

Synthesis of Ethoxylated Urethane and Modification with Cetyl Alcohol as Thickener*

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ABSTRACT

A suitable reaction system, and proper conditions were designed to produce desirable polyurethane base thickener with a calculated number average molecular weight. Initially an ethoxylated urethane prepolymer was synthesized by reaction of a polyethylene glycol ($\bar{M}_n=6000$) and dicyclohexylmethane diisocyanate using the step growth polymerization technique. Modification was carried out by reaction of cetyl alcohol with the resulting prepolymer. The synthesis of ethoxylated urethane was investigated by using FTIR. Also ¹H NMR was used for showing substituted hydrophobe parts. It was found that, the measured number average molecular weight of synthesized hydrophobically modified ethoxylated urethane (HEUR) was in agreement with the calculated \bar{M}_n . The thickening efficiency of the modified ethoxylated urethane was compared with a similar unmodified urethane. It was concluded that, the efficiency of modified ethoxylated urethane is very high in comparison with the unmodified one, although the synthesis conditions were similar for both modified and unmodified urethanes.

Key Words: HEUR, ethoxylated urethane, thickener, synthesis, modification, associative polymers

INTRODUCTION

Over the past several years, associative polymers have attracted widespread interest both from a theoretical and experimental point of view [1]. These materials are used for controlling the rheological properties of water-based fluids, such as cosmetics, paints and coatings.

Associative polymers contain a small amount of functional groups, which associate into multiplets in solutions [2]. These materials are composed of both water-soluble and water insoluble components; the water insoluble components interact in solution, and can also adsorb onto latex particles to form a microstructure that improves the rheological properties of a latex paint [3].

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The most commonly associative thickeners are hydrophobically modified compounds like: ethoxylated urethane (HEUR), polyacrylamide, alkaline soluble emulsion (HASE) and hydroxyethyl cellulose [5].

The early experiments on HEUR polymers were published in the mid-1980s' by Glass and his coworkers [6-7]. The first classic study of model polymers was done by Jenkins [8-9], although much of his work appears in his Ph.D. thesis [8]. An interesting paper was followed by Annable et al. [10], who examined similar materials. Both groups examined a series of hydrophobic ethoxylated urethane polymers prepared by condensing PEG of \bar{M}_n 8000 with isophoron diisocyanate in presence of a linear alcohol that serves to end-cap the polymer.

HEUR thickeners are prepared with two range molecular weight distributions. In the step growth process, with stoichiometric ratios, the monomers are consumed early, but high molecular weights are not realized until high conversions are achieved. A wide variation in HEUR molecular weight can be obtained by varying the ratios of reactant monomers. To achieve water solubility, a PEG diol is used. The molar ratio of NCO/OH is more than 1, and hence a prepolymer is produced with isocyanate terminal groups. The synthesis is followed by the reaction of the terminal isocyanate groups with hydrophobic alcohols or amines. In this way the synthesized S-G HEUR has wide molecular weight distribution.

In another method, PEG is reacted with a large excess of diisocyanate to produce a PEG with terminal isocyanate functionality, and the reaction is followed with hydrophobic alcohols or amines. By this method, HEUR is synthesized with narrow molecular weight distribution known as uni-HEUR [4].

In this work, the HEUR thickener was produced with S-G HEUR method. The Carothers equation was implemented for designing and controlling the reaction, and estimating the number average molecular weight.

EXPERIMENTAL

Materials

PEG of molecular weight 6000 (Merck) and dicyclo-

hexylmethane diisocyanate (H_{12} MDI) were used as received. Dibutyltin dilurate was supplied from Fluka. THF solvent (Merck) was dried with sodium wire and then it was distilled. Toluene solvent (Merck) was in contact with calcium hydride during distillation. Both solvents were stored with molecular sieve 0.4 nm beads. Cetyl alcohol (1-hexadecanol) was warmed to 50 °C for 1 h before being used. Petroleum ether with low boiling point was supplied from Pars Chimie.

Instruments

Infrared spectra were recorded on a Bruker-IFS 48 Fourier transform infrared spectrophotometer. 1H NMR spectra were obtained on a Bruker DRX 500 Avance Series. Thickener efficiency was investigated by a Brookfield Model DV-I.

Molecular Weight Calculation

Generally, any polyurethane prepolymer is a copolymer with a $B(AB)_n$ schematic structure, where A and B are referred to as polyol and diisocyanate, respectively. With this structural form and considering the eqn (1), the number average molecular weight is predictable, e.g. for a $\bar{M}_n=15500$, the weights of PEG (\bar{M}_n 6000) and H_{12} MDI must be used as 43 and 3 in grams, respectively.

$$\bar{X}_n = \frac{1+r}{1-r} \quad (1)$$

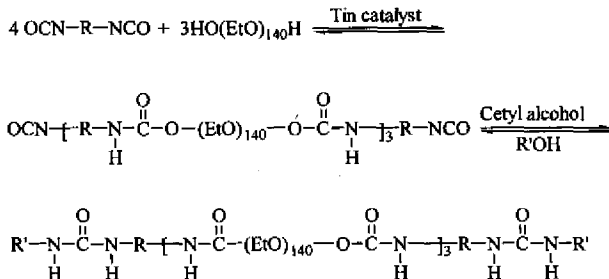
where, \bar{X}_n is the number average degree of polymerization and r is the molar ratio of OH groups to NCO groups.

For any molecular weight, and considering \bar{M}_w of polyol and diisocyanate, the amount of n is obtained. In fact the number n is the number average degree of polymerization. Simply, with determining n , the r is calculated via eqn (1).

Synthesis

The following synthetic procedure was used. The polyol (43 g) was weighed into a four-neck 500-mL round bottom flask. The flask was equipped with a magnetic stirrer, a dried pure nitrogen gas reflux column, and Dean Stark water trap. Nitrogen gas was dried and purified by passing through silica gel

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Scheme 1. Reaction scheme for synthesis of HEUR thickener.

column and solution of pyrogallol trap used for oxygen absorption. Approximately 250 mL of dry toluene was added to the flask. The solution was heated and refluxed, and three 40 mL volume Dean Stark water traps of toluene were removed. Then, the solution was cooled to 45 °C. The prepared solution of 0.15 g dibutyltin dilurate in THF and 3 g H₁₂MDI in dry toluene were added to the reaction flask. The reaction was continued to obtain a theoretical value of NCO content based on the mentioned NCO/OH ratio in the prepolymer. For this purpose, NCO content was determined using ASTM standard test method [11].

The residual isocyanate groups were reacted with a slight excess (1.2 equivalent excess) of cetyl alcohol. After the mono-functional alcohol addition, the reaction was allowed to proceed for 2 h (Scheme 1).

The HEUR thickener/toluene solution was precipitated in petroleum ether (3 volumes of petroleum ether to 1 volume of thickener solution), collected on a sintered glass funnel, and dried in a vacuum oven. Purification of the thickener was performed by dissolution in warm acetone, filtrating on a filter paper and its precipitation into petroleum ether. Final product was produced by collecting on a sintered glass followed by drying in a vacuum oven.

RESULTS AND DISCUSSION

PEG is a hygroscopic material and as a consequence removing water from it would be a very difficult task.

Also with THF, the same problem exists as well. An unwanted damaging factor is the reaction of the isocyanate with water. If the raw materials are dried completely, and conditions of the reaction system were chosen properly, the prepolymer is produced successfully.

The FTIR spectrum of the prepolymer product is presented in Figure 1. The presence of NCO groups in the structure of the prepolymer is observed at 2270 cm⁻¹. Also, the spectrum of prepolymer contains polyurethane characteristic bands in the regions of 1720 cm⁻¹ (carbonyl group in urethane band) and 3330 cm⁻¹ (NH stretching). The completion of reaction is shown in Figure 2. The spectrum of final product does not contain 2270 cm⁻¹ band related to unreacted NCO groups.

Figure 3 shows the ¹H NMR spectrum of synthesized HEUR in deuterated acetone. Appeared

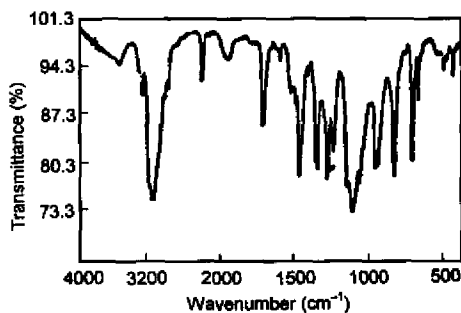


Figure 1. FTIR Spectrum of the synthesized prepolymer.

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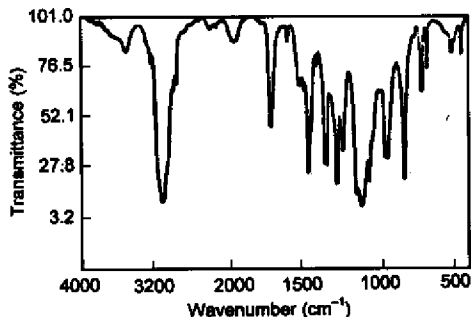


Figure 2. FTIR Spectrum of the synthesized HEUR.

peak in 1.3 ppm is an evidence for reaction between propolymer and cetyl alcohol. Other peaks in 2.05 and 3.6 ppm can be attributed to solvent and oxy-ethylene protons, respectively.

Molecular weights and molecular weight distribution were determined by a Waters Model 150 C gel permeation chromatography (GPC), with tetrahydrofuran as the mobile phase, a flow rate 1.5 mL/min, a column temperature of 30 °C, two styragel columns (HR3, HR4), run time 20 min and 500 μ L injection volume. A calibration curve was prepared with polystyrene standards. The molar ratio was chosen as obtaining a prepolymer with number average molecular weight 15000 via calculation. The results of GPC measurement were $\bar{M}_n=16500$ and PDI=1.4.

Experimental data were in agreement with predicted \bar{M}_n . Intrinsic viscosity was determined at 25 °C in double distilled deionized water (DDI), with the result of 0.19.

The thickener efficiency of the produced HEUR is shown in Figure 4. The viscosity of various solutions with different concentrations of HEUR in 100 mL DD water was measured by digital Brookfield viscometer. The data show association behaviour.

Unmodified ethoxylated polyurethane was compared with the HEUR (Figure 5). The prepolymer synthesis conditions were the same, but the reaction of Cetyl alcohol was omitted for the unmodified one. The Y-axis is in logarithmic scale. It is found that the role of hydrophobic group in thickener efficiency is very important, and its effect is of very extreme type.

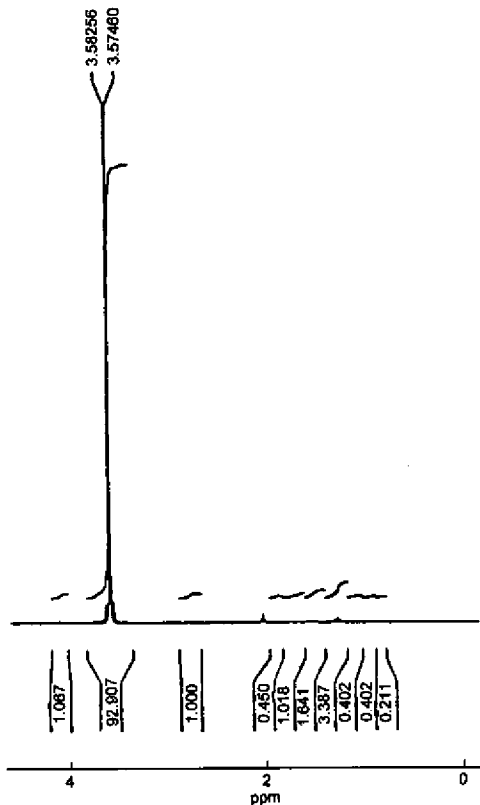


Figure 3. ^1H NMR Spectrum of the synthesized HEUR.

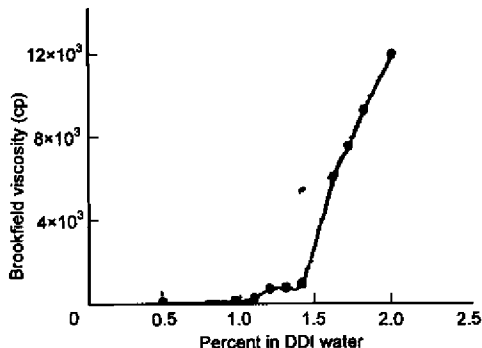


Figure 4. Thickening efficiency of the synthesized HEUR.

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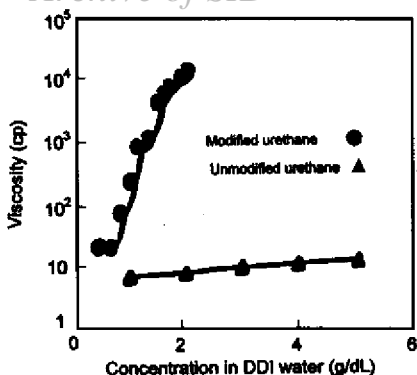


Figure 5. Effect of hydrophobic modification on thickening efficiency of an ethoxylated polyurethane.

CONCLUSION

In this work, we could run a suitable reaction system with proper conditions for synthesizing of HEUR thickener models. In this way, it is possible to make HEUR rheology modifier with a predetermined number average molecular weight. A model HEUR was synthesized with this system. It showed very good thickening efficiency.

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