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Influence of Molecular Weight Distributions on HEUR Aqueous Solution Rheology[1]

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ABSTRACT: Two series of hydrophobe-modified, ethoxylated urethane (HEUR) polymers were synthesized. The first series was prepared by the step-growth (S-G) polymerization of poly(oxyethylene) (POE) of $M_n = 6000$, with a slight excess of different aliphatic diisocyanates in a 4.2 to 3.2 mole ratio to produce a S-G polymer with M_n of ∼20 000. The terminal isocyanate groups were reacted with alkylamines of different hydrocarbon chain lengths. The second series was produced by reacting POE of $M_n = 20\,000$ with a large excess of the diisocyanate to produce POE with terminal isocyanate functionality, followed by reaction with alkylamines. The molecular weight distribution of the second series was narrow compared to the first series, prepared by S-G polymerization. The hydrocarbon chain length of the alkylamine, the coupling diisocyanate, and the molecular weight distributions were systematically varied by the proper choice of synthetic conditions. The changes in structures were correlated with the rheological behavior of aqueous HEUR solutions. Their aqueous solution behaviors also were evaluated in the presence of anionic and nonionic surfactants. HEUR thickeners prepared with bis(4-isocyanatocyclohexyl)methane (H_{12}MDI) were more effective in building viscosity than HEURs prepared from hexamethylene diisocyanate (HDI). In general, HEURs, with a narrow molecular weight distribution, gave higher aqueous solution viscosities than their corresponding broad molecular weight distribution counterparts at equal concentrations. Approximately twice the concentration of the broad molecular weight distribution HEUR with terminal $C_{12}H_{25}$−H_{12}MDI hydrophobes was required to achieve comparable viscosity with the narrow molecular weight distribution HEUR. Despite the differences in concentration, the storage and loss moduli responses were similar. Solutions with small terminal alkyl groups were predominantly viscous in their viscoelastic response. The size of the "effective" terminal alkyl groups dominated aqueous solution rheological responses of both narrow and broad molecular weight distribution HEURs.

Introduction

The focus of most hydrophobe-modified, ethoxylated urethane (HEUR) aqueous solution studies[4−9] has been to develop rheological models for HEUR flow behavior[4−6] and, in spectroscopic studies, to evaluate aggregation phenomenon.[7−9] In only one of these studies in which experimental materials were used was attention given to their synthesis and characterization, leading to questions about the structures of the HEUR thickeners. A structure−property relationship study should begin with what is defined in this article as a "uni-HEUR". There have been only a few efforts[7d,10−12] in this direction. Most publications reference a patent with multiple synthetic procedures. In one of these studies, the samples were prepared at high temperature in the presence of atmospheric oxygen, as a urethane thermoplastic would be prepared. Not surprisingly, the molecular weights were well below those expected for the reactant equivalences used. In the most recent study,[13] one of these samples, analyzed by ^{1}H NMR with a pulsed delay time of 20 s, had only 0.9 of the 2.0 expected terminal hydrophobes. The structure and participation of the diisocyanate, used to couple poly(oxyethylene) (POE) to the linear alkyl alcohol or alkylamine also has been generally neglected.

In our first study of model HEURs,[14] the influence of the terminal hydrophobe size was examined in a series employing an oxyethylene spacer length of ca. 600 units, the terminal units were isophorone urethane linked nonylphenols. In our second series,[15] the spacer length was varied and terminal $C_{18}H_{37}$−urethane units were studied in addition to isophorone urethane linked nonylphenol (NP) terminal units. The NP terminal model HEURs of the first study were generally higher in viscosity and more elastic in their solution response. This difference is likely due to the formation of hydrophobe groupings through allophanate formation with the higher reaction temperatures used in the initial studies. In the latter study,[15] the influence of the oxyethylene spacer length was examined and the optimum spacing, to balance intrahydrophobic associations with total hydrophobe concentration, was observed to be ∼500 oxyethylene units. These narrow molecular weight HEURs are referred to as uni-HEURs.[16]

An examination of the literature indicated that the molecular weight distributions were not considered when the rheology of HEUR thickener solutions was modeled. In these studies,[4,5] the model HEURs were reported to be synthesized by step-growth (S-G) polymerizations, known to produce broad molecular weight distributions, but the HEUR rheology was modeled as if the HEURs possessed narrow molecular weight distributions. In our S-G HEUR studies, the molecular weight distributions were broad.[17] The HEURs were prepared by reacting a slight excess of diisocyanate with POE of $M_n = 8000$, followed by reaction of the terminal isocyanate groups with alkylamines of increasing hydrocarbon chain lengths. When the alkyl group of the amine was kept constant and the coupling diisocyanate was changed, a change in aqueous solution viscosities were observed. The coupling diisocyanate influenced the "effective" size of the terminal alkyl group and, therefore, should be specified when the aqueous solution behavior of HEUR thickeners[17] is evaluated. The terminal hydrophobe sizes were not varied sufficiently in our second telechelic series, where the reaction conditions were similar to those used in the S-G syntheses, to allow an evaluation of molecular weight distribution effects on HEUR solution behavior. That is the objective of this study.

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Table 1. Molecular Weights of the Starting Poly(oxyethylenes)

POE MW	designation	M_n OH no.	M_n SEC	M_w SEC	PDI
6 000	$HO(EtO)_{140}H$	6 100	7 000	7 600	1.08
20 000	$HO(EtO)_{470}H$	20 600	23 100	28 400	1.23

The effect of molecular weight distribution on solution and melt rheology of polymers has been studied.[18-20] The rheology of solution polymers is dictated by the weight average molecular weight, as the higher molecular weight polymers were more capable of entanglements. If a linear polymer possessed a broad molecular weight distribution, the higher molecular weight fractions influenced the viscosity to the greatest extent. HEUR thickeners are unique because their molecular weights are generally too low to affect chain entanglements; the surfactant modification is responsible for the viscosity increase. As the molecular weight of the HEUR was lowered from 35 000 to ca. 20 000, a greater concentration of hydrophobe is present, and the lower molecular weight fractions are primarily responsible for the viscosity response.

The objective of this study is to demonstrate the influences of synthetic variables on the rheological behavior of HEUR associative thickeners. The hydrocarbon chain length of the alkylamine, the coupling diisocyanate, and the molecular weight distributions are systematically varied by the proper choice of synthetic conditions. The changes in structures are correlated with the aqueous solution behavior of HEUR thickeners.

Experimental Section

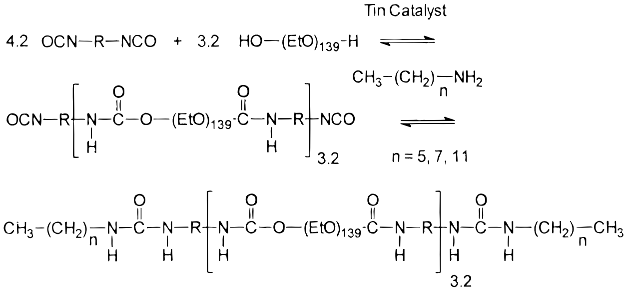
Starting Materials. POEs of molecular weights 6000 and 20 000 (Fluka) were used as received. Hexamethylene diisocyanate (HDI, 98%), hexylamine (99%), octylamine (97%), dodecylamine (98%), dibutyltin dilaurate (98%), *N,N′*-dimethylformamide (DMF, 99%), and 8-anilino-1-naphthalenesulfonic acid (ANS, 97%) were used as received from Aldrich. Bis(4-isocyanatocyclohexyl)methane ($H_{12}MDI$) was purified by vacuum distillation and stored under argon. Toluene (ACS Reagent Grade) was dried with either magnesium sulfate or sodium sulfate before use. Acetone (Baxter, 99.5%) and petroleum ether (Burdick and Jackson, purified) were used as received. Water was distilled and deionized (DDI water) through a Milli-Pore Q ion exchange and filtration system. The surfactants, sodium dodecyl sulfate (SDS, Aldrich, 98%) and an ethoxylated nonyl phenol surfactant, $NP(EtO)_{10}H$, (Tergitol, Union Carbide), were used without further purification.

Characterization of Starting Materials. Molecular weights of the parent POEs were determined by end group analysis, according to the pyromellitic dianhydride/imidazole method for determining hydroxyl numbers[21] and by size exclusion chromatography (SEC, Table 1).

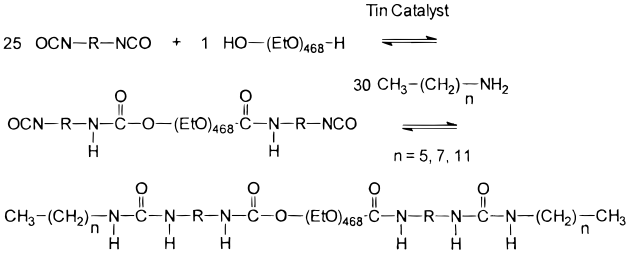
Synthesis of HEUR Thickeners with Broad Molecular Weight Distributions. The HEURs with broad molecular weight distributions were produced by the step-growth polymerization of $HO(EtO)_{140}H$ and a diisocyanate (HDI or H_{12}-MDI), according to Scheme 1. A stoichiometric ratio of 4.2 mol of diisocyanate to 3.2 mol of $HO(EtO)_{140}H$ was used to obtain a target number average molecular weight (M_n) of ~20 000.

The following synthetic procedure was used. A 500 mL, three-neck, round bottom flask was equipped with a mechanical stirrer, argon inlet, thermometer, and Dean Stark water trap. The $HO(EtO)_{140}H$ (about 50 g) was weighed into an argon-purged flask. Approximately 350−400 mL of dry toluene was filtered through a magnesium sulfate or sodium sulfate pad. The solution was heated to reflux, and four Dean Stark water traps of toluene (roughly 125 mL) were removed. After the trap filled a fifth time, the solution was cooled to 45 °C; and 0.2 g of dibutyltin dilaurate were added. The stoichiometric amount of diisocyanate was weighed into a 20 mL scintillation vial, diluted with dry toluene, and added to the reaction flask. The reaction was allowed to proceed for 60 min when HDI was used and for 60−240 min when $H_{12}MDI$ was used. The residual isocyanate groups were reacted with a slight excess (1.1 equiv excess) of alkylamine, weighed into a scintillation vial, and diluted with toluene, as described previously.[17] After the amine addition, the reaction was allowed to proceed for 30 min. 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 under reduced pressure (water aspirator). Purifications of the thickeners were performed by dissolution in warm acetone, gravity filtration, and precipitation into petroleum ether. The impurity in the HEUR thickener was a consequence of the step-growth polymerization. Unreacted diisocyanate was present in small quantities and reacted with the alkylamine to produce the corresponding diurea. As this byproduct contains no oxyethylene functionality, it will not dissolve in water; and aqueous solutions containing the byproduct will appear hazy or cloudy.

Scheme 1. Synthesis of Broad Molecular Weight Distribution HEUR Thickeners



Scheme 2. Synthesis of Narrow Molecular Weight Distribution HEUR Thickeners



Synthesis of HEUR Thickeners with Narrow Molecular Weight Distribution. A large excess of diisocyanate (25:1 ratio) was reacted with $HO(EtO)_{470}H$ to obtain POE end capped with isocyanate functionality with minimal step-growth polymerization; the isocyanato functional POE was reacted with an alkylamine. This reaction sequence produced HEURs with a target molecular weight of approximately 20 000, but with a narrow molecular weight distribution (Scheme 2). The experimental setup, isolation, and purifications were described previously, except $HO(EtO)_{470}H$ was used and the number of equivalents of reactants was 30 equiv of amine to 25 equiv of diisocyanate to 1 equiv of $HO(EtO)_{470}H$. The $H_{12}MDI$ thickeners with narrow molecular weight distributions required an extra step after the acetone purification. The thickener was dissolved in warm toluene, and a gel-like product was observed. This product was filtered from the solution, and the thickener was precipitated into petroleum ether.

Molecular Weight Determination. Molecular weight distributions were determined by size exclusion chromatography, using a Waters Model 510 pump, a Waters M730 data module, and a Waters Model R401 differential refractometer. Tetrahydrofuran was the mobile phase with a flow rate of 1.0 mL/min. A set of four Ultrastyragel columns was used with the following pore sizes: 100 000 Å; 2 × 10 000 Å; and 1000 Å. The column temperature was a constant 31 °C. Monodisperse molecular weight polystyrenes were used as universal calibration standards.

Table 2. HEUR Molecular Weight Distributions

terminal alkyl	M_n (SEC)	M_W (SEC)	PDI
$R-NH-CO-NH-R''-[-NH-CO-O-(EtO)_{140}-CO-NH-R''-]_3-NH-CO-NH-R$			
$C_6H_{13}-HDI$	18 000	28 300	1.57
$C_8H_{17}-HDI$	18 300	28 900	1.58
$C_{12}H_{25}-HDI$	18 400	27 300	1.48
$C_6H_{13}-H_{12}MDI$	17 600	29 100	1.65
$C_8H_{17}-H_{12}MDI$	21 100	32 100	1.52
$C_{12}H_{25}-H_{12}MDI$	20 700	32 400	1.56
$R-NH-CO-NH-R''-NH-CO-O-(EtO)_{470}-CO-NH-R''-NH-CO-NH-R$			
$C_6H_{13}-HDI$	24 400	28 000	1.22
$C_8H_{17}-HDI$	24 500	30 400	1.24
$C_{12}H_{25}-HDI$	24 200	30 200	1.25
$C_6H_{13}-H_{12}MDI$	22 600	28 100	1.24
$C_8H_{17}-H_{12}MDI$	24 000	29 400	1.17
$C_{12}H_{25}-H_{12}MDI$	20 800	27 100	1.31

Fluorescence Spectroscopy. Fluorescence emission spectra of the purified aqueous HEUR thickeners were recorded on a SPEX 2T2 Fluorolog fluorimeter, using a Xenon lamp as a light source. Solutions were prepared, using a 2×10^{-5} M stock solution of 8-anilino-1-naphthalenesulfonic acid (ANS). The stock solution was degassed with argon before use. The excitation wavelength to excite the probe was 377 nm, and the emission spectra were recorded from 400 to 600 nm for HEUR solutions with varying concentrations. The emission maximum of ANS in aqueous solutions occurs at 500 nm; it does not change significantly in the presence of POE. The maximum shifts to 490 nm when the POE is modified with large terminal hydrophobes. Aqueous probe solutions of surfactants or thickeners were prepared, according to the following procedure. The degassed surfactant or thickener solution was weighed into a 20 mL vial and diluted to a 2 g total weight with argon-purged distilled water. This solution was diluted to 10 g with the degassed probe solution to obtain a constant concentration of probe. Fluorescence spectra were recorded within an hour after preparing these solutions.

Purifications of the HDI thickeners were accomplished according to the procedure described in the Experimental Section. The thickeners with narrow molecular weight distributions contained large amounts of impurities because of the large excess of end capping reagents used. The $H_{12}MDI$ thickeners with narrow molecular weight distributions were difficult to purify because the impurity retained limited solubility in the organic solvents used to dissolve the HEUR. The two purification procedures did not completely remove the impurity, and aqueous solutions of these thickeners became cloudy at concentrations greater than 0.2 wt %. Fluorescence measurements of aqueous solutions of this series of HEURs were not performed.

Rheological Measurements. Intrinsic and reduced viscosities were run at 25.3 °C in both DDI water and DMF, using a Ubbelohde capillary viscometer. The steady state viscosity of higher concentrations of the thickeners and thickener/surfactant solutions were measured with a Brookfield cone and plate viscometer after a steady state viscosity was achieved. Flow profiles and oscillatory measurements were recorded, using a CarriMed CSL Controlled Stress Rheometer, Cleveland, OH.

Results and Discussion

Synthetic Conditions. In one of our initial studies,[14] the telechelic HEURs were prepared with two terminal hydrophobe groups. The rheological properties of aqueous solutions were examined to determine the effect of POE spacer length on viscosity. An HEUR thickener with a molecular weight of approximately 23 000 was the most effective rheology modifier when compared with lower (8000 and 14 000) and higher (35 000) molecular weight HEURs with the same terminal hydrophobe and the same aqueous solution concentration. As the molecular weight was increased from 20 000 to 35 000, a decrease in aqueous solution viscosity was observed. This was attributed to a decrease in the concentration of hydrophobe terminal groups with increasing molecular weight. When the POE molecular weight was decreased from 20 000 to 8000, the aqueous solution viscosities decreased because of the predominance of intramolecular associations relative to intermolecular associations.[15] This interpretation was based on a similar conclusion drawn from fluorescence studies of pyrene-labeled POE with an average of 100 and 200 oxyethylene units,[22] $M_n = 8800$. With these observations in mind, uni-HEURs and S-G HEURs were prepared with M_n of 20 000 for this study of molecular weight distributions.

Theoretically, HEUR thickeners from both telechelic and S-G syntheses have the same concentration of hydrophobe and number average molecular weight, based on the stoichiometry, and in this study, the external hydrophobes are the same. Only the molecular weight distributions would change. The broad molecular weight S-G HEURs have "internal hydrophobic groups" (the alkyl group of the diisocyanate coupler) present in the polymer backbone. In our previous study of S-G HEURs,[17] the internal hydrophobic groups did not form hydrophobic domains in aqueous solution and, therefore, can be neglected as a contributing factor to viscosity build in this study.

Size Exclusion Chromatography and Intrinsic Viscosities. Size exclusion chromatography (Table 2) and intrinsic viscosity measurements in DMF demonstrate that the HEURs with broad and narrow molecular weight distributions are of comparable molecular weights. In our initial studies, the telechelic uni-HEURs were noted to possess relatively narrow molecular weight distributions. They exhibited a maxima in viscosity when the oxyethylene unit spacing was ca. 500, and thus, a target M_n of 20 000 was chosen in our S-G syntheses. The S-G HEURs were prepared with different diisocyanate couplers and different hydrophobic amines in six independent syntheses. The similarity in molecular weights attest to the reproducibility of the synthetic procedure.

The molecular weights of the narrow distribution HEURs (Table 2) are similar in molecular weight and molecular weight distribution to the starting POE (Table 1). The chromatographs of two HEURs, one with a narrow and one with a broad molecular weight distribution, delineate the complex mixture of the products in the S-G polymerization (Figure 1). Three peaks are distinct in the broad molecular weight distribution HEUR; the peaks between 33.2 and 33.7 min, 34.2 and 34.7 min, and 35.7 and 36.2 min correspond to HEURs with three, two, and one $HO(EtO)_{140}H$ units,

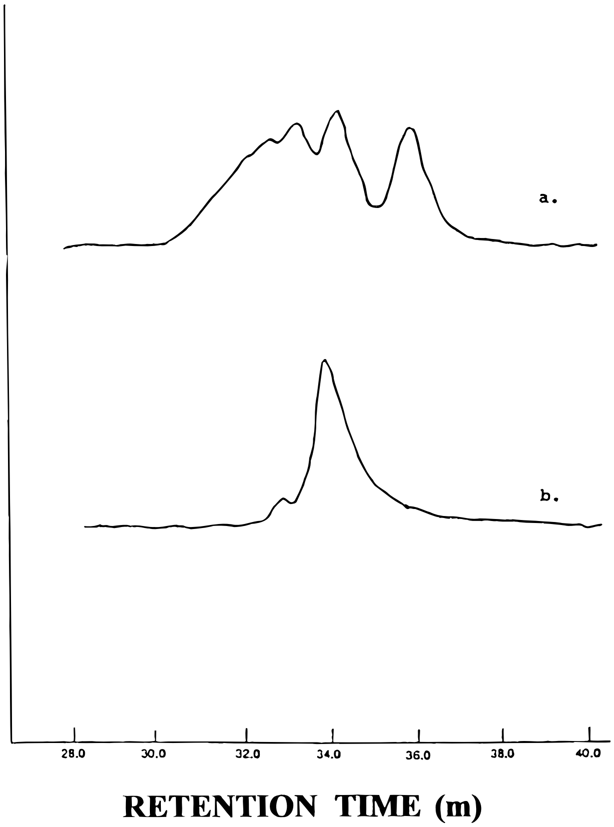


Figure 1. SEC chromatographs of HEUR thickeners: (a) $C_8H_{17}-H_{12}MDI-[-(EtO)_{140}-H_{12}MDI-]_3-C_8H_{17}$; (b) $C_8H_{17}-H_{12}MDI-(EtO)_{470}-H_{12}MDI-C_8H_{17}$.

while the higher molecular weight species blend together. In contrast, the chromatograph of the HEUR thickener with the narrow molecular weight distribution possesses one major peak at 33.2 min, corresponding to an HEUR with one $HO(EtO)_{470}H$ unit, and a small shoulder at 32.2 min, corresponding to an HEUR with two $HO(EtO)_{470}H$ units. In this synthesis, the excess diisocyanate was not sufficient in quantity to prevent chain extension; however, the majority (95% on the basis of peak area analysis) is the telechelic uni-HEUR thickener, $R-NH-CO-NH-R''-NH-CO-O-(EtO)_{470}-CO-NH-R''-NH-CO-NH-R$.

The chromatographs (Figure 2) and the molecular weights (Table 3) demonstrate that the reaction reached completion at 180 min. No further change in this complex mixture of products in the step-growth polymerization was observed after 180 min. This reaction time was then used for each thickener prepared with narrow and broad molecular weight distributions.

The intrinsic viscosities of the HEURs were measured (Table 4) in DMF. As the hydrophobe size is increased (this also includes the effective terminal size that encompasses both the terminal alkylamine and the diisocyanate unit that links it with the oxethylene chain), the reduced viscosities in water increase dramatically. The η_{sp} values in DMF remain close to the intrinsic viscosities in DMF that do not vary with variation in terminal hydrophobe size. This indicates that in DMF hydrophobic associations are absent. This would be expected, particularly in view of the tendency of cosolvents in aqueous solutions to disrupt such associations.[23,24] The intrinsic viscosities between the broad and narrow molecular weight distribution thickeners are similar, as are the molecular weight averages by SEC.

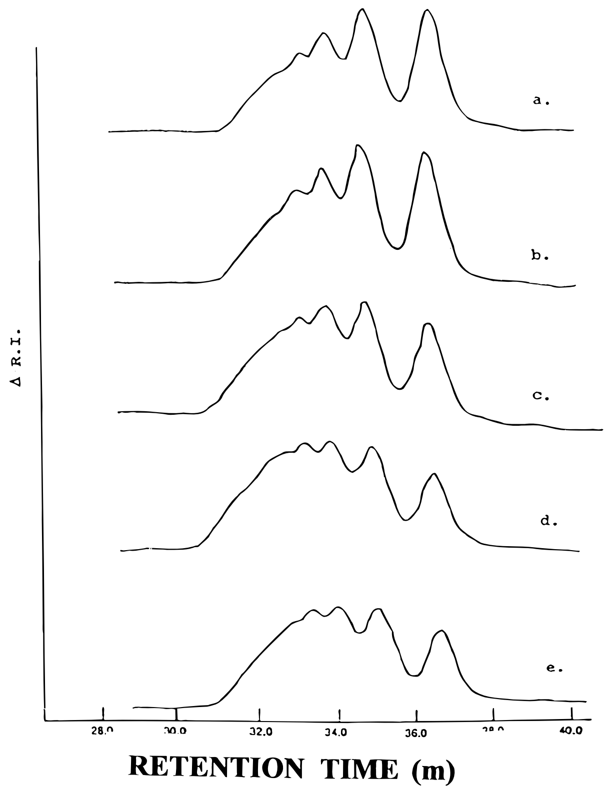


Figure 2. SEC chromatographs of $C_6H_{13}-H_{12}MDI-[(EtO)_{140}-H_{12}MDI]_3-C_6H_{13}$ HEURs as a function of reaction time: (a) 60, (b) 90, (c) 120, (d) 180, and (e) 240 min.

Table 3. Time Dependence of Measured Molecular Weights for Broad MW Distribution HEUR with Terminal $C_6H_{13}-H_{12}MDI$ Groups

time (min)	M_n	M_W	PDI
60	15 300	24 600	1.60
90	17 000	26 900	1.59
120	19 000	30 800	1.63
180	20 900	34 200	1.64
240	20 000	32 700	1.64

Fluorescence Spectroscopy. The fluorescent probe, ANS, is sensitive to the local environment. When the probe enters a region of different polarity, the wavelength at which a maximum in emission intensity occurs will shift. The diisocyantes, as internal hydrophobic urethane linkages, do not promote hydrophobic associations and the emmision maximum remains at 500 nm. As the terminal hydrophobe is added and increased in size, the excimer emmision shifts to 490 nm and increases in intensity. A comparison of the fluorescence emissions intensity of the broad molecular weight distribution thickeners with HDI (Figure 3) and H_{12}-MDI (Figure 4) indicates that when the hydrophobic amine is kept constant (i.e., $-C_6H_{13}$) and the diisocyanate is changed from HDI to $H_{12}MDI$, aggregation occurs at lower concentrations with the more hydrophobic $H_{12}MDI$, indicating that the size of the alkyl unit of the diisocyanate increases the effective hydrophobe size of the terminal alkyl groups. Changing the molecular weight distribution can also influence the formation of hydrophobic aggregates. Thickeners with a narrow molecular weight distribution and large hydrophobes can enter into hydrophobic aggregates more readily than a thickener with the same external hydrophobe, but with a broad molecular weight distribution. Fluorescence spectra of the $H_{12}MDI$ narrow distribution thickeners were not measured because the solutions contained an impurity, the diurea,[15] which could not be

Table 4. Reduced ($\eta_{red.}$) and Intrinsic [η] Viscosities of HEURs

terminal alkyl	$\eta_{red.}(H_2O)$	$\eta_{red.}(DMF)$	[η(DMF)]	$\eta_{red.}(H_2O)/\eta_{red.}(DMF)$
$R-NH-CO-NH-R''-[-NH-CO-O-(EtO)_{139}-CO-NH-R''-]_{3.2}-NH-CO-NH-R$				
$C_6H_{13}-HDI$	0.34	0.35	0.31	0.99
$C_8H_{17}-HDI$	0.35	0.36	0.30	0.98
$C_{12}H_{25}-HDI$	0.51	0.38	0.33	1.36
$C_6H_{13}-H_{12}MDI$	0.44	0.42	0.36	1.04
$C_8H_{17}-H_{12}MDI$	0.67	0.43	0.38	1.55
$C_{12}H_{25}-H_{12}MDI$	5.58	0.45	0.40	12.48
$R-NH-CO-NH-R''-NH-CO-O-(EtO)_{468}-CO-NH-R''-NH-CO-NH-R$				
$C_6H_{13}-HDI$	0.39	0.38	0.32	1.02
$C_8H_{17}-HDI$	0.40	0.37	0.32	1.07
$C_{12}H_{25}-HDI$	0.97	0.38	0.34	2.54
$C_6H_{13}-H_{12}MDI$	0.40	0.37	0.33	1.07
$C_8H_{17}-H_{12}MDI$	0.96	0.36	0.38	2.69
$C_{12}H_{25}-H_{12}MDI$	a	0.37	0.34	a

[a] HEUR phase separated in neat aqueous solutions, and capillary viscosity could not be measured. Reduced viscosities were measured at 0.5 g/dL, at 30 °C.

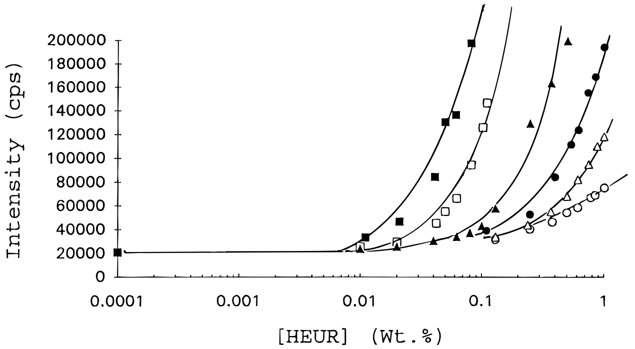


Figure 3. Fluorescence intensity (counts per second) as a function of HEUR concentration for HDI-based HEURs: (○, ●) $C_6H_{13}-HDI$; (△, ▲) $C_8H_{17}-HDI$; (□, ■) $C_{12}H_{25}-HDI$. (Open symbols) $R-NH-CO-NH-[(EtO)_{140}-R''-]_3-NH-CO-NH-R$; (closed symbols) $R-NH-CO-NH-R''-(EtO)_{470}-R''-NH-CO-NH-R$.

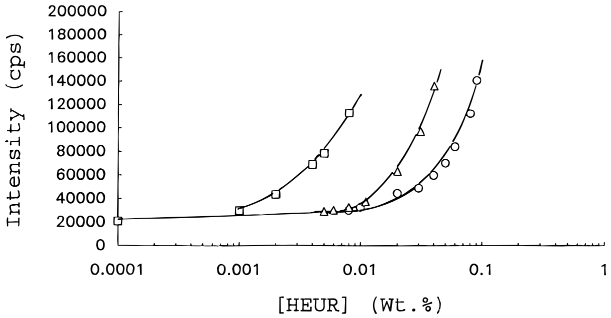


Figure 4. Fluorescence intensity (counts per second) as a function of HEUR concentration for $H_{12}MDI$-based HEURs: (○) $C_6H_{13}-H_{12}MDI$; (△) $C_8H_{17}-H_{12}MDI$; (□), $C_{12}H_{25}-H_{12}MDI$.

removed from the uni-HEUR. In addition the $C_{12}H_{25}-H_{12}MDI-(EtO)_{470}-H_{12}MDI-C_{12}H_{25}$ HEUR formed a viscous gel in neat aqueous solutions, and the fluorescence spectra could not be recorded without the presence of surfactant (0.002 M SDS).

Reduced and Low-Shear Viscosities. The reduced viscosities (Table 4) of the broad and narrow molecular weight distribution HEURs demonstrate that smaller external hydrophobes ($C_6H_{13}-HDI$ and $C_8H_{17}-HDI$) do not build viscosity readily at an aqueous solution concentration of 1.0 g/dL, regardless of the molecular weight distribution. The fluorescence measurements indicate that hydrophobic aggregates are formed at this aqueous concentration, but the associations are not strong enough to build viscosity. At a concentration of 1.0 wt %, the hydrophobic aggregates with larger external hydrophobes have a longer residence time within the hydrophobic aggregate, and an increase in viscosity is observed.

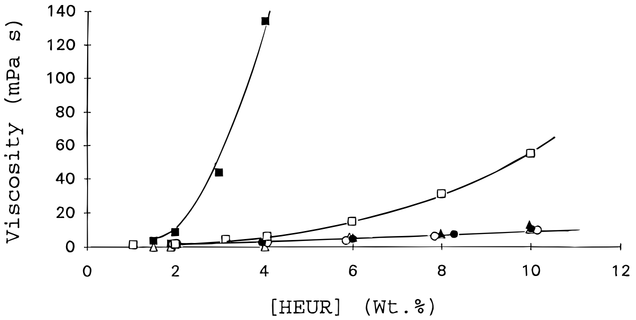


Figure 5. Steady state low shear rate (2 s^{-1}) viscosity dependence on HEUR concentration for HDI-based HEURs: (○) $C_6H_{13}-HDI$; (△), $C_8H_{17}-HDI$; (□) $C_{12}H_{25}-HDI$. (Open symbols) $R-NH-CO-NH-R''-[(EtO)_{140}-R'']_3-NH-CO-NH-R$; (closed symbols) $R-NH-CO-NH-R''-(EtO)_{470}-R''-NH-CO-NH-R$.

For the HEURs synthesized with HDI as the diisocyanate coupler, only the HEURs with $C_{12}H_{25}-HDI$ terminal hydrophobes exhibit a deviation from unity for the ratio of the reduced viscosity in water to DMF. The $C_{12}H_{25}-HDI-(EtO)_{470}-HDI-C_{12}H_{25}$ has a greater viscosifying ability relative to the $C_{12}H_{25}-HDI-[-NH-CO-O-(EtO)_{140}-CO-NH-HDI-]_3-C_{12}H_{25}$ HEUR (Table 4). The narrow distribution HEUR of $M_n \sim 20\,000$ forms a more uniform network with a minimal level of intramolecular associations.

Based on the reduced viscosity ratios in water and DMF, the HEUR thickeners with terminal $C_6H_{13}-H_{12}MDI$ and $C_8H_{17}-H_{12}MDI$ hydrophobes also exhibited a molecular weight distribution effect (Table 4). The $C_{12}H_{25}-H_{12}MDI-(EtO)_{470}-H_{12}MDI-C_{12}H_{25}$ phase separated in aqueous solution, presumably due to the strength and uniformity of the network and the presence of two hydrophobes on the POE chain. The concentration at which a macroscopic viscosity build occurs is referred to as the critical aggregation concentration (CAC). The low-shear viscosity as a function of thickener concentration for the HDI and $H_{12}MDI$ HEURs with broad distributions (Figures 5 and 6, respectively) demonstrates that the larger alkyl units of the $H_{12}MDI$ effect a greater increase in viscosity by increasing the effective size of the external hydrophobe. The $C_6H_{13}-$ and $C_8H_{17}-HDI$ HEURs do not exhibit large differences in viscosity build, regardless of the molecular weight distributions.

The presence of oxygen contiguous to the methylene groups in POE facilitates a quantitative estimate of the

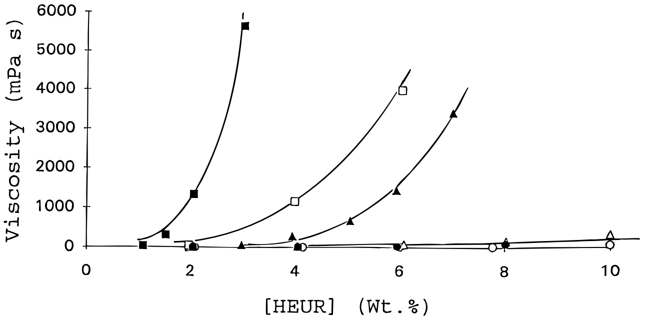


Figure 6. Steady state low shear rate (2 s^{-1}) viscosity dependence on HEUR concentration for H_{12}MDI-based HEURs: (○) C_6H_{13}−H_{12}MDI; (△) C_8H_{17}−H_{12}MDI; (□) $C_{12}H_{25}$−H_{12}MDI. (Open symbols) R−NH−CO−NH−R″−[(EtO)$_{140}$−R″]$_3$−NH−CO−NH−R. (closed symbols) R−NH−CO−NH−R″−(EtO)$_{470}$−R″−NH−CO−NH−R.

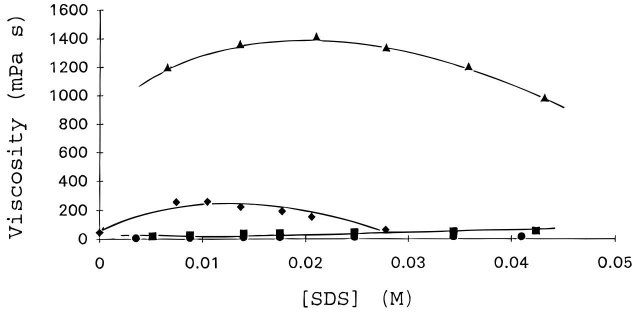


Figure 7. Steady state low shear rate (2 s^{-1}) viscosity dependence on SDS concentration for HDI-based HEURs: (Closed symbols) R−NH−CO−NH−R″−NH−CO−O−(EtO)$_{470}$−CO−NH−R″-NH−CO−NH−R. (●) 6% C_6H_{13}−HDI; (■) 6% C_8H_{17}−HDI; (▲) 6% $C_{12}H_{25}$−HDI; (♦), 3% $C_{12}H_{25}$−HDI.

degree of terminal substitution when octadecyl monoisocyanate is added directly to POE. In S-G HEUR synthesis the presence of internal hydrophobes complicates the analysis. Having alicyclic positions as in isophorone may facilitate the analysis[13] somewhat, but such an analysis may lack a truly quantitative value in this system. Perhaps the most sensitive spectroscopic analysis is the UV absorbance from aromatic structures: however, the UV emission of the HEUR prepared with tetramethylxylidene diisocyanate is not sufficient to quantitatively define the extent of terminal substitution. It is conceivable that the broad molecular weight HEURs may not be totally substituted in the terminal position and that this may contribute somewhat to the lower efficiency of the S-G HEURs. Given the influence of intrahydrophobic bonding of lower molecular weight HEURs and the significant amount of lower molecular weight HEUR in an S-G polymerization, the lower efficiency of the S-G HEURs would appear to be related to the high concentration of the 6000 POE with terminal hydrophobes that are not present in the uni-HEURs prepared with POE in the M_n 20 000 range.

Surfactant Effects. The influence of adding both an anionic (SDS) and a nonionic (NP(EtO)$_{10}$H) surfactant on the viscosity build of the broad and narrow molecular weight (MW) HDI HEURs and the H_{12}MDI HEURs was examined. The distinctive maxima in viscosity with increasing SDS concentration were not generally observed for HEURs with C_6H_{13}- and C_8H_{17}-modified HDI and H_{12}MDI terminal groups. The response to increasing SDS concentration of the narrow MW HDI HEURs are illustrated in Figure 7 and for the broad and narrow MW H_{12}MDI HEURs in Figure 8. As noted in aqueous solutions without surfactant, the narrow MW H_{12}MDI HEURs with the larger $C_{12}H_{25}$-terminal group achieve a higher viscosity than their broad MW HDI and H_{12}MDI analogues (Figure 8). Most previous studies on the HEUR type or the commercial HMHEC type of associative thickeners have observed a viscosity maximum at or below the critical micelle concentration (CMC) of SDS. In all of these studies, the hydrophobe has been large, $C_{16}H_{33}$−. In Figures 5 and 7 of our previous study[15] of uni-HEURs, the maxima occur at SDS concentrations higher than its CMC when the oxyethylene spacer length is decreased and when the hydrophobe size is decreased (i.e., $C_{18}H_{37}$− to nonylphenol). In the step-growth HEURs in this study, there is a broad molecular weight distribution (clearly indicated in Figures 1 and 2) and the broadness of the maxima in solution viscosities are related to the shorter sequence lengths in these polymers. The broad viscosity maxima also are related to the size of the terminal hydrophobes. The hexamethylene diisocyanate unit does not contribute significantly to the terminal hydrophobe size, probably due to the hydrophilicity of the two urethane linkage arising from the diisocyanates with only six methylene units. The dicyclohexylmethane group does not match the $C_{18}H_{37}$ when the alkylamine is small, C_6H_{13} or C_8H_{17}, again due to the hydrophilicity of the two urethane units. Thus, the results on the step-growth HEURs and the well-defined uni-HEURs are consistent. Some of the broadness in the maxima is probably also due to a change in micelle shapes and/or sizes. This is being addressed by changing the oxyethylene length in the nonionic surfactant, where there is substantial literature support for such a micelle shape change.

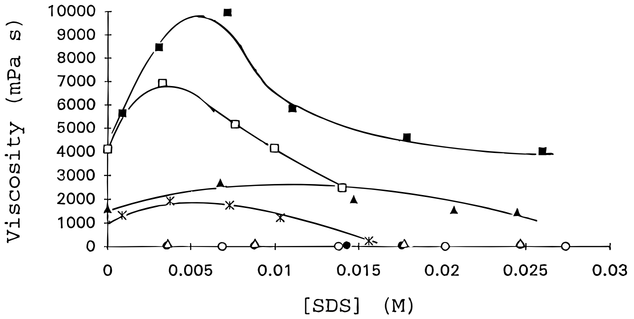


Figure 8. Steady state low shear rate (2 s^{-1}) viscosity dependence on SDS concentration for H_{12}MDI-based HEURs: (○) 6% C_6H_{13}−H_{12}MDI; (△) 6% C_8H_{17}−H_{12}MDI; (□) 6% $C_{12}H_{25}$−H_{12}MDI; (●) 6% C_6H_{13}−H_{12}MDI; (▲) 6% C_8H_{17}−H_{12}MDI; (■) 3% $C_{12}H_{25}$−H_{12}MDI; (*) 2% $C_{12}H_{25}$−H_{12}MDI. (Open symbols) R−NH−CO−NH−R″−[(EtO)$_{140}$−R″]$_3$−NH−CO−NH−R; (closed symbols) R−NH−CO−NH−R″−(EtO)$_{470}$−R″−NH−CO−NH−R.

In the presence of the nonionic, NP(EtO)$_{10}$H, surfactant, the HDI HEURs with broad (not shown) and narrow (Figure 9) molecular weight distributions do not exhibit a viscosity maximum with increasing surfactant concentration. In these studies, SDS facilitates greater viscosity build than NP(EtO)$_{10}$H, when the external hydrophobe of the HEUR is small, but NP(EtO)$_{10}$H facilitated more comparable solution viscosities when the external hydrophobe is large in H_{12}MDI HEURs (Figure 10). This suggests that larger terminal hydrophobes may alter the size of the mixed micelle to a greater extent with NP(EtO)$_{10}$H relative to SDS.

The area of surfactant influences is complex. For example if the SDS concentration is decreased below its CMC in hydrophobically-modified hydroxyethyl cellulose (HMHEC) solutions, very intricate thixotropic behavior

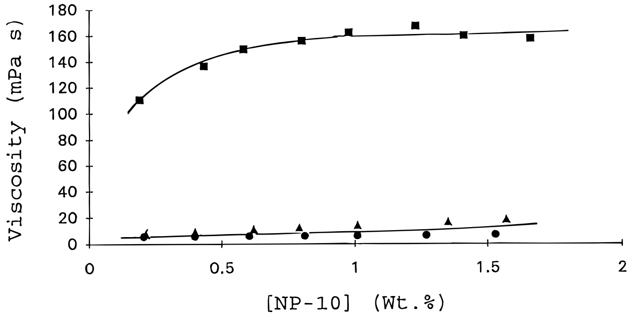


Figure 9. Steady state low shear rate (2 s^{-1}) viscosity dependence on $NP(EtO)_{10}H$ concentration for HDI-based HEURs: R−NH−CO−NH−R″−NH−CO−O−$(EtO)_{470}$−CO−NH−R″−NH−CO−NH−R, (●) 6% C_6H_{13}−HDI; (▲), 6% C_8H_{17}−HDI; (■), 6% $C_{12}H_{25}$−HDI.

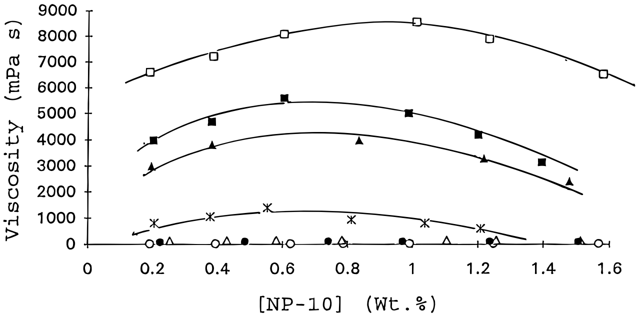


Figure 10. Steady state low shear rate (2 s^{-1}) viscosity dependence on $NP(EtO)_{10}H$ concentration for $H_{12}MDI$-based HEURs: (○) 6% C_6H_{13}−$H_{12}MDI$; (△) 6% C_8H_{17}−$H_{12}MDI$; (□) 6% $C_{12}H_{25}$−$H_{12}MDI$; (●) 6% C_6H_{13}−$H_{12}MDI$; (▲) 6% C_8H_{17}−$H_{12}MDI$; (■) 3% $C_{12}H_{25}$−$H_{12}MDI$; (*) 2% $C_{12}H_{25}$−$H_{12}MDI$. (Open symbols) R−NH−CO−NH−R″−$[(EtO)_{140}$−$R'']_3$−NH−CO−NH−R; (closed symbols) R−NH−CO−NH−R″−$(EtO)_{470}$−R″−NH−CO−NH−R.

is observed.[25] The nonionic surfactant has little influence on the viscosity of HMHEC solutions. When SDS is used with uni-HEURs, the lower molecular weight HEURs are thixotropic at low shear rate, become shear thickening at moderate shear rates and then exhibit shear thinning above 100 s^{-1} shear rates.[26] The shear thickening of water-soluble polymers cross-linked with boron compounds were related, through NMR measurements, to the transition from intramolecular cross-links to intermolecular cross-links with increasing shear rates.[27] The phenomena of surfactant influences in uni-HEUR solutions, however, is far more complex. With the higher molecular weight uni-HEURs a more complex tranisiton in thixotropic behavior is observed in the area of 100 s^{-1} shear rates. This type of rheological behavior can be induced in the lower moleular weight uni-HEUR aqueous solutions containing nonionic surfactants, but not in solutions containing SDS. These studies will be described in detail in a future manuscript.

Flow and Oscillatory Profiles. In an examination of the rheology of surfactant solutions, Hoffmann et al.[28,30] and Lobl et al.[29] have observed rodlike micelles to grow in number and in length as the concentration of the surfactant was increased. The appearance of an elastic response in the surfactant solution was correlated with an increase in the number of rods. The rods were proposed to overlap and interact, giving rise to a three-dimensional network and an elastic response. The influence of the alkyl chain length (from dodecyl to octadecyl) in a series of alkylpyridinium salicylates was observed,[31] in the presence of an equimolar concentration of NaCl, to give rise to an increased viscosity and elastic response, and the chemical relaxation time increased with increasing hydrocarbon chain length. In surfactant solutions with long alkyl chains and rodlike micelles, the chemical relaxation time was longer than the micelle rotation time. For shorter alkyl chains, the lifetime decreased with decreasing carbon chain length, and the chemical relaxation time became shorter than the rotation time. In this instance, the influence of rods on the rheological properties diminished, and the elastic response disappeared.

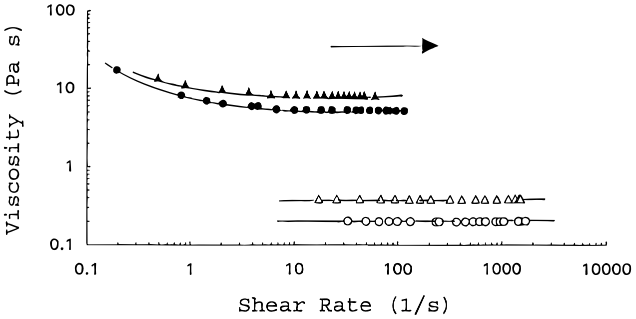


Figure 11. Viscosity with increasing shear rate ramp (3 m) for $H_{12}MDI$−based HEURs: (○, ●) 8% C_8H_{17}−$H_{12}MDI$; (△, ▲) 10% C_8H_{17}−$H_{12}MDI$. (Open symbols) R−NH−CO−NH−R″−$[(EtO)_{140}$−$R'']_3$−NH−CO−NH−R; (closed symbols) R−NH−CO−NH−R″−$(EtO)_{470}$−R″−NH−CO−NH−R.

In neat aqueous solutions of HEURs, the flow profiles and viscoelastic properties of the solutions may be altered by the size and shape of the terminal hydrophobe, the molecular weight distribution, and the HEUR concentration. Large terminal hydrophobes on HEUR thickeners give rise to solutions with elastic character.[10,11] Solutions of HEUR thickeners with smaller terminal hydrophobes exhibit a dominant viscous response. The combination of $H_{12}MDI$ with $-C_{14}H_{29}$ or HDI with $-C_{18}H_{37}$ as the terminal hydrophobe in step-growth polymers facilitates[11] a dominant elastic response at high frequencies. This can be related to the theories proposed by Hoffmann et al.[28−31] HEURs with two hydrophobes per POE chain and with sufficient spacer lengths between terminal groups facilitates two different hydrophobic aggregate associations, and the movement of both aggregates is restricted, similar to micelle−micelle overlap. For long terminal hydrophobes, the chemical relaxation time would be greater than the micelle rotation time, and the elastic character of the solution would increase.

In this study, the $H_{12}MDI$ series, when the alkyl chain length was increased from hexyl (C_6H_{13}−) to octyl (C_8H_{17}−) to dodecyl ($C_{12}H_{25}$−), exhibited progressive viscosity increases. Viscosity dependence on shear rate profiles were recorded for aqueous solutions of C_8H_{17}−$H_{12}MDI$−[−NH−CO−O−$(EtO)_{140}$−CO−NH−$H_{12}MDI$−$]_3$−C_8H_{17} HEUR and C_8H_{17}−$H_{12}MDI$−$(EtO)_{470}$−$H_{12}MDI$−C_8H_{17} at two different concentrations (Figure 11). The narrow molecular weight distributions exhibited significantly greater viscosities than the broader molecular weight S-G HEURs. The oscillatory profiles (Figure 12) indicate that both the uni-HEUR and the S-G HEUR have low elastic responses.

The flow and oscillatory response of $C_{12}H_{25}$−$H_{12}MDI$ with narrow and broad MW distributions are given in Figures 13 and 14. In aqueous solution the $C_{12}H_{25}$−$H_{12}MDI$ uni-HEUR phase separates, and a small quantity of sodium dodecyl sulfate (0.0008 M) was added to disrupt the phase separated, gel-like layer to achieve solubility. Phase separation is not observed in S-G

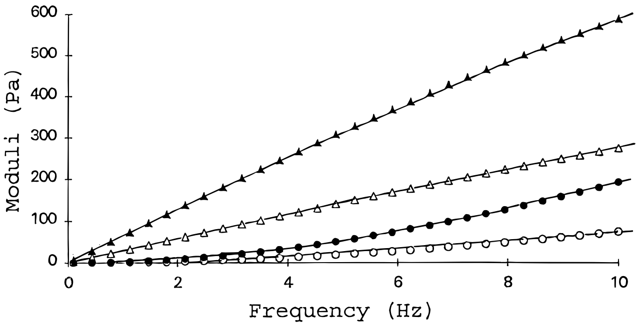


Figure 12. Moduli dependence on oscillation frequency for H_{12}MDI-based HEURs: HEUR structure, $C_8H_{17}-NH-CO-NH-H_{12}MDI-(EtO)_{470}-H_{12}MDI-NH-CO-NH-C_8H_{17}$, (○, ●) storage moduli, G'; (△, ▲) loss moduli, G''. (Open symbols) 8%; (closed symbols) 10%.

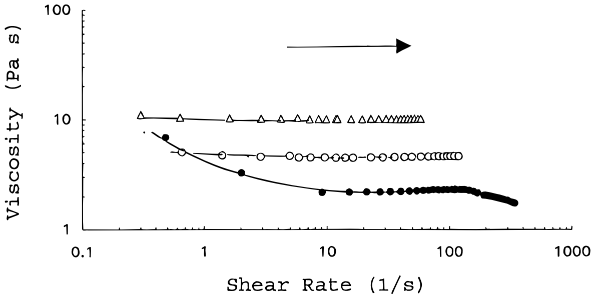


Figure 13. Viscosity with increasing shear rate ramp (3 m) for H_{12}MDI-based HEURs: (Open symbols) $R-NH-CO-NH-R''-[(EtO)_{140}-R'']_3-NH-CO-NH-R$; (closed symbols) $R-NH-CO-NH-R''-(EtO)_{470}-R''-NH-CO-NH-R$. (○) 6% $C_{12}H_{25}-H_{12}MDI$; (△) 8% $C_{12}H_{25}-H_{12}MDI$; (●), 3% $C_{12}H_{25}-H_{12}MDI$ with 8×10^{-4} M SDS.

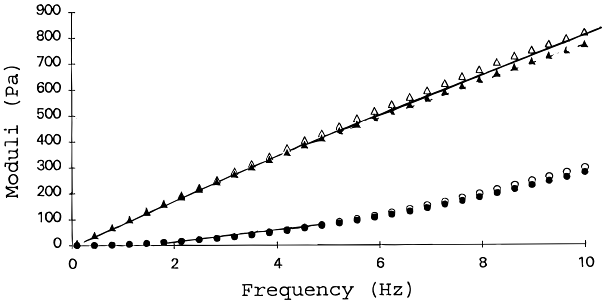


Figure 14. Oscillatory profiles for H_{12}MDI-based HEURs: HEUR structure, $R = C_{12}H_{25}$ and $R'' = H_{12}MDI$, (○, ●) storage moduli, G'; (△, ▲) loss moduli, G''. (Open symbols) 10% $R-NH-CO-NH-R''-[(EtO)_{140}-R'']_3-NH-CO-NH-R$; (closed symbols) 5% $R-NH-CO-NH-R''-(EtO)_{470}-R''-NH-CO-NH-R$ with 8×10^{-4} M SDS.

HEURs. The broad molecular weight distribution HEUR solutions at two concentrations was Newtonian, whereas the narrow molecular weight HEUR at a lower concentration was non-Newtonian at both low and intermediate shear rates (Figure 13). The oscillatory measurements (Figure 14) indicate that narrow MW distribution HEUR solutions are still primarily viscous (G'' is dominant). Twice the amount of the broad molecular weight distribution S-G HEUR with $C_{12}H_{25}-H_{12}MDI$ terminal hydrophobes were required to achieve viscosities comparable with the narrow molecular weight distribution uni-HEUR. Despite the differences in concentration, the oscillatory behavior was similar, and the storage and loss moduli were almost superimposable (Figure 14).

The viscosity differences can be attributed to the nature of the polymerization. The broad molecular weight distribution thickener possesses low molecular weight species (~6000), which are inefficient viscosifiers, and the level of hydrophobe is probably lower in the HEURs with broad molecular weight distributions. The presence of the impurity in all of the step-growth HEUR thickeners indicates that the hydrophobic amine was not quantitatively coupled to the POE backbone. This observation negated the possibility of assuming that broad molecular weight distribution HEURs can be modeled as narrow molecular materials with two terminal hydrophobes per POE chain.

Conclusions

Two synthetic procedures were developed to synthesize HEUR polymers with similar terminal hydrophobes and number average molecular weights but different molecular weight distributions. Terminal hydrophobe modification in broad molecular weight species may not be complete, and this may reduce the viscosity efficiency relative to the narrow molecular weight products. The broad molecular weight distribution HEURs with a number of species with distinct molecular weights formed an imperfect network, as the lower molecular weight species may be forming intramolecular associations.

HEUR thickeners prepared with H_{12}MDI as the diisocyanate coupler were more effective in building viscosity than HEURs prepared from HDI. Oscillatory rheological measurements indicated that the synthetic procedure influenced the absolute values of the storage and loss moduli. Twice the concentration of the broad molecular weight distribution HEUR with $C_{12}H_{25}-H_{12}MDI$ terminal hydrophobes was required to achieve viscosities comparable to the narrow molecular weight distribution HEUR. Despite the differences in concentration, the storage and loss moduli were similar. The size of the terminal alkyl groups and the molecular weight distribution were the dominant influences on the rheological responses of HEUR thickener solutions.

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