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ELECTRO-OPTICAL STUDIES ON SYNTHETIC POLYELECTROLYTES.
IV. ELECTRIC POLARIZABILITY AND CONFORMATION OF POLY-*N*-METHYL-2-VINYLPYRIDINIUM BROMIDE IN AQUEOUS SOLUTION.

Michel TRICOT, Claude HOUSSIER, Victor DESREUX
Laboratoire de Chimie-Physique, Université de Liège, (Sart-Tilman) B 4000 Liège, Belgium

and

Frans VAN DER TOUW
Gorlaeus Laboratoria der Rijksuniversiteit Leiden, Afdeling Fysische Chemie III, Leiden, The Netherlands

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Measurements of the relaxation time on aqueous solutions of the title polyelectrolyte as a function of the concentration and of the molecular weight show that its conformation at very high dilution can be better accounted for by a weakly bending rod or wormlike chain model, with persistence length ranging from 200 to 400 A. The analysis of the field strength dependence of the electric birefringence yields electric polarizability values which increase sharply with the dilution and are not significantly dependent upon the molecular weight. This has been tentatively interpreted on the basis of the theories derived by Oosawa and by Mandel and Van der Touw. The partially flexible model proposed by the latter authors allow to identify the electric polarizability calculated from electro-optical data to the specific dielectric increment measured in the high frequency range; both parameters appear to be molecular weight independent. The electric polarizability obtained from the Kerr effect would be originated in the induced dipoles caused by the delocalization of the bound counterions along rigid subunits whose length seems however to differ from the persistence length.

1. Introduction

The dielectric and electro-optical methods have been largely applied to the study of biological macromolecules for the purpose of gaining further insight into their conformation and electric properties in solution. Difficulties have been encountered in the interpretation of the electric polarization mechanism of natural polyelectrolytes such as DNA. This is why the study of the behaviour of synthetic polyelectrolytes used as model compound has been considered as a valuable approach to elucidate this mechanism. The latter polymers offer the advantage of being stable even in the absence of added salt and show very large conformational changes as a function of concentration and ionic strength. This paper is intended to show how the new theory recently developed by Van der Touw and Mandel [1] to interpret the dielectric behaviour of flexible polyelectrolytes (quaternized poly-2-vinylpyridine derivatives in the present study) may be also applied to the analysis of the electric birefringence of such polymers. It is thought that a similar interpretation would be also applicable to natural polyelectrolytes.

Until now, numerous studies of ultraviolet absorption, viscosity and conductivity have been made on the weak polybase behaviour of the poly-2-vinylpyridine neutralized at various degrees by different acids [2–4]. The degree of ionization and the activity coefficients of the small ions of the poly-2-vinylpyridinium salts in atactic and isotactic configurations [4] as well as the extension of the chains [2] have been discussed in function of several parameters such as the nature of the counterions, the degree of neutralization and the ionic strength. On the contrary, little attention has been paid to the strong polyelectrolytic behaviour of the poly-2-vinylpyridine quaternized by different alkylbromides. Some viscosimetric experiments performed on a poly-*N*-butyl-2-vinylpyridinium bromide in water seemed to indicate that this polysalt behaves as having a more extended and stiffer conformation than the corresponding poly-4-vinylpyridine derivative [5]. In addition, if a longer alkyl chain such as a dodecyl group is attached to the quaternary nitrogen atom, the polysalt then behaves as a polysoap and becomes highly compact even in dilute aqueous solution [6, 7].

Our previous works on quaternized derivatives of poly-4-vinylpyridine have clearly evidenced the usefulness of the electro-optical methods to determine the electric and optical parameters as well as to describe some hydrodynamic properties of polyelectrolytes. The influence of several parameters such as concentration, molecular weight, ionic strength and nature of the solvent has been investigated [8–14]. The peculiar importance of the latter parameter, i.e. the nature and polarity of organic solvents, has been exemplified in our previous studies which showed that the polyvinylpyridinium salts tend to a rather coiled conformation in some of these solvents [11, 13].

The purpose of the present work is to determine the conformation of poly-*N*-methyl-2-vinylpyridinium bromide in dilute aqueous solution and to express quantitatively its degree of extension and of rigidity, making use of various hydrodynamic models. We shall attempt to gain better insight into the effects of the flexibility on the electric polarizability parameters. The effect of the distance between the charged sites and the main chain will be examined by comparing the results with poly-2- and 4-vinylpyridinium salts.

The experimental values of the electric polarizability will be compared with those calculated by means of theoretical models based on the polarization of the counterion atmosphere along the polyion. The model of Oosawa [15], previously applied with a relative success to the cases of sonicated fragments of DNA [16] and of sodium carboxymethylcellulose samples [17], as well as the new model recently developed by Van der Touw and Mandel will be considered [18]. The latter theory takes into account the flexible character of the polyion and describes satisfactorily the dielectric behaviour of various synthetic polyelectrolytes [19], but, to our knowledge, it was never considered in the interpretation of electro-optical data.

2. Material and methods

The poly-2-vinylpyridine (2-PVP) has been prepared by radical polymerization with $\alpha - \alpha'$ azobisisobutyronitrile as initiator in benzene solution at 55°C. The atactic samples obtained were purified by repetitive precipitations with the methanol-diethylether solvent-non solvent system. The anionic polymerization of the 2-vinyl pyridine was performed by the method previously described by Natta et al. [20] using phenylmagnesium bromide in suspension in toluene as catalyst. The amorphous fraction of the polymer was eliminated by extraction with acetone at 60°C. The crude polymer was finally dissolved in methanol and precipitated in a mixture butanone/n-hexane. On the basis of the proton magnetic resonance spectrum recorded in $CDCl_3$, it has been verified that this anionic 2-PVP sample (H) possesses a highly isotactic configuration [21–23].

The 2-PVP has been fractionated using chloroform/n-hexane as solvent-precipitant systems. The viscometric average molecular weight of the 2-PVP fractions (table 1) has been determined with the relation of Arichi et al. [24] valid for the atactic poly-2-vinylpyridine in methanol at 25°C:

$$[\eta] = 11.3 \times 10^{-5} M_v^{0.73} \quad (1)$$

and with the relation established by Loucheux et al. [25] for the isotactic poly-2-vinylpyridine in ethanol + sodium acetate 0.1 M at 25°C:

$$[\eta] = 46.2 \times 10^{-5} M_v^{0.59} \quad (2)$$

The weight average molecular weight $\bar{M}_w$ of some 2-PVP fractions has been measured by light scattering in chloroform solution ($dn/dc = 0.139$ cm^3 g^{-1}) at 25°C ($\lambda = 546$ nm). The number average molecular weight of fractions C and D determined by osmometry in anhydrous ethanol showed that the fractionation procedure used yielded samples of low polydispersity index.

The quaternization of the fractions was carried out at 3°C in a nitromethane/methanol 98/2 v/v mixture during 120 h, under nitrogen, using a large excess of methylbromide. The quaternized samples were finally precipitated in anhydrous dioxane and dried under vacuum at 40°C. The quaternization degrees Q estimated by potentiometric titration and the average molecular weight $\bar{M}$ of the quaternized samples, calculated as pre-

Table 1
Molecular weights and degrees of quaternization Q of the samples

Fractions	Poly-2-vinylpyridine		Poly-*N*-methyl-2-vinylpyridinium bromide	
	$\bar{M}_v \times 10^{-5}$	$\bar{M}_w \times 10^{-5}$	Q	$\bar{M} \times 10^{-5}$
Atactic				
A	0.95	1.05	0.76	1.6
B	1.60		0.75	2.7
C	2.20	2.30	0.65	3.5
D	2.70	2.80	0.71	4.4
E	3.20		0.66	5.1
F	4.00		0.68	6.5
G	6.30		0.63	9.9
Isotactic				
H	2.60		0.69	4.2

viously reported [12, 14] are collected in table 1. The values of $\bar{M}_w$ for two poly-*N*-methyl-2-vinylpyridinium bromide (2-PVP.MeBr) have been measured by light scattering in methanol + sodium acetate 0.1 M ($dn/dc = 0.22$ cm^3 g^{-1}). $\bar{M}_w$ is slightly lower than the calculated molecular weight $\bar{M}$: 2.4×10^5 and 4.1×10^5 for fractions B and D respectively. Potentiometric titrations with NaOH 0.001 M indicated that the quaternization by free hydrobromic acid did not exceed 1%.

The measurements of the electric birefringence and birefringence relaxation have been performed as previously reported [12, 26]. Some of the results presented here were made with the new recording and computing electro-optical instrument recently described [27].

3. Results and discussion

The electro-optical data will be treated in a way similar to that used in our previous studies [8, 12, 13, 28]:

(i) The mean relaxation time values will be analysed on the basis of various hydrodynamic models in order to determine either the length L of the equivalent rigid rod (relation 5, ref. [13]) or the persistence length q and the radius of gyration $(\mathcal{R}_g^2)^{1/2}$ of the semi-rigid chain models.

(ii) The field strength dependence of the electric birefringence will be fitted with a set of three induced dipole moment orientation function $\Phi(\Delta\alpha_i)$ contributing to different extents ω_i to the total measured birefringence. The mean electric polarizability values $\Delta\alpha = \Sigma_i \, \omega_i \Delta\alpha_i$ will be considered for further discussion of the data [12].

(iii) The optical anisotropy factor $\Delta n_s/c$, where c is the concentration in g cm^{-3}, obtained from the birefringence extrapolated to infinite field strength Δn_s, will be used as a parameter reflecting the orientation of the pyridinium ring with respect to the macromolecular axis [10].

In steps (ii) and (iii), the average values of the results obtained by manual adjustments or extrapolation of the experimental data, and by computer fitting using a multiparametric non-linear least square program [29] will be considered. The deviations with respect to these average values will be taken as the errors on both the electric and optical anisotropy parameters.

3.1. Chain length and rigidity

The mean relaxation time $\bar{\tau}$ (calculated from the surface under the decay curve) was found to decrease with increasing field strength. This effect, frequently encountered with polymeric samples, can be attributed to polydispersity and flexibility effects. As the field strength increases, the degree of orientation of the smallest particles or of the chain segments, and hence their relative contribution to the total birefringence signal, will increase. For the same reason, the mean of the inverse of the relaxation time $(\overline{1/\tau})$ estimated from the initial slope of the decay curve [30, 31], increases with field strength. The product $\bar{\tau} \times (\overline{1/\tau})$ which is a qualitative indication of the polydispersity of the samples [31,32], is found of the order of 3 at high fields (12 kV/cm), and reaches values of 1.6–1.8 at low fields, for samples of low polydispersity (C and D).

We have determined the mean relaxation time values at high field ($E \sim 12$ kV/cm) in order to enable the measurements down to very low concentrations. The τ_0 values have been estimated by extrapolation of $1/\bar{\tau}$ versus c as for the dielectric relaxation data (fig. 1). It is worth noting that, in the case of measurements made on polyelectrolyte solutions in the absence of added salt, extrapolation to zero concentration is generally subjected to a large uncertainty. We however observed only a small difference between the $\bar{\tau}_0$ values and the $\bar{\tau}$ measured at the lowest concentration ($c \sim 0.002$–0.003 mg/cm^3), so that the $\bar{\tau}_0$ values can be applied to the determination of the length and rigidity parameters with sufficient confidence.

We assume in first approximation a rigid cylinder model [12] with axial ratios p (roughly estimated from the intrinsic viscosity) ranging from 300 to 500 for the lower (A and B) and higher (C to G) molecular weight samples respectively. The rotatory diffusion coefficient at infinite dilution $D_{r,0} = 1/6\,\bar{\tau}_0$ values yield L_0 values collected in table 2. Note that an error of 100% on p produced errors of less than 6% on L for axial ratios higher than 300. The ratio between the length L_0 and the degree of polymerization DP extrapolated to zero DP values (fig. 2) can be considered as a measure of the length h of the monomer unit. The value experimentally found, of about 2 ± 0.1 Å, is somewhat lower than the theoretical value ($h = 2.5$ Å). This feature arising here from the hydrodynamic properties is also displayed for the colligative properties [33]. The discrepancy between $h_{\text{effective}}$ and $h_{\text{theoretical}}$ is becoming larger at higher degrees of polymerization and can be possibly attributed to the partially flexible character of the polyvinylpyridinium salts at infinite dilution. The $L_0/\text{DP} = h_{\text{effective}}$ values for the 2-PVP derivatives are appreciably larger than those of 4-PVP derivatives (fig. 2) [8, 12]. Three factors should be taken into account in order to explain the difference of extension of the PVP chains. The larger extension of the 2-PVP salts might be attributed to the more intense electrostatic repulsion between the charged sites which are closer to the hydrocarbon backbone. Furthermore, the hydrophobic interactions between the lateral alkyl groups have been shown to reduce the extension of the poly-N-alkyl-4-vinylpyridinium salts [13]. But the lower degree of quaternization of the 2-PVP salts ($Q \approx 0.7$) with respect to that of the 4-PVP salts ($Q \approx 0.93$) should however yield a lower degree of extension for the former polyelectrolytes. The nature of the dominating factor cannot be established without a systematic study of 2- and 4-PVP samples quaternized to comparable extents with the same alkyl halide.

The comparison between atactic and isotactic 2-PVP.MeBr samples of similar molecular weight and

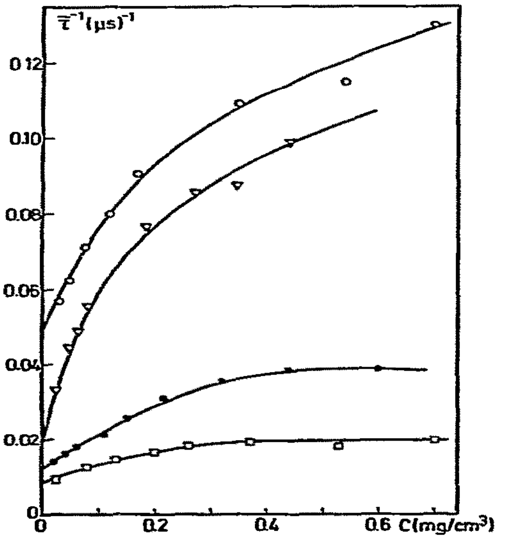

Fig. 1. Extrapolation of the average relaxation time to zero concentration for various fractions of 2-PVP.MeBr: (○) A, (▽) B, (●) C, (□) D.

Table 2
Molecular weight dependences of the average relaxation times and of the equivalent rigid rod length of the 2-PVP.MeBr samples at infinite dilution.

Samples	$\bar{\tau}_0$ (μs)	L_0 (Å)	L_0/DP (Å)
Atactic			
A	20	1440	1.60
B	50	1950	1.30
C	83	2380	1.12
D	118	2670	1.05
F	300	3650	0.96
G	750	5000	0.82
Isotactic			
H	100	2530	1.10

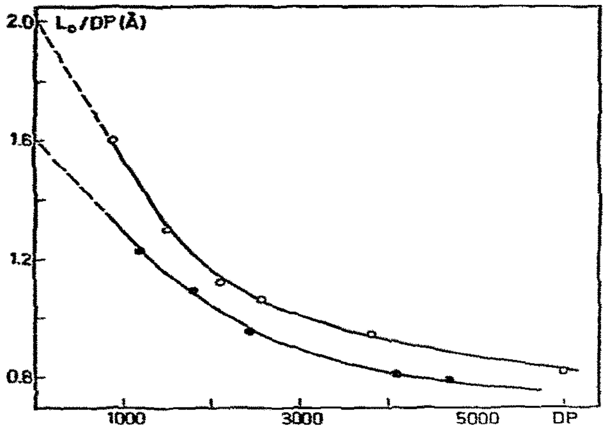

Fig. 2. Variation of the effective length of the monomeric unit at infinite dilution L_0/DP with the degree of polymerization for the 2-PVP.MeBr (○) and 4-PVP.BuBr (●) samples.

quaternization degrees (D and H, table 2) indicates that no significant difference can be detected between the lengths of the two polyelectrolytes at infinite dilution.

Our data can be better analysed on the basis of semi-rigid chain models, i.e. the weakly bending rod and the worm-like chain developed by Hearst [34], which allow the estimation of the persistence length q, from the molecular weight dependence of the rotatory diffusion coefficient. For the weakly bending rod, we used Hearst's relation in a slightly modified presentation recently given by Foweraker and Jennings [35] and applied to the determination of the chain stiffness of sodium carboxymethylcellulose samples. This relation can be expressed in the form:

$$\frac{\pi\eta_0 D_r M^3 h^3}{kTM_0^3} = 3\ln(Mh/2M_0 b_0) - 4.92 + 4(b_0/r_0)$$

$$+\frac{Mh}{4M_0 q}\left[(4.5\ln(Mh/2M_0 b_0) - 10.2 + 4(b_0/r_0)\right], \qquad (3)$$

where η_0 is the viscosity of the solvent, M_0 the molecular weight of the monomer unit (of the order of 172 with $Q \approx 0.7$) and h the length of the monomer unit. As this relation cannot be put in an analytical form, we have fitted the experimental data (table 2) with the aid of the multiparametric program mentioned above [29]. Assuming that the frictional parameters b_0 and r_0 introduced in the Hearst's theory are equal [34,35], we found at infinite dilution $q = 290$ Å, $b_0 = 5.5$ Å with $h = 2$ Å, and $q = 220$ Å, $b_0 = 3$ Å with $h = 2.5$ Å.

For the worm-like chain model, the slope of the linear dependence of $\eta_0 D_{r,0} M^2/kT$ on $M^{1/2}$ (following the form of the equation given in ref. [12]) allows to estimate persistence length value at infinite dilution of 240 Å (with $h = 2$ Å) to 190 Å (with $h = 2.5$ Å), and hence a smaller degree of rigidity than that obtained with the former model. The ordinate at the origin yields b_0 values comprised between 11 Å ($h = 2$ Å) and 5.5 Å ($h = 2.5$ Å). The assumption of Hearst and Stockmayer that b_0 is an approximated value of the rod diameter [36] seems verified in the present case.

On the basis of the worm-like chain model, we determined in a previous work q values at infinite dilution for the 4-PVP.BuBr samples which increase from 420 Å to 500 and 600 Å when h changes from 2.5 Å to 1.9 and 1.6 Å respectively [12, 14]. It thus appears that the 4-PVP salts are more rigid than the 2-PVP salts. The smaller degree of rigidity of the 2-PVP salts can result from the larger content of free pyridine units in the main chain. This would confirm the fact that the main part of the flexible joints in the polymer chain could be identified as the non-quaternized units, as previously suggested [12].

The worm-like chain model can also yield the average radius of gyration $(\mathcal{R}_g^2)^{1/2}$ from the knowledge of the persistence length q and the contour length $L_T = h \times \mathrm{DP}$, making use of the following relation in which $x = L_T/q$ [37]:

$$\mathcal{R}_g^2 = q^2\left\{\frac{x}{3} - 1 + \frac{2}{x}\left[1 - \frac{1}{x}(1 - e^{-x})\right]\right\}. \qquad (4)$$

The $(\mathcal{R}_g^2)$ values will be required below to estimate theoretically the electric polarizability.

We also attempted to follow the variation of the above parameters with the concentration c. The values of L, calculated with the relation valid for the rigid rod model, (with axial ratios ranging from 300 to 200 when going from low ($c \sim 0.12$ mg/cm^3) to higher concentrations are shown in fig. 3a for the sample A. The concentration dependence of the persistence length (with the assumption that $h = 2.5$ Å and $r_0 = 5.5$ Å, irrespective of c) for the 2-PVP.MeBr samples A and D is shown in fig. 3b. Both L and q values at different

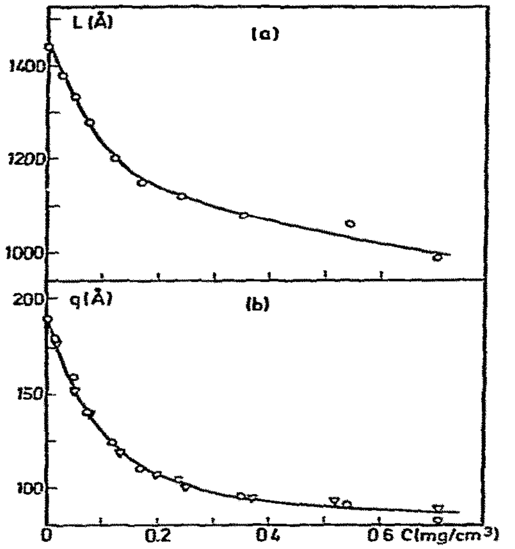

Fig. 3. Decreases of the chain length (a) and of the persistent length (b) with increasing polymer concentration for the 2-PVP.MeBr A (○) and D (▽) samples.

concentrations will be used here after in the calculation of the electric polarizability.

It should not be forgotten that models for uncharged particles are applied here. Interactions between the polyions and counterions or the mutual interactions between the polyions are not taken into consideration. In particular at the higher concentrations, the rotational diffusion can be influenced by these interactions and consequently the values of the parameters L, q and $(\mathcal{R}_g^2)^{1/2}$ are to be considered as apparent values. The value of q of about 80 Å at $c \sim 0.7$ mg/cm^3 is however comparable to that measured by Moan and Wolff [38] on a sodium carboxymethylcellulose sample with the elastic neutron scattering technique ($q \sim 50$ Å at $c = 1$ mg/cm^3). Even if cellulose derivatives and vinylic polyions possess very different backbones, we believe nevertheless that a value of the persistence length of the order of 50–100 Å is an acceptable order of magnitude for polyelectrolytes at finite concentration and in the absence of added salt.

3.2. Orientation mechanism and electric parameters

Under consecutive pulses of reversed polarity ($E \sim 3$ kV/cm) and of sufficiently long duration ($t_p \sim 0.5$ ms) for each pulse, the aqueous solutions of the various 2-PVP.MeBr samples showed particular shapes of the birefringence signals similar to those previously reported for 4-PVP.BuBr in dimethylsulphoxide [13], except for the change of sign of the anisotropy in the decay curve (fig. 4a). The maximum at the field reversal can be characterized by the ratio $r = (1 - \Delta_m)/(0.1547 + \Delta_m)$ where $\Delta_m = \Delta n_m/\Delta n_0$ is the ratio of the birefringence extremum over the value at the steady-state [39]. The negative values of r decreased towards zero (fig. 5a) at very low concentrations (at $c \sim 0.15$ mg/cm^3 for fraction A) and were higher the lower the degree of quaternization; if fraction C is excepted, r shows general tendency to increase with the molecular weight. The protonation of the unquatern-

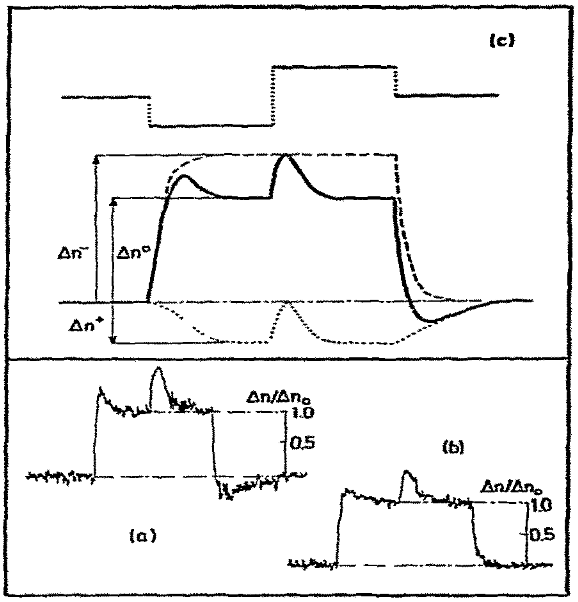

Fig. 4. a, b. Typical electro-optical signals recorded with the reverse-pulse technique on 2-PVP.MeBr F ($Q = 0.68$) solutions at $E \sim 3$ kV/cm and at $c = 0.36$ mg/cm^3 (a) or $c = 0.1$ mg/cm^3 (b). c. Schematical representation of the decomposition of an electro-optical signal into its positive Δn^+ and negative Δn^- birefringence components.

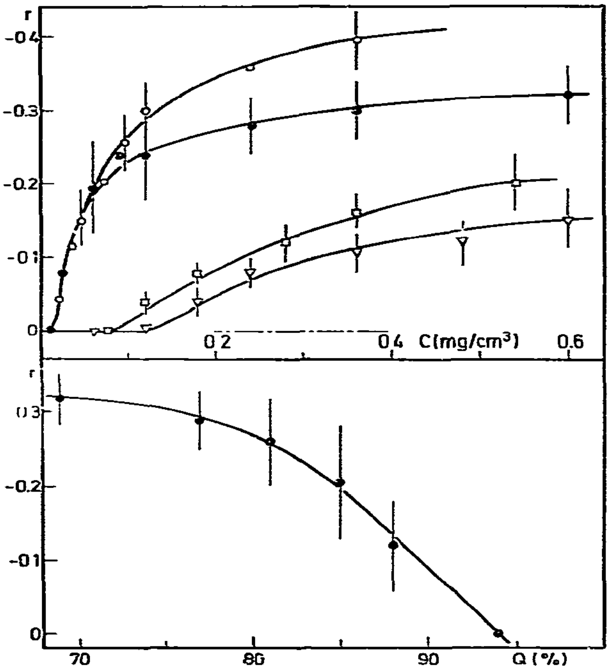

Fig. 5. a. Influence of the concentration on the r parameter measured with the reversing pulse technique on various 2-PVP.MeBr samples: (▽) A, (□) D, (●) F, (○) C. b. Variation of r with the degree of quaternization (modified by addition of hydrobromic acid) for a solution (c = 0.6 mg/cm^3) of 2-PVP. MeBr F.

ized pyridine residues by hydrobromic acid progressively reduced the value of r which vanished for $Q \sim 0.95$ (fig. 5b). This correlates with the fact that the 4-PVP. BuBr samples of high degrees of quaternization (Q = 0.90–0.95) did not show any transient at the pulse reversal in water [12].

Although the presence of a maximum at the field reversal could be accounted for by the presence of a transverse dipole moment [39], this interpretation could not explain the reversal of sign in the decay curve. In addition, the observed r values would imply very large values of the transverse dipole contribution (several thousands Debye units) and a reversal of the steady-state birefringence in a range of field strength where this was not experimentally observed. This particular behaviour arises probably from the presence of two molecular entities which display opposite birefringence signs (fig. 4c); the entity yielding a positive birefringence has a longer relaxation time and is oriented either by a permanent dipole moment mechanism or by a slowly induced dipole moment. As discussed in a previous paper [13], the positive birefringence may be caused by a large contribution of positive form anisotropy, so that no conclusion can be drawn about the sign of the intrinsic optical anisotropy of this entity. The orientation of two molecular entities with opposite birefringence signs has also been invoked in a study of a comparable behaviour observed with sonicated DNA [40]. The positive birefringence component does not always appear in the field-free relaxation process: at low concentration, extension of the chain might enhance the relaxation time of the negative birefringence component which then becomes preponderant (fig. 4b).

The nature of the entity with positive birefringence, present in small amounts in the polyelectrolyte solution, cannot be more precisely defined at the present stage of investigation. However, the correlation between this entity and the degree of quaternization suggests that it could result from associates due to the interaction between free pyridine units and quaternized groups of the polyelectrolytic chains. The presence of short sequences of free pyridine units is not excluded in such samples of lower degree of quaternization ($Q \sim 0.65$–0.75). Otherwise, the decrease of r with decreasing concentration suggests that the so-formed associates would be reversible.

No peculiar shape in the electro-optical signals has been detected in single pulse experiments for which pulses of very short duration ($t_p \sim 0.1$ ms) as compared to those applied in the reversing pulse technique were used. Owing to the faster rise process of the negative birefringence component (fig. 4c), we believe that this component has almost reached its steady-state value before the entity with positive anisotropy starts to be oriented. As long as pulses of short duration are used, the presence of associates in the solution should not influence markedly the steady-state birefringence and its field strength dependence, i.e. the optical and electrical anisotropy parameters. Furthermore, in what follows, we shall essentially analyse the electric birefringence data of samples of low molecular weight (A, D and H) for which the effect of the above described particular behaviour will be considered as negligible.

The average values obtained by the fitting procedure

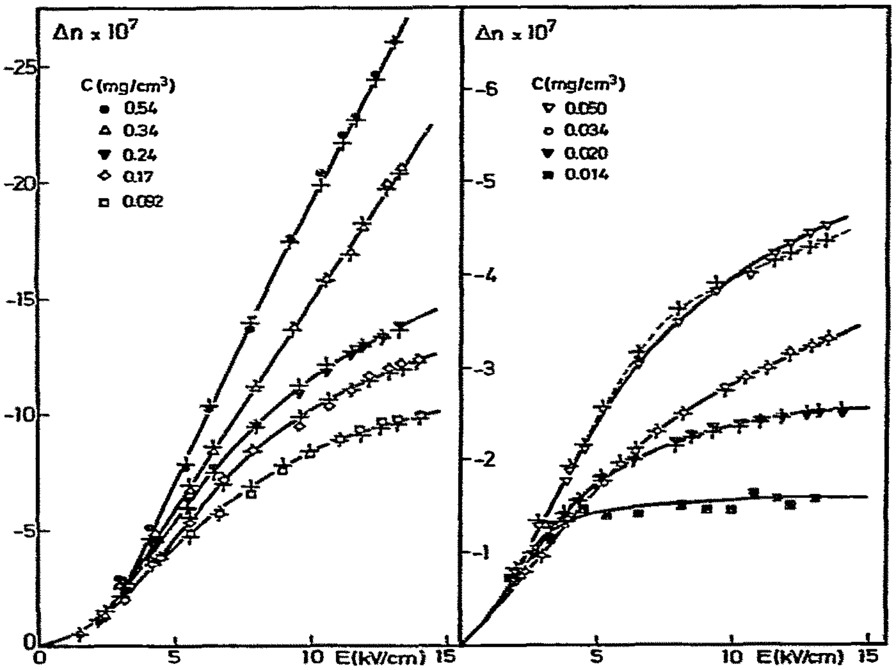

Fig. 6. Comparison of the experimental birefringence versus field strength curves with those (represented by crosses) theoretically computed using the $\Phi(\Delta\alpha)$ orientation function (2-PVP.MeBr A).

(fig. 6) agree (table 3) with the $\Delta\alpha$ derived from the Δn_s and the Kerr constant K_B values ($K_B = \Delta n_s\, \Delta\alpha/15\, kT$); K_B has been calculated from the initial slope of the Δn versus E^2 plots. We also tried to fit our data with the orientation function Φ (sinh) which takes into account a possible saturation of the induced dipole at high fields [41–43]. An agreement with the experimental data curve was only approached when the number of bound counterions per polyion of length L was taken to be close to 1, in which case the shape of the

Table 3
Birefringence at the saturation and electric polarizabilities (obtained from the fitting procedure and from the Kerr constant) at various concentrations for the 2-PVP.MeBr A sample.

c(mg/cm^3)	$-\Delta n_s \times 10^7$	$\Delta\alpha \times 10^{32}$ (F m^2)	$-K_B \times 10^{18}$ (V^2 m^{-2})	$\Delta\alpha \times 10^{32}$ (F m^2)
	(Fitting)		(Kerr constant)	
0.54	55.0	2.8	3.2	3.6
0.34	37.0	3.7	3.0	5.0
0.24	22.0	7.0	2.5	7.0
0.17	17.0	8.1	2.3	8.3
0.092	13.0	16.3	2.6	12.3
0.050	5.7	20.0		
0.034	3.8	30.0		
0.020	2.7	50.0		
0.014	1.9	65.0		

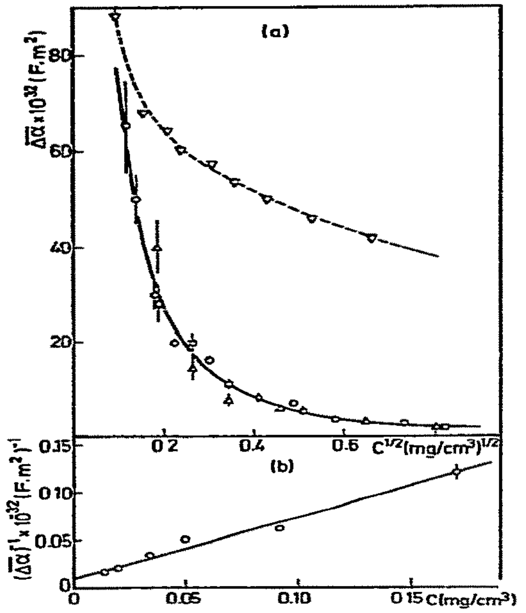

Fig. 7. a. Increase of the average electric polarizability with the dilution for the 2-PVP.MeBr samples A (○), D (△) and H (□); concentration dependence of the electric polarizability calculated on the basis of Oosawa's theory for the 2-PVP.MeBr sample A (▽). b. Extrapolation of the inverse of the average electric polarizability to zero concentration for the 2-PVP.MeBr sample A.

orientation function approaches that for a permanent dipole moment $\Phi(\beta)$. As already concluded by Kikuchi and Yoshioka in their study on potassium polystyrenesulphonate and poly-L-lysine hydrobromide samples, this result cannot be physically interpreted [41,42].

As already observed with the 4-PVP.BuBr samples [12,13], the mean polarizability increases sharply with the dilution (fig. 7a, table 3 and 4) but it is not appreciably influenced by the molecular weight (compare samples A and D, table 3 and 4) nor by the tacticity of the samples (compare samples D and H, table 4). The optical anisotropy factor $\Delta n_s/c$ was found to be almost independent of the concentration when c is lower than 0.2 mg/cm^3 and to by 30% larger for the atactic samples A and D: $\Delta n_s/c = -(11.5 \pm 1.5) \times 10^{-3}$ cm^3 g^{-1} than for the isotactic sample H: $\Delta n_s/c = -(8.0 \pm 1.0) \times 10^{-3}$ cm^3 g^{-1}.

3.3. Electric polarizability and conformation

There are various ways of interpreting the electric polarizability of polyelectrolytic macromolecules. The validity of the treatments developed by O'Konski [44], Schwarz [45] and Takashima [46] on the basis of surface conductivity phenomena, and by Mandel [47] and Oosawa [15] on the basis of a statistical approach of the behaviour of the distribution of the bound counterions, has been recently discussed by Weill and Hornick [16,48].

Oosawa's model takes into account the electrostatic repulsion between the bound counterions and was found to be the most satisfactory for interpreting the electric polarizability of DNA [16]. Within the framework of Oosawa's theory, following Weill and others [16,17], $\Delta\alpha$ can be expressed by the relation:

$$\Delta\alpha = \frac{N z^2 e^2 L^2 \phi}{12\, kT} \left[\frac{1}{1 + 2\lambda\phi \ln(R/d)}\right] , \qquad (5)$$

Table 4
Comparison of the average electric polarizability obtained by the curve fitting procedure and of the average values of the birefringence at saturation for the atactic D and isotactic H 2-PVP.MeBr samples.

2-PVP.MeBr D			2-PVP.MeBr H		
c(mg/cm^3)	$-\Delta n_s \times 10^7$	$\Delta\alpha \times 10^{32}$ (F m^2)	c(mg/cm^3)	$-\Delta n_s \times 10^7$	$\Delta\alpha \times 10^{32}$ (F m^2)
0.65	56.0	2.3	0.68	40.0	2.2
0.42	40.0	3.2	0.42	28.0	3.0
0.21	22.0	5.9	0.26	18.0	5.5
0.12	15.0	7.3	0.12	11.0	11.0
0.07	8.0	14.5	0.07	5.8	20.0
0.035	3.5	30.0	0.035	2.7	28.0

which differs from Mandel's equation [47] only by the corrective repulsion term $[1 + 2\lambda\phi \ln (R/d)]^{-1}$ where λ is the linear charge density:

$$\lambda = z^2e^2/4\pi\epsilon\epsilon_0' hkT. \quad (6)$$

ϵ_0' is the electric permittivity of a vacuum ($\epsilon_0' = 8.85 \times 10^{-12}$ $J^{-1}C^2m^{-1}$) and ϵ is the dielectric constant of the solvent. In these relations, N is the total number of counterions, L the length of the polyion, z the valency of the counterion and e the elementary electric charge. The polyelectrolytic solution is assumed to be constituted of cylindrical cells of radius R containing the polyion and its counterionic atmosphere. The fraction ϕ of bound counterions is located in a cylindrical volume of radius d; the fraction of osmotically free counterions is included in an external cylindrical volume of radius $(R - d)$ and those two phases are separated by a difference of potential $d\psi$ [49]. It should be also noted that both Mandel's and Oosawa's theories consider the longitudinal motion of the bound counterions along the long axis of a rod-like polyion and that the polarization in the transverse direction is considered as negligible. Even if relation (5) predicts the decrease of the electric polarizability with increasing ionic strength, it could not explain the discrepancy between the experimental and theoretical $\Delta\alpha$ values of a sodium carboxymethylcellulose sample at an ionic strength of about 10^{-3} [17].

The parameter R of relation (5) is directly related to the polymer concentration [50] and is given by:

$$R = (\pi c_p N_{AV} h)^{-1/2}, \quad (7)$$

where N_{AV} is Avogadro's number, c_p the concentration expressed in moles of monomer per unit volume; R and λ both depend on the value of the length of the monomer unit determined above. The calculation has been performed for the 2-PVP.MeBr sample A (Q = 0.76, M_0 = 177) which carries about 690 charged sites (N = DP × Q). For h = 2.5 Å, λ = 2.9, and taking into account the degree of quaternization, the effective linear density charge $\lambda' = \lambda \times Q$ is equal to 2.2.

From Oosawa's theory, it has been effectively shown that the fraction of bound counterions at infinite dilution [51] can be approximated by $\phi = 1 - 1/\lambda'$ ($\lambda' > 1$); thus $\phi = 0.54$. Making use of an appropriate computer program [50, 51], the theory of Oosawa also allows to calculate the electrostatic potential due to the highly charged polyion. By analogy with the energetical limit of the associated ion pairs of Bjerrum, the counterions submitted to a potential such as $e\Delta\psi/kT$ = 2 can be considered as electrostatically bound to the polyion. Thus, the distance at which $e\Delta\psi/kT = 2$ can be obtained (table 5) and identified to the radius d of the phase containing the bound counterions: the corresponding calculated ϕ values increase from 0.45 at c = 0.01 mg/cm^3 to values ranging from 0.58 to 0.60 when c changes from 0.027 to 0.44 mg/cm^3. In what follows, we shall consider the value ϕ = 0.54 estimated above, which nicely falls into the range of values calculated on the basis of the Oosawa's theory. As already suggested by Hanss and coworkers [17], it would however be preferable to determine ϕ experimentally by using a non-equilibrium method. In the theory of Mandel [47] and of Oosawa [15] the polyion is represented by a rigid rod. The length L should therefore be put equal to the length of the fully extended chain, i.e. h × DP = 2250 Å for sample A. The electric polarizability values $\Delta\alpha^{(0)}$, calculated for this sample using eq.

Table 5
Calculation of the electric polarizability at various concentrations for the 2-PVP.MeBr A sample, on the basis of the Oosawa's theory

c(mg/cm^3)	R(Å)	L(Å)	d(Å)	$\Delta\alpha^{(0)} \times 10^{32}$ (F m^2)	$\Delta\alpha^{(1)} \times 10^{32}$ (F m^2)
0.010	1930	1420	440	218	87
0.027	1170	1380	172	177	67
0.044	920	1330	135	177	62
0.060	780	1290	117	178	59
0.095	620	1240	100	184	56
0.130	540	1190	87	184	52
0.180	450	1150	74	185	49
0.280	370	1100	60	184	44
0.440	290	1050	48	186	41

(5) are summarized in table 5 together with the different parameters used. Comparison with the experimental values obtained for the various concentrations reveals a very important discrepancy, the calculated values being much too large.

The theory of Oosawa was derived for non-interacting macromolecules. It is often assumed that, due to repulsive interactions between different polyelectrolyte molecules, these molecules tend to shrink at higher concentrations as a consequence also of their flexible character. In an attempt to take into account these interaction phenomena, we assume now that the values L obtained from the rotational relaxation times using the rigid rod model and which are plotted in fig. 3a, represent the lengths of rods equivalent to the shrinked molecules and that the effect of the interactions on the polarizability are accounted for by the use of the experimental L values, leading to the polarizability values $\Delta\alpha^{(1)}$ (table 5). Fig. 7a compares the experimental curve obtained for the concentration dependence of the polarizability with the plot of $\Delta\alpha^{(1)}$ versus the concentration. It can be seen that the latter values are still larger than the experimental ones, in particular at the higher concentrations. There, the interaction effects are most important and the assumptions regarding the influence of polyion-polyion interaction may be most discutable; this makes conclusions in this region relatively unreliable. In addition, however, it should be emphasized that the discrepancy between the experimental and theoretical polarizability values, at low concentrations, would be much larger for the higher molecular weight samples since our data yield polarizability values almost independent of the molecular weight in contradiction with the prediction of Oosawa's theory. It is thus concluded that the theory of Oosawa is not very appropriate for the interpretation of the polarizability of flexible polyelectrolytes as deduced from electric birefringence experiments.

A new theoretical approach has been recently proposed by Van der Touw and Mandel [18] in order to explain the two dispersion regions of the dielectric increment generally observed for solutions of polyelectrolytes. In opposition to the treatment of Oosawa, this theory assumes that the correlation between the counterions can be neglected. The polyion is identified to a non-linear sequence of rigid subunits of length b. The bound counterions are "freely" moving along these subunits, whereas, in order to move along the whole chain, they must overcome potential barriers assumed to exist between the subunits. The relaxation time τ_b related to the local fluctuations in the distribution of counterions along the units b is much shorter than the relaxation time τ_s related to fluctuations in the overall distribution of the counterions along the whole chain. It has been shown [18] that the static dielectric increment $\Delta\epsilon_s$ and the dielectric increment $\Delta\epsilon_2$ associated to the high frequency dispersion region, both defined with respect to the permittivity of the solvent, can be expressed by the following relations:

$$3\epsilon_0' \, \Delta\epsilon_s / C_M = \frac{z^2 e^2 N \phi B}{12\, kT} (12 R_g^2 + b^2)\,, \qquad (8)$$

$$3\epsilon_0' \, \Delta\epsilon_2 / C_M = \frac{z^2 e^2 N \phi B}{12\, kT} b^2\,, \qquad (9)$$

where C_M is the number of polyions per unit volume. B is the ratio of the effective field acting on the polyion to the applied electric field; in the absence of any valuable theory allowing to estimate this parameter, it is generally put equal to unity [44]. R_g is the radius of gyration as defined in the theory of Van der Touw and Mandel [18] and the term $(12R_g^2 + b^2)$ can be identified to the term $12\mathcal{R}_g^2$ [52], where $(\mathcal{R}_g^2)^{1/2}$ is the conventional defined radius of gyration determined above (relation 4) for a wormlike chain.

This theory was successfully applied for the interpretation of dielectric measurements on several polyelectrolytes [19, 53]. In view of the fact that it does not consider interaction effects between polyelectrolyte molecules, extrapolation of the dielectric data to infinite dilution was required. It was found [19, 53] that the reciprocal of the specific increment obeys a linear relationship with respect to concentration, which finding brought about a possibility to extrapolate the data to zero concentration. In an attempt to treat the electrooptic data in an analogous way, the reciprocal of $\Delta\alpha$ was plotted as a function of the concentration and, as shown in fig. 7b, a linear relationship also holds in this case. Extrapolation to zero concentration (by linear least squares regression) yields $\Delta\alpha_0 = (120 \pm 60) \times 10^{-32}$ F m^2, this value being subject to a large error due to the very low $(\Delta\alpha)^{-1}$ values reached at low c.

The right hand side of eq. (8) is equal to the overall polarizability of the macromolecule arising from fluctuations in the counterion distribution along the whole chain for the system in equilibrium. Using equation (4) and the extrapolated value of the persistence length (fig. 3b) for the lowest molecular weight sample A at zero concentration a value for $(\mathcal{R}_g^2)^{1/2} = 335$ Å is found. Application of eq. (8) then yields for $\Delta\alpha_s$ a value of 265×10^{-32} F m^2, about two times larger than the experimental extrapolated value $\Delta\alpha_0$. If the assumption is also made here that the interaction effects between the polyions on the polarizability are only to be taken into account through the change in $(\mathcal{R}_g^2)^{1/2}$, the magnitude of which can be estimated using eq. (4) and the values for the persistence lengths obtained from the rotational relaxation times, eq. (8) can be applied at finite concentrations. It is found in this way that the differences between the experimental and calculated values of the polarizability becomes more and more important with increasing concentration.

In view of the fact that eq. (8) predicts a molecular weight dependence of the electric polarizability and the dielectric increment, not found experimentally for the polarizability determined by electrooptical methods nor for the high frequency dielectric increment $\Delta\epsilon_2$, we are led to the conclusion that the former is connected with the fluctuations in the distribution of the counterions along the subunits b. Under this assumption, the electric polarizability per subunit $\Delta\alpha_b$ is therefore related to $\Delta\epsilon_2$ and, from relation (9) and for monovalent counterions, is given by:

$$\Delta\alpha_b = \frac{3\epsilon_0' \Delta\epsilon_2}{C_M'} = \frac{e^2 \phi Q b^3}{12hkT}, \qquad (10)$$

where C_M' now represent the number of subunits per unit volume; the number of charged sites on a subunit b is equal to bQ/h. Using for $\Delta\alpha_b$ the measured value $\Delta\alpha$ for the 2-PVP.MeBr sample A and keeping h = 2.5 Å and $Q = 0.76$, eq. (10) yields b values increasing from about 320 Å at $c = 0.54$ mg/ml to about 900 Å at $c = 0.014$ mg/ml, whereas b reaches a value of about 1100 Å at zero concentration (table 6). The b values at finite concentration should be considered as apparent values, as it has to be assumed here again that the effect of the concentration on the polarizability is only reflected by a change of b, so that relation (9) and (10) remain valid at finite concentrations. These values are of the order of magnitude of values for b obtained for other vinylic polyelectrolytes from dielectric experiments [19, 53]. Therefore we reach the tentative conclusion that the polarizability found by Kerr effect measurements is directly related to the polarizability giving rise to the high frequency dielectric dispersion.

Table 6
Calculation of the length of the rigid subunit on the basis of the theory of Van der Touw and Mandel.

c (mg/cm^3)	$\Delta\alpha \times 10^{32}$ (F m^2)	b (Å) (h = 2.5 Å)
0	(120 ± 60)	(1100 ± 120)
0.014	65.0	910
0.020	50.0	830
0.034	30.0	700
0.050	20.0	610
0.092	16.3	570
0.170	8.1	450
0.240	7.0	430
0.340	3.7	350
0.540	2.8	320

4. Conclusions

Our observations have evidenced the semi-rigid chain behaviour of the poly-2-vinylpyridinium salts at infinite dilution. On the basis of models such as the worm-like chain or the weakly bending rod, we have expressed quantitatively the rigidity by means of persistence length values of the order of 200–250 Å for the former model and of 300–400 Å for the latter. It seems however impossible to conclude which of the two models gives the best description of the true conformation of the polyion. The finding that the persistence length and the $h_{\text{effective}}$ value for the 2-PVP. MeBr salts are respectively smaller and larger than the corresponding value for the 4-PVP.BuBr salts [12, 14] could reveal a specific conformational behaviour. Further investigations are needed to elucidate this in more detail.

The orientation and the disorientation processes of the polyelectrolyte in the electric field are complex phenomena which involve the motions of the whole particles superimposed to those of the rigid segments. This introduces the concept of the kinetic rigidity [54] of the chain submitted to a pulsed electric field. We must furthermore draw the attention on the fact that, in experiments performed in the absence of added salt, the rotational motion of the polyions and hence the relaxation time values could be influenced to a non-negligible extent by the so-called electroviscous effect, so as for viscometric experiments.

The electric polarizability values determined from the experimental orientation function are almost similar, at corresponding concentrations, for all the vinylic polyelectrolytes investigated, i.e. poly-*N*-methyl-2-vinylpyridinium bromide, poly-*N*-butyl-4-vinylpyridinium bromide [8, 12, 14], poly-3-ethyl-1-vinylimidazolinium bromide [8, 14] and sodium polystyrenesulphonate [55]. For all these rather flexible polyelectrolytes, the experimental orientation curves depart markedly from the theoretical curves for a pure induced dipole orientation mechanism although the reversing pulse method definitively established the occurrence of such a mechanism. The consideration of a three terms orientation function with different electric polarizabilities, assumed to account for flexibility and/or polydispersity effects, allowed to obtain a satisfactory fitting of the experimental data, while the function derived to take into account a possible saturation of the induced dipole at high fields did not. It seems probable that no single orientation function would allow to account for the very complex phenomena occurring during the orientation of the polyion in view of its flexible character.

To account for the influence of this flexibility on the electric polarizability, a new theory is applied successfully. This theory proposed by Van der Touw and Mandel [18] allows to explain the observed independence of the $\Delta\alpha$ values on molecular weight. The polarizability derived from the field strength dependence of the electric birefringence can be related to the specific dielectric increment at high frequencies which also is molecular weight independent. Within the framework of the model of Van der Touw and Mandel, the origin of this electric polarizability would be the delocalization of the bound counterions under the action of the external electric field along rigid subunits of length b. To make comparisons possible, it would be desirable to establish the relation between the model introduced by the latter authors and the other models like the worm-like chain and the weakly bending rod models applied to the interpretation of the hydrodynamic data. The b_0 value determined here for the 2-PVP.MeBr sample at infinite dilution, i.e. ~ 1100 Å, is markedly larger than the corresponding values obtained from dielectric experiments on the sodium salts of polystyrenesulphonic acid (b_0 ~ 430 Å), of polymethacrylic acid (b_0 ~ 420 to 530 Å) and of poly-L-glutamic acid (b_0 ~ 520 to 670 Å) [19, 53]. At the present stage, where experiments on the same samples using the electrooptic and dielectric techniques are not available, more definite conclusions cannot yet be drawn. A very detailed analysis of the electric birefringence within the framework of the model introduced by Van der Touw and Mandel will now be necessary to clarify the question whether it is possible to find a consistent interpretation of both dielectric and electrooptic data in terms of the same model. We hope to report on these points in a future work.

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