Study of the Effect of PEG Length in Uni-HEUR Thickener Behavior

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ABSTRACT: Four new models of Uni-HEUR associative thickener were designed and synthesized using various molecular weights of poly(ethylene glycol) (PEG) as hydrophilic segments. The PEG chain ends were capped with octadecyl isocyanate as hydrophobic segments. The structure of the prepared Uni-HEUR thickeners was confirmed by infrared spectroscopy. The steady shear viscosity measurements of aqueous solution of HEUR models showed that the relative size of hydrophilic segments to hydrophobic segments is very important. Oscillatory measurements confirmed the steady shear viscosity results. It is found, there is an optimum relative size of hydrophilic segments to hydrophobic segments to achieve the thickener with a good performance. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 111: 1751–1754, 2009

Key words: Uni-HEUR; hydrophilic; hydrophobic; associative; thickener

INTRODUCTION

Associative polymers are a group of thickeners used in water-based latex systems to adjust and to modify the rheology profiles. Also, they have wide application in foods and pharmaceutical products, and are used to enhance oil recovery.[1] Associative thickeners are water-soluble polymers onto which hydrophobic segments have been chemically attached, either to both or along the hydrophilic chain backbone. One of the most common types of associative thickeners is hydrophobically modified ethoxylated urethane (HEUR).[2]

Over the past two decades, a major part of past research works have been focused on HEUR systems. Topics include synthesis and characterization of HEUR models,[3–7] binding of the ionic and anionic surfactants with HEUR polymers,[8–12] interaction of HEUR thickener with other ingredients in the latices,[13–21] modeling and transient network theory or physical network formation,[22–25] rheological behavior of HEUR mixture in aqueous media,[26] and relationship between structure and rheological properties.[27,28]

HEUR associative thickeners are divided into two classes: S-G HEUR and Uni-HEUR, considering the synthesizing method or molecular weight distribution.[29] The synthesis process of S-G HEUR includes two steps. In the first step, polyethylene glycol (PEG) is reacted with excess diisocyanate, to achieve an isocyanate-terminated prepolymer. Then, S-G HEUR is formed by the reaction of the prepolymer with monofunctional aliphatic alcohol. This method provides a polyurethane thickener with a broad molecular weight distribution. Uni-HEUR is synthesized by direct addition of a monodiisocyanate to PEG, or by the addition of a large excess of diisocyanate to PEG, and is followed by the addition of an alkyl amine to the terminal isocyanate group. In this case, the obtained thickener has narrow molecular weight distribution which is related to the PEG molecular weight.

In our previous work,[29] the influence of the molecular weight of prepolymers on the viscoelastic properties of aqueous HEUR solutions were examined in a series of S-G HEUR thickeners.

Here, a series of Uni-HEUR was prepared by using different molecular-weight PEG and the effect of hydrophilic segment size was studied. The rheological behaviors of the thickener models both in aqueous solutions and with the presence of two latexes were examined.

EXPERIMENTAL

Materials and instrumentation

PEG of molecular weights 6000, 10,000, 15,000, and 20,000 were purchased from Merck (Germany).

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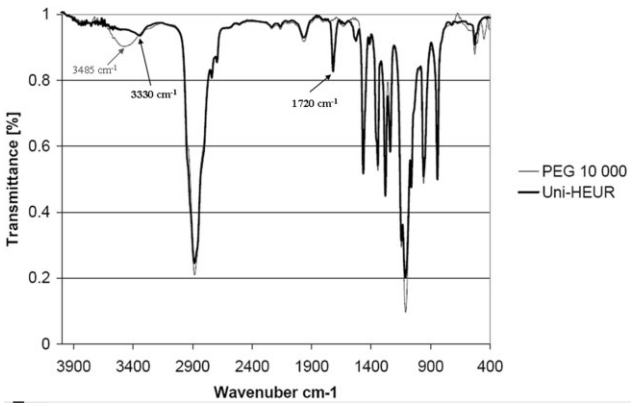

Figure 1 FTIR spectra of PEG and the synthesized Uni-HEUR model.

Octadecyl isocyanate (CH_3-$(CH_2)_{17}$-NCO; Sigma-Aldrich, Milwaukee, WI) was used as received. Dibutyltin dilurate used was obtained from Fluka (Switzerland). Petroleum ether with low boiling point was obtained from Pars Chemie (Iran). Industrial grade THF, toluene, and acetone were used as solvents.

Infrared spectroscopy was conducted on the samples using Bruker-IFS 48 model (Germany). The steady shear viscosity measurements were performed by implementing a Paar Physica MCR 300 rheometer (Austria) with cone and plate geometry. The cone angle and plate diameter were 2° and 50 mm, respectively. The temperature was set at 25°C.

Synthesis procedure

In this work, Uni-HEUR was obtained from direct reaction of PEG with octadecyl isocyanate. Octadecyl isocyanate contains only one isocyanate functional group. It can easily react with any trace of water in the reaction systems and reduce the level of substitution of hydrophobic segment to PEG. All raw materials, such as PEG, THF, and toluene, were dried to prevent this undesirable reaction.

PEG was dried by azeotropic distillation from toluene in the reaction flask. Octadecyl isocyanate was added to the mixture of PEG and toluene. Then five droplets of dibutyltin dilurate in 50 cc THF were added to the reaction system. The reaction vessel was a four-necked 500-mL round-bottomed flask. The flask was equipped with a magnetic stirrer and a dried pure nitrogen gas reflux column and located in an oil bath at 50°C. The reaction mixture was then continuously stirred for $\sim$ 1.5 h.

The reactor content was precipitated in petroleum ether (4 volumes of petroleum ether to 1 volume of reaction mixture), collected on a sintered glass funnel, and dried in a vacuum oven. Purification of the HEUR thickener models was performed by dissolution in warm acetone, filtering and collecting it on a filter paper, and precipitation in petroleum ether. The final product was obtained by collecting the thickener on a sintered glass, followed by drying in a vacuum oven. The average yield of thickener preparation was 76%.

RESULTS AND DISCUSSION

The FTIR spectra of PEG and the synthesized Uni-HEUR model are presented in Figure 1. As it can be seen, in the PEG spectrum an absorption band appeared at 3485 cm^{-1} which is related to the hydroxyl group of PEG. The appearance of the characteristic bands in the regions of 1720 cm^{-1} (carbonyl group of urethane) and 3330 cm^{-1} (NH stretching of urethane) and also the disappearance of OH absorption band of PEG (3485 cm^{-1}) in the Uni-HEUR spectrum confirm the reaction of PEG and octadecyl isocyanate and the bonding of the hydrophobic segments to hydrophilic ones.

Four Uni-HEUR models were synthesized. The specifications of the synthesized models are illustrated in Table I.

A qualitative primary test was performed for the initial evaluation of thickeners' performance. In this test, a 2% solution of thickener models in double distilled water was prepared and the viscosity was inspected visually. The Uni15M and Uni20M model solutions showed negligible build-up viscosity. It seems that their long hydrophilic segments, related to PEG 15,000 and PEG 20,000, causes weak association of thickener chains. Hence, in continuation, Uni6M and Uni10M which passed the initial test were studied.

The shear steady viscosity profiles as a function of shear rate for various concentrations of Uni6M are shown in Figure 2. The effect of Uni6M with 2% concentration is very negligible. There are two plateau regions in moderate shear rate for concentrations of 3 and 4%. The steady shear viscosity of Uni10M aqueous solutions is shown in Figure 3. All the concentrations of Uni10M show the same behavior, a plateau region, and shear thinning at high shear rate.

The low shear viscosity (0.1 s^{-1}) dependence on the concentration of Uni-HEUR model solutions is shown in Figure 4. These typical curves are regarded

TABLE I
The Synthesized Uni-HEUR Models Specification

Thickener model	Hydrophilic segment	Hydrophobic segment
Uni6M	PEG 6000	C_{18}
Uni10M	PEG 10,000	C_{18}
Uni15M	PEG 15,000	C_{18}
Uni20M	PEG 20,000	C_{18}

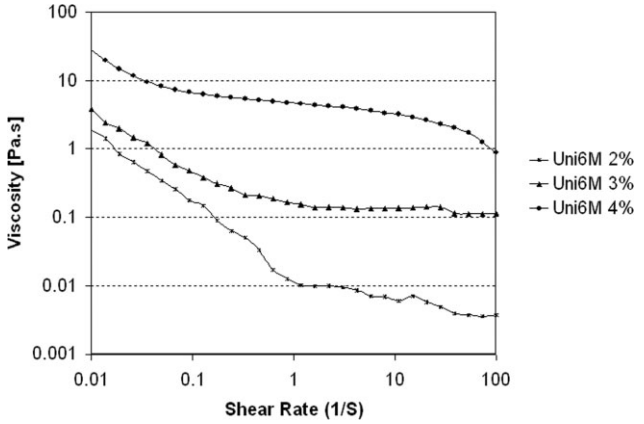

Figure 2 The steady shear viscosity profiles of Uni6M aqueous solutions.

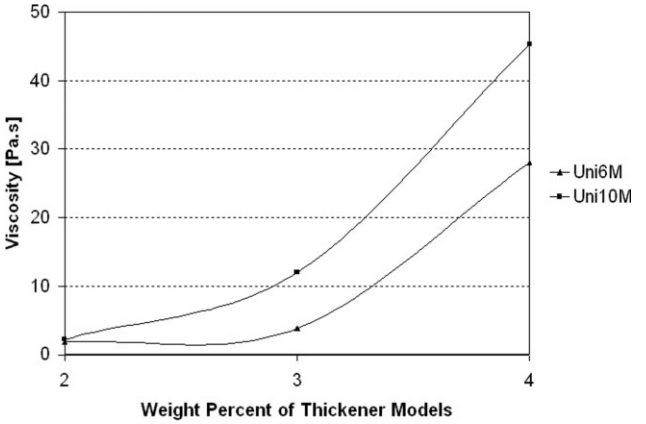

Figure 4 Comparison of low shear viscosity of Uni6M and Uni10M with thickening efficiency.

as thickening efficiency. The viscosity data of Uni10M are higher than Uni6M. Also, the rate of Uni10M curve is steeper in comparison to Uni6M curve.

HEUR thickeners at suitable concentration (more than critical concentration) associate to give flower-like micelles, which undergo secondary association to form secondary aggregates held together by bridging chains.[30]

The thickening efficiency of Uni6M is less than Uni10M (Fig. 4). It seems that in the case of constant hydrophobic segment length (C_{18}), by decreasing hydrophilic segment from PEG 10,000 to PEG 6000, the size of the flower-like micelles will be reduced and the bridge between them becomes unstable, which results in a weak association network.

Oscillatory measurements were carried out on aqueous HEUR model solutions. The storage and loss modulus as a function of frequency are plotted in Figure 5 for different Uni6M solutions of various concentrations. There is a convergence for loss and storage modulus only for Uni6M 3% aqueous solutions, while the other two samples (2 and 3%) do not show any converging. This is attributed to a very weak association network, as discussed for "thickening efficiency." However, the loss and storage moduli of various concentrations of Uni10M aqueous solutions have cross head point (Fig. 6). In other words, Uni10M HEUR model chains have the ability to make a strong association network, even in low concentration (2%).

Both steady shear viscosity and oscillatory measurements proved that the hydrophilic segment length relative to hydrophobic segment length is very important, and it has an optimum size to achieve a good performance in thickening efficiency.

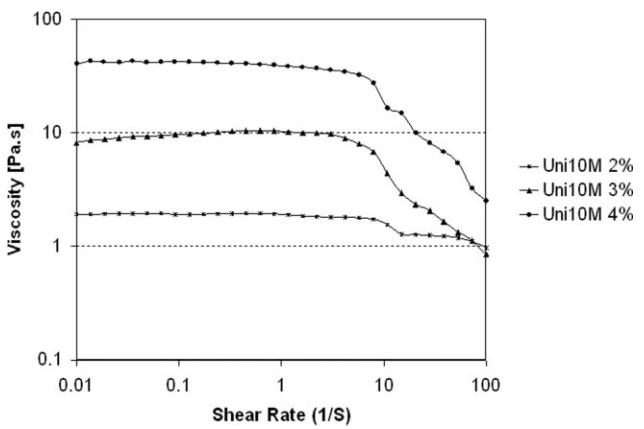

Figure 3 The steady shear viscosity profiles of Uni10M aqueous solutions.

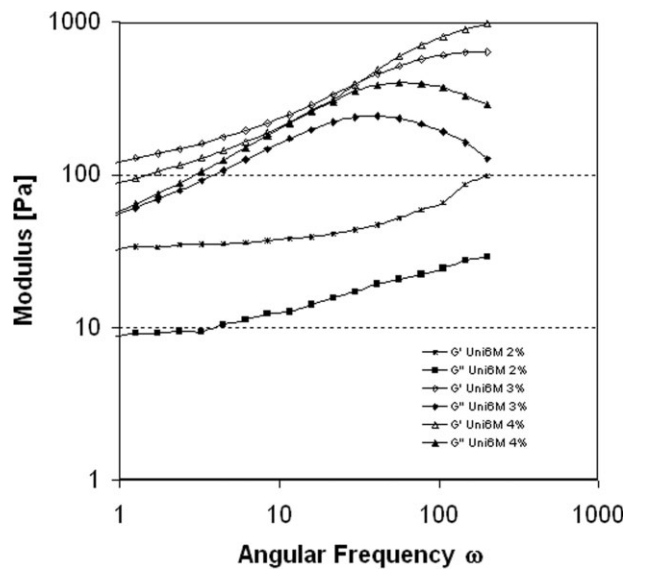

Figure 5 The storage and loss modulus (G', G'') versus frequency for Uni6M model for different concentrations.

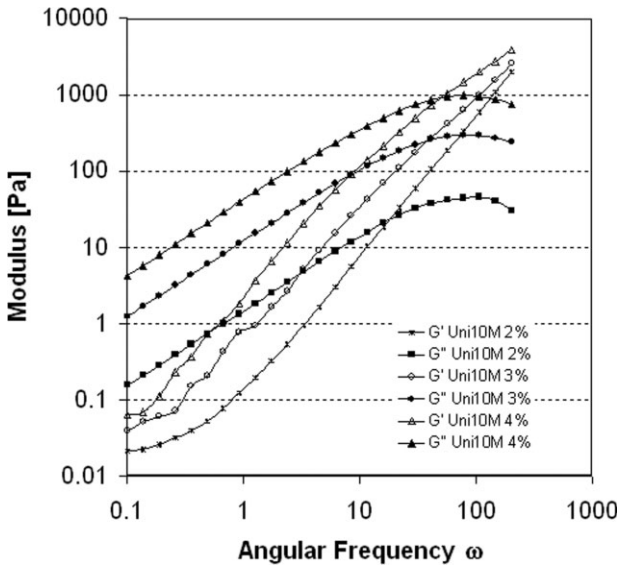

Figure 6 The storage and loss modulus (G', G'') versus frequency for Uni10M model for different concentrations.

CONCLUSIONS

Uni-HEUR models, namely, Uni20M, Uni15M, Uni10M, and Uni6M, were synthesized by reaction of octadecyl isocyanate and PEG with molecular weights of 20,000, 15,000, 10,000, and 6000, respectively. The models with higher relative length of hydrophilic to hydrophobic segments (Uni20M and Uni15M) showed very weak viscosity build-up. This is attributed to the nonstable micelles construction. Also, decreasing the hydrophilic segment length from Uni10M to Uni6M resulted in a decrease in the thickening efficiency. The decrease in hydrophilic segment length caused micelles size reduction and unstable bridging chains between micelles.

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