Interaction between Fluorocarbon End-Capped Poly(ethylene oxide) and Cyclodextrins

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ABSTRACT: Well-defined fluorocarbon end-capped poly(ethylene oxide) (PEO), known as F-HEUR, were synthesized by varying both fluorocarbon end groups and PEO chain length. Their solution properties were studied and compared with those of hydrogenated carbon end-capped PEO. Variation of the end-capped functional group from $-C_6F_{13}$ to $-C_8F_{17}$ gave rise to a significant shift in the solution rheological properties. The interaction between different cyclodextrins and these fluorocarbon derivatives of PEO was systematically examined by rheological, dynamic light scattering (DLS), isothermal titration calorimetric (ITC), and ^{19}F NMR techniques. The viscosity of F-HEUR solution was drastically reduced in the presence of methylated β-cyclodextrin (m-βCD) due to the disruption of intermolecular hydrophobic associations, but not observed for α- and γ-cyclodextrins. The destruction of F-HEUR network structure in the presence of m-βCD was reflected by the large reduction in the plateau modulus (G_N^0). The activation energies (E_a) determined from zero-shear viscosity decreased with m-βCD concentration until a molar ratio of 2; thereafter it remained constant. At high m-βCD concentration, subtle difference was observed for the complexes produced by $-C_6F_{13}$ and $-C_8F_{17}$ hydrophobic moieties. The inclusion complex formation between m-βCD and different fluorocarbon groups derived from ITC thermograms revealed a stoichiometry of 1:1 for C_6F_{13} but 1:1 and 2:1 inclusion complexes for C_8F_{17} at different m-βCD concentrations. DLS results showed a different mechanism for C_6F_{13} and C_8F_{17} fluorocarbon hydrophobes, which were in agreement with the results deduced from activation energies and ^{19}F NMR spectra. A mathematic model was adopted to describe the relationship between G_N^0 and m-βCD concentration.

Introduction

Associative polymers (APs) are hydrophobically modified water-soluble polymers composed of both water-soluble and water-insoluble components. Hydrophobic ethoxylated urethane (HEUR) is one class of AP produced by chain extension of poly(ethylene oxide) (PEO) with diisocyanate and end-capped with different types of hydrophobes as reported by several research groups.[1−4] Various association models have been proposed to describe the transient network structure and rheological behavior as summarized in two recent reviews.[5,6] In dilute solution, HEUR with different hydrophobic groups form micelles or aggregates through either closed or open association mechanisms. These flowerlike micelles or aggregates associate to form a 3-D network structure in semidilute concentration range, which dramatically increases the solution viscosity.

Fluorocarbon functional groups are interesting moieties and are of industrial importance because of their low surface energy, biocompatibility, and extreme hydrophobic properties. Similarly, conjugating fluorocarbon end-capped groups to PEO produces another type of associative polymer, known as F-HEUR. Because of the strong hydrophobic characteristic of the fluorocarbon, F-HEUR exhibits stronger hydrophobic association in aqueous solution and possesses a greater viscosifying effect than the corresponding hydrocarbon derivatives.[7−10] Thus, the behavior of model PEO end-functionalized with perfluorocarbon is of significant interest. From previous studies, a consistent description on the self-assembly and flow behaviors of F-HEUR has emerged.[7,10] In many respects, the phenomenon of self-assembly and network formation observed for telechelic fluorocarbon is similar to that of its hydrocarbon analogues. Above a critical micelle concentration, F-HEUR self-assembles in water to produce monodispersed flower-like micelles. In telechelic fluorocarbon, the onset of viscoelasticity coincides with the formation of an associative network of flowerlike micelles. One crucial difference between hydrocarbon and fluorocarbon telechelics is the range of relaxation time that characterizes the viscoelastic solutions in the transient network regime.

For predicting the performance of a hydrophobically modified polymer in a given application, it is important to understand the effect of hydrophobic modification on the macroscopic properties. Fundamentally, correlating the microscopic to the macroscopic properties of HEUR and the unmodified parent PEO polymer is critical to elucidate the effect of hydrophobic modification. One approach to study the effect of hydrophobic modification on the microscopic and macroscopic properties is to suppress the hydrophobic associations. This could be done by adding excess surfactant or diethylene glycol monobutyl ether to the solution of hydrophobically modified polymer.[11] However, such an approach is often complicated by the presence of other hydrophobic associations, such as surfactant/polymer interaction and solvent effect. A more desirable and specific approach to suppress the hydrophobic association is through the formation of inclusion complex with cyclodextrin (CD), a cyclic oligomer of α-D-glucose.[12] The inclusion complex formed between CD and hydrophobic moieties of HEUR polymer results in the destruction of micelles in dilute solution or associative network in semidilute to concentrated solutions.[13−16] Such an approach in removing the hydrophobic association has been used to characterize a single polymeric chain of a hydrophobically modified alkali-soluble emulsion (HASE).[17]

In contrast to the hydrocarbon moiety, fluorocarbon not only exhibits strong hydrophobic characteristic but also possesses

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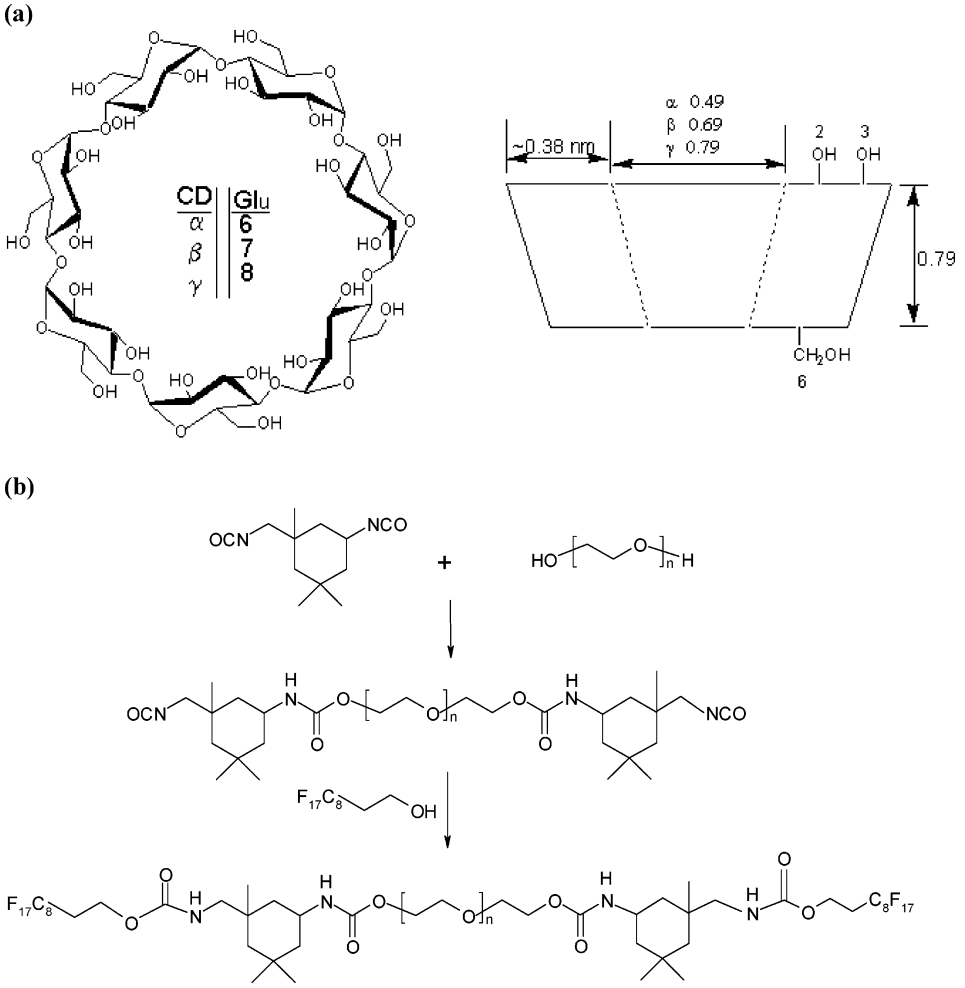
Scheme 1. (a) Chemical Structure and Specification of Different Cyclodextrins; (b) F-HEUR Synthesis Scheme



lipophobic characteristic. Several studies on the interaction between fluorocarbon surfactants and cyclodextrin have been reported.[18−21] It is evident that the fluorocarbon moiety can be hosted by the hydrophobic cavity of cyclodextrin. Zhang and co-workers studied the complex formation of β-cyclodextrin/perfluorocarbon modified water-soluble polymer by ^{19}F NMR,[22] and they found that the viscosity was greatly reduced by β-cyclodextrin which destroyed the intermolecular hydrophobic association. However, limited studies on the effect of different cyclodextrins on the associative behavior of fluorocarbon end-capped water-soluble polymers have been reported. The influence of cavity size and the cross-section area of hydrophobic moiety on the encapsulation efficiency of cyclodextrins on F-HEUR have not been reported. Thus, the present study seeks to examine the viscoelastic behavior of semidilute to concentrated F-HEUR solution in the presence of various types of cyclodextrins. The binding mechanism was elucidated by further examining the dilute solution characteristics using the ^{19}F NMR, ITC, and DLS techniques. A physical binding mechanism was proposed, and the plateau modulus representing the number of active chains was mathematically modeled by a sequential adsorption model.

Experimental Section

Materials. The F-HEUR polymers used in this study were synthesized from hydroxyl end-capped poly(ethylene oxide) (PEO) with nominal molecular weights of 20 000 g/mol ($M_w/M_n = 1.08$) (Dow) and 35 000 g/mol ($M_w/M_n = 1.20$) (Fluka). Isophorone diisocyanate (IPDI) was purchased from Sigma-Aldrich and distilled under vacuum prior to use. 3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-Heptadecafluoro-1-decanol, 3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluoro-1-octanol, and dibutyltin dilaurate (DBTDL) were purchased from Sigma-Aldrich. Cyclodextrins are crystalline, homogeneous, nonhygroscopic substances, which are toruslike macrorings built up from glucopyranose units (Scheme 1a). The α-, β-, and γ-cyclodextrins contain 6, 7, and 8 glucopyranose units, respectively. Because of the low solubility of β-cyclodextrin, methylated β-cyclodextrin (m-βCD) was used in this study, which has a similar cavity size but different cavity length with a typical substitution of 1.6−2.0 mol of CH_3 per mole of anhydroglucose unit.[23] The m-βCD was purchased from Sigma-Aldrich, and the other cyclodextrins were purchased from Cyclodextrin Technologies Development Inc. The deionized water was from Alpha-Q Millipore water purification system equipped with a 0.22 μm filter.

Synthesis of F-HEUR. F-HEUR polymers were prepared and characterized according to the method described below, where the prepolymer of PEO was prepared on a large scale by the reaction of PEO with excess of IPDI (1:200 equiv ratio) to avoid the formation of multi-PEO block. It was subsequently divided into smaller portions for further reaction with heptadecafluoro-1-decanol or tridecafluoro-1-octanol. In a typical synthesis (Scheme 1b), the prepolymer was prepared by adding 20 g of PEO ($M_n = 35$K, $M_w/M_n = 1.20$) to a 100 mL, four-necked, break-away reaction flask, equipped with a Dean Stark water trap and condenser, argon inlet tube, and mechanical stirrer. The PEO was dried by azeotropic distillation in toluene. About 30 mL of the toluene was removed through the Dean Stark trap, and 40 g of dry, distilled tetrahydrofuran and 20 g of IPDI were introduced. After reaction for 36 h at 45 °C, a small portion of the solution was withdrawn from the mixture and placed in methanol for size exclusion chromatographic

analyses. SEC trace indicated that there was no multi-PEO block formed during this reaction procedure. The remainder of the solution was concentrated and precipitated into petroleum ether, filtered, and dried under vacuum. The isocyanate content was determined by dibutylamine titration, and the prepolymer was stored under argon at dry ice temperature until it was ready for reaction with heptadecafluoro-1-decanol or tridecafluoro-1-octanol.

The following description of hydrophobic modification of telechelic prepolymer with heptadecafluoro-1-decanol or tridecafluoro-1-octanol is a representation of all end-capping reactions with hydrophobic, active-hydrogen containing compounds. In a 100 mL three-necked, round-bottom flask equipped with a magnetic stirrer, argon inlet tube, and thermometer, 5 g of the telechelic prepolymer (0.29 mmol of −N═C═O) was dissolved in 15 mL of dry, distilled THF. Dry heptadecafluoro-1-decanol or tridecafluoro-1-octanol (1.9 g, 8.5 mmol of −OH; 30 equiv of −OH to 1 equiv of −N═C═O) was dissolved in a small amount of THF and added to the flask, and the contents were heated to 40 °C. A drop of DBTDL was added to catalyze the addition reaction, and the mixture was stirred for 12 h. After the reaction was completed, it was filtered to remove triethylamine hydrobromide. The solution was concentrated and precipitated in *n*-hexane, filtered, and dried under vacuum. The procedure was repeated twice to ensure the complete coupling of the end groups. Finally, the crude polymer was dissolved in water at pH of 7−8 and extracted from methylene chloride. After drying over magnesium chloride for 12 h, the solvent was removed under vacuum and dried to obtain the purified polymer. The end-capping efficiency was ∼100% from ^{1}H NMR. Although the fluorohydrocarbon hydrophobic group enhances the miscibility with hydrocarbon hydrophobes, the fluorocarbon segments on the hydrophobic moiety is the dominant component. The nomenclature of these modified polymers is based on their fluorocarbon end-capping group and PEO molecular weight, i.e., F-HEUR-C8F17-35K for heptadecafluorodecane end-capped PEO of MW 35 000 Da; F-HEUR-C8F17-20K for heptadecafluorodecane end-capped PEO of MW 20 000 Da; F-HEUR-C6F13-35K for tridecafluorooctane end-capped PEO of MW 35 000 Da, and F-HEUR-C6F13-20K for tridecafluorooctane end-capped PEO of MW 20 000 Da.

Viscosity Measurements. The steady and dynamic rheological behavior of the polymer solutions were measured using a Controlled Stress Carri-Med CSL500 and controlled rate Contraves LS40 rheometers. The rheological measurements of low-viscosity solutions were conducted using the Contraves LS40 rheometer. The LS40 was fitted with the MS41S/1S concentric cylinder measuring system consisting of a cup of diameter 12 mm and a bob with the diameter of 11 mm and height of 8 mm. Other measurements involving more viscous solutions were performed on a CSL500 rheometer. A cone-and-plate with a 40 mm diameter and a 2° cone angle was used. The temperature for rheological measurements was controlled using a PolyScience water bath. The shear rate range of the steady flow measurements is from 0.001 to 100 s^{-1} on the LS40 and the shear stress range from 0.2 to 1000 Pa on the CSL500 instruments. The frequency-dependent moduli were measured over an angular frequency range of 0.03−200 rad/s, and the strain was kept below 1% to ensure that it is within the linear viscoelastic range.

Isothermal Titration Calorimeter (ITC). Calorimetric measurements were performed using a Microcal isothermal titration calorimeter (Microcal Inc., Northampton, MA). The microcalorimeter consists of a reference cell and a sample cell of 1.35 mL in volume, with both cells insulated by an adiabatic shield. The titration was carried out by step-by-step injections of concentrated titrant solution from a 250 μL injection syringe into the sample cell filled with dilute titrate solutions. The syringe is tailor-made such that the tip acts as a blade-type stirrer to ensure continuous mixing efficiency at 400 rpm. Using interactive software, an injection schedule was automatically carried out after setting up the number of injection, volume of each injection, and time interval between each injection. The details on ITC can be found elsewhere.[24]

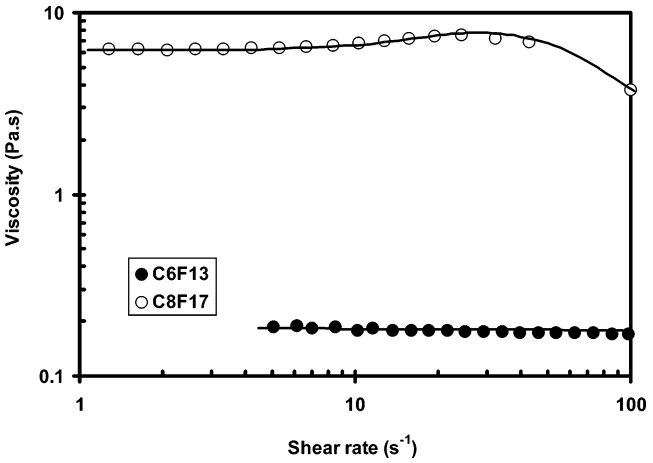


Figure 1. Steady shear flow curves of 2.0 wt % F-HEURs with different hydrophobes in aqueous solution at 20 °C.

NMR. The ^{19}F NMR spectra were recorded on a Bruker AM-360FT-NMR spectrometer operating at 339 MHz using a 5 mm quadrinuclear probe. The chemical shifts of the ^{19}F signals were referenced to aqueous solutions of $NaSO_3-CF_3$ at −78.25 ppm.

Dynamic Light Scattering (DLS). DLS sample solutions were conducted using a Brookhaven laser light scattering system equipped with a BI-9000AT digital correlator. The REPES routine in the GENDIST software package was used to analyze time correlation function with probe set to 0.5.

Results and Discussion

For 2.0 wt % F-HEUR-C6F13-35K, the viscosity (∼0.2 Pa·s) was almost independent of shear rate within the experimental shear rate regime (Figure 1). No shear thickening was observed in the moderate shear rate range, which was different from the behavior of telechelic associating polymers containing long hydrocarbon moieties.[4] The solution viscosity increased with polymer concentration. When the concentration was increased to 3.0 wt %, the low shear viscosity approached 1.0 Pa·s. In contrast, F-HEUR-C8F17-35K exhibited a typical rheological behavior similar to HEUR polymers containing strongly associating hydrocarbon end groups. The 2.0 wt % solution appeared to exhibit a slight shear thickening before the onset of shear thinning. A change in the hydrophobe from C_6F_{13} to C_8F_{17} groups resulted in an increase in the zero-shear viscosity of about 30 times, indicating a much stronger association of C_8F_{17} groups than that of C_6F_{13} groups. Varying the hydrophobic groups from C_6F_{13} to C_8F_{17} significantly altered the rheological properties, which also suggested that different association mechanisms must be in operation. Similar behaviors have also been observed by Winnik and co-workers.[25] On the basis of the thermodynamic criteria reported by Raspoud,[26] the formation of flowerlike association is possible for C_8F_{17}, but C_6F_{13} lies at the edge of the criteria.

Different types of cyclodextrin were used to study the cyclodextrin/F-HEUR-C8F17-35K interaction. Figure 2 compares the shear viscosity profiles of 2.0 wt % F-HEUR in the presence of different types of cyclodextrin at a cyclodextrin/F-hydrophobe molar ratio of 1. The viscosity profile of the α-CD/F-HEUR system was identical to that of F-HEUR solution in the absence of α-CD, which suggested that there was no interaction between α-CD and F-HEUR. However, γ-CD marginally reduced the viscosity of F-HEUR solution, and the characteristic shear thickening and shear thinning were preserved. In addition, the onset for the shear thickening and shear thinning behavior remained the same, which pointed to a weak interaction between γ-CD and F-HEUR. In contrast, the non-

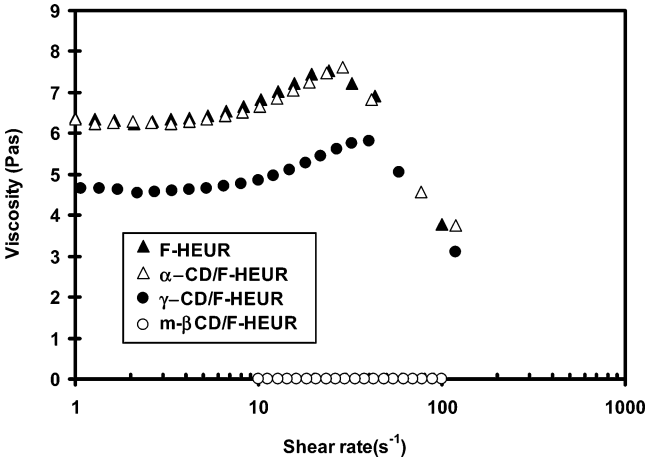


Figure 2. Viscosity profiles of 2.0 wt % F-HEUR-C8F17-35K aqueous solution in the presence of different cyclodextrins at 20 °C.

Newtonian viscosity profile of m-βCD/F-HEUR was reduced to a Newtonian viscosity of 0.005 Pa·s. The absence of shear thickening and shear thinning behavior after the addition of m-βCD suggested that the transient network formed by the associative junctions of fluorocarbon hydrophobes was completely destroyed through the strong interaction between m-βCD and fluorocarbon hydrophobic groups.

It has been reported by Palepu and co-workers that the relative size of cyclodextrin hydrophobic cavity is the decisive factor controlling the interaction between cyclodextrin and host molecules.[27] In order to form a guest−host inclusion complex, the size of hydrophobic cavity and the cross section of the guest molecules must be compatible to produce a stable complex. The diameter of a CF_2 group was estimated to be 0.5 nm, and that of a CF_3 group is 0.7 nm.[28] The cavity of α-CD (diameter ca. 0.5 nm) cannot accommodate the fluorocarbon chain with a CF_3 end group. Therefore, it was not possible for α-CD to form an inclusion complex with a fluorocarbon hydrophobe. In contrast, γ-CD has a larger cavity (diameter ca. 0.8 nm), and the fluorocarbon chain can loosely fit into the cavity. Thus, γ-CD can easily thread in and out of the fluorocarbon segment, and a stable complex cannot be produced. However, for m-βCD, the size of the inner hydrophobic cavity is 0.7 nm, which provided an excellent fit for the CF_3 group. Therefore, a fluorocarbon chain would be able to snugly fit inside the cavity of m-βCD molecule. Since the interior of the cavity is less polar than the aqueous phase, the inclusion of fluorocarbon chain into such a cavity reduced the contact between the fluorocarbon groups and the aqueous environment, which made such an inclusion complex energetically favorable.

The effect of m-βCD concentration on the steady shear viscosity of 2.0 wt % F-HEUR-C8F17-35K solution is shown in Figure 3. Addition of m-βCD dramatically reduced the steady-shear viscosities of the polymer solutions. The characteristic shear thickening and shear thinning region of HEUR solution became less apparent with increasing m-βCD concentration, and the onset of shear thickening and shear thinning shifted to higher shear rates. When m-βCD concentration was increased to 0.5 mol of m-βCD per hydrophobe, no shear thickening and shear thinning were observed. When m-βCD concentration was further increased to 1 mol of m-βCD per hydrophobe, the viscosity profile became Newtonian and possessed a relatively low viscosity of 0.005 Pa·s. Beyond this concentration regime, the viscosity did not show any significant reduction, suggesting that the fluorocarbon hydrophobes have been saturated with m-βCD molecules, and no additional interaction occurred between

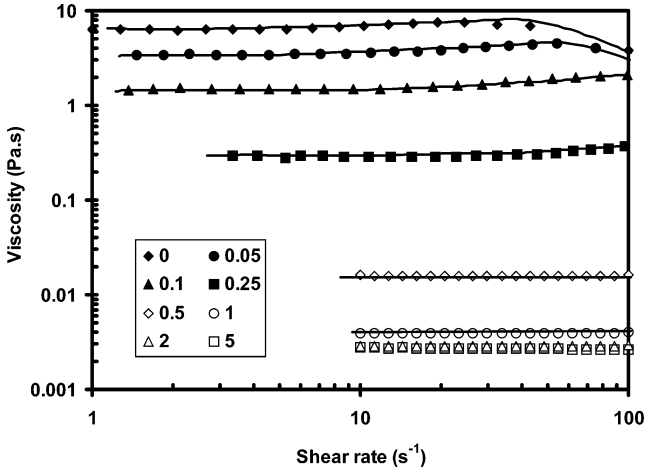


Figure 3. Effects of m-βCD concentration on the shear viscosity of 2.0 wt % F-HEUR-C8F17-35K aqueous solution at 20 °C. The number corresponds to the molar ratios of m-βCD to fluorocarbon hydrophobe [F].

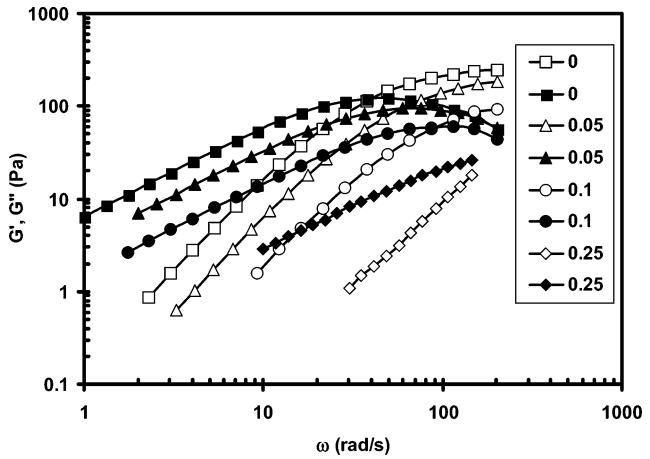


Figure 4. Dynamic moduli of 2 wt % F-HEUR-C8F17-35K aqueous solution with addition of different amounts of m-βCD at 20 °C. The number corresponds to the molar ratio of m-βCD to fluorocarbon hydrophobe [F]. Open symbols are G' and filled symbols are G''.

F-HEUR and m-βCD molecules. Compared with our previous study on the interaction between m-βCD and hydrocarbon HEUR,[29] it was apparent that m-βCD was more effective in destroying the F-HEUR network due to the stronger interaction between m-βCD and F-HEUR end groups.

A similar phenomenon was also observed for the dynamic rheological behavior, where the viscoelastic properties of F-HEUR solution could be fitted by a single element Maxwell model. At low frequencies, $G'(\omega)$ and $G''(\omega)$ possessed a slope of 2 and 1, respectively, and with increasing frequencies, $G'(\omega)$ approached the entanglement plateau region. Figure 4 shows the effect of m-βCD on the frequency dependence of elastic and loss moduli of 2.0 wt % F-HEUR-C8F17-35K polymer solution in the presence of different concentrations of m-βCD. The addition of m-βCD not only reduced both elastic and loss moduli but also increased their dependence on frequency. The greater dependence of moduli on the frequency is a sign of a weaker network structure due to the reduction in the number of mechanically active chains. When m-βCD/hydrophobe molar ratio exceeded 0.5, $G'(\omega)$ decreased to the point where it became undetectable. A Cole−Cole plot was constructed to describe the m-βCD/F-HEUR complex solution where the plateau modulus could be accurately determined from the intersection of the semicircle with the horizontal x-axis. If the fitting to the experimental data with the model is perfect, the G'' vs G' plot

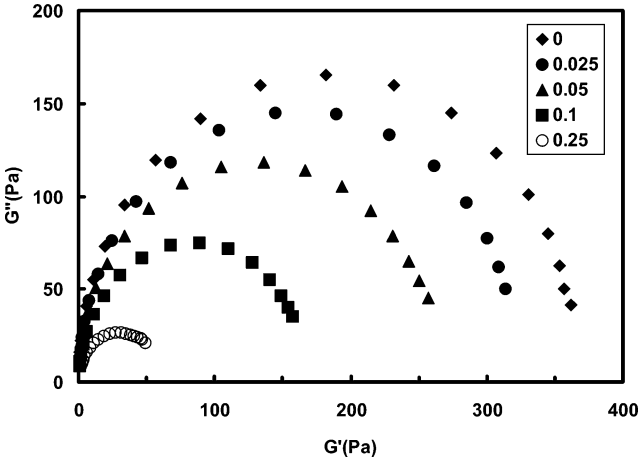


Figure 5. Cole−Cole plot of the dynamic properties of 2.0 wt % F-HEUR-C8F17-35K solution presenting different concentrations of m-βCD with the accompany fitting of the Maxwell model. The number corresponds to the molar ratio of m-βCD to fluorocarbon hydrophobe [F].

Table 1. Plateau Modulus and Relaxation Time for the m-βCD/F-HEUR System As Measured at 20 °C

[m-βCD]/[F] molar ratio	0	0.025	0.05	0.10	0.25
G_N^0 (Pa)	367	320	265	167	59
m	0.492	0.490	0.488	0.488	0.485
λ (s)	0.095	0.087	0.071	0.056	0.029

should form a semicircle as described by eq 1

$$G''(\omega) = [G'(\omega)G_N^0 - G'(\omega)^2]^m \quad (1)$$

where $m = 0.5$. Data which fitted the Maxwell model yielded a perfect semicircle when G'' was plotted against G'. The Cole−Cole plot for F-HEUR in the presence of different concentrations of m-βCD is shown in Figure 5 with fitted numerical values listed in Table 1.

For 2.0 wt % F-HEUR-C8F17-35K solution in the absence of m-βCD, the fitting yielded $m \sim 0.492$, which corresponded to an ideal fit to the Maxwell model. When m-βCD/hydrophobe molar ratio equaled 0.25, the fitting result of m was 0.485, suggesting that the single Maxwell model is still valid. It can be observed from Table 1 that both plateau moduli and relaxation times decreased with increasing m-βCD concentration. Comparing these results with the hydrocarbon HEUR system, the plateau modulus decreased more significantly than the relaxation time. At [m-βCD]/[F] ([F] represents fluorocarbon end group) molar ratio of 0.25, the magnitude of plateau modulus was only 1/6 of the original modulus in the absence of m-βCD, while the relaxation time remained at 1/3 of the original value in the absence of m-βCD. This implied that the reduction in solution viscosity is mainly attributed to the deactivation of the fluorocarbon moieties from the hydrophobic domains of the polymer network.

Figure 6 compares the effect of the m-βCD/hydrophobe molar ratio on the zero shear viscosity of F-HEUR-C8F17-20K and F-HEUR-C8F17-35K solutions. F-HEUR with a lower molecular weight (F-HEUR-C8F17-20K) exhibited a higher viscosity in the absence of m-βCD, and this was attributed to the relatively higher mole percentage of fluorocarbon hydrophobe. With the addition of m-βCD, both viscosities decreased. At [m-βCD]/[F] molar ratio of 1, the viscosity of the F-HEUR-C8F17-20K/CD system was identical to the F-HEUR-C8F17-35K/CD system, which suggested that the hydrophobic interaction of fluorocarbon HEUR and m-βCD was not related to the length of PEO chains.

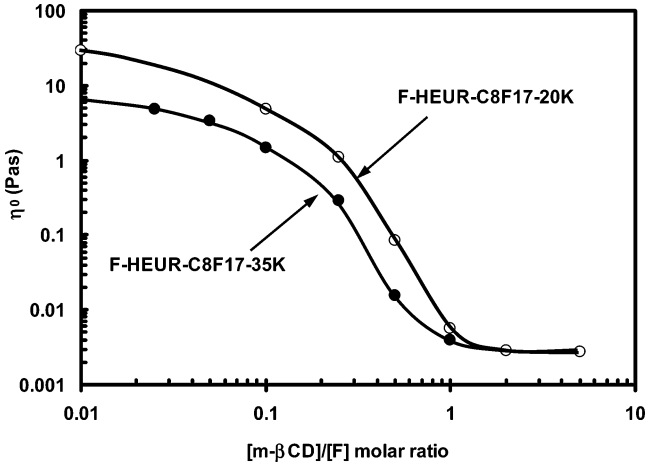


Figure 6. Effect of molecular weight on zero-shear viscosity of the F-HEUR and m-βCD mixed system at 20 °C.

The effect of temperature on the viscoelastic behaviors of F-HEUR in the presence of m-βCD was investigated as a function of m-βCD concentration. With increasing temperature, a reduction in G_N^0, λ, and η_0 was evident, and the decease in λ was more rapid than G_N^0. This suggested that increasing temperature enhanced the exit rate of hydrophobes from the associative junctions. At high temperatures, the viscoelasticity of the polymer solution exhibited larger deviation from the single Maxwell model. The temperature dependence of relaxation time and low shear viscosity obeyed the Arrhenius expression as shown in Figure 7a, and the activation energy was derived from the slope. It was evident that the activation energy determined from viscosity was larger than that obtained from relaxation time. The activation energies of the F-HEUR-C8F17-20K and F-HEUR-C8F17-35K systems were fairly identical, which suggested that the hydrophobic interaction was the major factor controlling the temperature dependence of the viscosity. The molecular weight of PEO chains has a negligible effect on the activation energy. The effect of m-βCD on the activation energy for the two F-HEURs was identical (Figure 7b), which confirmed the hypothesis that the temperature dependence of viscosity was dictated by hydrophobic interaction. At [m-βCD]/[F] molar ratio lower than 0.1, the activation energy was constant, and it exhibited a sharp decrease at a molar ratio of between 0.1 and 1.0. At [m-βCD]/[F] molar ratio greater than 2, the activation energy approached an asymptotic value that was very close to the activation energy of water.

The m-βCD/F-HEUR-C6F13-35K system possessed a smaller activation energy, since the hydrophobic interaction was weaker. When the [m-βCD]/[F] molar ratio exceeded 1, the activation energy was slightly larger than the F-HEUR with C_8F_{17} hydrophobe, suggesting that C_6F_{13} system still possessed a small fraction of weak intermolecular junctions since the association is controlled by the open association mechanism. From Figure 7b, it was observed that the activation energy of F-HEUR-C6F13-35K approached a minimum at a [m-βCD]/[F] ratio of 1, while the F-HEUR-C8F17-35K series reached a minimum at molar ratio of 2, which implied that the stoichiometry may be different for different fluorocarbon end groups. To further elucidate this phenomenon, ITC experiments were conducted on the dilute solutions with thermograms shown in Figure 8.

The changes in the complexation thermodynamics of CD are generally the results of several contrasting effects originating from the following: (i) penetration of the hydrophobic segment of the guest molecule into the CD cavity, (ii) dehydration of the guest, (iii) formation of hydrogen bonds, (iv) release of water

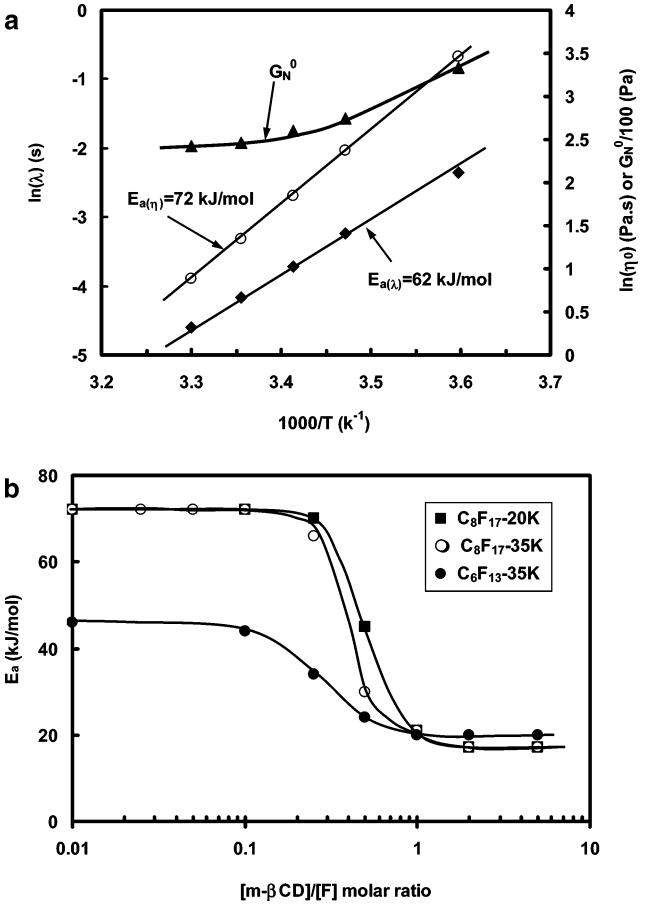


Figure 7. (a) Temperature dependence of η_0, λ, and G_N^0 of F-HEUR-C8F17-35K. (b) Activation energies from viscosity measurement of three different F-HEUR systems in the presence of m-βCD.

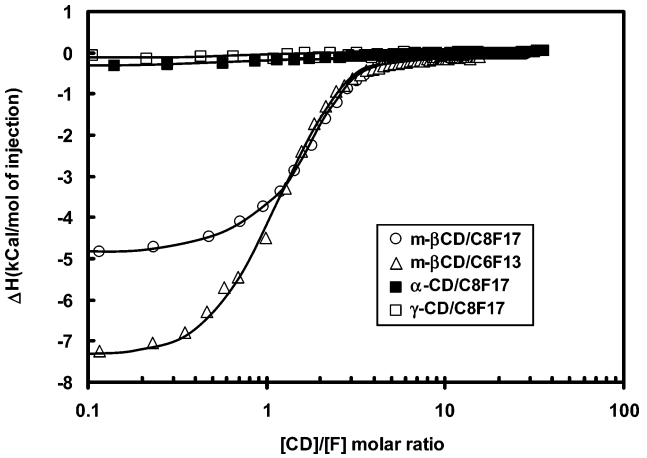


Figure 8. Isothermal titration calorimetric curves of 1 wt % CD into 0.1 wt % F-HEUR aqueous solution at 25 °C and 1 atm.

molecules from the CD cavity to bulk water, and (v) conformational changes of CD upon the inclusion of the guest molecule. Large negative enthalpy changes for m-βCD titrated into both F-HEUR with C_8F_{17} and C_6F_{13} were described by the sigmoidal titration curves, which represent the interaction between cyclodextrin molecules and the fluorocarbon hydrophobic moiety. The thermodynamic parameters were determined by applying a nonlinear least-squares fitting to the data (using ORIGIN software) based on a binding model to the same site for C_6F_{13} and C_8F_{17} moieties, and the derived parameters are summarized in Table 2. In comparison, there is no significant enthalpy change observed for the titration α- and γ-CD to the

Table 2. Thermodynamic Parameters Associated with the Interaction between m-βCD and F-HEUR As Determined from ITC at 25 °C and 1 atm

fluorocarbon groups	n	K (M^{-1})	ΔG (kJ/mol)	ΔH (kJ/mol)	$T\Delta S$ (kJ/mol)
C_8F_{17}	2	5.3×10^4	−26.9	−24.2	2.7
C_6F_{13}	1	4.9×10^4	−26.7	−41.8	−14.9

polymer solutions, which suggested the absent or weak hydrophobic interaction, which is in agreement with previous rheological data.

The large negative entropy changes usually arise from the large reduction in the translational and conformational freedoms of host and guest molecules upon complexation. On the other hand, large positive entropy changes are attributed to the relatively high flexibility of the guest molecule after complexation, and the extensive desolvation from the hydrophilic moieties of host and guest, or the release/restructuring of the water molecules inside and around the cavity.[30] From Table 2, it is interesting to observe that though the length of fluorocarbon hydrophobe is different, ΔG possessed identical values. However, the entropy is positive for the longer C_8F_{17} and negative for the shorter C_6F_{13} hydrophobes. This difference may be attributed to the different binding stoichiometry, where the C_8F_{17} hydrophobe is completely encapsulated by two cyclodextrin molecules, thereby removing all possible interactions between the fluorocarbon hydrophobes. Thus, a relatively high chain flexibility of guest is expected after complexation with m-βCD. However, the C_6F_{13} hydrophobe can only be encapsulated by one CD molecule with a small fraction of the hydrophobic segment exposed to bulk water. The exposed hydrophobic segments resulted in a weak interaction between the fluorocarbon hydrophobes, which reduced the flexibility of F-HEUR compared to the C_8F_{17} hydrophobic system. This description is consistent with the result derived from activation energies, where some extent of association was still present in the solution after the addition of m-βCD. For the cyclodextrin−surfactant mixture, it was also reported that with long hydrophilic segments a 1:1 complex was always formed for carbon number ≤6, and both 1:1 and 2:1 complexes were produced when the carbon number was greater than 6.[18,19]

Dynamic light scattering results conducted on the F-HEUR system in the presence and absence of m-βCD are shown in Figure 9. For translational decay mode, the decay rate Γ is related to the translational diffusion coefficient D by

$$\Gamma = Dq^2 = \frac{D(4\pi n)^2}{\lambda^2}\sin^2\left(\frac{\theta}{2}\right) \tag{2}$$

where q is the scattering vector, n the refractive index, λ the incident wavelength, and θ the scattering angle. Using the Stokes−Einstein relationship, the apparent hydrodynamic radius R_h can be determined:

$$R_h = \frac{kT}{6\pi\eta D} \tag{3}$$

where k is the Boltzmann constant, T the absolute temperature, and η the solvent viscosity.

Only one mode was evident from the decay time distribution functions of 0.1 wt % F-HEUR-C8F17-35K solution. The linear dependence of the decay rates on q^2 suggested that the relaxation mode is a translational diffusion mode, and the slope of decay rate vs q^2 corresponded to the translational diffusion coefficient of F-HEUR in solution. The measured R_h was 23 nm from DLS. On the basis of the molecular weight, the calculated monomeric

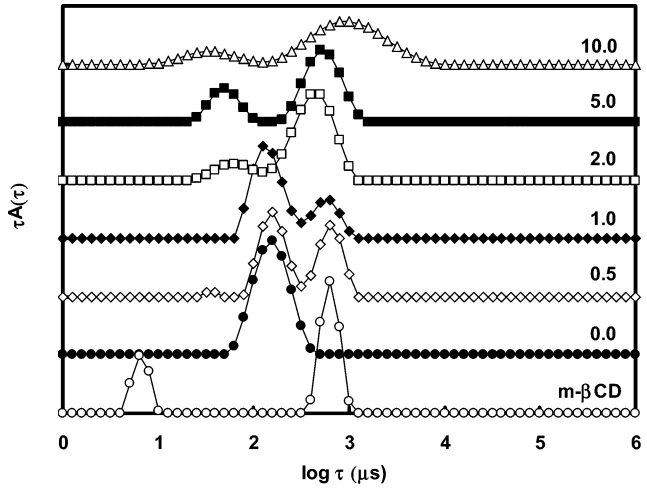


Figure 9. Decay time distribution of 0.1 wt % F-HEUR-C8F17-35K solution in the presence of different concentrations of m-βCD; the numbers correspond to the [m-βCD]/[F] molar ratio. Open circles are the decay time distribution of pure m-βCD in aqueous solution.

F-HEUR R_h was ~6 nm.[31] Thus, 23 nm is related to F-HEUR micelles in dilute solution. Upon the addition of m-βCD, the relaxation time distributions exhibited two distinct modes. The angular dependence of the decay time distribution functions indicated both translational characteristics are present. The fast mode relates to an R_h of ~23 nm, which is identical to the F-HEUR mode in the absence of cyclodextrin. The slow mode in the decay time distribution function has a hydrodynamic radius of ~92 nm, which corresponded to the cluster of aggregated m-βCD molecules as evident from the long time relaxation mode in the decay time distribution of m-βCD in water (open circles). The two translational modes in the decay time distribution of m-βCD solution corresponded to the apparent hydrodynamic radii of 1 and 90 nm, respectively, representing the unimeric m-βCD molecules and m-βCD aggregates. Similar results have also been observed for HEUR and the m-βCD system.[32] Coleman and co-workers examined the aggregation behavior of cyclodextrins and concluded that the solubility was related to the interaction of the aggregate structure and water.[33] Although the amount of m-βCD aggregates is relatively small, their contribution to the scattering intensity is significant due their relatively larger size. The scattered intensity scales with the number of particles dictated by C and is also proportional to R_h^6, where C is the concentration and R_h is the hydrodynamic radius of the scattering object. Thus, the scattering intensity is dominated by the slower diffusive component.[34] The disappearance of the unimeric m-βCD in the decay time distribution function of F-HEUR/m-βCD mixture reinforced the binding interaction between m-βCD and F-HEUR. By further increasing the cyclodextrin concentration, the relaxation times of the fast mode decreased until the cyclodextrin concentration reached 2 mol of m-βCD per hydrophobe. It then became independent of m-βCD concentration when [m-βCD]/[F] exceeded 2, and the size of hydrodynamic radius of 7 nm represented the size of PEO chain of similar molecular weight. In addition, the slow mode remained unchanged with increasing [m-βCD]/[F] molar ratio. Beyond a ratio of 10, larger cyclodextrin aggregates were formed in solution, which gave rise to the increase in decay time.

^{19}F NMR chemical shifts assignments were reported by Ribiero.[35] These heteronuclear correlations were observed in perfluoroheptanoic acid and combined with ^{19}F-decoupled ^{13}C and homonuclear ^{19}F NMR data; the resulting ^{19}F COSY can be used to derive a full set of unequivocal ^{19}F assignments.

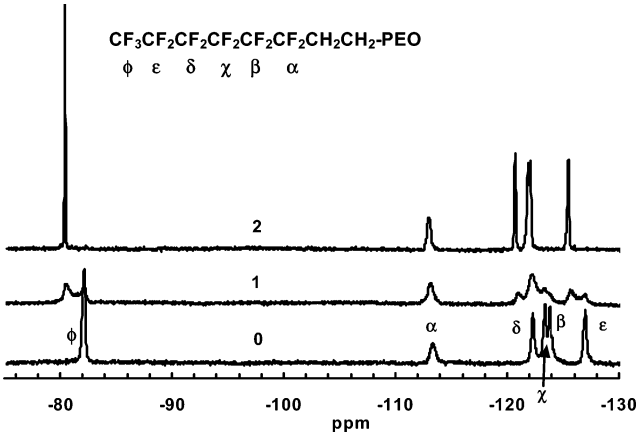


Figure 10. ^{19}F NMR peak assignments of C_6F_{13} end-capped F-HEUR and the effect of addition m-βCD on the ^{19}F NMR spectra of F-HEUR-C6F13-35K; the number corresponds to the [m-βCD]/[F] molar ratio.

Figure 10 revealed that the ^{19}F NMR spectra of F-HEUR-C6F13-35K are identical to that of perfluoroheptanoic acid. Therefore, the peak assignment of ^{19}F F-HEUR-C6F13-35K is analogous to perfluoroheptanoic acid.

Upon the addition of m-βCD, the CF_3 resonance due to the upfield aggregation at −82.2 ppm decreased, and a new CF_3 downfield resonance at −80.3 ppm was observed (Figure 10). At about 1 equiv of added m-βCD, the ratio of the downfield over the upfield resonance was about 3, and at 2 equiv of m-βCD the resonance at −82.2 ppm had virtually disappeared. A new distinct downfield resonance was also observed for the $-CF_2$ group upon the addition of m-βCD, and the ratios of the two resonances at a particular m-βCD concentration were identical to that of CF_3 resonances. For the other CF_2 groups, only downfield shifts were observed, and the broad resonances were visible in the intermediate range, and they became narrower at m-βCD/F-HEUR ratios greater than 1. The data were consistent with the formation of a 1:1 m-βCD/F-HEUR-C6F13-35K inclusion complex that exchanged slowly with the associated form on the ^{19}F NMR time scale. The resonance for the $-CF_2$ group close to the PEO segment was independent of m-βCD concentration, which suggested that the fluorocarbon end groups were only partially located inside the hydrophobic cavity, and one CF_2 groups remained outside the m-βCD cavity. This CF_2 might interact with neighboring fluorocarbon, resulting in an apparent larger activation energy as derived from the viscosity data compared to the F-HEUR-C8F17-35K system.

NMR chemical shifts assignment of C_8F_{17} group on one end of the perfluorocarbon-modified poly(ethylene glycol) was determined by Boschet et al.[36] For F-HEUR polymer with C_8F_{17} end groups, the ^{19}F NMR spectra were fairly identical (Figure 11). The ^{19}F NMR resonances of CF_3 upon the addition of m-βCD showed a similar trend as CF_3 of the C_6F_{13} end group. The CF_3 resonance at −82.2 ppm decreased, and a new CF_3 downfield resonance at −80.3 ppm was observed. At about 1 equiv of added m-βCD, the ratio of the downfield over the upfield resonance was about 3, and at 2 equiv of m-βCD the resonance at −82.2 ppm had virtually disappeared. The downfield resonance was also observed for the $-CF_2$ group upon the addition of m-βCD, and the ratios of the two resonances at a given concentration of m-βCD were identical to that of the CF_3 resonance. The resonance for the $-CF_2$ group next to the PEG segment was a single peak before the addition of m-βCD of ratio 1, and no shift was observed. But when the molar ratio was increased to 2, a downshift peak was observed, which suggested that all the fluorocarbon end groups were encapsulated

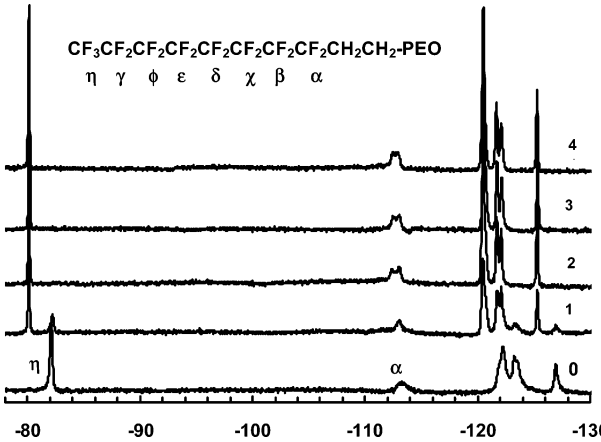


Figure 11. Effect of addition m-βCD on the ^{19}F NMR spectra of F-HEUR-C8F17-35K; the number corresponds to the [m-βCD]/[F] molar ratio.

by two m-βCD molecules, which suppressed the hydrophobic interaction between fluorocarbon hydrophobes. The results were consistent with the result from ITC, confirming the formation of a 2:1 m-βCD/F-HEUR-C8F17-35K inclusion complex.

Experimental findings support the formation of a 2:1 inclusion complex between m-βCD and F-HEUR-C8F17-35K but the 1:1 inclusion complex between m-βCD and F-HEUR-C6F13-35K. To further understand the binding interaction between m-βCD and F-HEUR, a mathematic model was developed. Karlson and co-workers attempted to interpret the binding isotherm between hydrocarbon HEUR and cyclodextrin by adopting the Langmuir adsorption model.[15] In addition, the Langmuir adsorption model was adopted to describe the interaction between cyclodextrin and hydrophobically modified ethyl(hydroxylethyl)cellulose, and good correlation between experiment data and theory was observed.[15,16] In their development of the model for describing the relationship between viscosity and cyclodextrin concentration, they assumed that the relaxation time for the relaxation process was independent of cyclodextrin concentration. For the m-βCD/F-HEUR system, it was also observed that the relaxation time decreased with increasing m-βCD concentration, and similar phenomena have also been observed for the m-βCD/HEUR system by Horsky and co-workers.[14a] Therefore, it was difficult to quantitatively predict the η_0/[cyclodextrin] relationship on the basis of the model proposed by Karlson and co-workers. In order to interpret the influence of m-βCD on the transient network structure of F-HEUR, we modified the previous adsorption model for describing the relationship between m-βCD concentration and plateau modulus of the polymeric network.

It was known the contribution to solution viscosity comes from both relaxation time λ and plateau modulus G_N^0:[4]

$$\eta = g\lambda G_N^0 \tag{4}$$

On the basis of the theory of rubber elasticity described by the transient network theory proposed by Green and Tobolsky,[37] G_N^0 is proportional to the number density of mechanically active chains ν

$$G_N^0 = \nu RT \tag{5}$$

where R is the gas constant and T is the temperature in kelvin. Since the binding interaction between end-capped fluorocarbon and m-βCD dissociates the F-HEUR associative junctions, the plateau modulus G_N^0 determined from dynamic oscillation experiments is independent of relaxation time and should be a more suitable parameter than the solution viscosity.

In dilute solutions beyond the cmc, F-HEUR self-assembles into flowerlike micelles comprising of a $C_nF_{2n+1}(CH_2)_m$ core surrounded by a swollen PEO corona with an averaged aggregation number N_{agg} ranging from 30 to 50.[38] Under such conditions, F-HEUR chains are in the form of looping chains with both ends associated into a micellar core. With increasing concentration beyond the overlap concentration C^*, these flowerlike micelles started to aggregate through the connection of bridging chains (both hydrophobic ends of one F-HEUR chain in different micelles) to produce a three-dimensional network. The 2:1 inclusion complex for m-βCD and the F-HEUR-C8F17-35K system determined from titration calorimetry was performed in the dilute solution regime, while the rheological experiments were conducted in the semidilute or concentration solution regime. Thus, the stiochiometry obtained from ITC experiments may not be applicable to the binding behavior in the semidilute to concentration solution regimes. It is reasonable to hypothesize that the formation of a 1:1 inclusion complex will result in the destruction of the transient network structure; hence, the 1:1 binding stiochoimetry could be used in deriving the mathematical relationship as described below.

Assuming that 1:1 "nut and bolt" complexes are formed between m-βCD and C_8F_{17} hydrophobe, the formation of the complex resulted in the deactivation of active junctions. The Langmuir adsorption model assumes that all binding sites are equivalent and each site can hold at most one molecule of adsorbate, and there are no interactions between the adsorbate molecules on adjacent sites of an ideal surface.[39] For telechilic end-capped PEO, the number density of mechanically active chain, ν, is related to the fraction of hydrophobic polymeric segments encapsulated by m-βCD (Θ), via eq 6:[14a]

$$(1-\Theta)^2 \propto \nu = \frac{G_N}{G_N^0} \tag{6}$$

where G_N is the plateau modulus of F-HEUR/m-βCD solution and G_N^0 represents the plateau modulus of F-HEUR solution in the absence of m-βCD.

In the mixed solution of F-HEUR and m-βCD, m-βCD could interact with bridging chains, looping chains, and dangling chains. However, only the interaction with bridging chain contributes to the viscoelasticity properties of the solution. Supposing K_b is the binding constant for the complex formation between F-HEUR and m-βCD, C_{CD} is total m-βCD concentrations and C_{hy} is the concentration of polymeric hydrophobic segments (= 2[F]). We found that the empirically modified form of the Langmuir isotherm given by eq 7 can account for the reduction in the ratio of bridging and looping chains with increasing CD concentration,[14b] where χ_b is an adjustable parameter.

$$K_b = \frac{\Theta}{(1-\Theta)(C_{CD} - \Theta\chi_b C_{hy})} \tag{7}$$

Thus

$$\Theta = \frac{1}{C_{hy}{}^*\chi_b}\left(\frac{K_b\chi_b C_{hy} + K_b C_{CD} + 1}{2K_b} - \sqrt{\left(\frac{K_b\chi_b C_{hy} + K_b C_{CD} + 1}{2K_b}\right)^2 - \chi_b C_{hy} C_{CD}}\right) \tag{8}$$

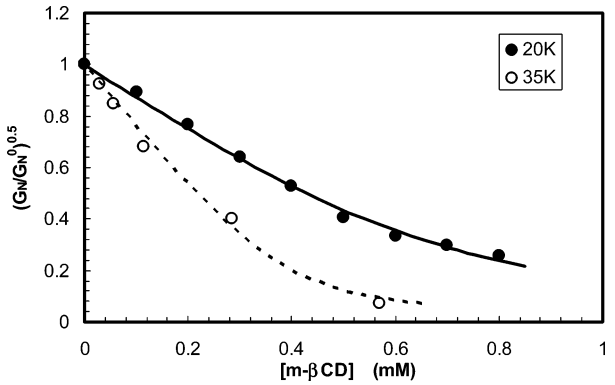


Figure 12. $(G_N/G_N^0)^{0.5}$as a function of m-βCD concentration in 2 wt % F-HEUR. Lines represent predictions from eq 9: ●, 20K; ○, 35K.

Table 3. Association Constant *K*, χ_b, and G_N^0 from Sequential Absorption Model; Data Fitted Using MATLAB Software

PEO MW	C_{hy} (mM)	K_b (mM^{-1})	χ_b	G_N^0 (Pa)
35K	1.14	44.1	0.34	365
20K	2.00	11.3	0.34	900

Combining eqs 6 and 8 yields

$$\left(\frac{G_N}{G_N^0}\right)^{1/2} = 1 - \frac{1}{C_{hy}{}^*\chi_b}\left(\frac{K_b\chi_b C_{hy} + K_b C_{CD} + 1}{2K_b} - \sqrt{\left(\frac{K_b\chi_b C_{hy} + K_b C_{CD} + 1}{2K_b}\right)^2 - \chi_b C_{hy} C_{CD}}\right) \quad (9)$$

Figure 12 compares the [m-βCD]/[F] molar ratio dependence of the plateau modulus of these two F-HEURs in the presence of different concentrations of m-βCD with fitted parameters summarized in Table 3. The binding constant for the 35K F-HEUR was about 4 times that of the 20K F-HEUR, as the lifetime of the 20K F-HEUR would be much larger than the 35K F-HEUR and hence will be less accessible for binding with m-βCD. However, the adjustable parameter χ_b for the two systems was identical. The fitting results for the 35K F-HEUR were compared with those from ITC, and both binding constants are fairly identical (40 vs 53 and 49 mM^{-1}). The slight difference is attributed to the presence of both looping chains and bridging chains in solution, where ITC only measured the averaged value and plateau modulus was only sensitive to bridging chains.

Conclusions

The fluorocarbon derivatives (C_6F_{13} and C_8F_{17}) of PEO with molecular weights of 20K and 35K g/mol were synthesized and characterized. The rheological property revealed that F-HEUR solution with C_8F_{17} end groups was viscoelastic but not for that with C_6F_{13} end groups. The interaction between m-βCD and these F-HEURs was studied by rheological, dynamic light scattering, isothermal titration calorimetric, and ^{19}F NMR techniques. The viscosity of F-HEUR solution was greatly reduced in the presence of m-βCD because of the disruption of intermolecular hydrophobic association. The results from oscillatory measurement indicated that the plateau modulus decreased with the addition of m-βCD. A modified sequential adsorption model was proposed to describe the relationship between G_N^0 and cyclodextrin concentration. The activation energies determined from the zero-shear viscosity decreased with m-βCD concentrations until a molar ratio of 2, and thereafter it remained constant. There is a small difference between the E_a for C_6F_{13} and C_8F_{17} end groups at high cyclodextrin concentrations, revealing some subtle differences in the complex produced by these two fluorocarbon end groups. It was observed from ITC thermograms that the complex formation of m-βCD and fluorocarbon group revealed an apparent stoichoimetry of 1 and 2 for C_6F_{13} and C_8F_{17}, respectively. Binding constants determined from ITC agreed with those obtained from the sequential binding model on the basis of dynamic rheological measurement. DLS results indicated that the presence of cyclodextrin can effectively remove the hydrophobic interaction. ^{19}F NMR showed a different mechanism for C_6F_{13} and C_8F_{17} fluorocarbon hydrophobes, which were in agreement with the results determined from activation energies and ITC.

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References and Notes

(1) Jenkins, R. D. The Fundamental Thickening Mechanism of Associative Polymers in Latex System: A Rheological Study. Ph.D. Thesis, Lehigh University, Bethlehem, PA, 1990.
(2) Jenkins, R. D.; Silebi, C. A.; El-Aasser, M. S. *Polym. Mater. Sci. Eng.* **1989**, *61*, 629.
(3) Annable, T.; Buscall, R.; Ettelaie, F.; Whittlestone, D. *J. Rheol.* **1993**, *37*, 695.
(4) Tam, K. C.; Jenkins, R. D.; Winnik, M. A.; Bassett, D. R. *Macromolecules* **1998**, *31*, 4149.
(5) Glass, J. E. *J. Coat. Technol.* **2001**, *73*, 79.
(6) Winnik, M. A.; Yekta, A. *Curr. Opin. Colloid Interface Sci.* **1997**, *2*, 424.
(7) Hogen-Esch, T. E.; Amis, E. J. *Trends Polym. Sci.* **1995**, *3*, 98.
(8) Zhang, K.; Hogen-Esch, T. E.; Boschet, F.; Margaillian, A. *ACS Polym. Prepr.* **1996**, *37*, 731.
(9) Berret, J. F.; Calvet, D.; Collet, A.; Viguier, M. *Curr. Opin. Colloid Interface Sci.* **2003**, *8*, 296.
(10) Cathebras, N.; Collet, A.; Viguier, M.; Berret, J. F. *Macromolecules* **1998**, *31*, 1305.
(11) Karlson, L.; Joabsson, F.; Thuresson, K. *Carbohydr. Polym.* **2000**, *41*, 25.
(12) Connors, K. A. *Chem. Rev.* **1997**, *97*, 1325.
(13) Akiyoshi, K.; Sasaki, Y.; Kuroda, K.; Sunamoto, J. *Chem. Lett.* **1998**, *1*, 93.
(14) (a) Horsky, J.; Mikesova, J.; Quadrat, O.; Snuparek, J. *J. Rheol.* **2004**, *48*, 23. (b) Karlson, L.; Thuresson, K.; Lindman, B. *Langmuir* **2002**, *18*, 9028.
(15) Karlson, L.; Malmborg, C.; Thuresson, K.; Soderman, O. *Colloids Surf., A* **2003**, *228*, 171.
(16) Karlson, L.; Thuresson, K.; Lindman, B. *Carbohydr. Polym.* **2002**, *50*, 219.
(17) Islam, M. F.; Jenkins, R. D.; Bassett, D. L.; Lau, W.; Ou-Yang, H. D. *Macromolecules* **2000**, *33*, 2480.
(18) Wilson, L. D.; Verrall, R. E. *J. Phys. Chem. B* **1997**, *101*, 9270.
(19) Wilson, L. D.; Verrall, R. E. *J. Phys. Chem. B* **1998**, *102*, 480.
(20) Junquera, E.; Tardajos, G.; Aicart, E. *Langmuir* **1993**, *9*, 1213.
(21) Guo, W.; Fung, B. M.; Chtistan, S. D. *Langmuir* **1992**, *8*, 446.
(22) Zhang, H.; Zhang, K.; Hogen-Esch, T. E. *Langmuir* **1998**, *14*, 4972.
(23) Immel, S.; Lichtenthaler, F. W. *Starch* **1996**, *48*, 225.
(24) Dai, S.; Tam, K. C. *Colloids Surf., A* **2003**, *229*, 157.
(25) Xu, B.; Li, L.; Yekta, A.; Masouni, Z.; Kanagalingam, S.; Winnik, M. A.; Zhang, K.; Macdonald, P. M. *Langmuir* **1997**, *13*, 2447.
(26) (a) Raspaud, E.; Lairez, D.; Adam, M.; Carton, J.-P. *Macromolecules* **1994**, *27*, 2956. (b) *Macromolecules* **1996**, *29*, 1269.
(27) Palepu, R.; Richardson, J. E.; Reinsborough, V. C. *Langmuir* **1989**, *5*, 218.
(28) Tiddy, G. L. T. In *Modern Trend of Colloid Science in Chemistry and Biology;* Birkhauser: Basel, 1985.
(29) Liao, D.; Dai, S.; Tam, K. C. *Polymer* **2004**, *45*, 8339.
(30) Rekharsky, M. V.; Inoue, Y. *J. Am. Chem. Soc.* **2002**, *124*, 813.
(31) Dai, S.; Tam, K. C.; Jenkins, R. D. *J. Phys. Chem. B* **2001**, *105*, 10189.
(32) Liao, D. Interactions between Cyclodextrin and Amphiphilic Polymer. Ph.D. Thesis, Nanyang Technological University, Singapore, 2006.
(33) Coleman, A. W.; Nicolis, I.; Keller, N.; Dalbiez, J. P. *J. Inclusion Phenom. Mol. Recognit. Chem.* **1992**, *13*, 139.
(34) Gaitano, G. G.; Brown, W. *J. Phys. Chem. B* **1997**, *101*, 710.
(35) Ribeiro, A. A. *J. Fluorine Chem.* **1997**, *83*, 61.

(36) Boschet, F.; Banger, F.; Margaillan, A.; Condamine, E. *Polymer* **2002**, *43*, 5329.
(37) Green, M. S.; Tobolsky, A. V. *J. Chem. Phys.* **1946**, *14*, 80.
(38) Tae, G.; Kornfield, J. A.; Hubbell, J. A.; Lal, J. *Macromelecules* **2002**, *35*, 4448.
(39) Richard, I. M. *Principles of Adsorption and Reaction on Solid Surfaces*; John Wiley & Sons: Singapore, 1996.

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