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Synthesis and Solution Properties of Hydrophobically-Modified Ethoxylated Urethanes with Variable Oxyethylene Spacer Lengths[†]

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ABSTRACT: The influence of the oxyethylene spacer length between terminal hydrophobes of hydrophobically-modified ethoxylated urethanes (HEURs) is examined through the synthesis of two series of well-defined terminally-modified HEUR thickeners. In the first series, octadecyl isocyanate is reacted with poly(oxyethylene) (POE) of varying molecular weight. In the second synthesis, excess isophorone diisocyanate is reacted with POE to prepare an isocyanato functional precursor, followed by reaction of the terminal isocyanate group with nonylphenol. Viscous aqueous solutions are obtained with only partial terminal modification of POE; with full terminal modification swollen gels are realized. At moderate concentrations the phase separation of HEUR thickeners is dependent on the size of the hydrophobe and the number of oxyethylene units between the hydrophobes. In both series of HEURs, the critical aggregation concentration is lowest when 500 oxyethylene units separate the terminal hydrophobes. In the presence of surfactant, both anionic and nonionic, the fully-modified HEURs also exhibit a maximum in viscosity when the spacer is ~500 oxyethylene units. The viscosities realized in both HEUR series are equal or greater (with smaller HEUR oxyethylene spacings) with the nonionic surfactant relative to the anionic surfactant, sodium dodecyl sulfate.

Introduction

When highly extended, the chemical bonds of macromolecules are broken,[1] and their viscosifying properties at low shear rates are not fully regained. Surfactant modification provides a means of minimizing this loss.[2] Aqueous solutions of high molecular weight polymers exhibit high elastic behavior, and in high deformation rate processing, this can be detrimental. Surfactant modification of water-soluble polymers can provide viscosities equivalent to high molecular weight polymers at low shear rates with significantly lower elasticity at higher deformation rates. In concept, the extent of the rheological changes due to the aggregation of the attached hydrophobes are dependent upon the size of the hydrophobes, the proximity of their placement, and the overall architecture of the water-soluble polymer.[3,4] Relating structural aspects of these "associative thickeners" to the performance of the modified water-soluble polymer is difficult because of the competing reactions and complexity of polymerization processes.

The synthesis of HEUR associative thickeners by step-growth addition of diisocyanates[5–7] with poly(oxyethylene)s (POEs) of intermediate molecular weight (8000–12 000) provides difficulties in structural characterizations. Broad molecular weight distributions[8] are obtained that complicate analysis of viscoelastic behavior[3,9] and there are two types of potential hydrophobes: internal hydrophobes[10] associated with the diisocyanate coupling unit and external hydrophobes added to the terminal isocyanate when the step-growth addition contains an excess of diisocyanate.

There have been two loosely defined approaches to understanding HEUR structural influences on solution properties: (1) synthesis of HEURs via step-growth polymerization with known components and (2) utilization of commercial materials. In the first approach, HEURs have been prepared using a broad synthetic design.[11] A more limited synthetic approach used only isophorone diisocyanate[12] as the coupler in the step-growth generation of HEUR polymers. In both studies experimental molecular weights were significantly lower than calculated stoichiometric values, indicating that the stoichiometry was altered or that products were degraded during synthesis and rectification steps, negating their usefulness in model studies. Products from the first synthesis have been examined by NMR to define rates of diffusion[13] of the "thickener". The isophorone products have been used extensively in fluorescence modeling[14] where "molecular weights calculated[15] on reaction stoichiometry" rather than measured SEC values are used.

A second approach is to analyze commercial products by gas chromatography in tandem with mass spectroscopy.[16] There are many pitfalls in this approach due primarily to various side reactions during degradation (openly discussed in the article) that limit unquestionable definition on HEUR structures. In the analysis of three commercial HEURs using this approach, opposing variances in molecular weight, terminal hydrophobe size, and the size of the alkyl group of the diisocyanate negate delineation of structural influences with solution properties. In light scattering studies[17] of their "analyzed" commercial HEUR, the necessity of studying well-defined HEURs was a clear conclusion.

Previous studies from this laboratory have examined commercial HEUR thickeners in coating formulations[18–24] and in aqueous solutions, alone and containing surfactants.[3] Such polymers create marked differences in coating and solution properties, even though they are chemically similar (i.e., by chemical composition they are >95% oxyethylene units). To define structural influences on solution properties, it is imperative that HEUR structures with controlled molecular weights, hydrophobe size, content, and placement be synthesized. That is the emphasis of this investigation. HEUR polymers are synthesized by two different procedures, but neither procedure results in internal hydrophobes as occurs in step-growth polymer-

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Table I. Molecular Weights of Poly(oxyethylene)s and Modified HEUR Derivatives

material	M_n(OH)	SEC		
		M_n	M_w	PDI
$HO(EtO)_{182}H$	8 140	8 935	10 354	1.2
$C_{18}H_{37}NCO$ mod-1		10 360	11 442	1.1
$C_{18}H_{37}NCO$ mod-2		11 946	12 837	1.1
$C_{18}H_{37}NCO$ mod-3		11 238	12 081	1.1
$HO(EtO)_{331}H$	14 340	15 044	17 778	1.2
$C_{18}H_{37}NCO$ mod-1		13 496	16 250	1.2
$C_{18}H_{37}NCO$ mod-2		16 600	18 823	1.1
$HO(EtO)_{531}H$	23 569	20 993	24 438	1.2
$C_{18}H_{37}NCO$ mod-1		18 303	23 562	1.3
$C_{18}H_{37}NCO$ mod-2		19 308	21 705	1.1
$HO(EtO)_{663}H$	29 219	33 408	37 237	1.1
$C_{18}H_{37}NCO$ mod-1		32 141	38 051	1.2
telechelic HEURs				
$(NPIP)_2(EtO)_{182}$		6 529	8 890	1.4
$(NPIP)_2(EtO)_{331}$		10 333	12 884	1.3
$(NPIP)_2(EtO)_{531}$		17 933	22 561	1.3
$(NPIP)_2(EtO)_{663}$		23 972	31 861	1.3

ization. In the first, terminal hydrophobes are generated by direct addition of octadecyl isocyanate to POE, with four different molecular weights. In the second, these POEs are end-capped with an excess of isophorone diisocyanate to achieve isocyanato functionality and then reacted with a hydrophobic alcohol. Complete end-capping is dependent on a variety of reaction conditions. POEs not fully derivatized can produce highly viscous solutions. The solution properties of these materials are compared in this study.

Experimental Section

Materials. Poly(oxyethylene)s of variable molecular weights were supplied by Union Carbide (8000) and by Fluka (12 000, 20 000, and 35 000). Octadecyl isocyanate was supplied by Miles and was gravity filtered before use. Toluene and petroleum ether were stirred for 24 h over 40-mesh calcium hydride and distilled under argon. *N,N*-Dimethylformamide was used as received. Tetrahydrofuran (Mallinckrodt, HPLC grade) was purged with argon prior to use. Water used in viscometric analysis and fluorescence experiments was distilled and passed through a Mill-Q (Millipore) ion exchange column. Dibutyltin dilaurate was obtained from Alfa, 8-anilinonaphthalenesulfonic acid (ANS) and sodium dodecyl sulfate (98%, SDS) were obtained from Aldrich, and (octylphenoxy)deca(oxyethylene) (Triton X-100, $C_8H_{17}C_6H_4O(EtO)_{10}H$) was obtained from Rohm & Haas.

Characterization of Starting Materials. All POEs were analyzed for molecular weights by end group analysis and size exclusion chromatography. The results are summarized in Table I. The hydroxyl number titration was performed according to the PMDA/IMDA method.[25] The phenyl isocyanate method was not used; recent work[26] has shown that this method leads to inaccurate results when the hydroxyl-containing polymers are POEs that contain acetate salts. Acetate salts, such as sodium and potassium acetate, will catalyze trimerization of the isocyanate and provide incorrect equivalent weights. The hydroxyl number procedure was modified in the amount of additional solvent used to determine the POEs of molecular weights 12 000 (50 mL), 20 000 (100 mL), and 35 000 (150 mL). These variations were made to maintain low viscosities during titration. For the POE of molecular weight 35 000 a lower number of equivalents (0.002) were used than the procedure designated to maintain a low viscosity during titration.

Synthesis of Octadecyl-Modified Poly(oxyethylene). A three-neck 500-mL round-bottom flask was equipped with an inlet for Drierite-treated argon and a thermometer, a reflux condenser and Dean–Stark water trap, and a mechanical stirrer. About 50 g of POE was weighed into the reaction flask, and 300 mL of dry toluene was added to the flask. The toluene was heated to reflux, and water was removed by azeotropic distillation. A total of 150 mL of toluene was removed in this manner. The flask was cooled to 40 °C, and 150 mL of dry, distilled THF and a catalyst, dibutyltin dilaurate (0.2 % by weight based on total solids) were added. Octadecyl isocyanate (1–4 equiv of NCO to 1 equiv of OH) was gravity filtered into the flask. The reaction was stirred for 6 h at 40–45 °C. The thickeners were precipitated into petroleum ether (1 volume of thickener solution/3 volumes of petroleum ether), collected on a sintered glass Buchner funnel, and dried with a water aspirator. The thickeners were further purified by dissolution in hot acetone, gravity filtration, and precipitation in petroleum ether (1 volume of thickener solution/3 volumes of petroleum ether). These HEURs are referred to as $(C_{18}H_{37}NHC(O)O)_x(EtO)_y$, where x designates the average number of hydrophobes per POE chain and y designates the number of oxyethylene units of the parent POE.

Synthesis of Telechelic Thickeners. Telechelic thickeners were synthesized according to the same synthetic procedures as described above except that, in this synthesis, a 100-equiv excess of isophorone diisocyanate was reacted with the POE (for 6 h) and the isocyanato functional POE was reacted with 110 equiv of nonylphenol. FT-IR spectra of POEs were recorded and compared to the FT-IR spectra of the telechelic prepolymer and the NPIP POEs to ensure that the isocyanate had completely reacted. The spectra of the modified POEs contain peaks between 1650 and 1675 cm^{-1}, corresponding to the urethane carbonyl group,[27] not present in the parent POE. The isocyanato functional POE was not isolated prior to nonylphenol addition. Purification of these HEUR thickeners was accomplished by dissolution in tetrahydrofuran and precipitation into petroleum ether several times. These HEURs are referred to as $(NPIP)_x(EtO)_y$, where NP and IP represent the nonylphenol and isophorone units and x and y maintain the designations given in the previous section.

Characterization of Thickeners. Infrared spectra were recorded on a Mattson Cygnus 25 Fourier transform infrared spectrophotometer. ^1H-NMR spectra of the octadecyl-modified POEs were recorded using a JEOL GSX 400-MHz Fourier transform NMR spectrometer with deuterated chloroform as the solvent and TMS as an external standard. Molecular weight distributions were measured by size exclusion chromatography (SEC) using a Waters M730 data module, a Waters R401 differential refractometer, tetrahydrofuran as the mobile phase, a flow rate of 1.0 mL/min, and a column temperature of 30 °C. SEC analysis was performed using three Ultrastyragel columns (Waters, one 500 Å and two 1000 Å) and one Styragel column (Waters, one 10 000 Å) with an effective molecular weight range of 2000–160 000 D. Calibration curves were constructed from polystyrene standards. Molecular weight data (as measured by SEC, calculated directly from the calibration curve) for the starting poly(oxyethylene)s and HEURs are listed in Table I for both the direct addition of octadecyl isocyanate and the nonylphenol telechelic series. Intrinsic viscosities were determined using a self-diluting capillary viscometer in water and *N,N*-dimethylformamide at 25.2 ± 0.1 °C. The efflux time of the solvent was 90–100 s. Fluorescence emission spectra of linear polymer solutions containing ANS (2×10^{-5} M) were recorded on a SPEX 2T2 Fluorolog spectrofluorimeter with a xenon light source. Polymer solutions with varying concentrations were made by dilution with a stock solution of ANS in water, and all solutions were degassed with argon prior to use. The polymer/probe solutions were irradiated with 377-nm radiation, and emission spectra were recorded from 400 to 600 nm. Low shear viscosities were recorded using a Brookfield cone-and-plate viscometer after a steady-state viscosity was achieved. Shear rate versus viscosity profiles and oscillatory measurements (following the procedures described in ref 3) were recorded using a Carri-Med controlled stress rheometer (4 cm, 2° cone). The data were taken in the linear viscoelastic region, and the scan conditions are reported in the legends of the respective figures.

Results and Discussion

Comments on the Syntheses and Characterizations. The quantitative reaction of exact stoichiometric amounts of poly(oxyethylene)s (POEs) and octadecyl isocyanate (Scheme I) is difficult because of the large difference in molecular weights of the two reactants and the uncertainty in molecular weights of the POEs used in this study. Another complicating factor is the reaction of water with

Scheme I. Synthesis of Octadecyl-Modified POE

$$H_{37}C_{18}NCO + HO\text{—}(CH_2CH_2O)_n\text{—}H \xrightleftharpoons[\text{catalyst}]{\text{tin}}$$

$$H_{37}C_{18}\text{—}NHCOO\text{—}(CH_2CH_2O)_{n-1}\text{—}CH_2CH_2O\text{—}CONH\text{—}C_{18}H_{37}$$

Scheme II. Reaction of Isocyanate with Water

$$R\text{—}NCO + H_2O \rightleftharpoons R\text{—}NH_2 + CO_2$$

$$R\text{—}NH_2 + R\text{—}NCO \rightleftharpoons R\text{—}NH\text{—}CO\text{—}NH\text{—}R$$

Table II. Extent of Hydrophobe Modification (^{1}H-NMR)

thickener	$(CH_2)/(OCH_2)$ expt	$(CH_2)/(OCH_2)$ theo	extent of modification[a]
$HO(EtO)_{182}H$			
$C_{18}H_{37}NCO$ mod-1	0.055	0.070	1.6
$C_{18}H_{37}NCO$ mod-2	0.052	0.061	1.7
$C_{18}H_{37}NCO$ mod-3	0.071	0.065	2.0
$HO(EtO)_{331}H$			
$C_{18}H_{37}NCO$ mod-1	0.030	0.042	1.4
$C_{18}H_{37}NCO$ mod-2	0.058	0.051	2.0
$HO(EtO)_{531}H$			
$C_{18}H_{37}NCO$ mod-1	0.018	0.030	1.2
$C_{18}H_{37}NCO$ mod-2	0.033	0.032	2.0
$HO(EtO)_{663}H$			
$C_{18}H_{37}NCO$ mod-1	0.029	0.023	2.0

[a] Values >2.0 are reported as 2.0.

the isocyanate[7] (Scheme II). POEs are hygroscopic and contain small amounts of water. In concept, the water can be removed by several procedures: azeotropic distillation using toluene, by melting the polyols under vacuum with stirring at 80 °C, or by freeze-drying techniques. The higher molecular weight materials with high melt viscosities were dried by azeotropic distillation, and for consistency, the lower molecular weight POEs also were dried in this manner. A portion of the solvent was retained in the reaction flask to inhibit mechanical degradation of the POE.[28]

When exact stoichiometric ratios of isocyanate to POE were used, a small quantity of an insoluble white impurity formed in the first 10 min of the reaction. FT-IR spectroscopy identified the impurity as *N,N'*-dioctadecylurea (Scheme II), indicating that drying the POE solutions by azeotropic distillation was not effective in removing all water in the system; therefore, the stoichiometric ratios are altered and incomplete modification occurs. The *N,N'*-disubstituted urea was separated from the HEUR by dissolution in acetone at 50 °C and gravity filtration while warm. The HEUR was precipitated from the clear solution by addition of petroleum ether. Complete modification of the POE was accomplished through the use of a four-fold equivalent excess of isocyanate. After purification of the $C_{18}H_{37}$ adducts, an experimental extent of modification was estimated from the ^{1}H-NMR spectrum ($\delta = 1.3$, hydrophobe methylene group; $\delta = 3.6$, oxyethylene methylene group[29]). A quantitative number for the CH_2-CH_2O units in the starting POE was obtained from the hydroxyl number titration molecular weight. The molecular weight (by hydroxyl number titration) of the POE is factored by the HEUR/POE SEC (number average) molecular weights to provide a "HEUR hydroxyl number molecular weight", which allows the number of CH_2O protons to be calculated. The theoretical number of CH_2 protons of the product is calculated assuming two octadecyl hydrophobes are present per POE chain. The experimental (from the NMR spectra) and theoretical (from the calculations described above) CH_2/CH_2O ratios provide a relative extent of hydrophobe modification (Table II). The ranking assumes that disubstituted ureas and excess reactants are completely removed from the HEUR.

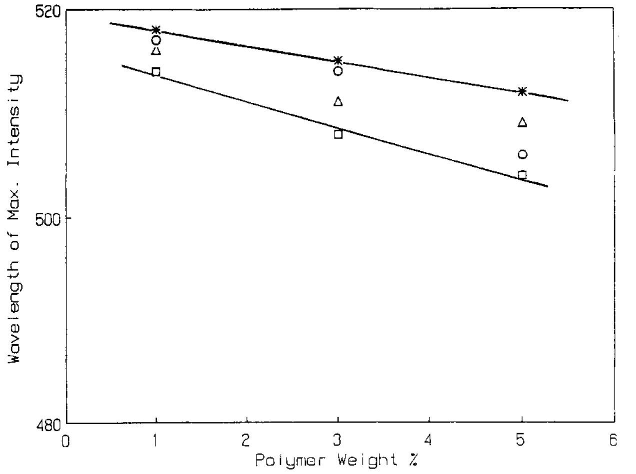

Figure 1. Maxima in fluorescence intensity of ANS/POE solutions as a function of polymer concentration: (○) POE-8140; (△) POE-14340; (□) POE-23569; (*) POE-29219.

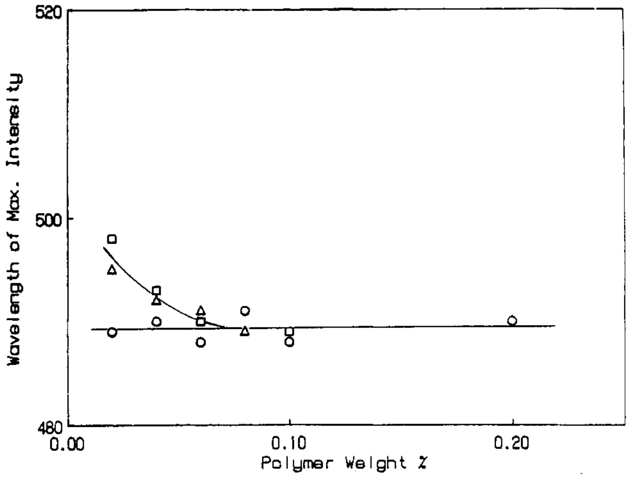

Figure 2. Maxima in fluorescence intensity of ANS/HEUR solutions as a function of HEUR concentration (wt %): (○) $(C_{18}H_{37}NHCOO)_{1.6}(EtO)_{182}$; (△) $[(C_{18}H_{37}NHCOO)]_{1.4}(EtO)_{331}$; (□) $(C_{18}H_{37}NHCOO)_{1.2}(EtO)_{531}$.

In the synthesis of the telechelic POEs, a large excess of the isophorone diisocyanate was used in a two-step addition procedure to prevent chain extension in the first sequence. The excesses of reactants and long reaction times permit the assumption of full hydrophobe modification, but the large quantities of the reaction product of the diisocyanate with the excess hydrophobe and residual hydrophobic alcohol or amine must be removed as described in the Experimental Section.

Fluorescence Spectroscopy and Intrinsic Viscosities. The fluorescent probe ANS[30,31] 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.[31] The emission spectra of aqueous POE/ANS solutions exhibit only a slight decrease in the maximum wavelength with varying concentration (Figure 1). In contrast, the emission spectra of the octadecyl-modified POE/ANS solutions (Figure 2) exhibit a large shift in a maximum wavelength with increasing concentration, indicating that the probe has entered a region of different polarity. It should be noted that the data in Figure 2 were obtained using *partially-modified* thickeners because the fully-modified thickeners phase separate in aqueous media (see below). The fluorescence measurements indicate that a hydrophobic region is formed at very low concentrations through the aggregation of the hydrophobes of the HEUR. For example, $(C_{18}H_{37}NHC(O)O)_{1.4}(EtO)_{331}$ and $(C_{18}H_{37}NHC$-

Table III. Intrinsic Viscosities of Partially-Modified Thickeners

	H_2O		DMF	
	$[\eta]^a$	$[\eta]^b$	$[\eta]^a$	$[\eta]^b$
$HO(EtO)_{182}H$	0.16	0.16	0.17	0.17
$(C_{18}H_{37}NHC(O)O)_{1.6}(EtO)_{182}$	0.17	0.19	0.16	0.17
$HO(EtO)_{331}H$	0.28	0.29	0.30	0.30
$(C_{18}H_{37}NHC(O)O)_{1.4}(EtO)_{331}$	0.24	0.31	0.27	0.27
$HO(EtO)_{531}H$	0.37	0.37	0.38	0.37
$(C_{18}H_{37}NHC(O)O)_{1.2}(EtO)_{531}$	0.51	0.56	0.37	0.37

[a] $[\eta]$ (dL/g) calculated by extrapolation of η_{sp}/c as a function of concentration to zero concentration. [b] $[\eta]$ (dL/g) calculated by extrapolation of ln η_{rel}/c as a function of concentration to zero concentration.

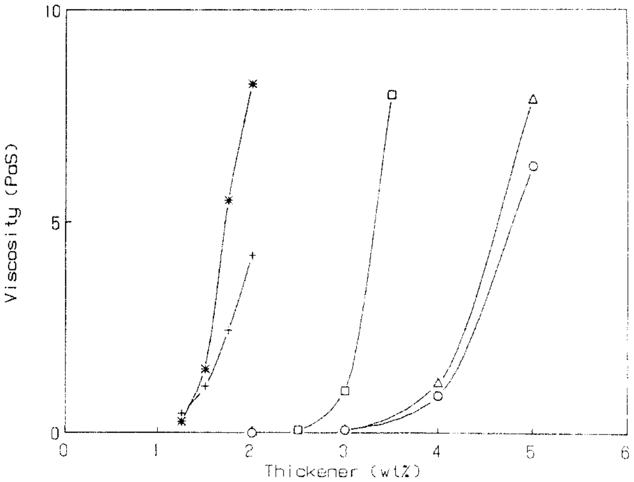

Figure 3. Low shear rate viscosity (2 s^{-1}) of $C_{18}H_{37}$-modified POE as a function of thickener concentration (wt %): (○) $(C_{18}H_{37}NHCOO)_{1.6}(EtO)_{182}$; (△) $(C_{18}H_{37}NHCOO)_{1.7}(EtO)_{182}$; (□) $(C_{18}H_{37}NHCOO)_2(EtO)_{182}$ with 0.002 M SDS; (*) $(C_{18}H_{37}NHCOO)_2(EtO)_{531}$ with 0.002 M SDS; (+) $(C_{18}H_{37}NHCOO)_2(EtO)_{663}$ with 0.002 M SDS.

$(O)O)_{1.2}(EtO)_{531}$ polymers exhibit a change in the maximum wavelength from 498 to 489 nm between the concentrations of 0.02% and 0.10% by weight, and the $(C_{18}H_{37}NHC(O)O)_{1.6}(EtO)_{182}$ thickeners exhibit maximum wavelength shifts at even lower concentrations (Figure 2), well below that used to extrapolate intrinsic viscosity values.

Intrinsic viscosities in organic media provide values unaffected by inter- or intrahydrophobic associations.[32] Small amounts of SDS are necessary to disrupt the gellike appearance of the fully-substituted HEURs; this would negate the importance of intrinsic viscosity data for the fully-modified HEURs. The intrinsic viscosities of the partially-substituted HEURs in water are reported in Table III. The intrinsic viscosity of $(C_{18}H_{37}NHC(O)O)_{1.2}(EtO)_{531}$ is high, despite its low average extent of modification. The data complement the conclusions drawn from the critical aggregation concentration (CAC, the transition point from a gradual to abrupt viscosity increase with increasing concentration; see Figures 3 and 4) and viscosity efficiencies with surfactant in the sections to follow. The partially-substituted HEURs contain unreacted POE and monosubstituted POE, which negate a significant interpretation of the results.

Phase Separation and Low Shear Rate Viscosity. The $(C_{18}H_{37}NHC(O)O)_{1.6}(EtO)_{182}$ and $(C_{18}H_{37}NHC(O)O)_{1.7}(EtO)_{182}$ thickeners, not fully-modified, formed homogeneous aqueous solutions. The thickener possessing the greatest hydrophobe content of this series, $(C_{18}H_{37}NHC(O)O)_2(EtO)_{182}$, exhibits a clear, phase-separated lower layer upon standing. This general phase separation trend was observed for all fully-modified $(C_{18}H_{37}NHC(O)O)_2(EtO)_x$ HEURs of varying oxyethylene molecular weights. Among the NPIP series the $(NPIP)_2(EtO)_{182}$ and $(NPIP)_2(EtO)_{331}$ thickeners exhibited phase-separated aqueous solutions, whereas $(NPIP)_2(EtO)_{531}$ and $(NPIP)_2(EtO)_{633}$ formed clear, homogeneous solutions. Thus, phase separation of HEUR thickeners is dependent on the size of the hydrophobe and the number of oxyethylene units between the hydrophobes and, as will be discussed in a future manuscript, on the molecular weight distribution of the HEUR.

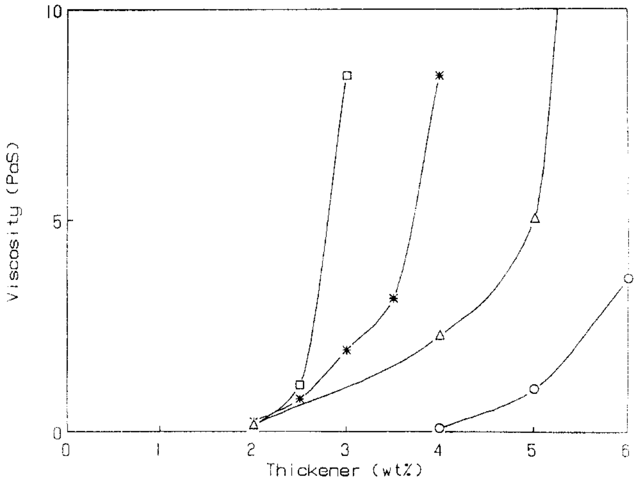

Figure 4. Low shear rate viscosity (2 s^{-1}) of NPIP-modified POE as a function of thickener concentration (wt %): (○) $(NPIP)_2(EtO)_{182}$ with 0.002 M SDS; (△) $(NPIP)_2(EtO)_{331}$ with 0.002 M SDS; (□) $(NPIP)_2(EtO)_{531}$ with 0.002 M SDS; (*) $(NPIP)_2(EtO)_{663}$ with 0.002 M SDS.

The viscosity dependence on concentration of two partially-substituted and three fully-substituted octadecyl derivatives is illustrated in Figure 3. With increasing extent of hydrophobe modification, the viscosity build occurs at lower concentrations. The fully-modified thickeners were studied with 0.002 M SDS, added to disrupt the gellike phase-separated lower layer. The fully-modified thickeners also reflect the influence of the oxyethylene spacer length. The $(C_{18}H_{37}NHC(O)O)_2(EtO)_{531}$ thickener exhibits a greater increase in viscosity at lower concentrations than either a fully-modified $C_{18}H_{37}$-HEUR with a smaller or larger oxyethylene spacer length. The same trend was exhibited by the $(NPIP)_2(EtO)_x$ model thickeners (Figure 4). Pyrene-modified POE exhibits a greater amount of intramolecular associations when separated by 100 oxyethylene units than when separated by 200 oxyethylene units.[33] This prior fluorescence study with the low shear rate viscosity data suggests that the shorter oxyethylene chain lengths promote intramolecular associations in aqueous media. When the oxyethylene spacer length is small, the hydrophobes from the HEUR thickener tend to enter the same hydrophobic domain. The viscosity increases with increasing spacer length, until the concentration of hydrophobes falls below an effective level for maximum domain participation. Thus, the two different series of model HEURs have delineated a common trend in surfactant-modified water-soluble polymers.

Surfactant Influences. The viscosity dependence of the fully-modified $(C_{18}H_{37}NHC(O)O)_2(EtO)_x$ HEURs on concentration of the anionic surfactant SDS and of the nonionic surfactant $C_8H_{17}C_6H_4O(EtO)_{10}H$ is illustrated in Figures 5 and 6, respectively. With the nonionic surfactant, the lower surfactant concentration represents that required to achieve soluble thickener solutions. A

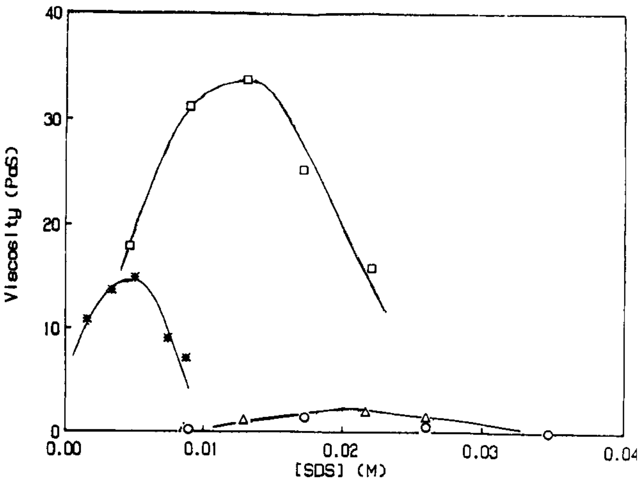

Figure 5. Low shear rate viscosity (2 s^{-1}) of 2 wt % $C_{18}H_{37}$-modified POE as a function of SDS molar concentration: (○) $(C_{18}H_{37}NHCOO)_2(EtO)_{182}$; (△) $(C_{18}H_{37}NHCOO)_2(EtO)_{331}$; (□) $(C_{18}H_{37}NHCOO)_2(EtO)_{531}$; (*) $(C_{18}H_{37}NHCOO)_2(EtO)_{663}$.

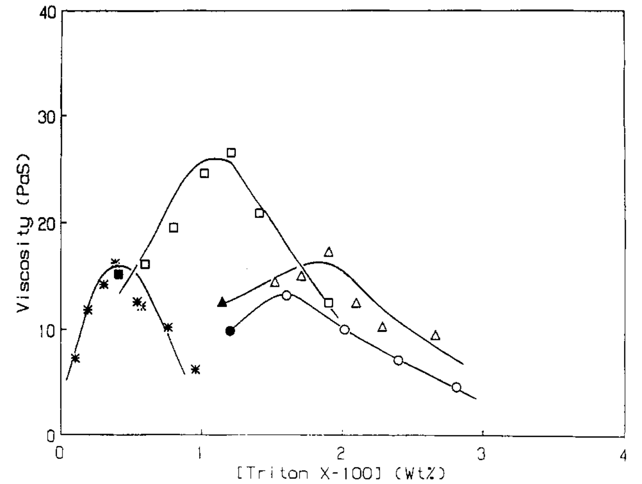

Figure 6. Low shear rate viscosity (2 s^{-1}) of 2 wt % $C_{18}H_{37}$-modified POE as a function of Triton X-100 concentration (wt %): (○) $(C_{18}H_{37}NHCOO)_2(EtO)_{182}$; (△) $(C_{18}H_{37}NHCOO)_2(EtO)_{331}$; (□) $(C_{18}H_{37}NHCOO)_2(EtO)_{531}$; (*) $(C_{18}H_{37}NHCOO)_2(EtO)_{663}$. Filled symbols represent the minimum amount of nonionic surfactant needed to achieve solubility.

molecular weight influence on the magnitude of the maxima is evident with both surfactants. As the number of oxyethylene units between the terminal hydrophobes is decreased, the concentration of terminal hydrophobes will increase (in constant weight percent studies). An increase in viscosity would be expected on the basis of an increasing hydrophobe content. This is not observed due to prevalent intramolecular associations. The optimum spacer length to achieve the highest viscosity appears to be approximately 500 oxyethylene units.

The highest viscosity in the NPIP series also occurs at this spacer length. The significant difference in hydrophobe size is the primary factor for the lower viscosity of the 4% $(NPIP)_2(EtO)_{182}$/SDS solutions relative to the viscosity of a 2.5% $(C_{18}H_{37}NHC(O)O)_2(EtO)_{182}$/SDS solution (Figure 7). The larger hydrophobe may effect an increase in viscosity by several modes. The most probable mechanism is chain entanglement of the larger and more flexible hydrophobe in the aggregate,[34] which increases the viscosity and residence time in an aggregate or surfactant micellar structure.

The nonionic surfactant effects a viscosity ca. equal in magnitude to that observed with SDS. This equality also is observed in the $(C_{18}H_{37}NHC(O)O)_2(EtO)_x$ series (Figures 5 and 6). In the current study, $C_8H_{17}C_6H_4O(EtO)_{10}H$ is used as the nonionic surfactant, instead of *b*-$C_{13}H_{27}O$(EtO)$_9$H. The aromatic-containing nonionic surfactant is used frequently in our competitive adsorption studies on model latices[35] because of the analytical (U.V.) sensitivity on the phenyl unit. Both nonionic surfactants effect viscosity increases similar in magnitude to that of SDS. Viscosity increases of this magnitude are not observed with nonionic surfactants when the associative thickeners are surfactant-modified (hydroxyethyl)cellulose or alkali-swellable emulsions.[36] These observations will be expanded upon in a later article with model HEURs prepared by step-growth mechanisms, where other significant differences are observed in the presence of SDS and $C_8H_{17}C_6H_4O(EtO)_{10}H$ when the size and shape of the terminal hydrophobes are varied.

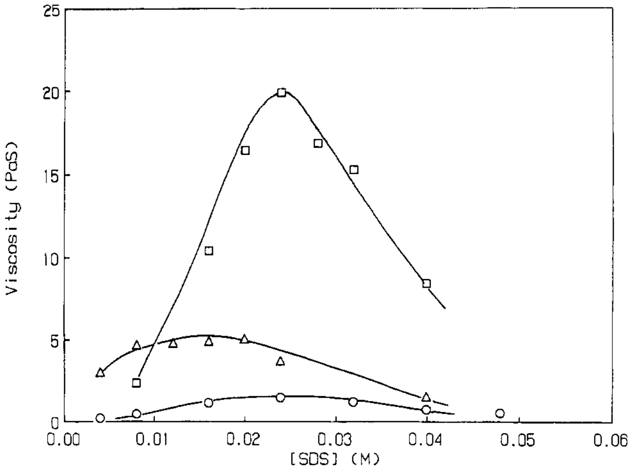

Figure 7. Low shear rate viscosity (2 s^{-1}) of modified POE as a function of SDS molar concentration: (○) 4% $(NPIP)_2(EtO)_{182}$, (△) 4% $(NPIP)_2(EtO)_{331}$; (□) 2.5% $(C_{18}H_{37}NHCOO)_2(EtO)_{182}$.

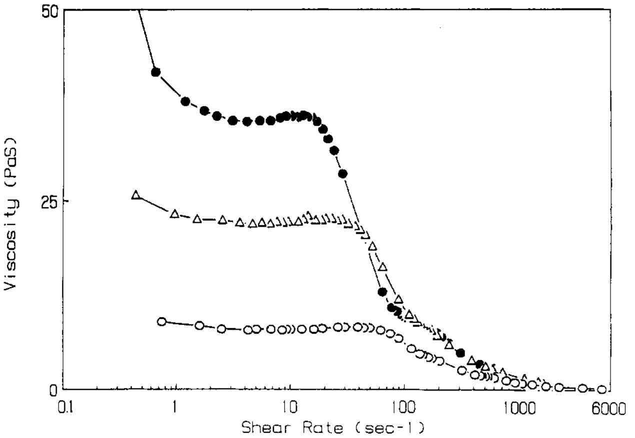

Figure 8. Viscosity as a function of shear rate (scan completed in 3 min) for $(C_{18}H_{37}NHCOO)_{1.4}(EtO)_{331}$ thickener: (○) 4 wt % solution; (△) 5 wt % solution; (●) 4 wt % solution with 0.012 M SDS.

Variations of Viscosity with Shear Rate. The SDS concentrations used in this section correspond to the levels required to achieve a viscosity maximum under steady-state conditions with the HEUR studied. Significant solution viscosity increases are observed when SDS is added to partially substituted HEURs that contain mixtures of di- and monosubstituted HEURs and unreacted POE. For example, the viscosity variances of $(C_{18}H_{37}NHC(O)O)_{1.4}(EtO)_{331}$ with increasing shear rate (total scan for these deformation studies was taken in 3 min) is given in Figure 8. Shear thickening is observed at moderate shear rates with this partially-modified HEUR, particularly in the presence of SDS. Shear thickening, previously observed in HEURs prepared by step-growth

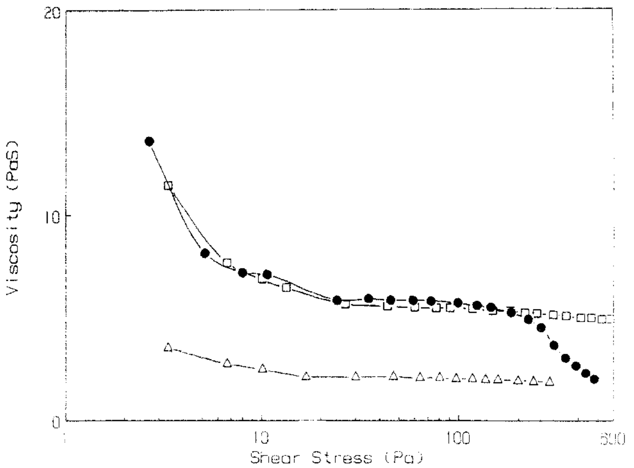

Figure 9. Viscosity as a function of shear stress for $(NPIP)_2(EtO)_{331}$ thickener (scan completed in 3 min): (△) 5 wt % solution; (□) 8 wt % solution; (●) 4 wt % solution with 0.024 M SDS.

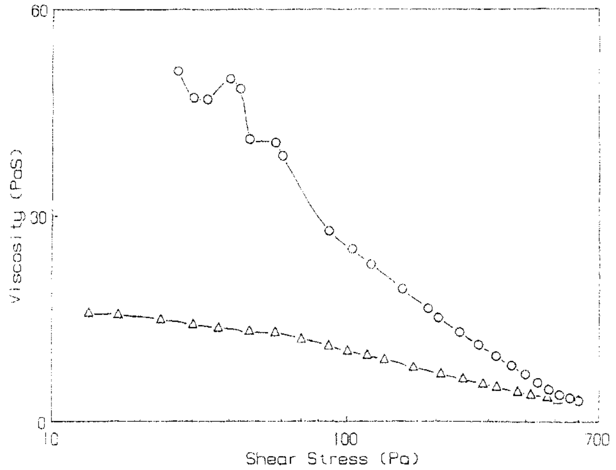

Figure 10. Viscosity as a function of shear stress for 5 wt % $(NPIP)_2(EtO)_{663}$ (scan completed in 6 min): (○) increasing shear stress; (△) decreasing shear stress.

polymerizations, is related to a transition from intra- to interhydrophobic associations as the deformation rate is increased.[3]

The addition of SDS to the fully-substituted, smaller hydrophobe $(NPIP)_2(EtO)_{331}$ thickener effects a viscosity increase comparable to twice the concentration of this fully-substituted telechelic HEUR without SDS (Figure 9). In the absence of SDS, this fully-modified thickener gives a swollen gel appearance, and at a lower concentrations, 4 wt %, it exhibits a clear nonviscous upper layer not observed in the 8 wt % solution. The higher concentration (i.e., 8 wt %) solution and the 4 wt % solution containing 0.024 M SDS appear to approach a yield stress. The surfactant solution network is unstable at higher deformation rates relative to the higher concentration of polymer without SDS (Figure 9). When surfactants are used at concentrations beyond that required for the viscosity maximum at low (2 s^{-1}) shear rates, the HEUR thickener viscosity remains constant over a greater range of higher deformations rates.[37,38]

As the spacer length is increased in the NPIP series at 3 wt %, the HEUR does not exhibit a gellike structure. The critical aggregation concentration is reached at a lower concentration, and a more effective network is generated because of the predominance of intermolecular associations (Figure 3 and 4). Shear thinning is evident in a 5 wt % $(NPIP)_2(EtO)_{663}$ solution (Figure 10), and a marked hysteresis is observed in this study. The shear viscosity of surfactant-modified, water-soluble polymers can be very sensitive to the sample's shear history.

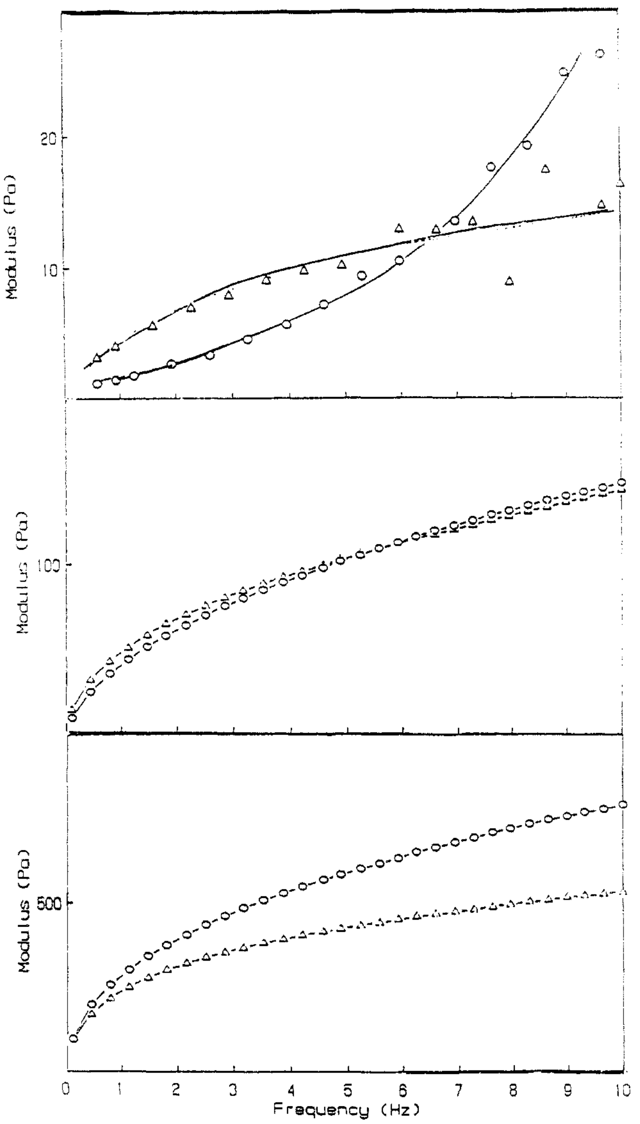

Figure 11. Storage (○) and loss (△) moduli as a function of frequency for $(NPIP)_2(EtO)_{663}$: (a) 3 wt % solution; (b) 5 wt % solution; (c) 8 wt % solution.

Oscillatory Rheology Studies. The above interpretations are supported by oscillatory measurements that allow the network structure to be estimated from the elastic component (storage modulus). In the $(NPIP)_2(EtO)_{>600}$ HEUR, the viscosity is markedly shear thinning and dramatically thixotropic (Figure 10). As the concentration of $(NPIP)_2(EtO)_{663}$ is increased from 3 to 8 wt %, the storage modulus is clearly the dominant contributor over the entire angular frequency range (Figure 11). When the spacer length is decreased, the hydrophobe concentration is increased at a given weight percent, but the oscillatory responses of $(NPIP)_2(EtO)_{331}$ (Figure 12) below the critical aggregation concentration exhibit little elastic contribution and SDS addition does not promote an elastic response.

As the hydrophobe size is increased [i.e., $(octadecyl)_x(POE)_y$], strong gels are observed with all spacer links, and soluble SDS solutions are very elastic. The partially-substituted product $(C_{18}H_{37}NHC(O)O)_{1.4}(EtO)_{331}$, although promoting large viscosity increases, exhibits a dominant elastic response only at high oscillatory frequencies and at high concentration (8 wt %, Figure 13). The addition of SDS promotes a significant network in a 4 wt % $(C_{18}H_{37}NHC(O)O)_{1.4}(EtO)_{331}$ solution (Figure 14), even though it is a mixture of components that include

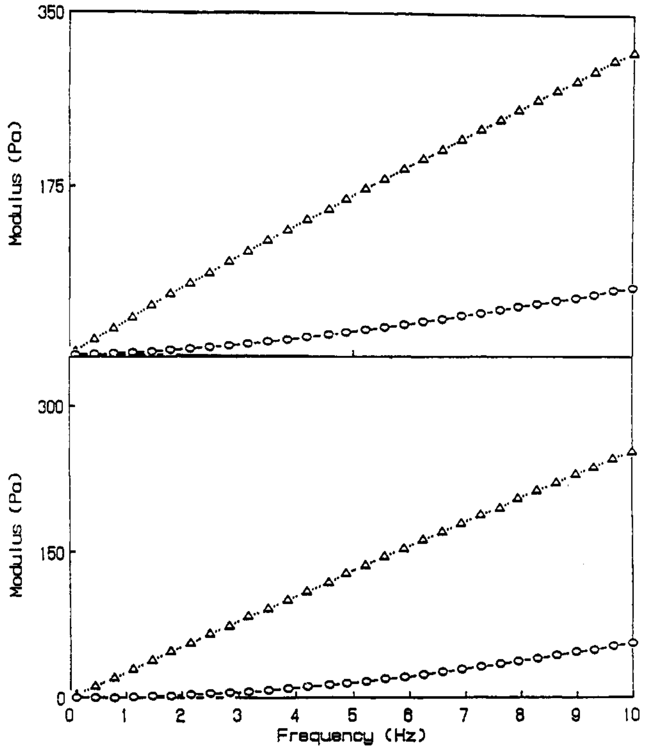

Figure 12. Storage (○) and loss (△) moduli as a function of frequency for $(NPIP)_2(EtO)_{182}$: (a) 8 wt % solution; (b) 4 wt % solution with 0.024 M SDS.

mono- and unsubstituted POE. The surfactant system exhibits a longer relaxation time (the reciprocal of the frequency at the storage/loss moduli crossover point[39]), reflecting a more complex aggregate than the HEUR at 8 wt % without SDS.

Conclusions

An examination of two well-defined series of hydrophobically-modified ethoxylated urethane (HEUR) polymers has provided some definition of the structural influences of HEUR thickeners on their role as rheology modifiers. For example, phase separation of HEUR thickeners in the absence of disperse phases is dependent on the size of the hydrophobe and the number of oxyethylene units between the hydrophobes. Solution viscosities also are influenced by these two parameters. Increasing the oxyethylene spacer length between the hydrophobe increases the solution viscosities by promoting less intramolecular and more intermolecular hydrophobic HEUR associations. This effect continues until the concentration of polymer hydrophobes, with increasing oxyethylene content, falls below an effective level for maximum domain participation.

The solution viscosity dependence on these parameters is evident with increasing HEUR concentration. The phenomenon also is evident in studies slightly above their critical aggregation concentration (4 wt %) with increasing surfactant concentration. The latter study includes both anionic and nonionic surfactants. Two observations are made that are definitive with respect to HEURs as rheology modifiers: (1) Nonionic surfactants effect viscosities equivalent to that of the classical anionic surfactant sodium dodecyl sulfate. This is not observed with other commercially important hydrophobically-modified, water-soluble polymers. (2) For HEURs with low polydispersity, the critical aggregation concentration is lowest when 500 oxyethylene units separate the terminal hydrophobes. In future papers the synthesis, characterization, and rheology of HEURs prepared by step-growth polymerizations will be presented and the effect of molecular weight distribution of the HEURs will be addressed.

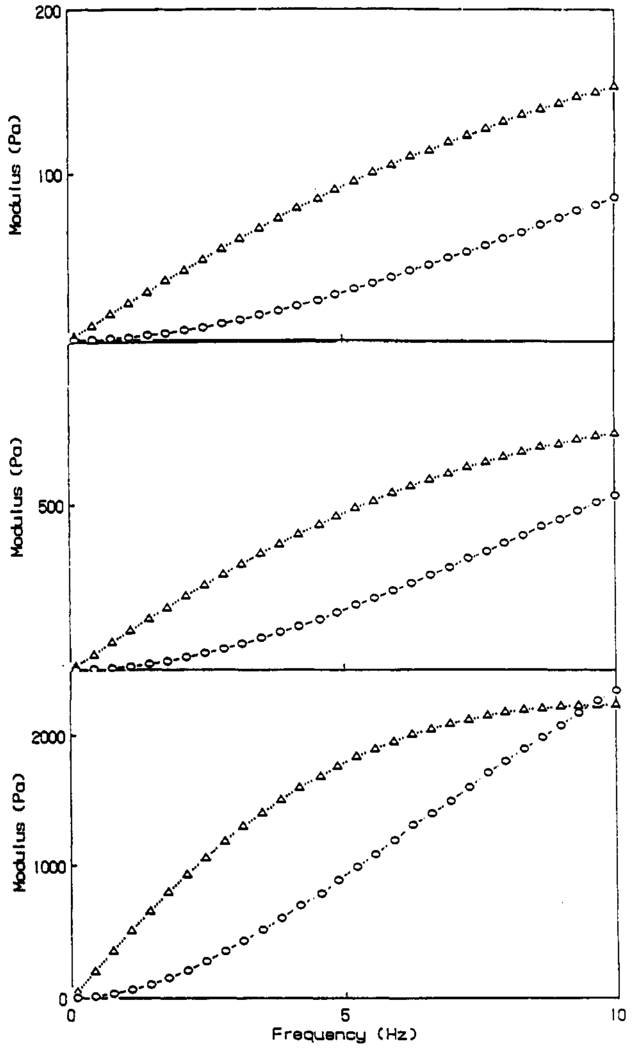

Figure 13. Storage (○) and loss (△) moduli as a function of frequency for $(C_{18}H_{37}NHCOO)_{1.4}(EtO)_{331}$: (a) 4 wt % solution; (b) 5 wt % solution; (c) 8 wt % solution.

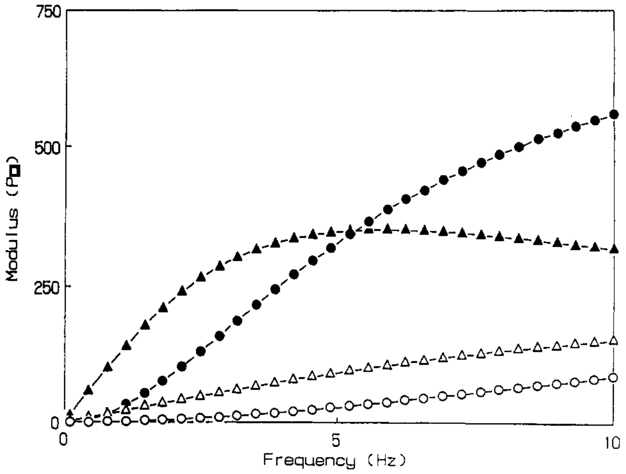

Figure 14. Storage (○) and loss (△) moduli as a function of frequency for 4 wt % $(C_{18}H_{37}NHCOO)_{1.4}(EtO)_{331}$: open symbols, no surfactant; closed symbols, 0.012 M SDS.

It might have been anticipated that the diisocyanate used in synthesizing the telechelic nonylphenol-capped HEURs would contribute to the overall hydrophobicity of the hydrophobe strength and that rheology comparable to that for the direct synthesis of octadecyl-modified HEURs would have been observed. With isophorone diisocyanate, there is no direct evidence in the studies to date that the rigid alicyclic structure contributes to the overall hydrophobicity of the terminal hydrophobe. In related studies from our laboratories other diisocyanates have been found to make such a contribution. Our studies in this area reveal that the influence of such diisocyanates is more complex and is under active study.

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