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Single Chain Characterization of Hydrophobically Modified Polyelectrolytes Using Cyclodextrin/Hydrophobe Complexes

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ABSTRACT: The characterization of hydrophobically modified alkali-soluble emulsions (HASE) using conventional techniques such as gel permeation chromatography or static light scattering is difficult because of the hydrophobic association. Two different approaches were taken to prevent the hydrophobic association of HASE polymers in aqueous solution: (1) hydrolyze the polymer to dislodge the hydrophobic constituents, and (2) use methyl-β-cyclodextrin, which has a hydrophobic cavity and a hydrophilic outer shell, to shield the hydrophobes from associating. Using these two approaches, the molecular weight (M_w), hydrodynamic radius (R_h), and radius of gyration (R_g) of single chains of these polymers were determined using gel permeation chromatography (GPC) and dynamic (DLS) and static (SLS) light scattering techniques. The molecular weight of the control polymer (i.e., polymers with similar composition but with no hydrophobe) is found to be $\sim 7.0 \times 10^5$ g/mol. The molecular weights of these polymers with C8, C16, and C20 hydrophobes were found to be $\sim 2.0 \times 10^5$ g/mol. By comparing GPC and SLS results, we were able to determine that, except for one chemical site, branching or grafting did not occur in the polymer chain during synthesis.

Introduction

Water-soluble hydrophobically modified polymers, also known as associative thickeners (AT), are being used as rheology modifiers primarily in the paint industry.[1] Hydrophobically modified alkali-soluble emulsion (HASE) polymers are a class of AT that is of increasing interest due to their low cost of production and ease of handling.[1−6] Typically, HASE polymers are synthesized by emulsion polymerization of monomers containing (1) carboxylic acid groups, ionized at pH $\geq$ 7, (2) acrylate groups, spacers between the charged groups, and (3) "macromonomer" segments that included pendent ethylene oxide terminated by hydrophobic groups. At low pH, the carboxylic acid groups are not ionized, and the polymer is insoluble in water. With an increase in pH, the carboxylic acid groups start to ionize, leading to solubilization of the polymers in water.[1,3]

The thickening efficiency of HASE polymers in solutions can derive from the combination of (1) the expansion of the high molecular weight backbone at high pH (due to electrostatic repulsion between ionized acid groups) and (2) the association between hydrophobes. The latter is particularly effective when the association is intermolecular.[1−4] An understanding of the aggregation mechanism and the interactions between the aggregates can lead to an improved control of the rheological properties of HASE polymers in their applications.

Several rheological studies have been conducted to understand the aggregation behavior of the HASE polymers. Jenkins et al. reported that HASE polymers showed dramatic increase in solution viscosity over the pH range of 6.0−7.5, beyond which the viscosity remained approximately constant.[1] English et al. studied the dependence of viscosity of HASE polymers on concentration at pH $\sim$ 9.0 using rheological measurements.[2] Their measurements suggested that there was more intermolecular association between the hydrophobic constituents at a higher concentration ($>$0.6 g/dL) than at a lower concentration. Tirtaatmadja et al. studied the dependence of viscosity of HASE polymers on the hydrophobe size and found that the strength of the hydrophobic association of HASE polymers increases with increasing hydrophobe size.[3,4] Kumacheva et al. used fluorescence techniques to study the pH-dependent aggregation behaviors of HASE polymers.[2] Their study found that HASE polymers showed intramolecular association at low pH ($<$6) and showed intermolecular association at higher pH. However, since the molecular weight and the chain architecture were not determined, much interpretation of these results has to be based on assumptions of these parameters. Characterizations of the single molecular parameters of these polymers are warranted.

In this paper, the determinations of the molecular weight (M_w) of a single molecule and the chain architecture of HASE polymers are presented. The hydrophobic association makes it difficult to use conventional techniques such as static light scattering or gel permeation chromatography in water to determine M_w. Several approaches can be taken to prevent this hydrophobic association while using these techniques to determine M_w. For example, one can use a suitable organic solvent or cosolvent to reduce the hydrophobic association.[1,7] However, organic solvents or cosolvents do not prevent association completely, and therefore interpreting light scattering data can become complicated.[1,7] Alternatively, one might attempt to use surfactant molecules to shield the hydrophobes from associating. However, at low concentrations, surfactant molecules can promote polymer association, and at high concentrations, the sur-

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factant molecules themselves can form aggregates. The third possible approach is to dislodge the hydrophobes by hydrolyzing the polymers. However, hydrolysis of the polymer can sometimes modify the polymer chains by cleaving chain branching or grafting that can occur during synthesis. A fourth option is to use cyclodextrin, a molecule with a hydrophobic cavity and a hydrophilic outer shell, to shield the hydrophobes. The last method was first demonstrated by Rohm and Haas Company to reduce hydrophobic interaction of associative thickeners.[8,9] There is no known surface activities of cyclodextrin molecules, and these molecules do not aggregate by themselves. Thus, when mixed with hydrophobically modified associative polymers, cyclodextrin is not expected to change the characteristics of the polymer molecule other than preventing the hydrophobic association.

In this study, we took a combination of the last two approaches. (1) The molecular weight (M_w), radius of gyration (R_g), and hydrodynamic radius (R_h) of single HASE polymer molecules at high pH were determined by using static (SLS) and dynamic (DLS) light scattering techniques after a majority of the hydrophobes were capped by methyl-β-cyclodextrin (m-β-CD) molecules. To determine the amount of m-β-CD molecules needed to cap the majority of the hydrophobes of HASE polymers, a titration of m-β-CD against hydrophobes was performed. (2) The same HASE polymers were hydrolyzed and characterized by aqueous GPC. The hydrolyzed samples were further investigated by light scattering techniques in this study.

One of the two tasks of the HASE polymer architecture study is to determine whether and where the branching or grafting has occurred in the chain during synthesis. The degree of branching or grafting primarily depends on the rates of hydrogen abstraction from the polymer by the initiator or propagating radicals, which is often directly related to the thermodynamic stability of the resulting radicals. The local structure of the monomer units along the chain can also contribute to the thermodynamic stability of the resulting radicals and make them favorable branching or grafting sites. For example, the abstraction of the tertiary hydrogen in ethyl acrylate (indicated by arrow "1" in Figure 1) can form a thermodynamically stable radical and is the most probable branching or grafting site.[10,11] Likewise, hydrogen abstraction from the carbon adjacent to the ester group, indicated by arrows "2" and "3" in Figure 1, can also participate in branching or grafting. In this paper, the discussion of the molecular architecture is focused on the possibilities of branching or grafting occurring from the sites indicated by arrows "1", "2", and "3" in Figure 1. The second task was to determine the randomness of the EA segments (i.e., if the EA segments are blocky).[1] Results from the aqueous GPC and the light scattering measurements of the hydrolyzed samples and the light scattering measurements of the nonhydrolyzed samples were compared to provide consistent interpretations of the architectural characteristics of these HASE polymers.

Experimental Section

Materials. The HASE polymers (Union Carbide, Cary, NC) were synthesized by emulsion copolymerization of a carboxylic acid monomer, a "nonassociative" acrylate monomer spacer, and an associative "macromonomer". Details of the synthesis procedure and characterization of the polymers studied were reported before by Jenkins et al.[3] Briefly, a "macromonomer" was first prepared by ethoxylation to 35 mol of an alcohol of appropriate hydrophobe length, followed by reaction with α,α-dimethyl-*m*-isopropenylbenzyl isocyanate (TMI). The macromonomer was then reacted with appropriate amounts of methacrylic acid (MAA) and ethyl acrylate (EA) in a conventional seeded semicontinuous emulsion polymerization under starved conditions. Carbon 13 and proton NMR showed that the composition of the final polymer was the same as the composition of the monomer feed used in the synthesis of the polymers.[1] The chemical compositions of these HASE polymers are listed in Table 1.

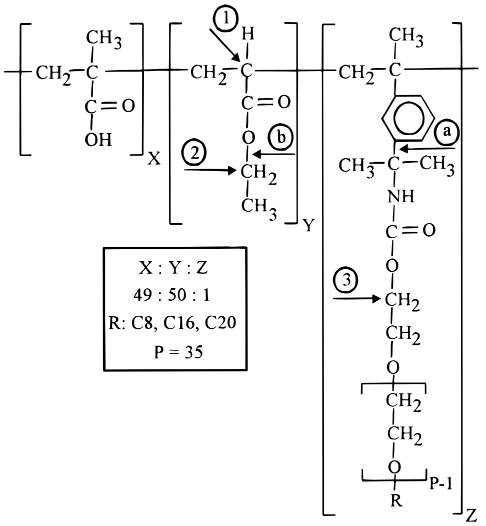

Figure 1. Target molecular architecture of HASE polymer used in this study.[3] Arrows "1", "2", and "3" indicate possible sites for branching or grafting to occur during synthesis. Arrows "a" and "b" indicate where the chain could be cleaved during hydrolysis.

Table 1. Chemical Composition of HASE Polymers

polymer designation	hydrophobe formulas	MAA:EA:MM	
		weight fraction	molar fraction
RDJ31-0	[a]	45.00:55.00:0.0	48.76:51.24:0.00
RDJ31-8	C_8H_{17}	39.10:46.39:14.51	49.00:50.00:1.00
RDJ31-16	$C_{16}H_{33}$	38.40:45.56:16.04	49.06:50.04:0.90
RDJ31-20	$C_{20}H_{41}$	38.14:45.25:16.61	49.06:50.04:0.90

[a] No hydrophobe.

The original HASE samples are latex particles in aqueous suspension at pH 5. The hydrodynamic radii, R_h, of the latex particles was ∼55.0 ± 3.0 nm determined by dynamic light scattering measurements of diluted suspensions.

Sample Preparation. The samples used for light scattering studies were dialyzed with deionized water for 3 weeks. The cellulose dialysis membranes (Spectra/Por) used were specified to retaine M_w above 25 000 Da. The dialyzed latex suspensions were then diluted to ∼2.0%, by weight, and filtered using 1.0 μm pore size glass-fiber microfilters and 0.45 μm pore size Nalgene microfilters. The HASE polymers were then ionized to pH 9 using filtered (0.2 μm pore size Nalgene filters) 0.1 M KOH solution. A fraction of the filtered polymer solution was evaporated to determine its concentration. The remaining solutions of the ionized polymers were then further diluted using filtered water, filtered KOH solution, and 0.1 M KCl solution (0.2 μm pore size Nalgene filters) to prepare a stock solution of 1.00%, by weight, at pH 9. All of the final samples were made by diluting the stock polymer solution with filtered water, KOH, and KCl; the purpose was to keep the pH of the solution at 9 and to keep the salt concentration the same for all the samples. Except for the dialysis, the sample preparation was conducted in a glovebox under a constant flow of dry, filtered air (0.2 μm Gelman Sciences online filter).

Methyl-β-cyclodextrin (Sigma Chemical Company, St. Louis, MO) was used in the complexation titration experiment. A

Table 2. Summary of Results from Two Different Batches of Samples with Different Ratios of the Number of Methyl-β-CD Molecules to the Number of Hydrophobes[a]

	nonhydrolyzed HASE					
	~44% capping (assuming $k_a = 100$ M^{-1})			maximum capping (~90%)		
	SLS		DLS	SLS		DLS
samples	$M_w \times 10^4$ (g/mol)	R_g (large) (nm)	R_h (large) (nm)	$M_w \times 10^4$ (g/mol)	R_g (nm)	R_h (nm)
RDJ31-0						
RDJ31-8	296 ± 12.4	88.0 ± 9.0	96.0 ± 5.2	21.2 ± 1.5	12.0 ± 1.5	17 ± 1.0
RDJ31-16	514 ± 15	113.0 ± 11.4	131.0 ± 7.1	23.6 ± 1.3	11.3 ± 1.4	16 ± 1.2
RDJ31-20	437 ± 12.8	121.0 ± 12.0	138.0 ± 7.5	18.2 ± 1.8	12.0 ± 2.0	14 ± 0.7

[a] In one batch, the ratio was 127:1 (~44% capping), and in the other batch the ratio was the maximum ratio obtained from the methyl-β-CD titration experiment (~90% capping).

Table 3. Summary of Results from GPC, DLS, and SLS

	hydrolyzed HASE				nonhydrolyzed HASE (maximum capping)		
	GPC	SLS		DLS	SLS		DLS
samples	$M_w \times 10^4$ (g/mol)	$M_w \times 10^4$ (g/mol)	R_g (nm)	R_h (nm)	$M_w \times 10^4$ (g/mol)	R_g (nm)	R_h (nm)
RDJ31-0	56.9 ± 0.57				73.1 ± 5.7	18.0 ± 2.0	23 ± 1.2
RDJ31-8	14.7 ± 1.63				21.2 ± 1.5	12.0 ± 1.5	17 ± 1.0
RDJ31-16	14.4 ± 0.7	16.7 ± 1.2	16.0 ± 1.5	19.0 ± 1.0	23.6 ± 1.3	11.3 ± 1.4	16 ± 1.2
RDJ31-20	8.1 ± 0.8				18.2 ± 1.8	12.0 ± 2.0	14 ± 0.7

stock solution of 0.5 M m-β-CD was prepared by dissolving m-β-CD in filtered solutions of water, 0.1 M KCl, and KOH (pH 9). Varying amounts of m-β-CD stock solution were added to a fixed amount of polymer. (The concentration of polymer solution was 8.0×10^{-4} g/mL, and the calculated moles of the hydrophobes was 7.1×10^{-8} mol.)

To prepare the hydrolyzed HASE polymers solutions for light scattering, a 1.0 wt % stock solution of hydrolyzed RDJ31-16 was prepared by dissolving dried and clean hydrolyzed polymers in filtered solution of water, 0.1 M KCl, and KOH (pH 9). The same filtration procedure for the light scattering studies of nonhydrolyzed HASE polymers was followed here. The polymer concentration range was between 7×10^{-4} and 9×10^{-4} g/mL with an increment of 5×10^{-5} g/mL. The samples were allowed to equilibrate for at least 24 h before use.

Aqueous GPC Measurements. Gel permeation chromatography was used to determine M_w of the hydrolyzed HASE polymers. The hydrolyzed HASE polymers were by hydrolysis at high pH and temperature, in which the hydrophobes of these polymers were dislodged. Because the hydrolysis of the ethyl acrylate group in the polymers would produce an equivalence of acrylic acids, a 50−50 random copolymer of MAA and acrylic acid was used as calibration standard in GPC. The GPC results for all four samples and the SLS results obtained from the hydrolyzed RDJ31-16 are summarized in Table 3.

Light Scattering Measurements (SLS and DLS). A goniometer (BI-200SM) and a digital correlator (BI2030AT), both from Brookhaven Instruments Corporation, were used for both DLS and SLS. A vertically polarized beam of an argon ion laser (Spectra Physics 2025) at the wavelength $\lambda_0 = 488$ nm was used as the light source. No polarization analyzer was used in front of the detector. The temperature of the sample cell chamber was kept at 25 ± 0.1 °C by using a water bath (Fisher Scientific model 9100).

The dynamic light scattering technique was used to determine the hydrodynamic size of a single molecule and the aggregates of HASE polymers in solution.[12,13] Standard analysis methods such as the double-exponential sampling method, exponential sampling method, second-order cumulant method, and CONTIN (Brookhaven Instruments Corporation, version 6.6) were used to determine the particle radius.[12,13] The DLS data were collected at scattering angles of 45° and 135°. The data analysis in all four different methods resulted in consistent values of R_h for all the HASE polymer solutions. The results presented in this paper were those obtained by analyzing the data using the CONTIN method.

The static light scattering technique was used to determine the molecular weights and radii of gyration of the single molecule and the aggregates of HASE polymers. The data analysis of SLS was done by using the Zimm equation:[14−16]

$$\frac{Kc}{\Delta I(\theta)} = \left(\frac{1}{M_w} + 2A_2c\right)\left(1 + \frac{16\pi^2 n_0^2}{3\lambda_0^2}\overline{\langle R_g^2\rangle_z} \sin^2\left(\frac{\theta}{2}\right)\right)$$

which relates excess scattering from the polymer solution $\Delta I(\theta)$ to the polymer concentration c and the scattering angle θ to determine M_w, R_g, and the modified second virial coefficient A_2. The constant K accounts for the experimental parameters such as the scattering volume, V, the distance from the scattering center to the detector, r, and the increment in refractive index with concentration dn/dc:

$$K = \frac{4\pi^2 n_0^2}{\lambda_0^4 N_A}\left(\frac{dn}{dc}\right)^2 \frac{I_0 V}{r^2}$$

where n_0 is the solvent refractive index, λ_0 is the wavelength of the incident light, N_A is the Avogadro number, and I_0 is the incident laser intensity. Calibration using toluene, for which the reported Raleigh ratio is $r^2 I(90°)/VI_0 = 4.0 \times 10^{-5}$ cm^{-1}, determined V/r^2. To analyze SLS data, $\Delta I(\theta)$ was measured at several concentrations and angles. The usual Zimm plot was then constructed by plotting $Kc/\Delta I(\theta)$ as a function of $\sin^2(\theta/2) + k'c$, as shown in Figure 2, where k' is an arbitration constant. Extrapolating $Kc/\Delta I(\theta)$ to zero angle or zero concentration determined M_w, R_g, and A_2.

Both R_h and R_g and the molecular weight of HASE polymers in the presence of m-β-CD were determined by DLS and SLS. In applying the standard Zimm plot, one usually assumes that polymer molecules do not aggregate with increasing concentration.[16−18] In reality, however, even with maintaining the same ratio of the number of m-β-CD to the number of hydrophobes, changing the polymer concentration can change the fraction of capped hydrophobes and, therefore, can change the size of the aggregates. As a compromise, the change of polymer aggregation with concentration was kept to a minimum by working in a relatively small concentration range in which R_h, measured by DLS, did not change with concentration. Thus, the assumption made in our Zimm analysis was that the aggregates did not change significantly in this concentration range as long as the R_h remained the same.

The SLS measurements were performed at scattering angles between 15° and 150°, at 5° intervals. However, in the final analysis, data obtained between the scattering angles 15° and 25° were removed due to large fluctuations in the scattering intensity at those angles. The increments in refractive indices

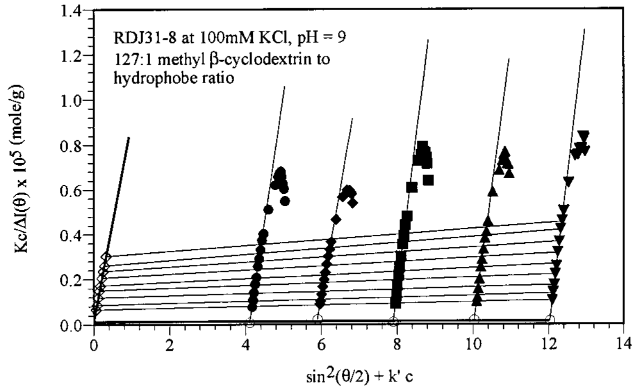

Figure 2. Zimm plot of HASE polymer with C8 hydrophobes (RDJ31-8) at pH 9, at the number of methyl-*β*-cyclodextrin molecules to the number of hydrophobes ratio = 127:1, and at 25 °C. The solid symbols represent actual data taken at several concentration and scattering angles. The hollow symbols represent the extrapolated values at zero degree angle and zero concentration.

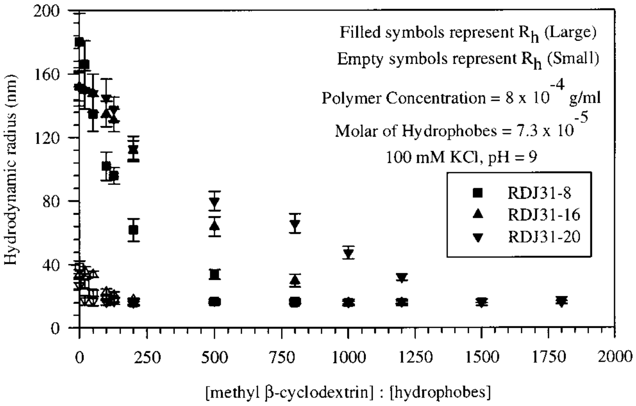

Figure 3. Hydrodynamic radii of the aggregates of the HASE polymers as a function of [methyl *β*-CD]: [hydrophobe] ratio. The polymer concentration is 8 × 10^{-4} g/mL. Note that the bimodal distributions for these polymers became a single mode above a certain ratio.

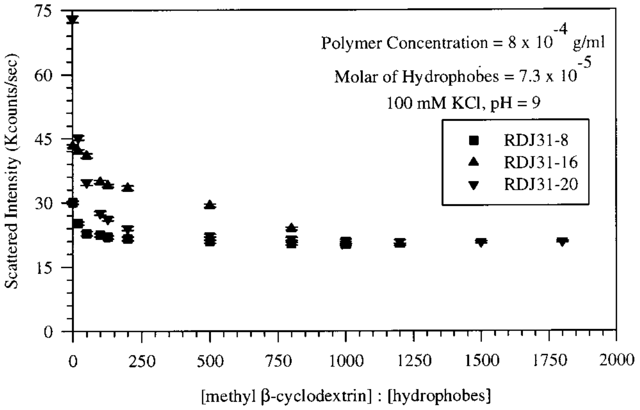

Figure 4. At the same conditions as that shown in Figure 3, the scattered intensity from the aggregates decreased as methyl *β*-CD was increased to the polymer solution. Note also that the scattering intensities leveled off at similar m-*β*-CD concentration where bimodal distributions became single mode.

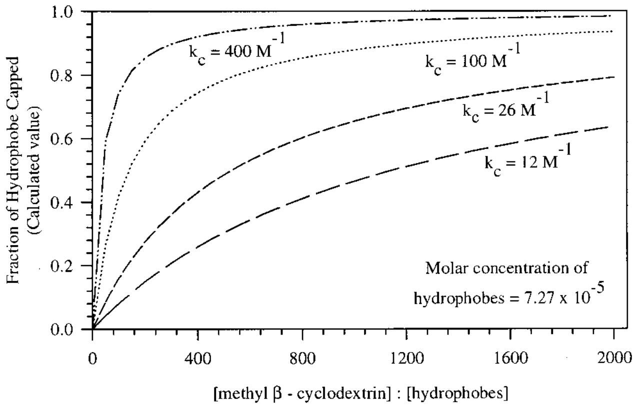

Figure 5. With the assumed 1:1 association between the hydrophobes and m-*β*-CD, the fraction of hydrophobes capped by m-*β*-CD molecules was calculated for different association constants and with a fixed molar concentration of hydrophobes at 7.27 × 10^{-5} M.

(*dn*/d*c*) of these polymers were measured using a differential refractometer (Laboratory Data Control Refractomonitor IV). At pH 9 and in 0.1 M KCl in water, *dn*/d*c* was measured to be 0.173, 0.147, 0.140, and 0.146 mL/mg for RDJ31-0, RDJ31-8, RDJ31-16, and RDJ31-20, respectively. The errors in the *dn*/d*c* measurements were estimated to be about 5%. The errors in all the other measurements shown below were determined from multiple measurements.

Results and Discussion

The m-*β*-CD Complexation Titration. The purpose of the complexation titration experiment was to determine the amount of m-*β*-CD needed to cap the majority of the hydrophobes on the HASE polymers, thus suppressing the hydrophobic association. The assumption here is that, once most of the hydrophobes were capped, the HASE polymers could not form interchain aggregates. Varying amounts of m-*β*-CD were added to a fixed amount of polymer (8.0 × 10^{-4} g/mL) in titration. DLS was used to monitor the R_h of the aggregates formed by HASE polymers. For RDJ31-0, the polymer without macromonomers, and thus no hydrophobes, data show that addition of m-*β*-CD did not change its R_h. As shown in Figure 3, without the addition of m-*β*-CD, the other three HASE polymers formed bimodal aggregates in 8.0 × 10^{-4} g/mL solutions. As the m-*β*-CD concentration was increased, the R_h of both aggregate groups decreased, and eventually only single modes were present. Presumably, the single mode was entities formed by individual, single HASE molecules. This assumption was supported by the fact that, at the m-*β*-CD concentrations where single modes started to appear, the total scattering intensities from the aggregates also started to level off, as shown in Figure 4. The amount of m-*β*-CD needed to suppress the interchain association varied with hydrophobe size, presumably due to the differences in the association constants between the different hydrophobes with the m-*β*-CD molecules.

Because of the multifunctionality of the HASE polymers, it is difficult to quantify the capping association constant from the R_h and scattering intensity data. However, with a reasonable assumption, estimates of association constant can be obtained. Assuming a first-order association, i.e., one m-*β*-CD molecule couples to one hydrophobe, we can calculate the fraction of hydrophobes capped as a function of the molar ratio of m-*β*-CD to hydrophobes. The results, calculated at a constant hydrophobe concentration (7.27 × 10^{-5} M) for different association constants, are shown in Figure 5. Assuming that ~90% of the hydrophobes are needed to be capped in order to completely suppress interchain associations, we can see, again from Figure 5, that the association constant k_a falls in the range of 100 and 400 M^{-1} with

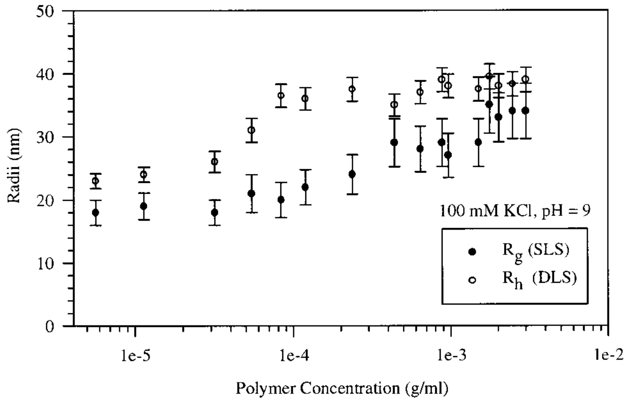

Figure 6. Hydrodynamic radius of RDJ31-0 measured as a function of polymer concentration (100 mM KCl). The radius increased at high polymer concentrations, indicating aggregation.

the larger k_a for RDJ31-20 and the smaller k_a for RDJ31-8. Similar values of k_a for polymers with similar hydrophobes and m-β-CD were reported by others.[19] We did look into the possibility of analyzing our scattering data with a hope to obtain the second virial coefficient as the hydrophobic association was decreasing; however, our data could not provide an unambiguous trend for A_2.

Molecular Weight of a Single Molecule (M_w). Data from multiple measurements of various experiments are used to determine the molecular weight of a single molecule. In the case of RDJ31-0, the hydrodynamic radius, obtained from DLS, did not change with the addition of the m-β-CD. The polymer concentration-dependent study showed that the hydrodynamic radius did not change when polymer concentrations were below 5×10^{-5} g/mL; however, the hydrodynamic radius did increase above that concentration, as shown in Figure 6. Several samples of RDJ31-0 were prepared between the polymer concentration range of 1×10^{-5} and 3×10^{-5} g/mL with an increment of 5×10^{-6} g/mL for the SLS measurements. The SLS results of RDJ31-0 indicate that its molecular weight is $73.1 \pm 5.7 \times 10^4$ g/mol and $R_g = 18.0 \pm 2.0$ nm, shown in Table 3.

For all other HASE polymers, two batches of samples were prepared with polymer concentrations ranging between 7×10^{-4} and 9×10^{-4} g/mL with an increment of 5×10^{-5} g/mL for SLS measurements. The number of m-β-CD molecules to the number of hydrophobes ratio was kept constant between the samples within each batch. In one batch, the ratio was 127:1, and in the other batch, the ratio was the maximum ratio obtained from m-β-CD titration experiments; see Figures 3 and 4. The reason for preparing two different batches of samples was to verify that the mass of an aggregate decreased with an increase in the m-β-CD concentration. The Zimm plot in Figure 2 shows the results for RDJ31-8 at the ratio of 127:1. The results from DLS and SLS measurements on these two batches, listed in Table 2, show that, with the exception of RDJ31-0, the mass of the aggregate and the radii decreased with the addition of m-β-CD. The results of GPC, DLS, and SLS from the hydrolyzed samples and the results of DLS and SLS from the nonhydrolyzed samples at the maximum m-β-CD to hydrophobe ratios are listed in Table 3.

To compare the GPC results of the hydrolyzed samples and the SLS results of the nonhydrolyzed samples with maximum capping, it is necessary to consider the molecular weight of the ethyl groups in the EA segments cleaved during hydrolysis. The molecular weight loss due to cleaving of the "macromonomer" segments is negligible, because the molar ratio of "macromonomer" in the polymer chain is small (1%).[1] Since the molar ratios of different components of each HASE polymers are known, the number of EA segments in each HASE polymers can be determined using M_w from either GPC or SLS measurements. The mass of the cleaved ethyl groups for RDJ31-0 is ~100 000 g/mol, while for other HASE polymers the cleaved amount is ~25 000 g/mol. After considering the contribution of the cleaved ethyl groups to M_w, we see the GPC and SLS results for all the HASE polymers, shown in Table 3, are within experimental error.

To summarize, the molecular weights M_w of the HASE polymers with hydrophobes RDJ31-8, RDJ31-16, and RDJ31-20 are found to be similar among themselves, $\sim 2 \times 10^5$ g/mol, but very different from that of RDJ31-0.

Single Chain Architecture. The combined GPC and light scattering results provided information on the molecular architecture of HASE polymers. As shown by arrows "1", "2", and "3" in Figure 1, there are possible sites for branching or grafting to occur during synthesis of HASE polymers. The similarity in M_w of the hydrolyzed and the nonhydrolyzed RDJ31-0 suggested that branching did not occur at the methane group in the ethyl segments, indicated by arrow "2" in Figure 1. The similarity of M_w of all other HASE polymers, hydrolyzed and nonhydrolyzed, also suggested that branching did not occur from the methane group in the "macromonomer" segments indicated by arrow "3" in Figure 1. However, this present study cannot determine whether branching or grafting occurred at the methine group in the ethyl acrylate segments denoted by arrow "1" in Figure 1.

Furthermore, the evidence of polymer aggregation of RDJ31-0 at high concentration and moderate salt (≥0.05 M KCl), see Figure 6, leads us to speculate that the aggregates were formed by either the hydrophobic EA segments or the methyl groups ($-CH_3$) groups in the MAA segments and that the EA segments were blocky. A further evidence of the blockiness of the EA segments was observed in a different study, where, despite the negative charges on the chain, RDJ31-0 adsorbed onto hydrophobic and negatively charged polystyrene (PS) latex at high polymer concentration and moderate salt (≥0.05 M KCl). Further adsorption study of the hydrolyzed RDJ31-0 (hydrolysis of RDJ31-0 transformed its EA segments into acrylic acid segments by replacing the ethyl groups with a hydrogen atom) onto PS latex is underway to verify the blockiness of the EA segments. The work on association and adsorption will be published elsewhere.

Conclusion

Experimental study to characterize single HASE polymer molecules was carried out by aqueous GPC, DLS, and SLS techniques. To determine the molecular weight (M_w) of a single polymer molecule, two different approaches were used to prevent the hydrophobic association of HASE polymers in solution. In one approach, the polymers were hydrolyzed at a very high pH and high temperature to dislodge the hydrophobic constituents. In the second approach, methyl-β-cyclodextrin was used to shield the hydrophobes from associating. The two approaches yield consistent results. The molecular weight of RDJ31-0 was found to be ~7.0 × 10^5 g/mol. The molecular weight of RDJ31-8, RDJ31-16, and RDJ31-20 was found to be ~2.0 × 10^5 g/mol. Neither group of polymers showed signs of branching or grafting, except for the uncertainty at a site in ethyl acrylate groups (indicated by arrow "1" in Figure 1). Moreover, aggregation of RDJ31-0, the one without pendent hydrophobes, points to the possibility of blocky EA along the chain backbone. To the best of our knowledge, this is probably the first application of methyl-β-cyclodextrin to determine the molecular weight of a single polymer chain. The approach of shielding the hydrophobes by cyclodextrin molecules can be applied to any polymer molecule with hydrophobic pendent groups.

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