

# The Effect of Molecular Weight on the Behaviour of Step-growth Hydrophobically Modified Ethoxylated Urethane (S-G HEUR) End-capped with Dodecyl Alcohol

Mohammad Barmar<sup>1\*</sup>, Mehdi Barikani<sup>1</sup>, and Babak Kaffashi<sup>2</sup>

(1) Department of Polyurethane, Fibers and Advanced Polymeric Materials, Iran Polymer and Petrochemical Institute, P.O. Box: 14965/115, Tehran, I.R. Iran

(2) Department of Chemical Engineering, Faculty of Engineering, University of Tehran  
Tehran, I.R. Iran

Received 17 November 2003; accepted 4 January 2004

## ABSTRACT

Two model thickeners of HEUR polymers were synthesized by step-growth polymerization of poly (ethylene oxide) (PEO) with dicyclohexylmethane diisocyanate ( $H_{12}$ MDI). First, the prepolymers were produced with different molecular weights by changing the molar ratios of the initial reactants. Then, S-G HEUR model thickeners were produced via reacting of the prepared isocyanate terminated prepolymers with mono-functional dodecyl alcohol. In this way, two polyurethane based model thickeners were obtained with different molecular weights arising from various hydrophilic lengths. The response of these S-G HEUR thickeners in aqueous solutions to both steady shear and oscillatory shear was determined. Considerable increases in thickening efficiency as decreasing molecular weight of model thickeners were observed. Also dynamic measurements verified the results obtained from the steady shear measurements about the effect of molecular weight on the viscoelastic properties of aqueous S-G HEUR solutions.

### Key Words:

S-G HEUR; hydrophile; hydrophobe; association; steady shear viscosity; oscillatory.

## INTRODUCTION

Hydrophobically modified ethoxylated urethanes (HEUR) are a well-known class of associative thickeners. These materials are divided in two main groups of Uni-HEUR and S-G HEUR. Uni-HEUR or HEURs with narrow molecular weights are

synthesized by direct addition of a monoisocyanate to PEO or the addition of a large excess of diisocyanate to PEO and followed by the addition of an alkyl amine to the terminal isocyanate groups. But S-G HEURs or HEUR thickeners with a distribution

(\*)To whom correspondence should be addressed.  
E-mail: M.Barmar@ippi.ac.ir

of molecular weights are produced by a step growth process. These materials are prepared by reacting a hydroxy-end-capped PEO with a diisocyanate and an aliphatic alcohol [1,2].

Over the past few years, several major studies of rheology of HEUR polymers in aqueous solution have been reported [3-8]. The research has been carried out in several areas, e.g. modelling of their viscoelastic behaviour, interaction of HEUR with ionic and non-ionic surfactants in aqueous solution [9-12].

The relationship between molecular weight distribution and properties of HEURs was studied by May et al. [13]. They synthesized two series of S-G and Uni-HEURs with approximately similar molecular weights of 20,000. It was concluded that, twice the concentration of broad molecular weight distribution HEUR was required to achieve viscosities comparable to the narrow molecular weight distribution HEUR. Kaczmarek and Glass investigated the influence of the ethylene glycol spacer length between terminal hydrophobic groups of a Uni-HEUR series with various hydrophobically modifications and molecular weight ranging from 10,000-24,000 [14]. Also the properties of aqueous solution of model HEURs with molecular weight ranging from 10,000 to 35,000 have been studied as a function of concentration, molecular weight, temperature, and hydrophobic end-cap, but the details of synthesis procedure, and raw materials' specification such as used PEO and diisocyanate, were not reported [15]. However, the solution properties of S-G HEUR models with molecular weight less than 10,000 have not been reported.

In this research work, the viscoelastic properties of HEUR associative thickeners as a function of molecular weight below 8,000 were studied on two S-G HEUR thickener models.

The models were synthesized via preparation of prepolymers by the step-growth polymerization of poly (ethylene oxide) ( $\bar{M}_n = 6,000$ ) with a proper amount of dicyclohexylmethane diisocyanate ( $H_{12}MDI$ ), with average molecular weight in the range of 6,000-8,000. Then, the synthesized prepolymers were fully end-capped with excess dodecyl alcohol. Both steady shear and oscillatory flow measurements were conducted to obtain the steady shear viscosity and dynamic viscoelastic properties of the S-G HEUR models.

## EXPERIMENTAL

### Materials and Methods

Poly (ethylene oxide) of molecular weight 6,000, dodecyl alcohol ( $C_{12}H_{25}OH$ ), toluene and tetrahydrofuran (THF) were supplied by Merck. Dicyclohexylmethane diisocyanate ( $H_{12}MDI$ ) with trade name of Desmodur W was used as received. The details of the synthesis procedure were described in our previous work [16].

The rheological properties of HEUR models aqueous solutions were measured on a Paar Physica rheometer model UDS 200, using a cone-and-plate fixture with a 75 mm diameter,  $2^\circ$  angle cone. The distance of gap was 0.05 mm. The samples were protected from water evaporation by using a solvent trap during the measurements. All rheology measurements have been performed at 293°K.

A standard procedure was used for all samples, to ensure that the HEUR model solutions are subjected to the same shear history. For the steady shear experiments, an equilibration time of 10 s was given at each shear rate to allow the system to reach steady state.

Dynamic viscoelastic properties of synthesized model solutions were measured in the oscillatory shear mode. The used frequency range was 0.06-314 Hz. The shear strain was 20%, which was chosen so that the measurement was carried out in the linear viscoelastic region. From strain sweep measurements ( $f = 1$  Hz,  $\gamma = 0.1-300\%$ ), the linear viscoelastic region was determined to be below 200% strain. In this region storage and the loss modulus are independent of the applied stress or strain.

## RESULTS AND DISCUSSION

The molar ratio of initial reactants, number average molecular weights and polydispersity indexes (PDI) of synthesized S-G HEUR models are given in Table 1. The molar ratios of OH/NCO were adjusted by weigh-

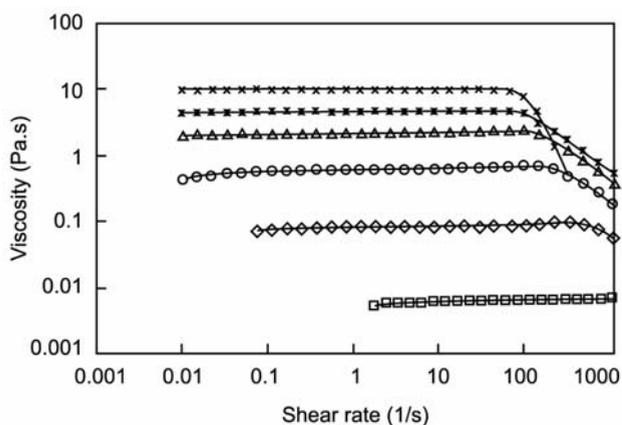
**Table 1.** Molecular weights of S-G HEUR models.

Thickener models	OH/NCO	$\bar{M}_n$	PDI
6-Dod	0.478	6204	1.9
15-Dod	0.703	7888	2.1

ing the proper amounts of the reactants. The data of molecular weights were obtained by gel permeation chromatography (GPC), using a Gyukotek model pump, and a "ERC 7512 (EKMA)" refractometer. Chloroform was the mobile phase with a flow rate of 1 mL/min. A Phenogel M 5  $\mu\text{m}$  column with 60 cm length was used. Polyethylene glycol (Polymer Labs) was used as universal calibration standards.

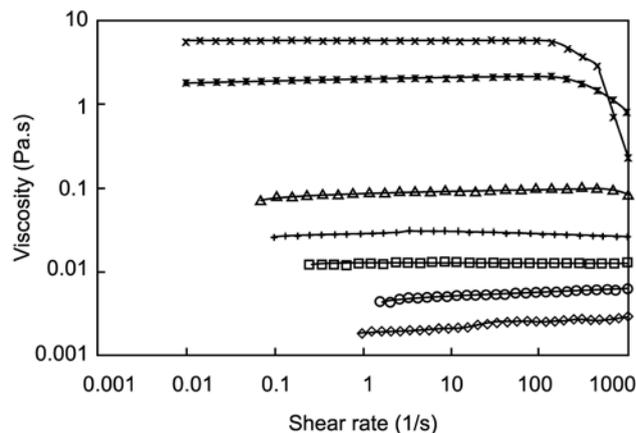
The steady shear viscosity profiles as a function of shear rate for aqueous solutions with various concentrations of S-G HEUR models 6-Dod and 15-Dod are illustrated in Figures 1 and 2, respectively.

The aqueous solutions are divided into two groups, medium and low viscosity due to differing of weight percent of thickeners. All of the samples show Newtonian behaviour, or shear rate independent viscosity at low shear rates. There is another region at higher shear rates, shear thinning for samples with higher viscosity. In this section, the viscosity rapidly decreases with increasing shear rate. The shear thickening is another behaviour of S-G HEUR thickener solutions with medium viscosity (6-Dod 1.5, 2, 2.5, 3, 4%, and 15-Dod 5, 7%). Several theoretical models have been proposed to describe the shear thickening behaviour in HEUR solutions. They fall into three main categories as shear-induced cross-linking, shear-induced non-Gaussian chain stretching and network reorganization [17]. The degree of shear thickening was reduced



(—x—) 4% Conc., (—x—) 3% Conc., (—▲—) 2.5% Conc., (—□—) 2% Conc., (—◇—) 1.5% Conc., (—□—) 1% Conc.

**Figure 1.** The steady shear viscosity of S-G HEUR models at various concentrations as a function of shear rate for 6-Dod thickener model.



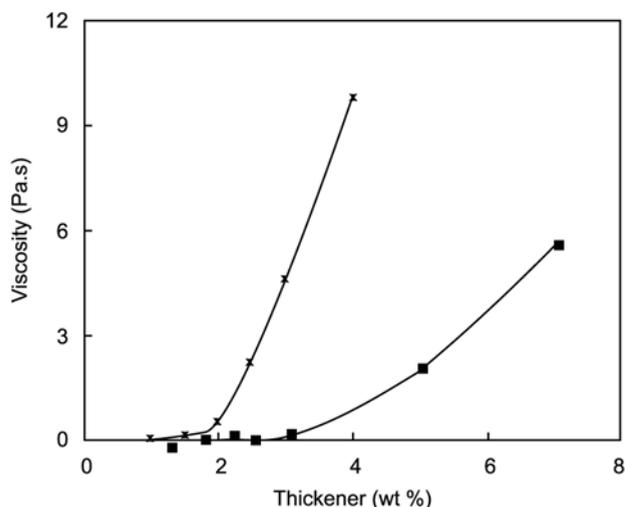
(—x—) 7% Conc., (—x—) 5% Conc., (—▲—) 3% Conc., (—+—) 2.5% Conc., (—□—) 2% Conc., (—□—) 1.5% Conc., (—◇—) 1% Conc.

**Figure 2.** The steady shear viscosity of S-G HEUR models at various concentrations as a function of shear rate for 15-Dod thickener model.

with increasing viscosity levels. For example, the shear thickening in the sample of 6-Dod with 4% concentration is too weak. In the samples with higher viscosity, the movement of the chains is very low, and hence it is not possible for any shear induced or network reorganization to take place.

By comparison between 4% solution of 6-Dod (Figure 1) and 7% solution of 15-Dod (Figure 2), it can be seen that, the lower concentration of 6-Dod (4%) solution gives higher viscosity. It seems that 6-Dod sample with lower molecular weight and shorter hydrophilic sizes compared with 15-Dod, shows stronger association network that improves the viscosity build-up and also viscosity profile sensitivity to shear rate (all of the samples have constant hydrophobic section size), i.e. shear thinning is started at lower shear rate for 6-Dod 4% solution.

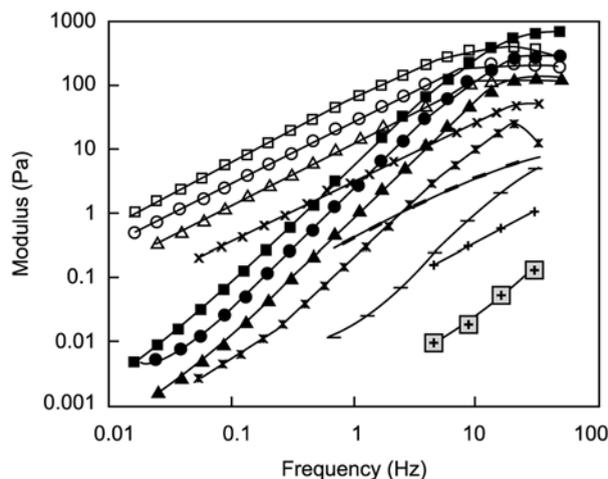
The thickening efficiency is evaluated from the zero shear viscosity [13-15]. The data were extracted from the Newtonian plateaus, and are compared in Figure 3. There are two important parameters in this typical curve, critical association concentration and slope of increasing viscosity with concentration. The critical association concentration is the concentration at which a macroscopic viscosity build-up is occurred. The value of this parameter for 6-Dod model is half of 15-Dod model. As already mentioned, with increasing S-G HEUR model molecular weight, the relative sizes of



(—x—) 6-Dod; (—■—) 15-Dod.

**Figure 3.** The comparison of zero steady shear viscosity of S-G HEUR models as a function of concentration ( $T = 20^\circ\text{C}$ ).

the hydrophobic length to the hydrophilic length decreases considering the constant terminal alkyl size. Therefore, the extent of association is lower, and higher weight percent of the thickener models are required for viscosity build-up to occur. Also, the rate or slope of increasing zero viscosity versus concentration curve for 6-Dod is higher than 15-Dod. It seems the phase separation rate in aqueous solution, related to the strength and uniformity of the network, is better for lower molecular weight S-G HEUR models with constant hydrophobic size. It was observed that the aqueous solutions of S-G HEUR models show linear viscoelastic behaviour for strain below 250%. Hence, the frequency sweeps were carried out in the range of 0.01–50 Hz at 200% shear strain. The storage and loss modulus as a function of the frequency for 6-Dod sample is plotted in Figure 4 for various concentrations. The same behaviour was shown for the 15-Dod model. The S-G HEUR model solutions with weak viscosity build-up did not show storage and loss modulus crossover. Despite the differences in concentration, the oscillatory behaviour was similar for all of the samples. The storage modulus ( $G'$ ) asymptotes to a constant value at high frequency. This plateau implies that the solution behaves as an elastic body in this region. The infinite storage modulus increases with increasing concentration. At low frequencies the solution behaves like a Newtonian fluid, as shown in steady shear measurements. Some authors have reported the storage and loss



(—■—)  $G'$  4%; (—□—)  $G''$  4%; (—●—)  $G'$  3%;  $G''$  3%; (—○—)  $G'$  2.5%; (—▲—)  $G'$  2.5%; (—△—)  $G''$  2%; (—x—)  $G'$  2%; (—x—)  $G''$  1.5%; (—x—)  $G'$  1.5%; (—□—)  $G'$  1.0%; (—+—)  $G'$  1%.

**Figure 4.** The storage and loss modulus ( $G'$ ,  $G''$ ) versus frequency for 6-Dod model at  $\dot{\gamma} = 0.2$  and  $T = 20^\circ\text{C}$  for different concentrations.

modulus of HEUR associative thickeners generally follow the single-relaxation Maxwell model [6, 18–20]. The relaxation time  $\lambda$  is an important parameter in investigation of viscoelastic behaviour of polymer solutions. In the present study, considering Maxwell viscoelastic model, the relaxation times were obtained from the intersection of the  $G'$  and  $G''$  curves.

The number of elastically effective chains ( $\nu$ ) is the other important parameters for investigation of association system. The simple theory of rubber elasticity was extended to transient networks by Green and Tobolsky [21]. They started from a rubber like system but assumed that the cross-links in the network are weaker connections than covalence bonds. Then, they predicted the magnitude of the plateau modulus  $G_\infty$  is related to the number of elastically effective chains per unit volume ( $V$ ):

$$G_\infty = g\vartheta RT \quad (1)$$

where,  $g$  is a correction factor which is approximately equal to unity for HEUR systems [12],  $\vartheta$  is the number of elastically effective chains per unit volume ( $\text{mol. m}^{-3}$ ),  $R$  is the gas constant and  $T$  is the temperature in Kelvin.

All of the viscoelastic parameters, i.e. relaxation

**Table 2.** Viscoelastic parameters of S-G HEUR models.

Viscoelastic parameters	6-Dod Concentration			15-Dod Concentration	
	2.5%	3%	4%	5%	7%
	$\lambda$ [S]	0.006421	0.009367	0.010687	0.004683
G' [Pa]	126	291	679	129	423
$\nu$ [1/mol]	$3.11904 \times 10^{22}$	$7.2035 \times 10^{22}$	$1.68082 \times 10^{23}$	$3.19331 \times 10^{22}$	$1.04711 \times 10^{23}$

times, infinite storage modulus and the number of elastically effective chains per unit volume of S-G HEUR models as a function of concentration are shown in Table 2. The relaxation times of S-G HEUR model solutions increase monotonically with concentration, but the rate of increasing in the 6-Dod model is more than 15-Dod model. Also, the number of effective chains of S-G HEUR models increases with increasing concentration as well. These results show, we have stronger association network in 6-Dod model, and in both models with increasing concentration of thickener, resulted more effectively association network, that presents higher efficient thickening system.

## CONCLUSION

Two S-G HEUR models were synthesized by a step growth polymerization with varying hydrophilic sizes with a constant hydrophobe, which contributed with dodecyl alcohol. The shear steady state viscosity measurements demonstrated on S-G HEUR models show two regions, Newtonian and shear thinning. Also, some samples show another region, shear thickening. The onset and the magnitude of shear thickening decreases as concentration increases. It was observed the thickening efficiency decreases with increasing the length of hydrophilic section, from 6-Dod to 15-Dod.

In oscillatory shear experiment, a good agreement was found between the data and single-relaxation Maxwell model. Then the relaxation time was calculated and compared. Also, the simple theory of rubber elasticity was applied to calculate the number of elastically effective chains per unit volume. The obtained data showed the similar phenomena with steady shear viscosity measurement. It was concluded from both of shear steady and oscillatory shear investigation, the

association strength could be varied by changing the length of the hydrophilic section. With the lower length of the hydrophilic section, the stronger association strength is achieved for the constant length of the hydrophobic section.

## REFERENCES

1. Yekta A., Xu B., Duhamel J., Adiwidjaja H., and Winnik M.A., Fluorescence studies of associating polymers in water: Determination of the chain end aggregation number and a model for the association process, *Macromolecules*, **28**, 956-966 (1995).
2. Glass J.E., Ed., *Hydrophilic polymers: Performance with environmental acceptance*, Adv. in Chem. Ser. 248, Chap. 10, ACS, Washington DC (1996).
3. Winnik M.A. and Yekta A., Associative polymers in aqueous solution, *Cur. Opin. in Col. & Inter. Sci.*, **2**, 424-436 (1997).
4. Lundberg D.J. and Glass J.E., Viscoelastic behaviour among HEUR thickeners, *J. Rheol.*, **35**, 1255-1274 (1991).
5. Tirtaatmadja V. Tam K.C., and Jenkins R.D., Superposition of oscillations on steady shear flow as a technique for investigation of the structure of associative polymers, *Macromolecules*, **30**, 1426-1433 (1997).
6. Tam K.C., Jenkins R.D., Winnik M.A., and Basset D.R., A structural model of hydrophobically modified urethane-ethoxylate (HEUR) associative polymers in shear flows, *Macromolecules*, **31**, 4149-4159 (1998).
7. Vorobyova O., Lau W., and Winnik M.A., Aggregation number determination in aqueous solution of a hydrophobically modified poly (ethylene oxide) by fluorescence probe techniques, *Langmuir*, **17**, 1357-1366 (2001).
8. Dai S., Tam K.C., and Jenkins R.D., Microstructure of dilute telechelic associative polymer in sodium dodecyl sulfate solutions, *Macromolecules*, **34**, 4673-4675 (2001).

9. Kaczmariski J.P., Targ M.R., Ma Z., and Glass J.E., Surfactant and salinity influences on associative thickener aqueous solution rheology, *Col. Sur. A*, **147**, 39-53 (1999).
10. Dai S., Tam K.C., and Jenkins R.D., Binding characteristics of hydrophobic ethoxylated urethane (HEUR) and an anionic surfactant: Microcalorimetry and laser light scattering studies, *J. Phys. Chem. B*, **105**, 10189-10196 (2001).
11. Alami E., Almgren M., and Brown W., Interaction of hydrophobically end-capped poly (ethylene oxide) with nonionic surfactants in aqueous solution. Fluorescence and light scattering studies, *Macromolecules*, **29**, 5026-5035 (1996).
12. Hulden M., Hydrophobically modified urethane-ethoxylate (HEUR) associative thickeners. 1. Rheology of aqueous solutions and interactions with surfactants, *Col. Sur. A*, **82**, 263-277 (1994).
13. May R., Kaczmariski J.P., and Glass J.E., Influence of molecular weight distributions on HEUR aqueous solution rheology, *Macromolecules*, **29**, 4745-4753 (1996).
14. Kaczmariski J.P. and Glass J.E., Synthesis and solution properties of hydrophobically-modified ethoxylated urethane with variable oxyethylene spacer lengths, *Macromolecules*, **26**, 5149-5156 (1993).
15. Annable T., Buscall R., Ettelaie R., and Whittlestone D., The rheology of solution of associating polymers: comparison of experimental behavior with transient network theory, *J. Rheol.*, **37**, 695-726 (1993).
16. Barmar M., Barikani M., and Kaffashi B., Synthesis of ethoxylated urethane and modification with cetyl alcohol as thickener, *Iran. Polym. J.*, **10**, 331-335 (2001).
17. Ma S.X. and Cooper S.L., Shear thickening in aqueous solution of hydrocarbon end-capped poly (ethylene oxide), *Macromolecules*, **34**, 3294-3301 (2001).
18. Annable T., Buscall R., and Ettelaie R., Network formation and its consequences for the physical behavior of associating polymers in solution, *Col. Sur. A*, **112**, 97-116 (1996).
19. Xu B., Yekta A., Li L., Masoumi Z., and Winnik M. A., The functionality of associative polymer networks: The association behaviour of hydrophobically modified urethane-ethoxylate (HEUR) associative polymers in aqueous solution. *Col. Sur. A*, **112**, 239-250 (1996).
20. Pham Q.T. and Russel W.B., Micellar solution of associative triblock copolymers: the relationship between structure and rheology, *Macromolecules*, **32**, 5139-5146 (1999).
21. Green M.S. and Tobolsky A.V., A new approach to the theory of relaxing polymeric media, *J. Chem. Phys.*, **14**, 80-92 (1946).