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Rheology control by modulating hydrophobic and inclusion associations in modified poly(acrylic acid) solutions

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Abstract

The rheology of modified poly(acrylic acid) (PAA) solutions can be tuned by controlling the inclusion interactions between α-cyclodextrins and alkyl hydrophobes. We demonstrate three modes of control: (1) using free cyclodextrins (CD) to displace hydrophobe–hydrophobe association in hydrophobically modified poly(acrylic acid) (HMPAA) polymers—which reduces fluid viscosity, (2) using competitive inclusion interactions where stronger SDS:CD binding can be used to 'unmask' CD:hydropobe inclusion interactions—which increases viscosity, and (3) employing HMPAA inclusion interactions with CD groups grafted to PAA chains (CDPAA)—which produces higher viscosities than purely hydrophobic association systems at the same concentration. The inclusion association between alkyl side-group in HMPAA and CD, either free or grafted onto PAA, obeys a 1-to-1 stoichiometry at low polymer concentrations (<1 wt%). In contrast to purely hydrophobically associating polymers, the CD:hydrophobe interaction is only binary, and, therefore, these associated networks should be ideal model systems to test theoretical predictions for associative fluids.

Keywords: Poly(acrylic acid); Rheology; Inclusion association

1. Introduction

Interactions among polymer chains give the ability to control solution rheology [1]. For example, hydrophobically modified water soluble polymers (HMP) are extensively used as rheology modifiers in paints, cosmetics, pharmaceuticals, foods, enhanced oil recovery, water treatment and controlled release of bioactive materials [2–4]. The hydrophobic interactions, and thus the solution viscosities, can be controlled by the type or density of hydrophobic groups [5–7], or the addition of salts or surfactants [8–11].

However, hydrophobic interactions do not provide the specificity to enable 'triggered' changes in rheology by minor changes in composition. The inclusion or 'host–guest' interaction between a cylcodextrin (CD) host and a hydrophobic guest is an ideal reversible, specific, physical interaction that can be exploited to modulate the rheology of polymer solutions. Cyclodextrins are cyclic oligosaccharides containing 6, 7 or 8 glucose rings, which are called α-, β- or γ-cyclodextrin, respectively. The internal cavity of a CD is hydrophobic and can accommodate suitable hydrophobic groups to form an inclusion complex [12–13]. For example, free CDs have been shown to reduce viscosity and viscoelasticity of HMP solutions by screening hydrophobic interactions [14–16].

More interestingly, if CDs are grafted onto polymer chains, novel polymer networks can be generated by host–guest interactions between polymers with hydrophobes and those with CD side-groups [17–20] as shown schematically in Fig. 1. The inclusion association between a CD and a hydrophobic guest group normally obeys a 1-to-1 stoichiometry. The theory of associative polymers has advanced significantly over the last decade [21–25]. However, the theories address only binary interactions, such that the associating network connectivity is independent of polymer concentration. The more advanced theories of associating

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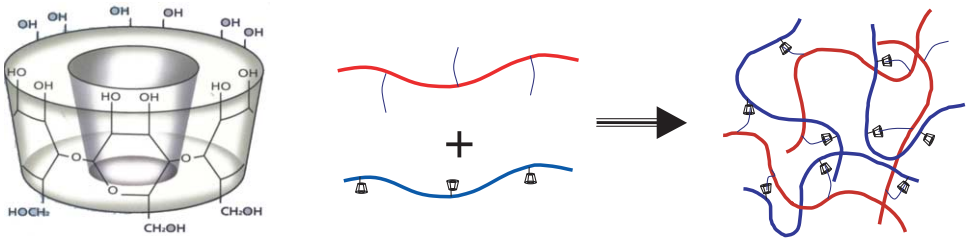

Fig. 1. (a) Cyclodextrin ring structure for α-cyclodextrin (six member rings) showing central hydrophobic cavity. (b) Schematic representation of association between poly(acrylic acid) (PAA) with hydrophobic grafts (HMPAA) and poly(acrylic acid) with cyclodextrin grafts (CDMPAA).

networks can address the differences between intra-chain associations and inter-chain associations as a function of polymer concentration [23], but not changes in aggregation number at the associating sites. A quantitative comparison between theory and experiment has not been possible due to the lack of a model system with only binary associative interactions. The traditional hydrophobically associative polymer networks are connected by clusters each containing 10–30 hydrophobic groups [26,27]. And the average number of hydrophobes in the cluster increases with increasing the polymer concentration [28]. The associative polymer networks based on CD inclusion interactions produce higher viscosities than purely hydophobically modified polymers alone and also provide an ideal model system to quantitatively test of theories of polymer association.

In this paper, we demonstrate how the rheological behavior of hydrophobically modified polyacrylic acid (HMPAA) aqueous solutions can be controlled through manipulation of hydrophobic and inclusion interactions. We show that the inclusion interactions can be used either to reduce solution viscosity by capping hydrophobic interactions upon addition of free CD or to enhance viscosity by displacing capped hydrophobes with a stronger binding inclusion interaction. Finally, we present a novel associative polymer network based on inclusion interactions between CDPAA and HMPAA, which shows higher viscosity solutions based on purely hydrophobic associations.

2. Experimental

2.1. Materials

Poly(acrylic acid)s (PAA) (M_w = 250 kg/mol, $M_w/M_n \approx 2$ and 140 kg/mol, $M_w/M_n \approx 2$) [29] were purchased from Aldrich. Octadecylamine (97%, Aldrich), 1-tetradecylamine (98%, ACROS Organics, NJ), dedecylamine (97%, Aldrich), 1-methyl-2-pyrrolidone (NMP) (99.5%, Aldrich), dicyclohexylcarbodiimide (99%, Aldrich), sodium dodecyl sulfate (SDS) (>99%, Sigma), sodium hydroxide (97%, EM Science, NJ) and methanol (99.5%, Aldrich) as well as α-cyclodextrin (Wacker Biochem. Corp.) were used as obtained. The 6-amino-a-deoxy-α-cyclodextrin were synthesized as reported previously [30].

2.2. Synthesis of poly(acrylic acid)s with α-cyclodextrin side-groups

Poly(acrylic acid)s with α-cyclodextrin side-groups (CDPAA) were synthesized by the reaction of monoamino cyclodextrin with carboxyl group in an aprotic solvent in the presence of dicyclohexylcarbodiimide (DCI).

In a typical run, 1.0 g (0.0139 mol –COOH groups) PAA with molecular weight of 250 kg/mol was dissolved in 30 ml NMP at 60 °C for 24 h. Then, 0.41 g monoamino α-cyclodextrin (dissolved in 4.0 g NMP) and 0.10 g DCI (dissolved in 2.0 g NMP) was introduced into the PAA solution under vigorous stirring. After reaction for 48 h at 60 °C, the system was cooled to room temperature. 35 ml 40 wt% NaOH aqueous solution was added, and the precipitate was washed with 15 ml 60 °C NMP twice and then by 20 ml methanol at room temperature. After filtration under vacuum, the solid product was dissolved in 12.5 ml DI water and precipitated in 100 ml methanol (twice).

The crude product was dissolved into 20 ml DI water and dialyzed (SpectraPor 3 tubing, molecular weight cutoff: 3500 g/mol) against DI water until the conductivity of water outside the tube was constant. The final dry products were obtained by freeze–drying after concentrating the solution to 10 wt% by evaporation.

2.3. Synthesis of poly(acrylic acid) with hydrophobic grafts

Following the procedure developed by Iliopoulos et al. [5], hydrophobically modified poly(acrylic acid)s (HMPAA) were prepared by grafting onto precursor poly(acrylic acid) alkylamines (dedecylamine, tetradecylamine or octadecylamine) in the presence of dicyclohexylcaroiimide (DCC), using *n*-methylpyrrolidinone (NMP) as solvent. Nomenclature for the modified poly(acrylic acid) is HMPAA*x*%*y*k*Cz*, where *x* is the mol% hydrophobic substitution, *y* is the PAA molecular weight in kg/mol and *z* is the number of carbon atoms in the alkyl side group. For example, HMPAA3%250kC18 means 3 mol% carboxyl groups in PAA with molecular weight of 250 kg/mol are substituted by *n*-octadecylamine.

2.4. Characterization

^{1}H NMR spectra were recorded on a Varian Inova-400 NMR spectrometer operating at 400 MHz at room temperature.

Samples were dissolved in D_2O at ca. 2 wt%. The degree of substitution for the carboxyl groups in PAA by α-cyclodextrin side-groups was determined according to Eq. (1):

$$\text{Substitution (mol\%)} = \frac{A_1/n}{A_2/2} \times 100 \quad (1)$$

where n is the number of dextrose units in cyclodextrin, A_1 and A_2 denote the peak areas of cyclodextrin at 4.85 ppm and the CH_2 peak at 1.30 ppm. The calculated substitution degree for α-CDPAA is 2.5 mol%.

The hydrophobic substitution level for HMPAA3%250kC18 was determined as 3.0% from the peak areas of CH_3 group (A_3) from *n*-octadecyl side-group at 0.63 ppm and CH_2 groups (A_2) from both PAA backbone (1.30 ppm) and *n*-octadecyl side-group (1.08 ppm) [5] according to Eq. (2):

$$\text{Substitution (mol\%)} = \frac{A_3}{A_2 - (2mA_3/3)} \times 100 \quad (2)$$

where m denotes the number of CH_2's in a hydrophobic side chain, e.g. $m=17$ for *n*-octadecyl side chain.

The steady and dynamic rheological measurements were performed on a Rheometrics DSR stress-controlled rheometer with 25 mm cone and plate geometry. The temperature was controlled to 25±0.1 °C by a Peltier plate. Samples for the rheological measurements were prepared as follows: the polymer was dissolved in a 0.1 M NaCl aqueous solution in order to screen the electrostatic interactions and the pH was adjusted to 7.0±0.2 using 0.1 M NaOH. The effect of pH and ionic strength on the rheology of hydrophobically modified PAA has been studied by Wang et al. [31]. They observed a viscosity maximum as a function of ionic strength (η_{max} at 0.17 M NaCl) and pH (η_{max} at pH 5). These maxima have been explained in terms of the competition between hydrophobic association and electrostatic repulsions. For this study, we have chosen the polymer precipitated in the sodium carboxylate form (PAA–Na) and dissolved in an aqueous solution with an ionic strength of 0.1 M NaCl at a pH of 7.0.

3. Results and discussion

3.1. Masking and recovery of hydrophobic association

3.1.1. Masking by α-cyclodextrin

Hydrophobic association can be masked by the addition of free CD as shown in Fig. 2 for a 0.5 wt% solution of HMPAA3%250kC18. The viscosity reduction is due to the loss of hydrophobic association as the hydrophobic groups form inclusion complexes with CDs. Essentially complete suppression of the hydrophobic interactions, and a reduction of viscosity by 50%, occurs when the molar ratio of CD to hydrophobic side-groups (C18) is greater than one [32].

For higher concentrations of HMPAA the effect of CD is even more pronounced. Fig. 3 shows the steady shear viscosities of 2 wt% HMPAA upon addition of CD. Three orders of magnitude reduction in viscosity is obtained upon the addition of two CD molecules per hydrophobe at 2 wt% HMPAA. The stoichiometry of CD needed to disrupt association is increased from a molar ratio of 1:1 to 2:1 (CD:C18) (Figs. 2 and 3). Shear-thickening is observed at shear rate around 0.01 s^{-1}, which is attributed to the shear-induced conversion of intra to inter molecular associations in hydrophobically associated system [33–37].

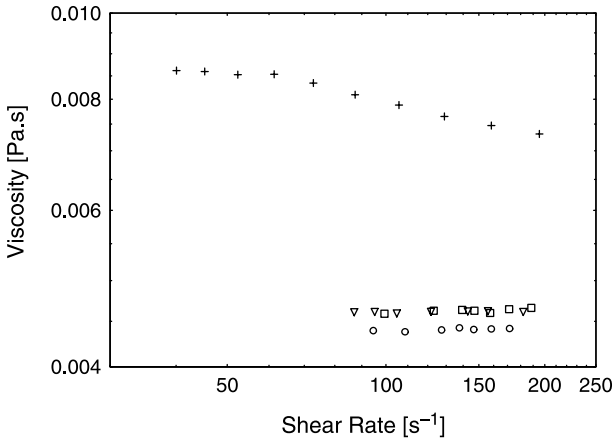

Fig. 2. Dependence of viscosity on the shear rate for 0.5 wt% HMPAA3%250kC18 in 0.1 M NaCl solution upon addition of CD (pH 7). The changing parameter is the molar ratio of added CD to hydrophobic side groups (CD:C18). Symbols denote: (+) 0.5 wt% HMPAA3%250kC18; (○) CD:C18=1:1; (□) CD:C18=2:1 and (▽) CD:C18=3:1.

The addition of CD is analogous to reducing the degree of hydrophobic substitution on the PAA chain. Rubenstein and Semenov [22] have shown that for a polyacrylamide substituted with dihexyl hydrophobes the zero shear viscosity scales with the number of stickers to the 3rd power. The system considered here with C18 hydrophobes has a stronger dependence on hydrophobe substitution: $\eta \sim (\text{HM})^7$ (Appendix A). While in his paper we are merely setting out the experimental phenomenology that controls this new associating polymer system, it is clear that the binary nature

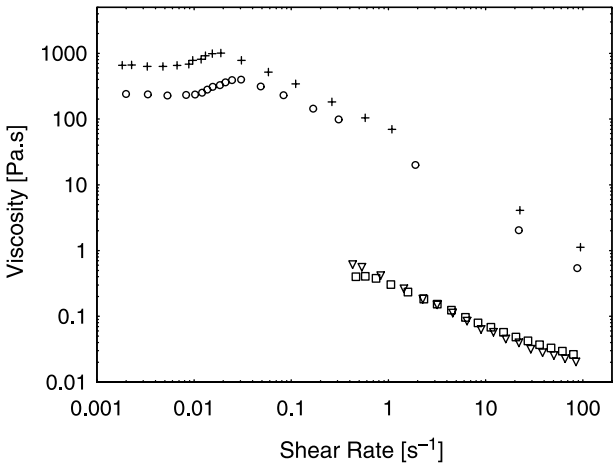

Fig. 3. Dependence of viscosity on the shear rate for 2 wt% HMPAA3%250kC18 in 0.1 M NaCl solution upon addition of CD (pH 7). The changing parameter is the molar ratio of added CD to hydrophobic side groups (CD:C18). Symbols denote: (+) 2 wt% HMPAA3%250kC18; (○) CD:C18=1:1; (□) CD:C18=2:1 and (▽) CD:C18=3:1.

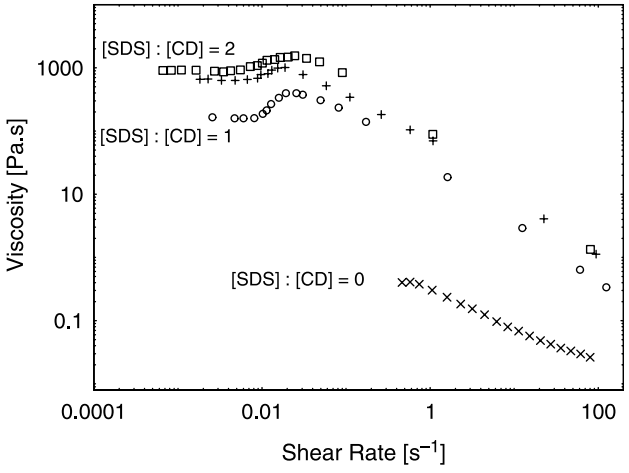

Fig. 4. Dependence of viscosity on the shear rate for mixed solution of 2 wt% HMPAA3%250kC18 and CD with molar ratio of CD:C18 = 2:1. The changing parameter is the molar ratio of added SDS to CD (SDS:CD). Curves denote: (+) 2 wt% HMPAA3%250kC18; (×) mixture of CD and HMPAA with CD:C18 = 2:1; (○) after addition of SDS with SDS:CD = 1:1 and (□) SDS:CD = 2:1.

of the interactions should correspond to the model of association addressed by Rubenstein and Semenov more closely than the system of hydrophobic association because the hydrophobic clusters have an indefinite aggregation number. The drop in viscosity by three orders of magnitude shown in Fig. 3 corresponds to the decrease in association below the percolation threshold [38]. Clearly these preliminary results provide the range of CD addition that should be probed in detail to compare against the theories of the dynamics of association solutions [21,22]. Further work is underway.

3.1.2. Recovery of viscosity by SDS 'unmasking'

Fig. 4 shows the viscosity of a 2 wt% HMPAA3%250kC18 solution with adequate CD added to mask hydrophobic associations—the zero shear viscosity is about 0.4 Pa s. Upon addition of SDS, the zero shear viscosity increases 500-fold at a molar ratio of SDS to CD of one, and reaches the viscosity equal to that of the original hydrophobically modified polymers when the SDS:CD molar ratio is 2:1. This corresponds to earlier observations of Abdala et al. [14] for a different polymer system.

This 'unmasking' has been exploited for the novel aqueous synthesis of hydrophobically modified polymers from water soluble monomers and hydrophobic monomers solubilized by CD [39]. However, further addition of SDS past the 2:1 stoichiometry decreases the viscosity of the polymer solution due to the disruption of hydrophobic association by excess SDS micelles (see discussion in Appendix A) [40]. The initial disruption arises from the stronger binding constant between CD and SDS relative to CD and hydrophobes. So, the viscosities of HMPAA solutions are easily tunable by addition of CD and SDS to modulate the hydrophobic and inclusion interactions.

3.2. Macromolecular assembly by inclusion association: CDPAA and HMPAA

The previous section considered only free CD added to HMPAA solutions. We now consider binary mixtures of polymers where one polymer is grafted by CD and the other by C18. The inclusion interactions between CDs and hydrophobic alkyl groups on different chains can form labile cross-links between polymers. Indeed, as shown in Fig. 5, the viscosity of mixtures from CDPAA and HMPAA can be higher than that of pure HMPAA solutions having only hydrophobic associations, and always much higher than that of CDPAA. The maximum in the shear viscosity appears at a molar ratio of CD to alkyl groups (CD:C18) of 1:1 at the polymer concentration of 0.5 and 1.0 wt% (Fig. 5(a) and (b)). Therefore, the CD and C18 complexation still obeys approximately a 1-to-1 association

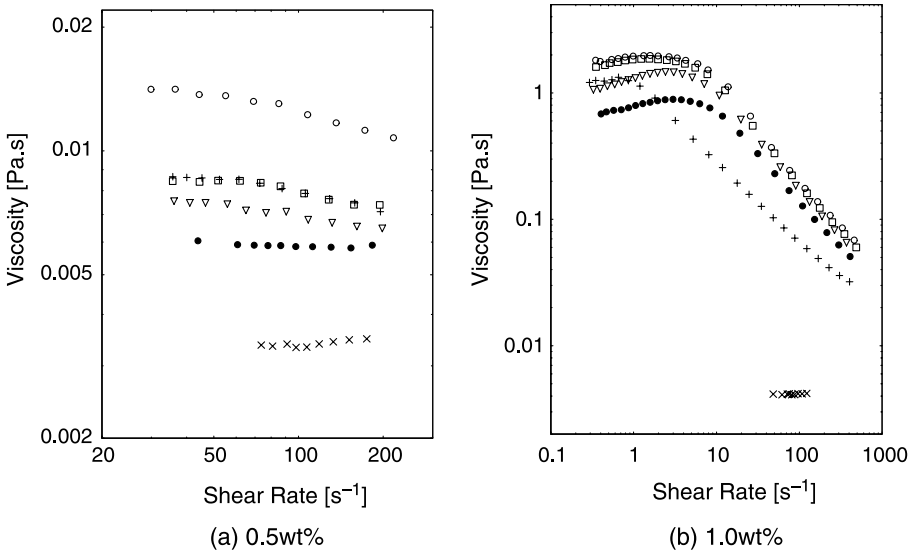

Fig. 5. Dependence of viscosity on the shear rate for mixed solutions of HMPAA3%250kC18 and α-CDPAA with different molar ratios of CD groups and hydrophobic side groups (CD:C18). Total polymer concentrations are (a) 0.5 wt% and (b) 1 wt%. Curves denote: (+) only HMPAA3%250kC18; (×) only α-CDPAA; (○) CD:C18 = 1:1; (□) CD:C18 = 2:1; (▽) CD:C18 = 3:1; (●) CD:C18 = 4:1.

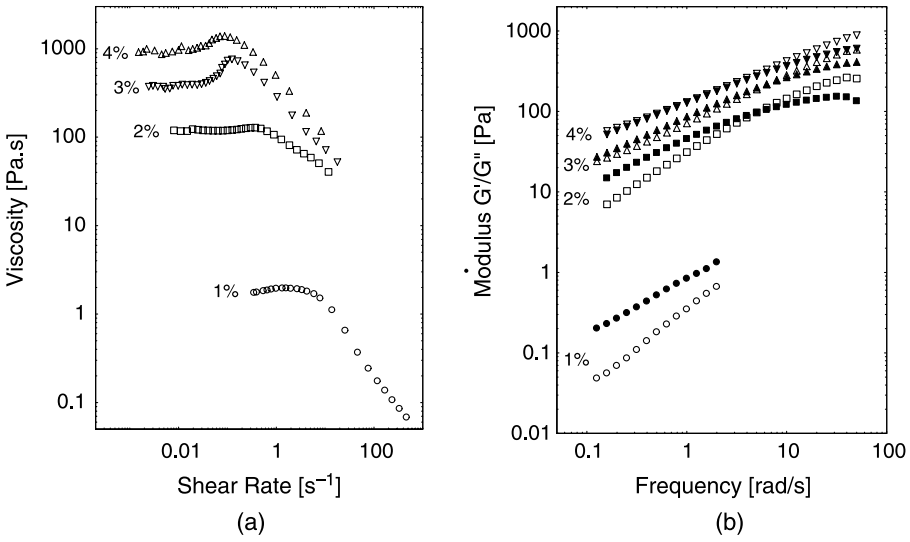

Fig. 6. Effect of concentration on steady shear viscosities (a), and frequency dependencies of the storage modulus G' (open symbols) and the loss modulus G'' (closed symbols) (b) for mixed solutions of α-CDPAA and HMPAA3%250kC18 at 1:1 molar ration in 0.1 M aqueous NaCl solution (pH 7). The changing parameter is total polymer concentration.

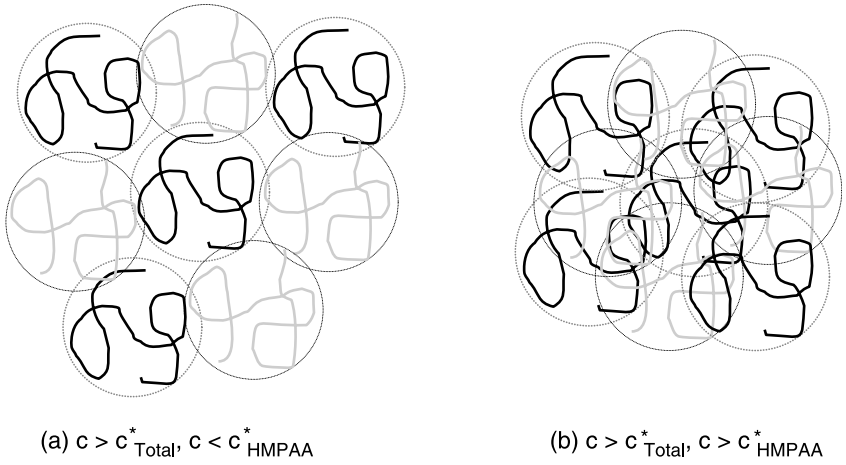

Fig. 7. Schematic representation of the macromolecular overlapping under the effect of concentration. The bold and grey lines denote HMPAA and CDPAA molecules, respectively.

stoichiometry even though the CD and C18 are grafted to polymer chains.

The viscosities of inclusion associated polymers increase significantly with increasing polymer concentration. The zero shear viscosity rises three orders of magnitude when the solution is concentrated from 1 to 4 wt% (Fig. 6(a)), and once in the strongly associating regime the viscosity scales as $\eta_o \sim c_p^{3.0}$. Shear-thickening appears in the steady shear viscosity

Table 1
Critical rheological parameters for HMPAA+CDMPAA inclusion associated polymer networks

c_p (wt%)	η_0 (Pa s)	$\dot{\gamma}_c(s^{-1})$	τ_c (s)	ω_c (rev/s)	τ_ω (s)	G_{pi} (Pa)	G_p (Pa)	$G_{pi}\tau_c$ (Pa s)	$G_p\tau_c$ (Pa s)	$G_{pi}\tau_\omega$ (Pa s)	$G_p\tau_\omega$ (Pa s)
1	1.4	3.8	0.26	2.4	0.42	4.5	–	1.2	–	1.9	–
2	122	0.6	1.7	0.8	1.3	100	260	170	440	130	330
3	401	0.11 (0.04)[a]	9.1 (25)[a]	1.0	1.0	200	550	1800 (5000)	5000 (14,000)	200	550
4	988	0.09 (0.03)[a]	11.1 (33.3)[a]	–	–	–	–	–	–	–	–

c_p, polymer concentration (wt%); $\dot{\gamma}_c$, shear rate at the onset of shear-thinning (s^{-1}); τ_c, relaxation time (reciprocal of shear rate) at the onset of shear-thinning (s); ω_c, frequency at the intersection point where $G'=G''$ (rev/s); τ_ω, relaxation time (reciprocal of frequency) at the intersection point (s); G_p, plateau modulus estimated from plateau value (Pa); G_{pi}, modulus estimated from the intersection point where $G'=G''$ (Pa).

[a] Denotes shear rates at the onset of shear-thickening.

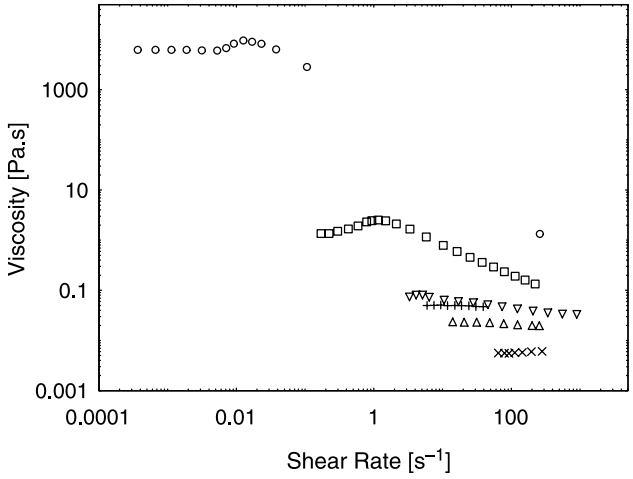

Fig. A1. Effect of polymer concentration on solution viscosities as function of shear rate for HMPAA3%250kC18 and its precursor in 0.1 M NaCl (pH 7) at 25 °C. Symbols from top to bottom denote: (○) 4 wt% HMPAA3%250kC18; (□) 1.5 wt% HMPAA3%250kC18; (▽) 1.2 wt% HMPAA3%250kC18; (+) 4.0 wt% PAA; (△) 1.0 wt% HMPAA3%250kC18 and (×) 1.0 wt% PAA.

profile at concentrations over 2 wt% (Fig. 6(a)). For purely hydrophobically associating polymers this shear thickening is interpreted as a disruption of intra chain association and formation of additional inter chain associations. For the binary CDPAA and HMPAA association the CDPAA cannot form intra chain associations. However, the HMPAA may. But at 2 wt% (1 wt% in HMPAA) the HMPAA chains are below their overlap concentration (Fig. 7). Therefore, one cannot argue that shear creates inter chain associations between HMPAA chains. However, the shear might create additional CDPAA:HMPAA associations or might disrupt intra chain hydrophobic associations to allow more inclusion associations. In the summary section, we will comment further on this.

The critical rheological parameters from Fig. 6 are listed in Table 1. The 1 and 2 wt% solutions show zero shear viscosities, relaxation times and plateau moduli that are consistent with the expectation for a single time constant Maxwell fluid (i.e. $\eta_0 = \tau G_p$, where τ is the fluid relaxation time, and G_p is the plateau modulus). For the higher concentrations $G'(\omega) \sim G'(\omega)$, which is the signature of a critical gel [41] with a power-law spectrum of relaxation times. A striking difference between the rheology of the purely hydrophobic associating solutions (Fig. A1) and the inclusion-based associating fluid (Fig. 6(a)) is the dependence of relaxation time on polymer concentration. For the purely hydrophobic associations increasing concentration leads to increasingly long relaxation times, while for the inclusion association to the relaxation time changes relatively little.

4. Conclusion

The viscosities of modified poly(acrylic acid) solutions are tunable by modulating hydrophobic and inclusion associations between C18 alkyl groups (HM) and α-cyclodextrins (CD). Hydrophobic association in HMPAA can be screened by adding free CD. The masking of the hydrophobic association occurs at approximately a 1:1 stoichiometric ratio of CD to HM at low polymer concentrations (<1 wt%) and at a 2:1 ratio for higher polymer concentrations. The viscosity, and hydrophobic association, can be recovered by introducing SDS. The ability to mask association with CDs and to unmask the association by displacing CD by the addition of SDS is a result of the order of binding constants: SDS:CD > HM:CD > HM:HM.

The binary mixtures of polymers with grafted hosts (CD) and grafted guests (HM) show higher viscosities than HMPAA or CDPAA solutions at the same concentration. The maximum viscosity of the mixture of HMPAA and CDPAA also appears at approximately a 1-to-1 stoichiometric ratio at low concentrations (≤1 wt%), which indicates that the network mainly involves binary association. The origin of shear thickening in the steady shear viscosity measurements remains unclear. It may either arise from shear inducing more favorable interactions between CD and HM groups or from intra chain hydrophobic associations that are disrupted by shear to allow formation of CD:HM inter chain associations. To distinguish between these mechanisms a host–guest system could be employed that does not induce intra chain association, for example, an association complex based on acid–base ionomers in non-polar solvents.

Finally, while we have merely laid out the phenomenology of the associations for this novel host–guest system, we believe that this will provide a model system to test theories of associating fluids.

Acknowledgements

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Appendix A. Rheological characterization of HMPAA

Because the rheology of associating polymers can be very sensitive to architecture, we present the solution viscosities of the pure hydrophobically modified polymers synthesized for this study. Since, the syntheses follow the procedures of Illiopolous [11] the general trends have been reported previously. However, we present these results because they provide a complete data set of the rheology of purely hydrophobically associating polymers to contrast with the data for CD mediated interactions presented in the body of the paper. Having both sets of data on the same HMPAA is important to compare models of association fluid rheology that will follow from this paper.

A.1. Effect of concentration

The steady shear viscosities of solutions of HMPAA3%250kC18 and its precursor as a function of shear rate are shown in Fig. A1. The increase in viscosity upon increasing polymer concentration is much more significant for hydrophobically modified PAA compared to its precursor. When HMPAA concentration increases from 1 to 4 wt%, the

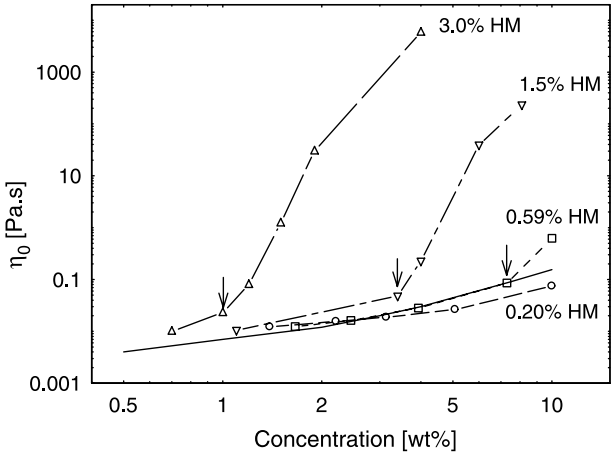

Fig. A2. Effect of hydrophobic substitution level on the relationship between zero shear viscosity and C18 HMPAA concentration in 0.1 M NaCl (pH 7). Curves denote: (△) HMPAA3%250kC18; (▽) HMPAA1.5%250kC18; (□) HMPAA0.59%250kC18; (○) HMPAA0.20%250kC18, and the solid line represents PAA with molecular weight of 250 kg/mol. Arrows show the estimated overlap concentration c^*.

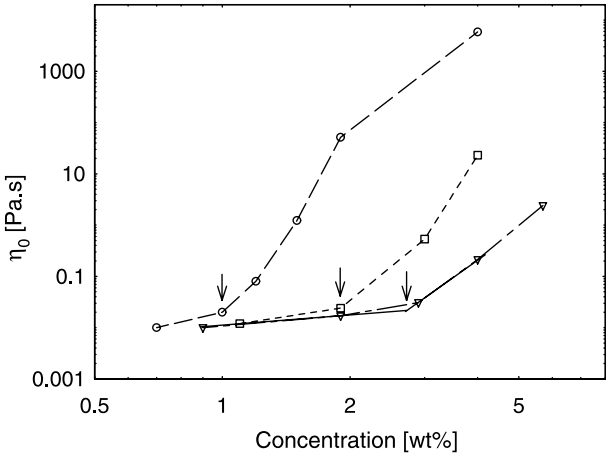

Fig. A3. Zero shear viscosity as a function of concentration for HMPAAs with various lengths of alkyl side-groups in 0.1 M NaCl (pH 7) at 25 °C. Symbols are: (○) HMPAA3%250kC18; (□) HMPAA3%250kC14 and (▽) HMPAA3%250kC12. Arrow shows the observed overlap concentration c^*.

viscosity increases by five orders of magnitude, while the viscosity increases only one order of magnitude for its precursor.

The non-specific hydrophobic interactions among alkyl side-groups in HMPAA allow the formation of both intra and inter molecular, micelle-like associations [4]. Only the inter molecular associations contribute to the enhancement of solution viscosity, while the intra molecular associations result in a collapse of chain dimensions and a reduction of viscosity. When the concentration reaches the overlap concentration c^*, the probability of inter molecular associations increases [4,5].

Another feature of the steady shear viscosity profile of HMPAA at concentration above c^* is the shear-thickening at moderate shear rates (Fig. A1) [4,34–38,42].

A.2. Effect of substitution degree

The concentration dependence of the zero shear viscosity of HMPAA solutions with various C18 substitution levels is shown in Fig. A2.

HMPAA3%250kC18 shows the lowest c^* of 1.0 wt% and the highest slope (dependence of the viscosity on concentration) among all the samples. When the hydrophobic substitution is reduced to 1.5%, c^* moves to 3.4 wt%. With further reduction of the substitution to 0.59%, c^* occurs at 7.3 wt%. There is no sharp upturn in viscosity up to concentrations of 10 wt% for the sample with the substitution of 0.20 wt%. The inter molecular hydrophobic associations depends strongly on the hydrophobe concentration or distance among hydrophobes.

Another interesting observation in Fig. A2 is that the zero shear viscosities of HMPAA0.2%250kC18 are even lower than that of its precursor PAA due to the intra molecular association. This has been observed for several associating polymer solutions [43,44] and can even lead to phase separation [45].

A.3. Effect of length of alkyl group

As shown in Fig. A3, the length of alkyl grafts in HMPAA has a pronounced impact on the concentration dependence of the zero shear viscosity. The observed overlap concentration c^* (Table 2) decreases while the concentration dependence increases as the hydrophobe alkyl length increases from C12 to C18 (Fig. A3) [6,31].

A.4. Effect of salt concentration

Since HMPAA is a polyelectrolyte, addition of salt changes the solution properties. Indeed, as shown in Fig. A4, the viscosities first increase with increasing ionic strength, reach a maximum at 0.1 M NaCl, and then drop with further addition of NaCl to 1 M. The appearance of a viscosity maximum results from the interplay of electrostatic and hydrophobic interactions [5,11,31].

A.5. Effect of SDS

In Fig. A5, the solution viscosities of HMPAA3%250kC18 increased three fold upon addition of SDS to a molar ratio of SDS:HM of 1:1 and decreased for higher SDS concentrations. This phenomenon has been reported by several authors for similar systems [6,7,10,11,40]. The initial addition of SDS creates mixed clusters containing surfactants and alkyl side-

Table 2
Observed overlap concentration of HMPAA

Polymer	Overlap concentration c^*
HMPAA3%250kC18	1.0
HMPAA1.5%250kC18	3.4
HMPAA0.59%250kC18	7.3
HMPAA3%250kC14	1.9
HMPAA3%250kC12	2.7

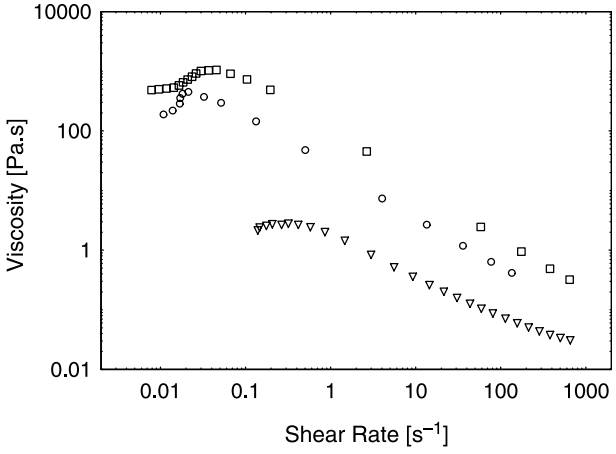

Fig. A4. Dependence of viscosity on the shear rate for 2 wt% HMPAA3%250kC18 at various salt concentrations (pH 7). Curves denote: (○) in DI water; (□) in 0.1 M NaCl and (▽) in 1 M NaCl.

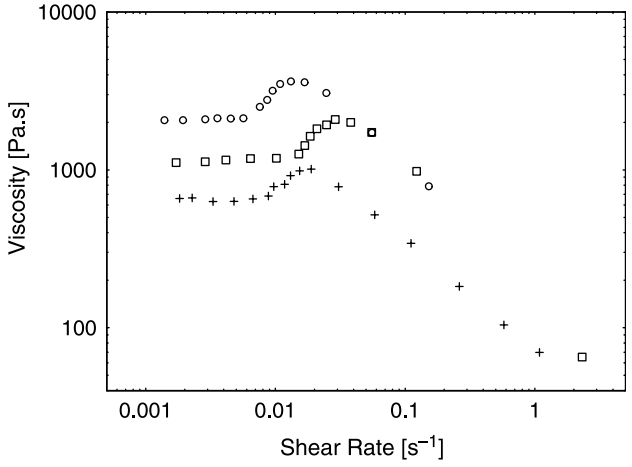

Fig. A5. Dependence of viscosity on the shear rate for 2 wt% HMPAA3%250kC18 solution upon addition of SDS. The changing parameter is the molar ratio of added SDS to hydrophobic side groups (SDS:C18). Curves denote: (+) 2 wt% HMPAA3%250kC18; (○) SDS:C18 = 1:1 and (□) SDS:C18 = 2:1.

groups. These clusters act as transient association sites and increase solution viscosity. However, upon further addition of SDS, such that the number of SDS micelles is greater than the number of grafted hydrophobes, the micelles 'mask' hydrophobic interactions among chains. The disruption of interchain associations results in a decrease in viscosity [11,40].

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