

Aggregation Behavior of Rodlike Ionogenic Polymers in Chloroform

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The rodlike ionogenic polymers poly(*p*-pyridylene-phenylene) and poly(*p*-pyridylene/phenylene-ethynylene) form polyelectrolytes when protonated with toluene sulfonic acid or ethane sulfonic acid in chloroform solution. This molecular modification, clearly indicated by a marked red shift of the UV absorption band, induces the formation of prolate, bundlelike aggregates, whose size and shape are obtained from their rotational dynamics as revealed by electric birefringence relaxation and their translational dynamics as measured by dynamic light scattering. The aggregates have a length of 400–600 nm and a high aspect ratio >15 . In general, the polyelectrolyte molecules are arranged with their long axes parallel to the long axis of the aggregates. They probably attract each other through the electrostatic interaction with counterions. The counterions are not bound to specific sites but may be shifted under the action of an external electric field to account for the highly anisotropic electric polarizability. When inert salt or excess sulfonic acid is added, these compounds seem to accumulate within the aggregates and influence the attractive forces. This is generally leading to an elongation of the aggregates and, in the case of added salts, even to a marked reduction of birefringence.

Introduction

Polyelectrolytes are substances with exceptional properties due to their high molar mass and large charge density. Despite their widespread appearance in biological systems and in industrial applications,^{1,2} there is still a lack of fundamental knowledge, particularly with regard to a quantitative treatment of counterion-polyion interaction. Stiff, rodlike polyelectrolytes like poly-*p*-phenylene (PPP) derivatives were synthesized and carefully studied as model systems because a significant simplification was anticipated from the exclusion of conformational freedom.³ This strategy, being successful in certain cases, has produced additional difficulties in others. Often, aggregation was observed when aqueous solutions of rodlike polyelectrolytes were investigated with or without additional salt.⁴ The dependence of self-organization on concentration, ionic strength, and valency of counterions in an aqueous environment was elaborated in detail.^{5,6}

In water, PPPs only dissolve, if at all, when they carry ionic groups. The backbone is very hydrophobic, and the entropy gain due to ion dissoziation is needed to produce a negative free energy of dissolution. Nonionic PPPs, on the other hand, dissolve in organic solvents of low polarity. If ionogenic PPPs are employed, they can be converted into polyelectrolytes, and the possible formation of supermolecular structures in low-polarity solvents can be studied.

In this work, the rigid rodlike and ionogenic polymers poly(*p*-pyridylene-phenylene) (PPPyP) and poly(*p*-pyridylene/phenylene-ethynylene) (PPPyPE) were investigated in chloroform (Figure 1). Conversion of the nonionic compounds into polyelectrolytes was achieved by protonation by sulfonic acids. The

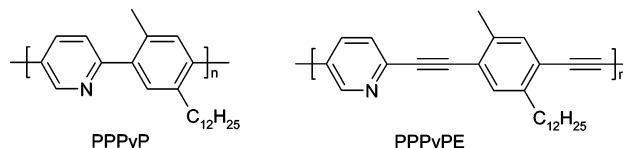


Figure 1. Chemical structures of PPPyP and PPPyPE.

dependence of the aggregation behavior of the polyelectrolytes on the degree of protonation and the concentration of different monovalent salts was studied by electric birefringence and light scattering.

Electric birefringence measurements are particularly suited to investigate polyelectrolytes in dilute solution because of the extraordinarily large signals observed.⁷ The method has therefore been frequently applied, mainly on aqueous systems.⁸ Application of an electric field to a polyelectrolyte solution leads to the orientation of the polyelectrolyte molecules. Because of anisotropy of their optical (high frequency) polarizability, this orientation causes birefringence. Orientation of polyelectrolyte molecules by electric fields, on the other hand, is readily achieved because of their extremely large anisotropy of the electric (low frequency) polarizability that can be traced back to the easy displacement of counterions along the polyions.⁹ A similar polarization mechanism exists for colloidal particles, where the ions in the electric double layer are equally easily displaced.¹⁰

Whether or not polyelectrolytes show corresponding features in organic solvents, where the ionic dissociation is significantly reduced or absent at all, is one of the central questions tackled in this work. Chloroform has a dipole moment of 1.15 D and exhibits a dielectric constant of $\epsilon = 4.72$ at 25 °C.¹¹ It is considered an inert low-polarity solvent of high polarizability, where ions are expected to form ion pairs or larger clusters. A second question therefore concerns the state of dissolution of rigid rodlike polyelectrolytes in chloroform, particularly the formation of aggregates.

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Theoretical Background

The steady-state birefringence, Δn_0 , brought about by non-interacting molecules or particles in solution, can be expressed by their optical anisotropy, $\Delta\alpha^{\text{opt}}$, the orientation factor, $P_2(\cos \theta)$, and the concentration, c , of the considered species

$$\Delta n_0 \sim c P_2(\cos \theta) \Delta\alpha^{\text{opt}} \quad (1)$$

If the molecules or particles do not possess a permanent dipole moment (as usually accepted for polyelectrolytes) and the electric field strength is sufficiently small ($P_2(\cos \theta) \ll 1$), the orientation factor is calculated as follows

$$P_2(\cos \theta) = \frac{\Delta\alpha^{\text{el}} E^2}{15kT} \quad (2)$$

where $\Delta\alpha^{\text{el}}$ is the anisotropy of electric polarizability, E is field strength, k is Boltzmann constant, and T is temperature. Combination of eqs 1 and 2 leads to Kerr's law¹²

$$\lim_{E \rightarrow 0} \Delta n = B\lambda E^2 \quad (3)$$

Here, B is the Kerr constant and λ the wavelength of the incident light.

The electric polarizability is a measure of how easily the counterions are shifted along a polyion or particle and therefore comprises some essentials of counterion–polyion interaction. In contrast, the optical polarizability depends on the electronic structure. For rigid rodlike polymers, it is essentially constant.

The transients observed after instantaneous application or cessation, respectively, of a constant electric field proceed according to

$$\Delta n = \Delta n_0(1 - \exp(-t/\tau)) \text{ or } \Delta n = \Delta n_0 \exp(-t/\tau) \quad (4)$$

(The first equation is valid only when permanent dipole moments are absent or negligible.) The characteristic relaxation time τ is related to the rotational diffusion coefficient, D_{rot} , of the molecules or particles by

$$D_{\text{rot}} = \frac{1}{6\tau} \quad (5)$$

D_{rot} depends on the size and shape of the particles. Considering ellipsoids of revolution, it can be calculated by the Perrin equation¹³

$$D_{\text{rot}} = \frac{3kT}{8\eta\pi a^3} \left[\ln \frac{2a}{b} - 0.5 \right] \quad (6)$$

where $2a$ and $2b$ are the lengths of the major and minor axes of the ellipsoid, respectively, and η is the viscosity of the solvent. D_{rot} is thus a useful parameter to estimate the shape of the particles of interest, and the transients observed in electric birefringence measurements provide a means of its determination. Of course, when the objects studied possess a distribution of sizes and shapes, the rise and decay of birefringence become multiexponential, and the estimate of adequate averages might be difficult.

Dynamic light scattering (DLS) mainly probes the translational dynamics of molecules or particles in solution. Appropriate data analysis,¹⁴ which is not reviewed here because of its widespread use, yields the translational diffusion coefficient,

D_{trans} , that is often expressed in terms of a hydrodynamic radius, R_h , via the Stokes–Einstein equation

$$D_{\text{trans}} = \frac{kT}{6\pi\eta R_h} \quad (7)$$

If the shape of the objects deviates strongly from spherical, the equations derived by Perrin seem more suitable.¹⁴ For prolate ellipsoids of revolution, he obtained

$$D_{\text{trans}} = \frac{kT}{3\pi\eta(2a)} \frac{1}{\sqrt{1 - \left(\frac{b}{a}\right)^2}} \ln \left[\frac{1 + \sqrt{1 - \left(\frac{b}{a}\right)^2}}{\left(\frac{b}{a}\right)} \right] \quad (8)$$

In the case of $b/a \ll 1$, this equation can be approximated as

$$D_{\text{trans}} = \frac{kT}{3\pi\eta(2a)} \ln \left(\frac{2a}{b} \right) \quad (9)$$

Materials and Methods

The synthesis of PPPyPE has already been described in detail elsewhere.¹⁵ PPPyP was synthesized in analogy to the Suzuki-type coupling reaction (cf. ref 16) by a palladium-catalyzed polycondensation of 2,5-dibromopyridine and 2,5-bis(boronic acid propane-1,3-diylester)4-dodecyl-toluene.

The molar mass distribution of PPPyP was determined by gel permeation chromatography (GPC). The originally obtained values based on polystyrene calibration were converted to actual molar masses by adopting a rescaling relationship derived from calibration measurements using a series of oligomeric, non-ionogenic *p*-phenylenes.¹⁵ The molar mass distribution is bimodal with $M_n = 8\,400$ g/mol and $M_w = 26\,000$ g/mol. This converts into contour length averages $l_n = 20$ nm and $l_w = 60$ nm, where the length of a repeat unit has been taken to be 0.84 nm.¹⁷

For PPPyPE, a number average molar mass of $M_n = 2\,900$ g/mol was obtained by vapor pressure osmometry. The molar mass distribution of this polymer is close to a Schulz–Flory distribution, as revealed by GPC. Hence the contour length averages can be estimated to be $l_n = 11$ nm and $l_w = 22$ nm by assuming a repeat unit length of 1.5 nm.

To generate polyelectrolytes, the uncharged polymers were protonated by *p*-toluene sulfonic acid (TSA) or ethane sulfonic acid (ESA): The uncharged PPPs were dissolved in chloroform that was stabilized by amlenes. ESA, being a liquid, could be added directly to the polymer solution by means of a microsyringe. TSA was added as a 1% solution in THF. (The amount of THF thus dissolved in chloroform was typically around 1 vol %.) The content of sulfonic acid is quantified by equivalents $x = \text{mol TSA or ESA per mol pyridylene functions}$. The solutions were allowed to stand for 2 days before measurements were made.

Tetrabutylammonium chloride, bromide, and thiocyanate were used as additional electrolytes in order to vary the ionic strength. These salts are readily soluble in chloroform.

The electric birefringence was measured at room temperature (22–23 °C) using a standard setup consisting of a He–Ne laser ($\lambda = 633$ nm), a Glan–Thompson polarizer, a Kerr cell, a quarter-wave plate, an analyzer, and a photomultiplier.^{8,18} A digital oscilloscope (Nicolet Corporation) that was fed by the photomultiplier recorded the birefringence signal. The Kerr cell was made up of a 50-mm quartz cuvette. In this cell, two stainless steel electrodes coated with gold were sited and spaced

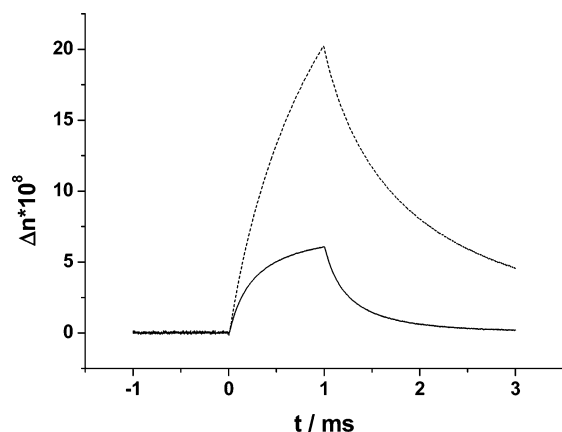


Figure 2. Typical birefringence signals: $c(\text{PPyP}) = 0.167 \text{ g/L}$ protonated with 0.9 equiv of TSA (full curve) or 4 equiv of TSA (dashed curve), $E = 6 \times 10^4 \text{ V/m}$.

by a Teflon fixture to 4.1 mm. A Cober pulse generator was used to apply direct current pulses with a typical duration of 1 ms and voltages of 100–500 V. All birefringence data were obtained by single electric field pulses.

By use of this apparatus, one can measure birefringence signals down to $\Delta n = 10^{-10}$. The solvent chloroform shows a negative birefringence of $\Delta n_0 = -10^{-9}$ at an electric field strength of $2.4 \times 10^5 \text{ V/m}$ ($\approx 1000 \text{ V}$). The polyelectrolyte solutions used in our experiments exhibit birefringence signals that are usually much larger than 10^{-8} even at applied field strengths of $6 \times 10^4 \text{ V/m}$ ($\approx 250 \text{ V}$).

Some typical signals obtained on solutions of protonated PPyP are shown in Figure 2. The birefringence signal is positive indicating that the axes of the highest electric polarizability and of the optical polarizability coincide. No steady state was reached during the duration of the pulse with any sample in this investigation. Therefore, the maximum value of the birefringence signal achieved after 1 ms was referred to when different systems had to be compared. The relaxation curve after cessation of the pulse was fitted with a single exponential in order to obtain an estimate of the mean relaxation time, τ . Although the decay is not really represented by a single exponential, this procedure is sufficiently exact to get reliable data.

DLS measurements were performed at 25°C on an ALV goniometer system with a multi- τ digital correlator ALV/LSE-5003. A He–Ne laser operating at a wavelength of $\lambda = 633 \text{ nm}$ was used as the light source. Intensity correlation functions were measured at scattering angles 60° , 90° , and 120° . They were converted into normalized field correlation functions, $g^{(1)}(\tau)$, by applying the Siegert relation. The distribution of decay rates, $G(\Gamma)$, was obtained via a CONTIN analysis, according to

$$|g^{(1)}(\tau)| = \int G(\Gamma) e^{-\Gamma\tau} d\Gamma \quad (10)$$

The characteristic Γ values were then used to calculate translational diffusion coefficients according to $D_{\text{trans}} = \Gamma/q^2$, with q being the scattering vector, $q = 4\pi n \sin(\theta/2)/\lambda$. The q^2 dependence of Γ was verified in all cases.

Results and Discussion

In the unprotonated form, both polymers do not show any detectable electric birefringence in chloroform solution at concentrations up to 0.17 g/L . This is in sharp contrast with solutions of the protonated samples, where large signals were obtained. The difference in birefringence between unprotonated

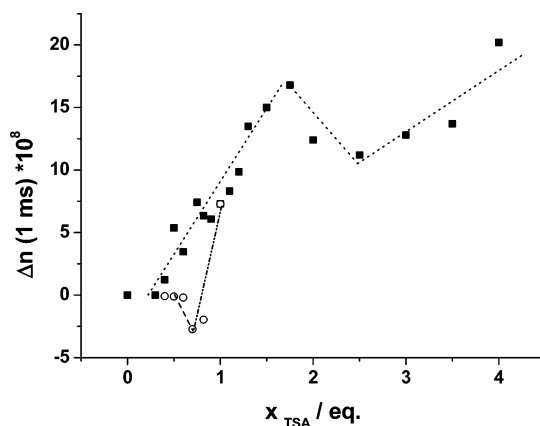


Figure 3. Dependence of the electric birefringence on the amount of protonating agent TSA: $c(\text{PPyP}) = 0.167 \text{ g/L}$, $E = 6 \times 10^4 \text{ V/m}$. (■) Fast addition of TSA, (○) successive addition of TSA (cf. text). Dashed lines meant to guide the eye.

and protonated solutions amounts to several orders of magnitude at least. Hence, the degree of protonation is an important quantity affecting either the structures formed by the corresponding species in solution, the polarization mechanism, or both. Therefore, the influence of the degree of protonation on the electric birefringence was studied systematically.

PPyP + TSA. Figure 3 shows the maximum birefringence produced by a 1-ms field pulse ($E = 6 \times 10^4 \text{ V/m}$) on a PPyP solution of concentration 0.167 g/L . (This corresponds to $5 \times 10^{-4} \text{ mol/L}$ of pyridylene moieties.) A detectable birefringence is first seen when 0.3 equiv of TSA per repeat unit of PPyP are added. The birefringence rises markedly upon increasing the amount of TSA to 1.5–2 equiv and then decreases somewhat and then increases again. This course of data points can be measured reproducibly. Generally, the birefringence is positive, indicating that the maximum electric polarizability points in the direction of the polymer backbone. (The maximum optical polarizability is assumed to be along the polymer backbone because of the conjugated π system).

The data considered so far are obtained by adding the appropriate amount of TSA (in form of a concentrated solution in THF) to the solution of the PPyP in chloroform. If this procedure is slightly altered, namely, that small quantities of TSA (corresponding to 0.1–0.2 equiv) are added one after the other, with ample time intervals (1–2 days) between successive additions, negative birefringence signals are observed at degrees of protonation around 0.7–0.9 (open symbols in Figure 3). Such data can also be reproduced. This observation shows that the way of protonation plays some role, at least in a limited range, and that one has to conclude that the structures formed are not necessarily equilibrium structures.

Another indication for nonequilibrium effects can be drawn from aging experiments. When measurements on the same solution are repeated after several days, the birefringence signals are usually some 10% larger than before. The increase slows down with aging time, but constant data are not obtained.

From the decay curves of the birefringence signals, characteristic relaxation times are determined. These relaxation times are used to estimate rotational diffusion coefficients. Figure 4 shows the dependence of D_{rot} on the amount of TSA. The data correspond to the measurements where the appropriate amount of TSA was added in one portion (full symbols in Figure 3).

Upon increasing the amount of acid, the rotational diffusion coefficient decreases continuously from 500 s^{-1} down to 150 s^{-1} , according to relaxation times from 250 to $1000 \mu\text{s}$. The

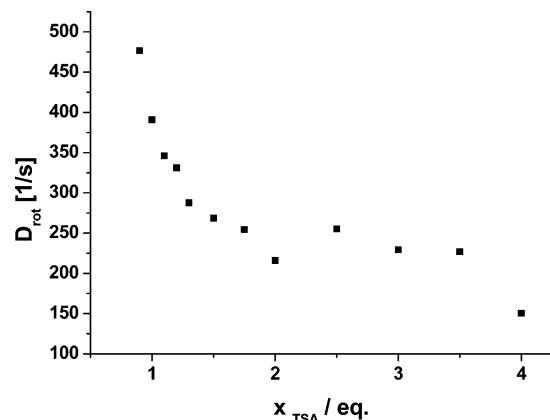


Figure 4. Dependence of the rotational diffusion coefficient on the amount of protonating reagent; $c(\text{PPyP}) = 0.167 \text{ g/L}$.

major change occurs in the range 0.8–2 equiv of TSA, which coincides with where the major change in $\Delta n(1 \text{ ms})$ takes place (cf. Figure 3). Diffusion coefficients obtained when TSA quantities are less than 0.8 equiv are not shown because of large and unsystematic scatter.

The rotational diffusion coefficients observed are 2–3 orders of magnitude smaller than expected for single PPyP molecules. (By assumption that the length of a rigid rodlike PPyP molecule is 60 nm (weight average) and the diameter is 1 nm, a rotational diffusion coefficient around 10^5 s^{-1} is obtained.) Hence, the particles present in solution and causing the electric birefringence must be appreciably larger than single molecules. The small rotational diffusion coefficients observed clearly indicate that extended molecular aggregates or clusters are formed, whose size seems to increase with rising amount of TSA. These aggregates have to be highly anisotropic to account for the birefringence. It is conjectured that the PPyP molecules are arranged in parallel thus forming a nematic-like structure within these discrete aggregates. The parallel arrangement of molecules accounts for a high optical anisotropy. The electrical polarizability has to be anisotropic as well in order to cause the orientation of the aggregates in an electric field. This fact is leading to the assumption that the counterions are not bound to specific sites but are easily shifted within the aggregates under the action of an external electric field. The anisotropy of electric polarizability is thus linked to the geometrical aspect ratio of the particles.

To confirm and complement these conclusions, DLS measurements were performed. The analysis of the measured correlation functions revealed two hydrodynamic radii or translational diffusion coefficients, respectively. Figure 5 shows the variation of these quantities with rising amount of TSA.

Obviously, there are large particles present, which are characterized by a hydrodynamic radius in the range of 55–63 nm, and small objects with a hydrodynamic radius around 5 nm. The relaxation corresponding to the large particles is the major contribution. (On the basis of scattering intensities, the ratio is 19:1.) It seems likely to associate the smaller radius with single polymer molecules, and the larger one with aggregates. The results of the DLS measurements do not vary perceptibly with the degree of protonation, unlike those of the electric birefringence. Also, variation of temperature between 8 and 39 °C did not produce any significant change. Static light scattering experiments performed on some selected samples gave a radius of gyration of $(76 \pm 4) \text{ nm}$.

The appearance of two relaxation times in DLS measurements is known from the literature. Liu et al. found such behavior in

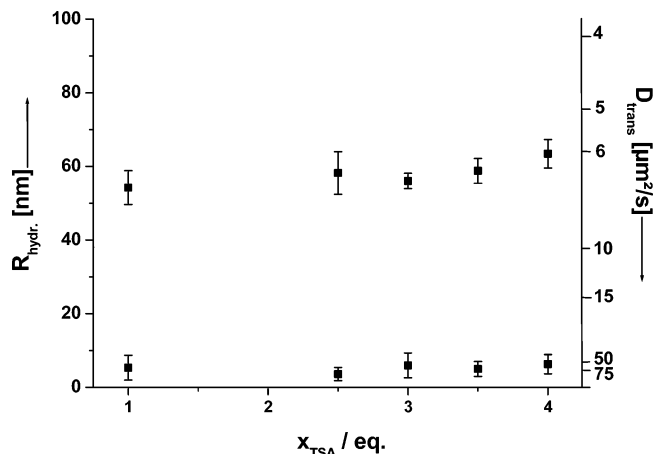


Figure 5. Dependence of the translational diffusion coefficients and the corresponding hydrodynamic radii of the two species detected by DLS on the amount of protonating agent: $c(\text{PPyP}) = 0.167 \text{ g/L}$.

their study of rigid rodlike polyelectrolytes in aqueous solutions.⁴ They interpreted the extramolecular structure as aggregates consisting of several macro ions and their condensed counterions, surrounded by a counterion atmosphere.

Combining the results obtained from electric birefringence measurements and from dynamic light scattering allows us to devise a more refined image of the aggregates. We assume for convenience that their shape be adequately approximated as an ellipsoid of revolution. Then, the Perrin equations for the translational and rotational diffusion coefficient, eqs 6 and 9, can be combined to calculate the size of the axes of the ellipsoid from experimental data for D_{trans} and D_{rot} . The shape of the particles is suitably expressed by quoting the length, $2a$, and the aspect ratio, $p = a/b$. Figure 6 shows the calculated values in dependence on the amount of added TSA.

Upon increasing the amount of TSA from 1 to 4 equiv, the length of the aggregates rises from about 400 nm to almost 600 nm, while the aspect ratio changes from 15 to approximately 40. This change is distinctly revealed in the rotational diffusion coefficient because of its strong length dependence, whereas the translational diffusion coefficient is only slightly affected. The long axis of the PPyP molecules must be parallel to the long axis of the aggregates in order to account for the positive birefringence.

As stated further above, the way of preparing the protonized sample can have an influence on the structures formed. By repeated addition of small portions of TSA with ample time intervals between successive additions, negative birefringence data were obtained in the range 0.7–0.9 equiv of TSA per monomer unit. These negative birefringence values are coupled with extremely long relaxation times, in some cases of the order of 10 ms. Some typical signals are depicted in Figure 7.

Unusually slow relaxations of birefringence indicate either very large clusters or an interconnected structure whose parts do not relax independently. Negative birefringence appears if the axis of the highest optical polarizability, namely, the polymer backbone, and the direction of the applied electric field are perpendicular to each other. Cates has devised a model to explain this phenomenon.¹⁹ He assumes that the polyelectrolyte molecules interact in a way that they are arranged parallel to form presmectic states in disclike aggregates. In an electric field, the disclike objects tend to orient the plane of the discs parallel to the field, so that the molecular axes of the PPyP molecules point transverse to the field. As the sign of the birefringence depends only on the optical polarizability of the polymer, the signal becomes negative.

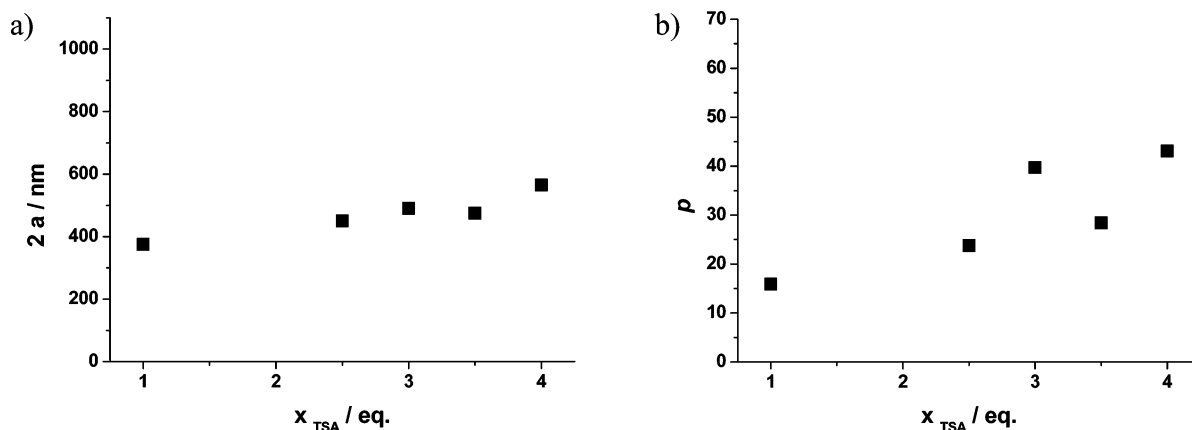


Figure 6. Dependence of the length of the major axis $2a$ (a) and the aspect ratio $p = a/b$ (b) of the ellipsoid on the amount of protonating agent.

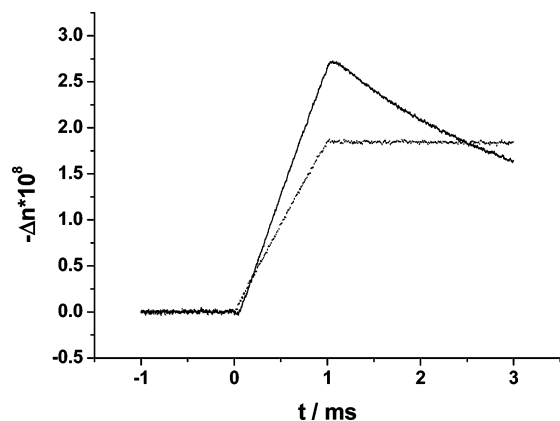


Figure 7. Typical birefringence curves observed when negative birefringence signals occurred; note the extraordinarily long relaxation times; $c(\text{PPPyP}) = 0.167 \text{ g/L}$ protonated with 0.72 equiv of TSA (full curve) or 0.82 equiv of TSA (dashed curve). $E = 6 \times 10^4 \text{ V/m}$.

In our experiments, negative birefringence appeared when TSA was added slowly and in successive portions to PPPyP solutions until a value of 0.9 equiv of acid was reached. Positive signals were obtained when the whole amount of acid was added at once. When the amount of TSA exceeded 0.9 equiv positive birefringence was found, irrespective of how the solution was prepared. Obviously the way of adding the protonating reagent is important only in a very limited range, where intermediate (metastable) structures may form. These structures are destroyed at higher amounts of TSA, leading to smaller aggregates with dimensions as shown in Figure 6. Whether or not Cates' model is applicable in our case remains speculation.

PPPyPE + TSA. When PPPyPE was employed as an ionogenic polymer and the influence of protonation by TSA was studied by electric birefringence and DLS, results similar to the ones just described were observed. Electric birefringence only appears after a threshold degree of protonation and augments when the amount of acid is further increased. The values of the electric birefringence of PPPyPE + TSA are comparable to those of the PPPyP + TSA system. The rotational relaxation times are also rising with protonation, in correspondence with rotational diffusion coefficients decreasing from 400 to 200 s^{-1} . DLS measurements reveal two hydrodynamic radii, around 57 and 4 nm, which may be attributed to single molecules and aggregates. A dependence of these radii on temperature is not observed.

PPPyPE is similar to PPPyP except for the wider spacing of the ionogenic groups. In the protonated form, the nominal linear charge density is practically only half as large as that of

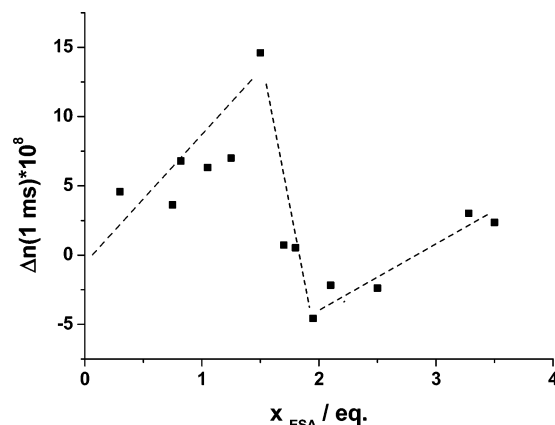


Figure 8. Dependence of the electric birefringence on the amount of protonating reagent ESA: $c(\text{PPPyP}) = 0.167 \text{ g/L}$, $E = 6 \times 10^4 \text{ V/m}$.

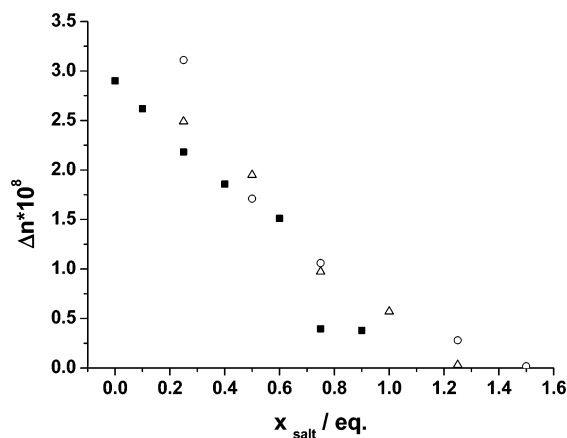


Figure 9. Dependence of the electric birefringence on the amount of added salt: (■) TBACl, (○) TBABr, (△) TBASCN, $c(\text{PPPyP}) = 0.0334 \text{ g/L}$ + 1.0 equiv of TSA, $E = 6 \times 10^4 \text{ V/m}$.

protonated PPPyP. Also, the degrees of polymerization or the lengths of the rodlike molecules differ appreciably between PPPyP and PPPyPE. Nevertheless, the aggregates formed in chloroform solution upon protonation with TSA are very similar. This means that the decisive criteria for the formation of aggregates and for their size and shape seem to be the fact that the molecules are rodlike and that their polarity is enhanced by protonation and formation of ion pairs with counterions. The actual length of the rodlike molecules seems to be of secondary importance, just as the nominal charge density.

PPPyP + ESA. As an alternative to TSA, ESA was used to protonate PPPyP. The maximum values of the electric birefrin-

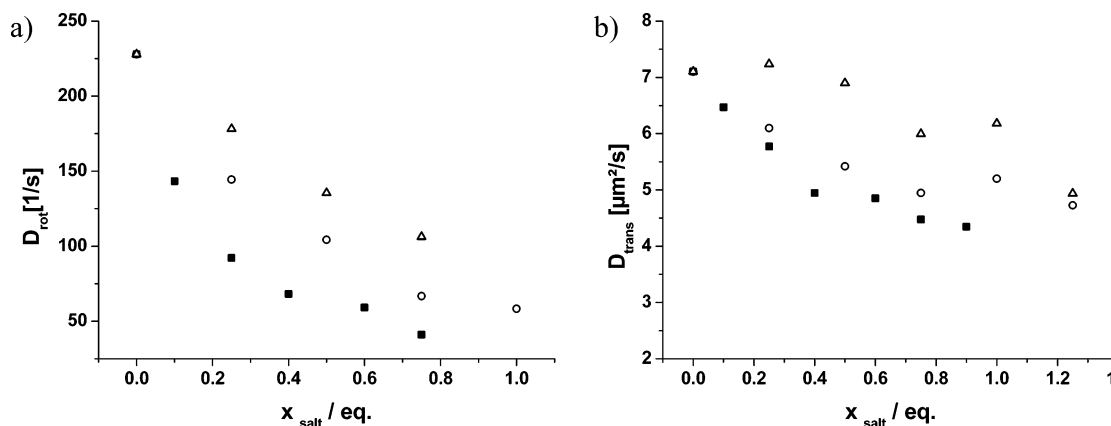


Figure 10. Rotational diffusion coefficient (a) and translational diffusion coefficient (b) as a function of the amount of additional electrolyte: (■) TBACl, (○) TBABr, (△) TBASCN, $c(\text{PPyP}) = 0.0334 \text{ g/L} + 1.0 \text{ equiv}$ of TSA.

gence obtained with 1-ms pulses are shown in Figure 8 as a function of the amount of ESA.

Similar to the results observed when TSA was used, the birefringence first appears at 0.3 equiv of acid. It increases upon addition of acid until a maximum value is reached at approximately 1.5 equiv. Then the birefringence drops sharply and even becomes negative in the range around 2 equiv of ESA. Further addition of ESA leads to another sign reversal.

This course of data, although seeming erratic at first sight, is in fact reproducible. In particular, no dependence on sample preparation was observed. The way of adding ESA directly or successively to the PPyP solution had no perceptible influence on the birefringence signals. There is also a common feature in Figures 3 and 8: The maximum of birefringence appears around 1.5 equiv of acid and is followed by a minimum at around 2–2.5 eq. This feature is underscored by showing the dashed lines. However, at high degrees of protonation the absolute values of the birefringence differ markedly when protonation is achieved by ESA instead of TSA.

The relaxation times obtained from the decay signals (data not shown) are more scattered than in the case when TSA is used for protonation. They rise with increasing amounts of ESA and become extremely long, of the order of several milliseconds, when the birefringence signal is negative. This is largely in accord with what was observed with TSA.

DLS measurements proved to be more difficult because the scattering intensities were mostly very weak. Obviously, the scattering contrast depends on the acid used for protonation, i.e., on the nature of the counterions enclosed in the aggregates. The few samples, whose intensity correlation curves could be analyzed, contained two species with hydrodynamic radii around 5 and 75–80 nm, indicative of single molecules and large aggregates. The aggregates are therefore somewhat larger when ESA is used for protonation.

Addition of Monovalent Tetrabutylammonium Salts to Polyelectrolyte Solutions. To check whether the size, shape, or stability of the aggregates formed upon protonation of PPyP can be controlled by other parameters, different tetrabutylammonium (TBA) salts were added as additional electrolytes. In chloroform, these electrolytes do not dissociate but are present in the form of ion pairs. Hence screening effects, as usually discussed when considering aqueous polyelectrolyte solutions, should not be relevant. On the other hand, ion pairs act as dipoles and may tend to form clusters with other polar species, such as the protonated PPyP, thus possibly influencing intermolecular interactions. A limited systematic variation was achieved by employing TBA salts with chloride, bromide, and thiocyanate

as anions, thus spanning the range from hard (nonpolarizable) to soft (polarizable) ions. Electric birefringence and DLS were again used to obtain information on the kind of aggregation of the polymers in solution.

Some typical results are shown in Figures 9 and 10. The polymer PPyP was first protonated by an equimolar amount of TSA. As a third solute, a TBA salt was added in quantities up to 1 equiv, corresponding to a maximum concentration of 10^{-4} mol/L . This leads to a marked decrease of the birefringence signal irrespective of which salt was used (Figure 9) and to a moderate decrease of the rotational and translational diffusion coefficients, which is strongest for the chlorides and weakest for the thiocyanates (Figure 10). The translational diffusion coefficients shown in Figure 10 are those of the aggregates. The corresponding hydrodynamic radii cover a range from 50 to 80 nm. A second species with hydrodynamic radius 5 nm was also detected in all these solution.

The reduction of the birefringence signal by adding salt to polyelectrolyte solutions is also known from aqueous solutions. In that case, electrostatic screening effects give rise to coil shrinkage, thus leading to a reduction of optical anisotropy and an increase of D_{rot} . In chloroform solution, the added salts are not dissociated, and similar screening cannot occur. Even so, adding TBA salt to the polyelectrolytes in chloroform leads to a marked decrease of the birefringence. However, the rotational and translational diffusion coefficients decrease as well, pointing to a growth of the aggregates. This opposed behavior upon adding salt is not expected and difficult to explain. One may speculate that the TBA salts prefer the more polar aggregates to chloroform and accumulate within the aggregates. If this enrichment of salt is leading to a reduction of the nematic-like order of the PPyP molecules and thus a reduction of the optical anisotropy of the aggregates, the size increase and concurrent drop of birefringence would be comprehensible. Alternatively, the enrichment of salt could cause a reduction of the spatial rigidity of the aggregates. When aggregates assume the form of bent rods, the anisotropy of electric polarizability is strongly reduced, and the maximum polarizability may even shift to the transverse direction.²⁰

Comparison with Figures 4 and 5 reveals that the effect of TBA salts is more pronounced than that of excess TSA. The latter is an ionogen, forming ions only under suitable conditions, while the TBA salts are ionophores. The ionic character drops in the sequence TBACl, TBABr, TBASCN, and TSA. The influence on the aggregates seems to run just in the same direction: the larger the ionic character, the higher the tendency of the salts to affect the size and shape of the aggregates.

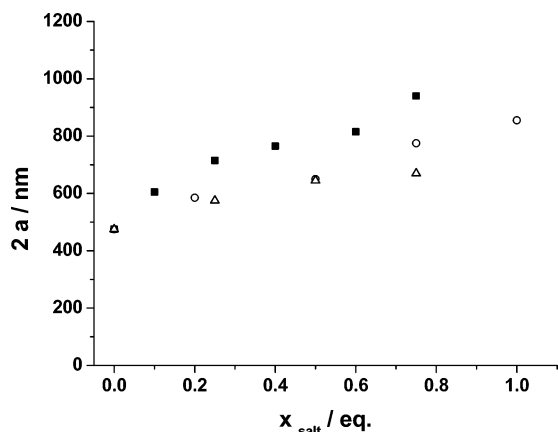


Figure 11. Dependence of the length of the major axis $2a$ of the ellipsoid on the amount of added salt: (■) TBACl, (○) TBABr, (△) TBASCN.

Combining the data for D_{rot} and D_{trans} and assuming that the aggregates have ellipsoidal shape, their lengths and widths were estimated. Figure 11 shows the dependence of the length, $2a$, as a function of the amount of TBA salts. $2a$ rises from the order of 400–800 nm and more. Concurrently, the aspect ratio also seems to grow from around 30 to 50–80. (The error in calculating the aspect ratio is quite large in this range; so we merely state that p is large and refrain from showing the data because of substantial scatter.)

Comparable results were obtained upon addition of TBA salts to PPPyPE samples protonated with TSA and to PPPyP samples protonated with ESA. The birefringence decreases significantly by raising the TBAX concentration, and the rotational diffusion coefficient drops somewhat indicating larger or longer aggregates.

Conclusions

The rodlike ionogenic polymers PPPyP and PPPyPE form molecular solutions in chloroform. Upon protonation with TSA or ESA, which is indicated by a marked bathochromic shift of the UV absorption band, the polymers aggregate. The size and shape of the aggregates can be deduced from the relaxation of electric birefringence and the correlation times determined by DLS. DLS shows that, besides aggregates, there are always single molecules in solution. The aggregates observed are not in an equilibrium state, since they seem to grow slowly with time and in some instances, a strong dependence on preparation conditions was observed. However, sufficiently reproducible results are obtained when the degree of protonation exceeds a certain threshold. Under these conditions, some general trends are noticed, which are observed irrespective of the nature of the polymer and the sulfonic acid.

The aggregates are prolate objects ($2a \approx 400\text{--}600$ nm) with a high aspect ratio. As the birefringence measured is mostly positive, we can conclude that the polyelectrolyte molecules are arranged with their long axes parallel to the long axis of the aggregates. The polyelectrolyte molecules probably attract each other through the electrostatic interaction with counterions, thus forming a bundlelike arrangement. One has to assume that the counterions are not bound to specific sites but may be shifted under the action of an external electric field to account for the large electric polarizability. The latter is markedly anisotropic because of the geometrical anisotropy of the aggregates, and this fact is the reason for the large electric birefringence values observed.

When TBA salt or excess sulfonic acid is added, these compounds seem to accumulate within the aggregates and influence the attractive forces. This is generally leading to an elongation of the aggregates (drop of rotational diffusion coefficient). The fact that the birefringence is concurrently reduced when TBA salt is added remains rather unclear and leaves room for speculation.

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