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# Structure of Polyelectrolyte Chains Confined in Nanoporous Glass

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ABSTRACT: We have investigated the structure of sodium poly(styrenesulfonate) in a bulk solution and when confined within the pores of the model nanoporous medium, Vycor. We have used the zero average contrast condition and SANS to separate the intramolecular (form factor), $P(q)$, and intermolecular contributions, $Q(q)$, to the total scattering. We find that the chains are more stretched in confined geometry than the bulk and sufficiently so as to highlight the large-scale disordered structure of Vycor. We show experimentally and prove theoretically that the asymptotic behavior of the observed interchain structure factor, $Q(q)$, is $\approx 1/q^2$ for free and $\approx 1/q$ for confined chains.

## Introduction

An understanding of polymer conformation in reduced dimensionality has enormous technological application, most notably for microfabrication and miniaturization, and has relevance to filtration, gel permeation chromatography, thin film lubrication, and enhanced oil recovery.[1] While neutron scattering has provided invaluable information on chain conformation in the bulk,[2] there have been relatively few scattering experiments of chains under confinement, and these mainly focus on neutral chains. The significantly more complex, and biologically relevant, situation of charged chains in confined geometry currently lacks an experimental framework with which to verify fundamental principles. Such knowledge has application to the novel technology of nanopore sequencing of individual DNA strands (i.e., charged polymers) using single-channel recording techniques, pertinent to the Human Genome Project, and the use of designed protein pores as components for biosensors.[3,4]

We have recently studied the effect of confinement of polystyrene polymers of varying molecular weight inside the model porous glass, Vycor, using small-angle neutron scattering (SANS) and showed that the radius of gyration of the confined chain is reduced relative to the equivalent bulk solution.[5] We focus here on the influence of confinement on the structure of the related, model charged polymer, fully sulfonated poly(styrenesulfonate) (PSSNa) when confined in Vycor and in the bulk. To remove the intense scattering from the porous medium, we use an appropriate mixture of protonated and deuterated water. Further, by employing solutions composed of either pure deuterated PSSNa or suitable mixtures of protonated and deuterated PSSNa, we have separated the intramolecular and intermolecular contributions to the total scattering and provide a theoretical understanding of their $q$-dependencies.

## Experimental Section

Vycor (Corning brand 7930) has a porosity of 28 vol % and a pore internal diameter of ca. 70 Å.[5,6] The SANS from Vycor exhibits an intense peak at $q_{\max}$ ca. 0.02 Å$^{-1}$ arising from the quasi-periodicity of the bicontinuous pore structure resulting from the spinodal decomposition process during the formation of the glass.[6] Vycor is highly susceptible to contamination; the following cleaning procedure was followed therefore. Disks, of 1 mm thickness and 14 mm diameter, were placed in a solution of 30% $H_2O_2$ in water which was then boiled for at least half an hour. After replenishing with fresh peroxide solution and further boiling, the disks were removed and dried in a desiccator under vacuum. The disks were subsequently transferred to a furnace, which was slowly heated to 500 °C, and kept at this temperature for at least 3 h before being returned to the desiccator prior to use. The disks were submerged in one of six $H_2O/D_2O$ mixtures (for at least 24 h) or one of the polyelectrolyte solutions (for varying periods as described in more detail below).

The scattering length density (SLD) of Vycor was determined by contrast variation experiments using mixtures of Millipore $H_2O$ (resistivity = 18 MΩ·cm) and $D_2O$. Each Vycor disk, along with several drops of the appropriate solvent, was placed in a "barrel" cell designed to prevent evaporation. Vycor nominally has an SLD of $3.55 \times 10^{10}$ cm$^{-2}$ [5] although the structure of Vycor is dependent on its formation, and therefore deviations from this value may occur.[9] Indeed, independent studies have reported the SLD of Vycor to be anywhere from $3.35 \times 10^{10}$ to $3.88 \times 10^{10}$ cm$^{-2}$.[7,10] Given this variation, we have thus determined the SLD of the lot of Vycor used in these studies by first conducting a series of contrast variation experiments. The intensity at $q_{\max}$ as a function of solvent contrast is shown in Figure 1a and gave the Vycor contrast match point of $3.79 \times 10^{10}$ cm$^{-2}$. This SLD corresponds to a mixture of 37.6% $H_2O$ and 62.4% $D_2O$. Vycor filled with this (matching) water mixture gave rise to the SANS signal shown in Figure 1b in which the correlation peak is absent, and the scattered intensity at $q_{\max}$ has reduced by 3 orders of magnitude. This water composition was used to prepare the polyelectrolyte solutions.

The zero average contrast (ZAC) method has been described in detail elsewhere;[11−13] we therefore describe the approach only briefly here. The scattering from a mixture of the protonated and deuterated forms of a single polymer species in a solvent (which can also be a mixture of protonated and deuterated species) is given by

$$I(q) = (\bar{\rho}_D - \bar{\rho}_H)^2 x(1-x) v \Phi N P(q) + (x\bar{\rho}_D + (1-x)\bar{\rho}_H - \bar{\rho}_0)^2 [v \Phi N P(q) + V \Phi^2 Q(q)] \quad (1)$$

where $I(q)$ is the total scattering intensity per unit volume (units cm$^{-1}$), $\bar{\rho}_D$, $\bar{\rho}_H$, and $\bar{\rho}_0$ are the SLD of the deuterated, protonated polymer, and solvent, respectively, $x$ is the mole fraction of deuterated chains, $v$ is the molecular volume of an H or D monomer, $V$ is the sample volume, and $\Phi$ is the volume

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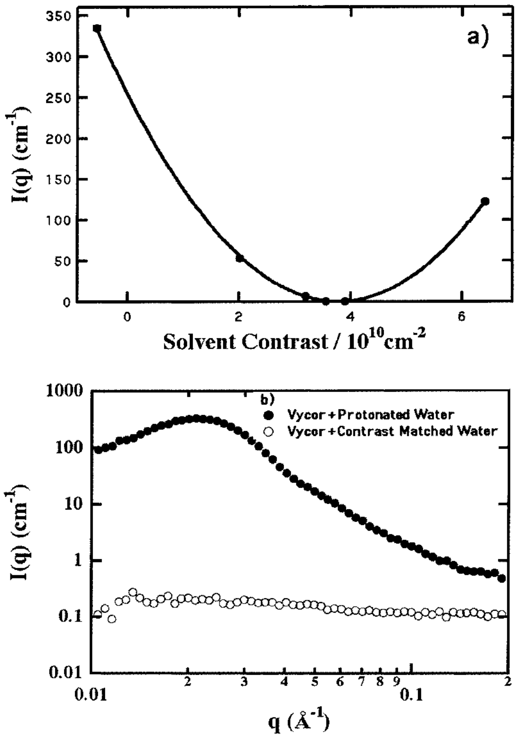

**Figure 1.** (a) SANS intensity at $q_{\max}$ vs solvent contrast in contrast-matching experiments. The minimum value of the parabola is the matching point for Vycor corresponding to 3.79 × $10^{10}$ cm$^{-2}$. (b) SANS from Vycor filled with $H_2O$ and with contrast-matching water.

fraction of polymer in solution. $P(q)$ and $Q(q)$ are the chain form factor and interchain structure factor, respectively.

When the average contrast between the polymer and solvent is adjusted to be zero, $x\bar{\rho}_D + (1 - x)\bar{\rho}_H - \bar{\rho}_0 = 0$, the scattering intensity is a function of the form factor only:

$$I(q) = (\bar{\rho}_D - \bar{\rho}_H)^2 x(1 - x)v\Phi NP(q) \qquad (2)$$

To maximize the scattering intensity, the composition of the polymer mixture is typically chosen to be of equal proportion of H and D chains; the solvent is then matched accordingly. However, to obtain $P(q)$ for the polymer under confinement a further requirement is necessary; the solvent must also contrast match the confining medium. This (ZAC) condition is satisfied for a mixture of 23.6 mol % PSS$^D$Na and 76.4 mol % PSS$^H$Na (SLD of PSS$^D$Na = 6.8879 × $10^{-10}$ cm$^{-2}$, PSS$^H$Na = 2.8321 × $10^{-10}$ cm$^{-2}$ [14]) but necessarily results in a further reduction in scattering intensity in these already weakly scattering systems.

The Debye length, $\kappa^{-1}$, is $4\pi\lambda_B\rho$ where $\lambda_B$ is the Bjerrum length (7.14 Å for water at room temperature) and $\rho$ is the monomer concentration. For a medium with neutral pores, a concentration is typically chosen such that $\kappa^{-1}$ is less than the pore diameter to enable chain penetration. Preliminary experiments used a ZAC concentration of 0.087 g cm$^{-3}$ (0.089 for PSS$^D$Na), i.e., with $\kappa^{-1} \approx 7$ Å, but chain penetration was negligible, indicating the charged nature of the pore surface. Subsequently, an increased concentration of 0.306 g cm$^{-3}$ was used for all ZAC solutions, except for the intermediate weight solution which was 0.238 g cm$^{-3}$. Similar deuterated-only solutions were also prepared for the low and high molecular weight chains with the same monomer concentration of 0.314 g cm$^{-3}$; this enables the later separation of $P(q)$ and $Q(q)$.[15]

All polyelectrolytes were fully sulfonated (Table 1) and dialyzed prior to solution preparation. Molecular weights and polydispersities are shown in Table 1. The cleaned Vycor disks were colorless and opalescent but, on entering the solution, became translucent, with bubbles subsequently being released, indicating displacement of air. The confined samples were studied after complete displacement of visible bubbles, corresponding to 2, 7, and 9 (40) days for the low, intermediate, and high molecular weight (low concentration) samples, respectively.

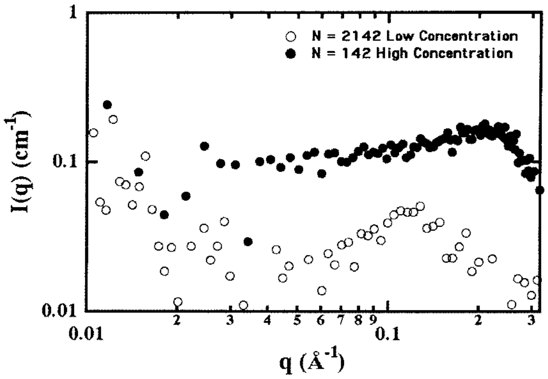

**Figure 2.** SANS from bulk PSS$^D$Na showing low molecular weight chain at 0.314 g cm$^{-3}$ and high molecular weight at 0.089 g cm$^{-3}$. Data have been shifted vertically for clarity.

**Table 1. Polyelectrolytes Used in This Study**

| $M_W$ (Da) | supplier | $M_W$/ $M_N$ | deg of sulfonation (%) | $N$ |
|---|---|---|---|---|
| 31 000 PSS$^H$Na | in-house | 1.1 | >95 | 150 |
| 25 000 PSS$^D$Na | in-house | 1.1 | >95 | 117 |
| 76 000 PSS$^H$Na | Polymer Standards Service | <1.1 | ≥99 | 369 |
| 77 400 PSS$^D$Na | in-house | 1.1 | >95 | 363 |
| 451 000 PSS$^H$Na | Polymer Source | 1.05 | 99.5 | 2189 |
| 425 000 PSS$^D$Na | Polymer Source | 1.04 | 98.8 | 1995 |

SANS experiments were performed on the SAD and SAND instruments at the Intense Pulsed Neutron Source, Argonne National Laboratory, and, for the low concentration studies of the high molecular weight chains, on the PACE instrument at Laboratoire Leon Brillouin, Saclay. For the polyelectrolyte experiments, run times were typically 11 h for the bulk experiments, 24 h for the confined experiments, and between 30 min and 6 h for the water solutions for the initial contrast match studies, depending on contrast. Absolute values of intensity were obtained from calibration against a standard sample of a 50:50 volume mixture of protonated and deuterated polystyrene ($M_W$ = 1.15 × $10^6$). The scattering background used was contrast-matched Vycor for the confined polymer and the same water mixture for the bulk solution. In the case of the confined experiments, we took the precaution of using the same disk for both the sample and background scattering runs to avoid effects from differences between individual Vycor disks (except for preliminary studies made on the low-concentration solutions).

## Results and Discussion

**Total Bulk Scattering.** The scattering at lowest $q$ from the bulk deuterated chain is weak due to the low compressibility of the system associated with electrostatic interactions. The principal feature is a peak at $q_{\max}$ ca. 0.25 Å$^{-1}$ corresponding to an average interchain distance of ca. 25 Å whose position is independent of molecular weight (Figure 2). The result for the preliminary study at lower concentration is also shown in which a peak is observed at $q_{\max}$ ca. 0.11 Å$^{-1}$, corresponding to a larger separation of ca. 60 Å. These values are in excellent agreement with previous studies.[14,16]

**Bulk Form Factor.** The overlap concentration, $c^*$, can be calculated from the formula $c^* \simeq M_w/N_A R_g^3$, where $N_A$ is Avogadro's number and $R_g$ is the radius of gyration of the chain.[17] For a fully extended chain, $R_g$ is $L/\sqrt{12}$, where $L$ is the contour length of the polymer

**Table 2. Radius of Gyration (Å) for the Chains at ZAC Used in This Study**[a]

| $\langle M_W\rangle_{ZAC}$ (Da) | $R_g$(neutral) (Å) | $R_g$(rod) (Å) | $R_g$(BD) (Å) |
|---|---|---|---|
| 29 500 | 36 | 85 | 40 |
| 76 300 | 58 | 262 | 70 |
| 445 000 | 143 | 1440 | 180 |
| 445 000 (low) | 143 | 1440 | 270 |

[a] $R_g$ limits based on neutral parent chain and rod conformations; values obtained from the Benoit and Doty (BD) eq 3 based on Sharp–Bloomfield model (Figure 3).

(= *Na* where *a* = monomer size = 2.5 Å). Calculated $c^*$ for the ZAC solutions are $4.52 \times 10^{-2}$, $6.79 \times 10^{-3}$, and $2.00 \times 10^{-4}$ g cm$^{-3}$. The experimental concentrations used are thus greater than the concentration above which the stretched chains can no longer freely rotate. Since $c^*$ is very low for these systems, the dilute regime is inaccessible to current neutron scattering experiments based on intensity considerations, and one is therefore inevitably obliged to work in the semidilute regime. For comparison, $R_g$ for the neutral parent polystyrene chain in a $\Theta$ solvent is obtained from the relationship $\langle R_g^2\rangle_z^{1/2} = 0.27M_w^{0.506}$.[18] $R_g$ limits for the molecular weights studied are summarized in Table 2.

From the SANS obtained from the ZAC solutions, we are sensitive only to the chain form factor since the scattered intensity is proportional to $P(q)$. Kratky plots for the ZAC solutions (not shown) exhibit a plateau region centered at $q$ ca. 0.05 Å$^{-1}$ (i.e., $I(q) \approx q^{-2}$) and, at higher $q$, varying as $q^{-1}$. The scattering vector associated with the crossover, $q^*$, corresponds to the transition between the asymptotic behavior of a Gaussian chain to that of a rod. One may then consider describing the polyelectrolyte chain by a wormlike model. Two parameters characterize such a chain: the contour length, $L$, and the persistence length, $l_p$. The persistence length of the chain is, in principle, obtainable from the crossover region, but des Cloizeaux has shown that, for an infinite chain, it may occur anywhere between $0.25/q^*$ and $1.5/q^*$; its position is thus too imprecise to be quoted in this way.[19] The persistence length can be extracted however by fitting the scattering curves to a Sharp and Bloomfield model for wormlike chains, providing $L > 10l_p$ and $ql_p < 2$.[20] Fits obtained are shown in Figure 3 with $L$ equal to 356, 919, and 5356 Å for the low, intermediate, and high molecular weight chains based on average degree of polymerization, $\langle N\rangle_{ZAC}$. The first requirement is satisfied for all solutions while the second is achieved by fitting the data over an appropriate $q$ range. The persistence length obtained is independent of the chain molecular weight at the high constant monomer concentration used (Table 3). Also shown for completeness are the results of the preliminary study of the high molecular weight system at low concentration (Figure 3d).

One may express $R_g$ as a function of $L$ and $l_p$ by the relation[21]

$$\langle R_g^{2}\rangle = l_p^{2}\left[\frac{L}{3l_p} - 1 + \frac{2l_p}{L} - \frac{2l_p^{2}}{L^{2}}\right]\left(1 - \exp\left(-\frac{L}{l_p}\right)\right) \quad (3)$$

For $L/l_p \ll 1$, this leads to $R_g^2 = L^2/12$ for a rod of contour length $L$. For $L/l_p \gg 1$, one obtains $R_g^2 = l_pL/3$ corresponding to a Gaussian coil. $R_g$ values obtained from (3) are also shown in Table 2. These values, based on the Sharp and Bloomfield model, are much closer to those for the Gaussian chain than the rod conformation as expected for the chain concentrations > $c^*$ investigated.

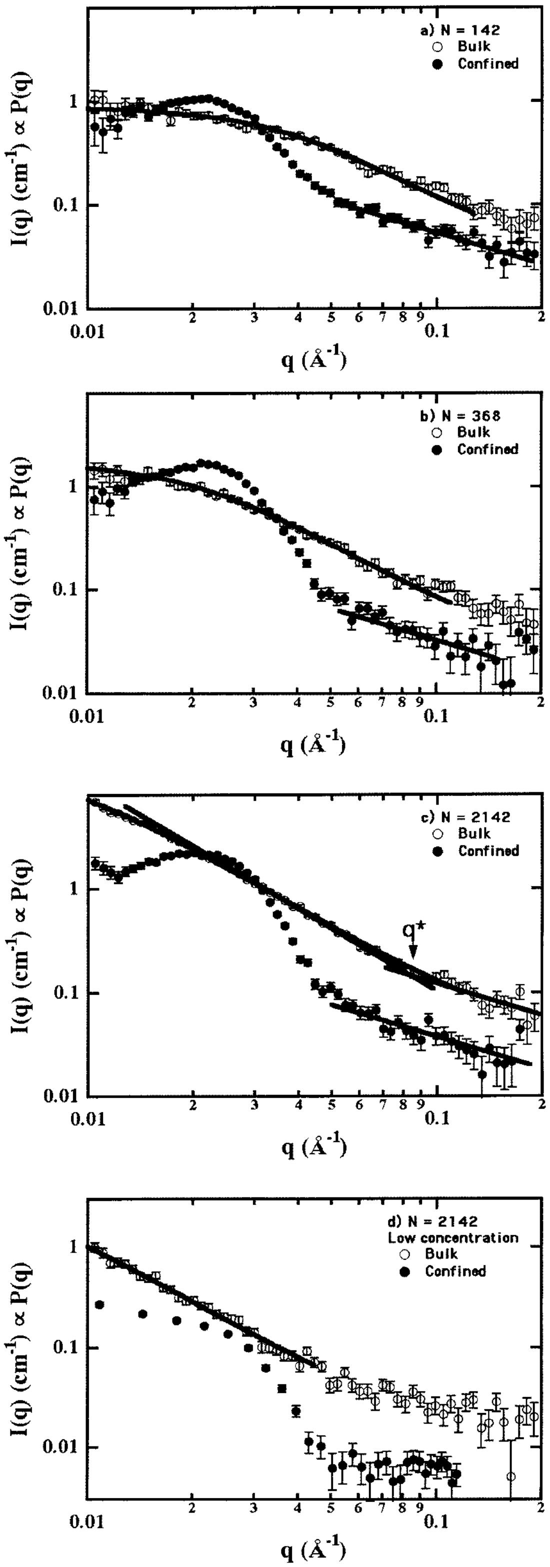

**Figure 3.** SANS from polyelectrolytes in ZAC condition in bulk and confined geometry. (a) Low, (b) intermediate, and (c) high molecular weight at 0.306 g cm$^{-3}$ and (d) high molecular weight at lower concentration of 0.087 g cm$^{-3}$. Bulk data have been fitted to the Sharp and Bloomfield model for wormlike chains for $ql_p < 2$. Also shown in (c) are $q^{-2}$ and $q^{-1}$ regions in the SANS which crossover at $q^*$.

**Confined Form Factor.** Figure 3 shows the scattering from the free and confined chains, illustrating the effect of molecular weight (Figure 3a–c) and con-

**Table 3. Fits to SANS from Bulk ZAC Solutions to Sharp−Bloomfield Model**[a]

| | 29 500 Da | | 76 300 Da | | 445 000 Da | |
|---|---|---|---|---|---|---|
| parameter | fit | pred | fit | pred. | fit | pred |
| Sf | 0.90(2) | 1.20 | 1.8(1) | 2.42 | 16.2(8)<br>[4.4(5)] | 18.1<br>[5.14] |
| $L$ (Å) | 356(0) | 356 | 919(0) | 919 | 5356(0) | 5356 |
| $l_p$ (Å) | 15(1) | | 17(1) | | 18(1)<br>[44(7)] | |

[a] Sf = scale factor $(\bar{\rho}_D - \bar{\rho}_H)^2 x(1 - x)v\Phi N$ (cf. eq 2), $x$ = mole fraction of deuterated polyelectrolyte in mixture = 0.236, $v$ = monomer volume = $108/N_A$ cm$^3$, $\Phi$ = volume fraction of polyelectrolyte in solution = 0.159 (low, high molecular weight), 0.124 (intermediate), and 0.045 (high molecular weight at low concentration), and $N$ = degree of polymerization = 142, 368, and 2142, respectively. Values in square brackets are those from low-concentration solution.

centration (Figure 3c,d). Preliminary experiments at low concentration (Figure 3d) indicated only partial penetration of the polyelectrolyte even after soaking for greater than 1 month. One would expect from the calculated Debye length that the solution would fully enter the Vycor; the observation that this is not so confirms the charged nature of the surface of the glass.

A comparison of the scattering at large scattering vectors ($ql_p \gg 1$) for subsequent, higher concentration solutions indicates that the intensity associated with the confined chain is approximately one-quarter that of the bulk solution ($I(q)_{\mathrm{confined}}/I(q)_{\mathrm{bulk}}$ = 0.36, 0.25, and 0.27 for $N$ = 142, 368, and 2142, respectively). Since Vycor has a porosity of 28%, such a reduction in high-$q$ scattering is in line with expectations and suggests that chains have fully entered. While the monomer concentration (for low and high $M_W$) is constant for bulk and confined states and greater than $c^*$, the average molecular concentration is not. Assuming a partition coefficient of unity and an average pore of length 300 Å and diameter 70 Å, we may estimate that the average number of molecules per pore is ca. 7, 2, and 0.5 chain(s), respectively. The principal feature in the scattering is a peak at $q$ ca. 0.02 Å$^{-1}$ whose intensity increases with polyelectrolyte molecular weight. This peak is located at approximately the same position as the pore−pore correlation peak observed from Vycor (Figure 1b).

The charged chain behavior is markedly different than that observed from previous experiments of the neutral parent polymer, polystyrene.[5] In the absence of adsorption, and for molecular weight ≤ 137 kDa, both the free and confined polystyrene scattering could be fitted successfully for $R_g \leq q \leq \approx$ (blob size)$^{-1}$ with a Debye model for ideal Gaussian chains (limit $q^{-2}$) with the confined chains exhibiting a lower $R_g$ than in the bulk. Further, it was shown that the neutral confined chains interpenetrate and are squeezed but not laterally stretched relative to the free chains.[5] For chains of molecular weight ≥ 137 kDa, however, the confined scattering showed a modest reappearance of the Vycor peak despite being under the ZAC condition.[5] Figure 4 illustrates this for polystyrene of $N$ = 3308 where a turning point is observed for the confined system at ca. 0.02 Å$^{-1}$. This feature was considered to indicate that the polymer chains were spanning pores over a range comparable to or longer than the Vycor pore−pore correlations; the associated scattering corresponding to the convolution product of the structure factor for Vycor with that of the polymer factor whose typical width in reciprocal space is $R_g^{-1}$. In the extreme case, an infinitely long chain *even* under the ZAC condition, able to span the entire bicontinuous structure of the medium, would give rise to a peak at the Vycor peak position because there would be an *intramolecular* component with an apparent repeat of ca. 300 Å. Within the Guinier regime ($qR_g$ < 1) then $P(q)$ in eq 2 may be replaced by $S_{\mathrm{Vycor}}(q)\exp(-q^2R_g^2/3)$.[5] In the present experiments, such an interpretation would seem reasonable if the charged chains under confinement were more extended than the corresponding bulk chains of the same contour length. Even for the shortest molecular weight chain under study, the length of the confined chain is sufficiently great as to enable such pore spanning to occur. Figure 3 shows that the rodlike conformation region does indeed extend to much lower $q$ than the corresponding bulk in all cases studied, indicating an increase in the persistence length under confinement. The low-$q$ cutoff for $q^{-1}$ scattering occurs at $q$ ca. 0.05 Å$^{-1}$, independent of molecular weight; below this $q$, the scattering around the Vycor peak masks the polymer scattering. We may exclude the possibility that this peak arises from a contrast mismatch since not only has the contrast match point of Vycor been verified, but the bulk ZAC scattering gives rise to $I(q)$, $l_p$, and $R_g$ in good agreement with the existing literature.[14] We also note that the Vycor peak intensity increases with molecular weight as would be expected if an increasing number of pores were connected by an extended chain.

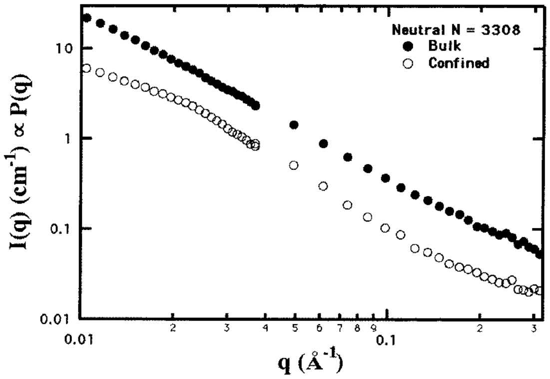

**Figure 4.** SANS for neutral 351 kDa polystyrene chains in ZAC condition in bulk and under confinement in toluene.[5]

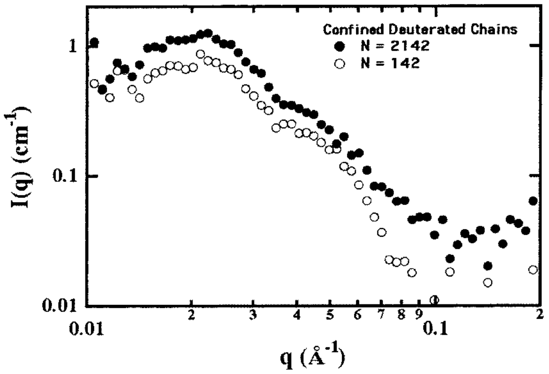

**Figure 5.** SANS from confined deuterated chains.

SANS from the confined deuterated polyelectrolytes in the matching solvent shows, in common with the ZAC chains, the Vycor correlation peak with the higher molecular weight chain exhibiting a higher maximum scattered intensity (Figure 5). For a fixed molecular weight, the deuterated sample gives rise to less scattering that the ZAC sample (cf. Figure 5 with Figure 3a,c) and arises due to the presence of intermolecular

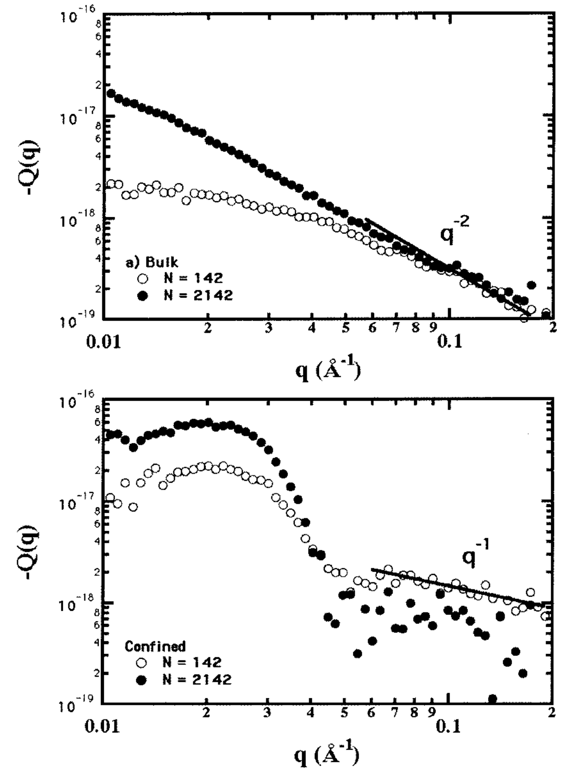

**Figure 6.** $Q(q)$ for (a) bulk and (b) confined chains for low and high molecular weights.

effects which are absent under the ZAC condition. A broad shoulder is present to the higher $q$ side of the correlation peak at $q$ ca. 0.04 Å$^{-1}$ whose position is independent of molecular weight. We note that similar scattering has been observed in other studies in which Vycor is filled with solutions of higher SLD than Vycor.[22] The presence of a so-called "skin effect" is however improbable from an electrostatic standpoint since the polymer and the surface of Vycor are both negatively charged. Further, we may exclude significant adsorption on the surface as, in the asymptotic limit, the (ZAC) scattering would have a form equal to $Aq^{-4} + Bq^{-1}$; in contrast, a clear $\approx q^{-1}$ behavior is observed.[5] An alternative explanation is an interchain correlation. Since the average internal diameter of the pores is 70 Å, we may immediately exclude a lateral chain separation of ca. 150 Å giving rise to this feature. It may however be related to modulation along the length of the chain or an effect related to the Vycor geometry.

**Interchain Structure Factor.** The combination of ZAC and fully deuterated chain scattering ($x = 1$ in eq 1) enables the separation of intrachain, $P(q)$, and interchain contributions, $Q(q)$. Using the measured $P(q)$ under the ZAC condition and inserting the known values for the prefactors into (1), we may obtain $Q(q)$ by an appropriate weighted subtraction from the deuterated chain-only scattering. This is shown in Figure 6a for free chains and in Figure 6b for chains under confinement. One of the striking features of our data is that the interchain structure factor, $Q(q)$, of the free and confined chains have well-defined asymptotic behavior. We observe that $Q(q)$ decays as $\approx q^{-2}$ for the bulk chains (Figure 6a) whereas the confined chain function decays only as $\approx q^{-1}$ (Figure 6b).

There have been very few experiments in which $Q(q)$ has been measured for free polyelectrolyte chains and none in which a quantitative analysis of the variation as a function of $q$ has been discussed.[15] Jannink et al. predicted that the asymptotic behavior of $Q(q)$ for semidilute neutral flexible chains to be $\approx q^{-d} + q^{-(2/\nu)+\omega}$ (where $\nu = 0.588$ and $\omega = 0.8$ in $d = 3$-dimensional space) $\approx q^{-3}$; this has been verified experimentally.[23] The asymptotic behavior will not be the same for charged chains as $\nu = 1$ and $\omega \approx 0$ for a locally rigid rod. With the second term dominating the asymptotic behavior, in the limit of high $q$, this yields $Q(q) \approx q^{-2}$. We may determine the asymptotic behavior of $Q(q)$ exactly, however, with the following treatment.

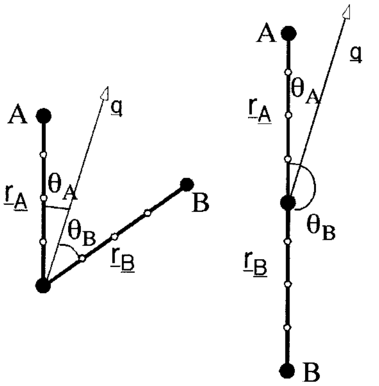

**Figure 7.** Model used to describe intermolecular scattering function, $Q(q)$, for two independent rods touching at one end. White circles represent monomer units; the black circles represent the extent of a single rodlike segment of a polyelectrolyte chain. (a, left) Random orientation or rods. (b, right) Parallel/antiparallel arrangement of rods.

The intermolecular interaction term, $Q(q)$, between polymer chains A and B with $N$ monomers can be calculated:

$$Q(q) = \frac{1}{N^2}\sum_{i_{A=1}}^{N}\sum_{j_{B=1,A\neq B}}^{N}\langle \exp(-iq\cdot(r_{i_A} - r_{j_B}))\rangle \qquad (4)$$

Now consider two rod segments on separate chains, each of size $\approx q^{-1}$, touching at one end as shown in Figure 7a. If the two rods are completely independent, then we may write for one rod−rod interaction:

$$Q(q)_{\text{rod-rod}} \propto \int_0^L \langle \exp(iqr_A \cos\theta_A)\, dr_A\rangle \int_0^L \langle \exp(-iqr_B \cos\theta_B)\, dr_B\rangle \qquad (5)$$

where we have taken both rods to have a common origin. Taking $Q(q)_{\text{rod-rod}} = A(q)\, B(q)^*$, where $A(q)$ and $B(q)$ correspond to each integral, we may write for the first term (cf. Appendix A)

$$A(q) = \left\langle \frac{1}{L}\left[\frac{1}{iq\cos\theta_A}[\exp(iqL\cos\theta_A) - 1]\right]\right\rangle \qquad (6)$$

Averaging over all orientations and setting $u = \cos\theta_A$, we may write

$$A(q) = \frac{1}{2L}\int_{-1}^{1}\frac{\exp(iqLu/2)}{iqu}[\exp(iqLu/2) - \exp(-iqLu/2)]\, du \qquad (7)$$

Since $\sin\phi = [\exp(i\phi) - \exp(-i\phi)]/2i$, and setting $x =$

$qLu/2$, we obtain

$$A(q) = \frac{1}{qL}\left[\int_{-qL/2}^{qL/2} \frac{\cos x \sin x}{x}\, dx + i\int_{-qL/2}^{qL/2} \frac{\sin^2 x}{x}\, dx\right] \quad (8)$$

The second term on the right-hand side is an odd function and has a zero integral. For $qL \to \infty$ and using the identity[25]

$$\int_0^{\infty} \frac{\cos x \sin x}{x}\, dx = \frac{\pi}{4} \quad (9)$$

we obtain

$$A(q) = \frac{\pi}{2qL} \quad (10)$$

Repeating the calculation for $B(q)^*$ and multiplying by $A(q)$ gives the interaction between rods in the system, of length $q^{-1}$, touching at a fixed origin. However, we could have chosen any one of $N$ origins, per polyelectrolyte chain, at which the two chains make contact. We thus have $N^2$ equivalent terms yielding

$$Q(q) = \frac{\pi^2}{4q^2L^2} \quad (11)$$

Thus, we have shown that the asymptotic limit of the interchain structure factor of a solution of uncorrelated rodlike particles is proportional to the square of the scattering amplitude from a single rod of size $q^{-1}$ and is independent of $N$. On the other hand, if we assume that the confined polyelectrolyte chains are locally aligned in the pores, i.e., $\theta_1 + \theta_2 = 0$ or 180° (Figure 7b), then, as for a single rod, the main contribution to $Q(q)$ will vary as $q^{-1}$. There is excellent agreement with this formalism for the bulk polyelectrolyte data, and while statistics limit our conclusions at high $M_W$, in the case of the confined chains, the low-$M_W$ system does indeed exhibit the $q^{-1}$ behavior as predicted for aligned rods.

We believe that the observed behavior in $Q(q)$ is a simple consequence of the charged chains in water (dielectric constant $\approx 80$), being confined by the low dielectric constant walls of Vycor glass (dielectric constant $\approx 3.85$). This would result in the electric field lines concentrating along the axial direction of the pores and enhancing the electrostatic interaction along the pore axis.[24] The effect may also be responsible for the stretched chain conformation as evidenced by the scattering peak and the asymptotic behavior of $P(q)$.

## Conclusions

We have investigated the structure of the polyelectrolyte PSSNa in a bulk concentrated solution and when confined in Vycor using SANS. We have employed the zero average contrast (ZAC) condition to separate the intramolecular (form factor), $P(q)$, and intermolecular contributions, $Q(q)$, to the total scattering. The chain conformation in the bulk solution is well-fitted to a Sharp and Bloomfield model for wormlike chains with a persistence length independent of molecular weight at the high monomer concentrations used. We find that the chains are more stretched in confined geometry than the bulk, as evidenced by the $1/q$ scattering region. They are also sufficiently extended as to highlight the large-scale disordered structure of Vycor; this effect increases with molecular weight. In addition, we have determined $Q(q)$ for both the bulk and confined states. The asymptotic behavior of the observed interchain structure factor is $\approx 1/q^2$ for free and $\approx 1/q$ for confined chains and is a consequence of the local rodlike structure of the chains. While the observed increase in chain rigidity may be an inherent effect of confinement or the weakly charged nature of the Vycor surface, we expect the former to be the dominant factor since the weakly charged Vycor surface is unlikely to significantly reduce the bound counterion fraction around the highly charged (fully sulfonated) backbone. However, we intend conducting parallel experiments in the presence of excess salt which may assist in determining the relative importance of these factors.

We are currently investigating PSSNa of lower contour lengths to preclude Vycor pore spanning so as to assist in fitting the full scattering function for the confined chains and also the kinetics associated with chain penetration.

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## Appendix

The scattering amplitude from a single rod of length $L$, whose axis, lying along a unit vector, $\mathbf{r}$, makes an angle $\theta$ with respect to the scattering vector $\mathbf{q}$ ($\mathbf{q}\cdot\mathbf{r} = qr\cos\theta$) and whose center is the origin, may be written[13]

$$a(q) = \frac{1}{L}\int_{-L/2}^{L/2} \exp(-iqr\cos\theta)\, dr \quad (A1)$$

Integrating yields

$$a(q) = \frac{2}{qL\cos\theta}\sin\left[\frac{qL\cos\theta}{2}\right] \quad (A2)$$

For a rod oriented along the scattering vector, the scattering intensity is equal to $|A(q)|^2$, but for a randomly oriented rod, we must average over all $\theta$, thus

$$I(q) = \frac{1}{4\pi}\int_0^{\pi}\left[\frac{2}{qL\cos\theta}\sin\left[\frac{qL\cos\theta}{2}\right]\right]^2 2\pi\sin\theta\, d\theta \quad (A3)$$

Integrating by parts yields

$$I(q) = \frac{2}{qL}\int_0^{qL/2} \frac{\sin^2 x}{x^2}\, dx \quad (A4)$$

In the limit of $qL \to \infty$, we may make use of the definite integral[25]

$$\int_0^{\infty} \frac{\sin^2 x}{x^2}\, dx = \frac{\pi}{2} \quad (A5)$$

giving the asymptotic intensity from a randomly oriented rod as

$$I(q)_{qL\to\infty} = \frac{\pi}{qL} \quad (A6)$$

## References and Notes

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