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ORIGINAL CONTRIBUTION

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The adsorption of hydrophobically modified carboxymethylcellulose on a hydrophobic solid: effects of pH and ionic strength

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Abstract Carboxymethylcellulose with 1.2% dodecyl groups (per glucose unit) was prepared by amidation with dodecylamine. This polymer behaves as a hydrophobically modified polyelectrolyte with the following thickening properties which are determined from viscosity data. It adsorbs from aqueous solution on spin-coated polystyrene films to various extents, depending on pH and ionic strength. The adsorbed amount has a surprising minimum at around pH 6 which coincides with a maximum in viscosity of a dilute solution, and with a very pronounced maximum in the hydrodynamic radius as determined from dynamic light scattering. To our knowledge, such behavior has not been reported before. It suggests that at low pH the polymer is present in the form of small aggregates which upon increasing the pH first swell and then break up into single molecules.

Key words Adsorption – polymer – carboxymethyl cellulose – hydrophobic – polyelectrolyte

Introduction

A hydrophobically modified water-soluble polymer (HMP) consists of a hydrophilic polymer chain which carries a small number of alkyl chains. These alkyl groups tend to associate in aqueous solution, thus forming reversible intra- and intermolecular bonds. At (very) low concentrations, intramolecular association is the dominating effect, and the molecules adopt compact conformations. At higher concentrations, intermolecular association leads to a network held together by reversible crosslinks, and very viscous solutions or weak gels result. The behavior can be seen as a combination of that of simple surfactants and that of polymers, which is the reason why HMPs have sometimes been called "polysoaps" [1]. The intra- and intermolecular association have recently been considered theoretically [1].

HMPs find extensive application as thickeners of aqueous solutions. Not surprisingly, numerous studies have dealt with the rheology of HMP solutions, as well as the influence of added surfactants thereon. It has been found that surfactants (in particular when these have opposite charge) tend to assist the network formation as long as their concentration is well below the cmc, but this effect disappears altogether when the cmc is reached [2]. Quite some work has been devoted to developing methods for synthesising HMPs with better control over the content and distribution of the hydrophobic moieties [3–5].

An interesting subclass of HMPs is that of hydrophobically modified polyelectrolytes (HMPEs). As HMPs these substances display associative behavior, but electrostatic repulsion between the polymer backbones tends to counteract this. As a result, the thickening behavior depends, in addition to other factors, also on pH and ionic strength. The interaction with surfactants of the same [6] or opposite charge [6–8] has been studied. Some naturally occurring polymers, for example humic acids, may be classified as HMPEs [9].

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By virtue of their alkyl groups, HMPs are surface-active. This makes them suitable as stabilizers of aqueous dispersions, emulsions, and foams. Systematic studies of the adsorption of HMPs are relatively scarce, though. Some work has been done on the adsorption of uncharged HMPs. For example, Tanaka et al. studied commercial thickeners like HM hydroxyethylcellulose on polystyrene latex [10]. Remarkably high adsorptions were measured in pure water (up to 6 mg/m^2) whereas the adsorption was reduced (although not entirely suppressed) by surfactants.

Even less is known about the adsorption of HMPEs. Over the last two decades, the adsorption of simple polyelectrolytes has been investigated in some detail and theoretical models have been developed [11, 12]. Some of the insights obtained may be applicable to HMPE adsorption, but an empirical basis for checking whether this is the case is almost entirely lacking. We therefore decided to make a modest start by investigating the role of electrostatic interactions in the adsorption of a cellulose-based HMPE on a hydrophobic substrate. As the hydrophobic substrate we chose polystyrene, spin-coated onto silicon wafers. On this substrate, CMC does not adsorb when it is fully dissociated, i.e., at pH 6 and higher.

Experimental

Materials

The HMPE that we studied was prepared from carboxymethylcellulose (CMC) by converting a small fraction of the carboxyl groups into alkylamide groups [13]. The parent CMC was a cotton-based sample with a weight-averaged molar mass of 450 000 (which corresponds to about 2500 monomer units per chain). This material has a much higher purity than standard commercial CMCs based on wood. In addition, it has been carefully characterized with respect to its chemical composition (substitution pattern) and its swelling behavior (persistence length) in aqueous solution [14]. The polydispersity index of CMCs prepared from cotton is usually around 2. Our sample had an average degree of carboxymethyl substitution (per glucose unit) of 0.77. A small fraction of the carboxyl groups was converted into dodecylamide groups, and the degree of dodecyl substitution was determined by means of nitrogen analysis and capillary zone electrophoresis to be 0.012 (per glucose unit). If we may assume that the reaction does not affect the chain length, this implies that each chain carries, on average, several tens of dodecyl groups.

It has been found that the conditions during alkylation may have dramatic effects on the solution properties of HM polymers [5]. If the reaction proceeds in a medium which is both a good solvent for the polymer and for the alkylamine, polymers are obtained which remain soluble up to high degrees of alkylation, and vicinal substitution (neighboring carboxylgroups) is hardly detected by NMR. If alkylation is carried out in a polar medium in which the polymer dissolves well but the amine much less, the polymers become insoluble at low degrees of alkylation and vicinal substitution occurs frequently. Hence, information on the distribution of dodecyl groups along the chains would be important. Unfortunately, this is difficult to obtain. The attachment of the alkyl groups takes place in hot ethanol in which dodecylamine is quite soluble, but the parent CMC is not. This may lead to some non-randomness in the substitution. It should be pointed out that even if the alkyl chains would be distributed entirely randomly, this does not imply a homogeneous sample. From simple statistical considerations one infers that especially at low degrees of substitution the sample should be heterogeneous in the sense that entire polymer molecules may differ considerably in their degrees of substitution. A tendency of the alkyl groups to cluster only adds to this heterogeneity.

All other reagents used (NaCl, NaOH) were analytical grade, demineralized water (Nanopure, Barnstead) was used throughout. Aqueous stock solutions of the polymer were prepared by dissolving 1 g into 1 l of water and stirring this mildly for 24 h. The solution so obtained is slightly turbid, due to a poorly dissolved fraction of polymer. The turbidity could not be removed by increasing the pH. The solution was therefore centrifuged, and the gel-like residue (which probably contains a fraction of polymer chains with a relatively high alkyl content) discarded. Finally, the carbohydrate content of the clear, viscous solution was assessed by the sulphuric acid–phenol method [15]; a concentration of 816 mg/l was found. All solutions used in the experiment were prepared from this stock solution.

As substrate we used polystyrene (PS) in the form of thin films spin-cast onto strips of silicon wafer. To this end, radically polymerized polystyrene with a weight average molar mass of 10^5 was dissolved in toluene (13.0 g/l) and spin-cast at 2000 rpm. When polystyrene was cast onto bare clean silicon, poor adhesion was often observed upon immersing the strips into water. This was attributed to the fact that the bare silicon wafer, which carries a thin layer of native silicon oxide, is very hydrophilic so that water tends to penetrate between the polystyrene and the silica thereby detaching the film. In order to improve the adhesion we hydrophobized the strips by prior treatment with a dilute (1%) solution of dimethyldichlorosilane in toluene.

Techniques

The adsorption of the HMPE from a flowing solution was followed by means of a reflectometer equipped with an impinging jet flow cell. This set-up has been discussed in detail by Dijt et al. [16] so that we shall limit ourselves here to a brief description.

Polymer solution enters the flow cell from a cylindrical hole in the wall facing the adsorbing substrate and hits the substrate perpendicularly. This flow configuration is referred to as "impinging jet" and produces a stagnation point on the substrate at the centerline of the jet. Polarized light from a small HeNe laser is reflected by the substrate, the angle of incidence being close to the Si/H_2O Brewster angle; the illuminated spot is chosen to coincide with the stagnation point. The reflected beam is split into its parallel (p) and perpendicular (s) components by a polarizing beam splitter and the ratio $S = I_p/I_s$ of their intensities is determined. It can be shown that under appropriate conditions the relation between S and the adsorbed amount is linear to a very good approximation [16]:

$$\Gamma = Q(S/S_0 - 1)\,,$$

where S_0 is the intensity ratio measured prior to adsorption and Q is a sensitivity factor which can be calculated from the refractive indices of silicon (3.8), polystyrene (1.59) and water (1.33), respectively, the thickness d of the polystyrene film and the refractive index increment dn/dc of the HMPE in water. It is known [17] that for electrolytes this latter quantity varies linearly with the degree of dissociation, i.e., it depends on pH and ionic strength. The refractive index increment was determined for CMC in 0.01 M HNO_3 (pH 2) where CMC is almost uncharged, and at pH 8, where it is fully charged [14]. The values obtained were 0.165 and 0.140 ml/g, respectively. We determined dn/dc for intermediate degrees of dissociation by linear interpolation between these values. As a result, Q varies for our set of experiments between 53 mg/m^2 (uncharged) and 45 mg/m^2 (fully charged). The combination of reflectometry with the impinging-jet flow cell is particularly suited to determine adsorptions as a function of time, and has indeed been employed successfully for kinetic studies of polymer adsorption [18].

Polymer solution viscosity measurements were carried out in an automatic Ubbelohde viscometer (Fica), using a cylindrical capillary of 0.92 mm diameter and 9 cm length. Rheological measurements on dispersions were carried out with a Bohlin controlled stress rheometer. Apparent diffusion coefficients of polymers in solution were determined by dynamic light scattering with an ALV light scattering spectrometer equipped with a 35 mW HeNe light source and an ALV-5000 multitau correlator.

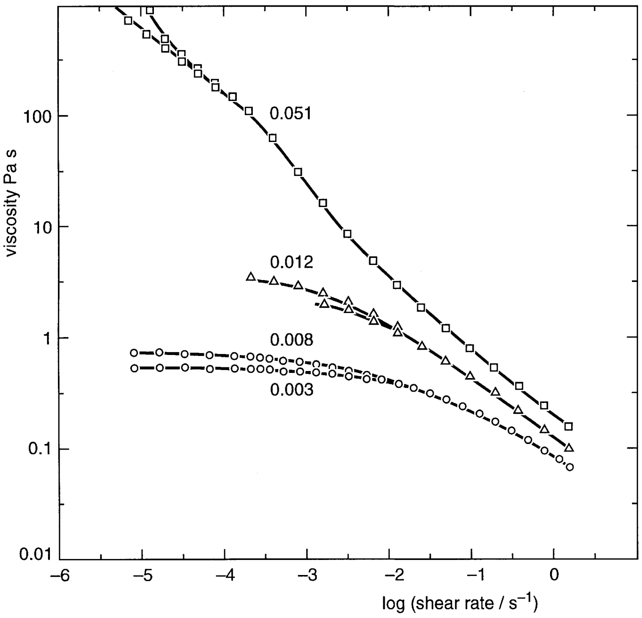

Fig. 1 Viscosity of 1% aqueous solutions of dodecyl-modified CMC as a function of shear rate. The content of dodecyl groups (in % with respect to glucose units) is indicated at each curve

Results and discussion

In Fig. 1 we show rheograms (viscosity as a function of shear rate) for four different HM-CMCs, all prepared from the same parent CMC. As is obvious from these data, the viscosity at low shear is most affected. For very low degrees of alkylation (0.003 and 0.008, respectively) there is little or no effect on the low shear (Newtonian) plateau. The sample with 1.2% dodecyl groups still has a plateau, but the viscosity there is almost ten times higher. For the last sample with 5.1% dodecyl groups the viscosity at the lowest shear rate is more than two orders of magnitude higher than that of the parent CMC, and the Newtonian plateau has disappeared altogether. All this proves that even low or modest alkylation has a dramatic effect on the rheology of these solutions. Such strong effects at low levels of dodecylation have been reported for samples with vicinal alkyl groups, suggesting that our material has also non-random alkylation.

For the remaining part of our paper we concentrate on the sample with 1.2% dodecyl groups. In Fig. 2 we show, for this sample, two representative examples of experimental adsorption curves, i.e., adsorbed mass Γ as a function of time t. The curves have both been measured at a polymer concentration of 100 mg/l, pH 8 and a flow rate of 0.08 ml/s, but they differ in the concentrations of added NaCl, which were 0.1 mol/l (upper curve) and 0.01 mol/l (lower curve), respectively. As can be seen, the adsorbed

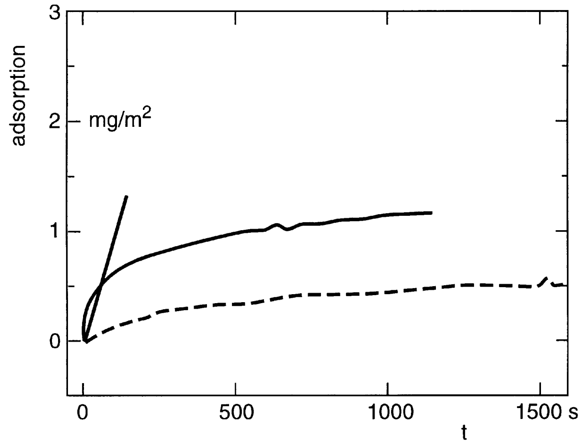

Fig. 2 Reflectometric adsorption curves (adsorbed amount as a function of time) for HM-CMC (1.2% dodecyl groups) at pH 8 on polystyrene. Upper curve: 0.1 M NaCl; lower curve: 0.01 M NaCl. The straight line indicates the expected limiting adsorption rate as calculated from the mean diffusion coefficient

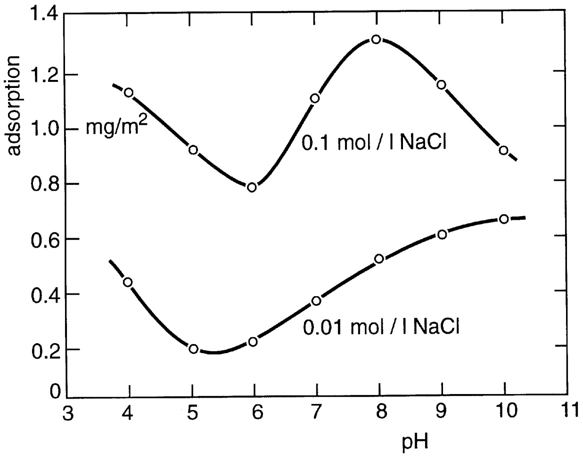

Fig. 3 Saturated adsorbed amount of HM-CMC on polystyrene films as a function of pH, for two concentrations of NaCl, as indicated

amount rises gradually with time in both cases. Both curves reach an almost constant (saturation) value. For the lower curve, this is after 1500 s and for the upper one after 3000 s (not shown), respectively. The initial adsorption rates differ considerably: that for 0.01 mol/l NaCl rises much more slowly. Clearly, salt has a strong enhancing effect both on the rate of adsorption and on the plateau value reached. This is not surprising, as CMC is fully charged at this pH and it should be expected that electrostatic repulsion between the HM-CMC molecules is strong at low ionic strength. Both the entry of molecules into the adsorbed layer and the final density that can be accomodated there will be adversely affected by this repulsion.

For comparison, we have drawn in Fig. 2 a line with a slope corresponding to the initial adsorption rate of the parent CMC, adsorbing from 0.1 mol/l salt solution on a hydrophilic substrate. This initial rate is entirely determined by the transport of polymer in solution and therefore depends on hydrodynamic conditions and on the diffusion coefficient of the molecules. As can be seen, HM-CMC at 0.1 mol/l salt has a *higher* initial adsorption rate than untreated CMC of the same molar mass. Since the hydrodynamic conditions were the same in both experiments, the difference in slope must imply that an important fraction of the HM-CMC diffuses faster than underivatized CMC. This could either be due to a reduction in average molar mass, or imply that HM-CMC molecules have a more compact structure than the CMC they were prepared from. At this point, we cannot decide between these two possibilities. The other point worth noting is that the rate of adsorption is considerably lower at 0.001 M salt. Under these conditions, an adsorption barrier due to electrostatic repulsion between the adsorbed layer and molecules approaching the surface begins to play a role [19].

In view of the importance of electrostatic effects it seems likely that the polymer charge and, hence, the pH is an important variable. In Fig. 3, the plateau adsorbed amount is given as a function of pH for the same two salt concentrations. Surprisingly, both curves have a *minimum* adsorbed amount in the pH range 5–6. In addition, the curve for 0.1 mol/l NaCl has a *maximum* at pH 8. As far as we know, a most peculiar pattern like this has not been reported before. Available data for adsorption of simple polyelectrolytes show consistently that the adsorption decreases with increasing charge on the polymer. There is evidence that polyampholytes and proteins (which can be considered as polyampholytes, too) tend to have a maximum adsorption in their isoelectric point [20]. However, CMC and HM-CMC carry only carboxylic groups, and are certainly not polyampholytes. It seems that the unusual pH dependence has something to do with the presence of the alkyl substituents.

As stated in the introduction, one expects that the repulsive interaction between the carboxyl groups on the chain will counteract association of the alkyl chains. As a consequence, the number of intra- and intermolecular bonds may begin to decrease when the pH becomes too high. This should be reflected by the viscosity of the solution: swelling of the polymer molecules should lead to an increase in the viscosity, but if disruption of intermolecular bonds dominates, the reverse is expected. We therefore measured the relative viscosity of HM-CMC

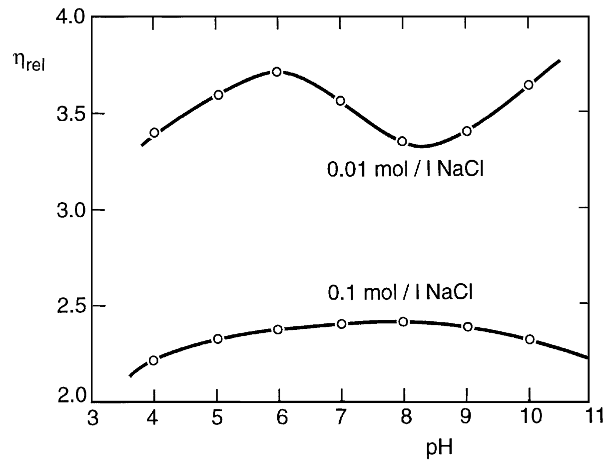

Fig. 4 Relative viscosity of HM-CMC solutions as a function of pH, for two concentrations of NaCl, as indicated

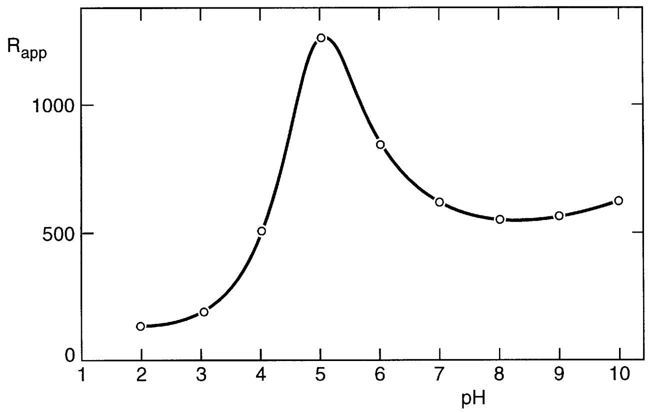

Fig. 5 Apparent diffusion radius R_{app} of HM-CMC molecules in aqueous solution at 0.01 M NaCl, as a function of pH

solutions as a function of pH, at a fixed concentration of about 800 mg/l and for the same two salt concentrations. The result is shown in Fig. 4. The viscosity in the case of 0.01 mol/l salt has two extrema at pH 6 and 8, respectively, like the adsorbed amount at 0.1 mol/l salt. The viscosity measured at 0.1 mol/l NaCl has a broad maximum around pH 6, but is rather featureless otherwise, probably because the concentration was too low to give clear effects. Another piece of information is obtained from dynamic light scattering measurements on the polymer solution. The data are presented in Fig. 5, and show that at 0.01 mol/l NaCl the apparent diffusion coefficient of the polymer has a deep minimum around pH 5. At low pH, diffusion is fast and the apparent hydrodynamic radius small. Increasing the pH from 3 to 5 causes a nearly tenfold increase in the apparent radius. Moreover, the data taken at pH 5 and 6 fluctuate strongly, as if the sample is very heterogeneous with respect to particle size.

All this brings us to the following scenario. In the pH range 4–6, the most likely solution process is swelling. The polymer is present in the form of soluble weak aggregates which grow enormously in size with increasing pH (see Fig. 5) causing a concomitant increase in viscosity. Probably, a sizeable fraction of the alkyl groups is associated. Adsorption of the neutral CMC on polystyrene was found to occur; other neutral polysaccharides (pullulan, dextran) have been found to adsorb on this surface, too. The hydrophobic dodecyl groups are expected to assist the anchoring of the polymer. The increase in the number of negatively charged groups leads to a decrease in adsorption; this is a common feature for weak polyelectrolytes caused by increasing electrostatic repulsion [21].

From pH 6 upward, the viscosity drops. In the same range, the diffusion radius of the aggregates in solution decreases. Apparently, a gradual break-up of aggregates occurs, which most likely is caused by the increasing electrostatic repulsion. Since the high charge density makes it very improbable that the liberated alkyl groups will associate within the same molecule, the solution now contains a population of HM-CMC molecules with an increased content of exposed hydrophobic groups. Our adsorption results in Fig. 4 indicate that these molecules adsorb to a higher extent, probably since they have more groups available for attaching to the substrate.

This process comes to an end when the electrostatic force, leading to break-up of intermolecular associations does not increase any further; this seems to be around pH 8. In the pH range 8–10 and at 0.1 mol/l NaCl we observe a downward trend in the adsorption. In the same pH range, there seems to be an upward trend in the viscosity at 0.01 mol/l NaCl. We have, as yet, no good explanation for these phenomena. One is inclined to think of a further gradual swelling of the individual polymer molecules but it seems unlikely that at pH 8 there is still a sizeable fraction of the rather strongly acidic carboxymethyl groups to be deprotonated [14].

The adsorption results for the lower salt concentration can be understood in the same way, the difference being that the increase beyond pH 6 is much more gradual. This seems to imply that carboxymethyl groups drawn together in the vicinity of a cluster of associated alkyl groups experience a stronger electrical field and are therefore less easily titrated when the pH is increased than acid groups having a more CMC-like surrounding. This agrees with the observation that pK_a of molecules in a micelle may shift considerably with respect to free molecules [22]. At low ionic strength this effect would be more pronounced, so that the titration extends over a larger pH range, and so

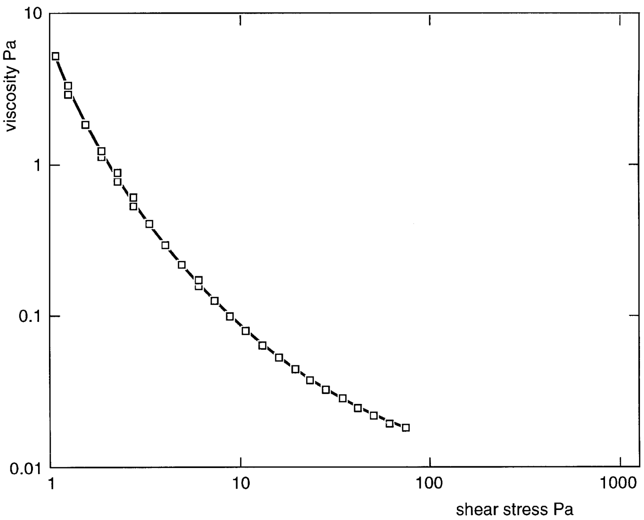

Fig. 6 Viscosity of 30% latex dispersion (particle radius 90 nm) with added HM-CMC, at pH 7 and 0.03 M NaCl, as a function of shear stress. The dispersion is clearly shear-thinning

does the aggregate break-up. The adsorption seems to attain a maximum value at about pH 10, but we have no data beyond this range so that we do not know whether a decrease follows at pH > 10.

From the observations reported above one might conclude that the sample of HM-CMC should also adsorb on hydrophobic latex particles. If this happens, one anticipates a strong bridging flocculation in concentrated latex dispersions. This was corroborated by experiments on sulphonate-stabilized polystyrene latex particles. Addition of HM-CMC turned the low-viscosity lattices into strong gels with a high modulus. Weaker interactions were evident when less hydrophobic acrylate latices were used. These thickened also upon addition of HM-CMC, but the lattices became viscous fluids or weak gels rather than very strong gels as in the case of polystyrene. The corresponding rheogram, taken at pH 7, is shown in Fig. 6.

A very striking observation in this context was that the thickening of the acrylate lattices did not occur when the dispersions were only briefly mixed and then left standing without stirring. Prolonged stirring proved necessary to produce the thickening effect. This would seem to imply that shear is essential to induce sufficient adsorption and bridging. Possibly, the shear disrupts intra- and intermolecular associations, thereby again enhancing transport towards the surface as well as the probability of polymer anchoring on particle surfaces. This supports the idea that conditions which cause break-up of intramolecular associations lead to enhanced adsorption.

Conclusions

HM-CMC with 1.2% dodecyl groups was prepared, and its interaction with hydrophobic polystyrene surfaces was studied. It was found that, whereas fully dissociated CMC itself does not adsorb, HM-CMC does, which must be entirely due to the hydrophobic interaction between the dodecyl groups and the PS surface. Upon addition of salt (at fixed pH), the adsorbed amount increases at all pHs studied. Apparently, repulsion due to unscreened charges lowers the adsorption. However, increasing the charge density on the chain by increasing the pH does not lead to a monotonic decrease of the adsorption. Instead, after an initial decrease in the pH range 4–6, the adsorption tends to increase for pH > 6. Since there are similar non-monotonic pH effects on the viscosity and the polymer diffusion coefficient (as measured by dynamic light scattering), we tend to interpret these effects in terms of swelling, followed by disruption of intramolecular hydrophobic domains. The latter process would liberate alkyl chains which can then bind to the substrate or to other chains, thus enhancing the adsorbed amount. This scenario of adsorption assisted by de-aggregation seems to be a unique feature of these associating HM-polymers, which may be interesting in the context of application as thickener or dispersant.

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