How Necklace Pearls Evolve in Hydrophobic Polyelectrolyte Chains under Good Solvent Addition: A SANS Study of the Conformation

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ABSTRACT: The chain conformation in sulfonated polystyrene PSSNa of a degree of sulfonation 0.34 ≤ f ≤ 1, i.e., of various hydrophobicity, is followed in mixtures of water and increasing content of tetrahydrofuran (THF), a good solvent of the hydrophobic polystyrene moieties (which improves the solvent quality of the mixture). This is achieved by measuring the chain form factor by small-angle neutron scattering using the zero average contrast method (ZAC). Polymer concentrations 0.17 and 0.34 M correspond in our case to the semidilute regime or its limit with dilute regime depending on the chain concentration. The main result is the monitoring with added THF of the pearl necklace conformation. This heterogeneous structure, made of wormlike chain parts (strings) and pearls, was observed formerly in water: when f decreases, the string contribution decreases, and the pearls size, characterized by a maximum in Kratky primitive chain parts (strings) and pearls, was observed formerly in water: when f decreases, the string contribution decreases, and the pearls size, characterized by a maximum in Kratky primitive length density distribution φ(q), as well as the modeling, suggest that while the sphere size varies a few, N decreases clearly with added good solvent. A link with the simulation of Liao et al. can be found. A second result, important in practice, is that all modeling of the scattering establishes that THF addition makes vanish an excess of low q scattering due to large compact spheres present in water. A third result is obtained after a “THF treatment” procedure, consisting of adding THF and then removing it by evaporation: (i) the spherical aggregates are washed out, and (ii) the pearl necklace conformation of the chain returns to the one in water solution before treatment. Therefore, the pearl necklace conformation of the hydrophobic polyelectrolyte in aqueous solution appears to be in an annealed equilibrium state resulting from hydrophobic attraction and electrostatic repulsion.

I. INTRODUCTION

Polymers (PE) can be “hydrophobic”, a very important class of polymers, where ionizable groups, which dissociate in water into hydrophilic parts bearing electrostatic charges, are combined with hydrophobic parts. These can be parts of the backbone in homopolymers, or repeat units of one type in copolymers, or moieties grafted to the backbone. This opens a huge range of opportunities in industry and of situations in biology.

Under certain conditions, essentially when strongly hydrophobic parts coexist with highly charged parts, an original model was proposed. It starts from the description of a hydrophilic single chain. In practice, this is an alignment of electrostatic blobs. It has been turned into the pearl-necklace model, where the balance between collapse and extension results in the formation of compact beads (the pearls) joined by narrow elongated strings. Simulation is consistent with this description.

In practice, due to the large volume they span over, semi-flexible chains overlap for lower concentration than flexible neutral chains. The semidilute regime is reached at lower concentration c*, above which many chains interact with each other; the highly charged polyelectrolytes in good solvent form an isotropic transient network. In the case of hydrophilic polyelectrolyte, the correlation length ξ, i.e., the mesh size of the isotropic transient network, scales with polyelectrolyte concentration as ξ ~ q−1/2, as observed by SANS and SAXS. Variable charge rates in good solvent, controlled via chemical synthesis or variable pH, have been also studied. The scaling has been extended to account for the partial charge and the
Oosawa–Manning condensation\textsuperscript{16,17} which agrees with SANS and SAXS measurements.\textsuperscript{18,19} In the case of hydrophobic polyelectrolyte, two semidilute concentration regimes have been predicted by Dobrynin et al.:\textsuperscript{4,6} the string-controlled regime and the bead-controlled regime. The string-controlled semidilute regime is similar to the one observed in the semidilute regime case for hydrophilic polyelectrolyte; it exists as long as the correlation length \( \xi \) of the solution is larger than the length \( \ell_{\text{so}} \) of a string between two following beads. Therefore, a classical polyelectrolyte behavior is expected, as for hydrophobic PE, and \( \xi \) scales as \( \xi \approx \ell_{\text{so}}^{1/3} \). For higher concentration where \( \xi \) has decreased enough to become of the order of \( \ell_{\text{so}} \) a bead-controlled semidilute regime is expected to take place; the correlation length \( \xi \) scales as \( \xi \approx \ell_{\text{so}}^{1/3} \), and the system behaves as a solution of charged beads of constant size.

The Dobrynin theory has received partial corroborating with the experiments on partially sulfonated polystyrene (PSSNa) in water, in the semidilute regime:

- When all chains have the same contrast with respect to solvent, the total structure function \( S_1(q) \) is measured. The single chain scattering, \( S_1(q) \), is not directly accessible (except in some dilute regimes where it can be extracted from \( S_T(q) \)). \( S(q) \) is measured by small-angle X-ray scattering (SAXS) and also by small-angle neutron scattering (SANS). It displays a “polyelectrolyte peak” with abscissa \( q^\alpha \). The length \( \xi \sim 1/q^\alpha \) scales as \( \xi \approx \ell_{\text{so}}^{1/3} \), where \( \alpha \) decreases from 0.5 to less than 0.4 when decreasing the chemical charge rate \( f \). Through \( \xi \), the correlation condensation has been evaluated, and it was found that the effective charge is strongly reduced\textsuperscript{18} compared to the hydrophilic case\textsuperscript{16,17} as explained later.\textsuperscript{18} It was also proposed that once the hydrophobic “pearls” formed, the low dielectric constant \( \epsilon \) inside the pearls may trigger the formation of ion pairs, explaining the observed reduction in osmotically active counterions.\textsuperscript{18}

- A further step was achieved by measuring directly the single chain scattering \( S_1(q) \) using small-angle neutron scattering combined with the zero average contrast method (ZAC). While totally sulfonated polystyrene showed a wormlike chain conformation,\textsuperscript{4} partially sulfonated showed the rising of a composite conformation of strings and pearls.\textsuperscript{5,20} The size of the pearls, as extracted from a fit of the maximum of the form factor of a monodisperse sphere, to the maximum of \( q^2S_1(q) \), was on the order of 1–3 nm and increased when the rate of sulfonation is decreased. This was in good agreement with the Dobrynin pearl-necklace model. More precisely, the data are well fitted with the Liao simulation of such model, including attraction due to hydrophobic interactions and condensed counterion correlation.\textsuperscript{23} There, beads were formed and contained both neutral and charged monomers. Their size distribution appeared very widely polydisperse, but the maximum for \( f = 0.36 \) could be perfectly reproduced (Figure 12b of ref 23).

Other systems showed pearl necklaces by involving specifically interacting alkaline earth cations,\textsuperscript{24,25} or conformational changes predicted (string–globule coexistence\textsuperscript{26}) by making charges mobile on the polyelectrolyte backbone.\textsuperscript{27} Other measurements than scattering concerned polymers deposited on to a surface: ellipsometry,\textsuperscript{28} AFM,\textsuperscript{29,30} in particular in liquid cell on PSSNa.\textsuperscript{31} Instead of varying the polymer, one could vary the solvent, e.g., by decreasing solvent quality through addition to water of miscible bad solvent, like acetone. SAX(N)S showed the coil to globule transition in dilute regime.\textsuperscript{32,33} In the semidilute regime, in polar organic solvent of poor quality, acetonitrile, atactic poly[2-(methacryloyloxy)ethyltrimethylammonium 1,1,2,3,3-pentacyanopropenide] ‘MPCP’ chains give two regimes with two scaling exponents \( \alpha \) being \(-1/2\) and \(-1/7\) in qualitative agreement with the pearl necklace model.\textsuperscript{4}

Conversely, the solvent quality can be increased.

- A first way of increasing solvent quality has been achieved by increasing temperature. While no effect was seen on both inter- and intrachain interactions for fully sulfonated PSSNa,\textsuperscript{35,36} partially sulfonated PSSNa showed gentle temperature dependence as \( f \) was decreased.\textsuperscript{35} Increasing solvent quality was also done using a polar organic solvent of good quality for the backbone, allowing at the same time significant ionic dissociation. Using DMSO for PSSNa chains,\textsuperscript{37,38} a classical wormlike chain scattering was found for \( S_T(q) \) and \( S_1(q) \), independently of \( f \), in agreement with Manning condensation.

- A second way of increasing solvent quality was to add to water small amounts of an organic solvent (good solvent) for the PSSN backbone. We found that \( S_T(q) \) depends at a given \( f \) on the amount of added organic solvent (THF),\textsuperscript{38} both for the peak and for the low \( q \) scattering.

However, in all these former papers dealing with the effect of adding solvent, we measured only \( S_1(q) \), which does not give directly the chain conformation. In the present work, we will measure the \( S_1(q) \), through the somehow sophisticated “zero average contrast (ZAC)” technique. Let us explain briefly the principle: we dissolve a mixture of normal “H” chains and deuterated “D” chains, in a mixture of normal and deuterated solvent with scattering density (SLD) equal to the average of the SLDs of the H and D chains (“zero average contrast” conditions). The SLDs difference (i.e., the contrast) of H chains with the solvent mixture, \( K_H \), will be equal to \(-K_D \); hence, the front factor of the sum of H–H, D–D, H–D, and D–H interchain contributions (\( K_H^2 + K_D^2 + 2K_HK_D \)) will cancel by symmetry, letting us with the HH and DD intrachain contributions, i.e., \( S_T(q) \).

\( S_T(q) \) will be measured in two conditions:

- either when adding to water a low proportion of an organic good solvent miscible with water (THF) or using “solutions treatment”, i.e., addition of good solvent followed by evaporation.

- or using another opportunity offered by such water–THF mixtures: it is possible, after adding THF for some time (hours), to evaporate it and substitute it by water in order to keep the same concentration. We call this “THF treatment”. This should enable us to check whether the solution in water is under thermodynamic equilibrium, since measuring \( S_T(q) \) by ZAC focuses on the chain.

We will vary the charge rates of PSSNa (\( f \)), but since water solubility is lost for \( f < 0.35 \), we stay above the Manning condensation threshold (\( f > 0.36 \) for our chains).

II. MATERIALS

II.1. Polymer Synthesis and Characterization. The hydrophobic polyelectrolyte used in this study is a copolymer of styrene and styrene sulfonate (PSS) (poly(styrene sulfonate)–(styrene)\textsubscript{n}) with sodium counterions. It was prepared by postsulfonation of polystyrene

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Macromolecules XXX, XXX, XXX–XXX
based on the Makowski procedure,\textsuperscript{39} which enables partial sulfonation and leads to a well-defined polyelectrolyte.\textsuperscript{40} The Vink method\textsuperscript{41} has been also used to synthesize the fully sulfonated PSS ($f = 1$).

In order to apply correctly the zero average contrast technique, the molecular mass distributions should be very close for the perdeuterated polystyrene (d-PS) and the nondeuterated polystyrene (h-PS). Moreover, the masses must be well-defined to allow data fitting. Hence, polymers with very close degree of polymerization (d-PS, $N_{\text{wD}} = 991$; h-PS, $N_{\text{wH}} = 923$) and a narrow mass distribution about 1.04 were purchased from Polymer Standard Service (Mainz, Germany). The average value, $N_{\text{wH}} + N_{\text{wD}} = N_{\text{w}} = 957$, will be used below in the Discussion.

Two sulfonation methods are used by our group. The Makowski procedure\textsuperscript{39} is a phase transfer, interfacial reaction for partial sulfonation. A dichloroethane polystyrene solution is mixed with anhydride acetic and sulfuric acid in proportions depending on the desired degree of sulfonation. A white layer appears between the two media. After 30–60 min, the aqueous phase is neutralized with sodium hydroxide, dialyzed against deionized water until the conductivity of the external dialysis bath remains stable. The solutions are then concentrated with a rotating evaporator and finally freeze-dried. The resulting white powder is better stored away from light.

The Vink method\textsuperscript{41} is commonly used to reach total sulfonation; one starts from a polystyrene (PS) solution in cyclohexane (a PS theta solvent at 35 °C), which is poured into a mixture of sulfuric acid with phosphoric acid. After stirring for half an hour, the mixture is let to rest for decantation. Separation in three phases is triggered by addition of ice. The phase containing PSSH (polysulfonic acid) is extracted and neutralized by an excess of sodium hydroxide. The obtained PSSNa solution is dialyzed, concentrated and freeze-dried.

The degree of sulfonation $f$ of the polyelectrolytes was varied between 0.35 (the limit for solubility in water) and 1 (fully charged), using Makowski method for $f < 1$ and Vink method for $f = 1$. The degree of sulfonation $f$ is

Figure 1. $^1$H NMR spectra of PSSNa $f = 0.34$ in d-DMSO and PSSNa $f = 0.80$ in D$_2$O.
thus always above the Manning condensation limit for the charge rate, equal to \(a/\lambda_B \approx 0.36\) for PS in water (a length of one unit, \(\lambda_B \approx 7\, \AA\), Bjerrum length in water).

The degree of sulfonation \(f\) has been determined by two methods. The first one is the elementary analysis of carbon, sulfur, and sodium (the comparison between the two ratios between sulfur/carbon and sodium/carbon in the dry sample allows the determination of the degree of sulfonation). The second method is \(^1\)H NMR measurements in d-DMSO or D\(_2\)O by using the different protons of the aromatic ring which are sulfonated or not sulfonated.\(^{22}\) In Figure 1, we give some \(^1\)H NMR spectra for different sulfonated PSSNa. We checked that both methods lead to similar results.

The corresponding characteristics of all these polymers are summarized in Table 1.

### Table 1. Characteristics of the Used Polymers\(^{24}\)

<table>
<thead>
<tr>
<th>PS/PSSNa</th>
<th>(M_0) (g/mol)</th>
<th>(V_{\text{mol}}) (cm(^3)/mol)</th>
<th>(M_a) (kDa)</th>
<th>(M_0/M_a)</th>
<th>(N_w)</th>
</tr>
</thead>
<tbody>
<tr>
<td>h-PS</td>
<td>104</td>
<td>111</td>
<td>96</td>
<td>1.04</td>
<td>923</td>
</tr>
<tr>
<td>d-PS</td>
<td>112</td>
<td>111</td>
<td>111</td>
<td>1.02</td>
<td>991</td>
</tr>
<tr>
<td>h-PSSNa</td>
<td>138</td>
<td>110</td>
<td>127</td>
<td>923</td>
<td></td>
</tr>
<tr>
<td>(f = 0.34)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>d-PSSNa</td>
<td>146</td>
<td>110</td>
<td>147</td>
<td>991</td>
<td></td>
</tr>
<tr>
<td>(f = 0.34)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>h-PSSNa</td>
<td>152</td>
<td>113</td>
<td>143</td>
<td>923</td>
<td></td>
</tr>
<tr>
<td>(f = 0.47)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>d-PSSNa</td>
<td>160</td>
<td>113</td>
<td>156</td>
<td>991</td>
<td></td>
</tr>
<tr>
<td>(f = 0.47)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>h-PSSNa</td>
<td>185</td>
<td>112</td>
<td>178</td>
<td>923</td>
<td></td>
</tr>
<tr>
<td>(f = 0.80)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>d-PSSNa</td>
<td>193</td>
<td>112</td>
<td>193</td>
<td>991</td>
<td></td>
</tr>
<tr>
<td>(f = 0.80)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>h-PSSNa</td>
<td>206</td>
<td>108</td>
<td>190</td>
<td>923</td>
<td></td>
</tr>
<tr>
<td>(f = 1)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>d-PSSNa</td>
<td>214</td>
<td>108</td>
<td>212</td>
<td>991</td>
<td></td>
</tr>
<tr>
<td>(f = 1)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*Value estimated from \(N_w\) of the parent PS.*

We can also observe in Table 1 that the final degrees of sulfonation are identical for the deuterated and the nondeuterated chains, within 1 or 2% error. We preferred to check the rate of \(f\) of d and h polymers separately because sulfonation can lead to different result beyond small differences in conducting the process; this can also be due to differences in the initial degree of aggregation and to a slight isotopic effect on the reactivity. In practice, after sulfonation of d-PS, several trials were conducted on h-PS until obtaining the same value of \(f\). In practice, after sulfonation of d-PS, several trials were conducted on h-PS until obtaining the same value of \(f\).

### II.2. Preparation of Solutions

The aqueous solutions were prepared by dissolving the desired amount of the dry polyelectrolyte in 1 or 2% error. We preferred to check the rate and H\(_2\)O with a divider. Note that our measurements of the solvent scattering did not differ on h-PS until obtaining the same value of \(f\). In practice, after sulfonation of d-PS, several trials were conducted on h-PS until obtaining the same value of \(f\). In practice, after sulfonation of d-PS, several trials were conducted on h-PS until obtaining the same value of \(f\). The corresponding characteristics of all these polymers are summarized in Table 1.

The aqueous solutions were prepared by dissolving the desired amount of the dry polyelectrolyte in the mixture D\(_2\)O/D\(_2\)O respecting the zero average contrast. This will be detailed in the next section III.1.

#### III. METHODS: SANS MEASUREMENTS

### III.1. Zero Average Contrast Method

We recall the fundamentals of the most convenient method by which the average form factor of one chain among others can be obtained.\(^{20,36,37}\) We start from the general expression of the scattered intensity:

\[
I(q) = \frac{1}{V} \sum_{\alpha \beta} \sum_{i,j} k_{ij} \exp[iq(R_{ij} - R_{ij}')]
\]

(1)

Here \(k_i\) (cm or Å) = \(b_i - b_i(V_{\text{mol}_i}/V_{\text{mol}})\) is the “contraction length” between one repeating unit of scattering length \(b_i\) and molar volume \(V_{\text{mol}_i}\) and a solvent molecule \((h, v_{\text{mol}})\).

Using a mixture of H and D chains of the same molecular weight distribution in a solvent constituted of D\(_2\)O, THF\(_d\), H\(_2\)O, and THF\(_d\) enables us to fulfill the ZAC conditions (see the Appendix) and get \(I(q)\) reduced to one part of eq 1:

\[
S_1(q) = \frac{1}{V} \sum_{i,j} \sum_{\beta=\alpha} \exp[iq(R_{ij}^\alpha - R_{ij}^\beta)]
\]

(2)

which corresponds to the correlations between monomers \(i, j\) of the same chain \(\alpha = \beta\) (intrachain scattering) so that

\[
I(q) = k_{ZAC}^2 S_1(q)
\]

(3)

which permits a direct measurement of intrachain scattering of one chain among all others, even in the semidilute regime. For fully charged h-PSS and d-PSS with a solvent composition 75% water and 25% THF, ZAC conditions correspond to a solvent constituted of 54.20% D\(_2\)O, 18.00% THF\(_d\), 18.00% H\(_2\)O, and 6.90% THF\(_d\).

The contrast length values for two solvent compositions, pure water and mixture of 25% THF/75% water, are listed in Table 3.

The values evaluated for the contrast lengths of the Na counterions with the H\(_2\)O/D\(_2\)O mixture and the other solvent compositions are low; their contributions to the scattering have therefore been neglected. This has been confirmed by a more refined evaluation accounting for hydration.\(^{43,44}\)

The \(S_1(q)\) limit at \(q\) tending to zero is

\[
\lim_{q \to 0} S_1(q) = c_P N_\text{AW} N_w P(q)
\]

(4)

where \(c_P\) should be expressed in mol Å\(^{-3}\) = 10\(^{-27}\) mol L\(^{-1}\) and \(N_w\) is the Avogadro number. Hence, from the definition of the form factor, we can write

\[
S_1(q) = c_P N_\text{AW} N_w P(q)
\]

(5)
The ZAC technique, first used by the Saclay group\textsuperscript{12,36} and used since on polyelectrolytes by other authors,\textsuperscript{42,43,45} is used here for the first time, to our knowledge, for a mixture of solvents.\textsuperscript{47} This makes it more delicate, as discussed in next section.

### III.2. Measurements and Data Treatment

SANS measurements have been performed on the PACE spectrometer at the Orphée reactor of LLB, CEA-Saclay, France. A range of scattering vectors $q = (4 \pi / \lambda) \sin (\theta / 2)$ between $5 \times 10^{-3}$ and $0.4 \text{ Å}^{-1}$ was covered using the following three settings: $D = 1 \text{ m}, \lambda = 5 \text{ Å}; D = 3 \text{ m}, \lambda = 10 \text{ Å};$ and $D = 5 \text{ m}, \lambda = 13 \text{ Å}$. Samples were contained in 2 mm thick quartz cells. All measurements were done at room temperature.

All data have been normalized using the incoherent scattering of a high proton content sample, here light water; the latter has been calibrated to obtain absolute values of $(1/\pi \lambda^4)$ in cm$^{-1}$, using Cotton’s method.\textsuperscript{46} The solvent contribution is subtracted from these corrected data. The subtraction of the solvent incoherent background is, however, quite delicate and deserves further remarks. At large $q$, in practice at $q > 0.2 \text{ Å}^{-1}$, the coherent part of the intensity is very small compared to the background due to incoherent scattering, which has several origins: (i) incoherent scattering from residual water adsorbed on the polymer dry chains (i.e., hydration water molecules), (ii) hydration water molecules adsorbed on the polymer dry chains (i.e., “residual water”, more than 10% in weight), (iii) incoherent scattering from protons in the h-PSSNa and deuteron in the d-PSSNa, and (iv) protons from water vapor molecules after contact with air. These small contributions are delicate to estimate and thus make us unable to know the exact quantity to subtract with accuracy better than 5%.

Such uncertainty has little influence for small $q$ but can lead to different shapes of the scattering curves for large $q$.

Also, mixing the components leads to an extra flat scattering, called Laue scattering or sometimes “mixing incoherent”, which is actually the scattering from the mixture of small elementary components such as different molecules (h and d) in a solvent.

For best results, and to eliminate as much as possible the effects of multiple scattering (though they are here very weak) which involve the cell geometry, we have prepared under the same conditions some blanks by mixing a nondeuterated and a deuterated solvent, $D_2$O with $H_2$O or water ($D_2$O + $H_2$O), with THF (THF$_h$ + THF$_d$) aiming at the same flat intensity.

Among the difficulties, we must note all the ones inherent to the mixing of THF and water, in particular, pay attention to the fact that the boiling point of d-THF is different from the one of h-THF. Unwanted consequences would be altering the incoherent background but—more drastic—to shift the system out of the ZAC conditions.

### IV. RESULTS

#### IV.1. Effect of Degree of Sulfonation in Pure Water

First let us describe the effect, in pure water, of the reduction of degree of sulfonation, in other words, of hydrophobicity (increase of fraction of polystyrene statistical segment, strongly hydrophobic). This is shown in Figure 2 which shows the behavior already observed,\textsuperscript{20} using the representation $q^{-2}S(q) / \phi$ versus $q$ at $\phi = 0.34 \text{ M}$. We recall that this representation is extremely sensitive to the data accuracy and therefore the most exacting one to detect changes at medium and high $q$. Of course, it must be completed by other representation, such as $\ln I - \ln q$ plots and $1/I(q)$ versus $q^2$ in the Guinier range (see next sections). This first description will enable us to define different terms characterizing these curves.

For the highest degree of sulfonation $f = 1$, we observe a behavior typical of the wormlike chain,\textsuperscript{22} at low $q$ we observe an increase in the Guinier regime (see the next paragraph) followed by an inflection toward a “plateau” (dotted gray line), characteristic of a Gaussian chain, $S(q) \sim 1 / q^2$. At immediately larger $q$, the curve displays a linear increase, representing the crossover toward $S(q) \sim 1 / q$ characteristic of a rodlike regime due to the rigidity of the polyelectrolyte chain at this scale. This crossover occurs at $q = q_{c1} = 6 / (\pi L_p)$, where $L_p$ is the persistence length which would be lie here between 40 and $50 \text{ Å}$ (see below), in agreement with former measurements\textsuperscript{37} for $\phi = 0.34 \text{ M}$ with no added salt.

For lower degrees of sulfonation $f < 1$, as seen before,\textsuperscript{20} a maximum progressively rises with the increase of hydrophobicity in Figure 2 at intermediate $q$. This maximum in $q^{-2}S(q) / \phi$ will be noted as a “bump” sometimes in the paper. It is very pronounced for $f = 0.47$ and for $f = 0.34$, the lowest values attainable before chain precipitation. On the contrary, it is quite soft for $f = 0.80$. For this degree of sulfonation, we observe, at lower $q$ than the foot of the “bump” ($q \sim 0.01 \text{ Å}^{-1}$) and at a height 3 times larger than for $f = 1$ (green dotted line), a short beginning of plateau, so short that we will prefer to call it a “shoulder”. The question whether this also corresponds to a “plateau”, characteristic of a wormlike chain (WLC), will be discussed in the Modeling section.

We can notice in the curves a slight shift between the last $q$ of the medium $q$ setting and the lowest $q$’s of the large $q$ setting.

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**Table 3. Values of the Different Contrast Lengths of Polymers in Different Solvents**

<table>
<thead>
<tr>
<th>solvent</th>
<th>PSSNa $f = 1$</th>
<th>PSSNa $f = 0.80$</th>
<th>PSSNa $f = 0.47$</th>
<th>PSSNa $f = 0.34$</th>
</tr>
</thead>
<tbody>
<tr>
<td>100% water</td>
<td>$\Phi_{D,O}$</td>
<td>0.750</td>
<td>0.697</td>
<td>0.653</td>
</tr>
<tr>
<td></td>
<td>$\Phi_{H,O}$</td>
<td>0.250</td>
<td>0.302</td>
<td>0.346</td>
</tr>
<tr>
<td>$k_{\text{ZAC}} = k_{\text{water}} (\times 10^{-12} \text{ cm})$</td>
<td>3.648</td>
<td>3.747</td>
<td>3.806</td>
<td>3.987</td>
</tr>
<tr>
<td>75% water</td>
<td>$\Phi_{D,O}$</td>
<td>0.542</td>
<td>0.503</td>
<td>0.470</td>
</tr>
<tr>
<td></td>
<td>$\Phi_{THF}$</td>
<td>0.180</td>
<td>0.167</td>
<td>0.156</td>
</tr>
<tr>
<td>/25% THF</td>
<td>$\Phi_{D,O}$</td>
<td>0.207</td>
<td>0.246</td>
<td>0.279</td>
</tr>
<tr>
<td></td>
<td>$\Phi_{THF}$</td>
<td>0.069</td>
<td>0.082</td>
<td>0.093</td>
</tr>
<tr>
<td>$k_{\text{ZAC}} = k_{\text{THF+water}} (\times 10^{-12} \text{ cm})$</td>
<td>3.778</td>
<td>3.830</td>
<td>3.852</td>
<td>4.023</td>
</tr>
</tbody>
</table>

---

**Figure 2.** Scattering in $q^{-2}S(q) / \phi$ representation of PSSNa in pure water, with decreasing degree of sulfonation $f = 1, 0.8, 0.47, 0.34$ for $\phi = 0.34 \text{ M}$. The table above shows the values of the different contrast lengths of polymers in different solvents.
A physical origin could be the angular collimation of the beam. In the first points of a given collimation, there is a large error on \( q \), such that the measured scattering can contain a part of the scattering at lower \( q \), which can be higher. This can be enhanced by the fact that we are looking at a maximum in a given representation (here the Kratky plot). It could also be an error on the data normalization, common to all the spectra, or a change in one given sample. Our policy is to keep the shift unless visualization and fitting remain difficult. This was the case for \( f = 0.80 \); hence, the scattering at large \( q \) was divided by a factor 1.1.

The data for \( f = 0.34 \) are very close to what observed in former work of LLB group.\(^{20}\) For \( f = 0.36 \), the curve for \( f = 0.47 \) is very close to the one for \( f = 0.34 \), the curve already reported for \( f = 0.64 \)\(^{20}\), consistently, in between the one for \( f = 0.47 \) and \( f = 0.80 \). As in the former work,\(^{20}\) we observe, at \( q = 0.06 \) Å\(^{-1}\) and \( q^2 S(q)/\xi_q \sim 0.00035 \) Å\(^{-5}\) mol\(^{-1}\) L, an even shorter beginning of plateau, which in this last case we definitely will call a “shoulder”.

At large \( q \), the same linear increase of \( q^2 S(q)/\xi_q \), as for \( f = 1 \) is observed for \( f = 0.80 \) (similarly to the \( f = 0.64 \) case). For lower \( f \), the curve also shows a linear part, but it is much lower. Note that accurate background subtraction in this \( q \) range is very difficult.

In former works, we claimed that the maximum of \( q^2 S(q)/\xi_q \) is the signature of spherical objects in the chain, more precisely of the pearls, which are parts of the pearl necklace conformation of the chain. Their size was related to the inverse abscissa of the maximum in \( q^2 S(q) \). More precisely, as stated in the Introduction, the low \( q \) one and the maximum in \( q^2 S(q) \) were well fitted for \( f = 0.34 \) with the Liao simulation;\(^{21}\) hence, this would be the same here for \( f = 0.34 \), since the data are very close to the former ones.\(^{20}\) There, beads formed at sufficiently high concentration contained neutral and charged monomers, with wide charge distribution. This will be detailed in the Modeling section. Note that if the ZAC condition was not respected, there would be a completely different signature due to the well-known “polyelectrolyte peak” in \( S_q(q) \) (not \( q^2 S(q) \)), which would arise around 0.05 Å\(^{-1}\) (this was examined in detail in a previous publication).\(^{21}\)

In summary, in pure water when the electrostatic charge rate \( f \) of the PE decreases, the pearl contribution increases. This is in satisfactory agreement with previous reported measurements\(^{20}\) and with the Liao et al. modeling\(^{21}\) while we cannot appreciate here clearly at this stage a change of pearl size since the abscissa of the maximum does not vary noticeably.

**IV.2. Effect of THF Addition on PSS Chain Conformation.** IV.2.1. A Purely Solvophilic Action. The effect of the addition of THF in the aqueous PE solution is the central point of this work. First, we observe in Figure 3, for \( c_p = 0.17 \) M, no effect of adding THF for PSSNa \( f = 1 \), i.e., for fully sulfonated chains. The plateau of \( q^2 S_1(q)/\xi_q \) keeps this value for all THF contents (it shows the same value as for \( q^2 S_1(q)/\xi_q \) with the other concentration \( c_p = 0.34 \) M) All scattering profiles overlap (except at very high \( q \), \( q > 0.3 \) Å\(^{-1}\), which is not meaningful since the subtraction of background is very delicate). Hence, we can infer that THF, up to 10% in volume, only acts on hydrophobic interactions but does not modify electrostatic interactions which are acting on the fully hydrophilic chain. The form factor has been fitted to the one of a wormlike chain with \( L_w = 45 \pm 3 \) Å for \( c_p = 0.34 \) M\(^{59}\) (not shown here), as found formerly.\(^{22}\)

IV.2.2. An Effect Increasing with PE Hydrophobicity. We now consider decreasing degrees of sulfonation \( f < 1 \).

![Figure 3](https://example.com/fig3.png)

**Figure 3.** Scattering in \( q^2 S(q)/\xi_q \) representation of PSSNa \( f = 1 \), for \( c_p = 0.17 \) M, in pure water and with 5% and 10% added THF. The gray dotted line indicates the “plateau” value.

![Figure 4](https://example.com/fig4.png)

**Figure 4.** Scattering in \( q^2 S(q)/\xi_q \) representation of PSSNa \( f = 0.80 \) in pure water for \( c_p = 0.34 \) M and with 10% and 25% added THF.

For PSSNa \( f = 0.80 \), the effect of THF addition is clearly seen in Figure 4. For \( c_p = 0.34 \) M, the maximum is reduced progressively when passing from 0% to 25% THF; there remains, however, the trace of a maximum even for 25% THF! The same behavior is observed at lower concentration \( c_p = 0.17 \) M (Figure S1.1a, only low \( q \)). We infer that the pearl signature is strongly reduced because the solvent is now a better solvent for the non-sulfonated polystyrene statistical units. Hence, for 25% THF we are close to the shape obtained for \( f = 1 \).

For \( f = 0.80 \) in 100% water, the onset of an effective “plateau” is clear, but its height is large: 0.7 \( \times 10^{-3} \) Å\(^{-5}\). This height (\( \sim 1/L_w \)) would correspond to a quite shorter persistence length \( L_w = 20 \) Å. This would correspond to a strong electrostatic screening, not expected at this ionic strength. Meanwhile, adding 10% THF makes immediately this plateau decrease strongly and return to the value of a WLC (see the effect of THF treatment, section IV.3). This suggests a different contribution (see Discussion).

For PSSNa \( f = 0.47 \), the effect of THF addition on the scattering profiles is very pronounced and clear-cut in Figure 5.
When passing from 0% to 5% THF, the only change is the vanishing of the shoulder at the left of the maximum (this effect is important; it will be detailed further when considering THF treatment). For 10%, the maximum decreases in height, and it is clearly shifted toward large $q$. For 25% THF, the “ghost” of a maximum ("bump") is seen as an inflection point around 0.15 Å$^{-1}$, while at large $q$ $q^2 S(q)$ catches up with the curve for 50% THF. For 50% THF, the inflection point vanishes completely such that the curve displays, at both low and large $q$, the shape of hydrophilic PSSNa of Figure 3. At $c_p = 0.17$ M for the same $f = 0.34$, the behaviors at 0%, 5%, and 10% THF are very similar (Figure S.I.1b). As well as for PSSNa $f = 0.34$ and 0.17 M for the same added percentage of 5% THF. Figure 7, as an example, shows that for PSSNa $f = 0.34$ the scattering profiles overlap, until large $q$ where the curve for $c_p = 0.17$ M is slightly higher. This behavior could be linked to the lower ionic strength or simply to uncertainty in background subtraction (to which a lower $c_p$ is more sensitive).

The same trend is seen in Figure S.I.2b,c both for 5% and for 10% THF (in one case, Figure S.I.2a, for 10% THF, $f = 0.17$ (in one case, Figure S.I.2a, for 10% THF, $f = 0.47$, we find no overlap, with no obvious reason).

IV.3. Effect of THF Treatment. Following our "THF treatment" procedure, the PE chains are dissolved in water and THF mixture, the THF is then removed by evaporation. For a simple comparison, we use the more global $\log S(q)$ versus $q$ representation in Figures 8a and 8b ($q^2 S(q)/c_p$ plots are given in Figure S.I.3a,b).

All figures lead to the same conclusion: for treated samples, all curves overlap. The one of the raw solution (pure water, no treatment at all) is different: it shows an extra scattering at lowest $q$. The vanishing of the extra scattering after treatment is pronounced for treated samples, all curves overlap, until large $q$ where the curve for $c_p = 0.17$ M is slightly higher. This behavior could be linked to the lower ionic strength or simply to uncertainty in background subtraction (to which a lower $c_p$ is more sensitive).

The same trend is seen in Figure S.I.2b,c both for 5% and for 10% THF (in one case, Figure S.I.2a, for 10% THF, $f = 0.17$ (in one case, Figure S.I.2a, for 10% THF, $f = 0.47$, we find no overlap, with no obvious reason).

IV.4. Determination of the Radius of Gyration and of the Molecular Weight. Until now, we have described the behavior over the full $q$ range, using most of the time Kratky plots, which mask the low $q$ behavior. We concentrate now on the low $q$ range, using a different representation, $c_q/R_g$ versus $q^2$ (also used in the so-called Zimm plot when coping with different $c_p$), which enables, by characterizing a linear regime, to fit to the expression

$$c_q/R_g = c_q/R_g^0 1/(N_{av} N_{so} (1 + q^2 (R_g^0)^2 z/3)) q < 1$$

(6)

yielding the values of the extrapolation at zero $q$, $N_{av}$ and the radius of gyration $R_g = (\langle R_g^2 \rangle z)^{1/2}$. This linear extrapolation is drawn, in the Figure 6, the level of the plateau corresponding to the shoulders observed for the three largest THF contents. At $c_p = 0.17$ M for the same $f = 0.34$, the behaviors at 0%, 5%, and 10% THF are very similar (Figure S.I.1d).
used because it is better adapted to polymer chains than the one using the Guinier plot.

**Effect of THF Treatment at Low q.** It is easier for understanding to start by THF treatment. We show an example in Figure 9a,b; more results are given in Table 4. Many other data are given in the Supporting Information.

<table>
<thead>
<tr>
<th>% THF</th>
<th>$N_w$</th>
<th>$R_g$ (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PSSNa $f = 0.34$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0 (untreated)</td>
<td>1491 ± 75</td>
<td>82 ± 4</td>
</tr>
<tr>
<td>5</td>
<td>948 ± 47</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>932 ± 46</td>
<td>83 ± 4</td>
</tr>
<tr>
<td>25</td>
<td>926 ± 46</td>
<td></td>
</tr>
<tr>
<td>PSSNa $f = 0.80$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0 (untreated)</td>
<td>1073 ± 53</td>
<td>150 ± 7</td>
</tr>
<tr>
<td>10</td>
<td>866 ± 43</td>
<td>155 ± 8</td>
</tr>
<tr>
<td>25</td>
<td>799 ± 40</td>
<td>155 ± 8</td>
</tr>
</tbody>
</table>

The results are consistent with those represented by the log $S_1$−log $q$ plots above. All scattering profiles corresponding to a THF treatment collapse on the same curve, while for the "genuine" samples, without treatment, $1/S_1(q)$ is lower. When $q$ tends to zero, it slightly bends down toward a lower intercept. The slope is nevertheless lower, such that the extracted radii of gyration before and after treatment do not vary. The lower intercept corresponds to a contribution of objects of higher mass, which are removed by treatment: only partly with 5% and completely for 10% and 25% THF.

**Effect of THF Addition at Low q.** The evolution of $1/S_1(q)$ at low $q$ with THF addition is similar and very consistent for all polyelectrolyte samples (Figure 10a–c) as well as the corresponding tables are good examples of this trend for PSSNa $f = 0.80$, 0.47, and 0.34 at $c_p = 0.34$ M. All straight lines tend to the same zero $q$ limit. Plots for $c_p = 0.17$ M are given in Figure S.I.4-1a,b,e as well as for other values of PSSNa $f = 0.55$ and PSSNa $f = 0.60$, for both $c_p = 0.34$ M and $c_p = 0.17$ M in Figure S.I.4-1c,d.

In Figure 11 (insert), we note that $N_w$ is noticeably higher for 0% THF than for the other THF contents, for all of which it remains...
In water, $N_w$ is higher due to the presence of large aggregates. With the presence of THF, the aggregates are dissolved. When increasing THF content above 5%, the apparent $N_w$ decreases and reaches a constant value, which is the one of the single chain as expected. Contrary to $N_w$, $R_g$ (main plot of Figure 11) is progressively increasing from 0 to 25% THF, at both $c_p = 0.34$ M (Figure 11) and $c_p = 0.17$ M (see in the Supporting Information the numerous table parts: parts a–f of Table S.I.4). Hence, when THF is added, $R_g$ increases, meaning that the chain unfolds. However, values measured for PSSNa $f = 1$ are never reached with adding THF: e.g., for PSSNa $f = 0.34$, $R_g$ increases until 130 Å, ≪200 Å for PSSNa $f = 1$, and even $f = 0.80$ with 25% THF reaches 170 Å only.

**Origin of Additional Low q Scattering.** As just seen in Figure 9a,b, in pure water, $1/S_1(q)$ curve intercepts are lower, i.e., $S_1(q \to 0)$ is larger, which is the signature of objects of larger mass. Let us now discuss the origin of this effect.

In principle, the ZAC symmetry allows to give the scattering $S_1(q)$ of the smallest nondivisible object, which is the chain. This would be true even if some chains (H and D chains) were belonging to aggregates, as long as they would be mixed together in the proportion fulfilling ZAC conditions, which we will call the “ZAC-aggregate condition”: in this case the average scattering length density of the aggregate is the one of the external solution, so that there is no contrast and the aggregate is “invisible”. At the same time, the aggregate behaves as a small droplet of solution in ZAC conditions, so that the internal H and D chains mixture yields their average $S_1(q)$, proportional to their mass as for chains in

![Figure 10. THF addition: plot of $c_p S_1(q)$ versus $q^2$ at low $q$, PSSNa $c_p = 0.34$ M: (a) $f = 0.34$; (b) $f = 0.80$.](image1)

![Figure 11. Evolution of the measured radius of gyration $R_g$ and apparent mass $N_w$ (insert) versus % of added THF, $c_p = 0.34$ M, and after addition and removal of the same percent of THF (hollow symbols; the average value is represented by a dotted horizontal line). Data are available in Tables S.I.1–f for $c_p = 0.34$ and 0.17 M.](image2)

![Figure 12. $q^2 S_1(q)/c_p$ for polydisperse pearls (calculated $R_0 = 25$ Å, $\sigma \sim 0.3$ dashed blue line) compared with experimental data from PSSNa $f = 0.34$, $c_p = 0.34$ M, 0% THF (red full circles).](image3)
solution. On the contrary, if the “ZAC-aggregate condition” is not fulfilled, aggregates may give higher scattering at small $q$, as observed. The fact that the scattering shows a bending down at low $q > 0$ in the log–log plot (see Figure 8a,b) means that these aggregates are not large: they can actually be seen from the dotted horizontal lines.

For all contents of added THF or after THF treatment, we can also check (Figure 10a–c) that the apparent $1/S_1(q\rightarrow0)$ in the $1/S_1(q)$ versus $q^2$ plots $\sim 1/N_s$ remains constant. This shows that in all these cases we observe the same object: one chain among the others. Meanwhile, the increase of $R_s$ with THF shows that the global dimension of these chains increases. In summary, we have thus two effects in the presence of THF: the aggregate dissolving effect and the chain unfolding effect, acting on the conformations of the chains themselves.

V. MODELING THE FORM FACTOR

We discuss here different approaches to model, compute, and fit the quantity $S_1(q)$. We will first check the different models using data for PSSNa $f = 0.34$, at a concentration 0.34 M, treated and untreated. Then we will consider the case $f = 0.80$. These three examples cover most of the types of scatterings observed for the other $f$’s, at different THF contents. Showing a complete modeling of all data would be too voluminous here; it is on the way to being published.

V.1. Pearls Sphere Form Factor. As seen above, in the larger $q$ range, hence inside the chain, $q^2S_1(q)$ is a convenient representation which magnifies the variation of a maximum: with THF addition, it decreases in height and slightly shifts to larger $q$. Let us first propose a simple modeling of this maximum. Figure S1.6a shows the fit of the maximum of the scattering of monodisperse spheres, with strong oscillations, as done formerly. These oscillations are suppressed in Figure 12 which shows that the maximum for low $f = 0.34$ % THF can be fitted satisfyingly in this $q$ range by the scattering from spheres, $S_1(q)$ for spheres with given $R_0$ (2.5 Å) and polydispersity $\sigma \sim 0.3$ (log-normal distribution). These spheres are the pearls of the pearl necklace conformation. Their large polydispersity $\sigma \sim 0.3$ agrees with the modeling of Liao et al.

Such simple fits give values of $(R_0, \sigma)$ listed for all $f$ and THF contents in Tables 6 and 7. However, it has several limitations:

<table>
<thead>
<tr>
<th>% THF</th>
<th>$R_0$ (Å)</th>
<th>polydispersity $(\sigma)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PSSNa $f = 0.34$</td>
<td>0</td>
<td>270 $\pm$ 1.5</td>
</tr>
<tr>
<td>10</td>
<td>270 $\pm$ 1.5</td>
<td></td>
</tr>
<tr>
<td>25</td>
<td>261 $\pm$ 1.5</td>
<td></td>
</tr>
<tr>
<td>50</td>
<td>260 $\pm$ 1.5</td>
<td></td>
</tr>
<tr>
<td>$\epsilon_p = 0.34$ M</td>
<td>230 $\pm$ 1.5</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>220 $\pm$ 1.5</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>210 $\pm$ 1.5</td>
<td></td>
</tr>
</tbody>
</table>

Table 6. Polydispersity $(\sigma)$ and Mean Pearl Size ($R_0$) as a Function of THF Treatment

<table>
<thead>
<tr>
<th>% THF</th>
<th>$R_0$ (Å)</th>
<th>polydispersity $(\sigma)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PSSNa $f = 0.34$</td>
<td>0</td>
<td>265 $\pm$ 1.5</td>
</tr>
<tr>
<td>10</td>
<td>250 $\pm$ 1.5</td>
<td></td>
</tr>
<tr>
<td>$\epsilon_p = 0.34$ M</td>
<td>240 $\pm$ 1.5</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>230 $\pm$ 1.5</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>220 $\pm$ 1.5</td>
<td></td>
</tr>
<tr>
<td>25</td>
<td>210 $\pm$ 1.5</td>
<td></td>
</tr>
</tbody>
</table>

Table 7. Polydispersity $(\sigma)$ and Mean Pearl Size $R_0$ as a Function of THF Addition, for $\epsilon_p = 0.34$ and 0.17 mol L$^{-1}$

<table>
<thead>
<tr>
<th>% THF</th>
<th>$R_0$ (Å)</th>
<th>polydispersity $(\sigma)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PSSNa $f = 0.34$</td>
<td>0</td>
<td>265 $\pm$ 1.5</td>
</tr>
<tr>
<td>10</td>
<td>250 $\pm$ 1.5</td>
<td></td>
</tr>
<tr>
<td>$\epsilon_p = 0.34$ M</td>
<td>240 $\pm$ 1.5</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>230 $\pm$ 1.5</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>220 $\pm$ 1.5</td>
<td></td>
</tr>
<tr>
<td>25</td>
<td>210 $\pm$ 1.5</td>
<td></td>
</tr>
</tbody>
</table>

Table 8. Fitting Parameters of Pearl Necklace-Rod and Pearl Necklace-FJC Models for PSSNa $f = 0.34$-100 Water, Untreated, and 10% THF Treated Solutions (A Rod Length, d Rod Diameter, and N Number of Subchains)

<table>
<thead>
<tr>
<th>$f$</th>
<th>$M$</th>
<th>$A$ (Å)</th>
<th>$d$ (Å)</th>
<th>$N$</th>
<th>$R_0$ (Å)</th>
<th>$Z-\sigma$</th>
<th>$R_0$ $10^{18}$ cm$^{-2}$</th>
<th>$r_0$ $10^{10}$ cm$^{-3}$</th>
<th>$r_0$ $10^{10}$ cm$^{-3}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PSSNa $f = 0.34$</td>
<td>0</td>
<td>3</td>
<td>65</td>
<td>2.5</td>
<td>4</td>
<td>24.9</td>
<td>2.1</td>
<td>6.4</td>
<td>2.13</td>
</tr>
<tr>
<td>Calculation Schulz using Zimm distribution</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PSSNa $f = 0.34$</td>
<td>0</td>
<td>16</td>
<td>37.6</td>
<td>2.5</td>
<td>6</td>
<td>23.2</td>
<td>2.1</td>
<td>6.4</td>
<td>2.26</td>
</tr>
<tr>
<td>Calculation Schulz using Zimm distribution</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PSSNa $f = 0.34$</td>
<td>0</td>
<td>16</td>
<td>37.6</td>
<td>2.5</td>
<td>6</td>
<td>23.2</td>
<td>11–0.29</td>
<td>2.1</td>
<td>6.4</td>
</tr>
<tr>
<td>Calculation Schulz using Zimm distribution</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PSSNa $f = 0.34$</td>
<td>0</td>
<td>16</td>
<td>42</td>
<td>2.5</td>
<td>5</td>
<td>22.9</td>
<td>2.1</td>
<td>6.4</td>
<td>2.27</td>
</tr>
<tr>
<td>Calculation Schulz using Zimm distribution</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PSSNa $f = 0.34$</td>
<td>0</td>
<td>16</td>
<td>45</td>
<td>2.5</td>
<td>5</td>
<td>22.9</td>
<td>11–0.29</td>
<td>2.1</td>
<td>6.4</td>
</tr>
</tbody>
</table>

Fixed parameter.
Scheme 1. Basis of Model 1 (Pearl Necklace–Rod) and Model 2 (Pearl Necklace–Freely Jointed Chain), after Lages et al.49

(i) Obviously the lowest $q$ range—for which, anyhow, the $q^2S_1(q)$ representation is not appropriate—should not be described through the scattering of individual spheres but by a necklace of spheres, corresponding to a radius of gyration $R_g$ much larger than for individual spheres. (ii) Moreover, in the medium and large $q$, Figure 12 evidences also that $S_1(q)$ is not enough to describe the signal in several different $q$ ranges. (iii) On the left side of the $q^2S_1(q)$ maximum, we observe an excess of scattering followed by the onset of a plateau, which can be called a “shoulder”. Because our example is for no added THF, this may contain the excess of intensity seen above in log–log and Zimm representations. (iv) On the right side of the maximum, at large $q$, we observe a slow increase, which we assume to be characteristic of wormlike conformation.

Meanwhile, the fitting of the maximum as in Figure 12 is very accurate, and we will see below that it is enough to determine all pearl radii. To obtain $R_g$, it will be used for all data.

V.2. Pearl Necklace Models. From what was just seen it is interesting to fit to a complete expression of scattering of Pearl Necklace chains. A first model, which we will note Pearl Necklace–Rod, by Schweins et al.,10 considers $N$ spheres of radius $R_g$ joined by $M = N - 1$ rods of length $A$ (i.e., the rim-to-rim length is $A - 2R_g$). A version is available on line in the SAS view suite.48 The strength is simplicity; the weakness is that even if our chains are in a wormlike conformation, their scattering is very different from the one of rods in the large and even medium $q$ range. An excellent improvement of this model due to Lages et al.49 considers pearls separated by a freely jointed chain (FJC) of several segments ($M$ for the whole total, with $g = M/N - 1$ rods identical in each FJC) is noted pearl necklace–FJC. This is illustrated in Scheme 1. Because it is not available in the SasView suite, we have introduced its mathematical expression—model 249—in Matlab software for computing and fitting.

We have by the same time introduced the mathematical expression given for pearl necklace–rod as “model 1”:59 we checked on one example that our computation fully coincides with the values given by SasView. The parameters are listed in Table 6.

In short, the model enables a balance between the sphere $S_a(q)$, the rod $S_m(q)$, and the crossed $S_0(q)$ contributions through the ratio between the scattering length of the spheres (respectively the rods) noted $m_s$ (respectively $m_r$) in the original paper (or $\mu_s$ and $\mu_r$ when multiplied by the square root of the number of chain per volume). Introducing the SLDs, $\rho_s$, $\rho_r$, and $\rho_0$ for the solvent, $m_s = (\rho_s - \rho_0)\pi d^4/4$ and $m_r = (\rho_r - \rho_0)\pi d^2/4A$. We chose and fixed for $\rho_r$ a sensible value using Table 3 for the scattering length of monomer in the rod, with a rod diameter $d = 2.5$ Å. We then fit $\rho_s$ assuming it varies via the inner monomer concentration in the pearls. The distance between spheres is also controlled through rod size $A$ or FJC number and size of segments, hence through $N$, $M$, and $A$. It results in an oscillation in $S_1(q)$ or in the shoulder in $q^2S_1(q)$ described above, which we will discuss in detail below. Polydispersity on $R_g$ has been applied, with a Schultz distribution, characterized by a parameter $z$ (the parameter $z$ in eq 24 of reference 49 is related to the number- and weight-averaged volumes $V_n$ and $V_w$ according to $V_n/V_w = (1/z + 1)$; this is close to a log-normal distribution with a parameter $\sigma = 1/(\sqrt{z} + 1)$). Finally modeling is also effective at lower $q$, for the effective radius of gyration (which depends on $\rho_0$ and $\rho_s$).

Table 5 enables us also to calculate the following: $m_s = (\rho_s - \rho_0)\pi d^4/4A$, $m_r = (\rho_r - \rho_0)(4\pi/3)R_g^3$, and $\sigma = 1/(z + 1)^{1/2}$. We have fitted $\rho_s$ to 2.13 for pearl necklace-rod and to 2.26 for pearl necklace-FJC. This gives for spheres a low contrast $\Delta\rho_s = \rho_s - \rho_0 = 0.03 (0.16)$, corresponding to a monomer volume fraction ($\phi = \sqrt{0.03/(6.4 - 2.1)} = 8\% (19\%)$; in other words, there is more than 92% (81%) of water in the sphere. Note that similar low values were found by...
Schweins et al.\textsuperscript{10} since they attributed a large occupied volume of 0.586 nm\textsuperscript{3} to each of their monomers, 37 times larger than the volume for a bare monomer (0.25)\textsuperscript{3} nm\textsuperscript{3}.

In Figure 13e, the three normalized contributions $S_{ss}$, $S_{rr}$, and $S_{sr}$ are represented. We used a log$(q^2S(q))$ versus $q$ representation, since their order of magnitudes are very

**Figure 13.** Fit for PSSNa $f=0.34$, 0.34 M, no added THF: a (log–log plot) and b (Kratky plot): with model \textsuperscript{149} (pearl necklace-rod), monodisperse (dotted blue line) or polydisperse (full red line), $A=65$ Å, four pearls, radius $R_0=24.9$ Å. c (log–log plot) and d (Kratky plot): with model \textsuperscript{249} (pearl necklace-freely jointed chain), monodisperse (dotted blue line) and polydisperse (full red line), $M=16$, $A=37.6$ Å, six pearls, radius $R_0=23.2$ Å. (e) Kratky plot of $S_{ss}$, $S_{rr}$ and $S_{sr}$, the three contributions normalized to $(Nm_s+Mm_r)^2$ of the pearl necklace FJC model (eqs 7, 16, 17, and 19 in Lages et al.\textsuperscript{49}) for fitting data from PSSNa $f=0.34$, 0.34 M solution.)
different, as it can be seen. The cross-term sphere-FJC is always negligible. The rod—rod contribution is minimal except at large q. In other words, where the spheres scatter, the rods do not, and vice versa.

Figure 14 now shows a Kratky plot for a solution of the same PEL, PSSNa f = 0.34 in water, after 10% THF treatment, with a fitting by pearl necklace FJC model with \( R_0 = 22.9 \text{ Å} \), \( M = 16 \) strings of 42–45 Å length and five pearls. What is important here is that, although the shoulder at low q has been made to vanish (as already described), it is possible to obtain a good fitting of this part.

The fit parameters when passing from solution 100% water (untreated, Figure 13b) and solution 10% THF treated, Figure 14) are quite similar (see Table 6). \( M \) is constant, the lower number of pearls decreases the maximum, which is partly balanced by increasing the number \( g = M/N - 1 \) of the rods and their length: \( N = 5, g = 4, A = 42 \text{ Å} \) instead of \( N = 6, g \sim 3, A = 37.6 \text{ Å} \) for the non-THF-treated PSSNa. Larger g means also more fluctuations of the FJC subchain, hence less correlation. This combination of effects is enough to get a lower signal at low q of the THF-treated solution or, vice versa, to cope with the higher signal for untreated solution using correlations between spheres.

Using the fit parameters, we can estimate to \( MA/2.5 \) the total number of monomers of length 2.5 Å in the FJC chains: \( 16 \times 37.6/2.5 = 240 \) (16\( \times \)45/2.5 = 288) monomers. The remaining monomers 957 \( \times \) 240 = 717 (667) are in the pearls. For six pearls finally it gives 119 (111) monomers/pearl. Using the pearl volume \( (R_0^3) \), we estimate to 0.439 (0.377) nm\(^3\) the average volume occupied by one monomer in a pearl (to compare with 0.586 nm\(^3\) for the different system of Schweins et al.\(^{15} \)).

**V.3. Fitting with an Additional Low q Contribution.**

Until now, above in the text, we have proposed the low q shoulder to be linked to a correlation distance between spheres (pearls) imposed by the presence of a rod or a chain between spheres. Since part of this low q shoulder vanishes upon THF treatment, we propose below another origin for that.

**Additional Contribution to Rod and FJC Models.** To fit the scattering of the nontreated PSSNa f = 0.34 solution (strong shoulder), we use the FJC form factor used to fit the THF treated solution (weak shoulder) and add an additional contribution from larger polydisperse spheres of 50 Å, individually dispersed. Figure 15 shows that the agreement is very satisfactory.

![Figure 14](image)

**Figure 14.** Fit of PSSNa f = 0.34, 0.34 M, after THF treatment with pearl necklace freely jointed chain,\(^{49}\) monodisperse (dotted blue line) and polydisperse (full green line).

![Figure 15](image)

**Figure 15.** Fits of PSSNa f = 0.34, 0.34 M, nontreated (red full circles): blue dotted line: poor fit with pearl necklace-freely jointed chain,\(^{49}\) polydisperse used to fit scattering of of PSSNa f = 0.34 THF-treated solution: a big difference with data appears clearly below 0.1 Å\(^{-1}\); full green line: good fit with a sum of the polydisperse pearl necklace freely jointed chain fit to PSSNa f = 0.34 THF-treated solution (blue dashed line) and of the scattering of a sphere of R = 50 Å, \( \sigma = 0.17 \) (long blue lines).

It could be a step further to consider, instead of a FJC, a wormlike chain for the string contribution. Since the corresponding expression of form factor is not available, we propose a simplistic approach, illustrated in Figure 16: we estimate \( S_1(q) \) as

![Figure 16](image)

**Figure 16.** Fit of \( q^2 S(q) \) for PSSNa f = 0.34, \( c_p = 0.34 \) M in pure water (full red circles) by the sum (full green line) of (i) \( \alpha = 0.88 \) times \( (\Delta p_{\text{bare monomer}})^2 \) times the form factor of a wormlike chain (J. des Cloizeaux\(^{50}\)), dotted blue line; (ii) \( \beta = 0.3 \) times \( (\Delta p_{\text{bare monomer}})^2 \) times the form factor of a polydisperse sphere of radius \( R_p = 30 \) Å and \( \gamma = 0.3 \), due to the pearls (dashed blue line); and (iii) \( \gamma = 1 \) times \( (\Delta p_{\text{bare monomer}})^2 \) times the form factor of spherical aggregates of radius \( R_{agg} = 60 \) Å with polydispersity \( \sigma = 0.5 \).
the weighed sum of the form factors of spheres, β S_1(q)_sphere and of wormlike chains, S_1(q)_wormlike, for this we are also prompted by the direct comparison between form factors of spheres and of the chain for f = 1, Figure S.I. 6c). Our sum neglects all cross-terms in the medium/large q range covered by the plot, since they have been shown to be very small in Figure 13c. To this sum, we add a third term, S_1(q)_aggregates the scattering from large polydisperse spheres of mean radius R_{agg} and variance σ_{agg} such that

S_1(q) = α S_1(q)_wormlike + β S_1(q)_sphere + γ S_1(q)_aggregates + B_k

As above, we add an adjustable part of the background B_k limited to 2 × 10^{-3} Å^{-3} mol^{-1} L.

In Figure 16 we show the best fit for α, β, and γ. We see that:
1. The large q range is better fitted by the WLC, as aimed at. The contribution of the strings, α, would also increase toward 1 for f < 1 when adding progressively THF, if complete dissolution of the pearls was observed (seen in this paper only for f = 0.47 and 50% THF). (2) Meanwhile, the low q shoulder for this nontreated solution can be fitted owing to additional contribution iii (aggregates).

Using the same simple sphere plus wormlike chain sum, we can address the scattering for PSSNa f = 0.6, c_0 = 0.34 M, where the maximum appears visually difficult to fit. The fit shown in Figure 17 is satisfactory at medium and large q. The maximum log–log plot in Figure 8b), while the measured R_q—from the 1/S_1(q) vs q—is not affected by aggregates: it is equal to 155 ± 5 Å before treatment and 150 ± 5 Å after (Table 4).

Eventually, it would be interesting and far more advanced to use the Liao et al. simulation to fit these results. However, this requires an extended computer modeling, and we are convinced that it should be combined anyway with the signal of aggregates, in the case of solution without THF treatment. Ignoring the aggregates, we believe Figure 4 of Liao et al. is the best available representation in real space. We recall that the scattering calculations of Liao et al. also lead to an apparent slight correlation between pearls. However we note in passing that our chains are slightly polydisperse, which may rub out also Liao’s correlation (particularly if “located close to the end of the chains”, as proposed by Liao).

VI. DISCUSSION

VI.1. Before Modeling. Low q Behavior and Radius of Gyration. In pure water, as observed earlier by Spiteri et al., the R_q’s depend increasingly on f. Two points are emerging with adding THF: (1) First for each f, R_q increases (Figure 11) by more than 50% for the lowest f, 0.34 and 0.47, and yet noticeably for f = 0.8: from 150 to 175 Å. This strongly suggests an unfolding of the chain due to a larger number of monomers in the strings or to a much larger sphere volume. (2) Second, while R_q increases, the zero q limit first decreases for the lower THF contents: this suggests the dilution of larger objects than a single chain, present in the solutions.

Looking at the log–log plots confirms that an extra scattering is present for the initial 100% water solutions and vanishes with THF. At large THF content, N_w becomes constant because the scattering from the large objects has vanished.

The vanishing of this low q scattering can find two explanations: (i) The spherical aggregates simply vanish. (ii) The spherical aggregates are dynamically dissolved and re-formed, in such a way that some H and D chains become mixed together inside each spherical aggregate. This is an interesting situation where the ZAC condition would be fulfilled inside the aggregates, so that we would measure the signal S_1(q) of those chains inside the aggregates. The ZAC method is not sensitive to interchains correlations and hence not to their aggregation. The low q limit would stay proportional to N_w after re-formation of the aggregates.

Discerning between the two cases i and ii can be made using the total signal S_T(q) (all chains labeled with respect to solvent), which shows repeatedly, beyond the expected thermodynamical chain concentration fluctuations, aggregates at low q. S_T(q) was previously measured for very similar solutions. As illustrated in the TOC of this reference, the low q scattering in S_T(q) vanishes after adding THF, which supports the simplest proposal i. Moreover, suppression of aggregates was connected to unambiguous differences in macroscopic properties, namely a simultaneous decrease of viscosity. However, even with THF treatment, a low q scattering subsisted in S_T(q), but it was 10 times lower, and this is usual for many polyelectrolytes.

After treatment by THF at 5%, 10%, or 25% and THF evaporation, we see in Figure 11 (and in Table S.I. 4-2a,b) that the radii return to their initial values, while the apparent N_w keeps the value measured in the presence of THF.

In summary, R_q and N_w data are nicely consistent all over the parameters explored. However, they are not enough to enable a unique description of evolution of numbers and volumes of spheres and strings. This is why modeling is important because it

Figure 17. Fit of q^3 S_1(q)/c_o for PSSNa f = 0.80, c_0 = 0.34 M in pure water, no THF treatment (full red circles) by the sum (full red line) of:

(i) α = 0.78 times (Δρ_{bare monomer})^2 times the form factor of a wormlike chain (J. des Cloizeaux) of length L = 975±2.5 Å, L_q = 45 Å, blue dots.
(ii) β = 0.025 times (Δρ_{bare monomer})^2 times the form factor of a polydisperse sphere of radius R_0 = 20 Å and σ = 0.17, due to the pearls, long blue dashes.
merges low $q$ behavior—where it will predict $R_g$—and large $q$
behavior—where it predicts the number of spheres and strings
and their sizes.

Medium–Large $q$ Behavior. Here also before modeling
some first conclusions can be drawn.

For THF Treatment. log–log plots at medium $q$ evidence
directly a perfect superposition of the curves for a sample as
prepared in water and for the same sample after THF treatment.
Therefore, apart from aggregates, the chain conformation in
water results from an annealed equilibrium (between hydro-
phobic attraction and electrostatic repulsion), giving rise to the
pearl necklace conformation. This is clear also in Kratky plots,
which superpose after THF treatment (within background
error), for $c_p = 0.34$ M (and also for $c_p = 0.17$ M).

VI.2. Discussion of Modeling Results. We attempted
above different modeling, and fitting, using for visualization
either log–log plots or the Kratky plots.

Sphere Correlations. In Kratky representation, models 1 and
2 of Lages et al.49 show a low $q$ shoulder, which we undoubtfully
attribute to assumed position correlations of spheres separated
by rods or FJC of size fluctuating around an average value, in the
sphere–sphere term. The rod–rod and sphere–rod cross-terms
are calculated but appear small in contribution apart at largest $q$.
This correlation shoulder (also predicted by Liao23) can account
for the one observed with 100% water non-THF-treated solu-
tion. However, in the presence of THF or after THF treatment,
where the observed shoulder is much reduced, the scattering can
be described by the same models, implying reduced sphere
correlation. Meanwhile, we have seen that it is also possible
to account for the shoulder by an extra scattering of larger compact
objects (spheres) added to model 1 and 2 or even to a simplistic
sum of sphere–sphere and string–string contributions.
Eventually, we conclude in favor of such extra scattering because
it also fits well with the observed variation of the zero $q$ limit (the
form factor of the chain itself has no reason to vary since it is
 proportional to the molecular weight of the chain).

This being settled, we can focus on the maximum in $q^2 S(q)$: it
has already been said above that it is enough to account for it with
a simple sphere model to obtain its radius $R_g$ and polydispersity $\sigma$
(log-normal), as given in Tables 6 and 7 for all solutions.

Pearls Size. After THF treatment, the pearls size is remarkably
constant at given $f$ (Table 6), whatever the THF content used for
the treatment. Hence, this is a very reproducible protocol.

In the presence of THF, the effect of THF content on pearl
size is not as strong as the effect of the degree of sulfonation $f$.$f$
makes vary $R_g$ more, as seen both in the present paper, and in a
former one.20 Note however that the range of variation of $R_g$ is
limited: values for $f = 0.34$ are 25.0 ± 1.5 Å20 and 27.0 ± 1.5 Å
here in this paper; 25.5 ± 1.5 Å for $f = 0.47$ here, and 22.0 ± 1.5 Å
for $f = 0.55$, 16 ± 1 Å for $f = 0.64$.20 And finally, in the present paper,
20.0 ± 1.5 Å for $f = 0.80$, i.e., not smaller than for $f = 0.64$
in the former paper.20

Meanwhile, the THF effect on the scattering is clear-cut: the
pearl contribution (which can be estimated from the amplitude
of the maximum of $q^2 S(q)$) decreases systematically with THF
addition. As suggested above, a first possibility could be the
decrease of monomer concentration inside the pearls. Note that it
would be a somehow surprising coincidence that in this case the
pearls diameter stays so similar. The second possibility is to
assume a decrease of their number. On average over all chains, this
would lead to changes in the effective linear density (as would
do a decrease in size). Such effective linear density will control
the average distance between chains, in other words the
“polyelectrolyte peak” abscissa will vary as observed formerly37
(see Concluding Remarks).

In parallel, at low $q$, THF effects are successfully evidenced in
the variation of $R_g$ (Figure 11), with a great consistency.

Under THF addition, the reduction in size of the pearls (Table 7)
is not always negligible (in particular, if we consider the
volume $\sim R_g^3$), but $R_g$ remains of the same order of magnitude:
27.0 to 21.0 ± 1.5 Å for $f = 0.34$, and similarly for $f = 0.47$;
(23.0–21.0) ± 1.5 Å for $f = 0.55$.

Number of Pearls. However, whereas the size can be
determined directly from the abscissa of the maximum, the
number of spheres $N$ in each chain cannot be determined
directly from the height of the maximum.

For $f = 0.80$, we can get information from the simple
approach of a sum of 2.5% of the form factor of a sphere ($R_g = 20$ Å)
form factor times the known contrast $(\Delta \rho_{\text{bare monomer}})^2$ and
of 78% of the form factor of a real wormlike chain (WLC) times
the same contrast $(\Delta \rho_{\text{bare monomer}})^2$. This would mean that there
are, out of 957 monomers, $0.78 \times 957 = 746$ string monomers in
chain (to be taken with caution since at large $q$ we depend on the
background subtraction) and 211 in the beads. Unfortunately, at
medium $q$, in this simple approach, the value of the sphere
maximum does not give access to the number $N$ of spheres.
We only have access to the product $N \times \Phi^*$, which should be
equal to 0.025. Keeping the same $N$ as for $f = 0.34$ analysis would
lead to $\Phi^*$ also close to the one for $f = 0.34$, of order 0.2, hence
limiting the effect of $f$ to the pearl size $R_g$ but we must be careful
since this approach is approximate.

Model Fits. Only the fits to models 1 and mostly 2 really
allowed us to get values for $N$, and hence for the number and
density number of monomers in the spheres, and for $M$, and
hence for the number $g = M/N - 1$ of monomers in the strings.
These numbers are obtained from the sphere correlation distances and from $R_g$ (hence log–log plots are also useful to
check the quality of the fit). The fits we have presented cover the
cases non-THF treated and THF treated for $f = 0.34$. The values of $N$ obtained lie between $N = 4$ (rod) and 6 (FJC) (5 for THF
treated). This is not far from what given by Figure 9a of Liao,23
for $c = 2.6 \times 10^{-3} \sigma^{-3}$ (0.34 M) and $N_p = 372$, $N = 2.7$;
extrapolated here for $N_p = 957$, $N$ becomes equal to 7. The
corresponding number of monomers in one bead in Liao23 was
40 on average (with a wide distribution of half-width 50 at half-
height; to compare with the 111 found above in Results).
In summary, orders of magnitude are consistent using the models
for three representative cases. This makes possible to apply them
to all the series of data in a following paper.

VI.3. Final Qualitative Remarks. Strength of the Effect
of THF Content. When passing from 0% to 5% THF, the main
effect is the vanishing of the low $q$ extra contribution, for all
values of $f$. From 10% to larger, the THF content effect shows
trends common to all $f$ but with some differences in strength.

We start by the example of $f = 0.47$ at $c_p = 0.34$ M because it is
particularly well clear-cut and exemplary. In Figure 5, we see that
when passing to 10% THF, the pearl contribution decreases, and
it decreases even more for 25% THF. The wormlike chain
contribution, quite small for 5 and 10% THF, increases quickly
at 25%, and we reach the full contribution of a WLC at 50% THF.

But for higher $f = 0.80$, the pearl contribution is decreased
as soon as the THF content reaches 10% THF, and it is hardly
noticeable at 25% THF.

On the opposite side, for lower $f = 0.34$, it requires more THF
to trigger the vanishing of pearls. When reaching 25% THF,
interactions between charged monomers appear to change deeply (strong reduction of electrostatic repulsions).

**Chain Concentration Effects.** We did not comment in detail the measurements made at concentration 0.17 M. This is an important piece of work, detailed in the Supporting Information. It is clear that they globally confirm the observations at 0.34 M. This is a very strong confirmation of our study. If the solutions are in dilute regime, the scattering should be proportional to \(c_p\) assuming one can neglect the effects of ionic strength. This is clear also in Kratky plots, which superpose after THF treatment. For \(c_p = 0.17\) M and \(c_p = 0.34\) M. This suggests that pearl necklaces are indeed in dilute regime, i.e., well dispersed in solution in most cases, at least when they are partially collapsed: e.g., for \(f = 0.34\) and 0.47. For \(f = 0.80\) and \(f = 1\), the radii of gyration are different (see Table S.I. 4-1a–f). The fact that the pearls contribution does not vary with concentration is partly in disagreement with Liao’s model.

VII. CONCLUDING REMARKS

We have demonstrated here that it is possible to measure, using zero average contrast, the form factor of partly hydrophobic chains in a mixture of solvents, namely aqueous solutions under addition of good solvent of the backbone. This experiment is delicate since four solvents (\(H_2O, D_2O, THF_1\) and \(THF_2\)) and two types of chains (h-PSS and d-PSS) are involved for each sulfonation rate and each percentage of solvent. Although the data could of course be improved by much longer measurements, or using more intense neutron beams, they are self-consistent over a large set. They confirm former measurements in water only, which showed a pearl necklace conformation as predicted theoretically, and as modeled using MD computer simulations. They agree with expectations and previous measurements of the total scattering function \(S_T(q)\): namely, the pearls contribution decreases with added good solvent. The corresponding variation of intensity is important and indubitable. Meanwhile, the range of variation of the pearls size, \(R_0\) and its distribution width, \(\sigma\), appears limited.

This limited range of \(R_0\) was already seen on \(S_1(q)\) in pure water when varying the sulfonation rate \(f\), as confirmed here with other values of \(f\). Larger values of \(R_0\) could not be reached due to the insolubility of the chains at \(f < 0.35\). The lower limit comes from the fact that at high \(f\), THF is a very good solvent, not sensitive to charge repulsion (THF low permittivity abates charge repulsion), and the wormlike conformation of PEL vanishes. Note also that the lower limit 16 Å is not far from the bare persistence length of polystyrene backbone, \(L_p = 10\) Å.

Beyond this limited range, the striking fact is that under good solvent addition the collapsed conformation vanishes more through the decrease of the number of pearls than through the decrease of their size. This has to be put in perspective with the clear variation of the peak absissa \(q^*\) of the “total scattering function” \(S_T(q)\), reported earlier (Figure 8 of ref 37). We will not discuss about other models considering different coexisting shapes of chains because we have no sufficient information. We simply conclude that as predicted by the Dobrynin–Rubinstein model the interchain electrostatic correlations are not linked directly to the spheres sizes, but more to an average distance \(2\pi/q^*\) between chains resulting from an average linear density of each chain. The latter can depend on the pearl number at constant pearl size. Therefore, in spite of the locally heterogeneous pearl necklace conformation, the average over space and time results in a well-defined repulsion distance.

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