



## Synthesis and Characterization of a Nonionic Urethane-Based Thickener

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### ABSTRACT

**H**ydrophobically modified ethoxylated urethanes have been synthesized using polyethylene glycol, hexamethylene diisocyanate and cetyl alcohol. These types of thickeners are categorized as nonionic associative thickeners. The HEURs were prepared in two steps. Initially an ethoxylated urethane prepolymer was synthesized through a reaction between a polyethylene glycol ( $M_n=6000$ ) and hexamethylene diisocyanate using the step growth polymerization technique, then modification was carried out by reaction of cetyl alcohol with the obtained prepolymer. HEURs were characterized using  $^1H$  NMR, FTIR and GPC techniques. The rheological properties of incorporated samples in different media proved the considerable thickening efficiency of the produced HEUR. Prog. Color Colorants Coat. 4(2011), 71-77. © Institute for Color Science and Technology.

### 1. Introduction

Polymers that act as associative thickeners in water are of considerable industrial importance in paint coatings, personal care products, and oil industries because of their dramatic ability to modify rheological properties. Associative polymers are a group of thickeners used in water-based latex systems to adjust and modify the rheology profiles. Also, they have wide applications in foods and pharmaceutical products in order to enhance oil recovery. Associative thickeners are water-soluble polymers onto which hydrophobic segments have been chemically attached, either to both ends or along the hydrophilic chain backbone. One of the most common types of associative thickeners is hydrophobically modified ethoxylated urethane (HEUR). They consist of chains with predominantly hydrophilic repeat units but also include a small fraction of hydrophobic sequences in

the main chain or as its side groups [1-6].

Associative polymeric thickeners constitute a particular family of commercial organic rheology modifiers including naturally derived and synthetic compounds. HEURs belong to this class and are actually nonionic block copolymers. They can be telechelic or random block copolymers in linear or branched structures. The synthesis of modified PEO with linkers such as ethers, esters, urethanes or diurethanes was reported elsewhere [7-9].

Other research groups have worked on the structure of HEUR associative thickeners consisting of a hydrophilic segment like poly (ethylene glycol) and the hydrophobic hydrocarbon groups located at the ends of the hydrophilic segments [10-12].

At the same time, at high shear rates, high viscosity is necessary to produce a good film thickness. On the other hand, low viscosity help good flowing-out and leveling

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on the surface at low shear rates. These seemingly mutually exclusive demands require the dispersion to exhibit time-dependent rheological properties specific to each particular type of application, in which the viscosity changes in a controlled way with shear rate. One method to achieve these rheological properties involves adding a water soluble polymer containing hydrophobic substituents as a rheology modifier to the dispersion. These associative polymers, when employed in this type of application to provide a more desirable rheology profile, are referred to “associative thickeners”. One of the major application of using associative thickeners is their effective thickening of small particle latex dispersions to provide water-borne coatings with high gloss levels. Urethane-coupled polyethylene glycol polymers containing hydrophobic end groups (HEUR polymers) constitute one class of associative thickeners widely used as rheology modifiers in the paints and other coating applications. While the structure written for these telechelic polymers have two hydrophobes on the ends of the polymer backbone, in practice, a significant fraction of these polymers lack an end group [13-14].

Commercially important HEUR polymers are prepared by a step growth process and also exhibit a heterogeneous mixture of molecular weights with various degrees of hydrophobic modification [15-16].

Hydrophobically end-capped poly(ethylene oxide)s continue to receive major attention since they form an important class of associating polymers. Particularly, due to their architectural simplicity with exact location of the associating groups, hydrophobically end-capped PEOs form an ideal model system for fundamental studies of rheology of associating polymers. The hydrophilic PEO chain is generally end-capped with hydrophobic stickers (alkyl, perfluoroalkyl or aromatic) attached by ether, ester or urethane linkages [17-19].

To the best of our knowledge, there is no report in the literature about the synthesis of HEUR using hexamethylene diisocyanate which is reported in this work using polyethylene glycol 6000, hexamethylene diisocyanate and cetyl alcohol.

## 2. Experimental

### 2.1. Materials

Polyethylene glycol with a molecular weight of 6000 and hexamethylene diisocyanate (HDI) were used as applied from Merck (Germany) without further purification. Hexamethylene diisocyanate (HDI) was stored under

argon prior to use. The catalyst of the reaction, dibutyltin dilurate (DBTDL) was also obtained from Merck. Toluene solvent (Merck) was dried with calcium hydride during distillation and was stored in a molecular sieve with 0.4 nm beads before use. Cetyl alcohol (Merck) was heated up to 50°C for 1h before using. Petroleum ether and acetone were used as applied from Merck. Deionized water was used for the preparation of polymer solutions. Toluene, tetrahydrofuran and petroleum ether were stirred for 24 h over a 40 mesh calcium hydride and distilled under argon. THF solvent (Merck) was dried with sodium wire. The nonionic surfactant under the trade mark of KENON6 was received from Kimiaganemrooz Company (Iran).

### 2.2. Instruments and characterization

Infrared spectra were recorded on a Perkin Elmer Spectrum 1 spectrophotometer. <sup>1</sup>H NMR spectra were obtained on a Bruker 500 MHz. Molecular weight and molecular weight distribution were determined by gel permeation chromatography (GPC), using a Waters model 150C, with tetrahydrofuran as the mobile phase, a flow rate of 1.5 mL/min, a column temperature of 30°C, two styrogel columns (HR3, HR4), run time 20 min and 500µL injection volume. A calibration curve was prepared with standard polystyrene.

#### 2.2.1. Rheological measurements

Rheological characterization was carried out using a controlled stress rheometer (MCR 300, Anton-Paar, Graz, Austria) with Couette geometry (inner diameter of 26.7, outer diameter of 28.4 mm and a cylinder length of 40 mm). All measurements were conducted at ambient temperature (23-25°C) and the samples were covered with a thin layer of an organic oil to prevent water evaporation.

The viscosity versus shear rate curves at constant temperatures were obtained from the steady shear rate sweep test. Thixotropy behavior was evaluated by hysteresis loop test in which the sample is subject to increasing and then reducing shear.

#### 2.2.2. Sample preparation for rheological measurements

Aqueous solutions of HEURs with various concentration levels were prepared by direct dissolving specified amount of polymer into 100 mL of distilled water. Each solution was gently stirred for 30 min to reach a

homogeneous state. Glycol polyester (2OAF) as nonionic surfactant (HLB=9.5) used in formulating HEURs.

In order to better examine the effect of synthesized HEUR addition on the rheological behavior, we mixed HEURs with a water-based resin of NA 58 received from Simab Resin, Iran. This is a very soft ( $T_g = -14\text{ }^\circ\text{C}$ ) nonionic emulsion resin with a solid content of 45 %.

As the viscosity of dispersion can be changed precisely with solid content [20], we used distilled water to adjust the total solid content of different samples to an identical level.

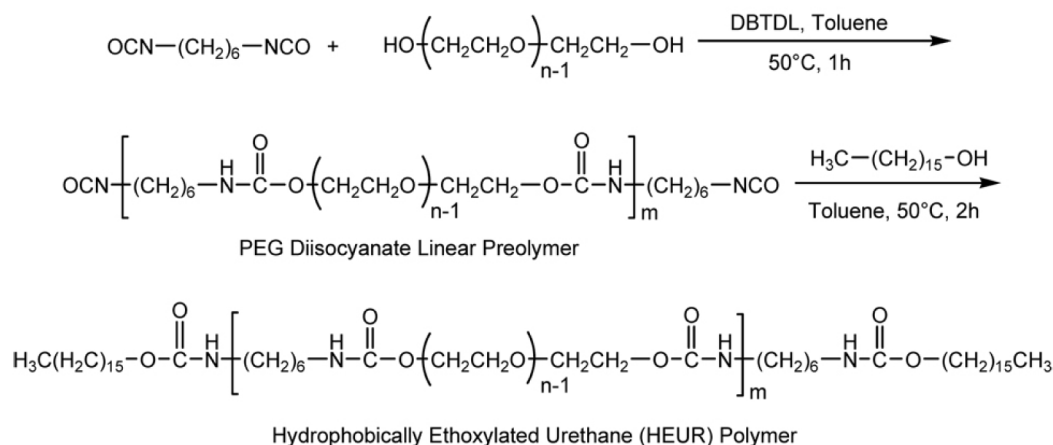
### 2.3. Synthesis of HEUR thickeners

The HEURs with broad molecular weight distributions were produced by the step-growth polymerization of PEG 6000 and hexamethylene diisocyanate (HDI), according to Scheme 1. A stoichiometric ratio of 2.1 mol of diisocyanate to 1.6 mol of PEG 6000 was used to reach an average molecular weight ( $M_n$ ) of 22000. Water reacts with diisocyanates easily. Thus, it is necessary to dry all the raw materials and solvents, i.e. PEG, THF and toluene. This was accomplished through azeotropic distillation of dried toluene and poly(ethylene glycol) mixture in a laboratory glass reactor. For the preparation of polyurethane thickeners, initially the polyurethane prepolymers having isocyanate end groups were prepared. Here, polyethylene glycol was reacted with hexamethylenediisocyanate. In fact, the prepolymer forms the hydrophilic section for the final polymer. After successful preparation of prepolymers, substitution

of the hydrophobic section on the prepolymer was carried out. This was achieved by reacting mono-functional alcohol with diisocyanate hooked to the end of prepolymer.

#### 2.3.1. Synthesis procedure

A 500 mL, three-neck, round bottom flask was equipped with mechanical stirrer, nitrogen inlet, and thermometer and a Dean Stark water trap was used as the reactor. The PEG 6000 (about 50 g) was weighed into an argon-purged flask. Approximately, 350-400 mL of dry toluene was filtered through a sodium sulfate pad. PEG was dried by the azeotropic distillation from toluene in a reaction flask. Then, the solution was cooled down to  $50^\circ\text{C}$  and 0.2 g of dibutyltin dilaurate was added. The stoichiometric amount of diisocyanate was weighed into a 20 mL dry toluene and added to the reaction flask. The reaction was allowed to proceed for 60 min. The residual isocyanate groups were reacted with a slight excess (1.1 equiv excess) of cetyl alcohol, and diluted with toluene. After adding the alcohol, the reaction was allowed to proceed for another 120 min. The reactor content was precipitated in petroleum ether (four volumes of petroleum ether and one 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 on a filter paper and further precipitation into petroleum ether. The final product was produced by collecting on a sintered glass followed by drying in a vacuum oven.



**Scheme 1:** Synthesis of hydrophobically modified ethoxylated urethane (HEUR) polymer.

### 3. Results and discussion

#### 3.1. Characterization of HEURs

The FTIR spectrum of HEUR is presented in Figure 1. The spectrum of final product does not contain 2270  $\text{cm}^{-1}$  band related to NCO groups. Figure 2 shows the  $^1\text{H}$  NMR spectrum of synthesized HEUR in  $\text{CDCl}_3$ .

A HEUR thickener with a molecular weight of approximately 22000 was the most effective rheology modifier when compared to lower (10000) and higher (35000) molecular weight HEURs with the same

terminal hydrophobes and the same aqueous solution concentrations. As the molecular weight was increased from 22000 to 35000, a decrease in aqueous solution viscosity was observed. This was attributed to a decrease in the concentration of hydrophobic terminal groups with increasing molecular weight. When molecular weight of HEURs was decreased from 22000 to 10000, the aqueous solution viscosities decreased because of the predominance of intramolecular associations compared to intermolecular associations.

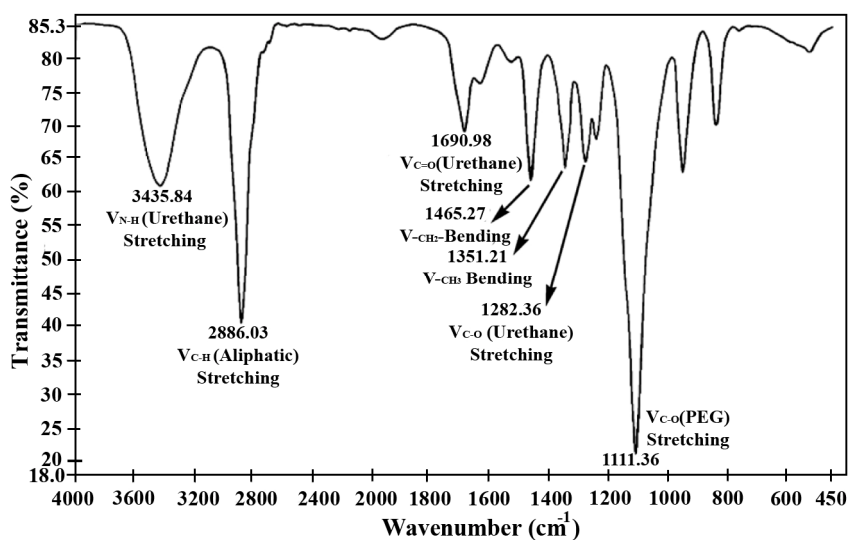


Figure 1: The FTIR spectrum of HEUR.

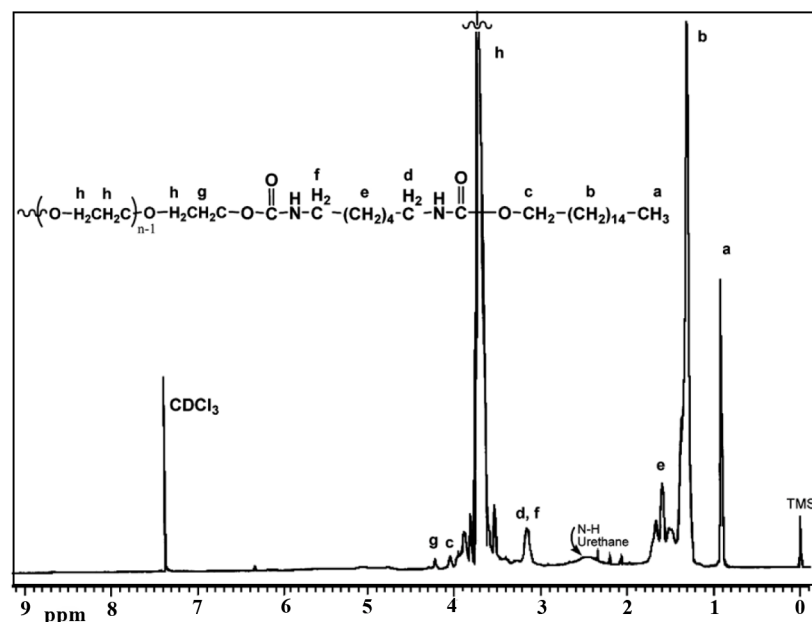


Figure 2:  $^1\text{H}$  NMR spectrum of synthesized HEUR in  $\text{CDCl}_3$ .

## 3.2. Rheological behavior

### 3.2.1. Steady shear viscosity in aqueous state

Figure 3 shows the variation of the steady shear viscosity versus shear rate and dashed lines represent thixotropy cycle for three different samples. The hysteresis loop test (like in Figure 3) gives an indication whether the sample is thixotropic or not.

In this figure, two aqueous samples with no surfactant addition show nearly Newtonian behaviors, where the change in viscosity versus the examined range of shear rate is negligible. Meanwhile, in the case of samples containing 1% wt. of surfactant, the viscosity becomes sensitive to shear rate and non-Newtonian behavior (shear thinning) can be observed. Similarly, this important effect of surfactant on the rheological behavior of HMHEC thickener in the waterborne paint [21], and HEUR thickener [22], have been reported by the other authors.

Figure 3 shows that for each sample, the viscosity curves obtain under decreasing shear rate nearly overlap the curves reported under increasing shear rate. Thus, the samples didn't show any considerable thixotropic or time-dependent behavior. Furthermore, the viscosity of these three aqueous samples containing HEUR thickener is clearly higher

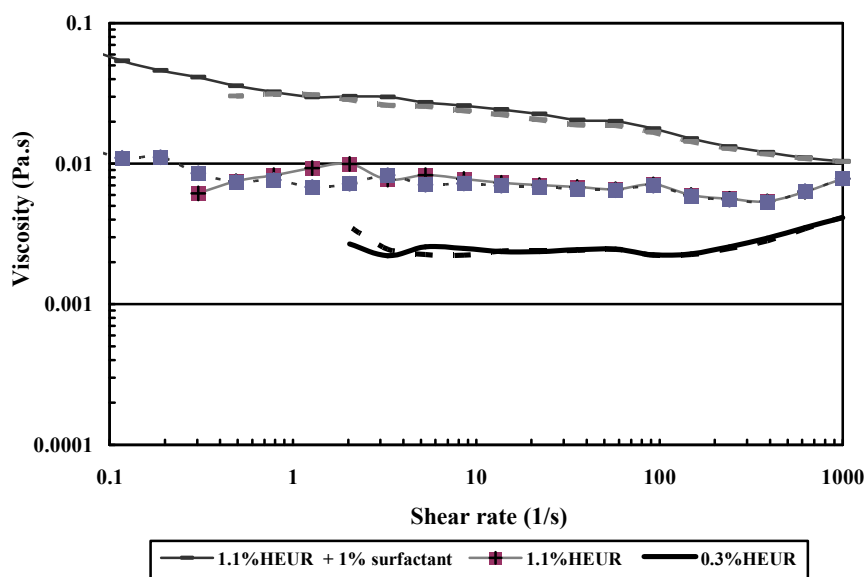
than that of pure water (0.001 Pa.s). This indicates the effect of thickener on the viscosity in the aqueous state.

### 3.2.2. Steady shear viscosity in the resinous dispersions

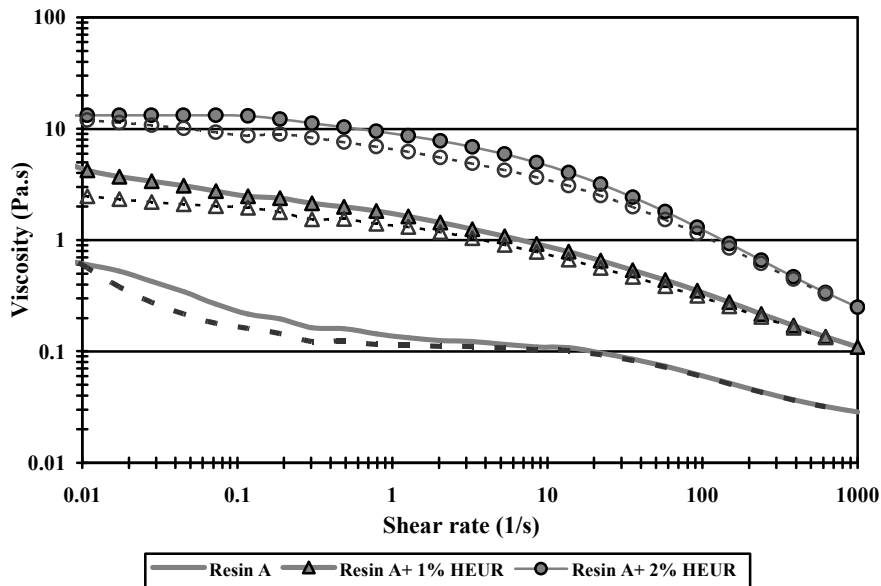
Figure 4 shows the variation of the steady shear viscosity versus shear rate and dashed lines represent thixotropy cycle for three different samples.

The pure resin and two other samples containing HEUR thickener show non-Newtonian behavior as shear thinning. Furthermore, the viscosity of two samples containing HEUR is much higher than that of pure resin. Clearly, adding just 1% wt. of thickener to the water-based resin, leads to an increase in viscosity by one degree of magnitude.

The non-Newtonian behavior of dispersion is characterized by a competition between viscous forces, Brownian motion of particles and colloidal interaction forces between the suspended particles, where colloidal forces become less significant at high shear rates. Figure 4 shows that the colloidal interaction forces between the thickener molecules and the resin particles and water are high enough to produce higher Newtonian viscosity ( $\eta_0$ ) in the low shear rate regims [23].



**Figure 3:** Variation of the steady shear viscosity versus shear rate for different aqueous samples containing HEUR, solid line: increasing shear rate, dashed line: decreasing shear rate (reversed).



**Figure 4:** Variation of the steady shear viscosity versus shear rate for different resinous samples, solid line: increasing shear rate; dashed line: decreasing shear rate (reversed).

Similar to the results of Figure 3 for the aqueous solution of the thickeners, Figure 4 shows that for resinous samples as well, there is not any considerable thixotropic or time-dependent behavior.

#### 4. Conclusions

Hydrophobically modified ethoxylated urethanes (HEURs) with broad molecular weight distributions were synthesized by the step-growth polymerization of PEG 6000 and a hexamethylene diisocyanate (HDI). A stoichiometric ratio of 2.1 mol of diisocyanate (HDI) to

1.6 mol of PEG 6000 was used to obtain an average molecular weight ( $M_n$ ) of 22000. It represented a very good thickening efficiency. The rheological properties of incorporated samples in different media proved the considerable thickening efficiency of the produced HEUR.

#### Acknowledgments

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