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Rheological and Structural Characterization of the Interactions between Cyclodextrin Compounds and Hydrophobically Modified Alginate

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Interactions in semidilute solutions of a hydrophobically modified alginate (HM-alginate) in the presence of hydroxypropyl-β-cyclodextrin (HP-β-CD) monomer or a β-cyclodextrin polymer (poly(β-CD)) have been characterized at different temperatures with the aid of rheology and small-angle neutron scattering (SANS). The viscosity results for the HM-alginate/HP-β-CD system reveal progressive deactivation of the hydrophobic associations as the concentration of HP-β-CD increases. For the HM-alginate/poly(β-CD) system, on the other hand, addition of poly(β-CD) sets up bridges between adjacent polymer chains and thereby strengthens the associative network. A novel shear-thickening effect is observed at fairly high shear rates for the HM-alginate/poly(β-CD) system, and this feature is influenced by temperature. Elevated temperature induces higher chain mobility and the formation of weaker network associations. Analyses of the SANS data disclosed that the association strength in HM-alginate/poly(β-CD) mixtures increases strongly with increasing cosolute concentration, whereas no effect or a moderate weakening of the strength can be traced in HM-alginate/HP-β-CD solutions upon addition of HP-β-CD. The value of the correlation length ξ is virtually not affected by the addition of cosolute for the HM-alginate/poly(β-CD) system, whereas the decoupling of hydrophobic moieties of the polymer upon addition of HP-β-CD gives rise to a smaller value of ξ, suggesting that the size of the heterogeneity patches is reduced. The SANS results suggest that compact association structures are formed in the HM-alginate/poly(β-CD) solutions.

Introduction

Interactions between polymers and cyclodextrin derivatives in aqueous solutions have attracted significant interest[1−14] in recent years due to the capacity of cyclodextrin to modulate the physicochemical properties of solutions of especially hydrophobically modified polymers. Cyclodextrins (CDs) are well-known[3,15] in supramolecular chemistry as molecular hosts capable of including, with a degree of selectivity, different guest molecules via noncovalent interactions in their hydrophobic cavities. The importance of host−guest complexes in biological systems motivates the current interest in supramolecular assemblies.[16] Cyclodextrins are cyclic oligosaccharides in the shape of truncated cones consisting of 6, 7, or 8 (α-1,4)-linked α-D-glucopyranose units, named α-, β-, and γ-CD, respectively. The number of units defines the size of the cavity and the flexibility of the compound. The CD structure provides an external hydrophilic region, where primary and secondary OH groups are located, and a rather hydrophobic inner cavity.[17] The most characteristic feature of the CD monomers is the cavity that enables them to form inclusion complexes with guest molecules of appropriate size, shape, and polarity. Previous studies[6,9,11−14] on aqueous solutions of hydrophobically modified polymers in the presence of β-CD monomers have revealed that the β-CD molecules encapsulate the hydrophobic moieties and thereby deactivate hydrophobic associations. Another class of supramolecular assemblies involves polymers of β-CD with a branched structure,[7,10] where the β-CD units are integrated in the skeleton. This β-CD polymer has a fairly high molecular weight, and it is expected in solutions of a hydrophobically modified polymer to form bridges between polymer chains with pendent hydrophobic tails and thereby, in contrast to the β-CD monomers, strengthen the intermolecular associations in the system.

In the present work, we have conducted rheological and small-angle neutron scattering (SANS) experiments on solutions of alginate and its hydrophobically modified analogue (HM-alginate) in the presence of the monomer hydroxypropyl-β-cyclodextrin (HP-β-CD) or a β-cyclodextrin polymer (poly(β-CD)). The principal aim of this study is to gain insight into the structural and dynamical differences of complexes formed between the hydrophobically modified polymer and HP-β-CD or with poly(β-CD). This investigation will disclose some novel rheological and structural features, for instance, the intriguing rheological behavior of the complexes formed between HM-alginate and the poly(β-CD) compound at different temperatures. Schematic illustrations of the structures of HM-alginate, HP-β-CD, and poly(β-CD) are displayed in Figure 1.

To the best of our knowledge, a systematic rheological and structural examination of the influences of cosolute addition and temperature on the effects of HP-β-CD deactivation of hydrophobic tails and poly(β-CD)-induced chain bridging of chains through poly(β-CD) have not been reported before. This will

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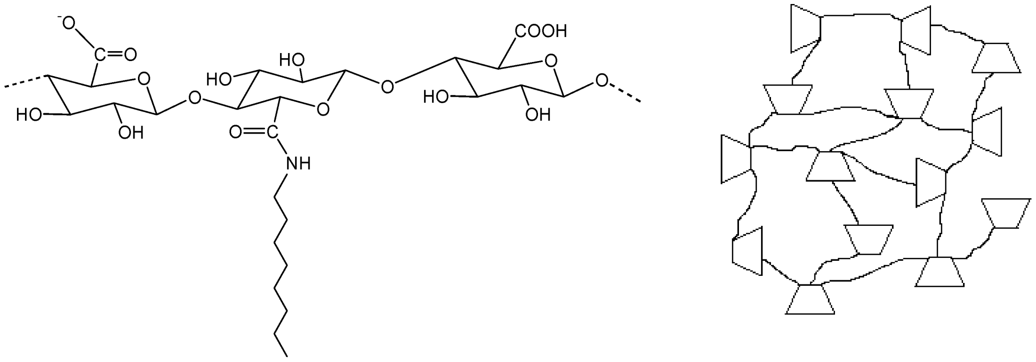
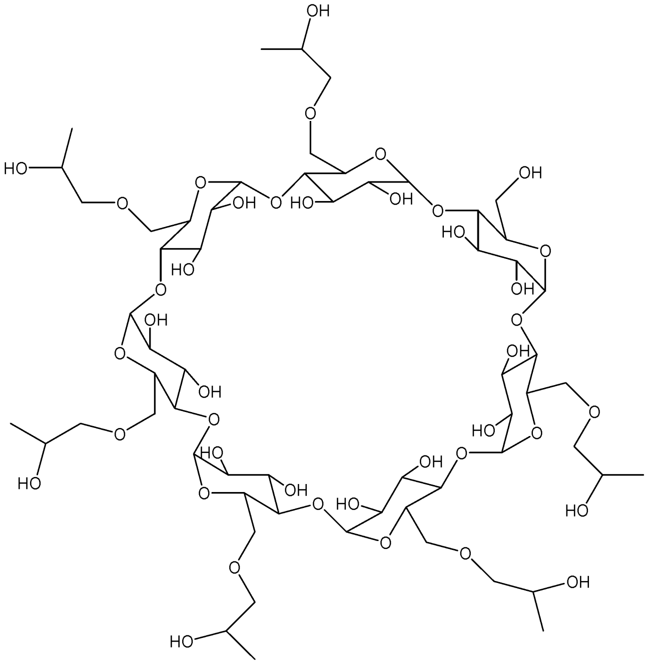


HM-alginate

Poly(β-cyclodextrin)



Hydroxypropyl-β-cyclodextrin

Figure 1. Schematic structures of HM-alginate, poly(β-CD), and HP-β-CD. The length of the hydrophobic tails in HM-alginate is about 7 Å. The value of R_g for poly(β-CD) is approximately 55 Å. The cavity of HP-β-CD has an inner diameter of ca. 7 Å and a depth of approximately 8 Å.

provide us with new information about how to modulate the association strength in systems with a hydrophobically modified polymer and cyclodextrin compounds.

Experimental Section

Materials and Solution Preparation. The alginate sample utilized in this work is designated LF 10/60 and was supplied by FMC Biopolymers, Drammen, Norway. 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 (G/M) ratio is 0.75. The pK_a values of G and M have been determined to be 3.7 and 3.4, respectively.[18] 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 the dialyzing membrane. By this procedure, the brownish-yellow color of the solutions disappeared.

The hydrophobically modified analogue, with attached C8 groups, was synthesized from the parent alginate sample by a method where the coupling agent 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride (EDC−HCl) was used to form amide linkages between amine-containing molecules and the carboxylate moieties on the alginate polymer backbone. This procedure has been described elsewhere,[19,20] and the characteristic data of this hydrophobically modified sample have been reported recently.[14] By using quantitative ^{1}H NMR spectroscopy and elemental analysis, the HM-alginate sample was found to contain 31 mol % of C8 groups.

Hydroxypropyl β-cyclodextrin (HP-β-CD) is a derivative of β-CD that has been modified by 5−6 hydroxypropyl chains, on average, and has been purchased from Aldrich (France). The polymer of β-cyclodextrin (poly(β-CD)), was synthesized by polycondensation with epichlorohydrin. Details of its synthesis[21,22] and structural characterization[10] are described elsewhere. The polymer exhibits a branched architecture in which β-CD molecules are modified by poly(2-hydroxypropyl)ether sequences of different lengths, possessing a free end or acting as a bridge between several CDs. The conformation of the copolymer can be quite compact because of its branched structure, which is illustrated schematically in Figure 1. The sample employed in this work is easily soluble in water, and its molecular weight has been measured by size exclusion chromatography coupled with a light-scattering detector; its weight-average molecular weight is M_w = 160 000, and its polydispersity index M_w/M_n = 1.9. Its radius of gyration has been measured by SANS[10] and is R_g = 55 Å. Its β-CD content, determined by ^{1}H NMR with a Bruker 200 MHz spectrometer, is 59 wt %.

All solutions were prepared by weighing the components, and the samples were dissolved in light (rheology measurements) or heavy (SANS experiments) water, followed by stirring for a few days to allow the solutions to homogenize.

Rheology. The steady shear viscosity experiments were carried out in 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 geometry was employed in all measurements. 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 value of the viscosity is practically not affected by this layer). The measuring device is equipped with a temperature unit (Peltier plate) that gives an effective temperature control (±0.05 °C) over an extended time for the temperatures considered in this work. The shear viscosity measurements were conducted over a wide shear rate range.

Small-Angle Neutron Scattering (SANS). The main SANS experiments were carried out using the KWS-1 and KWS-2 instruments at the research reactor FRJ-2 at the Forschungszentrum Jülich GmbH, Germany. The in situ rheo-SANS measurements were performed on the KWS-2 instrument by placing a commercial Rheowis-Fluid rheometer (LabPlus, Switzerland) directly in the beam, and the scattered SANS intensity was monitored continuously. This rheometer is strain controlled and was operated using Couette geometry where the outer cylinder is rotating. The gap between the outer and inner cylinders was 0.5 mm, giving a total path length for the neutrons of 1 mm. The shear cell is constructed of single-crystal sapphire material of which the transmission for neutrons is high, $T_{ec} \approx 0.8$. The applied constant shear rates were 2, 10, and 50 s^{-1}.

The measurements were conducted at three instrumental setups with sample-to-detector distances (L) equal to 2, 8, and 20 m. The collimation was chosen to be equal to L, except at 2 m where 4 m collimation was employed to reduce dead-time effects and to improve the resolution. The neutron wavelengths were $\lambda = 7$ and 6 Å with corresponding (fwhm) spreads of $\Delta\lambda/\lambda \cong 0.2$ and 0.1 at KWS-1 and KWS-2, respectively. The resulting scattering vector, $\mathbf{q}$, covered the approximate range $2 \times 10^{-3} \leq \mathbf{q} \leq 0.2$ Å^{-1}. The scattering vector $\mathbf{q}$ is given by $\mathbf{q} = (4\pi/\lambda)\sin(\theta/2)$, where θ is the scattering angle.

The raw data were corrected two-dimensionally for the empty cell scattering and background. The background scattering, primarily resulting from electronic noise, γ radiation, and fast-unmoderated neutrons, was measured using a Boron carbide sample to block the primary beam. Corrections for the spatial detector efficiency and sensitivity were made with a Plexiglas that also serves as a secondary standard for absolute calibration. The measured intensities were normalized to the monitor count rate of the incident intensity to take into account temporal variations of the output power provided by the reactor. The absolute value of the scattering cross section was determined by calibration against vanadium, and dead-time effects arising from saturation of the detector at high count rates were compensated for. After a radial average of the two-dimensional data, the measured scattering from the solvent was appropriately subtracted to obtain the coherent macroscopic scattering cross section of the system, $d\Sigma/d\Omega$ ($\mathbf{q}$), which is directly proportional to the scattered intensity $I(\mathbf{q})$.

All the samples were investigated in 2 mm Hellma quartz cells. They were prepared using pure D_2O as a solvent to minimize incoherent scattering and to maximize the scattering contrast between the solvent (with scattering length density $\rho_{D_2O} = 6.41 \cdot 10^{10}$ cm^{-2}) and the two polymers ($\rho_{HM-alginate} = 1.46 \cdot 10^{10}$ cm^{-2}; $\rho_{poly(\beta-CD)} = 2.29 \cdot 10^{10}$ cm^{-2}). Transmission values were determined in situ by a neutron monitor at $\mathbf{q} = 0$. Values were in the range between 70% and 90% depending on the concentration and conditions.

Results and Discussion

Rheological Properties. Figure 2 shows plots of the relative viscosity η_{rel} ($\eta_{rel} \equiv \eta/\eta_{water}$, with η_{water} the solvent viscosity) at 25 °C versus shear rate for HM-alginate solutions of different concentrations in the presence of various amounts of HP-β-CD monomers. All the polymer concentrations are located in the semidilute regime. At the lowest polymer concentration, the number of hydrophobic moieties is low, and the strength of the hydrophobic interactions is weak; hence, the effect of HP-β-CD addition on the relative viscosity is insignificant. As the polymer concentration increases, the effect of HP-β-CD addition becomes gradually more prominent. At the lower two polymer concentrations, the viscosity is only monitored down to a shear rate of about 1 s^{-1}, because the viscosity response is too weak at lower shear rates to produce reliable data. The progressive reduction of the viscosity at a given polymer concentration as the amount of HP-β-CD monomer rises can be ascribed to the inclusion of the hydrophobic tails, and thereby, the hydrophobic associations are inhibited.[13,14] The most pronounced shear-thinning effect is observed for the highest HM-alginate concentration without HP-β-CD, i.e., the system that exhibits the strongest association network and viscosity enhancement. The progressive decrease in viscosity as the shear rate rises indicates that the intermolecular junctions are disrupted at a rate faster than their rate of reformation, resulting in a decrease in the junction density and hence a drop in the viscosity.

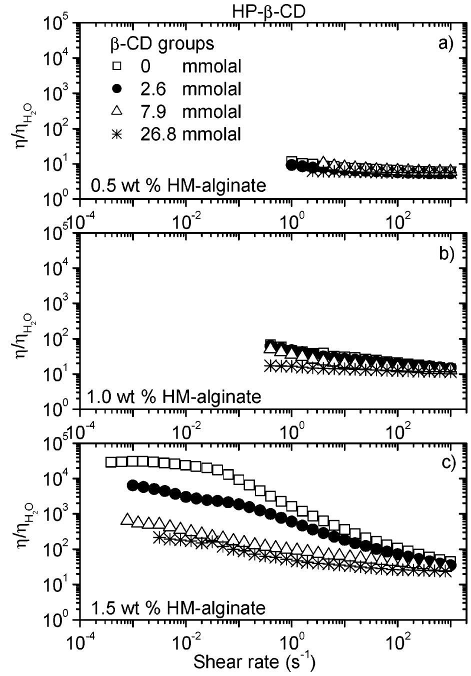


Figure 2. Comparison of shear rate dependence of the relative viscosity for HM-alginate solutions of different concentration in the presence of various amounts of HP-β-CD (every second point is shown).

Effects of HP-β-CD concentration on the relative zero-shear viscosity η_0/η_{water} in alginate and HM-alginate solutions of different polymer concentrations are illustrated in Figure 3. The values of η_0/η_{water} for the alginate solutions are not affected by the level of HP-β-CD addition, which signals that the interaction between alginate and HP-β-CD is weak. However, in the case of solutions of HM-alginate, we note that, for the highest polymer concentration, the decrease of η_0/η_{water} with increasing concentration of HP-β-CD is more than 2 orders of magnitude and the value of η_0/η_{water} approaches that of alginate. This finding implies that the hydrophobic stickers are gradually encapsulated and deactivated as the number of HP-β-CD molecules increases. An interesting result is observed for the lower two polymer concentrations, where the values of $\eta_{0,rel}$

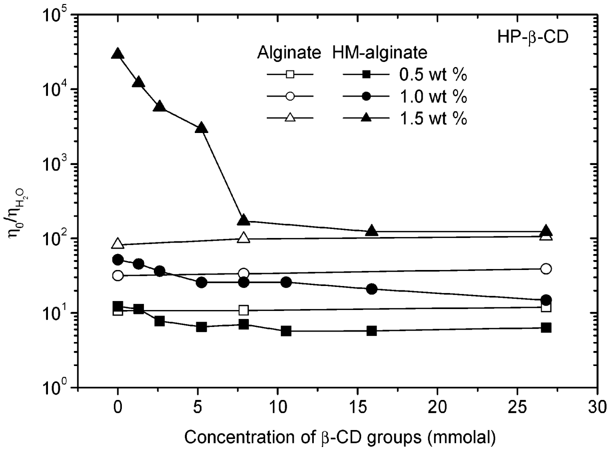


Figure 3. Effects of HP-β-CD addition on the relative zero-shear viscosity in alginate and HM-alginate solutions for the polymer concentrations indicated.

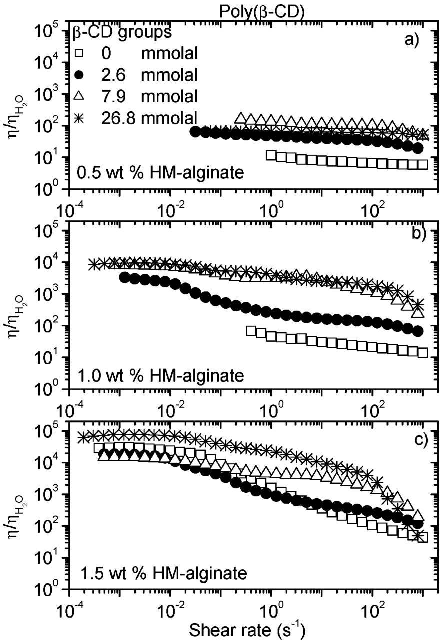


Figure 4. Effects of poly(β-CD) addition on the shear-rate dependence of the relative viscosity for HM-alginate solutions of different concentrations (every second point is shown).

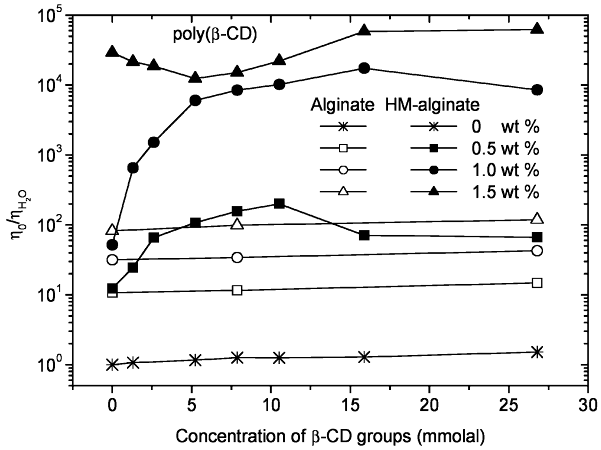


Figure 5. Comparison of the effects of poly(β-CD) addition on the relative zero-shear viscosity in solutions of alginate and HM-alginate of different concentrations. The concentration dependence of the relative zero-shear viscosity for poly(β-CD) in water is also included (*).

for the HM-alginate system at higher levels of HP-β-CD are considerably lower than the corresponding ones for the unmodified alginate. The onset of this effect occurs at a lower HP-β-CD concentration for the 0.5 wt % HM-alginate solution. This behavior can probably be rationalized in the following way. When the amount of HP-β-CD rises, the hydrophobic associations are decoupled, but because of the gradual complexation with HP-β-CD, the structure and flexibility of the polymer chains will be changed. This may lead to a loss of the connectivity in the network and the formation of a more fragmented network with a lower viscosity. For a lower HM-alginate concentration, this stage occurs at a lower level of HP-β-CD addition, because the number of hydrophobic stickers is small and only a little amount of the cosolute is needed to deactivate them. In the solution with the highest HM-alginate concentration, the entanglements play an important role, and the network will not disintegrate when the hydrophobic tails are decoupled.

The shear-rate dependencies of the relative viscosity for the same concentrations of HM-alginate and β-CD groups (as in Figure 2) in poly(β-CD) are depicted in Figure 4. In this case, a different situation appears where the CD polymer sets up bridges between adjacent HM-alginate chains, and thereby reinforces the network structure. This is reflected in the increase of η_{rel} with the β-CD concentration (up to 7.9 mmolal) observed in Figure 4a,b. However, when the stoichiometric balance between the hydrophobic moieties and the β-CD groups is approached, the rise of the viscosity is arrested, or it may even decrease. For the highest HM-alginate concentration, a more intriguing picture emerges that will be discussed below.

Figure 5 shows the effect of poly(β-CD) addition on the relative zero-shear viscosity at different polymer concentrations for the alginate and HM-alginate systems indicated. Despite that the molecular weight (M_w = 160 000) of poly(β-CD) is fairly high, the branched structure yields compact molecules with a low viscosity that changes very little with the concentration of poly(β-CD). This cosolute interacts weakly with alginate and has a very small effect on the viscosity of the alginate solutions. For the lower two HM-alginate concentrations (0.5 and 1.0 wt %), addition of poly(β-CD) results in strong viscosity enhancements that can be attributed to the formation of interpolymer bridges, which strengthen the network structure. This strengthening of the network continues until the hydrophobic sites in the network have been occupied by β-CD groups of the CD polymer. At higher levels of poly(β-CD) addition, the surplus of β-CD groups will lead to a situation where some of the hydrophobic stickers are encapsulated by poly(β-CD) molecules without forming interpolymer bridges. This process leads to lower values of η_0/η_{water}. For the highest concentration of HM-alginate, a fundamentally different pattern of behavior is observed. Initially, η_0/η_{water} falls off with increasing poly(β-CD) concentration, whereas at higher levels of poly(β-CD), the viscosity rises. This finding can probably be rationalized in the following scenario. At a high HM-alginate concentration, a "tight" and strongly entangled network is developed, and the probability for the poly(β-CD) species to find suitable hydrophobic sites on the polymer to establish more interpolymer connections is low. Instead, the poly(β-CD) entities act as the CD monomers and decouple some hydrophobic associations. As this kinetic process continues and the concentration of poly(β-CD) increases, this reduced degree of association gradually leads to more "open" network architecture, and more hydrophobic tails become available for coupling with poly(β-CD) molecules to form interpolymer bridges. This behavior gives

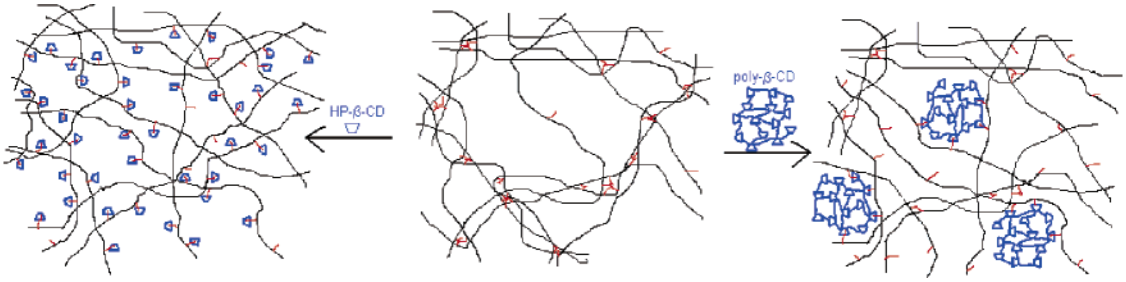


Figure 6. Schematic illustration of the effects of HP-β-CD or poly(β-CD) addition to semidilute solutions of HM-alginate.

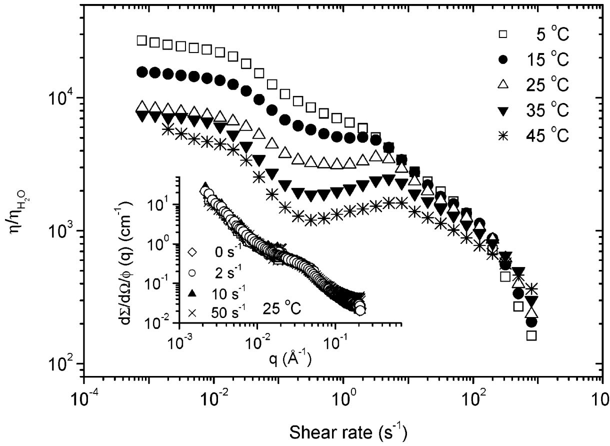


Figure 7. Effects of temperature on the shear-rate dependence of the relative viscosity for a 1 wt % solution of HM-alginate in the presence of poly(β-CD) (7.9 mmolal β-CD groups) (every second point is shown). The inset shows SANS scattered intensity data from in situ measurements on the same system at the continuous shear rates and temperature indicated.

rise to an augmented viscosity of the solution at higher levels of poly(β-CD) addition.

A schematic illustration of the effects of HP-β-CD and poly(β-CD) addition to semidilute solutions of HM-alginate on the formation of associative networks is depicted in Figure 6. We recall that addition of HP-β-CD leads to inclusion complexation and deactivation of the hydrophobic stickers, which will suppress the intensity of the hydrophobic associations, thereby promoting lower viscosity values. The presence of poly(β-CD) in HM-alginate solutions of moderate concentration will evoke a situation where different polymer chains are connected by poly(β-CD) bridges via their hydrophobic moieties. This leads to strengthening of the network and gives rise to the observed viscosity enhancement. At still higher cosolute concentration, when there is a surplus of poly(β-CD) molecules, the competition between interpolymer connections and deactivation of hydrophobic sites gives rise to some debridging and reduced viscosity of the system. At higher concentration of HM-alginate and low amounts of poly(β-CD), the viscosity results indicate that the network grows weaker because the compact architecture of the network prevents the formation of interpolymer bridges. Instead, the poly(β-CD) molecules act as cyclodextrin monomers by decoupling hydrophobic associations. At higher levels of poly(β-CD) addition, the reorganization of the network structure permits the arrangement of bridges.

Effects of shear rate and temperature on the relative viscosity for a HM-alginate solution (1 wt %) in the presence of poly(β-CD) (7.9 mmolal) are illustrated in Figure 7. The most conspicuous feature is the profiles of the viscosity curves with shear thinning at low shear rates, followed by shear thickening behavior at moderate shear rates and shear thinning at high shear rates. This can probably be explained within the following framework. When shear forces are applied, some intermolecular interactions are initially disrupted (shear thinning at low shear rates), and at higher shear rates, the alignment and stretching of the HM-alginate chains may lead to more hydrophobic sites on the chains becoming available in the formation of interpolymer bridges at moderate shear rates. At still higher shear rates, the network association is broken up, and the viscosity declines.

We note that, at low shear rates, the value of the relative viscosity drops as the temperature is increased. The conjecture is that the enhanced thermal mobility of the HM-alginate chains at elevated temperature restrains the evolution of interpolymer bridges. A closer inspection of the viscosity curves reveals that the maximum of the curve is shifted toward higher values of the shear rate with increasing temperature, and the maximum becomes more pronounced. The reason for this behavior may be that the temperature-induced augmented motions of the polymer chains and cosolute molecules are favorable for the shear-induced orientation and extension of the chains in the bridging process. It should be mentioned that this type of viscosity behavior is also detected for the highest HM-alginate concentration (1.5 wt %), whereas for the lowest polymer concentration (0.5 wt %), no sign of this feature has been found.

To investigate whether the viscosity changes are accompanied by structural alterations, in situ SANS rheological results at various shear rates, representing different stages on the viscosity curve, on the same system at 25 °C are displayed in the inset plot of Figure 7. All the SANS curves collapse onto a single curve, suggesting that on the mesoscopic dimensional scale probed in these SANS experiments no structural differences are unveiled at different shear rates. This suggests that no restructuring of the network occurs on the mesoscopic length scale. This result does not exclude the occurrence of structural alterations on a global dimensional scale. However, the interpolymer bridging of the HM-alginate/poly(β-CD) system is not observed at any of the studied compositions to affect the turbidity of the system. The tendency for a macroscopic phase separation is probably suppressed by repulsive electrostatic forces.

In Figure 8, effects of temperature on the relative zero-shear viscosity for solutions of HM-alginate of different concentrations in the presence of HP-β-CD or poly(β-CD) (all the samples contain 7.9 mmolal β-CD groups) are depicted. Virtually no temperature effect on $\eta_0/\eta_{\text{water}}$ is observed in the HM-alginate solutions with HP-β-CD. This is in contrast to the strong temperature dependence of the viscosity that was reported[13] for the same polymer in the presence of the β-CD monomer, which forms crystallites at low temperatures. These aggregates are not capable of deactivating the hydrophobic tails of the polymer, whereas in the case of HP-β-CD, this is not a problem, because this compound does not crystallize at falling temperature. In the presence of poly(β-CD), a fairly strong temperature effect is found at all HM-alginate concentrations. The weakening of the networks at elevated temperatures is ascribed to augmented

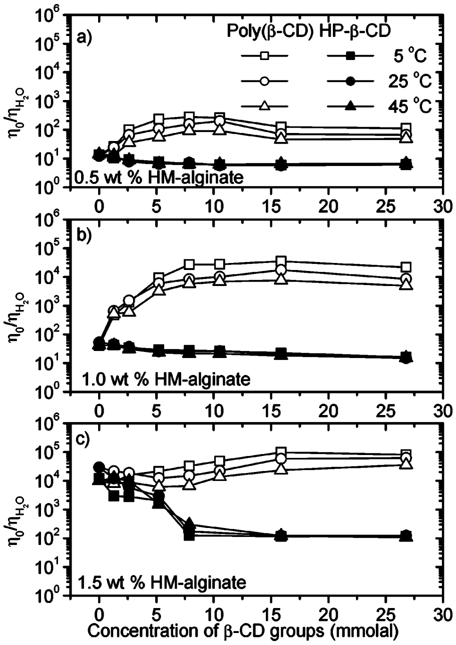


Figure 8. Effects of temperature and addition of cosolute (HP-β-CD or poly(β-CD)) on the relative zero-shear viscosity for HM-alginate solutions of different concentrations.

thermal mobility of the HM-alginate chains and the poly(β-CD) species, which reduces the tendency to form interpolymer bridges.

SANS Results. SANS experiments provide information about the structure of the system on a mesoscopic length scale. We found that the **q**-dependence of the scattered intensity over a wide **q** range could be well-described by the following functional form suggested by Hammouda et al.[23,24]

$$I(\mathbf{q}) = \frac{A}{\mathbf{q}^n} + \frac{B}{1 + (q\xi)^m} \tag{1}$$

where the first term describes Porod-like scattering from large clusters, and the second term is a Lorentzian type of function used to portray scattering from polymer chains in the intermediate and high-**q** regime. In the fitting of SANS data, the two factors A and B, the exponents n and m, and the quantity ξ are used as fitting parameters. The variable ξ denotes the correlation length for the polymer chains. In this model, the clustering strength can be characterized by the quantity $A/\mathbf{q}^n$. This model constitutes an attractive approach to analyzing the clustering effect in solutions of associating polymers over an extended q region. We are not aware of other models where the upturn of the scattered intensity at low **q** values and the behavior at higher **q** values are described well for this type of system.

Figure 9 shows the variation of the SANS scattering intensity as a function of **q**, together with the curves fitted with the aid of eq 1, for a solution of poly(β-CD) (1.8 wt % β-CD groups) and 1 wt % HM-alginate solutions without and with the addition of poly(β-CD) or HP-β-CD with the same amount (15.9 mmolal) of β-CD groups. In this case, the SANS measurements have been conducted at a stoichiometric ratio corresponding to one CD cavity for one alkyl C8 in the mixture. The experimental SANS data are well-fitted by eq 1, which is illustrated by a typical residual plot (see the inset) where small values and nonsystematic trends of the residuals are observed. It is merely for the poly(β-CD)/D_2O system (data from a previous SANS study[10] at Saclay, France, are displayed) that the linear Guinier region is observed, whereas for the other systems, only the tail of the low-**q** domain is seen in the spectrum. The data for the HM-alginate/poly(β-CD)/D_2O system exhibits an upturn in the small **q** range and higher values of the scattered intensity than for the HM-alginate/D_2O solution are detected. These features corroborate with the rheological results, suggesting that the interactions between HM-alginate and poly(β-CD) are strong. The scattered intensities in the low **q** domain for the HM-alginate/D_2O and HM-alginate/HP-β-CD/D_2O systems are almost coincident, indicating that the large-scale structures for this HM-alginate concentration are not significantly affected by the deactivation of the hydrophobic stickers.

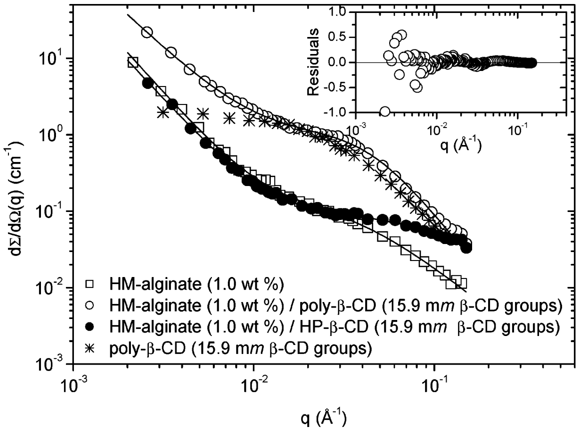


Figure 9. SANS intensity data (every fourth point is shown) plotted vs the scattering vector **q** for the systems indicated. The data (from Saclay, France) for the poly(β-CD)/D_2O system have been taken from ref 10. The solid curves have been fitted with the aid of eq 1. The inset shows a residual plot for the system indicated.

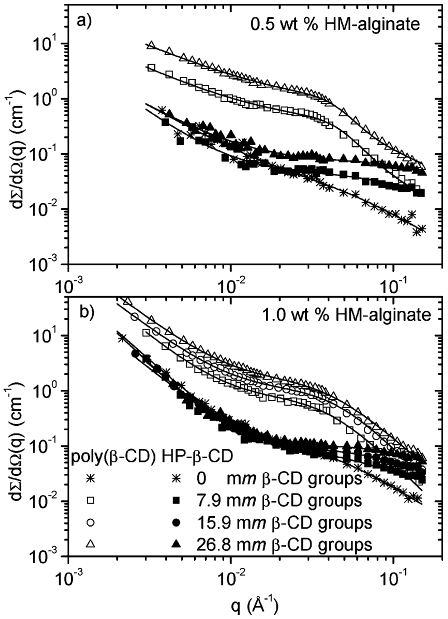


Figure 10. SANS scattered intensity (every fourth data point is shown) plotted vs the scattering vector **q** for the HM-alginate/HP-β-CD/D_2O (solid symbols) and HM-alginate/poly(β-CD)/D_2O (open symbols) systems at the conditions indicated. The curves are fitted by means of eq 1.

In Figure 10, the scattering profiles for different concentrations of HM-alginate without and in the presence of various concentrations of HP-β-CD or poly(β-CD) are depicted. An inspection of the SANS data for the HM-alginate solutions with different amounts of HP-β-CD reveals that the data points virtually collapse onto each other in the low **q** region, whereas a clear separation of the curves occurs at higher **q** values. This

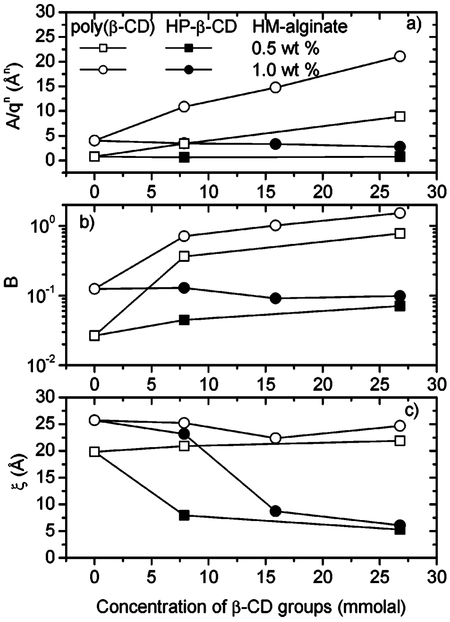


Figure 11. Effects of concentration of β-CD groups on the parameters determined from fits of the experimental SANS data for the HM-alginate/HP-β-CD/D$_2$O and HM-alginate/poly(β-CD)/D$_2$O systems with eq 1.

suggests that the addition of HP-β-CD to HM-alginate solutions has little impact on the large-scale structures, whereas changes on a more local length scale take place. The rather large scatter in the data at low **q** values for the samples with a low HM-alginate concentration is due to the weak signal at these conditions. In the case of the HM-alginate/poly(β-CD) systems, the profiles of the scattering curves are almost the same, but they are shifted toward higher values as the concentration of poly(β-CD) increases. The shift is approximately proportional to the change in the poly(β-CD) concentration. SANS measurements on these systems were also conducted at different temperatures, but no significant temperature effect could be traced.

Figure 11 summarizes the values and trends of the parameters obtained from the fitting of all the SANS data with the aid of eq 1. The quantity $A/\mathbf{q}^n$ characterizes the strength[24] of the associations at low **q** values and is depicted in Figure 11a at a fixed **q** value (0.003 Å^{-1}) for the systems indicated. The value of $A/\mathbf{q}^n$ is virtually constant or decreases slightly as HP-β-CD is added to the HM-alginate solutions, whereas in the presence of poly(β-CD), the value of $A/\mathbf{q}^n$ rises strongly with increasing poly(β-CD) concentration. These findings can be rationalized in the following way. The deactivation of hydrophobic interactions at the low HM-alginate concentration has practically no effect on the association strength parameter, whereas the moderate decrease of $A/\mathbf{q}^n$ at the higher HM-alginate concentration probably reflects decoupling of hydrophobic associations. In the case of poly(β-CD) addition, the interpolymer bridging process yields a strong association network, and this effect is intensified as the HM-alginate concentration increases (more stickers available for interpolymer bridging). The interpolymer coupling of chains is expected to give rise to an augmented clustering strength. The behaviors for both the HM-alginate/HP-β-CD and HM-alginate/poly(β-CD) systems are consistent with the reported rheological features for these samples (cf. Figures 3 and 5).

Parameter *B* (see Figure 11b) exhibits a modest change for the HM-alginate/HP-β-CD mixtures with increasing concentration of HP-β-CD, whereas the addition of poly(β-CD) to the HM-alginate solutions gives rise to a conspicuous increase of the variable *B*. This rise in the value of *B* may reflect enhanced composition fluctuations[24] in the samples because of the bridging process and the growth of clusters. Our conjecture is that the deactivation of hydrophobic interactions in the HM-alginate/HP-β-CD solutions has less repercussion on the concentration fluctuations than the interpolymer bridging of adjacent chains.

The variations of the correlation length ξ for the systems are illustrated in Figure 11c. The results for the HM-alginate/poly(β-CD) samples announce that the value of ξ is not significantly affected by the formation of bridges. The pronounced drop of the value of ξ for the HM-alginate/HP-β-CD solutions can probably be ascribed to the decoupling of hydrophobic interactions. In light of this behavior, the parameter ξ may reflect the size of semilocal heterogeneities in the sample induced by hydrophobic associations. When the hydrophobic tails are deactivated, the size of the heterogeneity patches should decrease.

Concerning the value of the parameter *m* that describes the **q** dependence of the scattered intensity in the highest **q**-range, care should be exercised in the interpretation, due to the low intensity level and high sensitivity to any effects (e.g. incoherent background) not fully compensated for. Using the system where the data quality is highest, HM-alginate(1.0%)/poly(β-CD), *m* values are found to be in the range 2.52−2.60, which is close to that obtained for poly(β-CD) alone (2.62). The latter value is significantly higher than expected (2) for an ideal chain, and this reflects the more compact branched structure[10] of the poly(β-CD) chains. Although not conclusive, this is an indication that the interaction between these two polymers does not affect much the inner structure of the poly(β-CD) chains, supporting a picture like that shown in Figure 6. Considering the size of the alginate chain (152 000 g/mol), it is reasonable to assume that one chain of HM-alginate may connect to several chains of poly(β-CD).

Conclusions

In this work, we have examined the effects of HP-β-CD and poly(β-CD) addition and temperature on the rheological and structure behaviors of semidilute solutions of alginate and a hydrophobically modified analogue (HM-alginate). No interaction effect is found between alginate and neither of the cosolutes. Addition of the HP-β-CD monomer in solutions of HM-alginate encapsulates the hydrophobic moieties and thereby deactivates the hydrophobic interactions. As a result, the viscosities of the HM-alginate solutions fall off as the concentration of HP-β-CD increases. For low polymer concentrations in the semidilute regime, decoupling of hydrophobic associations can lead to a fragmented network and values of the viscosity lower than those for the corresponding alginate solutions.

Addition of the branched β-CD polymer to the HM-alginate solutions gives rise to more intriguing features. In this case, the strength of the network is enhanced because of the establishment of bridges, mediated through poly(β-CD) species, between adjacent polymer chains, and the viscosity rises until a stoichiometric balance is reached between the β-CD units of poly(β-CD) and the hydrophobic sites on HM-alginate. However, when the HM-alginate concentration is sufficiently high (1.5 wt %), a different scenario emerges. In this case, an entangled and tight network evolves with architecture that makes it difficult (steric hindrance) to accommodate the poly(β-CD) entities in such a way that interpolymer bridges are formed. Instead, the poly(β-CD) molecules act as the monomer and decouple some hydrophobic associations, which gradually leads to a situation where interpolymer bridges can be formed and the viscosity increases.

The shear-rate dependence of the viscosity for HM-alginate/poly(β-CD) mixtures at different temperatures disclosed shear thinning and shear thickening behavior at unusually high shear rates. This attribute is ascribed to stretching and alignment of the polymer chains. However, rheo-SANS experiments at specific shear rates did not reveal any shear-rate-induced structural changes of the system on a mesoscopic scale. The viscosities of HM-alginate/poly(β-CD) solutions drop with increasing temperature, whereas no temperature effect can be detected for the HM-alginate/HP-β-CD system. This suggests that the thermal mobility of the polymer chains and the poly(β-CD) molecules reduces the ability of the system to generate interpolymer bridges.

The SANS results for all the systems (HM-alginate solutions of 0.5 and 1 wt % were considered here) were analyzed and could be well-described by a model proposed by Hammouda et al. In the framework of this approach, it was shown that the association strength of the complexes evolved in HM-alginate/poly(β-CD) mixtures increased strongly with increasing cosolute concentration, whereas no effect or a moderate weakening of the strength can be traced in HM-alginate/HP-β-CD solutions upon addition of HP-β-CD. This supports the rheological finding that the interpolymer bridges reinforce the network. The correlation length ξ for the polymer chains is virtually not affected by the addition of cosolute for the HM-alginate/poly(β-CD) solutions, whereas the deactivation of hydrophobic tails upon addition of HP-β-CD gives rise to reduction of the size of the heterogeneity patches. In this investigation, we have divulged several novel and fundamental structural and rheological differences between the HM-alginate/HP-β-CD and HM-alginate/poly(β-CD) systems.

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