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Effects of the Quantity and Structure of Hydrophobes on the Properties of Hydrophobically Modified Alginates in Aqueous Solutions

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Summary

Alginate is an important polysaccharide with applications in food industry, cosmetics and pharmacy. In this study, three hydrophobically modified alginates with different amount of various hydrophobic groups have been synthesized. Rheology and turbidity measurements have been carried out on polymer solutions in the concentration regime 0.005 - 2.0 wt %. The rheological results indicate that the introduction of hydrophobic groups induce the formation of intra- or intermolecular associations in the aqueous solutions depending on the polymer concentration and the hydrophobicity. The concentration dependency of the viscosity exhibit different power-law behaviors depending on the concentration regime and the hydrophobic modification. This has been scrutinized in view of theoretical scaling laws presented in the literature.

Keywords

Alginate, hydrophobic modification, rheology, turbidity, scaling laws

Introduction

Hydrophobically modified water-soluble polymers (HMWSP) consist of a hydrophilic backbone to which small amounts of hydrophobic substituents are incorporated as pendant chains, blocks, or terminal groups. Aqueous solutions of HMWSP exhibit interesting rheological properties which arise from intra- or intermolecular associations of the hydrophobic groups. In dilute polymer solutions, the molecules act mainly as individual units, and the intramolecular interactions are dominant. However, as the concentration increases, the intermolecular associations prevail. At a certain concentration, the overlap concentration, c*, a transition from dilute to semidilute regime occurs and a transient network is formed. The solution properties of these polymers can be controlled and manipulated by polymer design [1,2], and in this paper we will study the effect of adding various amounts of different types of hydrophobic groups to the polysaccharide alginate.

Sodium alginate is an anionic copolymer, comprising of β-D-mannuronic acid (M block) and (1→4)-linked α-L-guluronic acid (G block) units arranged in a nonregular blockwise pattern of varying proportion of GG, MG and MM blocks [3]. Hydrophobically modified alginates (HM-alginates) can be classified as hydrophobically modified anionic polyelectrolytes. Sinquin et al. have synthesized several HM-alginates with different hydrophobic chain lengths and studied the physicochemical properties of their aqueous solutions [4-7]. However, to the best of our knowledge, no further studies have been reported for the comparison of HM-alginates with different types of hydrophobes. As is well known, the physical properties of aqueous solutions of flexible associative polymers is dependent on several factors, such as hydrophobic chain length, hydrophobic content, type and arrangement of hydrophobic groups, and the charge density [1,2,8-13]. In this work, two types of hydrophobically modified alginates with different degrees of hydrophobic substitution have been synthesized. The effects of the structure and the content of the hydrophobic groups on the solution properties have been studied with the aid of rheology and turbidity measurements.

Experimental

Materials

The unmodified alginate used in this study was supplied by FMC Biopolymers, Drammen, Norway, designated LF 10/60 LS (# 912912). According to the specifications from the manufacturer, this sample has a weight-average molecular weight of 152 000 and the guluronic acid to mannuronic acid ratio (G/M) is 0.75. Dilute alginate solutions were dialyzed against pure water for several days to remove salt and other low-molecular weight impurities, and were thereafter freeze-dried. Regenerated cellulose with a molecular weight cutoff of 8000 was used as dialyzing membrane.

The three hydrophobically modified alginates examined in this study were synthesized by two different procedures. Two HM-alginate polymers with various hydrophobic pendant contents were synthesized via the Ugi multicomponent condensation reaction [14]. The n-octylamine groups (C8) were grafted onto the backbone of the alginate chain via the Ugi reaction with the theoretical hydrophobic modification ratio of 12 and 40 mol %. By using ^{1}H NMR (D_2O, 85 °C) with a 500 MHz Bruker DRX 500 spectrometer, the achieved degrees of modification of were estimated to be 5.4 and 15 mol %, respectively. The detailed synthesis procedure has been described previously [15,16], and the chemical structure of these HM-alginates is shown in Figure 1a. The products were named as HM_{UGI}m-alginate, where m denotes the hydrophobic modification ratio (mol %). For example, HM_{UGI}5.4-alginate is the HM-alginate with a modification ratio of 5.4 mol %. The diluted reaction mixture from the HM_{UGI}5.4-alginate synthesis was dialyzed against pure water for several days to remove the unreacted monomers as well as the low-molecular weight components, and thereafter freeze-dried. For the HM-alginate with high hydrophobic content (HM_{UGI}15-alginate), the diluted reaction mixture was first dialyzed against pure water and freeze-dried. The obtained polymer was dissolved again in an acetone/water mixture (20/80 % v/v), and was dialyzed against the mixed solvent for several days before freeze-drying. By this procedure, the unreacted chemicals were removed.

The third HM-alginate was synthesized by utilizing the coupling agent 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride (EDC.HCl) to form amide linkages between amine containing molecules and the carboxylate moieties on the alginate polymer backbone. The detailed synthesis and purification process of this HM-alginate has been described previously [17]. The structure of this hydrophobic modification is shown in Figure 1b, and the degree of hydrophobic modification was estimated to approximately 31 mol % by ^{1}H NMR. This sample has been denoted $HM_{EDC}31$-alginate. As can be seen from Figure 1, all the three HM-alginates contain a C_8-hydrophobic group. However, unlike $HM_{EDC}31$-alginate, the hydrophobic modification of $HM_{UGI}5.4$-alginate and $HM_{UGI}15$-alginate also contain a bulky side-group. This extra group can give rise to reduced flexibility, steric hindrances, and increased hydrophobicity.

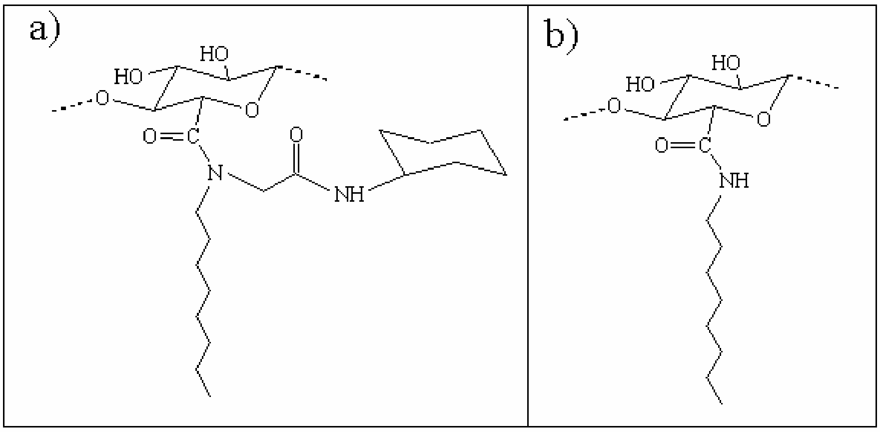

Figure 1. The chemical structures of the hydrophobic modifications of the alginate.
a) $HM_{UGI}5.4$-alginate and $HM_{UGI}15$-alginate. b) $HM_{EDC}31$-alginate.

Solution preparation

All solutions were prepared in Millipore^{TM} water by weighing the components. The dilute solutions were prepared by dilution from more concentrated samples.

Turbidity measurements

The transmittances of aqueous solutions of alginate and HM-alginates at different concentrations were measured with a temperature controlled Helios Gamma (Thermo Spectronic, Cambridge, UK) spectrophotometer at a wavelength of 500 nm. The apparatus is equipped with a temperature unit (Peltier plate) that gives stable temperature (25±0.1 °C) over an extended time. The turbidities, τ, of the samples are determined from the following relationship:

$$\tau = (-1/L)\ln(I_t/I_0) \qquad \textbf{(1)}$$

where L is the light path length of the cell (1 cm), I_t is the transmitted light intensity, and I_0 is the incident light intensity. All results from the spectrophotometer will be presented in terms of the turbidity.

Rheology

Steady shear measurements of the solutions were carried out on a Paar-Physica MCR 300 rheometer using a cone-and-plate geometry, with a cone angle of 1° and a diameter of 75 mm. This rheometer operates effectively with this geometry also on dilute polymer solutions, and even the viscosity of water can easily be measured over an extended shear rate domain. The samples were introduced onto the plate, and to prevent evaporation of the solvent, the free surface of the sample was always covered with a thin layer of low viscosity silicone oil (the viscoelastic response of the samples is not observed to be significantly affected by this layer).

Results and discussion

Effect of shear rate on the solution viscosities

Figure 2 depicts the effect of shear rate on the viscosity for solutions of unmodified and hydrophobically modified alginates at different concentrations. For the unmodified alginate, as can been seen from Figure 2a, a Newtonian plateau is observed in the whole shear rate region for the solutions with polymer concentration up to 1.0 wt %. When the concentration exceeds 1.0 wt %, the alginate solutions depict Newtonian behavior in the low to intermediate shear rate region, followed by moderate shear-thinning effects at high shear rates. This suggests the existence of some weak associations in the aqueous systems at higher polymer concentrations.

The analogous viscosity curves for solutions of HM_{UGI}5.4-alginate are displayed in Figure 2b. In this case, the profiles of the viscosity curves for the solutions with low polymer concentrations are similar as that of the unmodified alginate. At a high solution concentration (1.0 wt %), an interesting shear rate effect is observed. The zero-shear viscosity value is about one order of magnitude higher than that of unmodified alginate. Following the zero-shear viscosity plateau, a shear thickening effect emerges at low shear rates, suggesting shear rate induced structural reinforcements of the association complexes. At higher shear rates, the intermolecular junctions are disrupted, and shear thinning is observed. A clear hysteresis effect appears when the shear rate is reduced from high to low value, which indicates that the rate of reformation of the associations is not as fast as that of their disruption. Compared to the curve of HM_{UGI}5.4-alginate, the viscosity curves of HM_{UGI}15-alginate shown in Figure 2c depict a more pronounced shear-thinning effect at high polymer concentrations (above 0.5 wt %), and the values of viscosity are higher than that of HM_{UGI}5.4-alginate. Since the hydrophobic group content is raised from 5.4 % of HM_{UGI}5.4-alginate to 15 % for the HM_{UGI}15-alginate, the possibility of forming intermolecular hydrophobic junctions is enhanced in the semi-dilute regime, which results in increased viscosities at low shear rates.

Figure 2d shows the corresponding viscosity curves of HM_{EDC}31-alginate. It is obvious that at low polymer concentrations (up to 0.5 wt %), a Newtonian plateau is observed in the whole shear rate region for all the solutions, similar to what is found for the unmodified alginate. When the polymer concentration is raised to 1.0 wt %, shear-thinning effects are detected over a larger shear-rate regime than for the unmodified alginate. The plateau value at low shear rates is almost the same as that of the unmodified alginate, which is much lower than those of HM_{UGI}5.4-alginate and HM_{UGI}15-alginate. This phenomenon indicates that in the present case, the associations are very weak and easily to be destroyed. However, when the polymer concentration is increased from 1.0 to 2.0 wt %, the solution viscosities increase significantly, and a pronounced shear-thickening effect appears at low shear rates. As can be seen from Figure 1b, the hydrophobic side chain of HM_{EDC}31-alginate is a linear octyl chain, whereas the HM-alginate obtained from Ugi reaction has a cyclohexyl group connected to the octyl side chain, resulting in large steric hindrance, and also a higher hydrophobicity of each hydrophobic group.

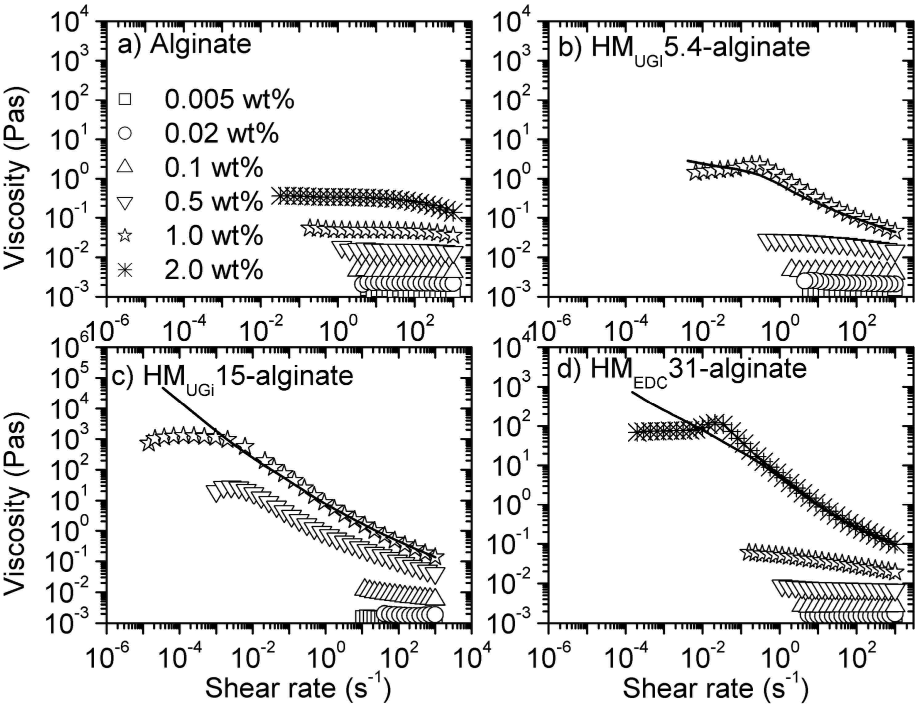

Figure 2. Steady shear viscosity profiles of various concentrations of aqueous solutions of: a) alginate b) HM_{UGI}5.4-alginate c) HM_{UGI}15-alginate d) HM_{EDC}31-alginate. The solid lines indicate the back curves (high to low shear rate) for the highest polymer concentration.

Zero-shear viscosity and turbidity

Figure 3a shows the dependence of zero-shear viscosity on the polymer concentration for the solutions of unmodified and hydrophobically modified alginate. At extremely low concentrations (c=0.005 wt %), the viscosities of the above four polymers approach one another. To show the viscosity change more clearly in the low concentration region, the zero-shear viscosity vs solution concentration was magnified in the inset plot of Figure 3a. The viscosity of HM_{UGI}5.4-alginate and the unmodified alginate display almost the same values in the concentration region between 0.005 to 0.1 wt %, beyond which the modified alginate displays higher viscosity than the unmodified one. The viscosities of solutions of HM_{UGI}15-alginate which has a higher hydrophobic content depict a more remarkable change with polymer concentration. In the concentration range of 0.005 wt % to 0.05 wt %, the unmodified alginate yields higher viscosities than the modified one; whereas the viscosity of HM_{UGI}15-alginate rises significantly when the polymer concentration is increased beyond 0.05 wt % and exceeds that of its unmodified analogue. Such trends are also observed for $\mathrm{HM_{EDC}}$31-alginate, but with the much higher crossover concentration of 1 wt %. Several studies on associative systems [18-20] have reported a behavior of lower viscosity for HM-polymer systems at low polymer concentrations, and this trend is attributed to the increasing hydrophobicity that leads to the formation of intramolecular interactions between the hydrophobic pendants along the same polymer chain.

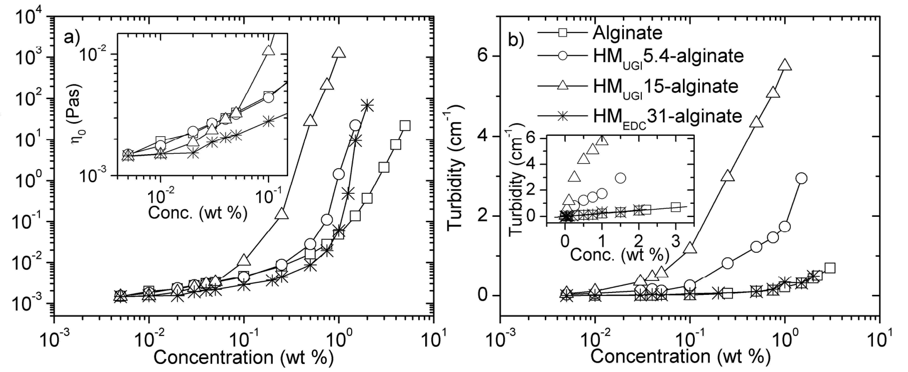

Figure 3. a) Dependence of zero-shear viscosity on concentration of unmodified and hydrophobically modified alginate. The inset plot shows the magnification of the concentration 0region between 0.005 and 0.1 wt %. b) Dependence of turbidity on polymer concentration for unmodified alginate and hydrophobically modified alginates. The inset plot shows the same data on a linear scale.

Figure 3b depicts the change of turbidity with polymer concentration for unmodified and hydrophobically modified alginates. In the inset plot, the same data is plotted on a linear scale, and if the enhanced turbidity is only due to an increased polymer concentration, we would expect a linear behavior of the turbidity in this inset plot (the Beer-Lambert law). As can be seen, the unmodified alginate and the $\mathrm{HM_{EDC}}$31-alginate both follow the Beer-Lambert law, while the $\mathrm{HM_{UGI}}$5.4-alginate and $\mathrm{HM_{UGI}}$15-alginate clearly exhibit a non-linear behavior. This indicates that the turbidity increase of $\mathrm{HM_{UGI}}$5.4-alginate and $\mathrm{HM_{UGI}}$15-alginate is due to the build-up of large associative structures, and from Figure 3b, it can be seen that the turbidity enhancement is evident even at low polymer concentrations. However, the $\mathrm{HM_{EDC}}$31-alginate exhibit the same turbidity as the unmodified alginate in the whole concentration range, and even though the viscosity at high polymer concentrations are much higher than that of its unmodified analogue, the hydrophobic associations that give rise to the viscosity change do not form large enough clusters to induce a raise in the turbidity values. The differences in the turbidity behavior between the $\mathrm{HM_{UGI}}$-alginates and the $\mathrm{HM_{EDC}}$31-alginate is probably due to the bulky cyclohexyl side-group on the $\mathrm{HM_{UGI}}$-alginates, which will give rise to steric hindrances and larger association structures than the smaller hydrophobic groups of the $\mathrm{HM_{EDC}}$31-alginate.

Scaling relationships of the viscosity

Polyelectrolyte solutions can be divided into several concentration regimes. In the dilute regime, the polymer concentration is low, and the separate polymer chains acts at individual units. As the polymer concentration is raised, the chains start to overlap with each other and a transient network is formed (semidilute regime). The overlap concentration, c*, marks the transition from the dilute to the semidilute regime. At still higher polymer concentrations, entanglement effects come into play, and the onset of this concentration regime is denoted c^e. At sufficiently high polyelectrolyte concentrations, the amount of counter-ions present in the solution will cause a significant salt effect. Rubinstein et al. [21] predicts that the behavior of polyelectrolytes at concentrations where the electrostatic blobs start to overlap, c^d, gives a behavior like that of entangled uncharged polymers, and we would expect the scaling-laws for polyelectrolytes at high salt concentrations to be valid in this region.

There are several theoretical works providing scaling-laws describing how the viscosity of polymer solutions depends on the concentration [21-27]. We have summarized the different scaling relationships from the literature of the specific viscosity, η_{sp}, the reduced viscosity, η_{sp}/c, and the zero-shear viscosity, η_0, as a function of the polymer concentration, c, for polyelectrolyte solutions in Table 1.

Table 1. Scaling-laws for polyelectrolyte solutions.

In the absence of added salt			High salt concentration			
$\eta_{sp}\sim c^{0.5\ (a)}$	$\eta_{sp}/c\sim c^{-0.5\ (a,b)}$	$\eta_0\sim c^{0.5\ (c,d)}$	$\eta_{sp}\sim c^{1.25\ (a)}$	$\eta_{sp}/c\sim c^{0.25\ (a)}$	$\eta_0\sim c^{1.25\ (c)}$	$c^*<c<c^e$
$\eta_{sp}\sim c^{1.7\ (a)}$	$\eta_{sp}/c\sim c^{0.7\ (a)}$	$\eta_0\sim c^{1.5\ (c)}$	$\eta_{sp}\sim c^{4.25\ (a)}$	$\eta_{sp}/c\sim c^{3.25\ (a)}$	$\eta_0\sim c^{3.75\ (c)}$	$c^e<c$

[a] Muthukumar [22].
[b] Fuoss et al. [23].
[c] Rubinstein et al. [21,24,25].
[d] Fuoss [26].

In Figure 4, the specific viscosity, the reduced viscosity, and the zero-shear viscosity are plotted as a function of the polymer concentration on a log-log scale. According to Muthukumar [22], the reduced viscosity of polyelectrolyte solutions in the absence of added salt increases with the polymer concentration in the regime c<c*, whereas there is a decline of η_{sp}/c in the region $c^*<c<c^e$, followed by a new raise when $c^e<c$. According to this, we have defined c* for our systems as the maximum of the reduced viscosity occurring at low polymer concentrations (Figure 4b and e). For the HM_{UGI}15-alginate, and the HM_{EDC}31-alginate, we do not observe this maximum in the considered concentration regime, and we have therefore not defined c* for these systems. The minimum in the reduced viscosity would denote the transition into the entangled regime, and we have defined c^e accordingly from Figure 4b, e, and k. As will be discussed below, HM_{UGI}15-alginate does not exhibit a negative slope of η_{sp}/c. For this system we have defined c^e as the concentration where there are a clear change in the slope of both η_{sp}/c and η_0 (Figure 4h and i). When the polymer concentration exceeds c^d, the electrostatic interactions are screened out, and we would expect a transition from the scaling-laws for polyelectrolytes without added salt to polyelectrolytes at high salt concentrations. This should result in an obvious change in the power-law behavior, and c^d is therefore taken as the concentration where there is a new change of the slopes in Figure 4. From the curves in Figure 4, the scaling relationships in the three different concentration regimes $c^*<c<c^e$, $c^e<c<c^d$, and $c^d<c$ has been examined, and the values of the fitted power-law exponents are plotted in Figure 5.

Scaling in the region $c^* < c < c^e$

As can be seen from Figure 5a and c, the observed scaling-law exponents of the specific and reduced viscosities for alginate in the region $c^* < c < c^e$ deviate significantly from the predicted values of Muthukumar [22]. The reason for this is unclear, but it might be due to associative interactions (e.g. hydrogen bonds) that counteract the repulsive polyelectrolyte forces. For the $HM_{UGI}5.4$-alginate, η_{sp} and η_{sp}/c exhibit approximately the same scaling behavior as for the unmodified alginate in this concentration regime, indicating that this low amount of hydrophobic modification has little effect on the scaling of these parameters.

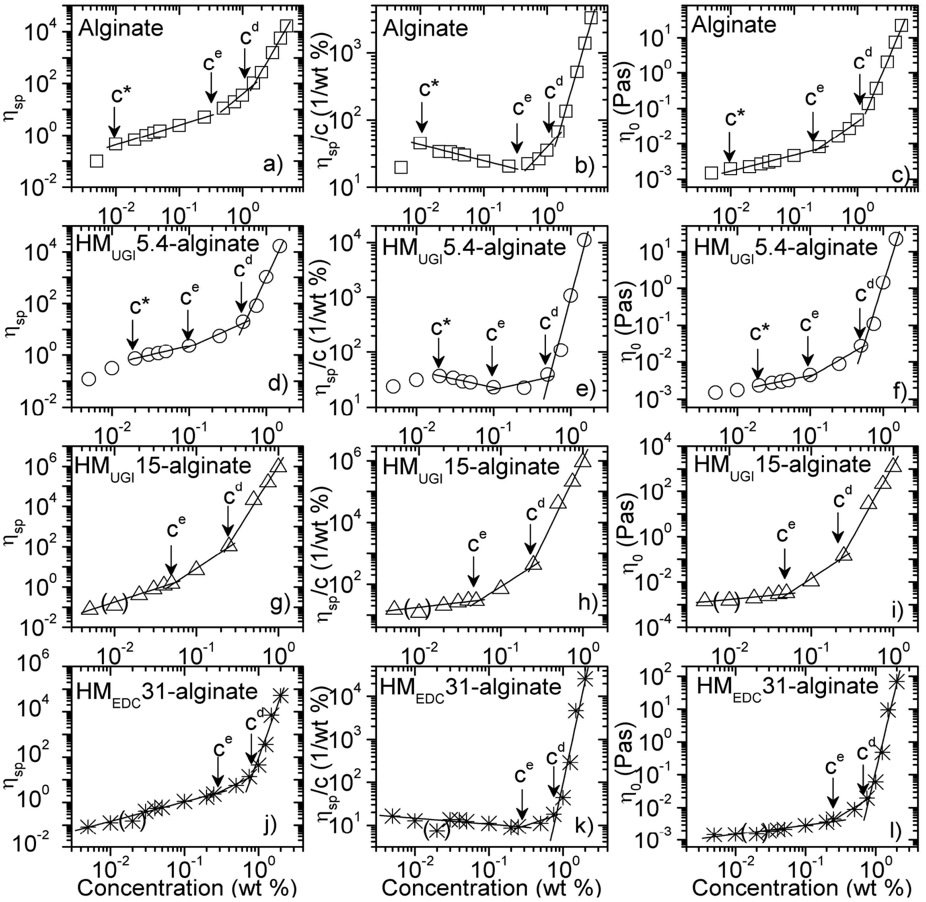

Figure 4. Log-log plot of the specific viscosity, the reduced viscosity, and the zero-shear viscosity as a function of the polymer concentration for the systems indicated. The slopes of the fitted lines are shown in Figure 5.

The $HM_{UGI}15$-alginate (Figure 4g, h, i) exhibits a behavior close to that of polyelectrolytes in the presence of salt in the region $c^* < c < c^e$. The disappearance of the typical polyelectrolyte upturn in the reduced viscosity as the polymer concentration is decreased has also been observed for hydrophobically modified polyelectrolytes previously [28]. The polyelectrolyte effect is usually attributed to the swelling of the polymer coils due to electrostatic repulsion. It seems that when a sufficient amount of hydrophobes is attached to the polymer, the attractive forces between the hydrophobic groups will cause the polymer coils to contract, and the polyelectrolyte effect disappears (Figure 4 h). In this concentration regime the $HM_{UGI}15$-alginate exhibits a power-law behavior of η_{sp} and η_{sp}/c which corresponds to Muthukumars theory for polyelectrolytes at high salt concentrations (Figure 5a and c), indicating that the hydrophobic interactions of this system effectively counteract the electrostatic repulsions.

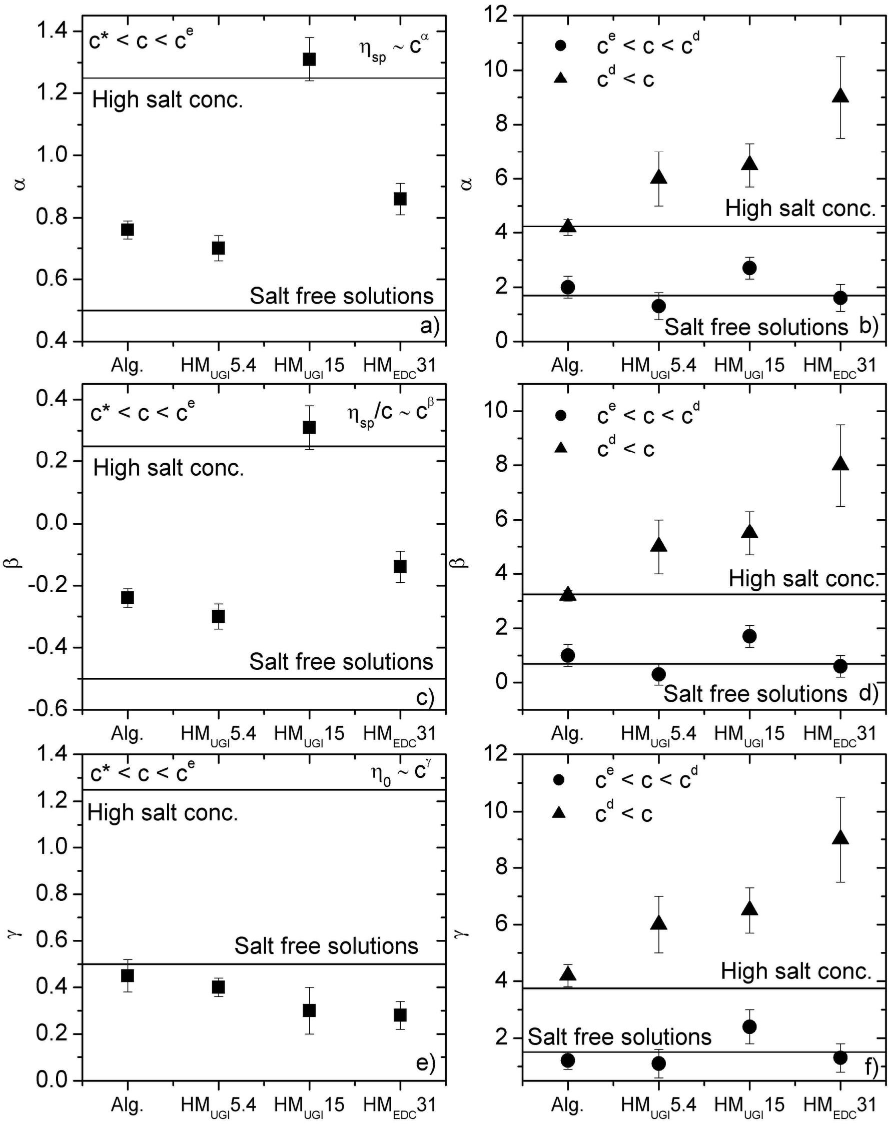

Figure 5. The fitted power-law exponents ($\eta_{sp} \sim c^{\alpha}$, $\eta_{sp}/c \sim c^{\beta}$, $\eta_0 \sim c^{\gamma}$) for the alginate and the hydrophobically modified alginates in the concentration regimes indicated. The upper and lower horizontal solid lines show the theoretical values (Table 1) for solutions with a high salt concentration and solutions without added salt, respectively.

From Figure 5a and c it can be seen that the $HM_{EDC}31$-alginate exhibit values of these scaling parameters in-between the alginate and the $HM_{UGI}15$-alginate. This suggests that the hydrophobic interactions of this polymer partly counteract the repulsive ionic forces, and even though $HM_{EDC}31$-alginate has twice as many hydrophobic groups as $HM_{UGI}15$-alginate, the hydrophobic interaction in this concentration regime is strongest for the $HM_{UGI}15$-alginate. The reason for this might be that the hydrophobicity of each hydrophobic group is stronger in the $HM_{UGI}15$-alginate due to the cyclohexyl group (Figure 1).

Even though the unmodified alginate sample deviates from the theory of Muthukumar in this concentration regime, the scaling of η_0 (Figure 5e) corresponds to the theory of Rubinstein et al. [21,24]. One would expect that the scaling of hydrophobically modified polymers should differ from that of the corresponding unmodified polymer due to the hydrophobic interactions. However, according to the theory of Dobrynin and Rubinstein [25], the concentration dependency of the zero-shear viscosity of hydrophobic polyelectrolyte solutions exhibit the same scaling-laws as is predicted for ordinary polyelectrolytes without stickers [21,24]. From Figure 5e it can be seen that the scaling behavior of the zero-shear viscosity clearly deviates from the theoretical values of Rubinstein et al. [25] for the hydrophobically modified alginates when $c^*<c<c^e$. For unknown reasons, it seems that the power-law exponent decreases with increasing amount of hydrophobic groups added to the polymer.

Scaling in the region $c^e<c<c^d$

In the concentration regime $c^e<c<c^d$ the only sample that deviates from the theoretical values are the $HM_{UGI}15$-alginate (Figure 5b, d, and f). The strong hydrophobic interactions in this sample induce scaling behaviors that lies in-between that of salt free solutions, and samples with high amounts of salt.

Scaling in the region $c^d<c$

Due to the large amount of counter-ions present in the concentration regime $c^d<c$, we would expect the samples to follow the same power-law behavior as polyelectrolytes at high salt concentrations, and this is indeed the case for the unmodified alginate (Figure 5b, d, and f). However, the hydrophobically modified alginates deviate significantly from the theoretical values of Table 1. And can be observed in Figure 5b, d, and f, all the scaling exponents are shifted towards higher values as the amount of hydrophobic groups on the polymer is increased. Since we expect the electrostatic interactions to be screened out in this region, scaling laws for neutral hydrophobic polymers should to be valid. Rubinstein and Semenov [27] predicts $\eta_0 \sim c^{6.8}$ in the regime $c^e<c<c^{ren}$, where c^{ren} is the concentration where the system exhibits a renormalized bond lifetime of the hydrophobic interactions, and $\eta_0 \sim c^{8.5}$ in the range $c^{ren}<c<c^s$, where c^s is the overlap concentration of the strands between stickers (hydrophobic groups). As can be seen from Figure 5f, the scaling exponent for the region $c^e<c<c^{ren}$ correspond to what is observed for $HM_{UGI}5.4$-alginate and $HM_{UGI}15$-alginate, while the $HM_{EDC}31$-alginate seems to be in the $c^{ren}<c<c^s$ regime.

Conclusions

In this work, we have investigated the rheology and turbidity of aqueous solutions of unmodified alginate and three hydrophobically modified alginates. The effects of polymer concentration, hydrophobic group structure and hydrophobic content have been studied. The main results can be summarized in the following way:

1. With the same structure of the hydrophobes, the change in the viscosity and turbidity are more pronounced when the hydrophobic modification ratio is increased.
2. The turbidity data shows that, unlike the unmodified alginate and the $HM_{EDC}31$-alginate, the $HM_{UGI}5.4$-alginate and $HM_{UGI}15$-alginate form large association structures as the concentration is raised.
3. At low polymer concentrations, the hydrophobicity of the $HM_{UGI}15$-alginate counteracts the repulsive polyelectrolyte forces, and the polymer loses its polyelectrolyte character. Even though the $HM_{EDC}31$-alginate has a higher degree of hydrophobic modification, this is only partially the case for this polymer due to the lower hydrophobicity of its hydrophobic groups.
4. The scaling behavior of the viscosity can to a large extent be explained by the different theoretical predictions, but due to the complexity of this system where both hydrophobic interactions and polyelectrolyte effects are important, there are some deviations from the theories.
5. The physicochemical properties of aqueous solutions of water-soluble polymers can be manipulated by introducing different amount of hydrophobic groups with various structures.

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