Novel associative polymer networks based on cyclodextrin inclusion compounds

ARTICLE

Modulation of Hydrophobic Interactions in Associative Polymers Using Inclusion Compounds and Surfactants

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Received February 10, 2003; Revised Manuscript Received July 29, 2003

ABSTRACT: We report the modulation of the solution rheology of a comblike, hydrobhobically modified alkali-soluble emulsion (HASE) associative polymer through addition of α- and *β*-cyclodextrins (CDs). The ring-shaped CDs with hydrophobic inner cores interact with the pendant macromonomer segments of the associative polymer containing hydrophobic end groups, leading to reduction in polymer solution viscosity and dynamic moduli by several orders of magnitude. We find no interactions between the CDs and the polymer backbone as substantiated by the fact that an analogous parent polymer without hydrophobes reveals no changes in the solution rheology in the presence of CDs. In contrast, the CDs encapsulate the hydrophobic groups on the associative polymer. This is confirmed by the complexation between the CD and a surfactant modified to resemble the hydrophobic macromonomer of the associative polymer as observed using ^{1}H NMR, differential scanning calorimetry (DSC), and thermal gravimetric analysis (TGA). The stoichiometric ratio of complexation between the CD and the hydrophobic macromonomer is determined independently from both NMR and yield data to be 5 mol of CD/mol of hydrophobe. Interestingly, the reduction in polymer viscoelasticity in the presence of CD is reversibly recovered upon subsequent addition of different nonionic surfactants that have a higher propensity to complex with the CD than the hydrophobic segments of the HASE polymer.

1. Introduction

Associative polymers are macromolecules with attractive groups either attached to the ends or randomly distributed along the backbone.[1] Hydrophobically modified alkali soluble emulsion (HASE) polymers are one class of water-soluble associative polymers that have a comblike structure with pendant hydrophobic groups randomly distributed along a polyelectrolyte backbone. HASE polymers have several advantages over other associative polymers in terms of cost and wide formulation latitude.[2] Consequently, they are currently being used in a range of applications, including paint formulations, paper coatings, and recently as glycol-based aircraft antiicing fluids[3−5] and also have potential for use in enhanced oil recovery and personal care products. These polymers are usually added to either modify the rheology of aqueous solutions or increase the stability of dispersions. Because of their high thickening ability, a few percent of HASE polymers can increase the solution viscosity by several orders of magnitude. This thickening ability is predominantly the result of the molecular hydrophobic associations that occur to minimize contact between the aqueous medium and the hydrophobic segments of the polymer; the hydrodynamic volume expansion upon neutralization of the carboxylic groups on the polymer backbone also plays a minor role in this regard.

Despite the importance of hydrophobic interactions to promote viscosity enhancement in this polymer system, there is also a need to remove these interactions in many instances. For example, the high solution viscosity of a concentrated solution is always associated with difficulty in handling during solution preparation and prior to end use. The hydrophobic interactions also make extracting information from characterization techniques, such as light scattering and gel permeation chromatography (GPC), cumbersome and less accurate. The removal of the hydrophobic interactions would simplify the information gained from these techniques and assist in understanding the behavior of these polymers. In addition, the properties of the hydrophobically modified polymers are usually compared to those of the unmodified parent polymer without hydrophobes to gain understanding about their microstructures and associating abilities. However, such an assessment may not be realistic because modified and unmodified polymers may differ by more than just the hydrophobic modification.[6] The ability to compare modified polymers with both active and deactivated hydrophobes provides a plausible basis for understanding their behavior.

In this study, we examine a powerful method to control the solution rheology of HASE polymers by means of removing the hydrophobic interactions using cyclodextrins to form inclusion compounds[6] with the macromonomer part of the HASE polymer. Cyclodextrins (CDs) are ring-shaped oligosaccharides consisting of 6, 7, or 8 glucose units (corresponding to α-, *β*-, and *γ*-CD) joined by α-1,4-glycosidic linkages. They have a hydrophobic inner core and a hydrophilic outer shell, thus making it possible for the hydrophobic segments of the polymer to reside inside them and form a complex referred to as an inclusion compound. Such a notion is supported from previous studies which reveal cyclodextrins to have superior tendencies to interact with the hydrophobic segments of different hydrophobically modified water-soluble associative polymers, including hydrophobically end-capped poly(ethylene oxide),[7−12] poly(ethylene glycol)s (PEGs) bearing hydrophobic ends (naphthyl and phenyladamantyl),[13] *N*,*N*-dimethylacryl-

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10.1021/ma034173v CCC: $25.00
Published on Web 09/06/2003

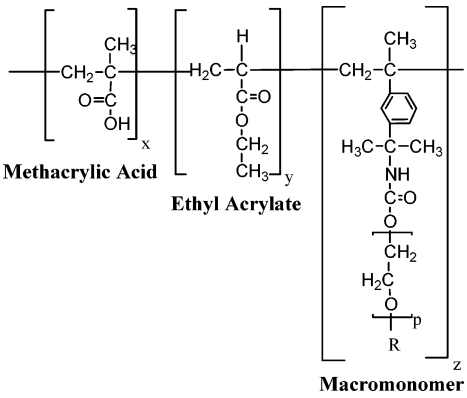


Figure 1. Schematic representation of a HASE associative polymer and the molecular constitution of the HASE polymer used in this study. R refers to the $C_{22}H_{45}$ hydrophobe, $p = 40$, and $x/y/z = 43.57/56.21/0.22$ by mole.

amide−hydroxyethyl methacrylate copolymer hydrophobically modified with adamantyl groups,[14−16] hydrophobically modified ethyl(hydroxyethyl) cellulose,[6] hydrophobically modified, degradable, poly(malic acid),[17] isobutene maleate polymer with pendant hydrophobic 4-*tert*-butylanilide,[18] hydrophobically modified ethoxylated urethanes,[19] hydrophobically modified alkali-soluble emulsion polymers,[20,21] and hydrophobically modified Dextran.[22] Cyclodextrins have also been reported to form inclusion compounds with many nonionic surfactants.[23−39]

In this work, we focus on investigating the effects of α- and *β*-cyclodextrin addition on the rheology of HASE polymer solutions, understanding the mechanism of cyclodextrin polymer complexation and evaluating the reversibility of these interactions. As such, we examine initially the extent of rheology changes upon CD addition and the existence, if any, of quantitative relationship between the molar ratio of CDs to the polymer hydrophobes on solution rheology. To isolate whether the observed changes are due to interactions of the CD with the macromonomer containing the hydrophobes or with the polymer backbone, we take a two-prong approach. The interaction between the CDs and the polymer backbone is studied using the unmodified parent polymer without hydropobes. On the other hand, a commercially available surfactant, RhodaSurf, was modified to resemble the macromonomer part and used to simulate the interaction between the macromonomer part of the HASE polymer with the CDs. A range of techniques including NMR, DSC, and TGA are used to study the complexation and formation of an inclusion compound between the CDs and the hydrophobic macromonomer Finally, the reversibility of the CD−polymer complexation and ability to recover the original solution rheology is investigated through addition of nonionic surfactants. A higher affinity of the CD to form an inclusion compound with the surfactant would lead to the release of the polymer from the CD and a concomitant reversal of rheology.

2. Experimental Section

2.1. Materials. The model associative polymer used in this study is a hydrophobically modified alkali-soluble (HASE) polymer synthesized by UCAR Emulsion Systems (Dow Chemical) via emulsion polymerization of methacrylic acid (MAA), ethyl acrylate (EA), and a hydrophobic macromonomer (Figure 1). This macromonomer is end-capped with $C_{22}H_{45}$ alkyl hydrophobes that is separated from the backbone by 40 ethylene oxide (EO) units. Details of the preparation method can be found in a previous publication.[40] In addition to the hydrophobically modified polymer, an unmodified polymer that has the same structure as the modified polymer with the $C_{22}H_{45}$ hydrophobes replaced by an equivalent amount of methyl groups was also used. Both the modified and the unmodified polymers were prepared in an identical manner and are believed to have the same molecular weight. The polymer latexes were dialyzed against deionized water using a cellulosic tubular membrane for at least 3 weeks with daily change of water. After dialysis, the polymer was freeze-dried, and 5% solutions were prepared and neutralized to pH of 9 ± 0.1 using 1 N NaOH with the ionic strength adjusted to 0.1 M KCl.

$C_{22}EO_{40}$ surfactant under the commercial name of RhodaSurf was provided by Dow Chemical Co. The surfactant was modified to resemble the macromonomer part (MW 2287 Da) of the HASE polymer through reaction with α,α-dimethyl meta-isopropenyl benzyl isocyanate (TMI (meta), American Cyanamid) as shown in Scheme 1. The nonionic surfactant, nonylophenol poly(ethylene glycol) ether with degree of ethoxylation of 4 (NP4), was provided by Dow Chemical Co. Industrial grade α- and *β*-cyclodextrins were supplied by Cerestar and used as received.

2.2. Methods. The steady and dynamic rheological behavior of the polymer solutions were measured using a stress-controlled rheometer (Rheometrics DSR II) fitted with appropriate cone and plate, parallel plates, and couette geometries. Details on the rheological techniques are provided in previous publications.[41−44]

^{1}H NMR data were obtained using a 500 MHz Bruker DRX NMR spectrometer. All spectra were acquired at 298 K using tetramethylsilane (TMS) as internal standard, and all samples were prepared in DMSO-*d*6. The instrumental parameters for acquisition of the one-dimensional proton spectra were as follows: tuning frequency 500.128 MHz, spectral width 13.2 ppm, number of data points 32K, relaxation and acquisition times 1.0 and 2.47 s, respectively, pulse width 10.5 *μ*m, tip angle 90°, and number of transients 16.

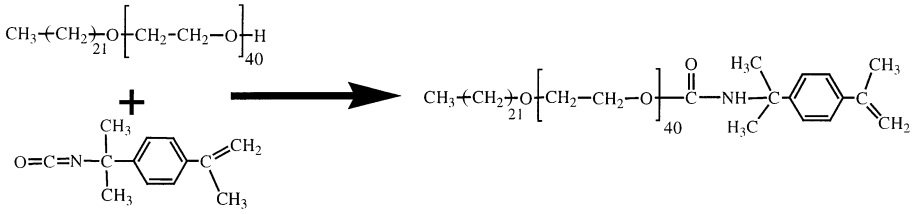
Differential scanning calorimetry (DSC) was carried out on 3−8 mg samples with a Perkin-Elmer DSC-7 thermal analyzer equipped with a cooler system. A heating rate of 10 °C/min was employed, and an indium standard was used for calibration. Before each scan, samples were annealed at 200 °C for 3 min to erase thermal history, followed by a flash quenching to −100 °C at 500 °C/min. Thermal gravimetric analysis (TGA) measurements were carried out on a Perkin-Elmer Pyris 1 thermogravimetric analyzer. Approximately 20 mg samples were heated from 25 to 600 °C, and the weight loss was recorded as a function of sample temperature.

3. Results and Discussion

3.1. Effect of CDs on Solution Rheology. The effects of both α- and *β*-CD on the steady shear viscosities of a 3% HASE solution are shown in parts a and b of Figure 2, respectively. With the addition of CDs, the steady shear viscosities of the polymer solutions decrease dramatically. Moreover, at about 15 mol of CD per hydrophobe, it seems that there is no further reduction in the solution viscosity for both α- and *β*-CD; however, the final viscosity obtained using α-CD is about 1 decade lower that that obtained using *β*-CD.

Similar findings are obtained from dynamic rheological measurements. Figure 3a,b demonstrates the effect of α- and *β*-CD on the frequency spectrum of the elastic (G') and viscous (G'') moduli of 3% HASE polymer solutions. The addition of either α- or *β*-CD reduces both the elastic and viscous moduli and increases their dependence on frequency. The decrease in the elastic modulus reflects a reduction in the number of active junctions between HASE polymer chains due to the deactivation of the hydrophobic groups; transient net-

Scheme 1



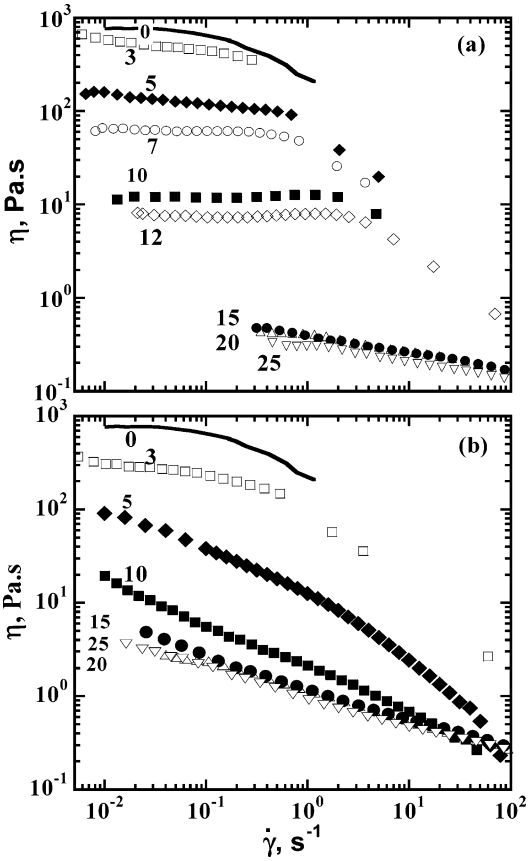


Figure 2. Effects of addition of (a) α-cyclodextrin and (b) *β*-cyclodextrin on the steady shear viscosity of 3% HASE associative polymer solution. Numbers correspond to the moles of cyclodextrin per moles of hydrophobe.

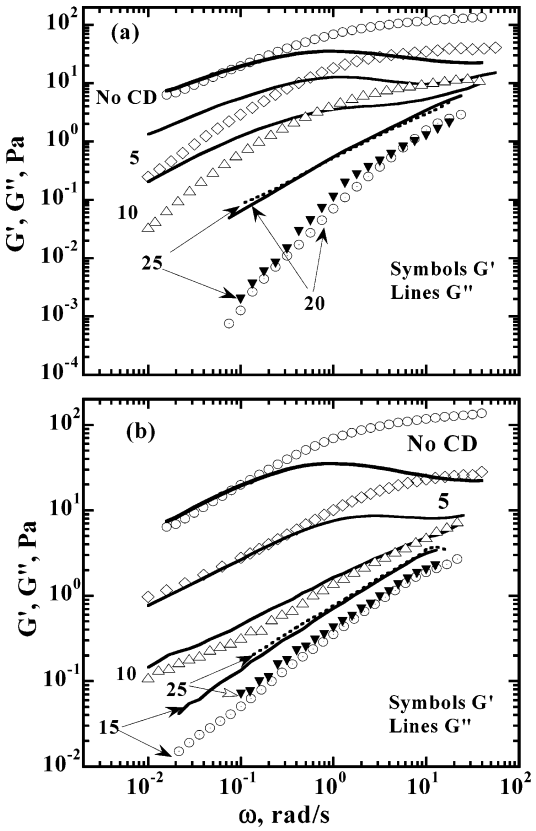


Figure 3. Effects of addition of (a) α-CD and (b) *β*-CD on the dynamic elastic (*G′*) and viscous (*G″*) moduli of a 3% HASE associative polymer solution. Numbers correspond to the moles of cyclodextrin per mole of hydrophobe.

work theory predicts that the elastic modulus is directly proportional to the number of active junctions.[45] The higher dependence on the frequency is a sign of weaker network structures due to the reduction of the number of active hydrophobes. The addition of CD above that of 15 mol of CD per mole of hydrophobe has no effect on either the level of the moduli or their dependence on frequency. Moreover, the maximum reduction in the moduli, vis-à-vis the final moduli values, is about 2 decades lower with α-CD than those obtained with *β*-CD. These results are consistent with the steady shear findings.

The decrease in solution viscoelasticity upon addition of CD suggests that the CD interacts with either the polymer backbone, the hydrophobic macromonomer, or both. To determine whether any interactions occur between the CDs and the polymer backbone, an unmodified polymer with similar structure and molecular weight to that of the HASE polymer was used. The unmodified polymer was synthesized in the same manner as the HASE polymer, but with the C_{22} hydrophobes replaced with an equivalent amount of CH_3 groups. Parts a and b of Figure 4 illustrate the effects of adding varying amounts of *β*-CD to a 1% unmodified polymer solution on both the steady shear viscosity and the dynamic moduli, respectively. We find that the addition of *β*-CD, regardless of the amount added, has no effect on the steady shear viscosity of the unmodified polymer solution or on the frequency spectrum of the dynamic moduli. This suggests that there are no interactions between the *β*-CD and the polymer backbone, and any effect of CDs on the rheology of the HASE solution occurs primarily from the interaction between the CDs and the hydrophobic segments of the HASE polymer.

3.2. Macromonomer−Cyclodextrin Complexation. An extensive array of experiments were undertaken to decipher the interactions between α- or *β*-CD with the macromonomer part of the polymer, the structure of which resembles that of a nonionic surfactant with the C_{22} alkyl group as the hydrophobic segment and the 40 EO units as the hydrophilic segment of the surfactant. As a first step, a macromonomer−CD inclusion compound (IC) was formed by mixing a 1% aqueous solution of macromonomer with a 1% aqueous solution of α- or *β*-CD. Different proportions of the solutions were used to yield different CD/macromonomer molar ratios (0.5−50). Upon addition of α-CD to the macromonomer

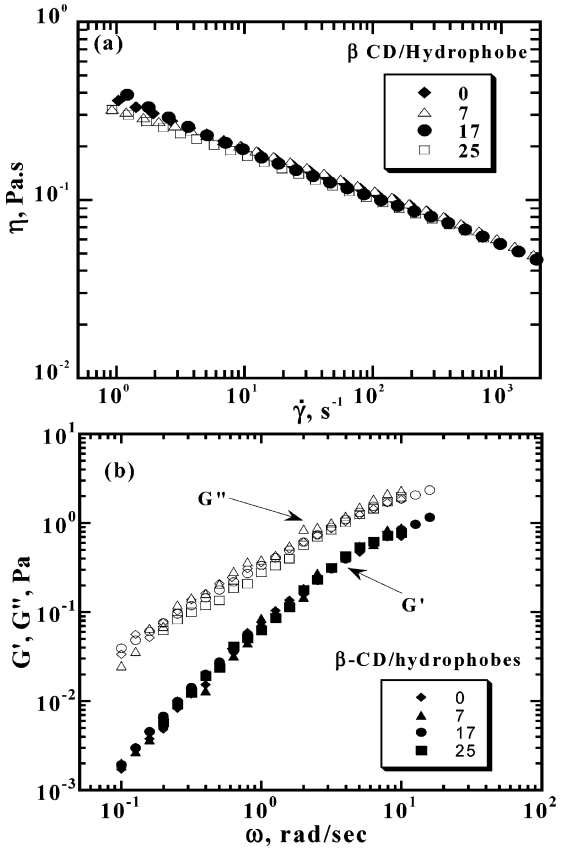


Figure 4. Effect of addition of various amounts of β-CD on the (a) steady shear viscosity and (b) dynamic elastic (G') and viscous (G'') moduli of a 1% unmodified polymer solution. This polymer is analogous to the HASE associative polymer used but with the hydrophobic groups replaced by CH_3 groups.

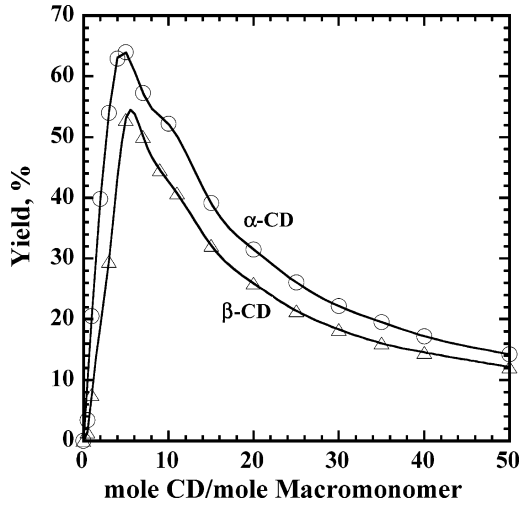


Figure 5. Yield of macromonomer−CD inclusion complexes as a function of the molar ratio of CD/macromonomer.

solution, a cloudy solution was formed immediately. In contrast, it took several hours after the addition of β-CD for the solution to become cloudy. The cloudiness of the solution is a sign of complexation between the CD and the hydrophobic macromolecule. Three days after mixing the two components, the complexes were isolated by centrifugation, filtration, washing with water, re-centrifugation, refiltration, and freeze-drying.

Figure 5 shows the IC yield as a function of the CD to macromonomer molar ratio for α-CD and β-CD. The IC yield was calculated as the weight of the dried IC divided by the total weight of the surfactant and the CD. As seen from this Figure, the IC yield increases with increasing CD to macromonomer molar ratio, reaching a maximum at a ratio of about 5 mol of CD to 1 mol of macromonomer before starting to decrease. This behavior is suggestive of the complexation process being stoichiometric. Figure 5 also reveals that α-CD gives a higher yield compared to β-CD. The difference in the yield between α and β-CD can be attributed to the difference in the annular size of the two. α-CD has a ring size of about 5.7 Å in which the hydrophobic segments of the macromonomer would have a snug fit. On the other hand, the annular size of β-CD is larger (∼7.8 Å),[46] giving the macromonomer sufficient room to move in and out. In fact, it has been reported by others, as well, that while α-CD was able to form inclusion compounds with poly(ethylene glycol) and oligoethylene, β-CD was not.[47]

A larger maximum yield value of the α-CD−macromonomer complex (∼65%) compared to the β-CD−macromonomer complex (∼54%) is consistent with the rheology data in Figures 2 and 3, which indicate that α-CD is more effective in deactivating the hydrophobic groups and reducing viscosity and modulus. However, the ratio of CD to hydrophobes where the maximum viscosity/modulus reduction occurs, 15 to 1, is different than the stoichiometric ratio, 5 to 1, where the maximum yield is obtained. This can nonetheless be easily explained if the yield is calculated on the basis of the macromonomer weight rather than weight of both the macromonomer and the cyclodextrin. If we do this, the yield increases continuously rather than passing through a maximum.

To interpret the CD/hydrophobe ratio at which the maximum reduction in viscosity/moduli occurs, we can calculate the percentage of active hydrophobes (hydrophobes that are not complexed with CD) as a function of the molar ratio of added CD/hydrophobes. This can be done following the scheme

$$m\mathrm{CD} + \mathrm{C_{22}EO_{40}}\sim \rightleftharpoons n\mathrm{CD_5}{-}(\mathrm{C_{22}EO_{40}}\sim) + (m - 5n)\mathrm{CD} + (1 - n){-}(\mathrm{C_{22}EO_{40}}\sim)$$

Using the initial molar ratio of CD/macromonomer (m), the fraction of hydrophobes complexed (n), and the yield of their complex (y), the percentage of active hydrophobes can be calculated as follows by assuming a 5/1 stoichiometric complexation ratio:

$$\text{moles of macromonomer in 1 g of feed } (F) = \frac{1}{mM_{\mathrm{CD}} + M_{\mathrm{macro}}} \text{ moles}$$

$$\text{moles of complexed macromonomer } (P) = \frac{y}{5M_{\mathrm{CD}} + M_{\mathrm{macro}}} \text{ moles}$$

$$\%\ \text{active hydrophobes} = \left(\frac{F - P}{F}\right) \times 100$$

where M_{CD} is the molecular weight of the CD and M_{macro} is the macromonomer molecular weight. The percentage of active hydrophobes based on the yield data and calculated according to this scheme is shown in Figure 6. We observe a rapid initial decrease in the percentage of active hydrophobes followed by a very slow decrease at CD/macromonomer molar ratios above 15. We also

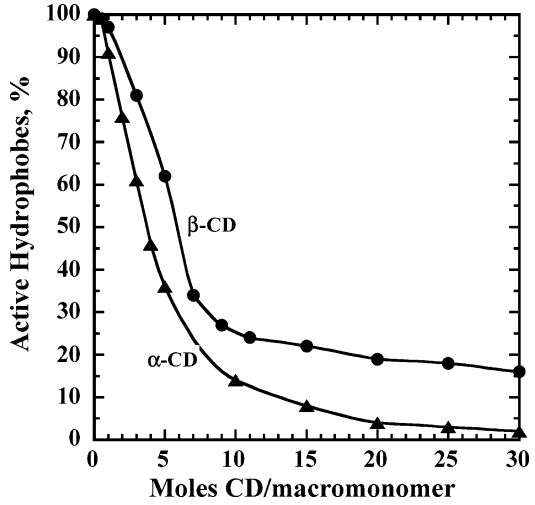


Figure 6. Effect of the CD/hydrophobe molar ratio on the percentage of active macromonomers present, calculated on the basis of the yield data in Figure 5.

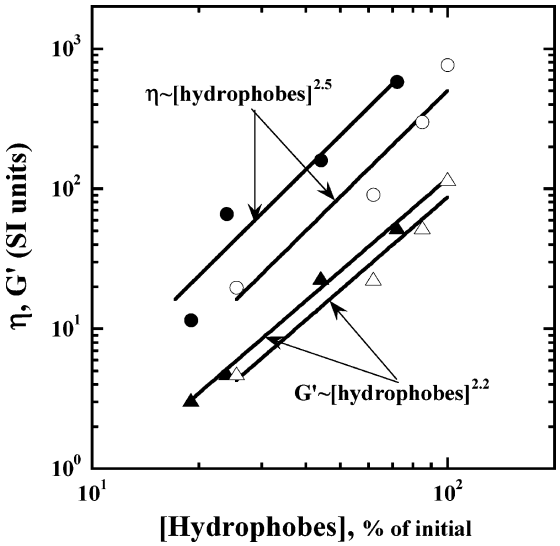


Figure 7. Effect of the active hydrophobes concentration on the steady shear viscosity at fixed shear rate 0.01 s^{-1} and elastic modulus at fixed frequency 10 rad/s. The change in the active hydrophobe concentration is due to the encapsulation with α-CD (open symbols) *β*-CD (open symbols). Active hydrophobe concentration has been calculated as in Figure 6.

find that the percentage of active hydrophobes at a CD/hydrophobe molar ratio of about 15 is less than 10% for α-CD compared to about 20% for *β*-CD. The presence of fewer active hydrophobes when using α-CD compared to *β*-CD is consistent with the enhanced effects produced by α-CD, compared to *β*-CD, on the steady shear viscosity and dynamic moduli of concentrated HASE solutions.

Calculating the number of active hydrophobes in the solution allows scaling the rheological properties with the concentration of the hydrophobic groups. Figure 7 shows scaling of the steady shear viscosity at a fixed shear rate (0.01 s^{-1}) and the elastic modulus at a fixed frequency (10 rad/s) as a function of the concentration of the hydrophobic groups. Here the change in the concentration of the hydrophobic groups is a result of their encapsulation with α- or *β*-CD. The scaling exponents for both the viscosity and the elastic modulus seem to be independent of the type of CD as the case should be. More interestingly, the scaling exponents of

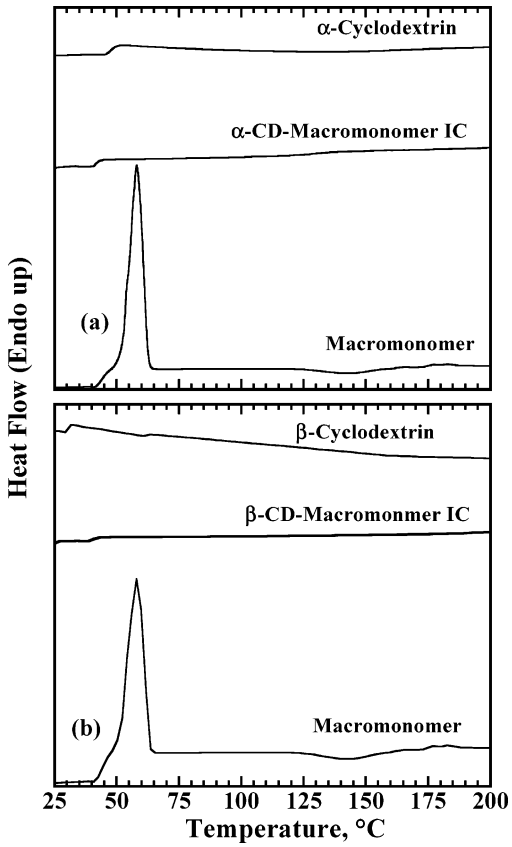


Figure 8. DSC scans of (a) α-CD, macromonomer, and their inclusion compound and (b) *β*-CD, macromonomer, and their inclusion compound. The scans shown are for the second heating taken after heating the samples at 200 °C for 3 min to erase any thermal history.

2.5 and 2.2 for the viscosity and elastic modulus, respectively, are analogous to scaling exponents observed experimentally for η or G' with polymer concentration for the same[44] or similar HASE polymers[48,49] for $c > c_e$ (the entanglement concentration). However, the 2.5 exponent for η is lower than that predicted by the sticky reptation model.[50] The agreement between the scaling of the rheological properties with the hydrophobic group concentration and with the polymer concentration reflects the strong dependence of rheology on the hydrophobic interactions. These dependences hold true as long as the polymer chains are kept in the same concentration regime. It should be noted that while the active number of the hydrophobic groups will not affect the chain entanglement, changing the polymer concentration would.

3.3. Characterization and Interaction Modes of CD−Macromonomer ICs. The DSC technique was used to confirm complex formation and to determine whether the "inclusion compound" separated via centrifugation contained any free macromonomer. Figure 8a,b shows the DSC thermograms of the macromonomer, α-CD, *β*-CD, and their ICs. The DSC thermograms of the macromonomer−α-CD and macromonomer−*β*-CD complexes show no endothermic peak where the melting point of the free macromonomer is expected. This confirms the absence of free macromonomer in the ICs.[38]

The complexation between CDs and the macromonomer also impacted the thermal stability of both CDs and the macromonomer. Figure 9a,b shows the TGA data of α-CD, *β*-CD, macromonomer, and their ICs. The TGA data for α- and *β*-CD show the onset of weight loss at

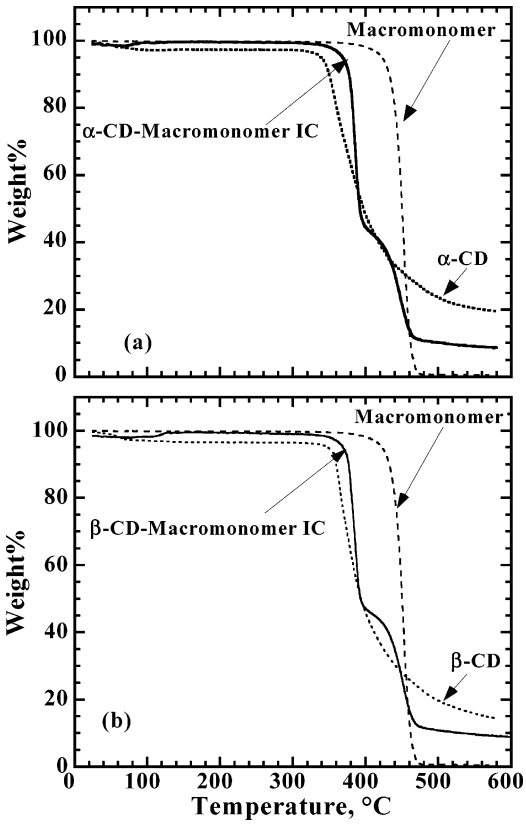


Figure 9. TGA scans for (a) α-CD, macromonomer, and their inclusion compounds and (b) *β*-CD, macromonomer, and their inclusion compounds. Samples were heated at 20 °C/min under nitrogen.

about 315 and 325 °C, respectively. Both α- and *β*-CD have a residue of about 20% at 500 °C. On the other hand, the macromonomer has a higher temperature onset for weight loss of about 400 °C and much lower residue, about 1% at 500 °C. The macromonomer−CD ICs have an onset between that of the macromonomer and the CDs (about 340 °C) and a residue of about 10% at 500° C. The improved thermal stability of the CDs due to complexation has been observed in other cyclodextrin ICs.[51,52]

Figure 9 also reveals that the macromonomer−CD ICs have a multistep decomposition profile. After the onset of weight loss, there is a rapid decomposition up to about 40% residue. This is followed by a very slow but small decomposition regime for a few wt % at about 400 °C and a final rapid decomposition until a final residue of about 10% is reached. Similar multistep profiles have been observed with 4-arm poly(ethylene glycol)−α-CD IC, 4-arm poly(ethylene glycol)−*γ*-CD IC,[52] and $C_4\pi$ C_4EO_8−α-CD IC[51] and has been attributed to the dethreading of the guest (macromonomer) during the TGA run.[51]

Further insights into the complexation between the CDs and the macromonomer have been obtained using ^{1}H NMR. Figure 10a,b shows the ^{1}H NMR spectra for α-CD, *β*-CD, the macromonomer, and their ICs recorded in DMSO-*d*6. Both the methylene protons in the alkyl C_{22} and EO_{40} in the ICs are shifted downfield as shown in Figure 11a,b. The complexation stoichiometric ratio can be obtained by comparing the integral area under the H_1 proton for the CD (4.80−4.82 ppm) with that of the methylene protons of the alkyl C_{22} from the macromonomer (1.20 ppm) in the IC spectrum. These peaks are fully resolved and free from any overlap with other peaks. The stoichiometric ratio obtained from the ^{1}H NMR data is about 5, which is consistent with that obtained from the yield data (Figure 5). Moreover, the formation of inclusion compounds is confirmed by the ^{1}H NMR spectra; a very significant shift is observed for cyclodextrin protons labeled as OH_2 and OH_3. Smaller shifts are observed for the other cyclodextrin protons and both the aliphatic and the ethylene oxide protons on the macromonomer (Figure 11).

Two intriguing issues that remain to be resolved are how much of the macromonomer is encapsulated by the CD and whether such complexation is static or dynamic in nature. Because the height of each CD bracelet is ∼7.9 Å,[46] a fully extended macromonomer would require ∼20−25 threaded CDs for complete coverage. However, as noted above, we observe a CD−macromonomer complex stoichiometry of ∼5, so only roughly one-fifth to one-fourth of the $C_{22}-EO_{40}$ chain is complexed by the CDs. Although tentative, we can offer further suggestions regarding the complexation of the macromonomer with CDs based on the ^{1}H NMR observations presented in Figures 10 and 11. Let us consider the following two scenarios: (i) all CDs are moving along and possibly threading onto and off of the $C_{22}-EO_{40}$ macromonomer chains rapidly on the NMR time scale (MHz), and (ii) some of the CDs are rapidly moving along and possibly threading and dethreading onto and off of the macromonomer as in (i), whereas the remaining CDs remain complexed with the macromonomer for longer times. It is reasonable to suppose that CDs may only thread the macromonomer chain from the C_{22} end and not from the bulky TMI (meta) end-containing methyl groups. This is because Harada et al.[53] report that the presence of dimethyl groups effectively prevents complexation of polyisobutylene with α-CD (0% yield) and *β*-CD (9% yield). Steric hindrances by methyl groups have also been reported in preventing complexation of poly(propylene glycol) with α-CD.[54] It has also been observed that disubstitution of benzene end-caps on poly(propylene glycol) prevents it from forming inclusion compounds with any type of CD.[54] Both of these observations strongly suggest that threading of the macromonomer by CDs is limited to the C_{22} end and not from the bulky TMI (meta) end. As a consequence, scenario (i) would be expected to evidence ^{1}H NMR spectra for the macromonomer−CD complexes with CH_2 protons from both the C_{22} and EO_{40} portions of the macromonomer chains resonating upfield from their positions in the free macromonomer. This appears to be the case for the C_{22} CH_2 protons, as seen in Figure 11a. However, in Figure 11b we note that the CH_2 protons belonging to the EO_{40} portion of the complexed macromonomers, while also shifted upfield from their uncomplexed resonance frequencies, exhibit even higher field shoulders on their main resonance peaks. This is suggestive of two different populations of EO_{40} CH_2 protons, with the majority of EO units experiencing rapidly moving CDs, while the smaller remaining population are complexed and covered by the CDs for a longer period of time, as described in scenario ii.

We therefore suggest, that at any given time, one-fifth to one-fourth of the $C_{22}EO_{40}$ macromonomer chain is complexed and therefore covered by CDs, with CDs able to rapidly move along most of the $C_{22}EO_{40}$ chain and possibly thread/unthread onto/from the C_{22} end. In addition, a minor population of the EO_{40} macromonomer units, which are likely those closest to the bulky TMI

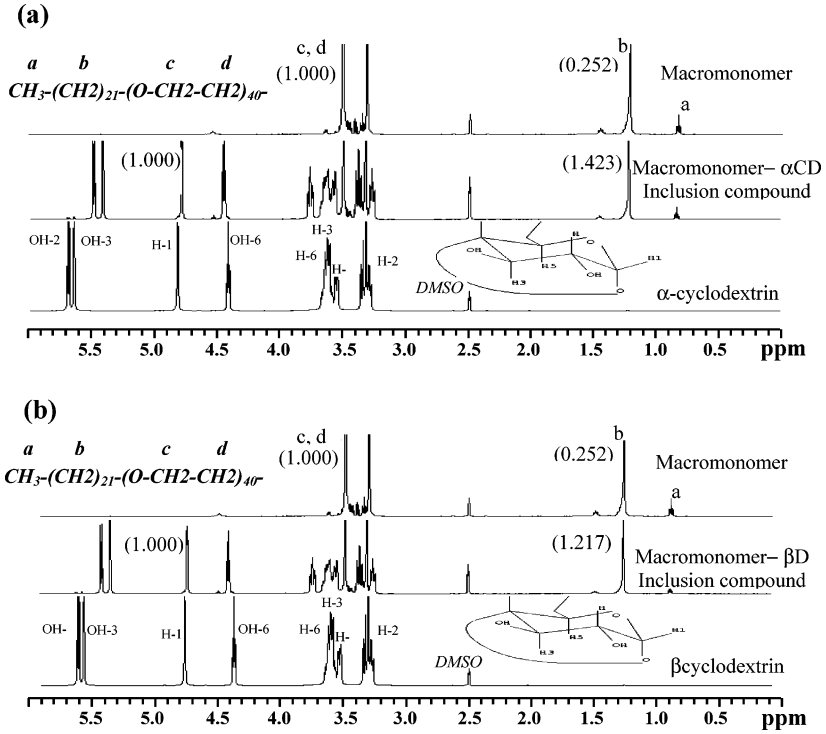


Figure 10. 500 MHz ^{1}H NMR spectra of (a) macromonomer, α-CD, and their inclusion compound and (b) macromonomer, *β*-CD, and their inclusion compound. All spectra were acquired in DMSO-*d*6.

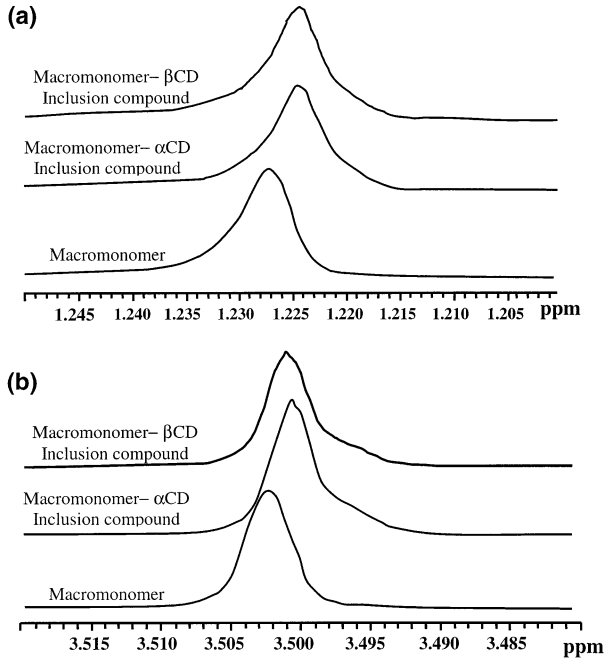


Figure 11. Part of the 500 MHz ^{1}H NMR spectra showing (a) the aliphatic CH_2 protons of the macromonomer and its inclusion compounds with α-CD and *β*-CD, and (b) the CH_2-CH_2-O protons of the macromonomer and its inclusion compound with α-CD and *β*-CD. All spectra were acquired in DMSO-*d*6.

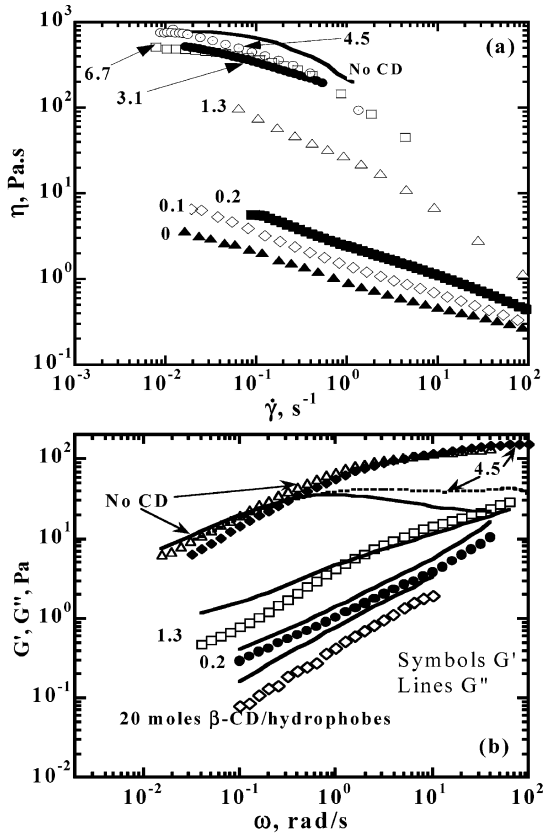


Figure 12. Effect of adding macromonomer to a 3% HASE polymer solution that has had its hydrophobic interactions deactivated by 20 mol of *β*-CD. (a) Steady shear viscosity and (b) dynamic elastic (*G*′) and viscous (*G*″) moduli of the polymer solution. Numbers in figure denotes amount of macromonomer added to the solution in mM.

(meta) end, remain complexed and covered by CDs for longer times. Future NMR relaxation studies will be necessary to substantiate the suggestions we have tentatively offered here concerning the detailed characteristics of the macromonomer−CD and HASE−CD complexes.

3.4. Recovery of Solution Rheology. In the previous sections, we presented an approach to reduce the viscoelasticity of HASE solutions through complexation with CDs to form inclusion compounds. This complexation yields a solution with a final viscosity or dynamic modulus several orders of magnitude lower than the

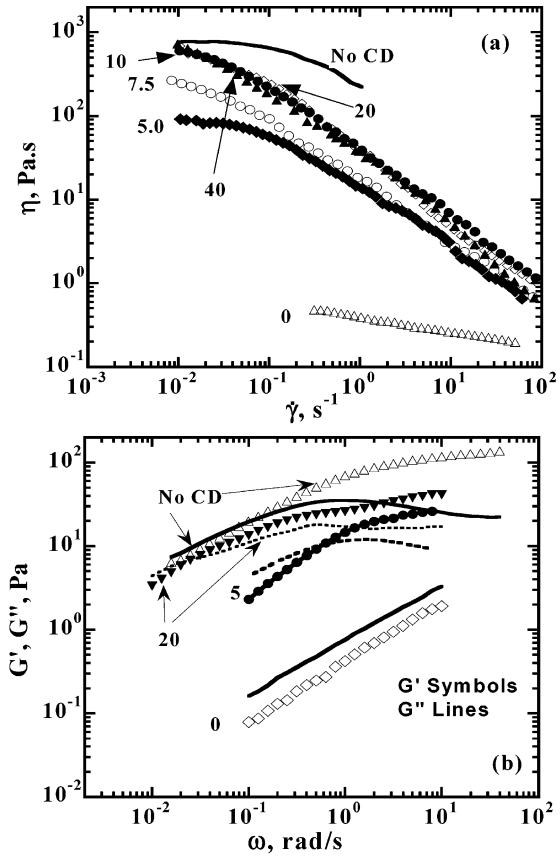


Figure 13. Effect of NP4 surfactant addition to a 3% HASE polymer solution that has had its hydrophobic groups deactivated by 20 mol of β-CD. (a) Steady shear viscosity and (b) dynamic elastic (G') and viscous (G'') moduli of the polymer solution. Numbers in figure denotes amount of NP4 surfactant added to the solution in mM.

original solution. The question that needs to be resolved is whether the HASE solution can recover its viscoelastic characteristics and to what extent. Since the macromonomer part of the HASE polymer interacts with the CDs, the addition of more macromonomers to the HASE solution that is complexed with CD would shift the equilibrium between the polymer and the CDs away from their complexed state, as CD−macromonomer complexes are formed. This, in turn, would free some of the hydrophobic groups in the polymer and enhance solution viscoelasticity.

To test this hypothesis, we have added different amounts of macromonomer to a HASE solution complexed with CD. Parts a and b of Figure 12 show the effect of macromonomer addition on the steady shear viscosity and the dynamic moduli, respectively, of a 3% HASE that was complexed with 20 mol of β-CD per hydrophobes. The addition of the macromonomer increases the solution viscosity, and a complete recovery of the zero shear viscosity is reached with about 4.5 mM macromonomer. The macromonomer addition also increases both the elastic and loss moduli and reduces their dependence on frequency. In fact, with 4.5 mM macromonomer the plateau elastic modulus reaches that of the original solution. Further surfactant additions decrease the steady and dynamic rheological properties. This decrease in the steady and dynamic rheological properties can be explained on the basis of the interaction between nonionic surfactants, CD, and HASE polymer. A portion of the macromonomer added is encapsulated by CD, a part interacts with the polymer, and the remaining stays as free macromonomer. Beyond a certain concentration, the macromonomer interacts negatively with the polymer, leading to a reduction in viscosity and viscoelastic properties. This has been reported for interaction between nonionic surfactants and HASE polymers[55−57] and can be explained as a result of the concentration of free surfactant reaching its upper critical micelle concentration (cmc).

The effect of a nonionic surfactant, nonylophenol surfactant with 4 EO units (NP4), on the steady shear viscosity and the dynamic moduli of a 3% HASE solution complexed with 20 mol of α-CD per hydrophobes was also examined and is illustrated in Figure 13a,b. With the addition of about 40 mM surfactant the zero shear viscosity is fully recovered, but the viscosity profile is different than that of the original solution. With added surfactant, the solution shows a higher degree of shear thinning compared to the original solution. Similar findings are also obtained from the dynamic measurements, with an increase in the level of the dynamic moduli and lower dependence on frequency with the addition of NP4 surfactant.

Despite the recovery of the zero shear viscosity and the plateau modulus, there are, however, differences in the steady shear profile and dynamic spectrum of the recovered and the original solutions. The differences that are observed in either the macromonomer or NP4 surfactant cases likely are a result of the fact that both the added macromonomer and NP4 also interact directly with the HASE polymer.[48,55−57]

4. Conclusions

The use of inclusion compounds and surfactant provides a viable approach to control the hydrophobic associations and concomitant solution rheology of HASE polymers. The complexation of the normally associating hydrophobic macromonomer components with α- and β-cyclodextrins reduces the steady shear viscosity and dynamic moduli of the HASE solutions by several orders of magnitude. Correlation of the viscosity and elastic modulus with hydrophobe concentration reveal power-law dependences with scaling exponents analogous to that observed with respect to polymer concentration. Furthermore, it is possible to reversibly recover the high viscoelastic characteristics of HASE solutions containing cyclodextrins by treatment with surfactants that compete with the hydrophobic portions of HASE for complexation with the cyclodextrins. As a consequence, cyclodextrins and surfactants in combination can be judiciously employed to lower the viscoelasticity of HASE solutions during processing, while subsequently recovering the high viscosity and viscoelastic properties that are sought in their applications.

Acknowledgment. The authors gratefully acknowledge the support and help of Dow Chemical Co., UCAR Emulsions, for providing various samples for this study.

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MA034173V