

Chapter 20

Small-Angle Neutron Scattering on Neutral and Cationic Guar Galactomannan

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We investigate the local structure of aqueous solutions of guar, a naturally occurring polysaccharide. Small-angle neutron scattering (SANS) results are presented for both the native neutral polymer and for salt solutions of a cationically modified guar in D₂O based systems. The intermediate wavevector range of the neutron spectra carries a signature of a Gaussian or nearly Gaussian chain with a decay close to q^{-2} . A crossover to a smaller slope at higher wavevectors, indicative of a local rigidity, was observed for all. The chain structure revealed by SANS is independent of temperature in the range of 9-50°C.

Guar is a naturally occurring polysaccharide known mostly for its ability to noticeably increase solution viscosity at relatively low concentrations. Naturally occurring forms of this neutral polymer as well as its derivatives (*i.e.* having cationic or hydrophobic substitutions) have applications that span a broad range of industries including cosmetics, pharmaceutical, food and oil industries. In the cosmetic industry, for example, it is used as a skin protective agent (1) and as a conditioner in shampoos (2). In pharmaceuticals, on the other hand, its presence is known to influence digestion in chickens (3) and also to control nutrition in camels (4). Randomly distributed galactose units along a mannose backbone at the approximate ratio of 1 galactose unit to 1.6 mannose units insure good polymer solubility in water through steric effects (Figure 1a). However, it is believed that the random nature of the substitution leads to inter- and intrachain association through the guar chain segments which are galactose-poor (5,6). These interactions are noncovalent and form stable intersegmental junction zones which can span several sugar units along the backbone. These associated regions have important consequences for the structure of the chains and for the physical behavior of the solution. In particular, aggregates are often presumed to be present even in dilute solutions and make the physical characterization of the polymer by common light-scattering measurements ambiguous (7,8).

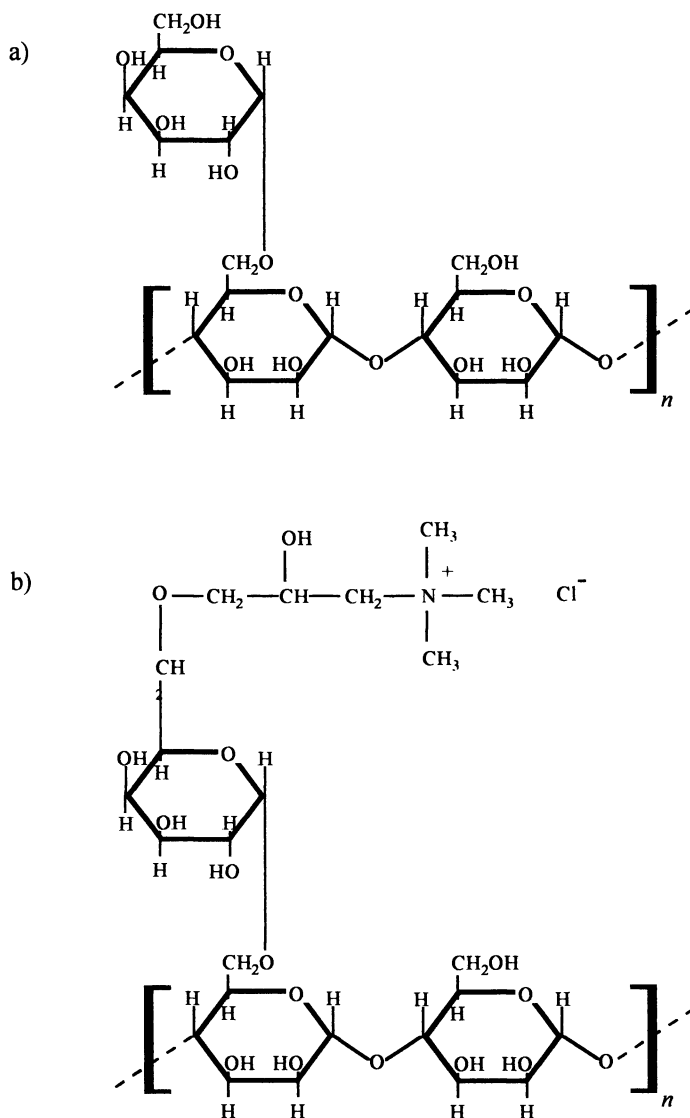


Figure 1. Molecular structure of (a) neutral and (b) cationic forms of guar. Note that the galactose units are randomly distributed at a ratio of 1 for every 1.6 mannose units. Also, the quaternary propylammonium is randomly attached to 14% of the mannose and galactose units.

In this study, small-angle neutron studies were performed on the native (neutral) form of guar and on cationic guar, a modified form of neutral guar more commonly used in cosmetic applications. Our particular sample has quaternary propylammonium groups distributed randomly along the chain (Figure 1b). The measurements on cationic guar were performed in the presence and absence of 0.1 M NaCl, with the focus of work being on the former. For a monovalent salt in water, the electrostatic screening length (Debye length) equals $0.304/c^{1/2}$ giving 9.6 Å for 0.1 M NaCl. This is approximately twice the length of a sugar unit along the backbone (5.4 Å) (9). It was hoped that this salt concentration would be high enough to effectively eliminate long-range electrostatic repulsion while retaining enough short range repulsion to hinder formation of inter- and intrachain associations. SANS measurements were performed on solutions at concentrations greater than the overlap concentration. Such concentrated systems were necessary to increase the signal-to-noise ratio allowing reasonable statistics to be obtained within a 12-24 hour timeframe. Also, to increase the scattering contrast between polymer and solvent, D₂O was used as the solvent. It is known for other molecules, however, that H₂O is a somewhat better solvent than D₂O (10) which may have some effect on the conformation of the polymer in solution. This fact must be remembered when comparing to H₂O-based systems.

Background

Scattering experiments provide information on the conformation of macromolecules in solution. Real space features with a characteristic dimension of l can be determined from the scattering spectra at wavevectors of $q \sim 1/l$. Moreover, the mass density of the macromolecules often follows a power-law distribution, leading also to power-law forms of the scattered intensity. For instance, the characteristic chain dimension of polymer chains (R) increases with the polymerization index (N) to a certain power, $R \sim N^{1/D_f}$, where D_f is the fractal dimension (11). In the case of Gaussian chains, $D_f=2$ and the intensity scattered at intermediate wavevectors ($a^{-1} \gg q \gg R^{-1}$ where a is the monomer length) decays as $I(q) \sim q^{-D_f} = q^{-2}$. On the other hand, the intensity scattered by rigid rod molecules ($D_f=1$) has a slower decay— $I(q) \sim q^{-1}$. A polymer molecule will often appear flexible at large lengthscales (intermediate wavevectors), but more rigid at local lengthscales (large wavevectors) since the monomers and their connections between each other provide some intrinsic rigidity to the backbone. Thus, the scattering profiles of polymer chains exhibit a crossover from larger to smaller fractal dimensions with increasing wavevector indicating a change in apparent rigidity at the different lengthscales.

Experimental Method

Guar was obtained in its unmodified (neutral) and cationic form from Rhodia Inc. Both polymers were purified by centrifugation to remove insoluble impurities, precipitated with isopropyl alcohol, and dried under vacuum. The final moisture content of the powder was ~8.7%. The intrinsic viscosity, $[\eta]$, of neutral guar

solutions at room temperature was determined to be 21 dl/g. For the cationic polymer, quaternary propylammonium groups (which remain fully ionized in aqueous solutions without pH adjustment) are randomly attached to fourteen percent of the sugar units on the chain backbone. The intrinsic viscosity of the cationic guar depends on the salt concentration, ranging from 454 dl/g without added salt to 16.2 dl/g in 0.5 M NaCl (at room temperature). Such variations in the intrinsic viscosity are typical for polyelectrolytes (12). The overlap concentration, estimated from $c^* \sim 4/[\eta]$, corresponds to 0.19 g/dl and 0.25 g/dl (upper bound) for the neutral and cationic guar, respectively. D₂O (99.9% pure) obtained from Cambridge Isotope Laboratories was filtered (with a hydrophilically modified PTFE Millipore filter, 0.2 μ m) directly into clean glass vials with screw cap tops. The solutions were made by adding the guar powder to the filtered D₂O and manually shaking to disperse the powder. They were then rotated on a spinning wheel at a low speed for 1-2 days at room temperature to allow for full dissolution of the polymer. After dissolution, the solutions were stored at 6 °C except during neutron scattering runs. The NaCl was added to the D₂O and solubilized prior to adding cationic guar. The concentrations were 0.25%, 0.46%, 0.70%, and 1.1% (by weight) for the neutral guar in D₂O and 0.25%, 0.46%, 0.65%, and 0.91% (by weight) for the cationic guar in 0.1 M NaCl in D₂O. A 0.46% cationic guar solution in the absence of salt was also prepared.

Small-angle neutron scattering measurements were performed using the time-of-flight small-angle diffractometer at the Intense Pulsed Neutron Source (IPNS) in Argonne National Laboratory. The details of the instrument setup and operation are described elsewhere (13). Large sample cells with a 5 mm pathlength were used since guar scatters weakly in D₂O. Data from q values ranging from 0.00494 Å⁻¹ to 0.247 Å⁻¹ were collected over 12 hours (for concentrations greater than 0.25%) and 24 hours (for concentrations of 0.25% and for the solvents without polymer). All measurements were taken at 25°C except for 2 runs on 0.46% neutral guar solutions at 9.5°C and 50°C. All data were treated according to methods used by Argonne National Laboratory which correct for solvent and parasitic scattering and place the data on an absolute level using standards. Within the range of polymer concentrations studied here, the amount of H₂O in the bulk (from exchange of hydrogen along the polymer chain with deuterium in the bulk and from residual moisture in the guar powder) is less than 0.1%.

Results and Discussion

The intensity values for the neutral and cationic guar solutions are plotted in absolute terms in Figure 2 normalized by concentration. Error bars are not shown in order to make the graph more readable, but vary from approximately $\pm 5\%$ at intermediate wavevectors to $\pm 10\%$ at high wavevectors. Data at wavevectors above 0.13 Å⁻¹ are omitted since incoherent scattering effects are more significant there. The data collapse onto a single curve at wavevectors above 0.01 Å⁻¹ for the neutral guar and 0.02 Å⁻¹ for the cationic guar. The curves do not show a well-defined plateau at the lowest measured wavevectors indicating that neutrons are probing the internal structure of the molecule (at dimensions $\ll R$). In general, the data show two slopes. This feature is more easily seen when the data for each concentration are

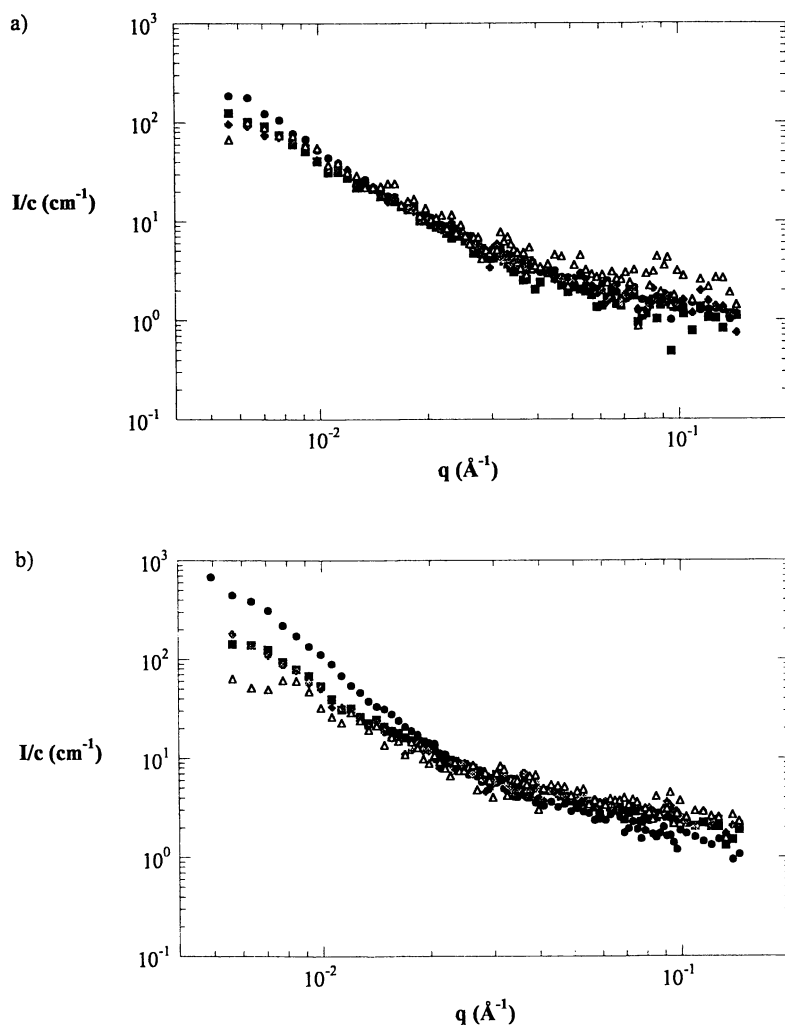


Figure 2. Neutron scattering spectra for (a) neutral guar in D_2O [(●) 1.1%; (■) 0.70%; (◆) 0.46%; (△) 0.25% concentration by weight] and (b) cationic guar in D_2O -based 0.1 M NaCl [(●) 0.91%; (■) 0.65%; (◆) 0.46%; (△) 0.25% concentration by weight].

plotted separately and in different manners. An example is shown in Figure 3 for neutral guar at 0.46% concentration. Figure 3a shows the data plotted in the same way as in Figure 2. Neglecting the first few data points (which are at the limits of the capabilities of the instrument), two lines were fit through the data giving slopes of -2.0 and -1.0 at the lower and higher ends of the neutron spectra, respectively. These slopes represent the fractal dimension of the polymer and indicate a crossover from a more flexible structure at larger lengthscales to a more rigid structure at smaller lengthscales. Reinforcing this finding, Figure 3b shows a Kratky plot where Iq^2 vs. q is plotted on linear scales. The plot shows a flat region at lower wavevectors indicating q^{-2} behavior and an increase in the slope at high wavevectors indicating a change to smaller power law behavior. For comparison, lines with power law behavior of q^{-2} and q^{-1} are also shown. Plotted in this way, such crossovers are clearly seen for all of the samples, both neutral and cationic, although the exact power law behavior varies somewhat. Moreover, the crossovers appear independent of concentration for each guar, giving $0.033 \pm 0.005 \text{ \AA}^{-1}$ for neutral guar and $0.025 \pm 0.002 \text{ \AA}^{-1}$ for cationic guar. It is reasonable that the crossover point for the cationic guar occurs at lower wavevectors than for neutral guar. This represents a larger "rigid" lengthscales for the cationic guar and suggests that some local repulsion still exists even in 0.1 M NaCl. Also, the cationic guar has a larger average monomer size due to the attachment of charge groups to the backbone, making the polymer in a steric sense even more rigid.

Data at other guar concentrations were analyzed similarly and are summarized in Table I. The correlation factors describing the quality of the fitted data are 0.98 or greater at intermediate wavevectors. At higher wavevectors the data are more difficult to fit, with correlation factors ranging from 0.74 (for the 0.25% neutral guar solution) to 0.97. Note that some of the slopes at higher wavevectors are not reported; the measured slopes are less than one giving a fractal dimension that has no physical meaning within the framework of the power law discussed earlier. With some variability, the neutral guar displays a fractal dimension of ~ 2 at low wavevectors ($0.006 \text{ \AA}^{-1} \leq q \leq 0.03 \text{ \AA}^{-1}$) and ~ 1 in the range $0.03 \text{ \AA}^{-1} \leq q \leq 0.13 \text{ \AA}^{-1}$. Thus, neutral guar exhibits Gaussian behavior at intermediate lengthscales and rigid rod behavior at smaller lengthscales, displaying the signature of a random walk polymer with local rigidity.

Table I. Summary of power law behavior for neutral and cationic guar.

<i>Neutral Guar in D₂O</i>			<i>Cationic Guar in 0.1 M NaCl (D₂O-based)</i>		
<i>Guar concentration n (wt. %)</i>	<i>slope in intermediate q range</i>	<i>slope in high q range</i>	<i>Guar concentration (wt. %)</i>	<i>slope in intermediate q range</i>	<i>slope in high q range</i>
1.1%	-2.26	-1.04	0.91%	-2.89	-1.04
0.70%	-2.01	-0.98	0.65%	-2.04	----
0.46%	-2.03	-1.01	0.46%	-2.18	----
0.25%	-1.94	----	0.25%	-1.84	----

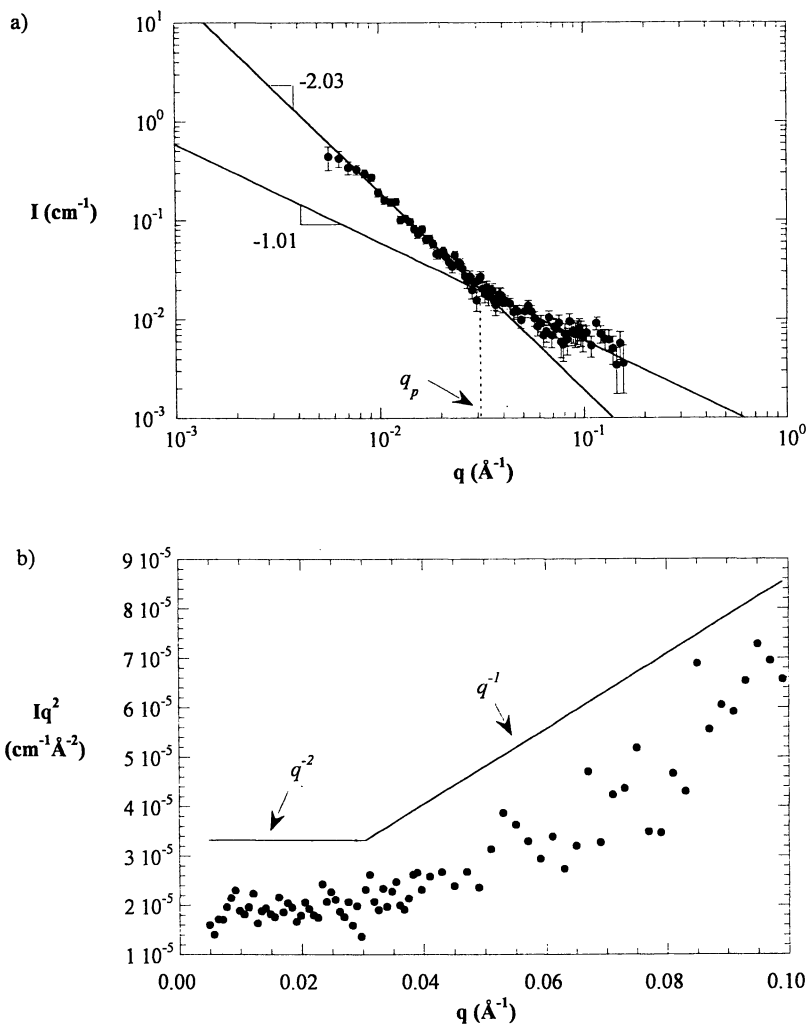


Figure 3. Neutron scattering spectrum for 0.46% neutral guar in D₂O. a) Logarithmic plot of I vs. q ; b) Linear plot of Iq^2 vs. q (Kratky plot). Lines showing q^{-2} and q^{-1} power law behavior are also shown.

The cationic guar data vary more widely in the wavevector range $0.006 \text{ \AA}^{-1} \leq q \leq 0.13 \text{ \AA}^{-1}$, with a slope close to 3 at the highest concentration that decreases with the polymer concentration. While electrostatic effects may encourage some swelling at the lowest concentration, the total increase in the ion concentration from contributions due to the polymer is less than 3%. This small increase is not expected to reduce long range repulsion significantly enough to completely account for such large changes in the polymer conformation. Hence, the large slope at the highest concentration may indicate increased interaction among chains, perhaps due to incomplete polymer dissolution. Both the 0.91% cationic guar solution and the 1.1% neutral guar solution exhibited some elastic qualities making polymer dissolution more difficult. Considering these factors, no definite concentration dependence in the fractal dimension can be ascertained.

The slopes for cationic guar in the higher- q region are less than 1 except at the highest concentration. The absence of a clear q^{-1} regime might be due to the charged nature of the polymer. Not only are charged monomers more bulky structurally, but counterion contributions to the scattering profile may mask the signature of local rigidity. Figure 4 makes this statement more clear. It shows the neutral and cationic guar at 0.46% concentration plotted together and includes all measured q values, even those above 0.13 \AA^{-1} where the signal-to-noise ratio is considerable. At intermediate wavevectors ($0.01 \text{ \AA}^{-1} \leq q \leq 0.03 \text{ \AA}^{-1}$) the data coincide whereas at large wavevectors ($q \geq 0.03 \text{ \AA}^{-1}$) the data diverge. Typically, all intensity profiles will eventually flatten out to zero slope at high enough wavevectors as the neutrons probe molecular rearrangements within the monomer itself.

Polysaccharides are weak scatterers of neutrons mostly because of the exchange of hydrogens along the backbone with deuterium in the bulk. This not only reduces the contrast between the polymer and solvent, but it also increases the total amount of incoherent scattering. Thus, in order to get good scattering statistics, the data must be collected for long time periods, making the experiments more difficult. Recall that the data in this study were collected for 12 to 24 hours both for the sample and solvent. Up to this point, incoherent scattering was not subtracted from the measured data. To estimate the error from incoherent scattering one must include the presence of hydrogen from the polymer and from residual moisture in the guar powder before addition to water. Estimates reveal a small increase in the slopes extracted from data at intermediate wavevectors (up to 2%), but a moderate increase at high wavevectors (up to 22%). Also, the effect on the crossover position is minimal ($\sim 1\%$). Hence, even though incoherent scattering increases with guar concentration, the crossover position stays the same. Thus, the change in slopes in the intensity data is not a manifestation of improper background subtraction, but rather an intrinsic characteristic of the guar chain.

Regardless of the type of guar or the concentration, a change in the fractal dimension from a number greater than one at intermediate wavevectors to approximately one at higher wavevectors is usually associated with a persistence length of the polymer. This length represents a contiguous portion of the chain where the directional orientation the monomers at either end of this portion becomes uncorrelated (14). The wormlike chain is often used as a polymer model when the

fractal dimension changes from 2 to 1. For an ideal wormlike chain, the crossover in the scattered intensity (I) from intermediate to high wavevectors has been shown by des Cloizeaux (15) to obey

$$I = C \left(\frac{2}{3} \frac{1}{q^2} + \frac{l_p \pi}{q} \right). \quad (1)$$

Here l_p denotes the persistence length and C is a constant. Note that the intensity as written here has two asymptotes at high and low- q values with a crossover point, q_p , at

$$q_p = \frac{2}{3\pi l_p}. \quad (2)$$

Within the framework of this model, l_p was found to be approximately 7 Å for neutral guar at 0.46% which is slightly larger than the length of a sugar molecule along the backbone, 5.4 Å (9). A similar calculation on the neutral guar data at 0.7% concentration gives a persistence length of approximately 6 Å.

The values obtained here for the persistence length seem surprisingly small. Polystyrene chains, for example, have been reported to have a persistence length of ~9 Å (16). However, the reported persistence lengths are usually extracted by fitting the lower and middle q -range of the scattering spectra, typically from zero wavevectors to the end of the plateau region in the $q^2 I(q)$ representation. The lowest of our scattered data belong already to the plateau. Moreover, we do observe a clear crossover from the plateau to the next linear regime, allowing for the use of the asymptotic form equation (1). The differences in numbers are certainly to be attributed to differences in the extraction methods, and not to differences in the properties of the chains. For instance, considering the steric hindrance of the mannose units and the high frequency of galactose side chains, the persistence length of guar is expected to be larger than the persistence length of polystyrene. Indeed, if we estimate the value of q_p for polystyrene from the data in reference 17, and compare it with our results, we would be lead to a persistence length of guar 2-2.5 times larger than that of polystyrene.

Other techniques also yield different values for the persistence length. Robinson *et al.* (7), for instance, find a value of ~37 Å for neutral guar in H₂O using intrinsic viscosity measurements. These measurements probe global properties of the solution and, hence, are affected by the molecular weight and polydispersity as well as by inter- and intra-chain interactions. Extrapolations to infinite dilution may rule out inter-chain interactions, but intra-chain interactions may still be present. Hence, the intrinsic viscosity would be higher than in the absence of these interactions, leading to a higher-than-real persistence length. Alternatively, small-angle neutron scattering probes the local features of the polymer.

In addition to the SANS studies previously discussed, a measurement was performed on cationic guar in the absence of salt (at 0.46% (by wt.) concentration) to show the extent of screening in the 0.1 M NaCl case. Figure 5 shows that the characteristic features are still present in the absence of salt, but the crossover point is

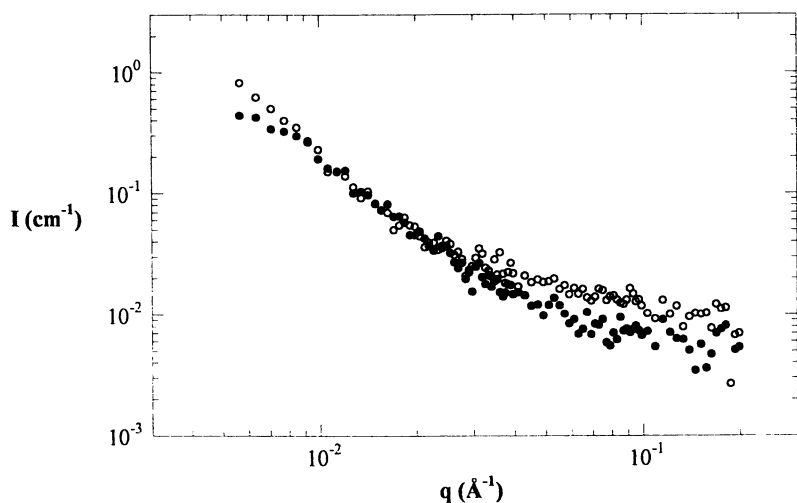


Figure 4. Comparison of neutron scattering spectra for 0.46% neutral guar in D_2O (●) and 0.46% cationic guar in D_2O -based 0.1 M NaCl (○).

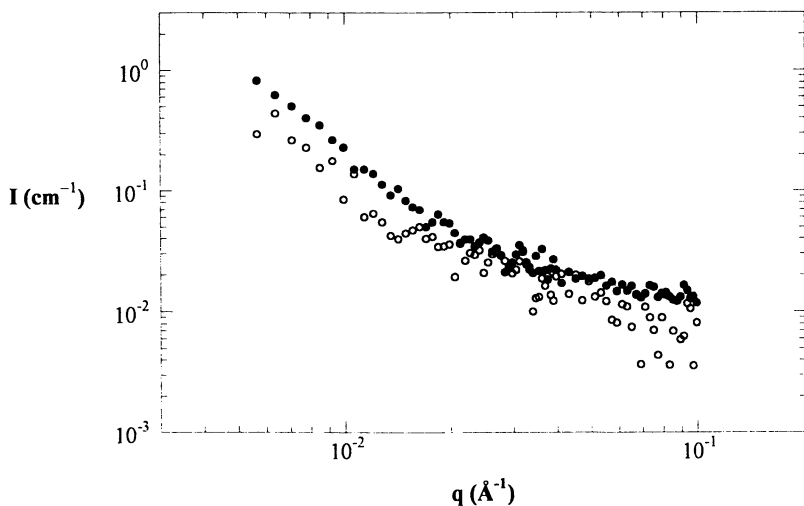


Figure 5. Comparison of 0.46% cationic guar in presence (●) and absence (○) of 0.1M NaCl.

shifted to lower q values as expected for a polymer with the persistence length increased by electrostatic repulsion. Indeed, without salt the crossover occurs approximately between 0.013 \AA^{-1} and 0.020 \AA^{-1} , as compared to $\sim 0.025 \text{ \AA}^{-1}$ in the presence of 0.1 M NaCl . This corresponds to a 40-100% increase in the persistence length, which is somewhat lower than would be expected from an Odijk calculation. In Figure 5, the scattering intensities of the two samples differ slightly. This may simply reflect increased scattering from the electrolyte surrounding the guar molecule which also may increase the signal-to-noise ratio for that sample, giving less scattered data.

In the last part of the study, the influence of temperature on the conformation of the polymer was investigated (Figure 6). Three temperatures were investigated, 9.5°C , 25°C , and 50°C , and no difference in the static organization of the polymer was detected within the available q range of the instrument. In fact, the collapse of the data at each temperature suggests rather good reproducibility of all the results, despite some scatter in the data.

Conclusion

Small-angle neutron scattering experiments were performed on concentrated neutral and cationic guar solutions, the latter in the presence of salt. Here we reported, to our knowledge, the first measurements on the local structure of such a system. The polymer was found to have a conformation close to that for a Gaussian chain at

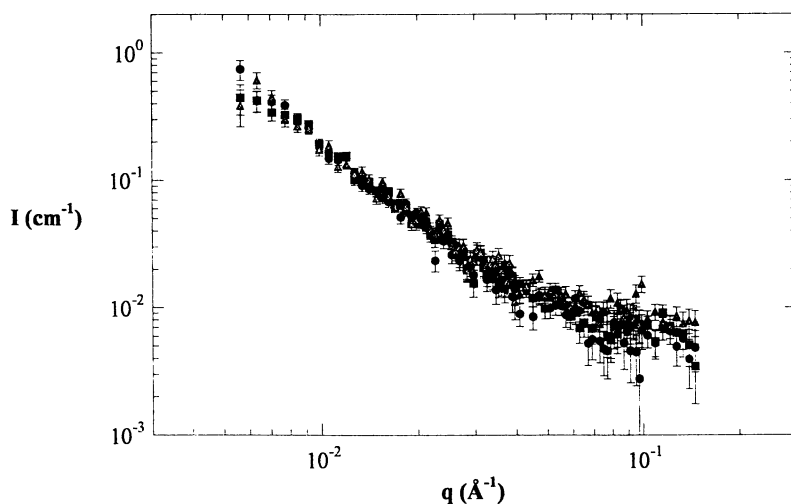


Figure 6. Temperature dependence of neutron scattering spectra for 0.46% neutral guar in D_2O : (●) 9.5°C ; (■) 25°C ; (▲) 50°C .

intermediate lengthscales. The scattering profiles are typical of those for polymers with intrinsic rigidity, with a q^{-1} slope at high wavevectors. Crossovers from the two regions occur at roughly the same q values, around $0.033 \pm 0.005 \text{ \AA}^{-1}$ for neutral guar and $0.025 \pm 0.002 \text{ \AA}^{-1}$ for cationic guar. Electrostatic effects on the cationic guar were partially screened in the presence of salt, but appeared strong enough to influence the scattered intensity at the higher end of the measured q range. Incoherent scattering does not appear to strongly affect the results. Last, the static properties of the neutral polymer do not change within temperature range 9.5°C to 50°C.

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