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A ferrocene-functionalized hydrophobically modified ethoxylated urethane: Redox-responsive controlled self-assembly and rheological behavior in aqueous solution

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KEYWORDS: Redox-responsive; controlled self-assembly; rheological behavior; ferrocene; telechelic polymers; hydrophobically modified ethoxylated urethane.

ABSTRACT: In this work, we present a novel redox-responsive ferrocene-functionalized hydrophobically modified ethoxylated urethane (**Fc-HEUR**) model polymer. The effects of redox-induced hydrophobicity change of ferrocenyl hydrophobes on the self-assembly and rheological properties of **Fc-HEUR** in aqueous solution were investigated. In view of the redox-induced change in the hydrophilic–lipophilic balance of polymer, the **Fc-HEUR** polymer in aqueous solution can reversibly self-assemble into spherical micelles and larger micellar aggregates of different nanoscales, and also disassemble by redox reactions immediately. Moreover, we have demonstrated that a rearrangement of micellar junctions

takes place through a bridge-loop or loop-bridge transition in the concentrated polymer solution followed by redox reactions, meanwhile, which induces a great change in rheological properties of the polymer solution: A viscoelastic liquid for the reduction state **Fc-HEUR** and a viscous liquid for the oxidation state  $Fc^+$ -HEUR due to their different relaxation behavior. Particularly, the associative structures and rheological properties of the **Fc-HEUR** aqueous solution can be reversibly controlled by redox reactions. This work will be useful not only for understanding of the thickening mechanism of stimuli-responsive HEURs but also for development of reversible self-assembly and controlled rheological fluids, which may have some special application in drug delivery systems, catalyst supports, sensors, and microfluidic devices.

#### **INTRODUCTION**

Telechelic amphiphilic polymers composed of a hydrophilic main chain and two hydrophobic end groups can aggregate into various nanostructures in aqueous solution.<sup>1-4</sup> As an important class of telechelic associative polymers, hydrophobically modified ethoxylated urethanes (HEURs) composed of a hydrophilic poly(ethylene glycol) (PEG) main chain and two hydrophobic end groups linked to the main chain through urethane groups can self-assemble into flower-like micelles, large aggregates, and even network structures with increasing polymer concentration (C).<sup>5-6</sup> Particularly, HEURs in aqueous solution can form flower-like micelles consisting of the flower loops (hydrophilic backbone) and the micellar cores (hydrophobic end groups) above a critical aggregation concentration (cac).<sup>7</sup> Above a critical percolation concentration ( $C_p$ ), these flower-like micelles will form large aggregates of micelle through the

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bridge connection of the hydrophilic chain between adjacent micelles, and eventually a dynamic network of micellar junctions is developed, leading to the solution viscosity increases sharply with increasing C.<sup>5</sup> Therefore, HEURs are also a kind of excellent thickening agents to regulate solution viscosity in water-borne coatings, inks, cosmetics, medicines and many other fields in the past decades.<sup>6, 8-11</sup>

In order to demonstrate the aggregation and rheological behavior of HEUR aqueous solution, many theories or models have been developed. Winnik's loop-bridge model expounded that the polymer chains in aqueous solutions will undergo a series of bridge-bridge. loop-bridge and bridge-loop transitions under shear, leading to interesting rheological behavior.<sup>12</sup> According to the transient network theory, the end hydrophobes can exchange between neighbouring micellar cores at the same time, and the network is temporal and can relax in a finite time scale.<sup>13-14</sup> Numerous research have demonstrated that the temperature, solution concentration, molecular weight and its distribution, hydrophilic backbone and type of end groups have a great influence on the solution rheological behavior of HEUR.<sup>15-16</sup> However, there remain many challenges to synthesis of HEURs comprising different types of units, which interact with one another to perform desired rheological properties. A major challenges we face are that the rheological properties of these "classical" HEURs can be tuned only by either changing temperature, concentration, solvent, or by synthesizing a new HEUR.<sup>17-19</sup> It is worth noting that the influence of hydrophobes including the the hydrophobic chain length, size, and structure on the rheological behavior of HEUR solution is disproportionately significant so that considerable efforts have been made to demonstrate the effects of the hydrophobes on the solution rheological behavior of HEURs, although the

hydrophobes comprise only a small part of the HEUR polymers.<sup>18, 20</sup> For instance, Elliott synthesized a series of narrow distribution model HEUR, and studied influence of terminal hydrophobe branching on the solution rheological behavior.<sup>20</sup> We also reported several Percec-type dendron-functionalized HEURs and studied the influence of hydrophobic tail number on the solution rheological behavior.<sup>17</sup> In view of the effects of end groups, the use of stimuli-responsive moieties to act as hydrophobes in HEURs is particularly attractive. The reversible hydrophobicity change of stimuli-responsive hydrophobes may lead to a rearrangement of micellar junctions in HEUR solution upon exposure to stimuli, thereby altering the solution rheological properties in a controlled manner.

Recently, we reported the photo-responsive aggregation and rheology of an azobenzene-functionalized HEUR (Azo-HEUR) in aqueous solution.<sup>21</sup> The light-induced reversible hydrophobicity change of Azo hydrophobes leads to a rearrangement of micellar junctions through loop-bridge and bridge-loop transitions in HEUR solution and thus a change of solution rheological properties upon alternative exposure to UV and visible light, which provides a new strategy and perspective for tuning the solution rheological properties and understanding the thickening mechanism of stimuli-responsive HEURs. However, the Azo-HEUR shows a slow responsive rate and a small magnitude of response to light irradiation, which may limit its practical applications. As is known to all, ferrocene (Fc) is one of the most interesting stimuli-responsive compounds due to its synthetic convenience, reversible redox activity, and reversible amphiphilicity change and thus has been successfully used for fabrication of many redox-responsive self-assembly systems.<sup>22-25</sup> Compared to photo-responsive Azo groups, hydrophobic Fc groups can be quickly oxidized to yield

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hydrophilic ferrocenium cations (Fc+) and then reversibly recover by chemical means, which results in a significant and reversible hydrophilicity change without changing the molecular structures, because only the gain and loss of electrons occur in the redox process of ferrocenyl groups.<sup>26-27</sup> Thus it is particularly appealing to develop novel redox-responsive HEURs with a rapid responsive rate and a great magnitude of response by using ferrocenyl group as hydrophobes. However, little study on the redox-responsive self-assembly and controlled rheological behavior of HEURs in aqueous solution has been reported up to present.

In the present work, we present a novel redox-responsive ferrocene-functionalized narrow distribution model HEUR polymer (Fc-HEUR) to construct a novel redox-reversible self-assembly and controlled rheological system with a quick responsive rate and a large magnitude of response. Fc-HEUR was synthesized by the additive reaction of PEG with excess of diisocyanates and 4-(11-ferrocenylundecyloxy) benzyl alcohol (2), as shown in Scheme 1. The redox-controlled self-assembly and rheological behavior of Fc-HEUR in aqueous solution were investigated by UV-Vis absorbance spectrophotometry, surface tension test, dynamical light scattering (DLS), transmission electron microscopy (TEM), and steady and oscillatory shear measurements. We have demonstrated that a redox-induced reversible hydrophobicity change of Fc hydrophobes cause a rearrangement of micellar junctions and a great change of the rheological properties of **Fc-HEUR** aqueous solutions. This work will be useful not only for understanding of the thickening mechanism of stimuli-responsive HEURs, but also for preparation of reversible self-assembly and controlled viscosity systems, which may have some special application in drug delivery systems, catalyst supports, sensors, microfluidic devices, and smart rheological fluids.



Scheme 1. Synthetic routes of 4-(11-ferrocenylundecyloxy) benzyl alcohol (2) and Fc-HEUR polymer

# **EXPERIMENTAL SECTION**

#### Materials

Methyl 4-hydroxybenzoate (Aldrich, 99%), poly(ethylene glycol) (Flakes, average Mn=20000), dibutyltin dilaurate (DBTDL) (Aladdin, 98%) and 3-isocyanatomethyl-3,5,5-trimethylcyclohexyl isocyanate (IPDI, BASF, 98%) were used as received. 11-Bromoundecyl ferrocene was synthesized according to our previous report.<sup>28-29</sup> Toluene, petroleum ether, tetrahydrofuran (THF) and *N*,*N*-dimethylformamide (DMF) were stirred for 24 hours over 40 mesh calcium hydride and distilled under argon before use.

#### Instruments

The <sup>1</sup>H-NMR and <sup>13</sup>C-NMR spectra were recorded on a Bruker 600 MHz spectrometer. The carbon and hydrogen contents were determined with a Vario EL elemental analyzer. Mass Spectrum were recorded on a Bruker (Agilent1290 / maXis

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impact) Ultrahigh pressure liquid chromatography/high resolution mass spectrometry. The relaxation time distributions of the micelles and aggregates was analyzed at 25 °C by dynamic light scattering (DLS), a Malvern Nano-ZS 90 Zetasizer using a monochromatic coherent He-Ne laser (633 nm) as the light source. Molecular weights and molecular weight distributions of polymers were measured by gel permeation chromatography (GPC) with a Waters 515 pump/M717 data module/ R410 differential refractometer, using THF as the mobile phase with a flow rate 1.5 ML/min and monodisperse polystyrene as the standard with a column temperature of 40 °C. UV-vis absorption spectra were determined on HITACHI U-3010 UV/Vis а spectrophotometer. Transmission electron microscopy (TEM) images were obtained from a JEM-2100HR Microscope with an accelerating voltage of 200 kV, and samples were taken through the homemade atomizer to aero-spray cellulose-coated copper grids and then stained by 2 wt% uranyl acetate before observation. Surface tensions were obtained from a surface tension meter (Dataphysics OCA20, Germany) at 25 °C. Fourier transform infrared (FT-IR) spectra were obtained on a Thermo Nicolet 6700 spectrometer using KBr substrates. The rheological properties of HEUR polymers in aqueous solution were measured on an ARG-2 controlled stress rheometer (TA Instruments Inc) with a cone-plate geometry (40 mm diameter and  $2^{\circ}$  cone angle). Silicone oil was applied to seal the cone-plate in order to protect from water evaporation. Both steady-state shear and oscillatory measurements were recorded at indicated temperature to obtain the shear rate versus viscosity profiles and the viscoelastic properties of polymer solutions.

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#### Synthesis of 4-(11-ferrocenylundecyloxy) benzyl alcohol (2)

The synthetic route of **2** is shown in Scheme 1. First, a mixture of 11-bromoundecyl ferrocene (2.00 g, 4.76 mmol) in 20 mL of dry DMF, methyl 4-hydroxybenzoate (0.66 g, 4.34 mmol) and anhydrous potassium carbonate (3.00 g, 21.7 mmol) were added to a 100 mL round-bottomed flask with a magnetic stirrer. The mixture was allowed to react for 24 h at 80 °C and then extracted with methylene dichloride, purified by silica gel column chromatography to give 2.25 g yellow solid compound **1** (yield: 95 %).<sup>30</sup> <sup>1</sup>H NMR, <sup>13</sup>C NMR and mass spectrometry confirm that compound 1 is synthesized successfully, as shown in Figure S1. <sup>1</sup>H-NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm): 7.97 (d, 2H, Ar-*H*), 6.89 (d, 2H, Ar-*H*), 4.09-4.03 (m, 9H, *H*(Cp), 4.00 (t, 2H, -CH<sub>2</sub>-O-Ar), 3.88 (s, 3H, -O-CH<sub>3</sub>), 2.30 (t, 2H, Cp-CH<sub>2</sub>-), 1.79 (m, 2H, -CH<sub>2</sub>-CH<sub>2</sub>-O-Ar), 1.49-1.28 (m, 16H, -CH<sub>2</sub>-). <sup>13</sup>C-NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm): 166.8, 162.9, 131.5, 122.3, 114.0, 89.6, 68.5, 68.2, 67.0, 51.7, 31.1, 29.5, 29.3, 29.1, 25.9. Anal. Calcd for C<sub>29</sub>H<sub>38</sub>O<sub>3</sub>Fe: C, 71.02%; H, 7.81%. Found: C, 70.85%; H, 7.94%. ESI-MS, m/z calcd for [M+Na]<sup>+</sup>C<sub>29</sub>H<sub>38</sub>O<sub>3</sub>FeNa: 513.46, found: 513.21.

Secondly, compound 1 was reduced to produce compound 2. LiAlH<sub>4</sub> (0.23 g, 6.00 mmol) was added to a three-necked 150 mL round-bottom flask with 20 mL of dry THF. The flask was cooled at 0 °C under an atmosphere of dry argon, and then a solution of 1 (1.00 g, 2.00 mmol) in dry THF (10 mL) was added by dripping slowly. After addition of 1, the mixture was stirred at room temperature for 2 h, and the reaction endpoint was determined by thin layer chromatography (TLC). Afterwards, a small quantity of H<sub>2</sub>O was added slowly to quench the reaction. The product was

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extracted with methylene dichloride, and further purified by silica gel column chromatography (eluent: petroleum ether/ethyl acetate = 5:1 in volume) to yield 0.78 g yellow solid compound **2** (yield: 85 %). The <sup>1</sup>H NMR, <sup>13</sup>C NMR and mass spectrometry spectra of **2** is given in Supporting Information Figure S2. <sup>1</sup>H-NMR (600 MHz, CDCl<sub>3</sub>) δ (ppm) 7.26 (t, 2H, Ar-*H*), 6.88 (d, 2H, Ar-*H*), 4.60 (s, 2H, Ar-CH<sub>2</sub>OH), 4.22-4.26 (m, 9H, *H*(Cp), 3.94 (t, 2H, -CH<sub>2</sub>-O-Ar), 2.18 (t, 2H, Cp-CH<sub>2</sub>-), 1.77 (m, 2H, -CH<sub>2</sub>-CH<sub>2</sub>-O-Ar), 1.44-1.28 (m, 16H, -CH<sub>2</sub>-). <sup>13</sup>C-NMR (600 MHz, CDCl<sub>3</sub>) δ (ppm): 158.9, 132.9, 128.6, 114.5, 89.8, 68.6, 68.2, 67.1, 65.0, 31.0, 29.5, 29.3, 29.2, 26.0. Anal. Calcd for C<sub>28</sub>H<sub>38</sub>O<sub>2</sub>Fe: C, 72.72%; H, 8.28%. Found: C, 72.95%; H, 8.17%. ESI-MS, m/z calcd for [M+Na]<sup>+</sup>C<sub>28</sub>H<sub>38</sub>O<sub>2</sub>FeNa: 485.43, found: 485.21.

#### Synthesis of Fc-HEUR polymer

Scheme 1 shows the synthetic route of **Fc-HEUR** polymer, which was synthesized according to our previous work. Firstly, the dry PEG 20,000 was dissolved in dewatered toluene and then excess amount of IPDI (4 equiv of NCO to 1 equiv of OH) along with DBTDL (0.2 % of the total mass of reactants) as the catalyst were added to the flask. After 3 h of the reaction at 80 °C under nitrogen, excess amount of **2** (6.6 equiv of NCO to 1 equiv of OH) was added into the reaction mixture as the end-caper. The reaction temperature was raised to 90 °C, and the reaction lasted for 4 h. Afterward, **Fc-HEUR** was obtained by re-precipitating the warm polymer toluene solution in petroleum ether (3 volumes of petroleum ether to 1 volume of toluene solution) to remove unreacted **2** and diisocyanate residues. Then, the solution was filtered. The precipitate was dissolved in hot toluene and re-precipitated in petroleum

ether again. Finally, pure **Fc-HEUR** was obtained by drying under vacuum at 40 °C for 24 h.

#### **Preparation of Samples**

**Fc-HEUR** polymer was dissolved in deionized water and stirring for several hours at 60 °C until it was fully dissolved, and then the **Fc-HEUR** aqueous solutions with different concentrations were obtained. The **Fc<sup>+</sup>-HEUR** aqueous solutions were prepared by adding stoichiometric oxidant  $Fe_2(SO_4)_3$  and stirred several hours until the systems reach well-distributed steady state. These solutions were kept at room temperature for further studies.

#### **RESULTS AND DISCUSSION**

#### **Characterization of DHEUR polymers**

The **Fc-HEUR** polymer was characterized in detail by GPC, <sup>1</sup>H NMR and FTIR spectra. The  $M_n$  determined by GPC is 22,800 and polydispersity index PDI is 1.21. <sup>1</sup>H NMR and FTIR spectra confirm the successful synthesis of **Fc-HEUR** polymer, as shown in Figure S3. The percentages of end-capping reaction defined as the end-capping ratio (ECR) is a very important parameter of HEUR polymer. The absorption intensity of **2** at 428 nm in the THF solution is proportional to its concentration (Figure S4). Hence, we can determine the content of the Fc groups from UV-Vis absorbance of **Fc-HEUR** in THF solution by the standard curve. The ECR of **Fc-HEUR** polymer was calculated to be 96.2% according to eq 1.

$$\text{ECD} = \frac{n_{\text{Fc}}}{\frac{C_{\text{HRUR}} \times 2}{M_n}} \times 100\% \quad (1)$$

where  $n_{\rm Fc}$  is the molar concentration of ferrocene groups in THF solution of **Fc-HEUR** calculated by the standard curve,  $C_{\rm HEUR}$  is the mass concentration of **Fc-HEUR** in THF, and  $M_{\rm n}$  is the number average molecular weight of **Fc-HEUR** polymer. It means that the majority of polymer has two expected end-groups per chain, which is consistent with the previous results.



Figure 1. UV-visible absorption spectra of Fc-HEUR solution (15.0 g/L) before and after oxidization.

#### Reversible redox activity of polymers in solution

As previously described, the Fc groups can be quickly transformed into the ferrocenium salt (Fc<sup>+</sup>) and undergo reversible redox reactions through chemical and electrochemical means.<sup>25, 31-32</sup> As expected, **Fc-HEUR** can be rapidly oxidized into **Fc<sup>+</sup>-HEUR** by adding 0.50 equiv of oxidants  $Fe_2(SO_4)_3$  corresponding to the total Fc units in polymer, and the latter can be immediately reduced by stoichiometric reducing agents Vitamin C (VC, 0.50 equiv) again. Particularly, the redox transformation of ferrocenyl groups can be observed through UV-vis absorption spectra.<sup>22, 33</sup> As shown in Figure 1, the absorption peak at 436 nm of Fc groups disappears and a new absorption peak at 627 nm corresponding to Fc<sup>+</sup> group appears after oxidation by  $Fe_2(SO_4)_3$ , indicating that **Fc-HEUR** is fully oxidized into **Fc<sup>+</sup>-HEUR**. In

addition, after adding reducing agents Vitamin C, the oxidation absorption peak at 627 nm disappears and the initial absorption peak of Fc groups recovers, indicating that  $Fc^+$ -HEUR is completely reduced into Fc-HEUR. Thus Fc-HEUR has good redox reversibility in aqueous solution.



#### Surface tension change of FcHEUR aqueous solution

**Figure 2.** Dependence of equilibrium surface tension ( $\gamma$ ) on concentration *C* of **Fc-HEUR** aqueous solution at 25 °C before and after oxidization.

As aforementioned, the redox reaction of ferrocenyl groups in **Fc-HEUR** will lead to a great change in polymer amphiphilicity, which can be confirmed by surface tension tests. As shown in Figure 2, the aqueous solutions of **Fc-HEUR** have nearly the same surface tensions ( $\gamma$ ) as water at very low concentrations. With the increase of *C*,  $\gamma$  decreases sharply and then reaches to a constant value. We can obtain the *cac* value of polymer in aqueous solution from the turning point of curve. The determined *cac*<sub>red</sub> value is 0.07 g/ L for **Fc-HEUR**. Interestingly, after oxidization by Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>, the *cac*<sub>ox</sub> value increases to 5.0 g/ L for **Fc<sup>+</sup>-HEUR**. This suggests that **Fc<sup>+</sup>-HEUR** shows much larger hydrophiphilicity than **Fc-HEUR**. According to

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previous researches,<sup>22, 25</sup> the change in the hydrophilic–lipophilic balance of **Fc-HEUR** before and after oxidization will change its solution aggregation behavior, thereby altering the viscoelastic properties of concentrated polymer solution *via* a rearrangement of hydrophobic associative structure or networks.

#### Redox-responsive reversible self-assembly of Fc-HEUR in solution

In order to verify the above considerations, the redox-responsive reversible self-assembly of **Fc-HEUR** in aqueous solution was investigated by TEM and DLS. Figure 3 shows the TEM images of **Fc-HEUR** solution at different concentrations. For 1.0 g/L aqueous solution of **Fc-HEUR**, which is above its *cac*<sub>red</sub>, only spherical micelles are observed, and their sizes are about 30-40 nm in diameter (Figure 3a). Interestingly, with increasing *C* from 1.0 g/L to 3.0 g/L, the number of spherical micelles gradually increases (Figure 3b). For the solution of 7.0 g/L, larger irregular structures are observed (Figure 3c), indicating the formation of micelle aggregates.<sup>34</sup> Figure 3d shows the characteristic relaxation time distributions of **Fc-HEUR** in aqueous solution at indicated concentrations obtained by DLS. When *C* is very low (1.0 to 3.0 g/L), there is only one fast relaxation mode, which is assigned to the flower-like micelles. With increasing *C* to 5.0 g/L, a slow relaxation mode is observed besides the fast mode, indicating that the *C*<sub>p</sub> value of **Fc-HEUR** in aqueous solution is  $\geq$ 5.0 g/L and larger aggregates of micelle are formed through bridging hydrophilic chains between adjacent micelles according to an open association mechanism suggested by Chasssenieux *et al.*<sup>34-36</sup>



**Figure 3.** TEM images of **Fc-HEUR** micelles in 1 g  $L^{-1}$  (a), 3 g  $L^{-1}$  (b) and 7 g  $L^{-1}$  (c) aqueous solutions; (d) The characteristic relaxation time distributions of the reduction state **Fc-HEUR** aqueous solutions at indicated concentrations.

Interestingly, for 3.0 g/L aqueous solution of **Fc-HEUR**, which is between its  $cac_{red}$  (0.07 g/L) and  $cac_{ox}$  (5.0 g/L), spherical micelles (Figure 4a) are totally disassembled (Figure 4b) after oxidation by  $Fe_2(SO_4)_3$ , and reversibly recover after reduction by Vitamin C again (Figure 4c). DLS results confirm the reversible changes of the characteristic relaxation time



**Figure 4.** TEM images of **Fc-HEUR** (3.0 g/L): (a) micelles, (b) irregular fragments after oxidization by Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> and (c) micelles after reduction by Vitamin C; (d) Reversible changes of the characteristic relaxation time distributions determined by DLS at C= 3.0 g/Lbefore and after oxidization by Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>; TEM images of **Fc-HEUR** (7.0 g/L): (e) micellar aggregates, (f) micelles after oxidization by Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> and (g) micellar aggregates after reduction by Vitamin C; (h) Reversible changes of the characteristic relaxation time distributions determined by DLS at C= 7.0 g/L before and after distributions DLS at C= 3.0 g/L before and after oxidization by Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>. Moreover, for 7.0 g/L aqueous solution of **Fc-HEUR** (*C*> *cac*<sub>ox</sub>), the large aggregates of micelle (Figure 4e) are turn into micelles of 30–70 nm diameter after oxidation by Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> (Figure 4f), and reversibly recover after reduction by vitamin C again (Figure 4g), indicating that **Fc<sup>+</sup>-HEUR** in aqueous solution has a much larger *C*<sub>p</sub> than **Fc-HEUR**. Figure 4 hshow the characteristic relaxation time distributions of **Fc-HEUR** in aqueous solution determined by DLS before and after oxidization by Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>. The DLS results indicate that small micelles and large aggregates of micelle in **Fc-HEUR** solutions are tuned into larger micelles in **Fc<sup>+</sup>-HEUR** 

solutions. The fact that the characteristic relaxation time distribution or the size of the micelles in  $\mathbf{Fc}^+$ -**HEUR** solutions (Figure 4e) is larger than that of **Fc-HEUR** solutions should be attributed to stronger electrostatic repulsions between  $\mathbf{Fc}^+$  groups and a larger aggregation number of micelle in  $\mathbf{Fc}^+$ -**HEUR** than in **Fc-HEUR** with the increase of hydrophilicity of micellar cores. The above observation indicates that redox-responsive reversible self-assembly of **Fc-HEUR** in dilute aqueous solution is successfully achieved by chemical redox method.

#### **Redox-controlled rheological behavior of Fc-HEUR in solution**

As previously discussed,  $Fc^+$ -HEUR in aqueous solution has a much larger  $C_p$  than Fc-HEUR. This means that the redox of ferrocenyl groups may lead to redox-responsive solution rheological change of Fc-HEUR via a rearrangement of hydrophobic associative structure or networks when  $C \ge C_p$ . As we expected, the macroscopic viscosity change of Fc-HEUR solutions at 25 °C before and after oxidization was clearly observed (Figure 5). The solution of **Fc-HEUR** (30.0 g/L) in the reduction state is so viscous that it does not flow (Figure 5A). The steady shear measurements indicate that the **Fc-HEUR** solution takes on a typical Newtonian fluid at low shear rates and undergoes shear thinning at high rates. This should be attributed to the formation of a physical network of micellar junctions.<sup>37-38</sup> After oxidization by Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>, the solution changes its colour from yellow to dark blue immediately, and low or zero shear viscosity  $\eta_0$  (approximately represented by  $\eta$  at  $\dot{\gamma} = 0.01$ s<sup>-1</sup>) in the Newtonian region decreases strongly from 1938 Pa.s to 1.6 Pa.s, indicative of a great change in network structures due to a redox transition of Fc to Fc<sup>+</sup>. The reason is that when hydrophobic Fc end groups are transformed into hydrophilic ferrocenium  $Fc^+$ , initial hydrophobic network composed of large micellar aggregates in Fc-HEUR solution would become unstable due to the change in hydrophilic-lipophilic balance and a rearrangement of micellar junctions through a bridge-to-loop transition is necessary to meet a new thermal

equilibrium. As a result, initial hydrophobic network is breakup into micelles and small micellar aggregates. Interestingly, after adding reducing agents Vitamin C, the solution viscosity recovers its initial value immediately due to hydrophobicity change of end groups induced by  $Fc^+$  to Fc conversion. It is noted that this viscosity change can be cycled at least two times by redox reactions (Figure 6). This means that the rheological properties of the **Fc-HEUR** solution dependent upon the redox states of Fc groups in the solution can be readily controlled by reversible redox reactions.



**Figure 5.** (A) A plot of steady shear viscosity  $\eta$  *vs.* shear rate  $\hat{\mathbf{y}}$  (B) Storage modulus *G'* and loss modulus *G''* dependence on angular frequency  $\omega$  for **Fc-HEUR** aqueous solution (30.0 g/L) before and after oxidation.



**Figure 6.** Macroscopic viscosity change of **Fc-HEUR** aqueous solution (30.0 g/L) for two oxidation-reduction cycles.

#### Dynamic viscoelastic property of Fc-HEUR aqueous solutions

Furthermore, oscillatory shear measurements were performed in the linear viscoelastic region to understand the effects of redox reaction of Fc end groups on the associative structure and viscoelasticity of the **Fc-HEUR** aqueous solution. Dynamic strain sweep experiments were carried out to satisfy the linear viscoelastic constraint, and the strain in oscillatory shear measurements was kept under 1%.<sup>39</sup> Figure 5B shows the storage modulus *G'* and loss modulus *G''* as a function of angular frequency  $\omega$  for the 30.0 g/L aqueous solution of **Fc-HEUR** in the reduction and oxidation state at 25 °C. For the reduction state **Fc-HEUR**, at low frequency region (approximately from 0.03 to 0.51), *G'* increases with a slope of 2, *G''* with a slope of 1, and *G'* is less than *G''*. Furthermore, with increasing  $\omega$  (approximately from 0.51 to 100 rad/s), *G'* asymptotes to a constant value higher than *G''*, while *G''* exhibits a maximum and a crossover of *G'* and *G''* curves is observed at about 0.51 rad/s. This plateau

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modulus is analogous to a classical rubber plateau modulus ( $G_0$ ), suggesting that the solution shows elastic behavior at high frequencies and viscous liquid behavior at low frequencies.<sup>40</sup> The viscoelasticity of the **Fc-HEUR** solutions can be described by the following single Maxwell model<sup>41-42</sup>:

$$G'(\omega) = \frac{G_0 \omega^2 \tau^2}{1 + \omega^2 \tau^2}$$
(2)  
$$G''(\omega) = \frac{G_0 \omega \tau}{1 + \omega^2 \tau^2}$$
(3)

where  $G_0$  is the plateau modulus,  $\omega$  is the angular frequency, and  $\tau$  is the relaxation time. After fully oxidized by Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>, both *G* and *G* of the solution significantly decrease, and *G* is always less than *G*, indicating that **Fc<sup>+</sup>-HEUR** solution shows viscous liquid behaviour. This means that isolated micelles and small micellar aggregates play a dominant role in **Fc<sup>+</sup>-HEUR** solution due to the fast relaxation of Fc<sup>+</sup> end groups. Moreover, after adding reducing agents Vitamin C, both the  $G_0$  and the relaxation time  $\tau$  recover the initial values, and the **Fc-HEUR** aqueous solution come back into the initial viscoelastic fluids.



**Figure 7.** A plot of the zero-shear viscosity  $(\eta_0)$  *vs.* on polymer concentration *C* of **Fc-HEUR** aqueous solution in the reduction and oxidation state.

# Influence of polymer concentration on aggregation and rheological properties of Fc-HEUR aqueous solutions

Previous researches have demonstrated that polymer concentrations greatly affect the associative structure and rheological properties of HEUR aqueous solutions.<sup>17, 43</sup> Thus the steady shear measurement were performed for **Fc-HEUR** aqueous solutions at different concentrations at 25 °C, as shown in Figure S5. When *C* increases from 15.0 g/L to 40.0 g/L, the zero/low-shear viscosities ( $\eta_0$ ) of the reduction state **Fc-HEUR** solutions increase sharply from 30.6 Pa.s to 5066 Pa.s (Figure 7), and the onset of shear-thinning shifts to slight lower shear rates (Figure S5). Analogous results are observed in the oscillatory shear measurement for **Fc-HEUR** aqueous solutions at indicated concentrations (Figure S6). For **Fc-HEUR** solutions,  $G_0$  values increase and the point of intersection G'/G'' occurs at lower  $\omega$  with the increase of *C*, indicating a gradually enhanced number density of actively micellar junctions. However, after oxidization by Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>, no shear thinning is observed in the oxidation state **Fc<sup>+</sup>HEUR** solutions due to the fast relaxation of Fc<sup>+</sup> end groups and the zero/low-shear

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viscosities change slightly from 0.03 Pa.s to 3.66 Pa.s when *C* increases from 15.0 g/L to 40.0 g/L (Figure 7). Meanwhile, the oscillatory shear measurements also show that the  $\mathbf{Fc}^+$ -**HEUR** solutions behaviour as viscous liquid in the tested  $\omega$  range, indicating that Isolated micelles and small micellar aggregates are dominant in  $\mathbf{Fc}^+$ -**HEUR** solutions. The above observations were confirmed by DLS measurements also. The characteristic relaxation time distributions of the oxidation state  $\mathbf{Fc}^+$ -**HEUR** aqueous solutions at indicated concentrations are shown in Figure 8. When *C* increases to 15.0 g/L, a slow relaxation mode is observed, indicating that  $\mathbf{Fc}^+$ -**HEUR** begins to form micelle aggregates in solution (Figure 8d). Moreover, the peak intensity of slow relaxation modes significantly increases and the distribution of relaxation time/size evolves with the concentration C (Figure 8), indicating that more and larger aggregates of micelle are formed through bridging in  $\mathbf{Fc}^+$ -**HEUR** solutions. This means that a rearrangement of network takes place after oxidization by  $\mathbf{Fe}_2(\mathbf{SO}_4)_3$  and a large number of bridged active chains in initial  $\mathbf{Fc}$ -**HEUR** solutions are transferred into the loops of micelles through bridge-to-loop transitions.



**Figure 8.** The characteristic relaxation time distributions of the oxidation state **Fc-HEUR** aqueous solutions at indicated concentrations.

Based on the above discussion, a proposed model is shown in Figure 9 to describe the redox-responsive associative structure change of the **Fc-HEUR** aqueous solution. In this model, **Fc-HEUR** in aqueous solution will form micelles, larger aggregates and physical network with increasing C. After oxidization by  $Fe_2(SO_4)_3$ , a rearrangement of network through a bridge-loop transition takes place to greatly decrease the number density of effective elastic chains and the relaxation time of the network, as a result, a hydrophobic physical network formed in **Fc-HEUR** in aqueous solution is transformed into micelles and micellar aggregates in **Fc<sup>+</sup>-HEUR** solutions. Moreover, after reduced by Vitamin C, a loop-bridge transition happens again, and the solution recover initial physical network, performing excellent reversibility.



**Figure 9.** Schematic of the formation of networks with increasing C and the redox-responsive rearrangement of micellar junctions by the redox of ferrocenyl groups.

#### CONCLUSIONS

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A ferrocene-functionalized narrow distribution model HEUR polymer (Fc-HEUR) was synthesized, and the redox-controlled self-assembly and rheological behavior of Fc-HEUR in aqueous solution was demonstrated. The redox reactions of Fc end groups induce a reversible change in hydrophilic-lipophilic balance of polymer. Accordingly, the Fc-HEUR can reversibly self-assemble into spherical micelles and larger micellar aggregates of different nanoscales in solution and also disassemble by redox reaction. Meanwhile, a rearrangement of micellar junctions takes place through a bridge-loop or loop-bridge transition in the concentrated solution of Fc-HEUR, leading to a quite different rheological behavior of the polymer solution. Particularly, the associative structure and rheological properties of the Fc-HEUR aqueous solution can be reversibly controlled by adding oxidants and reducers. The results indicate that the redox reactions of Fc end groups affect not only the network connectivity but also the relaxation behavior of the Fc-HEUR solution. The work will not only provide new insights into the thickening mechanism of stimuli-responsive HEURs, but also open a new perspective of stimuli-responsive reversible self-assembly and redox-responsive viscosity systems, which have some special application in drug delivery systems, catalyst supports, sensors, microfluidic devices, and smart rheological fluids.

#### ASSOCIATED CONTENT

Supporting Information. Additional figures including <sup>1</sup>H-NMR, <sup>13</sup>C-NMR and mass spectrometry of compound 1 and 2. <sup>1</sup>H NMR and FTIR of Fc-HEUR polymer. The standard curve obtained from UV-Vis measurement. The steady shear viscosity  $\eta$  against shear rate for different concentrations of polymer solution. Storage modulus *G*' and loss modulus *G*''

dependence on angular frequency  $\omega$  for different concentrations of polymer solution. This

material is available free of charge via the Internet at http://pubs.acs.org.

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#### Notes

The authors declare no competing financial interest.

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### Insert Table of Contents Graphic and Synopsis

A ferrocene-functionalized hydrophobically modified ethoxylated urethane: Redox-responsive controlled self-assembly and rheological behavior in aqueous solution

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In this work, a novel redox-responsive ferrocene-functionalized hydrophobically modified ethoxylated urethane (**Fc-HEUR**) model polymer was prepared to demonstrate the effects of redox-induced reversible hydrophobicity change of ferrocenyl hydrophobes on its self-assembly and rheological properties in aqueous solution.



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