Delta n_s}$, it is seen that the orientation function for the low molecular weight samples B and C approaches that for a pure induced dipole moment $\Phi(\gamma)_{1\,\text{term}}$. On the contrary, the experimental orientation functions, which are identical for the high molecular weight samples D, E, and F, approach

Table II

Birefringence at Saturation and Electric Polarizability Values Obtained by Different Calculation Procedures (Sample C)

	graphical procedure			fitting with $\Phi(\gamma)$			mean values		fitting with $\Phi(\chi)$			
c, g·L^{-1}	$-\Delta n_s \times 10^7$	$\Delta\alpha \times 10^{32}$, F·m^2	$K_B \times 10^{18}$, V^{-2} m^2	$-\Delta n_s \times 10^7$	$\Delta\alpha \times 10^{32}$, F·m^2	$\bar{Y}^a$	$-\Delta n_s \times 10^7$	$\Delta\alpha \times 10^{32}$, F·m^2	$-\Delta n_s \times 10^7$	$\Delta\alpha \times 10^{32}$, F·m^2	n	$\bar{Y}^b$
0.348	83.4	4.62	6.4	84.8	4.28	0.0085	84.1 ± 0.7	4.45 ± 0.16	88.6	4.41	2.10	0.024
0.214	48.6	6.08	4.9	49.2	6.57	0.0032	48.9 ± 0.3	6.32 ± 0.25	56.3	5.58	1.38	0.030
0.144	35.2	7.86	4.6	35.8	7.78	0.0084	35.5 ± 0.3	7.82 ± 0.04	40.7	7.10	1.58	0.023
0.103	24.5	9.80	4.0	24.9	9.20	0.0067	24.7 ± 0.2	9.5 ± 0.30	27.5	8.66	1.77	0.022
0.077	19.0	10.04	3.1	18.6	9.45	0.0088	18.8 ± 0.2	9.75 ± 0.30	20.4	9.65	1.79	0.031
0.057	13.9	10.55	2.4	13.7	10.15	0.0130	13.8 ± 0.1	10.35 ± 0.20	15.6	10.40	1.41	0.018
0.043	10.2	10.11	1.7	10.2	9.89	0.0057	10.2 ± 0.0	10.0 ± 0.10	11.1	10.14	1.51	0.021
0.031	7.8	11.52	1.5	8.0	11.62	0.0045	7.9 ± 0.1	11.57 ± 0.05	8.7	12.95	0.97	0.022

[a] $\bar{Y} = 0.0074$. [b] $\bar{Y} = 0.024$.

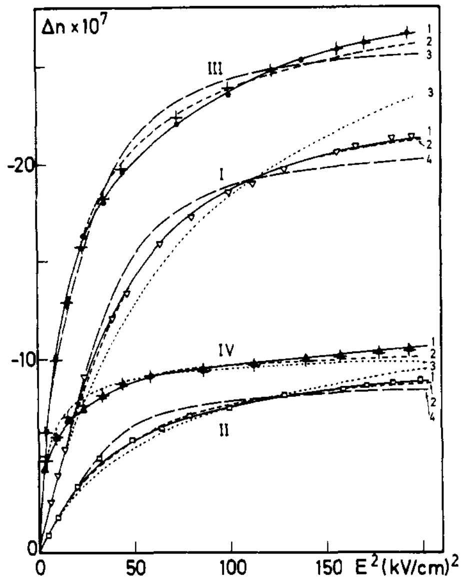

Figure 5. Some examples of fitting with various orientation functions for two NaPSS samples; the data issued from these fittings are collected in Table IV.

the shape of $\Phi(\beta)$ over a wide field strength range but depart markedly therefrom in the limit of high degree of orientation ($\Phi > 0.7$–0.8). In their study on potassium poly(styrenesulfonate), Kikuchi and Yoshioka[2] stated that their experimental orientation curves are similar, irrespective of molecular weight, and that all resemble $\Phi(\beta)$ but also tend progressively to $\Phi(\gamma)$ at very high electric fields. They did not detect, however, orientation curves which approached $\Phi(\gamma)$, even with low molecular weight samples. This could arise from the effect of the polydispersity of their fractions. The main feature of Figure 4 is that, even with samples of narrow molecular weight distributions, the use of a single theoretical orientation function is not sufficient to describe the field strength dependence of the birefringence of such polyelectrolytes at all molecular weights.

Even though the bipolar pulse experiments and the polyelectrolyte structure seem compatible only with a purely induced polarization mechanism, we tentatively fitted our data with the $\Phi(\beta,\gamma)$ and $\Phi(\beta)$ functions (eq 4 and 5). Both yielded unsatisfactory $\bar{Y}$ values, as shown in Table III, except for the high molecular weight samples E and F: $\Phi(\beta)$ accounts for the orientation of these samples, but only by using a weighted sum of orientation functions corresponding to different permanent dipole moments. Figure 5 shows some results of fitting for samples C and E at two concentrations; the values given by the various fitting procedures are collected in Table IV. In several cases, the fittings with $\Phi(\beta)$ yielded two rather close values of μ_i and the addition of a third μ_i term did not improve markedly the $\bar{Y}$ value.

The discrepancy between the experimental orientation functions with respect to $\Phi(\gamma)$ could be also attributed to the saturation of the polarization at high fields, as suggested by Kikuchi and Yoshioka;[2,8] therefore we have tried to fit our data by using the function $\Phi(\chi)$ (eq 12). In this case, it is assumed that the saturation of the ionic polarization occurs before the saturation of the orientation of the polyions. Table III indicates that the $\bar{Y}$ values, of the order of 0.02–0.03 for all the samples, are higher than those obtained with $\Phi(\gamma)_{3\,\text{terms}}$. According to the fact that we make use in the present case of only three adjustable parameters (Δn_s, $\Delta\alpha$, and n) instead of four or six with $\Phi(\gamma)$, we can, however, consider that the fittings with $\Phi(\chi)$ are

Table III
Comparison of $\bar{Y}$ Values Yielded by the Fittings Using Different Orientation Functions

sample	$\Phi(\gamma)_3$ terms	$\Phi(\gamma)_2$ terms	$\Phi(\gamma)_1$ term	$\Phi(\beta, \gamma)$	$\Phi(\beta)_1$ term	$\Phi(\beta)_2$ terms	$\Phi(\beta)_3$ terms	$\Phi(\chi)$
B	0.011	0.010	0.061	0.014	0.105			0.023
C	0.0074	0.015	0.083	0.025	0.115	0.115		0.024
D	0.0070	0.033		0.057	0.029	0.022	0.014	0.034
E	0.0058	0.036		0.070	0.037	0.013	0.0088	0.018
F	0.010	0.079		0.084	0.055	0.021	0.011	0.024

Table IV
Comparison of Some Fitting Results for Two NaPSS Samples at Two Concentrations (Figure 5)

sample	c, g·L^{-1}	function	no. of electric terms	ω_i, $\Delta\alpha_i$[a] or ω_i, μ_i[a]	μ_{Debye}	$\Delta\alpha \times 10^{32}$, F·m^2	$-\Delta n_s \times 10^7$	Y	curve no.
C	0.103 (I)	$\Phi(\gamma)$	1	9.59		9.59	21.7	0.070	4
		$\Phi(\gamma)$	2	35.7%, 18.47 + 64.3%, 5.16		9.20	24.9	0.007	1
		$\Phi(\beta)$	2	40%, 4610 + 60%, 4910	4790		42.3	0.160	3
		$\Phi(\chi)$	1	8.66; n = 1.77		8.66	27.5	0.022	2
	0.043 (II)	$\Phi(\gamma)$	1	10.60		10.60	8.9	0.105	4
		$\Phi(\gamma)$	2	48%, 17.08 + 52%, 4.06		10.30	9.8	0.006	1
		$\Phi(\beta)$	2	15%, 5480 + 85%, 4900	4990		15.5	0.121	3
		$\Phi(\chi)$	1	10.14; n = 1.51		10.14	11.1	0.021	2
E	0.103 (III)	$\Phi(\gamma)$	2	29%, 84.47 + 71%, 10.0		31.6	28.8	0.030	3
		$\Phi(\gamma)$	3	11.9%, 136.7 + 50.2%, 24.5 + 37.9%, 3.4		29.8	29.3	0.003	1
		$\Phi(\beta)$	2	17.8%, 11500 + 82.2%, 10280	10500		34.6	0.013	+
		$\Phi(\chi)$	1	33.0; n = 0.57		33.0	31.8	0.017	2
	0.036 (IV)	$\Phi(\gamma)$	3	15.1%, 396.1 + 44.8%, 65.2 + 40.1%, 3.5		90.4	11.5	0.007	1
		$\Phi(\beta)$	1	24550	24550		11.0	0.088	3
		$\Phi(\beta)$	3	23.6%, 46100 + 56%, 18700 + 20.4%, 5400	22450		12.5	0.005	+
		$\Phi(\chi)$	1	161.0; n = 0.17		161.0	11.4	0.017	2

[a] The electric polarizabilities and the permanent dipole moments are expressed in 10^{-32} F·m^2 and in Debye units respectively.

satisfactory (Figure 5). The Δn_s values are generally somewhat larger than the average values calculated with $\Phi(\gamma)$, while the electric polarizabilities agree generally for the low molecular weight samples. Some discrepancy in the $\Delta\alpha$ values has been observed for the high molecular weight samples at high dilution (Table IV). However, the main feature of the latter fittings lies in the fact that the parameter n, defined as the number of mobile counterions, remains of the order of unity: n varies between 2 and 1 for samples B and C and between 1 and 0.2 for the other samples. Such low n values are inconsistent with the effective charges borne by the polyion and differ therefrom by several orders of magnitude. Similar values previously reported[2,7,8] would be possibly explained by the fact that the counterion repulsion has been neglected, an effect that would necessarily reduce the n value.

3. Concentration and Molecular Weight Dependences of the Electrooptical Parameters. The mean values of the birefringence at saturation decrease linearly with concentration for $c < 0.15$ g·L^{-1} (Figure 6a). The optical anisotropy factor $g_a - g_b$ at infinite dilution can be estimated with the aid of the relation

$$\Delta n_s = \frac{2\pi c\bar{v}(g_a - g_b)}{n_0} \tag{25}$$

where n_0 is the refractive index of the solvent (1.3325) and $\bar{v}$ the partial specific volume measured by pycnometry: $\bar{v}$ = 0.565 ± 0.005 cm^3·g^{-1} for the NaPSS in water. Figure 6b shows that $g_a - g_b$ remains constant at high molecular weight but appreciably decreases with $\bar{M}_n$ for $\bar{M}_n < 2 \times 10^5$.

The variations of the average electric polarizabilities with concentration reflect the so-called polyelectrolytic effect, i.e., a sharp increase of $\Delta\alpha$ with dilution. Similarly, with the poly(vinylpyridinium) salts, the electric polarizability can be extrapolated to zero concentration in a plot of $(\Delta\alpha)^{-1}$ vs. c. Although such plots appear linear for samples A, B, and C over the whole concentration range (Figure 7a) and for sample D when $c < 0.15$ g·L^{-1}, a pronounced curvature is observed for the high molecular weight samples E and F (Figure 7b). In the latter case, a linear variation is obtained for $(\Delta\alpha)^{-1}$ vs. c^2 (Figure 7b). We have presently

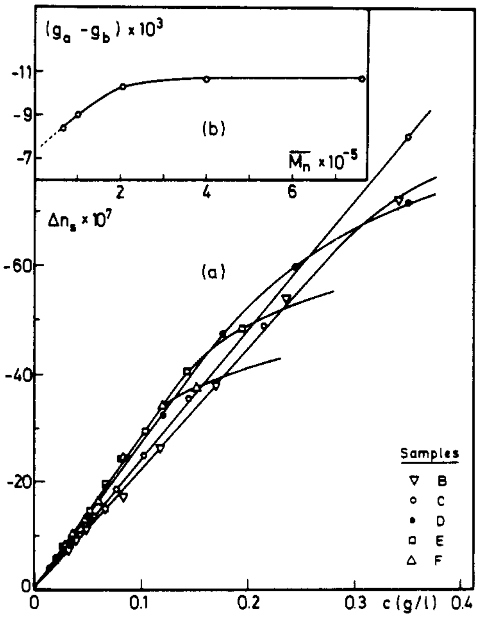

Figure 6. Concentration dependences of the birefringence at saturation for different NaPSS samples (a) and variation of the optical anisotropy factor with the molecular weight (b).

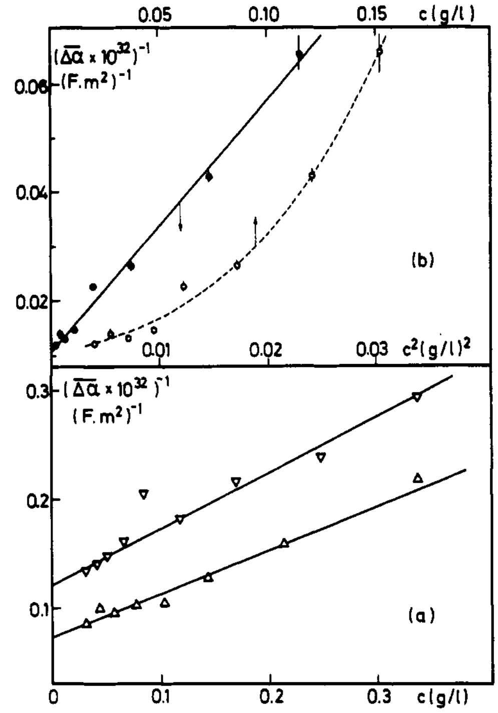

Figure 7. Extrapolation of the electric polarizability values to zero concentration for samples B (▽), C (△), and F (○, ●).

Table V
Optical Anisotropy Factors, Electric Polarizabilities, and Contour Lengths of the NaPSS Samples

sample	$-(g_a - g_b) \times 10^3$	$\Delta\alpha_0 \times 10^{32}$, F·m²	B^* or B^{**}	L_T, Å
A	7.77	0.90 ± 0.05	1.57[a]	407
B	8.41	8.2 ± 0.2	0.51[a]	860
C	9.01	13.7 ± 0.6	0.40[a]	1282
D	10.29	138 ± 17	0.19[a]	2730
E	10.70	130 ± 8	2.70[b]	5390
F	10.70	95 ± 7	2.32[b]	10900

[a] B^*, in L·g^{-1}. [b] B^{**}, in L^2·g^{-2}.

no satisfactory explanation for this $(\Delta\alpha)^{-1}$ dependence. Following the observations of Mandel and co-workers,[16,43] the inverse of the reduced dielectric increment $(\Delta\epsilon/c)^{-1}$, directly related to the inverse of the electric polarizability, also varies linearly with c, whatever the molecular weight of the polyelectrolyte. Linear least-squares regression analysis yields the electric polarizability values at infinite dilution, $\overline{\Delta\alpha_0}$, given in Table V with correlation coefficients higher than 0.99. The values of the slopes B^* (or B^{**} for the c^2 dependence) of polarizability–concentration relationships are also given.

The variation of the electric polarizability at infinite dilution and that measured at a very low concentration (close to 0.03 g·L^{-1}) with molecular weight are shown in the bilogarithmic plot of Figure 8. It is worth noting that the electric parameters extrapolated to zero concentration can be considered as free from electrostatic and hydrodynamic interactions. Two molecular weight domains can be distinguished, more clearly than on the basis of the optical anisotropy factor. At low molecular weight ($\bar{M}_n < 2 \times 10^5$), $\overline{\Delta\alpha_0}$ increases with a power of 2.6 ± 0.2 of the molecular weight. Such a strong dependence of $\Delta\alpha$ vs. M indicates a rigid chain behavior of our polyions at infinite dilution. At high molecular weight ($\bar{M}_n > 2 \times 10^5$), $\overline{\Delta\alpha_0}$ remains almost independent of molecular weight, or even slightly decreases. The lower $\overline{\Delta\alpha_0}$ found for sample F certainly arises from its lower degree of sulfonation ($\delta = 0.7$). Our results may be compared with those of Kikuchi and Yoshioka for potassium poly(styrenesulfonate). At very low concentration ($c = 0.01$ g·L^{-1}), they found $\Delta\alpha$ values of about 6.1×10^{-32}, 7.8×10^{-32}, 44.5×10^{-32}, and 278×10^{-32} F·m^2 for samples of viscometric-average molecular weight equal to 0.45×10^5, 0.71×10^5, 2.62×10^5, and 7.66×10^5, respectively (Figure 7 of ref 2). The quantitative agreement is very good for the second of these samples with the value we determined for sample B (Table V). However, they obtained a continuous increase of $\Delta\alpha$ with M, with an exponent of M of the order of 1.5, over a molecular weight range identical with that presently studied (Figure 8).

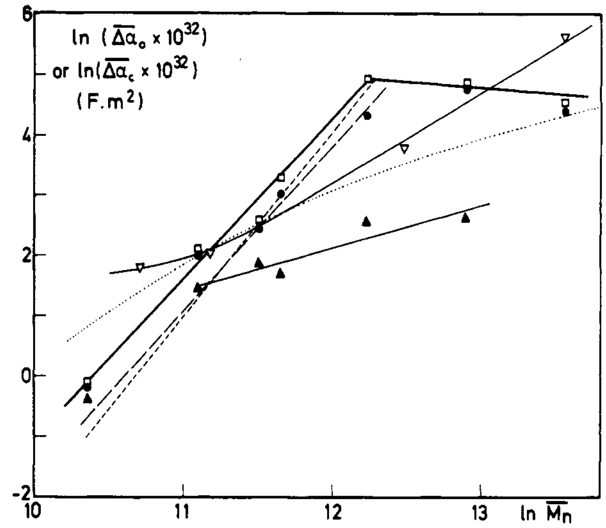

Figure 8. Molecular weight dependences of the electric polarizability experimental values at zero concentration (□), at concentrations of the order of 0.20–0.25 g·L^{-1} (▲), and at concentrations equal to 0.075, 0.032, 0.031, 0.021, 0.028, 0.027, and 0.020 g·L^{-1} for samples A, B, C, G, D, E, and F, respectively (●). Experimental values (▽) for KPSS at $c = 0.01$ g·L^{-1} from Kikuchi and Yoshioka;[2] calculated values (Table VI) according to Manning (- - -), Fixman (— — —), and Elias and Eden (···).

The discrepancy in the exponents could arise from a larger polydispersity of the KPSS samples of Kikuchi and Yoshioka, obtained by fractional precipitation. The presence of high molecular weight species in the fractions could possibly reduce the slope of the $\Delta\alpha$ vs. M dependence. Otherwise, in the high molecular weight range, the $\Delta\alpha$ values of KPSS continue to increase in opposition with our observation on the NaPSS samples. We also stated previously[11] that the electric polarizability of the poly(2-vinylpyridinium)salts was also almost molecular weight independent, but we only investigated the high molecular weight range ($M > 1.6 \times 10^5$). We can tentatively explain this difference by the fact that both the poly(2-vinylpyridinium) salts and the sodium poly(styrenesulfonates) of high molecular weight presently studied (D, E, and F) are not fully charged: δ ranges from 0.63 to 0.76 for the former[11] and from 0.70 to 0.80 for the latter (Table I). On the contrary, the KPSS prepared by Yoshioka et al.[1,2] from a polymerization of the potassium p-styrenesulfonate monomer has a degree of charge equal to unity. In our case, we should consider that, owing to the presence of uncharged sites (or of short sequences of them) in the main chain, the delocalization of the counterions occurs only on subunits of the chain. It will be necessary to compare the electric polarizability for two NaPSS samples of similar molecular weights but different degrees of charge in order to clarify this question.

4. Comparison between the Experimental and

Table VI
Calculation of the Electric Polarizability on the Basis of the Theories of Mandel, Manning, and Fixman

sample	$\overline{\mathrm{DP}}_n$	δ	N	L_T, Å	λ_{eff}	ϕ	$\Delta\alpha_{Mandel} \times 10^{32}$, F·m^2	$\Delta\alpha_{exptl} \times 10^{32}$, F·m^2
A	163	0.88	143	407	2.55	0.608	7.6	0.9
B	344	0.89	306	860	2.58	0.612	73	8.2
C	513	0.89	456	1282	2.58	0.612	242	13.7
D	1093	0.81	885	2732	2.35	0.574	2000	137.8
G	558	1.00	558	1395	2.90	0.655	374	27.8

sample	X	$\Delta\alpha_{Manning} \times 10^{32}$, F·m^2	$\sigma \times 10^{10}$, m^{-1}	$\gamma_a^2 \times 10^{-12}$, molecules·m^{-2}	K	$\gamma_a L/2$	$\frac{1 - 2\tanh(\gamma_a L/2)}{\gamma_a L}$	$\Delta\alpha_{Fixman} \times 10^{32}$, F·m^2
A	0.051	0.39	0.214	7.71	0.218	0.0565	0.00107	0.54
B	0.050	3.68	0.218	5.71	0.165	0.1027	0.00350	3.78
C	0.050	12.2	0.218	5.05	0.146	0.1440	0.00686	11.1
D	0.058	117.0	0.186	4.84	0.119	0.3006	0.02910	85.3
G	0.043	15.9	0.262	4.10	0.142	0.1412	0.00659	13.9

Calculated Electric Polarizabilities. Only the $\overline{\Delta\alpha}$ values in the low molecular weight range (3×10^4 to 2×10^5) will be compared here to those calculated on the basis of the theoretical treatments of Mandel,[10] Manning,[22] and Fixman.[24] Even though the present measurements were performed in the absence of added salt, we consider that a residual bulk ionic strength of the order of 10^{-5} mol·L^{-1} is present in our solutions. Indeed, our samples have been dialyzed, and contact between the solutions and atmosphere has been avoided as long as possible. However, possible contamination by carbon dioxide or ionic traces cannot be excluded. With some Δn vs. E curves recorded for samples C and D at low concentrations in water and NaCl 10^{-5} M, we verified that no difference was detected in the $\overline{\Delta n_s}$ and $\overline{\Delta\alpha}$ values within the limit of experimental errors.

The number of ionic sites N is equal to the number-average degree of polymerization, $\overline{\mathrm{DP}}_n$, multiplied by the degree of sulfonation (Table VI). The length of the polyion is taken equal to the theoretical contour length, L_T, or $\overline{\mathrm{DP}}_n \times b$. The value of 2.5 Å used for the contribution of the monomer unit to the chain length is somewhat larger than that experimentally found on the basis of the birefringence relaxation experiments.[44] The theoretical linear density charge at 293 K is 2.9 but we must take into consideration an effective value of this parameter. Indeed, owing to the presence of unsubstituted benzene rings in our NaPSS samples, the average distance between charged sites is longer than the length of the monomer unit and is equal to b/δ. It ensues (eq 15) that the effective linear density charge λ_{eff} is equal to $\lambda\delta$. This λ_{eff} value was then used to calculate the fraction of bound counterions ($\phi = 1 - \lambda_{eff}^{-1}$) (Table VI). According to Manning,[45] the latter parameter remains practically independent of ionic strength, provided that I is lower than 0.1 mol·L^{-1}. The variation of ϕ appearing in Table VI is only due to the slight decrease of the degree of charge as the molecular weight increases. As often observed, the $\Delta\alpha$ values obtained with the aid of the Mandel's relationship (eq 10) are much larger, by factors of 8–14 in the present case, than the experimental ones. On the contrary, the application of Manning's corrective factor X (with $\kappa = 10.36 \times 10^6$ m^{-1})

$$X = (1 - 2(|z|\lambda_{eff} - 1)\ln \kappa b)^{-1} \qquad (26)$$

yields $\Delta\alpha$ values slightly lower than the experimental ones. The discrepancy is only of the order of 2.2–2.3 for samples A and B, and a good agreement is noticed for the two high molecular weight samples (Table VI). In fact, $\Delta\alpha_{Manning}$ varies with the third power of the molecular weight. At lower ionic strength ($I = 10^{-6}$ M), $\lambda_{eff} = 2.6$, $\phi = 0.615$, and $\kappa = 3.14 \times 10^{-6}$ m^{-1}, X is then of the order of 4% whereas it ranges between 5 and 6% at $I = 10^{-5}$ M (Table V). As a comparison, we also calculated the $\Delta\alpha$ value of a fully charged NaPSS sample ($\delta = 1$) whose viscosimetric-average molecular weight is equal to 1.15×10^5[46] and hence similar to that of sample C. The experimental $\Delta\alpha$ values, 20.2×10^{-32} and 27.8×10^{-32} F·m^2 at $c = 0.021$ g·L^{-1} and at infinite dilution, respectively, higher than the corresponding values for sample C, agree with the $\Delta\alpha$ vs. M variation depicted in Figure 8. A difference by a factor of about 2 is, however, noticed between the calculated and experimental $\Delta\alpha_0$ values (Table VI).

In the case of 1:1 added electrolyte ($z_1/(z_1 - z_2) = 1/2$), Fixman's relationship (eq 19) is reduced to

$$\Delta\alpha_{Fixman} = \frac{2\pi\epsilon\epsilon_0 KL}{\gamma_a^2}\left[1 - \frac{2\tanh(\gamma_a L/2)}{\gamma_a L}\right] \qquad (27)$$

A value of 8 Å is adopted for the radius a of the poly(styrenesulfonate) polyion. The number of bound counterions per unit length, σ, has been estimated as follows: the number of charged sites per unit length is δ/b, but only a fraction ϕ of counterions is really bound to the polyion, so that $\sigma = \delta\phi/b$. Introducing the number of ionic sites $N = L\delta/b$ and replacing γ_a^2 by its value given by eq 20, we find

$$\Delta\alpha_{Fixman} = \frac{N\epsilon\epsilon_0\phi}{2 \times 10^3 c_1 N_A}\left[1 - \frac{2\tanh(\gamma_a L/2)}{\gamma_a L}\right] \qquad (28)$$

The values of σ, γ_a^2, K, $\gamma_a L/2$, and the term in brackets in relation 28 are given in Table VI for 10^{-5} M ionic strength. The values of $\Delta\alpha_{Fixman}$ found in this way agree qualitatively with the experimental ones, although they remain lower, too. Furthermore, these calculated $\Delta\alpha$ values are in good concordance with those estimated from Manning's theory, at least for the four samples A, B, C, and G, even though the two theoretical approaches are quite different. The exponent of the $\Delta\alpha$ vs. M dependence, of the order 2.7, is very close to the experimental exponent (namely, 2.6 ± 0.2). The best concordance between experimental and calculated $\Delta\alpha$ values is obtained for sample C (Table VI). The $\Delta\alpha$ values estimated for this sample in 10^{-6} and 10^{-4} M NaCl are 11.22×10^{-32} and 10.30×10^{-32} F·m^2, respectively. As the theory is subjected to some uncertainty on the real thickness of the layer of the condensed counterions, we also tested the calculation of $\Delta\alpha$ with a radius larger than 8 Å. $\Delta\alpha$ increases with a and reaches values of 5.0×10^{-32} and 14.0×10^{-32} F·m^2 for samples B and C when a radius of 16 Å is used. However, it must be recalled that a basic assumption in Fixman's treatment considers that the thickness of the bound counterions layer is negligible with respect to the radius of the cylinder. In this regard, Fixman called attention to the fact that the calculation should be considered with care in the case of very low ionic strength. From the single point of view of the estimation of the $\Delta\alpha$ parameter, the calculation according to Fixman becomes very inaccurate in the limiting case of very small $\gamma_a L$ values, i.e., for short chains at low ionic strength since the $\gamma_a L$ and tanh $(\gamma_a L)$ terms are very close. Qualitatively, Fixman's theory predicts the decay of the electric polarizability as the ionic strength increases and as the dielectric constant of the solvent decreases, in fairly good agreement with the observations. Quantitatively, it yields a good order of magnitude of the electric polarizability.

Two other contributions to the understanding of the electric polarizability of polyelectrolytes have recently appeared. In their approach, Rau and Charney[47] considered that the polarizability of the free ionic atmosphere surrounding the polyion might also contribute to the total electric polarizability according to the equation

$$\Delta\alpha_{\text{ionic}} = \frac{4\pi\epsilon_0\epsilon}{\kappa^3}\left(\frac{z}{z'}\right)F(l,r) \tag{29}$$

where z and z', respectively, represent the charge of the counterion in the ion atmosphere and the average charge of a counterion in the condensed layer. $F(l,r)$ is a rather complex function which depends on the ionic strength through the Debye–Hückel screening parameter and on the length L and radius a of the polyion through the $l = \kappa L/2$ and $r = \kappa a$ parameters. For very thin rods ($r \ll l$), $F(l,r)$ is independent of r, and, provided that $l \leq 4$, $F(l)$ becomes approximately proportional to $l^{1.85}$, so that $\Delta\alpha_{\text{ionic}}$ is proportional to $l^{1.85}/\kappa^{1.15}$;[47] i.e., $\Delta\alpha_{\text{ionic}}$ increases as the ionic strength decreases. For our NaPSS samples B and C in 10^{-5} M NaCl ($\kappa = 10.36 \times 10^6$ m^{-1}), we obtain very large values of $\Delta\alpha_{\text{ionic}}$ (26×10^{-32} and 55×10^{-32} F·m^2, respectively), i.e., 3–4 times larger than the experimental ones. Such a contribution added to the electric polarizability of the bound counterions leads to an overestimation of the total electric polarizability.

In the treatment of van Dijk et al.,[48] the influence of the counterion exchange between the free and bound phases is considered. van Dijk et al. define a length Z given by

$$Z = (u_D kT/K_r)^{1/2} = (D/K_r)^{1/2} \tag{30}$$

where u_D, D, and K_r represent, respectively, the counterion mobility along the polyion, the diffusion constant of these ions, and the rate constant for the exchange between the free and bound phases. It is shown that this exchange process does not influence the electric polarizability when this length Z is much larger than the length of the rod ($Z/L \gg 1$), so that $\Delta\alpha$ depends on L^3 as in eq 10. On the contrary, this dependence is reduced to a first power of the length if $Z/L \ll 1$ and the electric polarizability is much smaller, in fact decreased by a factor $12(Z/L)^2$. Using the mobility of the sodium ions at infinite dilution ($u_D = 3.1 \times 10^{11}$ m s^{-1} N^{-1}) and the rate constant for the counterion exchange, estimated to about 9×10^4 s^{-1} at a concentration of 5×10^{-5} monomol·L^{-1} (corresponding to $c \simeq 0.01$ g·L^{-1} for NaPSS), van Dijk et al. found Z to be of the order of 1200 Å.[48] In the limit of the very low concentrations used in this study, it ensues that the critical ratio $Z/L = 1$ would be reached for samples C and G (Figure 8), and one might expect a $\Delta\alpha$ dependence which would tend progressively to the first power of M at higher molecular weight. One must nevertheless keep in mind that the mobility of the bound ions could be modified through the polyion–counterion interactions with respect to the mobility of the freely moving Na$^+$ ions considered here. At a higher polyelectrolyte concentration (10^{-3} monomol·L^{-1} or $\sim$0.2 g·L^{-1} for NaPSS), Z is decreased to about 350 Å and $Z/L < 1$. The experimental $\Delta\alpha$ values at concentrations of the order 0.20–0.25 g·L^{-1} increase with a power of 0.70 ± 0.14 of the molecular weight, not too different from unity if we except sample A, for which the ratio Z/L is rather close to unity (Figure 8). These estimations must be considered with caution because the polyion–polyion interactions cannot be neglected and the effective lengths differ markedly from the contour lengths at such high concentrations. As we already noticed, the problem with our high molecular weight samples is that their degree of sulfonation is too low (Table I); measurements on fully charged NaPSS samples would be required to clarify this problem. We intend to examine if the predicted $\Delta\alpha$ vs. M dependence is verified at high molecular weight in the same manner as the $\Delta\alpha$ vs. M^3 dependence is approached at low molecular weight.

Such a change of the slope of the $\Delta\alpha$ vs. M dependence has been detected by Elias and Eden in their electric birefringence study of DNA restriction fragments.[49] The cubic dependence is verified when the number of base pairs does not exceed 124 whereas a first power dependence is reached for sizes greater than 267 base pairs. These authors also stated that the $\Delta\alpha$ values calculated on the basis of Fixman's and Manning's theories remain lower than the experimental ones. In order to fit their $\Delta\alpha$ vs. M dependence, they modified Mandel's relationship in an empirical way by replacing the rod length L of eq 10 by a length l_p which is a function of the persistence length q:

$$l_p = q[1 - e^{-(\text{RPB})\times(\text{BP})/q}] \tag{31}$$

where RPB is the length per base pair (3.15 Å) and BP the number of base pairs. These parameters can be identified in our case to the length of the monomer unit, $b = 2.5$ Å, and to the degree of polymerization, DP, respectively. Moreover, the interaction between counterions is accounted for by an empirical parameter $\Pi(c)$, so that eq 10 is expressed as

$$\Delta\alpha = \frac{Nz^2e^2\phi l_p^{\,2}}{12kT}\Pi(c) \tag{32}$$

Elias and Eden obtained a good fit of their data by adjusting $\Pi(c)$ to 2.3 and taking q equal to 500 Å.[49] We also tested this empirical procedure by using the DP, N, and ϕ values collected in Table VI. These parameters are equal to 2155, 1725, and 0.570 for sample E and 4360, 3050, and 0.507 for sample F. Adopting a persistence length of 300 Å, as estimated from the molecular weight dependence of the relaxation time on the basis of Hearst's treatment,[44] we obtain with $\Pi(c) = 1$ a continuous curvature (Figure 8) which does not reach the cubic dependence in the low molecular weight region.

In spite of its empirical character, the procedure suggested by Elias and Eden is, however, able to take into account the progressive conformational change of the polyion from the straight rod to the wormlike coil as the molecular weight increases.

5. Electric Polarizability and Polydispersity. We tried to see if the narrow molecular weight distribution of our samples would be compatible with a distribution of polarizability as used in our analysis with the orientation function. We selected as an example a fraction with $\bar{M}_n = 1.0 \times 10^5$ and a polydispersity $\bar{M}_w/\bar{M}_n = 1.1$, close to the characteristics of fraction C (Table I). The molecular

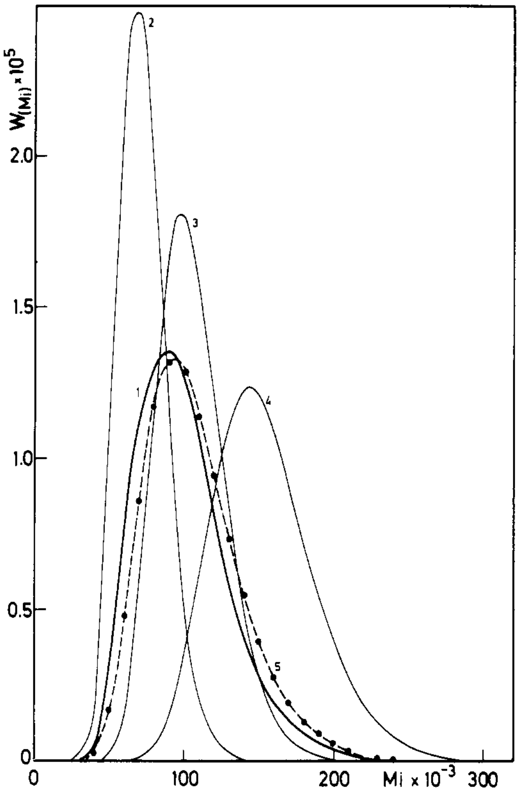

Figure 9. Decomposition of the molecular weight distribution into three components, assuming a normal logarithmic distribution law.

weight distribution was assumed to obey a logarithmic normal distribution law[50,51] which can be expressed as

$$W(M_i) = \frac{1}{M_i \nu \pi^{1/2}} \exp\left(-\frac{1}{\nu^2} \left(\ln \frac{M_i}{M_m} \right)^2 \right) \qquad (33)$$

where $M_m = (\bar{M}_n \bar{M}_w)^{1/2}$ is the molecular weight corresponding to the median value of the distribution and ν is the standard deviation of ln M, directly related to the polydispersity by $\bar{M}_w/\bar{M}_n = \exp(\nu^2)$. Such a distribution (curve 1 of Figure 9) can be decomposed into three distribution functions $W_j(M_i)$, centered on number-average molecular weights equal to 0.7 × 10^5, 1.0 × 10^5, and 1.5 × 10^5, respectively, but characterized by a smaller polydispersity index of 1.05 (curves 2, 3, and 4 of Figure 9). Considering that each function $W_j(M_i)$ contributes with fractions ω_j to the total distribution function, we can evaluate the latter by a simple weighted sum $W(M_i)_{\text{calcd}} = \sum_j \omega_j W_j(M_i)$. Assuming contributions ω_j of 30, 60, and 10% for the distributions with the $\bar{M}_n$ equal to 0.7 × 10^5, 1.0 × 10^5, and 1.5 × 10^5, respectively, we found that the $W(M_i)_{\text{calcd}}$ function is rather close to the initial distribution function (compare curves 1 and 5 of Figure 9).

The electric polarizability of a sample with $\bar{M}_n$ = 1.0 × 10^5 is equal to 11.0 × 10^{-32} F·m^2 as theoretically estimated or to 13.7 × 10^{-32} F·m^2 as experimentally measured (Table VI). Considering that $\Delta\alpha$ is proportional to $M^{2.6}$, the respective $\Delta\alpha_j$ terms calculated for the $\bar{M}_n$ = 0.7 × 10^5 and 1.5 × 10^5 centered distributions will range from 4.4 × 10^{-32} to 5.4 × 10^{-32} F·m^2 for the former and from 20 × 10^{-32} to 39 × 10^{-32} F·m^2 for the latter. The agreement between the calculated ω_j and $\Delta\alpha_j$ and the experimental ω_i and $\Delta\alpha_i$ values used for the fitting of some Δn vs. E curves for sample C in the limit of low concentrations is quite satisfactory (Table VII). This indicates that our fitting procedure using two or three electric terms can be justified on the basis of a polydispersity effect, even for samples with narrow molecular weight distributions. We believe nevertheless that the polydispersity is not the only factor responsible for the departure of our orientation functions from the $\Phi(\gamma)$ function; we also obtained good fittings based on the $\Phi(\chi)$ function making use of only one electric polarizability term. In a future work we shall try to correlate more quantitatively the distributions of relaxation time and polarizability to the distribution of molecular weights.

Table VII
Comparison of the Calculated $\Delta\alpha$ Values (Expressed in 10^{-32} F·m^2) and Their Respective Contributions with the Corresponding Values Derived from the Fitting with $\Phi(\gamma)$ for Sample C

ω_j, $\Delta\alpha_j$ (calculated)	$\overline{\Delta\alpha}$
30%, 4.4 + 60%, 11.0 + 10%, 20.0	9.9
30%, 5.4 + 60%, 13.7 + 10%, 39.0	13.7

c, g·L^{-1}	ω_i, $\Delta\alpha_i$ (experimental)	$\overline{\Delta\alpha}$
0.057	10.4%, 27 + 54.4%, 11.5 + 35.2%, 3.0	10.1
0.043	9.8%, 26 + 50%, 12.5 + 40.2%, 2.8	9.9
0.031	7.1%, 50 + 59%, 12.5 + 33.9%, 2.0	11.6

Conclusions

The major conclusions which can be drawn from the present study may be summarized as follows:

i. Orientation Function. Several new orientation functions have been proposed to describe the field strength dependence of the electrooptical anisotropy for polyelectrolytes, considering a saturation of the induced dipole at high fields.

We did not analyze our data with the functions used by Hogan et al.[52] and by Sokerov and Weill[7] to describe the electrooptical behavior of high molecular weight DNA since they both predict a linear dependence of the anisotropy on the first power of the field at low fields, a feature which we never observed with our synthetic polyelectrolytes. The function $\Phi(\chi)$ derived by Kikuchi and Yoshioka does not have this drawback and it yielded relatively satisfactory fittings of our data.

In order to very satisfactorily account for our observation by a pure induced orientation mechanism, we had to use two or three polarizability terms for the fitting with the $\Phi(\gamma)$ function. Although this procedure used in all our previous studies may be questioned from a mathematical point of view, we showed here that the small residual polydispersity of the samples was sufficient to justify such an approach. This argument could probably not be invoked in the case of the DNA restriction fragments which also did not follow the shape of the classical $\Phi(\gamma)$ function. It would be interesting to see if the empirical function recently used by Diekman et al.[53] to fit the electric dichroism orientation curves of such DNA fragments could also satisfactorily account for our data on NaPSS.

It seems even more difficult to understand the change in the shape of the orientation function with molecular weight observed in this study, and also noticed with the DNA fragments.[54] We cannot accept the idea that the molecular mechanism of orientation of polyions, induced or permanent dipole moment, could change as a consequence of the increase in molecular weight. In addition to the progressive saturation of the polarizability, we would need to simultaneously take into account the polydispersity and flexibility effects, the latter arising from the conformational change from a rodlike to a wormlike structure appearing as the molecular weight increases. This reinforces our opinion that the shape of the orientation function is not a good criterion to distinguish between various orientation mechanisms, even if large orientation degrees are experimentally reached.

ii. Electric Polarizability. Irrespective of the way in which the above analysis was made ($\Delta\alpha$ deduced from Kerr constant or any satisfactory fitting with $\Phi(\gamma)$ or $\Phi(\chi)$), the electric polarizability values obtained were always of the same order of magnitude so that their comparison with the theoretical estimations is not affected thereby. At infinite dilution or at very low concentration, we observed a dependence of $\Delta\alpha$ on a power of 2.6 with respect to the molecular weight, in fairly good agreement with the Manning and Fixman theories, which predict exponents of 3 and 2.7, respectively.

Larger discrepancies appear in the literature results for DNA restriction fragments. Stellwagen[54] and Diekman et al.[53] observed a quadratic dependence of the electric polarizability on the number of base pairs, whereas Elias and Eden[49] obtained a cubic dependence at very low molecular weight and a tendency to a first power dependence at high molecular weight. This was explained by the progressive bending of DNA chain. According to the recent analysis of van Dijk et al.,[48] a change from an M^3 to an M dependence of $\Delta\alpha$ could also be predicted by taking into account the exchange process between free and bound counterions.

The theories of Manning and Fixman give a good order of magnitude for the electric polarizability, which, however, remains smaller than the experimental value. We believe that the discrepancy, which does not exceed a factor of 1.5–2, cannot be explained by the fact that the polarizability of the bond valence electrons has been neglected. This term is much smaller than the polarizability of the counterions in the particular case of the carbon–carbon σ bonds in the main backbone of vinylic polyelectrolytes. Otherwise, the fraction of bound counterions, which was not determined experimentally, remains also subject to some uncertainty. Westra and Leyte[55] have reviewed the different criteria adopted to define the fraction of bound counterions, which can vary between the limit values of $1 - \lambda^{-1}$ and $1 - (2\lambda)^{-1}$, i.e., between 0.66 and 0.83 for a fully charged vinylic polyelectrolyte ($\lambda = 2.9$). The former value, recommended by Oosawa[13] and Manning[56] and choosen for our calculations, appears to be the most valid at infinite dilution.[55]

On the contrary, if we estimate, according to the treatment of Rau and Charney,[47] the polarizability of the free counterions surrounding the polyion and if we add this contribution to the polarizability of the bound counterions, we obtain $\Delta\alpha$ values much larger than the experimental ones. This overestimation of the free counterion contribution could arise from the low ionic strength conditions of the present study. We believe nevertheless that such a contribution would be able to explain the discrepancy between the experimental $\Delta\alpha$ values and those calculated for the polarization of the bound counterions alone.

We intend to report in a further paper results on the conformation of the NaPSS polyions at various ionic strengths and on the persistence length derived from the molecular weight dependence of the relaxation time. Attention will also be given to the analysis of the transitory states, rise and decay processes, in connection with the polydispersity of the samples.

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