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Novel Hydrophobically Modified Ethoxylated Urethanes End-Capped by Percec-Type Alkyl Substituted Benzyl Alcohol Dendrons: Synthesis, Characterization, and Rheological Behavior

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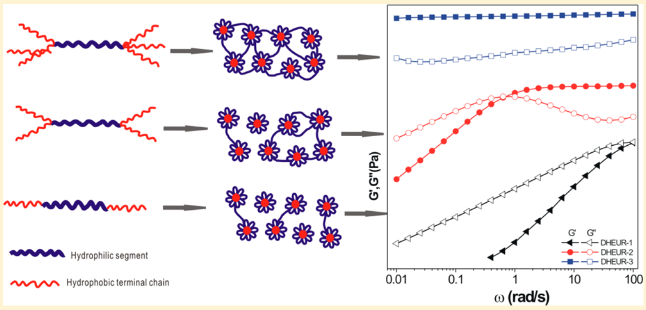
Supporting Information



ABSTRACT: Novel dendron hydrophobically modified ethoxylated urethanes (DHEUR) with almost the same molecular weights, molecular weight distributions, and identical hydrophilic portion but different terminal hydrophobic group numbers were prepared by using Percec-type alkyl substituted benzyl alcohol dendrons as new end-cappers. These DHEUR polymers in solution possess interesting associative and rheological behavior. For **DHEUR-1** with 4-mono(decyloxy)benzyl alcohol (**2**), the solutions are dominantly composed of the isolated and separated micelles and exhibit Newtonian behavior in a wide shear rate range accompanied by shear thinning at high shear rate region. **DHEUR-2** with 3,5-di(decyloxy)benzyl alcohol (**4**) in solutions form a relatively more complete network through dominant micellar junctions and process a relatively higher solution viscosity and similar solution viscosity behavior to **DHEUR-1**. However, shear thinning behavior shifts to a lower shear rate region due to a relatively longer relaxation time. Interestingly, the solutions of **DHEUR-3** with 3,4,5-tri(decyloxy)benzyl alcohol (**6**) have developed a complete physical network and show pronounced shear thinning behavior over the whole shear rate range. The oscillatory measurements further confirm that a gradually developing associative network leads to their different solution rheological behavior, i.e., viscous fluid (**DHEUR-1**), viscoelastic fluid (**DHEUR-2**), and elastic body (**DHEUR-3**) with increasing the hydrophobic tail number of dendrons. Furthermore, the rheological activation energy of these DHEUR polymers increases with the increase of terminal hydrophobic group numbers, indicating that DHEUR polymers with more hydrophobic tail chains need more energy potential barrier for the disengagement of hydrophobes from micelles due to stronger association strength. In general, the results demonstrate that the terminal hydrophobic tail number of dendrons plays a key role in determining the associative and rheological behavior of DHEUR in solutions. This work opens a new perspective for more efficient thickeners and also promises the potential of these DHEUR polymers in waterborne coating, cosmetics, dyestuff, medicines, and so on for the first time.

■ INTRODUCTION

Associative polymers which comprise hydrophilic backbone and hydrophobic end groups have gained considerable attention over the past decade. When associative polymers dissolve in aqueous solution, their hydrophobic groups associate with each other in both intramolecular and intermolecular. This leads to the formation of network structures. For their amphiphilic property,[1] associative polymers have been widely applied in many fields, including waterborne coatings, ink, oil production and cosmetics as rheology control agents, and DNA sequencing where the network structure acts as a sieving medium.[2] The rheological properties, such as viscosity increasing and shear thinning and thickening, are the major uses of associative polymers.[3] Therefore, these polymers are commonly referred to as associative thickeners. Hydrophobically modified ethoxylated urethane (HEUR) is a class of representative associative thickener. Compared to traditional thickeners such as polyacrylates and cellulose derivatives, HEUR polymers have noticeable thickening effect even at relatively smaller doses and lower molecular weights.[4] This has led to the use of HEUR polymers as effective rheology modifiers for improving the rheological properties in paints and coating industry and in some other applications, such as cosmetics, dyestuff, and medicines.

The basic structure of HEUR is composed of poly(ethylene glycol) (PEG) chains as hydrophilic segment chain-extended by diisocyanates and two hydrophobe groups such as alkyl phenyl,[5] fluorocarbons,[6−9] or aliphatic alkyl[10−12] attached through urethane on both ends. Above a critical aggregation concentration (CAC), HEUR in aqueous solutions form flower-like micelles.[13,14] The hydrophobic segments associate with each other and form micellar cores and the hydrophilic

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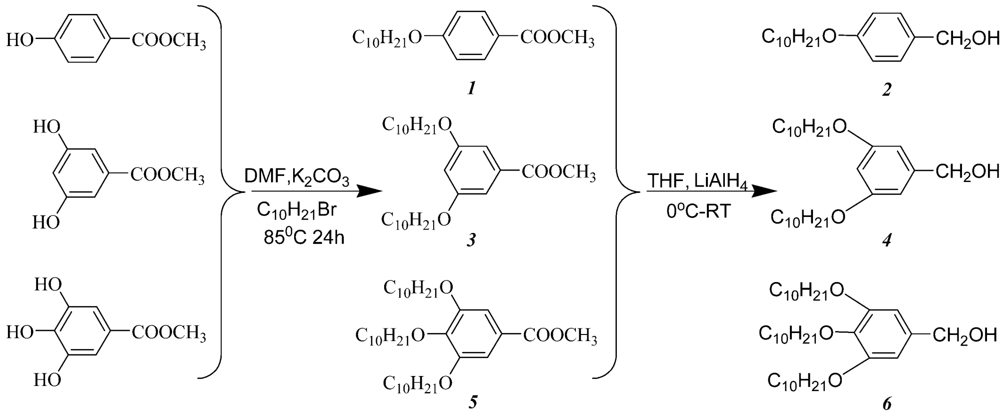
Scheme 1. Synthetic Route of Mono-, Di-, and Trisubstituted Benzyl Alcohol Dendrons



backbone come into being flower loops. When the concentrations are low, the micelles are isolated, separated, and difficult to associate with each other. However, at higher concentration these flower-like micelles connect mutually through the bridge connection of the hydrophilic chains bridge. As a result, a network structure is formed and the viscosity increases.[15−19] Thus, hydrophilic groups, molecular weight, molecular weight distribution, and parameters of hydrophobic end-capper agents are important factors in determining the thickening effect of HEUR associative thickeners.

Previous research has been focused on the thickening effect of HEUR associative thickeners.[12,20−29] Barmar et al.[21] studied the influence of the hydrophilic group of HEUR prepolymer on the viscoplastic property. For HEUR with different lengths of the hydrophilic segment but same hydrophobic ends, a stronger association is achieved with a reduced length of the hydrophilic section. The Glass group[12,22−25] reported that an HEUR thickener with a molecular weight of probably 23 000 was the most effective rheology modifier. For HEUR polymers with the same molecular weights but different molecular weight distributions, a broad molecular weight distribution would result in a defective network, so thickening efficiency might be reduced. The parameters of hydrophobic end-capper agent including the hydrophobic chain length, the size, and structure of the hydrophobic groups exert significant influences on thickening performance of HEUR polymers. HEUR polymers associate with each other to form flower-like micelles only if their end groups are sufficiently hydrophobic because low end chain lengths has unfavorable hydrophobic interactions.[30] For example, Kim et al.[26] investigated the effect of the end chain length of the hydrophobic groups on the thicken efficiency. They found that HEUR polymers with end chain lengths of C_{12} and C_{18} had completed transient networks structures, but HEUR with that of C8 did not. This means long end chains are beneficial to the formation of both more compact micelles and transient networks at low concentrations for HEUR. Barmar et al.[27] studied the effect of the structure of the hydrophobic groups on the thicken efficiency. For HEUR end-capped respectively by cetyl alcohol, dodecyl alcohol, and cyclohexanol, only HEUR with cyclic end group did not exhibit viscoelasticity. Rheology behavior of HEUR polymers with variable terminal hydrophobic size was reported by Lundberg et al.[22] As the concentration of HEUR increased, the size of terminal hydrophobic groups affected the magnitude of the viscosity. A high viscosity was obtained when the linear HEUR end-capped by the terminal nonylphenol. This indicated that the hydrophobic association would be enhanced with increasing the size of hydrophobic chain. However, nearly all the studies of HEUR focused on hydrophobes of a single substituted alkyl tail chain linked to the PEG spacer through urethane.

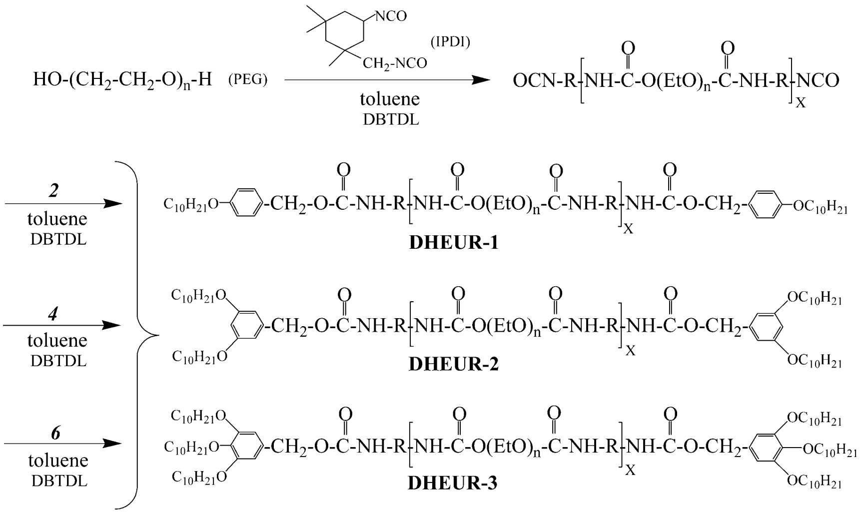
It is well know that dendrons are one of most interesting architectural motifs and have been utilized as powerful building blocks for construction of complex nanostructures and supramolecular systems due to the abundant variation in the composition and structure.[31−33] In our previous article, based on an amphiphilic dendron−coil macromonomer (3,5-di(*n*-hexadecyloxy)benzoyloxy polyoxyethylene methacrylate), the Percec-type alkyl substituted benzoic acid dendron was successfully introduced into the hydrophobically modified alkali-soluble emulsion (HASE) polymer by emulsion copolymerization.[34] Our results confirmed that the dendron hydrophobically modified alkali-soluble emulsion (DHASE) polymer resulted in a significant increase in terms of DHASE solution viscosity with increasing the content of the Perce-type dendron, representing an obvious thickening effect. We attempted to introduce the Percec-type dendron into the HEUR polymers to enhance hydrophobic associative networks. However, the combination of synthetic thickeners with linear polyurethane block and dendritic hydrophobic moiety are not common data. Little is known about the rheological behavior of the dendron-end-capped HEUR polymers as well.

In this study, three kinds of alkyl substituted benzyl alcohol dendron with one, two, and three hydrophobic alkyl chains, i.e., 4-mono(decyloxy)benzyl alcohol (**2**), 3,5-di(decyloxy)benzyl alcohol (**4**), and 3,4,5-tri(decyloxy)benzyl alcohol (**6**), were used as new end-capper agents. Novel dendron hydrophobically modified ethoxylated urethanes (DHEUR) were prepared by the step-growth polymerization of poly(ethylene glycol) (PEG) with a slight excess of diisocyanates followed by the reaction of the terminal isocyanate groups with the Percec-type dendrons. The associative structures and rheological behavior of these novel DHEUR polymers in aqueous solutions were studied. The objective of this study is to obtain detailed insights into rheological behavior of these novel DHEUR polymers and demonstrate the potential of these Percec-type alkyl substituted benzyl alcohol dendron as new end-capper agents in HEUR associative thickeners in the future.

■ EXPERIMENTAL SECTION

Materials. Methyl 4-hydroxybenzoate, methyl 3,5-dihydroxybenzoate, and methyl 3,4,5-trihydroxybenzoate (all from Aldrich, 98%) were used as received. Other reagents, such as tetrahydrofuran (THF)

Scheme 2. Synthetic Route of Three DHEUR Polymers



and *N,N′*-dimethylformamide (DMF), were all analysis grade chemicals and freshly distilled prior to use. 1-Bromodecane (Aladdin, 98%) was distilled before use. Lithium aluminum hydride (Aladdin, 99%) was used as received. Poly(ethylene glycol) (PEG) with the molecular weight of 6000 was purchased from Aldrich. Dibutyltin dilaurate (DBTDL) (98%) was used as received from Aladdin. 3-Isocyanatomethyl-3,5,5-trimethylcyclohexyl isocyanate (IPDI) from BASF was distilled under vacuum and stored under argon before use. Toluene and petroleum ether were stirred for 24 h over 40 mesh calcium hydride and distilled under argon. The mono-, di-, and trisubstituted benzyl alcohol dendrons, i.e., 4-mono(decyloxy)benzyl alcohol (**2**), 3,5-di(decyloxy)benzyl alcohol (**4**), and 3,4,5-tri-(decyloxy)benzyl alcohol (**6**), were synthesized mainly according to the method reported by Percec and co-workers[35,36] with some modifications (Scheme 1).

Measurements. ^{1}H NMR spectra were obtained on a Bruker Avance Digital 400 MHz spectrometer. The carbon, hydrogen, and nitrogen contents (wt %) were determined with a Vario EL elemental analyzer. Fourier transform infrared (FTIR) spectra of DHEUR polymers were recorded on a Thermo Nicolet 6700 spectrometer using KBr pellets at room temperature (25 °C). Molecular weights and molecular weight distributions of DHEUR 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, distributed polystyrene as standard, and a column temperature of 40 °C. The rheological properties of DHEUR 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° 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 25 °C to obtain the shear rate versus viscosity profiles and the viscoelastic properties of the DHEUR solutions.

Syntheses of 3,4,5-Tris(decyloxy)benzyl Alcohol (6). First, methyl 3,4,5-tri(decyloxy)benzoate (**5**) was synthesized (Scheme 1) according to the method reported in our previous paper.[31] The ^{1}H NMR spectrum of **5** is given in Supporting Information Figure SI1. ^{1}H NMR ($CDCl_3$, TMS) δ (ppm): 0.89 (t, 9H, $-CH_3$), 1.28 (m, 36H, $-(CH_2)_6-$), 1.48 (m, 6H, $-CH_2-CH_2-CH_2-O-Ar$), 1.79 (m, 6H, $-CH_2-CH_2-O-Ar$), 3.89 (s, 3H, $-CO_2-CH_3$), 4.02 (m, 6H, $-CH_2-O-Ar$), 7.26 (s, 2H, $-ArH-CO_2-CH_3$). Anal. Calcd for **5**: C, 75.38; H, 11.24; O, 13.22. Found: C, 75.64; H, 11.53; O, 12.82.

Second, **6** was synthesized by chemical reduction from **5**. $LiAlH_4$ (0.45 g, 11.91 mmol) was weighed and placed under an infrared lamp for 0.5 h to remove water and was then was dissolved by dry THF (20 mL) and added to a three-necked 150 mL round-bottom flask which was oven-dried. The flask was cooled at 0 °C in an ice−water bath and under an atmosphere of dry argon. A solution of **5** (4.8 g, 8.32 mmol) in dry THF (60 mL) was added by dripping slowly. After addition of **5** within an hour, the ice−water bath was removed and the temperature was increased to 30 °C. The reagents were stirred at 30 °C for 2 h, and the reaction end point was determined by thin layer chromatography (TLC). Subsequently, a small quantity of H_2O was added to consume the unreacted $LiAlH_4$. 30 mL of hydrochloric acid was used to neutralize the reaction. The mixture was transferred to a separator funnel and extracted three times by adding dichloromethane. Next, the liquid ballistic under layers was obtained, dried over $MgSO_4$, and filtered to remove the solvent. The product was further purified by silica gel column chromatography (eluent: petroleum ether/ethyl acetate = 5:1 by volume) to yield 4.5 g (98.1 wt %) of white solid **6**. The ^{1}H NMR spectrum of **6** is given in Supporting Information Figure SI2. ^{1}H NMR ($CDCl_3$, TMS) δ (ppm): 0.88 (t, 9H, $-CH_3$), 1.27 (s, 36H, $CH_3-(CH_2)_6-$), 1.46 (s, 6H, $-CH_2-CH_2-CH_2-O-Ar$), 1.79 (m, 6H, $-CH_2-CH_2-O-Ar$), 3.97 (m, 6H, $-CH_2-O-Ar$), 4.59 (s, 2H, $-Ar-CH_2-OH$), 6.55 (s, 2H, $-ArH-CH_2-OH$). Anal. Calcd for **6**: C, 76.96; H, 11.79; O, 11.09. Found: C, 77.14; H, 11.85; O, 11.02.

3,5-Di(decyloxy)benzyl alcohol dendron **4** and 4-mono(decyloxy) benzyl alcohol dendron **2** were synthesized following a similar procedure to **6**. The ^{1}H NMR spectrum of dendron **2** is given in Supporting Information Figure SI3. ^{1}H NMR ($CDCl_3$, TMS) δ (ppm): 0.88 (t, 3H, $-CH_3$), 1.27 (m, 12H, $-(CH_2)_6-$), 1.45 (q, 2H, $-CH_2-CH_2-CH_2-O-Ar$), 1.61 (m, 1H, $-Ar-CH_2-OH$), 1.77 (q, 2H, $-CH_2-CH_2--O-Ar$), 3.95 (t, 2H, $-CH_2-O-Ar$), 4.61 (m, 2H, $-Ar-CH_2-OH$), 6.89 (d, 2H, $-O-HAr-$), 7.28 (d, 2H, $-ArH-CH_2-OH$). Anal. Calcd for **2**: C, 77.16, H, 10.59 O, 12.10. Found: C, 77.32, H, 10.67 O, 11.93.

The ^{1}H NMR spectrum of dendron **4** is given in Supporting Information Figure SI4. ^{1}H NMR ($CDCl_3$, TMS) δ (ppm): 0.88 (t, 6H, $-CH_3$), 1.27 (m, 24H, $-(CH_2)_6-$), 1.44 (q, 4H, $-CH_2-CH_2-CH_2-O-Ar$), 1.66 (m, 1H, $-Ar-CH_2-OH$), 1.78 (q, 4H, $-CH_2-CH_2-O-Ar$), 3.93 (t, 4H, $-CH_2-O-Ar$), 4.61 (m, 2H, $-Ar-CH_2-OH$), 6.37 (t, 2H, $-O-HAr-$), 6.5 (d, 2H, $-ArH-CH_2-OH$). Anal. Calcd for **4**: C, 77.01, H, 11.41 O, 11.41. Found: C, 77.36, H, 11.73 O, 10.93.

Synthesis of DHEUR Polymers. *Synthesis of Isocyanate-Terminated Polyurethane Prepolymers.* Before polymerization of DHEUR, traces of water which can react with diisocyanates easily must be removed from the reaction vessel to prevent the chain termination. The processes can be completed through azeotropic ditillation of PEG with toluene. In a four-necked 250 mL round-bottom flask, equipped with a magnetic stirrer, a nitrogen inlet tube, a condenser with Dean-Stark trap, and a thermometer, 5 g (0.83 mmol) of PEG with an average molecular weight of 6000 dissolved by 80 mL of toluene was added. The temperature was increased to 112 °C to remove the water by azeotropic distillation of PEG in toluene with stirring for 2 h. A total of 30 mL of solvent was removed to obtain dry PEG in toluene solution. Following dewatering, the flask was cooled; the Dean-Stark trap was remove and replaced by a reflux condenser. The nitrogen was added continuously into the reaction system, and 0.24 g (1.1 mmol) of IPDI (4 equiv of NCO to 3 equiv of OH) as raw material along with 0.011 g of DBTDL (0.2% of the total mass of reactants) as the catalyst were added into the flask. After 2 h of the reaction at 80 °C under the protection of nitrogen, the isocyanate-terminated polyurethane prepolymers were obtained.

*Synthesis of DHEUR Polymers End-Capped with **2**, **4**, and **6**.* After preparation of the isocyanate-terminated polyurethane prepolymer, the end-capping reaction was performed by adding a toluene solution of 0.17 g of **2**, 0.25 g of **4**, and 0.34 g of **6** into the four-neck round-bottom flask. The reaction temperature was further increased to 90 °C, and the end-capping reaction lasted for 3 h. Afterward, the **DHEUR-1**, **DHEUR-2**, and **DHEUR-3** were obtained. The general reaction is given in Scheme 2.

Purification of DHEUR Polymers. The warm DHEUR toluene solutions were precipitated into petroleum ether (3 volumes of petroleum ether to 1 volume of thickener solution) in order to remove unreacted benzyl alcohol and diisocyanate residues. Later, the solution was collected on a sintered glass funnel and filtered to remove the solvent. The purified products were dissolved in hot toluene, reprecipitated into petroleum ether, and filtered with filter papers. Finally, **DHEUR-1**, **DHEUR-2**, and **DHEUR-3** polymers were obtained by drying under vacuum at 40 °C for 12 h.

Preparation of Samples. Weighted amounts of DHEUR polymers were dissolved in Millipore Milli-Q water by stirring at room temperature until they were totally dissolved. Finally, the aqueous solutions of DHEUR with different concentrations were obtained.

RESULTS AND DISCUSSION

Characterization of DHEUR Polymers. GPC measurements are shown in Table 1 for the three DHEUR polymers. As can be seen, these DHEUR polymers have almost the same molecular weights and molecular weight distributions. A target M_n of probably 22 000 which is the scope of the proposal of the Glass group[22,24,25] has been chosen in our syntheses by adjusting the molar ratio of NCO/OH. The FTIR spectra are shown in Figure SI5 for the three DHEUR polymers. The strong characteristic absorption band at ca. 2200−2300 cm^{-1} corresponding to the stretching vibration of isocyanate groups of IPDI disappears, and a new absorption band appears at ca. 1716−1721 cm^{-1} corresponding to the stretching vibration of carbonyl group of carbonate, indicating that isocyanate groups reacts with hydroxyl groups to form carbonate.

Table 1. Molecular Weights and Molecular Weight Distributions of Three DHEUR Polymers

polymers	M_n	M_w	PDI
DHEUR-1	21 000	29 100	1.38
DHEUR-2	21 300	31 900	1.49
DHEUR-3	23 500	34 100	1.45

The ^{1}H NMR spectrum is shown in Figure 1 for the purified **DHEUR-3** polymer. The ^{1}H NMR spectra of the purified **DHEUR-1** and **DHEUR-2** polymers follow similar trends and are represented in Supporting Information Figures SI6 and SI7. The number of alkyl groups per HEUR association polymer chain can be sought from an ^{1}H NMR analysis for HEUR polymers with a single substituted alkyl tail chain.[28] For these DHEUR polymers, the degree of end-capping reaction can be defined as end-capping ratio (ECR) of hydrophobic alkyl chain according to a similar procedure,[28] correlation with the number of end alkyl group per DHEUR polymer chain

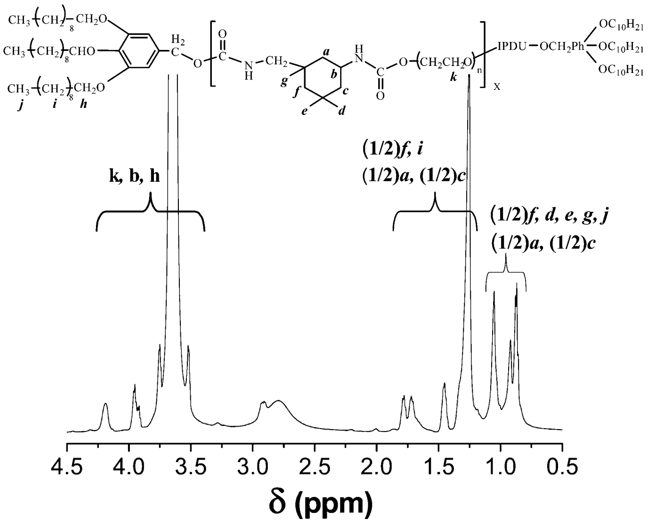


Figure 1. ^{1}H NMR spectrum of **DHEUR-3** polymer.

In the range of chemical shifts δ from 0.7 to 1.8 ppm for **DHEUR-3** (Figure 1), there is a significant overlap of the proton resonances of the alkyl tail ($C_{10}H_{21}O$) of the Percec-type dendron end-cappers and the isophorone diurethane (IPDU) moieties. In δ range between 0.7 and 1.1 ppm, the integration $I_{(0.7-1.1)}$ of the NMR signals compose by 12 protons contributed by IPDU and 3 protons contributed by the alkyl group $C_{10}H_{21}O$, which can be described by eq 1. In the range of 1.1−1.8 ppm, IPDU contributes 3 protons, while each $C_{10}H_{21}O$ group contributes 16 protons. The integration $I_{(1.1-1.8)}$ can be described by eq 2. There is also an overlap of the proton resonances of PEG, $C_{10}H_{21}O$, and IPDU moieties in δ range of 3.5−4.3 ppm. In δ range between 3.5 and 3.8 ppm, the integration $I_{(3.5-3.8)}$ consist of 544 protons contributed by PEG, 1 proton contributed by IPDU, and 2 protons contributed by $C_{10}H_{21}O$, which can be described by eq 3. As the average IPDU number is always one more than the average PEG number in DHEUR polymer chain, eq 4 can be obtained.

$$I_{(0.7-1.1)} = 3N_{(C_{10}H_{21}O)} + 12N_{(IPDU)} \tag{1}$$

$$I_{(1.1-1.8)} = 16N_{(C_{10}H_{21}O)} + 3N_{(IPDU)} \tag{2}$$

$$I_{(3.5-4.3)} = 544N_{(PEG)} + N_{(IPDU)} + 2N_{(C_{10}H_{21}O)} \tag{3}$$

$$N_{(IPDU)} = N_{(PEG)} + 1 \tag{4}$$

In eqs 1−4, N is the average number of group per DHEUR polymer chain. According to the integral area of the above three δ range from ^{1}H NMR spectra of DHEUR polymers, $N_{(IPDU)}$, $N_{(PEG)}$, and $N_{(C_{10}H_{21}O)}$ can be calculated by applying the above equations.

The number-average molecular weight M_n (NMR) and the end-capping ratios of hydrophobic alkyl chain can be obtained in terms of the calculation eqs 5 and 6

$$M_n(\text{NMR}) = 6000N_{(PEG)} + 222N_{(IPDU)} + \frac{M_i}{i}N_{(C_{10}H_{21}O)} \tag{5}$$

$$\text{ECR} = \frac{N_{(C_{10}H_{21}O)}}{2i} \times 100\% \tag{6}$$

where M_i is the molecular weight of the Percec-type dendron end-cappers and i is the number of terminal hydrophobic tail chains of the Percec-type dendron end-cappers.

The results derived from ^{1}H NMR measurements are summarized in Table 2 for these DHEUR polymers. The molecular weights derived from ^{1}H NMR are consistent with the values from GPC measurements. The end-capping ratios of the three DHEUR polymers are above 87%, indicating that the majority of the Percec-type dendron end-cappers are successfully introduced into the molecular chain of DHEUR polymers and only little DHEUR have fewer than the two expected end-cappers per chain, which is consistent with the results reported by other authors.[25,28,37]

Table 2. ^{1}H NMR Characterization of Three DHUER Polymers

polymers	$N_{(PEG)}$	$N_{(IPDU)}$	$N_{(C_{10}H_{21}O)}$	M_n(NMR)	ECR (%)
DHEUR-1	3.22	4.22	1.8	20 731	90
DHEUR-2	3.21	4.21	3.48	20 848	87
DHEUR-3	3.33	4.33	5.28	21 975	88

Steady Shear Behavior of DHEUR Aqueous Solutions. The steady shear viscosity η profiles as a function of shear rate γ for DHEUR aqueous solutions at indicated concentrations are illustrated in Figure 2. The shear rates incremented from 0.01 to 1000 s^{-1} in logarithmically spaced steps (5 points per decade). Prior to measurement, an equilibrium time of 10 s was given at each experiment to ensure the shear stress reaches a constant value.[38] As shown, the shear viscosity of the three DHEUR solutions processes interesting behavior.

For **DHEUR-1**, the solution viscosity is very low and shows essentially Newtonian behavior in a wide γ range for each concentration, while a highly shear thinning behavior appears in a high γ region (approximately 40−100 s^{-1}), where the viscosity rapidly falls with increasing γ. As aforementioned, the hydrophobic segments of HEUR polymers in aqueous solution can associate to form micellar cores and the hydrophilic backbone come into being flower loops. When the micelles are isolated and separated, they are difficult to associate with each other. However, when these flower-like micelles connect mutually through the bridge connection of the hydrophilic chains, thus a network structure is formed and the viscosity is increased.[15−19] As the network is temporal and weak, so the network can be destroyed by the shear stress. When the shear rate exceeds the inverse of relaxation time, i.e., the disengagement rate of the hydrophobe from micellar junction surpasses the rate at which micellar junction can be re-formed,[15] the network is destroyed and the viscosity rapidly drops.[39] Clearly, the isolated and separated micelles should play a dominant role in **DHEUR-1** solutions, while micellar junction through the bridged connection of the hydrophilic chains is secondary. Therefore, **DHEUR-1** polymers in solution cannot develop a complete physical network to give a high viscosity. Furthermore, a short relaxation time also reduces a rapid shear-thinning behavior to occurs at high γ, which is almost independent of the polymer concentration, suggesting that the polymer concentration do not significantly influence on the association and relaxation behavior of **DHEUR-1** polymer. The relaxation behavior of HEUR polymer is attributed to the disengagement rate of the hydrophobe from micellar junction.[15] Thus, the relaxation time is related to the association degree of transient network and shear-thinning

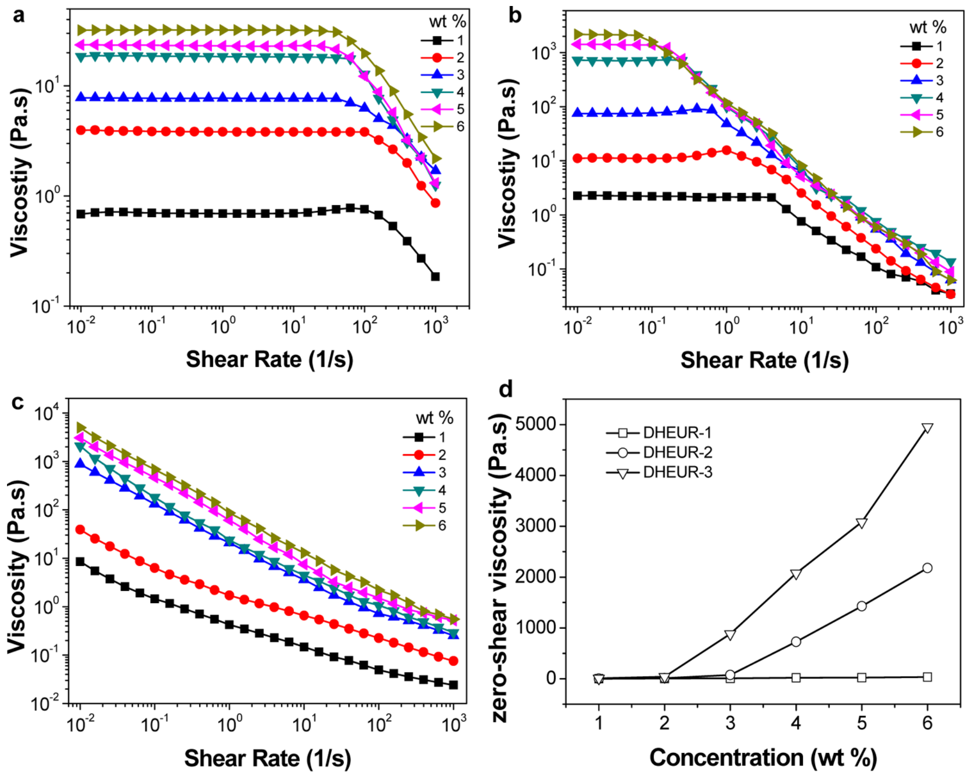


Figure 2. Plots of steady shear viscosity vs shear rate for (a) **DHEUR-1**, (b) **DHEUR-2**, and (c) **DHEUR-3** aqueous solutions at indicated concentrations (wt %). Zero-shear (0.01 s^{-1}) viscosity as a function of DHEUR concentration (d).

behavior of HEUR solutions. The more complete the associative network is, the longer the relaxation time is. It should be mentioned that shear thickening behavior is also observed before shear thinning appears at intermediate γ (approximately from 10 to 100 s^{-1}) in low polymer concentrations, which is the same as the behavior of telechelic association polymer.[7,19,29,40−44] The shear thickening of HEUR solutions has been verified by some recent publications.[5,40,45−47] The shear thickening may result from a rearrangement of the molecular chain of DHEUR stretch from intramolecular aggregation to intermolecular association under shear. So the viscosity increase is due to more intermolecular association. With the increase of the concentration, the degree of shear thickening is debased because of the establishment of intermolecular association.

DHEUR-2 solutions have similar steady shear flow behavior to **DHEUR-1** solutions, and shear thickening is also observed at low polymer concentration, but the solution viscosity is relatively higher and represents essentially Newtonian only in a narrow γ range. On the contrary, a highly shear thinning behavior shifts to low γ region (approximately from 0.05 to 5 s^{-1}). This means that **DHEUR-2** in solutions process a longer relaxation time than **DHEUR-1**. Clearly, the flower-like micellar junctions through the bridge connection of the hydrophilic chains should be dominant in **DHEUR-2** solutions besides some isolated and separated micelles. Furthermore, the shear rate at which shear thinning occurs significantly reduces as the solution concentration increases, suggesting the increase of the bridged micellar junctions and thus a relatively longer relaxation time. This indicates that the polymer concentration has an important influence on the associative structure and the relaxation behavior of **DHEUR-2** solutions due to the change of the micellar junctions. The difference in associative structures and the relaxation behavior for **DHEUR-1** and **DHEUR-2** solutions should attribute to the number of hydrophobic end groups in their molecular structures.

The solutions of **DHEUR-3** show very high solution viscosity and especially pronounced shear thinning behavior over the whole γ range. This indicates that **DHEUR-3** polymer in solution form a complete physical network through the micellar junctions to greatly improve the thickening effect due to more hydrophobic alkyl tails without isolated and separated micelles. So the relaxation time tends to infinity according to previous discussion. In other words, even though the shear rate is very low, the disengagement rate of the hydrophobe from micellar junction would surpass the rate at which micellar junction can be re-formed. As a result, **DHEUR-3** polymer in solution shows a rapid shear thinning behavior over the tested γ range. As aforementioned, the **DHEUR-3** have almost the same molecular weights, molecular weight distributions, and nearly identical hydrophilic portion with both **DHEUR-1** and **DHEUR-2** polymers but more terminal hydrophobic group numbers. Thus, it comes to conclusion that the number of hydrophobic tail chain has a significant effect on the viscosity behavior of these novel DHEUR polymers due to their different hydrophobic associative structures.

In order to clearly demonstrate the effect of hydrophobic tail chain number on thickening efficiency of DHEUR, a plot of the zero-shear (0.01 s^{-1}) viscosity η_0 of DHEUR solutions as a function of polymer concentrations is shown in Figure 2d. For **DHEUR-1**, η_0 is low and increases slightly with the polymer concentration, and a linear relationship between the value of η_0 and polymer concentration in the examined range can be observed. Note that η_0 of **DHEUR-2** solutions increases sharply when the concentration is over 3 wt %. Analogously, **DHEUR-3** solutions show a mutation of η_0 above the concentration of 2 wt %. The difference in η_0 should be attributed to the different hydrophobic associative structures of these DHEUR polymers, which agrees with data reported by other authors.[4,6,15,48,49] The more terminal hydrophobic tail chain number the DHEUR have, the more significant thickening efficiency the DHEUR aqueous solutions get. Thus, both **DHEUR-2** and **DHEUR-3** solutions promise significant thickening efficiency due to their stronger hydrophobic association than **DHEUR-1** solutions. The results further indicate that the number of the hydrophobic end groups in these DHEUR polymers plays a key role in determining the viscosity behavior.

Oscillatory Shear Measurement of DHEUR Aqueous Solutions. The above steady shear measurement has indicated that the different viscosity behaviors of these DHEUR aqueous solutions should be due to the difference in their associative structures. In order to verify the associative network structures, the oscillatory shear measurement is performed to investigate viscoelastic behaviors of DHUER aqueous solutions. DHEUR aqueous solutions show linear viscoelastic behavior at strain below 100% according to strain sweep measurements. In this linear viscoelastic region, oscillatory shear measurement of DHEUR aqueous solutions is conducted in angular frequency range ω from 10^{-2} to 10^{2} rad/s. The storage modulus G' and loss modulus G'' of DHEUR aqueous solutions at indicated concentrations as a function of the angular frequency ω is shown in Figure 3. As an illustration, DHEUR solutions at concentrations of 1, 3, and 5 wt % are given.

Figure 3a illustrates the changes of G' and G'' dependence on ω for **DHEUR-1**. At each concentration, the G'' increases with a slope of one and G' with a slope of two in the whole ω range. G' and G'' intersected at ω close to the maximum one. G'' is higher than G' over the frequency range, which reflects that there is no rubbery plateau evident. They behave like Newtonian viscous fluids, indicating that the associative junction is weak and micellar aggregation play a dominant role.

Figure 3b illustrates the plots of G' and G'' as a function of ω for **DHEUR-2**. At low frequency region (approximately from 0.01 to 1), G'' increases with a slope of one, G' with a slope of two, and the value of G'' is less than that of G', indicating a similar viscous behavior to **DHEUR-1** solutions. Interestingly, with increasing ω (approximately from 1 to 100), G' asymptotes to a constant value higher than G'', while G'' exhibits a maximum and a crossover of G' and G'' is observed. This plateau modulus is analogous to a classical rubber plateau modulus (G_0). This plateau implies that the solution behaves in this region as an elastic body. This suggests the formation of the associative network,[50−52] which should be attributed to the large number of mechanically active micellar junctions. Thus, **DHEUR-2** solutions show a viscoelastic behavior with elastic regions at high ω and viscous regions at low ω. With the increase of concentration, G_0 value increases and the point of intersection G'/G'' comes out at lower ω, indicating that the associative network is more and more complete and the relaxation time of associative network get longer and longer due to the increase of micellar junctions. The relaxation time can be obtained by fitting the G' and G'' data of **DHEUR-2** aqueous solution from the single Maxwell model, consisting in an elastic component connected in series with a viscous element. The single Maxwell model is described by the following equations.[15,21,29,40]

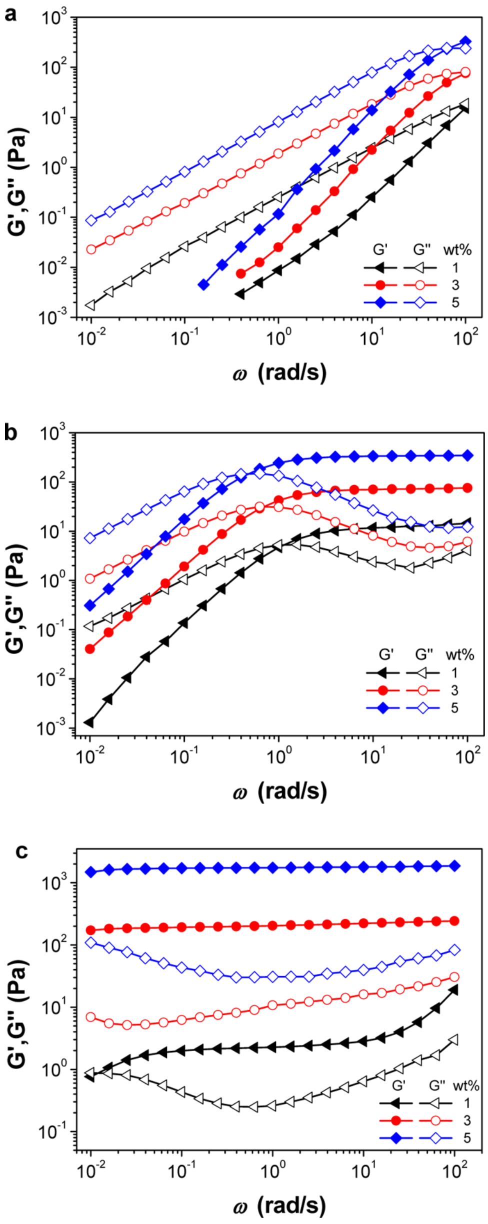


Figure 3. Storage modulus G' (closed symbols) and loss modulus G'' (open symbols) modulus dependence on angular frequency ω for (a) **DHEUR-1**, (b) **DHEUR-2**, and (c) **DHEUR-3** aqueous solutions at indicated concentrations.

$$G'(\omega) = \frac{G_0\omega^2\tau^2}{1 + \omega^2\tau^2} \tag{7}$$

$$G''(\omega) = \frac{G_0\omega\tau}{1 + \omega^2\tau^2} \tag{8}$$

where G_0 is the plateau modulus, ω is the angular frequencies, and τ is the relaxation time. The fitting data according to the Maxwell eqs 7 and 8 are shown in Figure 4a–c; the solid line represents the best fit to the single Maxwell model. The fitting plots of **DHEUR-2** solutions possess similarity as long as the concentration is over 1 wt %. From the fitting data, the plateau modulus G_0 and the relaxation time τ can be obtained. The concentration dependence of the relaxation time for **DHEUR-2** solutions obtained from fitting of the Maxwell model is plotted in Figure 4d. As is seen, the relaxation time increases as the concentration increases, which is consistent with previous steady shear measurements. The results indicated that **DHEUR-2** solution form a relatively more complete network with increasing polymer concentration and exhibit significant viscoelastic behavior.

A Cole–Cole plot of G' vs G'' is another way to investigate the viscoelastic behavior of telechelic associating polymers.[6,15] The Cole–Cole plot can be described by the following eq 9 obtained by rearranging eqs 7 and 8:

$$G''(\omega) = [G'(\omega)G_0 - G'(\omega)^2]^m \tag{9}$$

where the exponent m equal to 0.5. The data of a Maxwell fluid should be in the form of a semicircle. Figure 5 shows Cole–Cole plots for **DHEUR-2** solutions at three concentrations (1, 3, and 5 wt %) with the accompanying fitting of the Maxwell model shown in solid lines using eq 9. Perfect semicircles can be observed and G_0 determined from the intersection of the semicircle with the horizontal x-axis are consistent with the values obtained from fitting of the Maxwell model. This further confirms the fitting of oscillatory measurement data to the single element Maxwell model.

Figure 3c illustrates the plots of G' and G'' versus ω for **DHEUR-3.** Note that in the whole ω range the value of G' is higher than that of G''. Moreover, G' is independent of the ω examined in this work and remains a constant value. A clear rubbery plateau is observed, indicating the **DHUER-3** solutions behave like a highly elastic body due to the formation of a complete physical network with strong associative cross-linking. Thus, the system has infinite relaxation time in this tested range, which is in accord with the steady shear viscosity measurements.

From above results, one can draw one conclusion that the number of hydrophobic tail chain is a significant contributing factor affecting on the associative structures and rheological behavior of these DHEUR polymers in solutions. The more hydrophobic tails for dendron end-cappers favor the formation of a complete physical network with strong micellar junctions, which achieve high thickening efficiency.

Influence of Temperature on Rheological Behaviorof DHEUR Aqueous Solutions. The rheological activation energy is an important property of associative polymers and represents the potential barrier for disengagement of the hydrophobic chain from micellar junction. In order to obtain the rheological activation energy of these DHEUR polymers, the influence of temperature on the viscoelastic response is investigated for the three DHEUR aqueous solutions. The steady state and oscillatory shear measurements were performed for these DHEUR solutions with fixed concentration at different temperatures ranging from 15 up to 65 °C. Figure 6a shows the effect of temperature on steady shear viscosity η for 5 wt % **DHEUR-1** aqueous solutions. As can be seen, η decreases with increasing temperature. Similar results are observed for **DHEUR-2** in Figure 6b and **DHEUR-3** in Figure 6c. For **DHEUR-1** and **DHEUR-2**, the onset of shear shinning shift to the lower γ, and **DHEUR-3** remain shear shinning behavior over the whole γ range as temperature decreases. These steady shear experiments indicate that the associative structures of these DHEUR polymers in solutions almost retain no change, but their relaxation time becomes shorter with increasing temperature, which will be discussed below through oscillatory shear measurements.

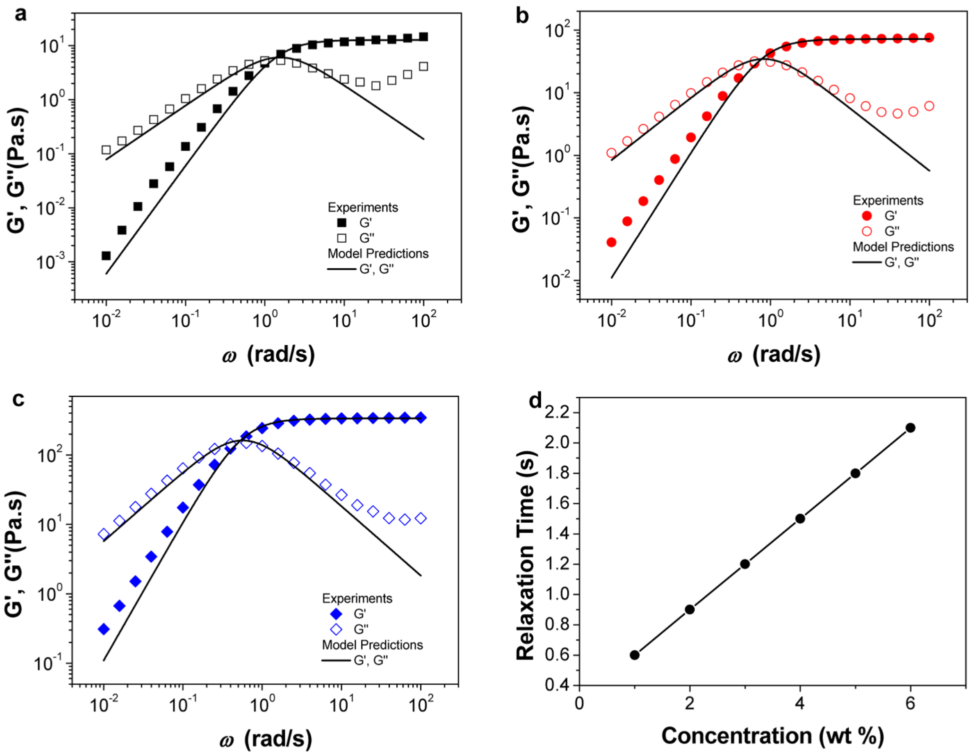


Figure 4. Fitting of single Maxwell model to the oscillatory measured data of **DHEUR-2** aqueous solutions at various concentrations: (a) 1, (b) 3, and (c) 5 wt %. The relaxation time obtained from fitting to single Maxwell model as a function of concentration of **DHEUR-2** solutions (d).

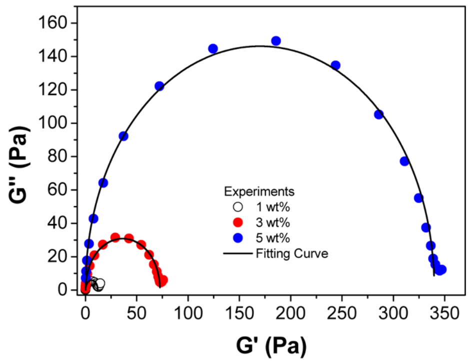


Figure 5. Cole−Cole plots of storage modulus G' vs loss modulus G'' for **DHEUR-2** solutions at indicated concentration with the accompanying fitting of the Maxwell model shown by solid lines.

The temperature dependence of zero-shear viscosity η_0 extracted from the steady shear experiments can be fitted by the Arrhenius equation expressed as[53]

$$\eta_0(T) = Ae^{E_m/RT} \tag{10}$$

where E_m is the activation energy representing the potential barrier to disengagement of the hydrophobic chain from micellar junction, T is the thermodynamic temperature, A is a pre-exponential constant, and R is the gas constant, equal to 8.31 J mol^{-1} K^{-1}. The η_0 profile as a function of temperature in Arrhenius form for 5 wt % DHEUR aqueous solutions is shown in Figure 6d. Clearly, η_0 follows an Arrhenius temperature dependence, with a linear relationship between the natural log of η_0 and 1/T. The rheological activation energys E_m obtained from the slope of linear fittings are 61, 117, and 140 kJ mol^{-1} for **DHEUR-1**, **DHEUR-2**, and **DHEUR-3**, respectively. A higher E_m value suggests stronger association interaction at a given polymer concentration.[8,54] The values of E_m for these DHEUR polymers increase with the increase of terminal hydrophobic tail chain number, further confirming that the number of hydrophobic end groups is a significant contributing factor affecting the strength of the association junctions.

To verify the influence of temperature on association and relaxation behavior of DHEUR polymers, G' and G'' profiles as a function of ω are shown in Figure 7a−c for 5 wt % DHEUR solutions at various temperatures. As an illustration, the data only at temperature of 15, 35, and 55 °C are given for these DHEUR solutions. It is clearly observed that the association behavior of the DHEUR solutions maintains no change under different temperature; i.e., **DHEUR-1** has only viscous behavior with short relaxation time τ, **DHEUR-2** behaves as viscoelastic fluid with a relatively longer τ, and **DHUER-3** is highly elastic with infinite τ. For 5 wt % **DHEUR-2** aqueous solution, the temperature dependence of τ obtained by fitting the G' and G'' data from the single Maxwell model is shown in Figure 7d in Arrhenius form, based on the transient network theory proposed by Tanaka and Edward.[55] Just like η_0, τ also exhibits a similar temperature dependency and a typical Arrhenius relationship. E_m evaluated from the relaxation date possesses a value of 100 kJ mol^{-1}, which is close to the data determined from viscosity measurements. As temperature increases, the network association strength become weaker, and terminal hydrophobic chains exit from the micellar junctions more easily, which result in τ decreasing.[45] Furthermore, as τ decreases with increasing temperature, the onset of shear thinning shift to higher γ, verifying the previous steady shear measurements.

Structural Models of DHEUR Polymers. To illustrate the change of associative networks, an overview of structural models for these DHEUR polymers in aqueous solution is detailed in Figure 8. The systems are composed of flower-like

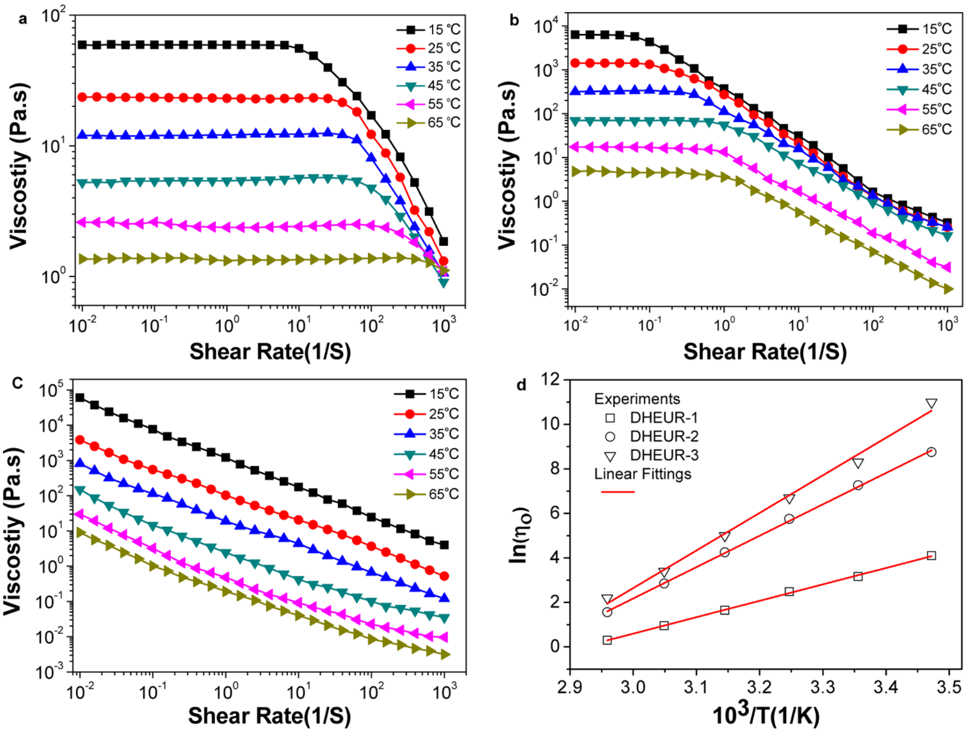


Figure 6. Steady shear viscosity profiles as a function of shear rate for 5 wt % of (a) **DHEUR-1**, (b) **DHEUR-2**, and (c) **DHEUR-3** aqueous solutions at different temperatures. Arrhenius plots of zero-shear viscosity η_0 for 5 wt % DHEUR aqueous solutions (d).

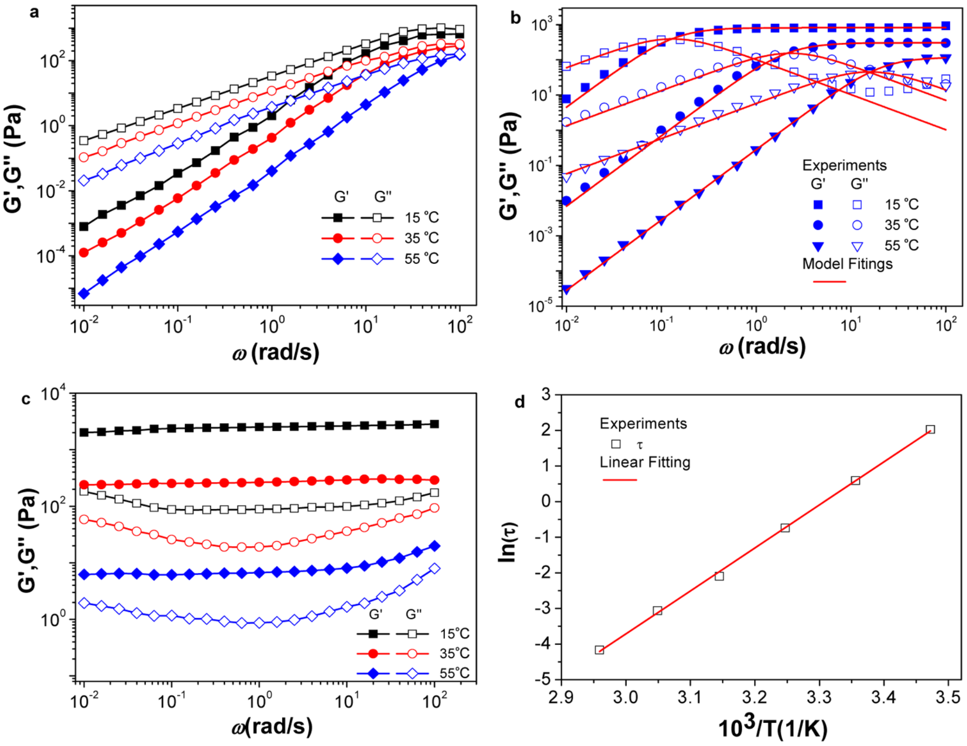


Figure 7. (a) Storage modulus G' (closed symbols) and loss modulus G'' (open symbols) modulus dependence on angular frequency ω for (a) **DHEUR-1**, (b) **DHEUR-2**, and (c) **DHEUR-3** aqueous solutions at 5 wt % at various temperature. (d) Arrhenius plot of relaxation time τ for 5 wt % **DHEUR-2** aqueous solutions.

micelles and chain bridged junctions. The end hydrophobic groups of DHEUR aggregate to form the core of flower-like micelles, and hydrophilic segments form the loops or bridged junctions of flower-like micelles. Flower-like micelles can connect mutually to form micellar junctions. Those active junctions through the bridged connection of the hydrophilic chains are temporary. The lifetime of those junctions is very short. Since the junctions in the network are dynamic, they are broken and re-formed all the time by thermal energy. So the capacity to rupture and re-form the existing junctions allows the

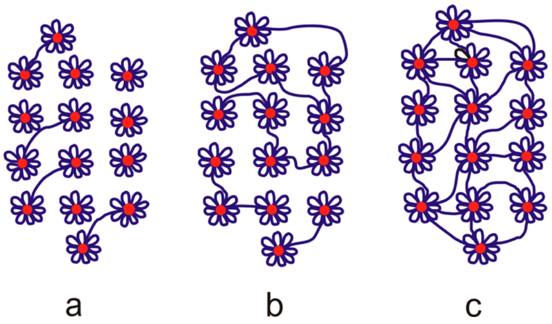


Figure 8. Schematic diagram of structural models of (a) **DHEUR-1**, (b) **DHEUR-2**, and (c) **DHEUR-3** polymers in aqueous solution. The terminal hydrophobic groups of DHEUR aggregate to form the core of flower-like micelles and hydrophilic segments form the loops and bridged junctions of flower-like micelles.

networks to relax applied stress of strains. When the number of terminal hydrophobic tails increases from one to two and to three, the association is stronger and stronger, and the network structures tend to reach more and more complete, and thus the relaxation time is longer and longer.

Figure 9 shows the steady shear viscosity as a factor of shear rate for DHEUR aqueous solutions and the accompanying structural models of micelles at different shear regions. As shown in Figure 8, **DHEUR-1** solutions are dominantly composed of the isolated and separated micelles, and a complete physical network of micellar junctions could not be developed. Hence, **DHEUR-1** solutions show Newtonian behavior in wide shear rate range. However, the relaxation time is very short. When the shear rate is very high, the disengagement rate of the hydrophobe from micellar junctions surpasses the rate at which micellar junction can be re-formed, so those secondary micellar junctions is also destroyed and the shear-thinning behavior occurs, while shear-thickening should be caused by a rearrangement of the molecular chain from intramolecular aggregation to intermolecular association at intermediate shear rates at high shear rate region. **DHEUR-2** polymers have stronger hydrophobic association interactions than **DHEUR-1**, so they can form more bridged micellar junctions than **DHEUR-1**. **DHEUR-2** solutions represent a relatively more complete network through dominant micellar junctions, although some isolated and separated micelles are present. So, **DHEUR-2** solutions process high viscosity. However, dominant micellar junctions cause shear thinning behavior to occur at lower shear rate due to a relatively longer relaxation time, although they show a similar solution viscosity behavior to **DHEUR-1**. **DHEUR-3** have more hydrophobic tail chains and thus stronger hydrophobic association interactions than **DHEUR-2**, so **DHEUR-3** in solutions can form the most complete transient networks by the micellar junctions through the bridged connection of the hydrophilic chains, leading to a significant increase in viscosity values and rapidly shear thinning behavior over the whole γ range due to a very long relaxation time.

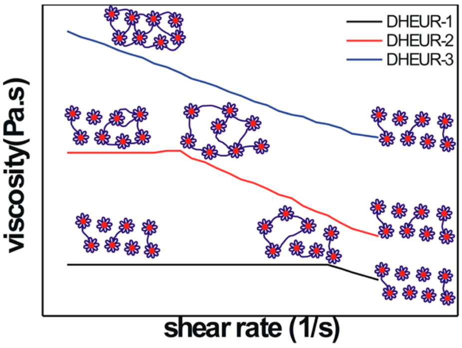


Figure 9. Steady shear viscosity vs shear rate of DHEUR aqueous solutions and the accompanying structure models of micelles at different shear regions.

CONCLUSIONS

Novel dendron hydrophobically modified ethoxylated urethanes (DHEUR) were prepared by using Percec-type alkyl substituted benzyl alcohol dendrons as new end-cappers. These DHEUR polymers have almost the same molecular weights, molecular weight distributions, and nearly identical hydrophilic portion but different terminal hydrophobic group numbers. The end-capping ratios of these DHEUR polymers are above 87% estimated from their ^{1}H NMR measurements; thus the majority of the Percec-type dendron end-cappers are successfully introduced into DHEUR polymers chain. These DHEUR polymers in solution exhibit significantly different rheological behavior due to their different associative structures. **DHEUR-1** solutions are dominantly composed of the isolated and separated micelles and exhibit Newtonian behavior in a wide shear rate range accompanied by shear-thinning at high shear rate region due to a short relaxation time. **DHEUR-2** solutions represent a relatively more complete network through dominant micellar junctions and process a relatively higher solution viscosity but a similar solution viscosity behavior to **DHEUR-1**. However, shear thinning behavior occurs at lower shear rate due to a relatively longer relaxation time. **DHEUR-3** solutions have developed a complete physical network and show only pronounced shear thinning behavior over the whole γ range due to a very long relaxation time. The results indicate that interesting rheological behaviors such as viscous fluid (**DHEUR-1**), viscoelastic fluid (**DHEUR-2**), and elastic body (**DHEUR-3**) can be triggered by increasing the terminal hydrophobic tail number of dendrons. Furthermore, the rheological activation energy of these DHEUR polymers increases with the increase of terminal hydrophobic group numbers, indicating that DHEUR polymers with more hydrophobic tail chains need more energy potential barrier for the disengagement of hydrophobes from micelles due to stronger association strength. In general, the results indicate that the number of terminal hydrophobic tail chain plays a key role in determining the rheological behavior of the DHEUR aqueous solutions. This study opens a new perspective for more efficient thickeners and further confirms the potential of these novel DHEUR polymers in waterborne coating, cosmetics, dyestuff, medicines, and so on for the first time.

ASSOCIATED CONTENT

Supporting Information

^{1}H NMR spectra of dendron **5**, **6**, **2**, and **4**; FTIR spectra of the three DHEUR polymers; ^{1}H NMR spectra of **DHEUR-1** and **DHEUR-2** polymers. 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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