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Interaction between Hydrophobically Modified 2-Hydroxyethyl Cellulose and Sodium Dodecyl Sulfate Studied by Viscometry and Two-Dimensional NOE NMR Spectroscopy

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S Supporting Information

ABSTRACT: Interaction between an anionic surfactant, sodium dodecyl sulfate (SDS), and a nonionic polymer, 2-hydroxyethyl cellulose (HEC) hydrophobically modified with benzoyl chloride (bmHEC), is studied by viscometry and two-dimensional nuclear Overhauser effect NMR spectroscopy (2D NOESY) in a semidilute regime of bmHEC. The hydrophobicity of bmHEC was varied with different substitution of benzoyl group to HEC macromolecules. In general, the low-shear viscosity of 1 wt % bmHEC aqueous solution is increased with added SDS surfactant having concentration from 0 to 0.5 wt %, and then decreased significantly with a further addition of surfactant to 3 wt %. The activation energy of transient network formation in 1 wt % bmHEC aqueous solution present with SDS surfactant is found to be dependent with SDS concentration, which varies from 32.7 to 69.80 kJ/mol. The maximum activation energy takes place when 0.5 wt % SDS is added, which coincides with that of the maximal viscosity. The 2D NOESY displays that the surfactants actually interact with bmHEC not only on the hydrophobes, namely benzoyl groups, but also the polymer backbone, i.e., glucose units. In contrast, no interaction is revealed by 2D NOESY in the aqueous system containing SDS surfactant and HEC polymer.
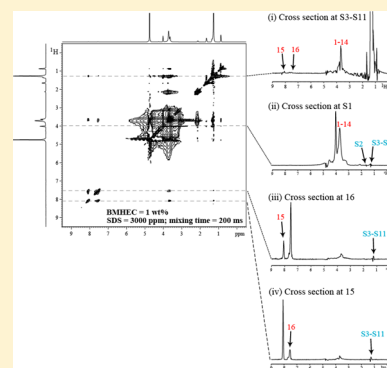
1. INTRODUCTION

More and more research efforts have been made toward the aqueous surfactant–polymer complex systems recently,[1−4] as surfactants and polymers are often conjointly formulated for their specific functions in a wide range of applications, such as cosmetics and personal-care products, foods, pharmaceuticals, oil-enhanced recovery, and shale-gas production, as well as many others of significant commercial interest.[1,2,5,6] Surfactants are commonly used as emulsifiers to enhance solubility and dispersibility of hydrophobic components, while polymers are often utilized as thickeners. For example, in the slickwater fracturing process for shale-gas production, surfactants are injected into the well to reduce interfacial tension between the fluid and formation materials, and gels prepared from guar gum or hydroxyethyl cellulose are introduced to thicken the fracturing liquid to reduce the fluid loss from the fracture.[5,6] However, specific interactions between surfactants and polymers may alter the fluid properties in these surfactant–polymer complex systems, leading to formation of either viscous aggregates or fluidic liquids.[2,7]

Regarding the use of aqueous soluble polymers as thickeners, hydrophobic modification on polymers, i.e., by grafting a small portion of hydrophobes to polymers, has been introduced during the last few decades to greatly increase the efficacy of polymers as thickening agents.[1,2,7−12] Explicitly, the viscosity enhancement of these hydrophobically modified (HM) polymers can be mainly ascribed to the temporary formation of hydrophobic association network, either by inter- or intrachains, among hydrophobes of these HM polymers in

aqueous media even at relatively lower polymer concentrations.[1,2,7,9−11] Alternatively, the hydrophobic interaction between hydrophobes on HM polymers contributes to the viscosity enhancements in the dilute regime.

The thickening effect of the aqueous HM polymer solutions could be strengthened even more by an introduction of proper surfactants near their critical micelle concentrations (CMCs).[2,11,12] Generally, the added surfactants will tend to interact with the hydrophobic moieties of aqueous-soluble HM polymers.[1,2,7,9−12] Therefore, the cross-links of the HM polymers could be reinforced as several hydrophobes from different HM polymers could be solubilized in the same micelle. However, such entanglement of polymer chains will be weakened at a higher concentration of added surfactants, in which the hydrophobes of the HM polymers are saturated and masked with excess surfactant micelles.[2] Consequently, the viscosity of the surfactant–polymer complex solution becomes even lower than that of pure HM polymer at the same polymer concentration.[2,7,11,12] Namely, added surfactants could either increase or decrease the viscosity of the HM polymer solution, dependent on the interaction between surfactant molecules and HM polymers. Currently, the effect of added surfactants to the rheological behavior of the surfactant-HM polymer complex system still attracts much research attention.[1,2,7,9−12] However, the mechanism on the molecular interaction between surfactant

molecules and macromolecules is not yet fully understood and still under extensive research. Hence, in this work, we have chosen a hydrophilic polymer, 2-hydroxyethyl cellulose (HEC), and an anionic surfactant, sodium dodecyl sulfate (SDS), as our model surfactant–polymer complex system studied with viscometric analysis and the NMR technique in an attempt to provide insights to the mechanism of the surfactant–polymer interaction.

In general, viscometry could give the enveloped behavior of intermolecular interactions in the flow system, whereas the NMR spectroscopy looks at the magnetic interaction of certain atomic nuclei. Marcura and Ernst demonstrated that two-dimensional NMR experimental techniques appeared particularly promising for the study of intra- and intermolecular cross relaxation in macromolecules.[13] Especially, two-dimensional nuclear Overhauser effect spectroscopy (NOESY) has been proven as a powerful technique in determination of molecular structure of large molecules.[14,15] For example, cross-peaks on the 2D NOESY indicate proximity of protons (within 5 Å) that are not necessarily chemically bonded.[13−15] Alternatively, NOESY can reveal the spatial information on protons on proximal but different molecules. In 1996, Gjerde et al.[16] published the first paper in the open literature reporting the use of the 2D NOESY technique in the study of surfactant–polymer interaction between sodium dodecyl sulfate and poly(ethylene oxide). Afterward, more and more research works on the investigation of surfactant–polymer complexes using NOESY techniques have been conducted.[17−33] Most of these works focused on the effects of surfactant concentrations to the interaction between surfactants and polymers. Hence, in this work, we attempted to study the effect of the hydrophobicity of polymers to the surfactant–polymer interaction. Simply, we utilized 2-hydroxyethyl cellulose and its hydrophobically modified analogues prepared by grafting benzoyl groups to HEC as our model polymers for studying their interaction with SDS, one common anionic surfactant. Notably, both HEC polymer and SDS surfactant are commonly formulated in many applications.

In brief, HEC macromolecules are hydrophilic enough, so as not to tentatively interact with SDS molecules, according to the NOESY analysis in this study. In contrast, hydrophobic modification on HEC macromolecules induces obvious molecular interaction between polymers and SDS molecules. The hydrophobes, i.e., benzoate, are introduced to HEC via esterification with benzoyl chloride. With different molar ratios of benzoyl chloride to HEC present in esterification, the hydrophobically modified 2-hydroxyethyl cellulose (bmHEC) with different degrees of hydrophobic substitution could be obtained. Additionally, all experiments in this work were conducted with polymer concentrations above their overlap concentrations. In this report, we will give the details of our observation on the effect of hydrophobic modification to the interaction of the surfactant–polymer system. The conjecture on the interaction mechanism of the hydrophobically modified HEC polymer and SDS surfactant will be discussed.

2. EXPERIMENTAL SECTION

2.1. Materials. HEC (M_w= 250 000 g/mol) was purchased from Aldrich. According to the information provided by the supplier, the degree of hydroxyethyl substitution (DS) and the molar substitution of ethylene oxide groups (MS) are one and two, respectively, per $\beta_{1\rightarrow4}$ linked D-glucose unit. The degree of polymerization (DP) was estimated at about 817, according to

our GPC characterization. Benzoyl chloride, lithium chloride, N,N-dimethylacetamide (DMAc) and triethylamine (TEA) were supplied from Riedel-de Haën. Sodium dodecyl sulfate (SDS), acetonitrile (ACN) and N,N-dimethylformamide (DMF) was acquired from Mallinckrodt Baker. Deionized water from a Milli-Q purification system (Millipore, USA) having resistivity greater than 18.2 MΩ-cm was used in preparing samples and the mobile phase. All chemicals were of reagent grade and used as received.

2.2. Esterification of HEC with benzoyl chloride. The procedure on hydrophobic modification of HEC with benzoyl groups was modified from the Heinze–Liebert method[34] and schematically shown as Figure 1 and described in details as
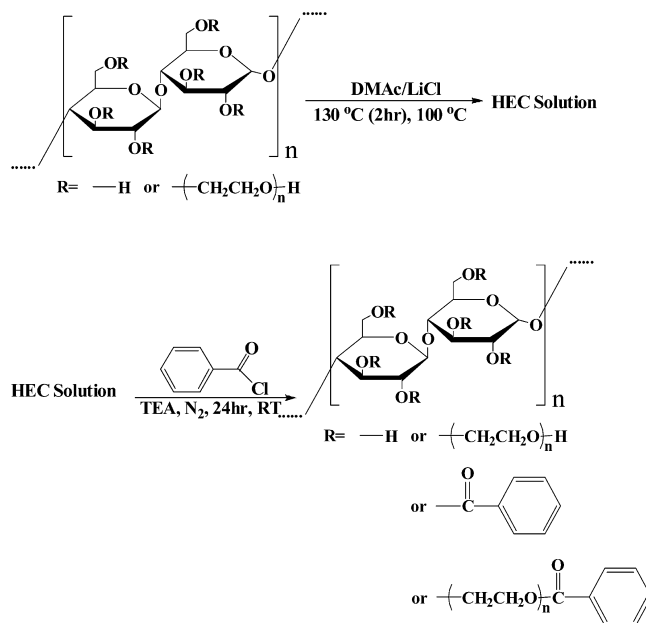

Figure 1. Schematic procedures on hydrophobic modification of HEC with benzoyl chloride.

follows. HEC (6 g, 14.56 mmol based on $\beta_{1\rightarrow4}$ linked D-glucose unit) was dissolved with 240 mL of DMAc at 130 °C under continuous stirring for 2 h. After the HEC slurry was gradually cooled down to 100 °C, 18 g of anhydrous LiCl was added. By cooling to room temperature under stirring for overnight, the HEC was completely dissolved and ready for subsequent esterification with benzoyl chloride.

TEA (2.43 g, 24.01 mmol) diluted with 5 mL of DMAc was added into the reactor containing as-prepared HEC clear solution and left still under N_2 atmosphere for 30 min. Subsequently, solution of benzoyl chloride (3.37 g, 23.97 mmol) in 5 mL DMAc was introduced dropwise into the reactor to start the esterification reaction, which proceeded for 24 h under continuous stirring until water (2.16 g, 120 mmol) was poured into reactor to stop the esterification reaction. In brief, the hydrophobically modified 2-hydroxyethyl cellulose (bmHEC) used in this work was mainly obtained from a feed ratio as 1.65 mol of benzoyl chloride per unit of $\beta_{1\rightarrow4}$ linked D-glucose of HEC, unless specified.

2.3. Purification of bmHEC. The reaction mixture was filtered slowly with a filter paper, so that the filtrate was gradually dipped into acetone and precipitated out. The polymer-contained precipitate was collected by filtration again and further purified with Soxhlet extraction for nearly 48 h until
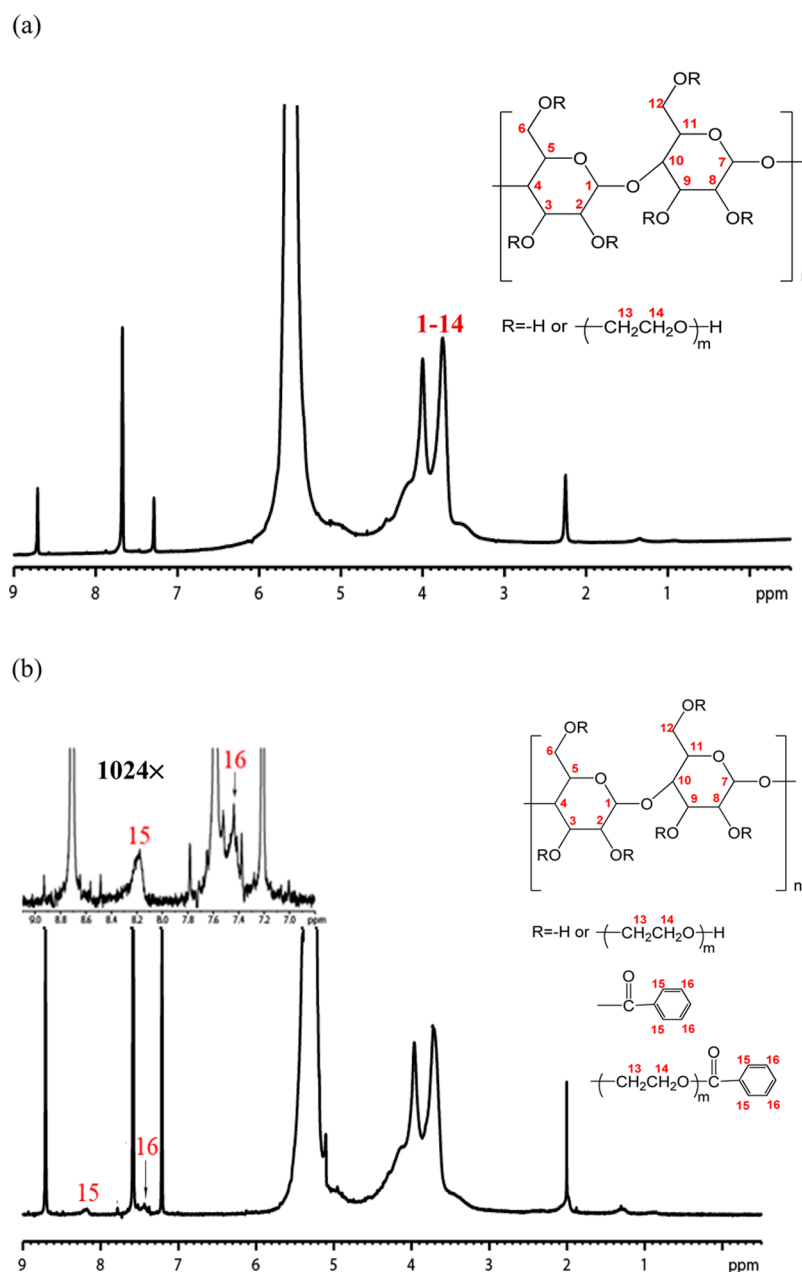
Figure 2. Characterization of HEC and bmHEC by NMR. (a) ^{1}H NMR spectrum of HEC (250 K) in pyridine-d$_5$, and (b) ^{1}H NMR spectrum of bmHEC in pyridine-d$_5$.

no white precipitate was found when a drop of 1N AgNO$_3$ solution was dipped into the condensate collected in the thimble. The solvent used was the azeotrope of water and acetonitrile (i.e., ACN/water =83.7/16.3 by weight). Subsequently, the polymer was vacuum-dried at 50 °C for 72 h. The purity of the obtained bmHEC was further checked with ^{1}H NMR analysis.

2.4. Gel Permeation Chromatography (GPC) Measurements. The molecular weights of HEC and bmHEC were characterized with GPC. The GPC system consists of an ERC-3415α degaser, HPLC pump from Lab Alliance, a Rheodyne 7725i Injector with a 100 μL sample loop, and a PN 3110 differential refractometer from Postonova Analytics. Separation was carried out at 30 °C using Jordi Gel DVB columns with a length of 250 mm and an ID of 10 mm (Cat. No. 15022 and 15023). The mobile phase was 0.5 wt % LiBr in DMF with a

flow rate set at 1 mL/min. Polystyrene standards supplied from Tosoh were used for calibration.

2.3. Viscosity Measurements. Viscosity measurements were performed using proper Ubbelohde viscometers in a temperature-controlled water bath, following the procedures and operating instructions given in the ASTM Test Methods D445 and D446. Anhydrous glycerol and deionized water were used as references to calibrate these kinematic viscometers. In brief, the efflux time of a fixed volume of liquid is directly proportional to its kinematic viscosity. Moreover, the ASTM D446 suggests that the kinetic energy correction can be negligible if the flow time is more than 200 s. Therefore, no kinetic energy correction was applied in this work, since the efflux times of the tested solutions through the capillary of the selected viscometer were always greater than 6 min.

2.4. NMR Measurements. All NMR experiments were performed at 299 K on a Bruker Avance 500 spectrometer at a proton resonance frequency of 500.13 MHz. The proton chemical shifts were referenced to the HOD signal at 4.70 ppm. The 2D NOESY spectra were acquired with the standard pulse program $(90°\text{-}t_1\text{-}90°\text{-}t_m\text{-}90°\text{-acquisition})$ of the Avance 500 spectrometer. For each NOE spectrum, 256 slices were recorded in the t_1 dimension, and the number of scan was 32 (2048 data points for each scan). The FID was treated by square-shifted sine bell weighting functions in both dimensions.

3. RESULTS AND DISCUSSION

3.1. Characteristics of HEC and bmHEC. The obtained bmHEC and its unmodified analogue HEC were characterized with various methods, including GPC for molecular weights, NMR for degree of benzoyl substitution on bmHEC and intrinsic viscosity measurements for determination of overlap concentrations.

Successful graft of benzoyl group on the bmHEC is evidently shown from ^{1}H NMR analysis (Figure 2). Figure 2 shows the ^{1}H NMR spectra of HEC and bmHEC in pyridine-d_5, along with proper assignments on chemical shifts. Pyridine-d_5 is known to possess three ^{1}H chemical shifts at 7.22, 7.58, and 8.74 ppm, respectively.[35] By comparing the proton-NMR spectrum of bmHEC with that of HEC, the chemical shifts of the induced protons on grafted benzoyl groups are 8.18 ppm (H-15, *ortho*-position) and 7.46 ppm (H-16, *meta*-position). Note that the signal of the proton at *para*-position is overlapped with the strong signal of pyridine-d_5. The degree of benzoyl substitution (bs) could then be calculated from the NMR spectra, e.g. the ^{1}H spectrum of the *ortho*-protons (H-15) in this work. Consequently, the degree of benzoyl substitution per unit of $\beta_{1 \to 4}$ linked D-glucose unit on bmHEC was found to be 0.09. Alternatively, one benzoyl hydrophobe was grafted on HEC per 11 units of $\beta_{1 \to 4}$ linked D-glucose. Notably, each $\beta_{1 \to 4}$ linked D-glucose unit on HEC has 6 hydroxyl groups available for esterification reaction and, therefore, the maximum degree of benzoyl substitution is 6.

Reducing the initial molar ratio of benzoyl chloride-to-HEC in feed by half to 0.82, the degree of benzoyl substitution on the bmHEC is only 0.017. In contrast, increasing the initial molar ratio of benzoyl chloride-to-HEC in feed to 2.47 and above, the obtained bmHEC is so hydrophobic to be scarcely dissolved in water. Hence, the impurities left on the bmHEC hindered an accurate measurement on the degree of benzoyl substitution.

The bmHEC with different degree of benzoyl substitution has shown different viscometric behavior (Figure 3). Generally, the higher the degree of benzoyl substitution on a polymer, the more viscous the aqueous polymeric solution. Approximately, the viscosity of 1 wt % bmHEC (bs = 0.09) is about 1.9−1.6 times larger than that of 1 wt % HEC (i.e., bs = 0) at temperatures from 10 to 60 °C. Likewise, the viscosity of 1 wt % bmHEC (bs = 0.017) is about 1.3 times higher than that of 1 wt % HEC solutions. Explicitly, a slight graft of benzoyl groups to HEC alters obviously the viscosity of the polymeric solutions.

The average molecular weights of HEC template and bmHEC were obtained with GPC (Figure 4). The molecular weights by weight of HEC and bmHEC were estimated around 336 700 g/mol and 360 000 g/mol, respectively. With grafted benzoyl group, the polydispersity index of bmHEC was slightly increased to 1.198, in contrast to 1.08 for the unmodified analogue, HEC, used as a template. Hence, according to the
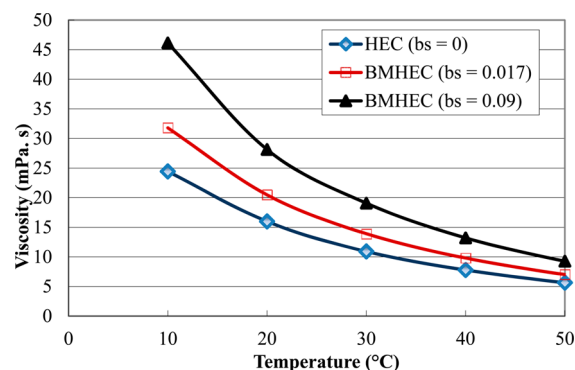

Figure 3. Viscosity of 1 wt % HEC solution and 1 wt % bmHEC solutions prepared from bmHEC with different degrees of benzoyl substitution (bs).
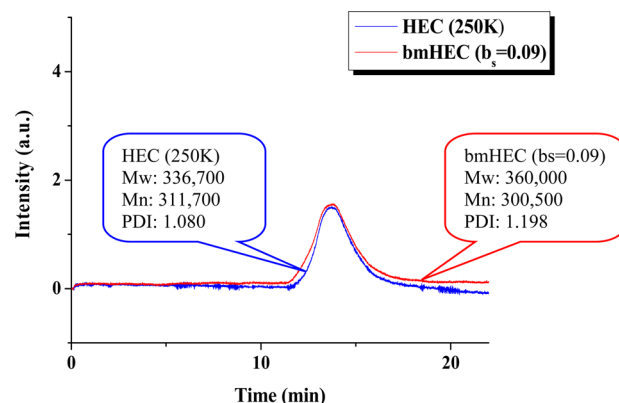

Figure 4. Molecular weights of HEC and bmHEC characterized by GPC.

GPC results, each macromolecule of HEC used in this work contains in average 817 units of $\beta_{1 \to 4}$ linked D-glucose.

The overlap concentration C^* of either bmHEC or HEC polymer in water could be evaluated from its intrinsic viscosity using the capillary viscometry. The intrinsic viscosity $[\eta]$ could be expressed as follows:[10,36]

$$[\eta] = \lim_{C_p \to 0} \frac{\eta_{sp}}{C_p} \tag{1}$$

where η_{sp} and C_p are specific viscosity and polymer concentration. Explicitly, the specific viscosity is a fractional change in viscosity of solution upon addition of polymer:

$$\eta_{sp} = \frac{\eta_{solution} - \eta_{solvent}}{\eta_{solvent}} \tag{2}$$

where $\eta_{solution}$ and $\eta_{solvent}$ denote the viscosity of solution and solvent, respectively. In practice, the intrinsic viscosity is regarded as the extrapolated value of (η_{sp}/C_p) at zero polymer concentration $(C_p = 0)$. Assuming that each polymer coil in the dilute solution behaves like a hard sphere with a radius equal to the radius-of-gyration of the polymer, the overlap concentration could be roughly approximated to the reciprocal of the intrinsic viscosity of the polymer.[10,36]

The intrinsic viscosities of this bmHEC polymer and its unmodified analogue HEC are found to be ca. 3.22 dL/g and 3.33 dL/g, respectively. That is, the overlap concentrations of this bmHEC polymer and its unmodified analogue HEC are 0.31 and 0.30 g/dL, respectively. The corresponding radii of

gyration of bmHEC and HEC are 35.84 and 35.45 nm. Hence, it is ensured that the concentration of the bmHEC polymer at 1 wt % under investigation in this work is in the semidilute concentration regime.

3.2. Interaction of bmHEC and SDS Studied with Viscometry. Viscometry measurement could provide insight and information in molecular interactions of a fluid system to a macroscopic level. Additionally, capillary viscometry gives a convenient way to determine the molecular weights of macromolecules via the Mark−Houwink equation.[10,36] Hence, in this work, capillary viscometers with proper capillary diameters were employed to yield the zero-shear viscosity of polymer−surfactant solution.

Effects of temperature and surfactant concentrations on viscosity of 1 wt % polymer solutions were investigated and presented in Figure 5. Furthermore, variations on the
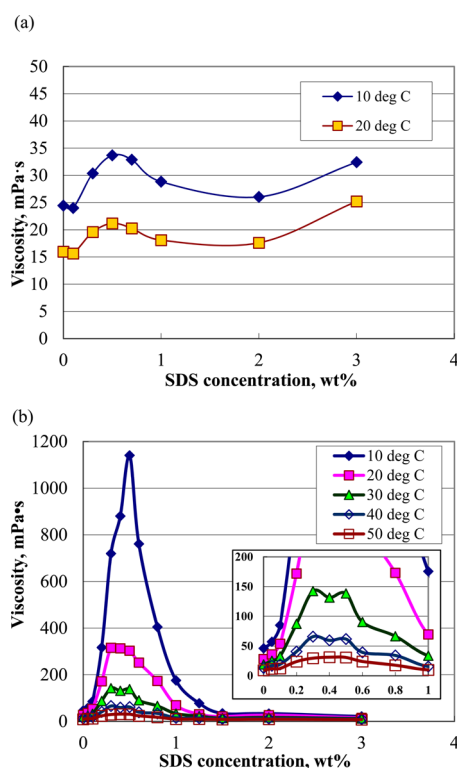
(a)

(b)

Figure 5. Viscosity of 1 wt % HEC and 1 wt % bmHEC solutions in the presence of sodium dodecyl sulfate (SDS). (a) Viscosity of 1 wt % HEC solution in the presence of SDS, and (b) viscosity of 1 wt % bmHEC solution in the presence of SDS.

temperature-dependent viscosity were employed to yield the surfactant-dependent information on transient network formation in 1 wt % bmHEC solution (Figure 6). Obviously, surfactant molecules did not pose a significant effect on the viscosities of the 1 wt % HEC solutions (Figure 5a). For example, the viscosity of 1 wt % HEC solution at 20 °C increases from 16 to 21.2 mPa·s with concentration of SDS added from 0 to 0.5 wt %, and gradually to 25.2 mPa·s in the presence of 3 wt % SDS. In contrast, despite only slight substitution of benzoyl groups on HEC, namely bs = 0.09, being achieved, a dramatic effect on the viscosity of 1 wt % bmHEC was imposed by surfactants at proper concentrations (Figure 5b).
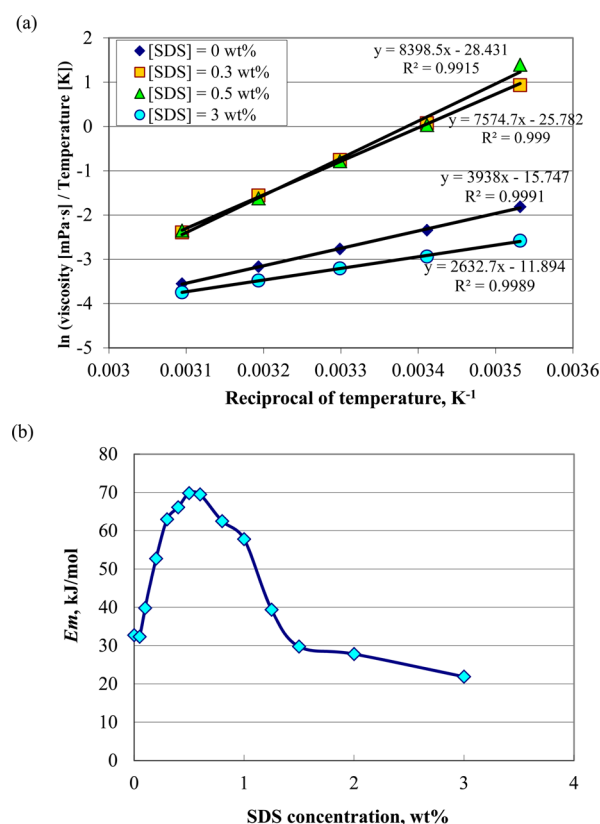
(a)

(b)

Figure 6. (a) Temperature dependence of viscosity of bmHEC in the presence of SDS and (b) the activation energy, E_m (kJ/mol), of transient network formation in 1 wt% bmHEC solution as a function of SDS concentration present.

In general, the viscosity of 1 wt % bmHEC solution increased with an increasing surfactant concentration to an apex where about 0.3−0.5 wt %, ca. 1−2 CMCs, of SDS was present in the solutions. For instance, the viscosity of 1 wt % bmHEC solution at 20 °C increased from 28.1 mPa·s, in the absence of any SDS, to 315.5 mPa·s in the presence of 0.3 wt % SDS. A further increase in surfactant concentration would diminish the viscosity of 1 wt % bmHEC solutions, even to a level lower than that of surfactant-free polymer solution. For instance, the viscosity of 1 wt % bmHEC solution present with 3 wt % SDS is decreased to 15.5 mPa·s only.

Such SDS-concentration-dependent viscosity of bmHEC solution could be further elucidated with the changes in activation energy of hydrophobe disentanglement in bmHEC-SDS solution. Based on the pioneer work of Green and Tobolsky on transient networks to account for entanglement or reversible physical bonds formed, the zero-shear viscosity η_0 is given as follows:[10,36]

$$\eta_0 = \frac{\nu_0 \cdot k_B T}{\beta_0} = \frac{\nu_0 \cdot k_B T}{\omega_0} \cdot \exp\left(\frac{E_m}{k_B T}\right) \tag{2}$$

where $\beta_0 = \omega_0 \cdot \exp(-E_m/k_B T)$ represents the dissociation rate of transient network with an activation energy E_m that follows an Arrhenius behavior; ν_0 and ω_0 denote for the number density of effective or elastic chains at zero shear and characteristic frequency of thermal vibration on these chains; and k_B and T are for the Boltzmann constant and the absolute temperature. Therefore, the activation energy of transient
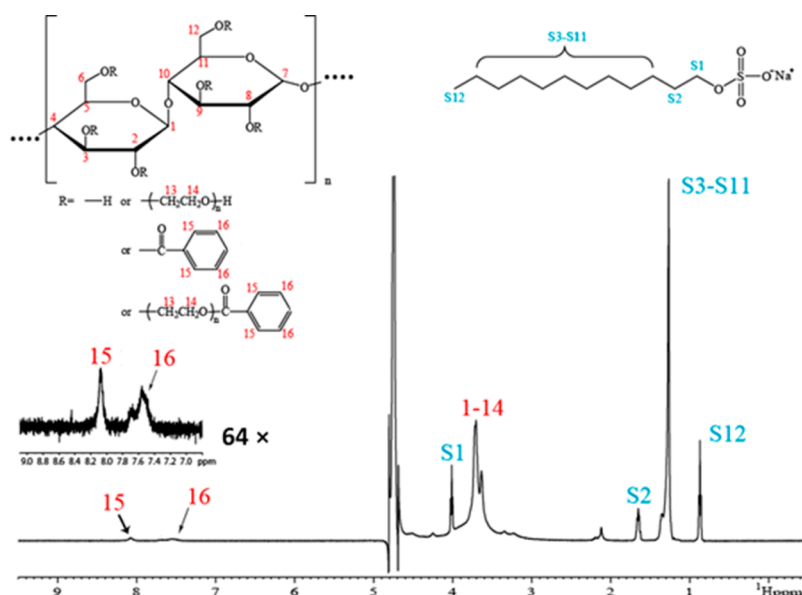
Figure 7. ^{1}H NMR spectra and assignments of ^{1}H chemical shifts for the bmHEC/SDS/D$_2$O solution. The concentrations of SDS and bmHEC were 0.3 and 1 wt %.
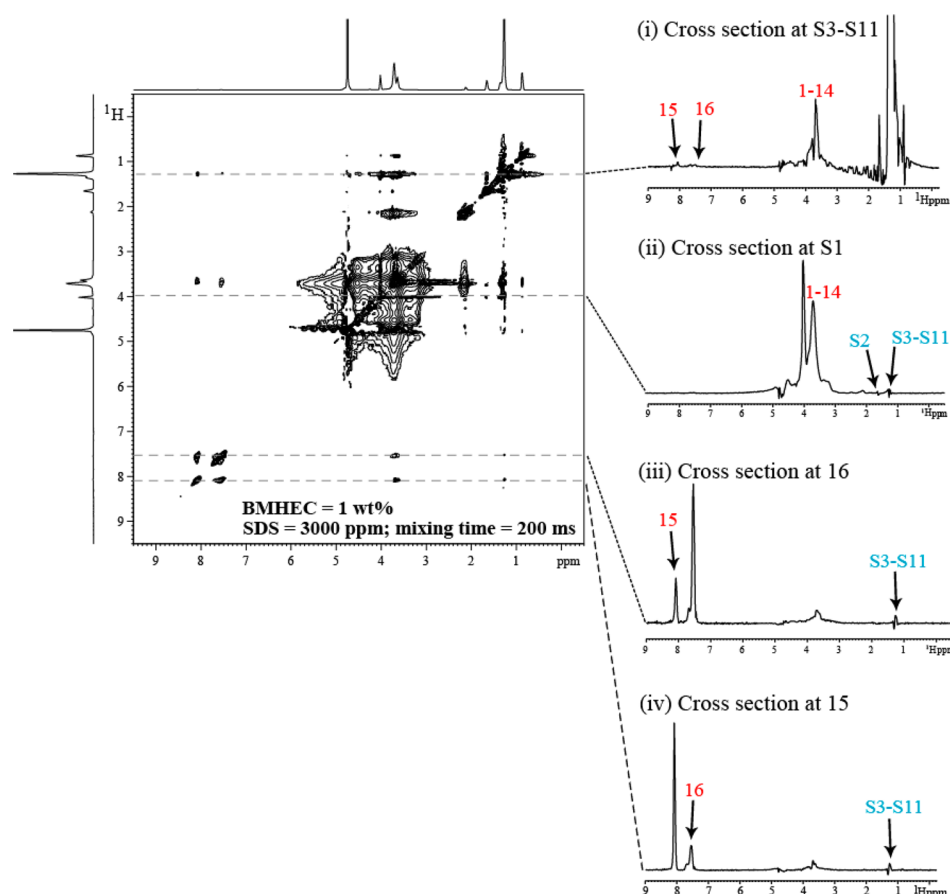

Figure 8. ^{1}H−^{1}H 2D NOSEY spectra of the bmHEC/SDS/D$_2$O system. The concentrations of SDS and bmHEC were 0.3 and 1 wt %. The mixing time is 200 ms, and the contour levels in the spectra are linearly spaced.

network formation E_m could be deduced from the slope of a plot on $\ln(\eta_0/T)$ versus T^{-1}.

In this work, the zero-shear viscosity of 1 wt % bmHEC solution with/without SDS added and 1 wt % HEC exhibits quite a good Arrhenius dependence on temperature[7,11,12,34] (Figure 6a). As a result, the activation energies for the hydrophobe disentanglement in 1 wt % bmHEC (bs =0.09) solution and 1 wt % bmHEC (bs =0.017) are 32.74 and 30.69 kJ/mol, respectively, comparable to other associative polymers,[7,11,12] whereas that of 1 wt % unmodified HEC solution is

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29.96 kJ/mol. With more SDS introduced to 1 wt % bmHEC solution, the activation energies increased to about 69.8 kJ/mol, when 0.5 wt % SDS were present, and, then decreased to a value, e.g., 21.9 kJ/mol with 3 wt % SDS present, smaller than that of pure bmHEC solution (Figure 6b). Additionally, the activation energy of hydrophobe disentanglement changes suddenly in between 0.05 and 0.1 wt % SDS present in the polymer solutions, which implies that the onset of significant binding of surfactant to polymers occurs in this range. In other words, the critical aggregate concentration (CAC) of the SDS-bmHEC in 1 wt % polymer solution falls into this range.

As aforementioned, the degree of benzoyl substitution on bmHEC is low. Hence, bmHEC and its unmodified analogue HEC possess similar physicochemical properties, for instance, the molecular weight, the overlap concentration and the radius of gyration, the viscosity in surfactant-free polymer solution, and the activation energy of transient network formation of polymer in aqueous solution. However, addition of appropriate surfactants to polymer solutions, e.g., sodium dodecyl sulfate, alters the fluid properties of the surfactant−polymer complex systems significantly. This work demonstrates that SDS introduced to both solutions of bmHEC and HEC leads to two contrasting results in viscosity. In an SDS−bmHEC complex system, SDS aggregates at a concentration around its CMC could provide a hydrophobic environment that could bridge hydrophobes on adjacent polymers, leading to enhanced hydrophobic interactions.[2,7,11,12] Indeed, this associated binding behavior has been observed and reported in the literature.[2,7,11,12] Evidently, the 2D NOE measurement to be discussed in the next section has shown such hydrophobic interaction in the SDS−bmHEC complex system. However, when excess surfactant molecules are present in bmHEC solution, hydrophobes would be individually solubilized in surfactant micelles and, consequently, intermolecular hydrophobic interactions would be shielded. Therefore, viscosity and activation energy of hydrophobe disentanglement in an SDS−polymer complex system at high SDS concentrations are decreased to a level even smaller than those of surfactant-free polymer solution.[2,7,11,12]

3.3. Short-Range Interaction of bmHEC and SDS Studied with NMR Analysis.
Figure 7 shows the ^{1}H NMR spectrum and assignments for proton chemical shifts in the bmHEC/SDS systems. Deuterium oxide, D_2O, was used as the solvent in an attempt not to interfere with the proton NMR measurement and not to distort the interaction existing in the aqueous system of bmHEC and SDS. The ^{1}H shifts on SDS, bmHEC and benzoyl hydrophobe grafted on bmHEC are labeled in Figure 7. Notably, the significant proton shift near 4.7 ppm mainly arises from HOD in D_2O solvent. In this SDS/bmHEC/D_2O system, the proton shifts from surfactant and polymers are distinguishable.

The 2D NOESY experiments of polymer/SDS/D_2O were carried out to study the surfactant−polymer interaction. Figure 8 illustrates the 2D ^{1}H−^{1}H NOSEY spectra in the SDS/bmHEC/D_2O system. The concentrations of SDS and bmHEC were set at 0.3 and 1 wt %, respectively, in which the hydrophobic interaction in SDS-bmHEC complex system is relatively the strongest as shown by viscometry (Figure 5(b)). The 1D spectrum could be found along the diagonal in Figure 8. There exist observable off-diagonal cross peaks on the 2D NOESY of SDS/bmHEC/D_2O system. These NOE cross peaks are attributable to the interaction between alkyl protons of surfactant and protons on hydrophobes and backbone of

polymer. The 1D cross-sectional NOE spectra on specific protons are also shown to give more detailed NOE information on these specific protons (Figure 8).

2D NOESY measurements were also performed in SDS/HEC/D_2O system (Figure S1 in the Supporting Information). As predicted from viscometry on nonexistence of associative bindings between SDS and the unmodified HEC, no corresponding cross peaks between SDS surfactant and HEC polymer have been observed.

Combined with information on the buildup rate of the NOE cross peaks shown in Figure 9, it is evident that the alkyl chains
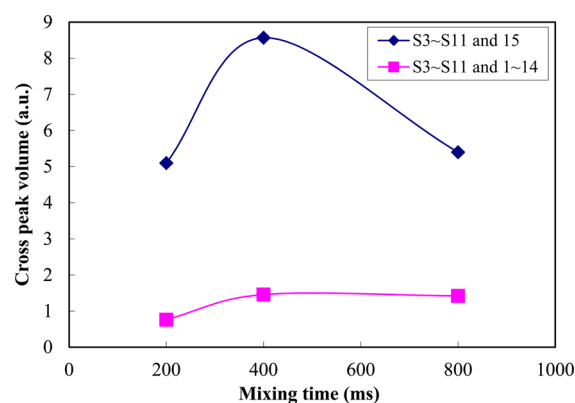

Figure 9. Normalized buildup curve of cross-peak volume of S3−S11 of SDS and 15 of bmHEC as well as that of S3−S11 of SDS and 1−14 of bmHEC from ^{1}H−^{1}H 2D NOSEY spectra of the bmHEC/SDS/D_2O system.

of sodium dodecyl sulfate have interacted with the polymer backbones and benzoyl groups on bmHEC polymers, as shown in the 2D NOESY spectra and the 1D cross section along both axes of SDS alkyl protons and hydrophobe protons of bmHEC. For example, the cross section at Proton S1, viz., α-methyl next to sulfate on SDS, has witnessed the NOE peaks from protons on cellulose backbone (1−14), as well as other alkyl protons of SDS. This implied that Proton S1 of SDS is in the proximity of protons on the polymer's cellulose backbone. On the cross section along Protons S3−S11 of SDS, NOE peaks from protons located on the hydrophobe and cellulose backbone of bmHEC could be discerned. Notably, successful grafting of benzoyl group on the cellulose backbone of HEC is also reflected in the existence of correlational proton−proton cross peaks between the hydrophobe and cellulose backbone of the polymer. Interestingly, the terminal protons of SDS's hydrophobic tail (S12) and the protons of α-methyl next to sulfate on SDS (S1) have yielded cross peaks with protons on cellulose backbones (1−14), but not the protons of the hydrophobes on bmHEC (15−17). One possible cause mainly arises from the fact that very few hydrophobes are grafted to each bmHEC backbone.

Figure 9 presents the normalized volume of the NOE cross peak between SDS alkyl protons, labeled as S3−S11, and various protons on bmHEC as a function of mixing times. Three different mixing times at 200, 400, and 800 ms were chosen. The cross-peak volumes shown in Figure 9 have been normalized by the number of interacting protons on each $\beta_{1\rightarrow4}$ linked D-glucose unit of the bmHEC polymer. That is, on average, there are 22 protons on carbon atoms labeled as 1−14 per $\beta_{1\rightarrow4}$ linked D-glucose unit of bmHEC, and only 0.18

protons on average on *ortho* carbons, labeled as 15, of benzoyl hydrophobe in each $\beta_{1\rightarrow4}$ linked D-glucose unit.

In general, as mixing time increases, the NOE cross-peak volume increases and, then, decays or levels off with a further increase in mixing time (Figure 9). For example, when mixing time rises from 200 to 400 ms, it doubles the volume of the NOE cross-peak between Protons S3−S11 of SDS and Protons 1−14 on the cellulose backbone of bmHEC. The nonlinear relationship on cross-peak volume with mixing time shown in Figure 9 implied that the NOE cross-peaks at short mixing time, e.g., t_m = 200 ms, mainly arise from dipole−dipole interactions from adjacent protons located within 0.5 nm, explicitly the nuclear Overhauser effect, rather than spin diffusions of protons.[35,37] Certainly, Figure 9 also reveals that protons on surfactant molecules have proximally interacted with protons of bmHEC located both on benzoyl groups and cellulose backbones. More specifically, the normalized volume of NOE cross-peak between Protons S3−S11 of SDS and Proton 15 on the *ortho* carbon of the benzoyl hydrophobe is obviously larger than that between S3−S11 protons and 1−14 protons on the cellulose backbone of bmHEC. This suggests that SDS molecules would preferably interact with benzoyl hydrophobe of bmHEC rather than cellulose backbone of bmHEC polymer. In our conjecture to the interaction between the bmHEC macromolecules and SDS molecules, the backbone of the bmHEC macromolecule may pass through the palisade layers of SDS micelles, with benzoyl hydrophobes solubilized in the hydrophobic interiors of SDS micelles. Hence, a necklace-like structure could probably describe the SDS-bmHEC interaction well (Figure 10).[2]
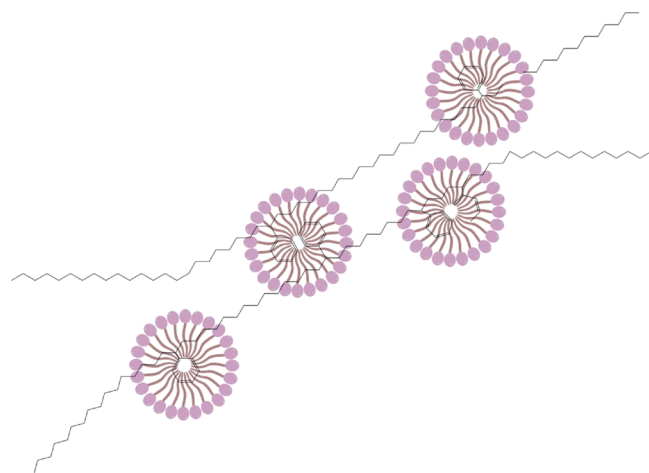

Figure 10. Schematic illustration of the bmHEC−SDS interaction model.

4. CONCLUSIONS

Varying the feed ratio of benzoyl chloride to the HEC template in esterification, bmHEC with different hydrophobicity was obtained. Proper addition of sodium dodecyl sulfate to the bmHEC solutions could dramatically increase the viscosity of the bmHEC solutions. In general, the low-shear viscosity of bmHEC was increased 60-fold with addition of surfactant from 0 to ca. 0.3−0.5 wt % and then decreased to a value smaller than that of pure bmHEC with further addition of surfactant to 3 wt %. The activation energy of transient network formed by 1 wt % bmHEC and SDS surfactant molecules was found to range from 32.7 to 69.8 kJ/mol as a function of surfactant concentration. The maximum activation energy coincided with 0.5 wt % SDS added. The 2D NOESY spectra displayed that the surfactants might interact with polymer not only on the benzoyl hydrophobes, but also the cellulose backbone of the polymers. That is, 2D NOESY reveals that both cellulose backbone and hydrophobes of bmHEC polymer could really interact with the hydrophobic alkyl chain of SDS surfactants. However, the normalized volume of NOE cross-peak suggests that SDS would preferably interact with the benzoyl hydrophobe of bmHEC rather than the cellulose backbone of bmHEC polymer.

■ ASSOCIATED CONTENT

ⓢ Supporting Information

2D NOSEY spectra of the HEC(250k)/SDS/D$_2$O system. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

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