A Perspective on the History of and Current Research in Surfactant-Modified, Water-Soluble Polymers

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In this review of surfactant-modified, water-soluble polymers, a definition of terms and their historical development is given for each associative polymer type. Studies that have contributed to a fundamental understanding of the structural influences of these associative polymers on the solution behavior of such thickeners are reviewed critically avoiding the sales approach and over exuberance[1] exhibited in so many publications in this area of coatings science.

GENERAL ASPECTS OF THE OVERVIEW

A clarification of material terms is given in the following. A brief history on each class of polymer is given and followed by research developments in each area in the Adsorption and Stabilization Section primarily from 1996, when the last book[2] this author edited was published.

Hydrophobically-Modified Poly(AcrylaMide)

In applications, a hydrophobically-modified monomer, CH_2=CHCONHR, is copolymerized by a chain growth mechanism with hydrophilic acrylamide and acrylic acid monomers. In most of the original Exxon studies, these polymers were referred to as RAM. The details in controlling structural features in HMPAM synthesis are give in the Adsorption and Stabilization Section and presented in detail in Chapter 7 of reference 118.

Hydrophobically-Modified Ethoxylated Urethane

Hydrophobically-modified Ethoxylated Urethanes (HEURs) are generally synthesized commercially by a step-growth polymerization of a diisocyanate (in slight excess) with a 6,000 to 8,000 molecular weight oxyethylene diol (POE). This produces a broad distribution of products, generally with isocyanate terminal linkages, that are then reacted with hydrophobic alcohols. In general, all of the terminal positions in the gamish of products are not substituted, and the lower molecular weight substituted POEs form strong intramolecular hydrophobic associations due to small spacer lengths between the terminal hydrophobes. This is important since the internal urethane linkages do not contribute to hydrophobic domain associations. Narrow molecular weight HEURs can be produced by the direct reaction of higher molecular weight POEs with monoisocyanates. They can also be synthesized through the reaction of POEs with a large excess of a diisocyanate (to avoid chain extension of the POE) and then reacting this isocyanate intermediate at both termini with a hydrophobic alcohol or amine. The reaction schemes were originally given in references 20 and 21.

Hydrophobically-Modified Derivatives of HydroxyEthyl Cellulose and Ethylhydroxyethyl Cellulose

As discussed in the first text in this series (Advances 213, reference 8), the world's most abundant polymer, cellulose, is water-insoluble. Various industrial organizations use an alkali-water cellulose (A/C) dispersion process to disrupt the intra- and inter-hydrogen bonding in cellulose. A/C is then reacted with a variety of adducts to produce cellulose ethers that are water-soluble. The general structures of such products are given in Chapter 1 in reference 8 and their hydrophobe modification is discussed in Chapter 10 of reference 2.

Hydrophobically-Modified Alkali-Swellable Emulsion

Methacrylic acid and ethyl acrylate are the primary monomers of a Hydrophobically-modified Alkali-

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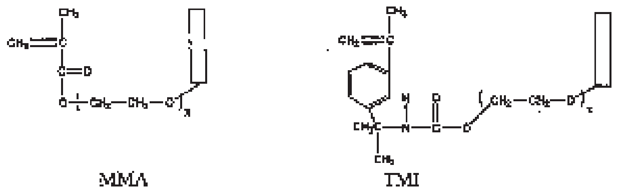
Swellable Emulsion (HASE) thickener, generally in equal amounts. They are terpolymerized with a relatively small amount of a hydrophobically-modified monomer (HPM) and 0 to 20 wt% of a divinyl crosslinker is used to hold the latex together when the acid groups are neutralized to increase the viscosity. The highly swollen "particles" have a refractive index close to that of water, and the dispersion appears to be water-soluble. Some portion of the distribution of products should be soluble. The product also contains crosslinks to minimize the dynamic uniaxial extensional viscosity that would be present in a high molecular weight soluble thickener. A semi-continuous emulsion polymerization is used in the synthesis of HASE thickeners. The structure of the two most commonly used HPMs are:



DRIVING FORCES FOR THE ACCEPTANCE OF ASSOCIATIVE THICKENERS

There are generally four parameters responsible for the commercial acceptance of surfactant-modified, water-soluble polymers.

(1) Minimizing the extensional viscosity of thickened solutions and aqueous dispersions. In non-coating applications, this is reflected in less mechanical degradation[3] of the thickener. In coatings this relates to lower elasticity and less spatter[4] in roll applications and better misting[5] in spray applications.

(2) Obtaining coating formulations with higher viscosities at high shear rates[6] ($>10^4 s^{-1}$).

(3) Achieving lower viscosities at low shear rates[6] ($<2\ s^{-1}$) in coating formulations that have met the criterion in (2), particularly in formulations containing small particle latices (<100 nm).

(4) Stabilizing disperse phases in aqueous media that result in better applied coating properties, such as film gloss.

ASSOCIATIVE POLYMERS: STRUCTURAL DISTINCTIONS

Hydrophobically-Modified Acrylamide

High molecular weight (10^7) acrylamide polymers are synthesized by a free radical, chain-growth polymerization. Polymers are produced because of the high propagation to termination rate constant ratio and the propagating radical's low chain transfer to monomer. Polyacrylamides (PAMs) are produced as copolymers with acrylic acid (HPAMs) for petroleum applications because the neutralized comonomer acid units mini-

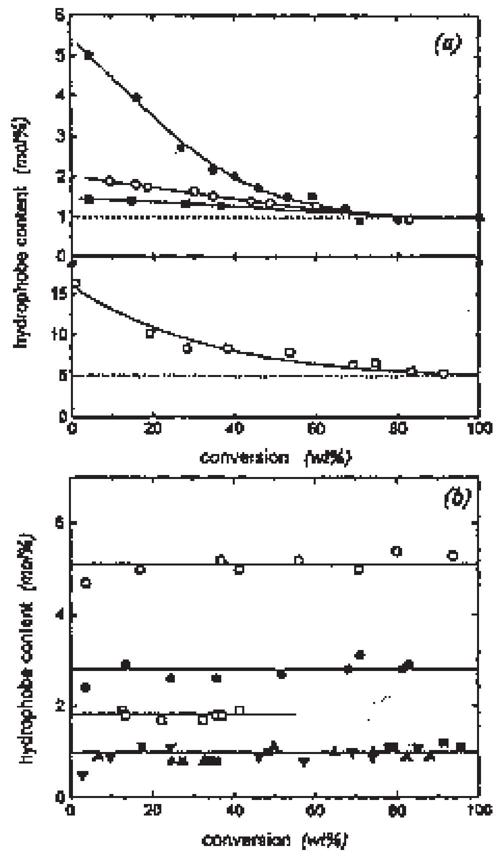


Figure 1—Variation of the copolymer composition as a function of conversion for the copolymerization of acrylamide with various N-monosubstituted acrylamides (a); and N,N-disubstituted acrylamides (b) at different initial contents in the monomer feed ((H), mol%) and different N_H values; (a) N-butylphenylacrylamide, (H) = 1; N_H = 1.5 (■), N_H = 2.6 (O), N_H = 9.9 (•). N-hexylacrylamide, (H) = 5, N_H = 7.7 (❑) and (b) N-methyl-N-hexylacrylamide, (H) = 5, NH =7.7 (0); (H) = 3, NH = 3 (•), N-methyl-N-ethylphenylacrylamide, (H) = 2, N_H = 4.1 (❑). N,N-dihexylacrylamide, (H) =1, NH = 1 (■); N_H = 2.7 (▼), N_H = 4 (▲); from reference 13.

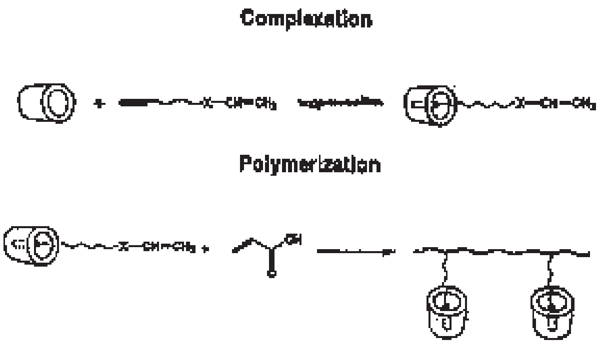


Figure 2—Cyclodextrin mediated solution polymerization of a hydrophobically-modified monomer with acrylic acid. Free radical initiator.

mize adsorption[7] on subterranean substrates. However, high molecular weight HPAM polymers are difficult to solubilize and notorious for their susceptibility to mechanical degradation.[8] Preparation of HPAM polymers via inverse emulsion polymerizations was one approach to bypassing the mechanical degradation problem during solubilization, but this did not address their instability during application. Hydrophobe modification was intended to minimize mechanical degradation. Dow and Exxon workers (the patents are listed in reference 3, pages 396 and 410, and will not be relisted here) considered this. Hydrophobe modification would provide the physical bond that could rebuild the hydrodynamic volume, and thus viscosity, at low deformation rates. Separation of the hydrophobe by oxyethylene (EO) units from the main chain and the use of the solubility sensitivity of the EO units to salts and temperature were also considered as a means of enhancing the viscosity at elevated temperatures in this early work, a concept being revisited today.[9]

One of the major concerns in the Dow and Exxon studies was the tendency of the hydrophobes to form multiblock units in the HMPAM copolymers. The number and length of the hydrophobic blocks vary with the initial number of hydrophobes per micelle when prepared by an aqueous micellar copolymerization. In addition to this complexity, compositional variations with conversion occur in a chain-growth polymerization. This was not evident to several academic investigators in the 1980s and '90s. Candau's group in Strasbourg France recognized it during this period (*Figure* 1). In the 1996 period covered in this update, they observed that disubstituted acrylamides lead to a copolymer composition independent of the degree of conversion. This was not observed in monosubstituted acrylamide copolymerizations. Solubility measurements on both types of hydrophobes indicate that micellar dynamics are not responsible for this behavior; the difference in polarity between the bulk phase and the micellar phase is the parameter of importance. This microenvironment effect modifies the reactivity ratios of those hydrophobes capable of forming hydrogen bonds, whereas the reactivity of the disubstituted amides (e.g., dihexylacrylamide) remains unaffected,[10,11] and the composition does not vary with the extent of conversion. The hydrophobes are randomly placed along the poly(acrylamide) backbone, and the length of the block was adjusted by varying the surfactant content used in the synthesis (i.e., by varying the number of hydrophobes per micelle).

The results stress the major role of the hydrophobe distribution in the copolymer for good control of the thickening efficiency of association.[12] These studies have been reviewed[13] recently as part of the associating polymer symposium in Fontevraud, France in November 1997 and will not be discussed in detail here. Candau and Selb discuss the most recent use of specific surfactants to accomplish uniform distribution of the hydrophobic monomers in Chapter 7 of reference 118.

The influence of disubstituted-acrylamide monomers on the rate of polymerization also was highlighted in the work of Hogen-Esch's group. The free-radical copolymerizations of N, N-dimethylacrylamide (DMA) and 2-(N-ethylperfluorooctanesulfonamido)ethyl acrylate (FOSA), monitored simultaneously by F-19 and ^{1}H-NMR spectroscopy, indicated that DMA and FOSA are incorporated[14] at the same relative rates throughout the chain-growth polymerization. These results are discussed, not because RAM or HMPAM polymers are used to thicken coating formulations, but because these fundamental studies are pertinent to HASE thickeners that are primary thickeners in waterborne coatings. HASE thickeners will be discussed later.

A Unique Approach: Capping the Hydrophobe

Aqueous and micellar polymerization processes are economical methods of producing polymers, but as is apparent from the previous discussions, long sequence runs of the hydrophobic monomer will occur, without using an excess of an appropriate surfactant in a micellar process. In an attempt to prepare acrylic acid copolymers with a surfactant monomer such as R–(EO)$_x$–methacrylate (R=$C_{12}H_{25}$– or $C_{18}H_{37}$–; x=20) in water, Lau observed[15] an inhomogeneous polymerization in a semi-continuous emulsion process, in which the less soluble surfactant monomer polymerized preferentially. An insoluble phase was formed while the acrylic acid rich polymer remains fully soluble. He overcame the solubility barrier by optimizing the solubility of the surfactant monomer through formation of an inclusion complex with beta-cyclodextrin (ß-CD). A random copolymerization of the two monomers, illustrated in *Figure* 2, was observed.

The complexation of the hydrophobe is fully reversible, and the ß-CD moiety can be readily displaced from the polymer hydrophobe by the addition of surfactant. The unshielding of the hydrophobes results in an increase in thickening efficiency through association (*Figure* 3). The use of ß-CD as an analytical tool in

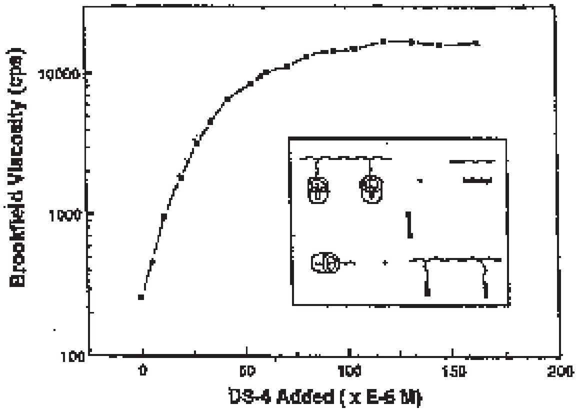


Figure 3—Increases in viscosity with surfactant (DS-4) concentration, reflecting freedom of the polymer hydrophobe from β-cyclodextrin complex. HMPAA M_n ~ 48,000, (four hydrophobes per thickener molecule), 3% solution at pH 9.

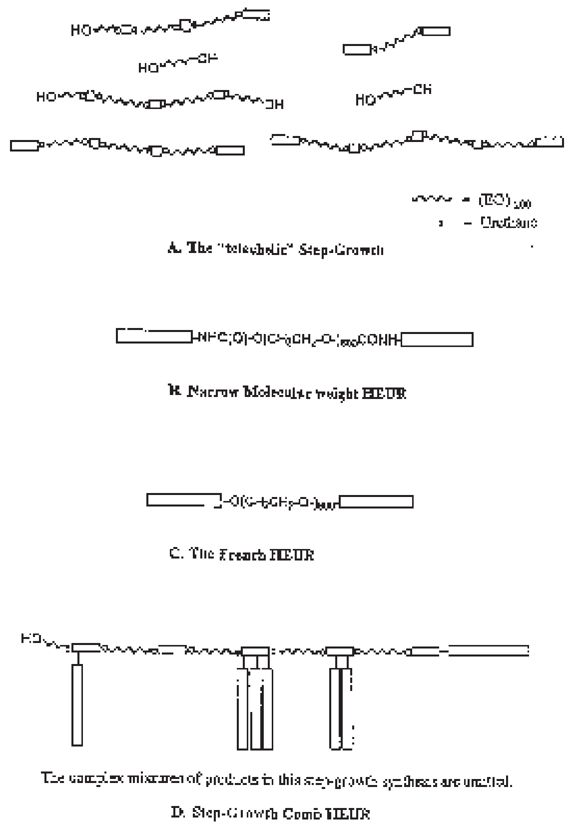


Figure 4—Structures of different HEURs that have been investigated.

associative thickener studies has been described in adsorption[16] studies (given in detail in Chapter 16 of reference 121) and in characterization[17] of HMHEC and HASE thickeners. Wenz and his students describe a unique study of polymer complexes among water-soluble polymers containing hydrophobes and those containing ß-CD groups in Chapter 17 of reference 118.

HEURs

One is impressed with the detail in synthesis and characterization of block copolymers. The area of hydrophobe-modified, water-soluble polymers has only recently approached this level. HEUR thickeners represent an area where unambiguous model associative thickeners can be synthesized and studied; however, much of the research quality in this area has been poor. What is referenced and discussed in the following are the quality studies that have been reported. Cartoon illustrations of HEUR types considered in this subsection are depicted in *Figure* 4. The syntheses of these products are given in references 2 and 3.

SYNTHETIC APPROACHES: A decade ago, after several years of examining commercial associative thickeners to see if there was a significant variation in their influence on coating properties,[18] we initiated model HEUR syntheses,[19,20] using a large excess of diisocyanate to inhibit chain extension of the diol. This provides a polyether with terminal monoisocyanates that can be reacted with a variety of alcohols or amines with variable size alkyl groups to produce a variety of terminal HEUR hydrophobe sizes (Scheme 1 in Chapter 11 of reference 118). One could refer to these as telechelic HEURs, but those studying the S-G HEURs, to draw attention away from the S-G connotation and its broad distribution of products, have used this term, so we designated our narrow molecular weight models as “uni-HEUR.” One can also achieve a narrow molecular weight HEUR by direct addition of a monoisocyanate to a polyether diol,[21] and we also pursued this route to synthesize uni-HEURs. Without synthesizing toxic monoisocyanates in an academic laboratory, one is limited to commercial monoisocyanates with large hydrophobes via this route.

Francois’ group at the University of Strasbourg followed a parallel scenario of first examining commercial products[22] and then undertaking a model synthesis of polyethers with terminal hydrophobes. Based upon their analysis of Rohm and Haas’ RM-8, their subsequent models contained $C_{12}H_{25}$– terminal hydrophobes. These model syntheses did not use isocyanates; a Williamson synthesis placed the hydrophobes in terminal positions[23] with ether connecting linkages. We will refer to this as the “French HEUR,” even though it does not contain urethane linkages. In the middle of the studies described in the following, Almgrens’ group compared hydrophobically-modified polyether diols prepared by both the Williamson synthesis and by coupling with an isocyanate.[24] Both polymers contained $C_{12}H_{25}$ end caps with a $–(EO)_{304}–$ spacer length and were 85% end capped. The results indicate that this subtle difference in polymer architecture dramatically influences the initial association and the clouding of the polymer in water. The urethane linkage starts to aggregate earlier but has a higher clouding temperature; however, at higher polymer concentrations (above 2-3 wt%), the differences in solution behavior and transport dynamics are less significant. Fluorescence, dynamic light scattering, NMR self-diffusion, turbidimetry, and viscosity measurements were used in these studies. It is likely that there would be a significant difference between these thickeners with different hydrophobe interlinks in acidic media due to hydrogen bonding. In basic media, characteristic of the primary applications media for HEURs, a significant difference would not be expected.

In the other significant HEUR study of this period, Annable and co-workers[25] stated that their HEUR synthesis followed the procedure described in the well-referenced Rohm and Haas patent.[26] This is, of course, deliberately vague, for patents make broad claims that describe all possibilities. The Rohm and Haas product is a step-growth thickener. In a private discussion at the 1995 symposium on associative polymers in Loen, Norway, Annable indicated that their products were NOT synthesized by a step-growth process. Recently, Lau of Rohm and Haas has synthesized narrow molecular weight HEURs by the direct addition of large hydrophobe monoisocyanates to polyetherdiols for those in need of real model HEURs in North America.

Most moderate or high molecular weight commercial HEURs are synthesized by a step-growth polymerization process that produces a broad mixture of products[27,28] (*Figure* 4A). From a commercial viewpoint this is not a bad product, for the inefficient thickening of a S-G HEUR requires a coatings formulator to use more of the product. The amount of "thickener" added is one of the main parameters in achieving higher viscosities at high shear rates (10^4 s^{-1}) for small particle latex coatings.[29] The poor viscosifying properties of low molecular weight hydrophobically-modified POE and unreacted POE in a step-growth HEUR synthesis allow the addition of more "thickener" to achieve a "formulation viscosity," but such mixtures are poor products for "fundamental studies." Step-growth HEURs were synthesized in Europe for fundamental studies and these materials were examined, particularly by Hulden,[30] but when the impurities in the step-growth products were realized, studies of these thickeners were stopped. All of the European studies after that point have been conducted with the well-characterized French HEUR. Not all of these samples studied in Sweden were prepared in Francois' group. A sentence in Persson's publication[31] acknowledges Helgren as the individual who prepared the materials in some of the Swedish studies. In this area, as in many other areas in chemistry, there is a general distinction between those who prepare materials and those who gather data on those materials from automated machinery.

A series of step-growth HEURs also was prepared and studied in North America. They were prepared by a commercial supplier and sampled to various academics in North America; it represented a high profile, low cost marketing effort. The synthesis of the S-G HEURs that was used is described in general terms in a well-referenced thesis.[32] The materials were reacted in the melt until the melt was too viscous to stir. The products were then "cured" in an oven for several hours. Different stoichiometries of diisocyanate to diol were used to obtain different molecular weights; however, all of the HEURs produced had essentially the same molecular weight. Considering the high temperatures and presence of oxygen in the curing process, this is not surprising. Two of the HEURs were only slightly higher in molecular weight than the POE used in the synthesis. In publications, the theoretical molecular weights calculated from reaction stoichiometry, not the experimental values, have been reported to retain uniformity with their previous publications and with other research groups who have received the same samples.

Our earlier direct reactions of monoisocyanates with polyetherdiols in equal amounts did not provide complete substitution of both hydroxyl groups due to the difficulty in totally removing water from the diol.[21] The partially substituted HEURs are inefficient viscosifiers (*Figure* 5). This study denoting the importance of the extent of terminal substitution led Winnik's group to examine the extent of terminal substitution of the commercially sampled S-G HEURs. Some materials had less than 0.9 substitution of the two terminal positions.[33] The best of the materials had a degree of substitution of 1.7.

With the possibility of degradation and branching through the oxyethylene chain and trimerization of the isocyanate units at high reaction temperatures, it is difficult to imagine all of the hand waving such commercially supplied materials have received. Unlike the turnaround in Europe, the study of these materials has continued with little real technical benefits to the area. Those interested in a direct comparison of narrow molecular weight model HEURs with step-growth HEURs, of the same compositions prepared under less brutal mixing and temperature conditions are referred to a relatively recent publication.[34] In the paragraphs to follow, the recent literature studies (1996 to May 1999) of real model HEURs are reviewed.

SOLUTION BEHAVIOR OF MODEL HEURs: In prior studies, Annable and co-workers characterized the rheological response of HEURs by a Maxwellian viscoelastic response. This was consistent with a picture in which stress relaxation occurs via disengagement of a chain end from an association followed by rapid Rouse relaxation of the stressed chain. In a recent study of HEURs and unmodified PEG homopolymers of the same molecular weight, the phase behavior observed is described by a modified form of the Flory-Huggins theory to account for the associations between hydrophobic end groups of the associating polymer chains.[35] The overall polymer concentrations of both phase-separated solutions were measured and found to be identical. In contrast, the viscosities of the two phases were several orders of magnitude different, suggesting that the polymer species in one phase are predominantly HEURs, whereas those in the other phase are mainly unmodified POEs. The two-phase region was observed only when the overall polymer concentrations were above two percent and the mole fraction of the HEUR was

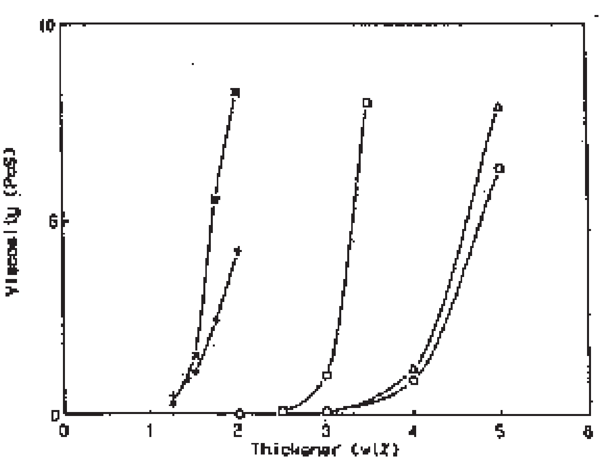


Figure 5—Low shear rate viscosity (2 s^{-1}) of $C_{18}H_{37}$-modified POE as a function of thickener concentration (wt%): (O) $(C_{18}H_{37}\text{-}NHCOO)_{1.6}(Et0)_{182}$; (Δ)$(C_{18}H_{37}NHCOO)_{1.7}(Et0)_{182}$; (❑)$(C_{18}H_{37}\text{-}NHCOO)_2(Et0)_{182}$ with 0.002 M SDS; (*) $(C_{18}H_{37}NHCOO)_2(Et0)_{531}$ with 0.002 M SDS; (+) $(C_{18}H_{37}NHCOO)_2(Et0)_{663}$ with 0.002 M SDS, from reference 21.

below 0.65. It was indicated that these results could be explained quantitatively by considering the effects of association within the Flory-Huggins scheme. The critical mole fraction of HEUR is predicted to be 0.68, in agreement with experimental observations. In the latter case, the tendency for phase separation between the two species of polymers is found to increase rapidly as the hydrophobe size on the associating polymer molecules is increased.[36] It was argued that phase separation is driven by entropic rather than enthalpic considerations.

It is interesting to note that experimental phase separation in our studies has been a problem in fully substituted HEURs at low concentrations, but has not been a problem with step-growth HEURs, in our studies or in those of many other investigators. It has been observed in separate studies[37,38] that blending HEUR thickeners with hydroxyethyl cellulose, a common practice in coating formulations in the 1980s, leads to phase separation in coating formulations. In an earlier text, it is reported that the mixing of hydrophobically-modified, hydroxyethyl cellulose with HEURs led[39] to a more predictive method of formulating coating viscosities at high shear rates. It would be interesting to assess the relative role of enthalpic and entropic contributions to phase separation in these types of blends. To the author's knowledge such studies have not been conducted.

In a very recent study by Russel's group, "the first clear observations" of an entropy-driven phase transition between a dilute micellar "gas" and a disordered but highly associated micellar "liquid" were reported with aqueous solutions of fully end-capped $C_{16}H_{33}$– and $C_{18}H_{37}$–$(EO)_{750}$ –HEURs. Dynamic light scattering and capillary viscometry were used to determine the radii and aggregation numbers of the micelles and, together with the coexisting concentrations, permit estimates of the strength of the entropic attraction through an adhesive hard-sphere model.[40]

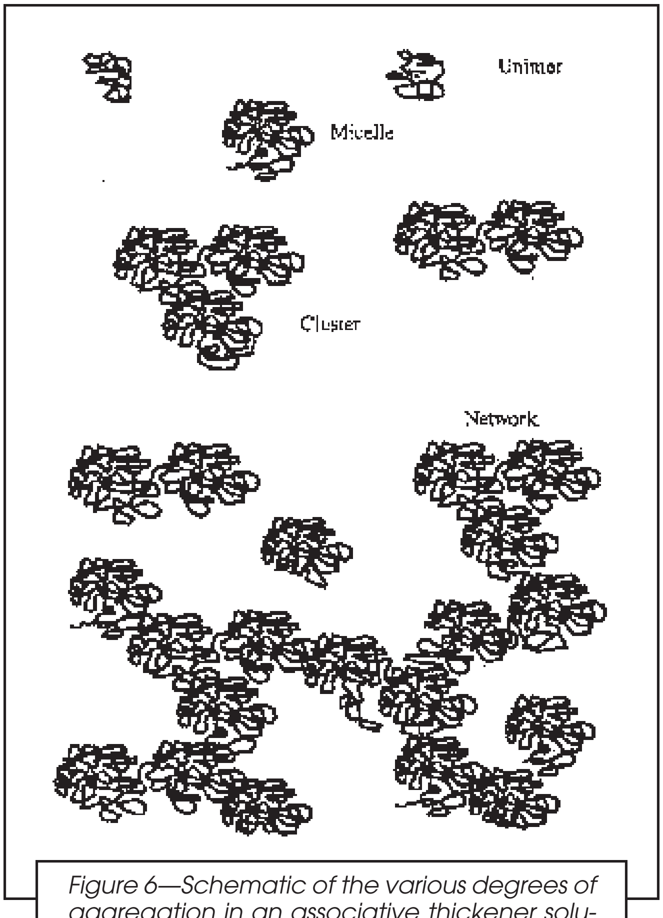


Figure 6—Schematic of the various degrees of aggregation in an associative thickener solution with increasing concentration.

Earlier studies with the French HEUR (*Figure* 4C) revealed that two two-phase regions appear: (1) at low polymer concentration, upon heating above the temperature traditionally called the cloud-point temperature (CPT), and (2) at high polymer content, upon cooling below the crystallization temperature of the PEO chains.[41] Transitions from the micellar solutions to a cubic phase are observed when temperature and molecular weight decrease. Neutron scattering experiments were performed on solutions that exhibit Newtonian or shear-thickening and shear-thinning behaviors as a function of the shear rate. No modification of the scattering patterns was observed in the Newtonian regime; a phase separation is observed during the shear-thinning step.[42]

In other studies of the French HEUR, it was observed that the effect of the hydrophobic end-groups on the self-diffusion (NMR method) of $H_{25}C_{12}$ $(EO)_{200}C_{12}H_{25}$ thickeners is proportional to the polymer concentration and inversely related to the temperature.[43] The variation of the self-diffusion coefficient follows an Arrhenius behavior. The resulting apparent activation energies, $E_{a,}$, increase with polymer content from 15 to 55 kJ/mol in the range 0.5-5.0 wt%, whereas the unmodified PEO exhibits an almost constant E_a of about 25 kJ/mol in the same concentration ranges. Activation energies derived from self-diffusion and low shear viscosity measurements were found to be similar. The distribution of self-diffusion coefficients observed in HEUR systems is discussed in terms of distribution of aggregate sizes at low HEUR content and homogeneity of the network at higher contents. In other studies the distribution of relaxation times from dynamic light scattering indicates three important diffusive modes[44] in the concentration range 3×10^{-3} to 5×10^{-2} g/ml. A fast mode in the dilute region is attributed to unimers or small oligomeric aggregates of $H_{25}C_{12}(EO)_{460}C_{12}H_{25}$. At concentrations near the point where the viscosity rises, an intermediate mode appears. This mode is considered to reflect the cooperative motions of the formed network. There have been many cartoon drawings of the transitions of HEURs in aqueous solution. The one given in *Figure* 6 is from Persson's thesis cover.[45]

In the study of the French HEUR with three spacer lengths, the short spacer (8,000 EO units) exhibited a two-step association model. In the first association, well-defined small clusters are identified; however, these units have a tendency to aggregate. The two steps are not as distinct as observed in non-aqueous telechelic ionomers. In the studies from Durand's laboratory,[46] the two steps were observed to occur simultaneously for larger EO spacers. An examination of these HEURs in the Russian literature, using light scattering and high-speed sedimentation, suggests that the aggregates of HEURs with shorter spacer lengths consist of five macromolecules, whereas the aggregates of long-chain polymers consist of three macromolecules. This would be dependent on the terminal hydrophobe size and concentration. Returning to the urethane linked hydrophobe, Winnik's group has recently found the aggregation behavior of well defined $C_{16}H_{33}$ and $C_{18}H_{37}$ HEURs using two fluoresence phobes, ethylpyrene and pyrene, to be 16 and 21, respectively.[47] The difference is based on the relative solubility of the probes and is discussed in his review of fluorescence studies in Chapter 10 of reference 118.

In our earlier studies,[21] HEURs with small and large EO spacing between hydrophobes (i.e., isophorone urethane linked nonylphenol units only) increased in viscosity with increasing HEUR concentration, but only with the small spacer (200 EO units) was the increase in viscosity NOT associated with an increasing storage modulus. This would be consistent with the "flowered micelle" in many publications; however, in a number of investigations that we have conducted since this early study, HEURs with small EO lengths have exhibited a storage modulus dominance as the viscosity increases with concentration. The studies therefore do not support a flowered micelle. It exists, at best, only under very limited conditions, and that is a conclusion supported by most of the experimental work cited. Indeed a very basic study[48] of pyrene capped POE with variable EO spacings observed that the excimer to monomer ratio in the intramolecular excimer region decreases as the EO spacing increases (*Figure* 7). This basic reference is one that is referenced only by Hulden. The pyrene labeled POE with the largest EO spacing in this 1987 study is less than a third of the length in the HEUR exemplified in the Rohm and Haas commercial product that so many academics have emphasized in their studies. The 1987 study indicates that the tendency to intra-hydrophobically bond will be lower with the larger EO spacing.; therefore, the flowered micelle appears to be an artifact from the study of a poorly defined HEUR. In the >30,000 molecular weight range that most studies have emphasized, the flowered micelle conformation is not likely to occur. Borisov and Halperin in Chapter 8 of reference 118 summarize the theoretical treatment of the conformation of HEURs in aqueous solutions.

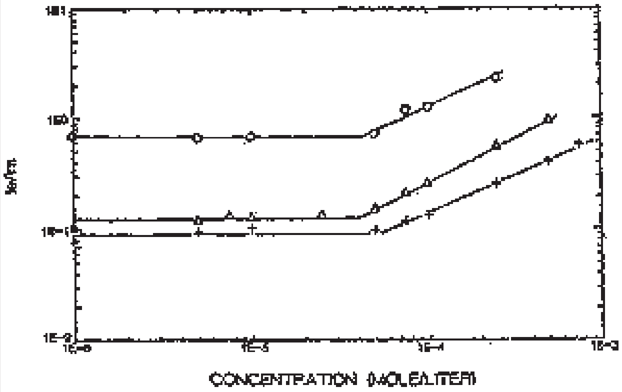


Figure 7—Log-log plot of I_e/I_m ratios as a function of polymer concentration in deionized water for Py-PEG-Py samples of different PEG molecular weights at 298 K: (❑) Py-PEG-Py (4800); (Δ) Py-PEG-Py (9200); (+) Py-PEG-PY (11, 200); (•) phase separation observed.

Comb Type HEURs: In the 1970s, there were numerous patents issued to Dow and Exxon in the RAM or HMPAM area, and there are numerous patents on hydrophobically-modified, alkali-swellable emulsions (HASE) discussed in a section that will follow. Comb type HEUR thickeners arose from the perceived need to by-pass the Rohm and Haas patent.[26] There is a good reason, from a business viewpoint, for being late to the market with an HEUR thickener; every pound gained in sales resulted in lost cellulose ether thickener sales. If there were anywhere near the teeth required in a comb, the intra-hydrophobic associations would collapse the chain and it would be an inefficient viscosifier. The term comb polymer simply infers that there are hydrophobes dangling from the backbone.

In relatively recent times, comb architecture HEUR thickeners have been sampled and evaluated in academic laboratories; in view of the past history of this type of collaboration, the comb polymers were remarkably well characterized. The comb-HEURs, however, are synthesized by a step-growth process, and the limited nature of the thickeners studied provide only limited insights as to what this type of hydrophobe placement can provide. Comb-HEURs are based on the step-growth reaction of POE (M_n=8400) with isophorone diisocyanate and a hydrophobe modified 1,2-diol. After purification, one polymer in this recent study contains 47 µm mol of $C_{14}H_{29}$-groups per gram (ca. 2.5 groups per polymer, ^{1}H-NMR), a second contained 55 µm mol of $C_{14}H_{29}$-groups per gram (ca. 8.8 groups per polymer).[49]

The composition of the 8.8 groups per polymer is close to the commercial comb-HEUR, SCT-200, studied more than a decade ago.[50] This commercial thickener achieved only temporary success because it was too surfactant sensitive. This was corrected in the commercial HEUR SCT-270 thickener, also included in our early studies. In the recent study, the polymer solutions exhibit a strong increase in low shear viscosity for concentrations between 1 and 2 wt%, and a sharp shear thinning transition at a shear rate of ca. 100 s^{-1}. In the studies of this comb-HEUR a decade ago, significant shear thickening also was observed.[51] In the recent study, each micelle contains an average of 15 hydrophobic groups (fluorescence decay experiments). Both dynamic light scattering and pulsed-gradient spin-echo NMR experiments indicate the hydrodynamic radii of the individual micelles formed are on the order of 20-25 nm. Secondary association occurs at concentrations above ca. 0.2 wt%.

The biggest (and perhaps only) asset of the comb-HEUR is their adsorption on and stabilization of disperse phases,[52] discussed in the Adsorption and Stabilization section.

Hydrophobically-Modified Carbohydrate Polymers

Many water-soluble polymers are prepared from carbohydrate polymers. The one that dominated the coatings thickener area from 1961 to the mid-1980s was hydroxyethyl cellulose (HEC). A discussion of cellulose chemistry and its derivatization is given in Chapter 1 of reference 8 and Chapter 10 in reference 2. When HEUR thickeners began to take root in the waterborne coatings market, HEC was hydrophobically-modified (HMHEC). Two other carbohydrate polymers will be discussed in this section: hydrophobically-modified guaran (or guar gum) (HMHPM) and chitosan.

Hydroxyethyl Cellulose Derivatives: Two types of hydrophobically-modified, hydroxyethyl cellulose are discussed in this review. The first type deals with hydroxyethyl cellulose (HEC), described in Landoll's original patent,[53] and whose solution behavior was described in reference 3 by Sau and Landoll and by Goodwin, et al.[54] The second type is the hydrophobe modification of Ethylhydroxyethyl cellulose (EHEC). The initial HEC modified contained 2-2.5 moles of oxyethylene units per repeating anhydroglucose unit. With hydrophobe modification, the number of EO moles was increased to slightly more than three to ensure solubility in the current HMHEC. EHEC, like methylcellulose, is surface active without hydrophobe modification, but it also has been hydrophobically-modified. The oxyethylene segments have been quantified with respect to their placement on the cellulose chain[55]; the oxyethylene units seldom grow beyond two units in length from the cellulose chain. The placement of ethyl groups in EHEC has not been defined, but could be approximated from the distribution of methyl groups in methylcellulose. Placement of the hydrophobes in both HEC and EHEC has not been defined and this is also true for any fluorescence probes attached to the mainchain. To the author's knowledge there have been no new developments among hydrophobically-modified cellulose ethers, so we will move on to the next type of hydrophobically-modified carbohydrate polymer.

Guaran: The structure of guaran or guar gum is significantly more complex than the structure of cellulose. It consists of a simple mannopyranose mainchain (mannose has the 2–OH group in an axial placement; the 2–OH group of glucose in cellulose is in an equatorial position). This alone would make it more water insoluble than cellulose, but guaran contains C–6 galactopyranose branches (there is a difference in the 4–OH placement of galactose relative to glucose). The branching disrupts mainchain hydrogen bonding and crystallinity among the mannose units (*Figure* 8).

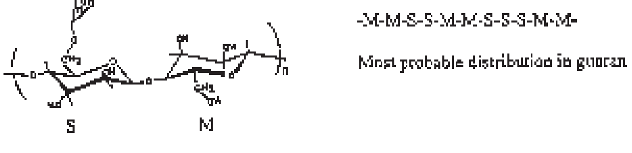


Figure 8—Composition and general structure of guaran or guar gum.

The primary complexity in guaran arises from the placement of the galactose branches on the repeating mannose backbone. In guaran, the ratio of M to G is 2:1, but the galactose branches are not uniformly placed.[56] This structural arrangement results in unique associations leading to "supramolecular order" and viscosity dependence on concentration[57] to the 5.1 power. It is a highly entangled polymer at moderate concentrations. Unlike cellulose, which comes in a pure crystalline state, commercial guaran comes with crushed seed hulls and with ca. 12% of a protein mixture. Part of the purification process (which is never quantitative) involves derivatization of guaran with propylene oxide (HPG). The placement of propylene oxide units on the guaran polymer, a Herculean research effort, has been reported,[58] but like other carbohydrate polymers, hydrophobe placement in a recent commercial guaran[59] is unknown. Based on the data in the patent, even the amount of hydrophobe added to guaran is unknown; however, the hydrophobes used are very large (e.g., mixtures of $C_{22}H_{45}$– to $C_{28}H_{57}$–) and these large hydrophobes are effective in promoting associations in aqueous solution. Aubry and Moan have made some interesting observations[60] with this associative polymer. In their study the samples were presheared at a fixed shear stress for a fixed time. Initially, a large viscosity peak was observed. This was followed in time by a lower steady-state value of the shear viscosity. The transient behavior reveals the existence of a structure that can be destroyed rather quickly when applying a critical shear stress. The steady state flow curve of the hydrophobically interacting HPG shows a discontinuity at a critical shear stress, σ_c=60 Pa. This has been observed in other associative thickener types but its occurrence varies with the structure of the thickener. In the guaran study, the discontinuity of the flow curve at σ_c is not the mark of a gel fracture but corresponds to the point of total destruction of the hydrophobic junction network. Just before the discontinuity and over a short shear stress range, a tendency to shear thicken is observed. This is related to the existence of a competitive process related to the kinetics of association and dissociation, as it has been in other associative thickener systems. At the end of that regime (i.e., just before the discontinuity), the shear rate measured is independent of concentration over 0.75 to 1.5 wt% and has a value of ca. 10 s^{-1}. The characteristic time, defined as the inverse of that shear rate, gives a satisfactory approximation of the order of magnitude of the average lifetime of the associating junctions: 0.1 s. This generally corresponds with other associative thickeners at this concentration. The critical shear stress for complete destruction of the hydrophobic junctions network follows the scaling law, $\sigma_c \sim c^{1.7}$, over the concentration range 0.5-1.5% w/w. The discontinuity presented in this guaran study has been observed in both HEUR and HASE solutions. Similar observations for the "new" HASE resins are discussed in Chapter 23 in reference 118. The viscosity dependence on shear rate of an HMHPG with a higher hydrophobe modification superimposes at high shear rates on an HMHPG of lower substitution, denoting that at high stresses the hydrophobic interactions no longer hinder the chain dynamics and the behavior is that of the non-modified sample.

CHITOSAN: Chitosan is a carbohydrate polymer that offers simplicity because there is an amine group in the 2-position of every repeating pyranose ring (*Figure* 9). The amine group can react preferentially over the numerous hydroxyl groups present, and thereby cause some symmetry of placement for the hydrophobe. Hydrophobe-modification alone would not produce a water-soluble chitosan polymer, but in acidic media, the amine groups can be hydrophobically-modified and protonated. The cationic charges provide water solubility.

Nystrom's group in Oslo has studied, by dynamic light scattering (DLS), the semidilute acidic solution properties of this product with two different degrees of C_{12}-aldehyde substitution. The time correlation data obtained from DLS experiments revealed the existence of two relaxation modes, one single exponential at short times followed by a stretched exponential at longer times. The value of the slow relaxation time increases with increasing concentration and hydrophobicity. The reduced slow relaxation time exhibits a weak temperature dependence for both UM-chitosan and HM-chitosans.[61] Non-linear shear thinning behavior is found at higher shear rates. The magnitude of this effect depends on pH, amount of surfactant, polymer concentration, and hydrophobicity of the polymer.[62]

HASE Thickeners

Alkali-Swellable Emulsions (ASEs) have been around for decades, as a low cost viscosifier, primarily in textile dye applications. The first patent on the hydrophobe modification of ASEs was issued to Sonnabend[63] (Dow); it is discussed in Chapter 10 of reference 2. Their historical development is discussed by Shay,[64] and Jenkins, DeLong and Bassett have also discussed them, with respect to component influences in Chapter 23 of reference 2. As noted in the previous review of this area, the primary components of an HASE thickener are methacrylic acid and ethyl acrylate. Ethyl acrylate is chosen because of its low glass transition temperature and its high hydrophilicity.[65,66] Methacrylic acid is chosen because it will enter the micelle at a low pH. Acrylic acid polymerizes substantially in the aqueous phase, even at low pH.

The conformations of polyacrylic and polymethacrylic acids in aqueous solutions depend on both pH and polymer concentration. At low pH the polyelectrolytes have a hypercoiled spherical conformation. At a pH of ~6 the polymer coils begin to open; at higher pH (ca. 8) the chains are stretched due to the electrostatic repulsion of the anionic groups. A further increase in the pH leads to a recoiling of the polyelectrolytes. This is attributed to an increase in the ionic strength of the solution. At a constant pH in the semidilute concentration region,[67] an increase in the polymer concentration effects a recoiling of the polyelectrolyte chain. Light scattering measurements of filtered solutions of PMAA at higher pHs observe the solutions to be aggregate free. For the partially neutralized PMAA, a discontinuity appears in the range of the conformational transition.[68] In much earlier studies using fluorescence probes,[69] it was observed that PMAA forms microdomains below a pH of 4, but not in higher pH solutions. Since HASE thickeners generally contain 50% MAA, they are primarily polyelectrolytes. An increase in the salt content in the solution causes a reduction in viscosity for all HASE thickeners. This has been demonstrated in four separate publications,[70-73] but it is often ignored in many publications in attempts to draw parallels with nonionic HEUR thickeners. The hydrophobes on the monomer (illustrated previously) used in the emulsion synthesis are spaced from the monomer with EO units; the ether atoms of the EO units will complex with the carboxylic acids units.[74] This is a strong interaction in acidic media but only a moderate one in alkaline solutions when the neutralizing unit is an amine, commonly used in coating formulations.

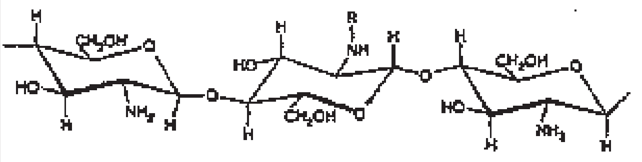


Figure 9—Structure of chitosan

HASE thickeners are synthesized by a chain-growth process, and therefore, should have some characteristics in common with HMPAM or RAM technology discussed earlier. There are two contrasts when compared with HMPAM thickeners. The first is the crosslinking agent used in the synthesis of HASE resins to hold portions of the matrix together when the acid groups are expanding on neutralization.[65,66] This also minimizes the dynamic uniaxial extensional viscosity[75] that results in poor roll[4] and spray[5] applications of coatings. This limits total solubilization on neutralization, but enhances the shear viscosity. A crosslinking agent is used in the original Sonnabend patent and in all patents that have followed. Although the original and the other prior HASE patents are not mentioned in recent HASE publications, the use of crosslinkers is declared in the "new technology" HASE patents,[76] that academics reference in their publications.

The second contrast in an HASE vs. HMPAM thickener comparison is the semi-continuous process used in the synthesis of HASE emulsions. The hydrophobic monomer is held back with lower amounts of the other monomers until the latter stages of the polymerization. This is a necessary procedure in the synthesis of commercial methacrylate latices, when 2-4 wt% MAA is added late to ensure carboxylate group placement on the latex surface for stabilization. This is not needed for an emulsion that contains 40-50% MAA and a hydrophilic comonomer (i.e., ethyl acrylate). In the "new technology" with large hydrophobe HASE thickeners, the largest faux pas is ignoring the technology of HMPAM thickeners discussed in the first section of this article. The generation of smaller particle size latices with most of the hydrophobic monomer in these secondary emulsion drops should occur (*Figure* 10), as was observed in the HMPAM syntheses. In a semi-continuous emulsion process, this is encouraged. Given these complexities, HASE thickeners cannot be considered as models, even though they are touted as such in certain academic studies. Given this insight, the current HASE literature is reviewed in the following.

Increases in viscosity were observed[77] in 1 wt% aqueous HASE "solutions" with increasing hydrophobe sizes (C_{12} to C_{20}). In an examination of variable oxyethylene lengths (2.5, 10, and 40 units) between the urethane linkage of TMI and the hydrophobe unit, an optimum thickening efficiency is observed at 10 moles of an oxyethylene spacer.[78] This seems a little low in view of the 20 EO minimum needed for maximum viscosity in Dow's original styrene/maleic acid/hydrophobically-modified termonomer thickeners and 40 EO moles needed for maximum viscosity in methacrylate thickeners. The interaction of the carboxylate units with the ether oxygens of the EO unit may dictate this in HASE thickeners. It may also be an artifact of the hydrophobic monomer in closer sequences arising in the smaller particle latex sizes during their synthesis.

The major contribution from Tam's laboratory has been in the superposition of oscillations on steady shear flow as a technique for investigating the structure of associative polymers solutions. A steady shear deformation is applied to the fluid, and once the steady state is achieved, a small amplitude oscillation is imposed on the sample. It is very similar to the approach that Dodge and Kreiger applied in studying coating flows.[79] HASE solutions at high pH exhibit a viscosity dependence on shear stress that reveals two distinct regions where network rupture is prominent, at a stress of 2 Pa and between 40 and 50 Pa. The relaxation time is reduced by four orders of magnitude as the stress is increased from 1 to 60 Pa, while a much smaller decrease in viscosity is observed. In similar studies with the $C_{16}H_{33}$– step-growth marketing HEUR, at 2.0 wt%, within the shear-thickening region, the plateau modulus is larger than in the Newtonian region. This is interpreted as the result of a shear-induced increase in the density of mechanically active chains or higher aggregates in the network structure.

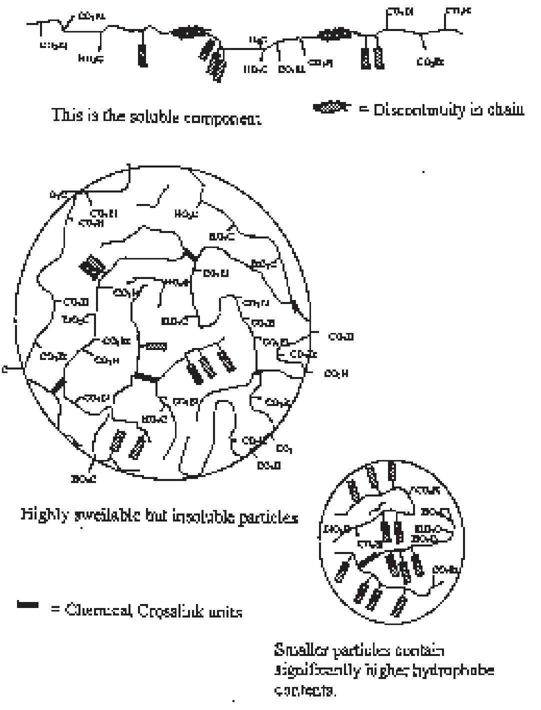


Figure 10—Generalized structure and complexity of a HASE thickener mixture.

HASE thickeners with large hydrophobes have major disadvantages[39,80] in high quality architectural coatings. Such thickeners produce very shear thinning waterborne coatings as the number of intermediate size hydrophobes increase (reference 2, Chapter 24, *Figures* 13 and 14 for HASE influences on coatings rheology). This reflects the depletion flocculation behavior of hydroxyethyl cellulose thickened coatings that formulators wanted to avoid. This is also reflected in HMHEC thickened coatings. The crosslinked HASE thickeners, however, do not add to the extensional viscosity of the formulation as is observed in a high molecular weight HEC thickened small particle latex coating. With increasing size or number of hydrophobes in HASE resins, a decrease in film gloss is observed (*Figure* 11). The carboxylate groups effect adsorption on the pigment (TiO_2) surface, and the large hydrophobe interactions in the aqueous phase of the adsorbed HASE resin apparently flocculate the pigment and result in the lower film gloss. When the pigment has been prestabilized (discussed later) with a low molecular weight hydrophobe containing polyacid, association with the hydrophobes of HMHEC promote improved gloss (*Figure* 11).

HASE thickeners have the lowest production costs of any associative thickener, and there is always a market for low cost materials. The markets are identified in Chapter 21 of reference 118. Some of the markets for HASE thickeners include paper coatings, where early water retention in high kaolinite formulations is an asset, lower cost architectural coatings that are high in clay content, and airplane deicers (a market where glycol ethers are important and shear thinning viscosity and yield stress values are assets).

The above comments are made with previous studies in mind. For example, in earlier studies on roll spatter,[4] a relatively low molecular weight, acrylic acid/ethyl acrylate (Acrysol G-110, Rohm and Haas) was used as a thickener. The vinyl acrylic latex coating had a significant dynamic uniaxial extension viscosity (DUEV) and spattered excessively. This we attributed to a high molecular weight fraction in the commercial material. In later studies at NDSU,[119] we added low concentrations of a six million mole wt. POE to a low mole wt. (i.e., 20,000) POE at high concentrations (~20 wt%). Neither POE, at their respective concentrations, exhibited a DUEV, but the combination provided a substantial DUEV and this POE/POE combination exhibited a significant ribbing pattern on a Giardano coater. This influence of high molecular weight fractions can be circumvented via the crosslinking discussed in HASE patents.

There have been recent introductions of non-crosslinked HASE thickeners[120]; this does not seem compatible with the previous statements. In our recent study of HEUR structural influences on spray behavior, we unexpectedly observed that large hydrophobes resulted in lower DUEVs than higher concentrations of HEURs with smaller hydrophobes.[5] This difference resulted in the desirable misting with the larger hydrophobe HEUR. The newer non-crosslinked HASE thickeners have larger hydrophobes than the ones we have studied and it may well be that the larger hydrophobes can offset the broad molecular weight distribution with high molecular weight tails in a copolymerization of ethyl acrylate and acrylic acid, resulting in better application behavior.

It also has been suggested that the new HASE resins are capable of achieving high gloss coatings. Ethyl acrylate/acrylic acid copolymers are well hydrated and affect good flow and leveling behavior in a coating when not crosslinked. While the stabilizing or destabilizing influence of a thickener on TiO_2 is important to film gloss, the latex can also influence the flow and leveling behavior of a coating and thus film gloss. A decade ago, it was noted that associative thickeners are very "system specific." Our observations reflect the film gloss of crosslinked HASE thickened coatings with small particle latexes, which reflect that the greater the number of hydrophobes in a HASE thickener, the poorer the film gloss.

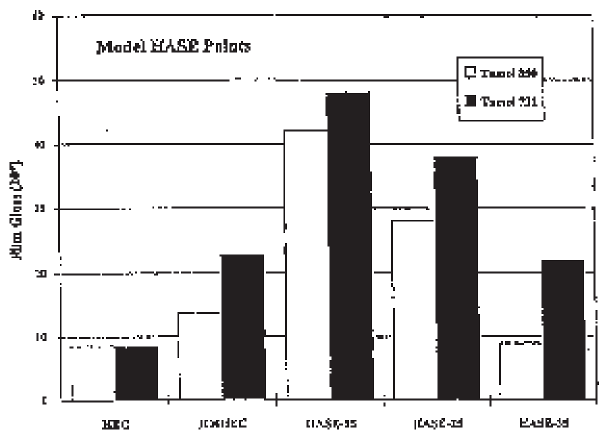


Figure 11—The film gloss (20°) study of Al_2O_3/TiO_2 pigment pretreated with commercial dispersants with 121 nm acrylic latex and model HASE thickeners. Tamol 731 is a maleic acid co-oligomer containing alternating alpha olefin HPs.

ASSOCIATIVE POLYMER INTERACTIONS WITH SURFACTANTS

Anionic Surfactants

The associative thickener (AT) concentration used in most application formulations is small, and therefore the number of hydrophobes in solution is very low. Although hydrophobic domains are formed at even lower concentrations (as reflected in fluorescence studies), they are not effective in promoting viscosity if the only interaction available is with the other AT hydrophobes. The addition of surfactant, specifically an anionic one such as sodium dodecyl sulfate (SDS), will initiate an increase in viscosity at low AT concentrations. With increasing surfactant concentration, the associative thickener solution will increase in viscosity, reach a maximum, and then decrease in viscosity as the surfactant concentration continues to increase, generally above the CMC of the surfactant. The anionic surfactant must have greater than an eight-carbon hydrophobe to effect this viscosity increase. The first delineation of this phenomenon this author remembers is that by Gelman[81] and by Sau and Landoll[54] for HMHEC (illustrated graphically in *Figures* 15 and 16 of their chapter). There have been numerous studies of this phenomenon. Anionic surfactant thickening has been observed in HMPAM studies by Candau's group[82] and in HASE and in HEUR solutions by many others. The incorporation of long chain alcohols and alkyl ethoxylates in SDS micelles is a well-known interaction that allows greater packing in the SDS aggregate. Viewing HEUR as a long chain ethoxylated alcohol, the interaction of SDS and HEURs is understandable, as is the inclusion of HEC in SDS micelles. The phenomenon is more complex with both HEUR and HMHEC thickeners as SDS also interacts with the EO segments on each polymer.

HASE thickeners are negatively charged polyelectrolytes, but their solution viscosities are also enhanced by anionic surfactants. This is probably related to the salinity associated with HASE thickeners in alkaline media. An increase in salinity is known[83] to transform the spherical nature of SDS micelles into rod-like structures and increase their viscosity. A recent examination of SDS in saline solutions, using more sophisticated techniques than in the original studies, has estimated[84] a hydrodynamic length of approximately 150 nm, with a radius of about 2 nm for SDS at 10–80mM in a 0.8 M NaCl concentration. This behavior is likely to play a part in the increased viscosity of HASE thickeners observed in SDS solutions.

In general the viscosity maximum occurs with all thickeners below the anionic surfactant's CMC. In our model HEUR studies, the maximum in viscosity occurs at 5 mM SDS (vs 8.2mM, the CMC of SDS) with a ca. 30,000 molecular weight EO spacer. The number of SDS molecules per micelle drops from 60 to 40 with the accommodation of 6 to 10 sterically restricted HEUR hydrophobes.[85] As the spacer length between hydrophobes decreases the viscosifying ability of the thickener[21] decreases and a higher HEUR concentration is required to achieve the viscosity maxima. A higher

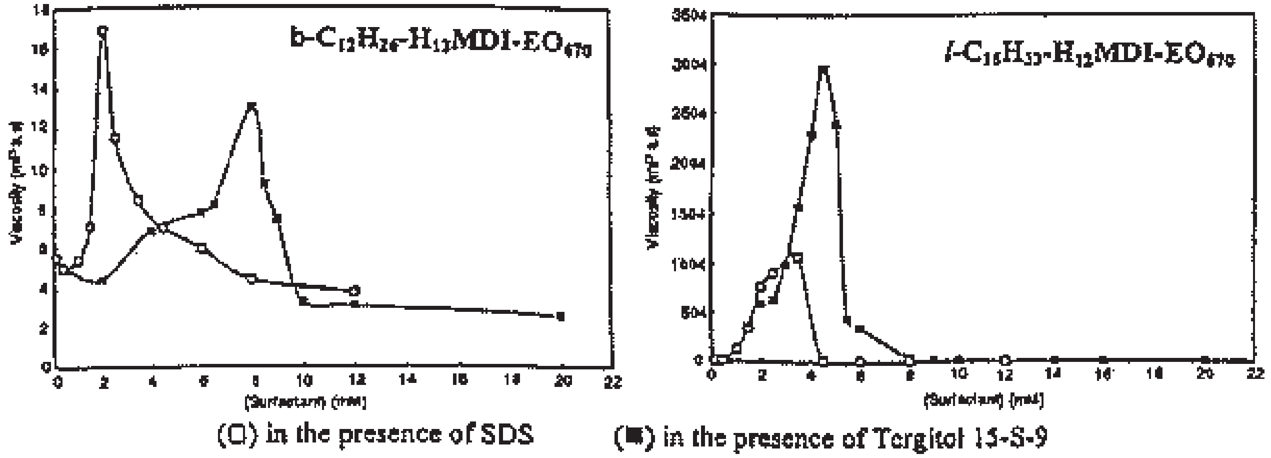


*Figure 12—Influence of the terminal hydrophobe size on the surfactant viscosity maximum with SDS (anionic, open symbol) and Tergitol 15-S-9 (nonionic, closed symbol) surfactants. (HEUR concentration=1.77 * 10^{-4}M; shear rate=$2s^{-1}$)). The influence of branching is discussed in reference 85.*

SDS concentration is also required to observe the viscosity maximum, but the ratio of SDS and HEUR hydrophobes remains essentially the same,[85] irrespective of the spacer length.

Nonionic Surfactants

The first surfactant study of a model HEUR thickener[19] observed that a classical nonionic surfactant like Triton X-100 was as effective in enhancing the solution viscosity of the thickener as SDS. Nonionics are effective in viscosifying HEURs with terminal hydrophobes as small as $–C_8H_{17}$.[20] This is surprising given the following: (1) its attachment to a 30K M.W. POE, (2) that micelle formation in an anionic surfactant requires a $C_8H_{17}–$ or greater hydrophobe size, and (3) that the small hydrophobe was connected to POE by a relatively small isophorone diisocyanate. With a nonionic surfactant the maxima generally occurs[19-21] at much higher concentrations than the CMC of a nonionic surfactant (e.g., at 33 CMCs in our first study). This also happens to represent the same number of micelles that are present at one CMC of SDS; we will return to this phenomenon later in this section, for it is far more complicated than this. Hulden did not see that in her study of SG HEURs nor is it dramatically evident in SG HEUR/surfactant studies we have recently reported.[73]

The nature of the association with nonionic surfactants has been investigated by self-diffusion coefficient distributions from pulsed-gradient spin-echo nuclear magnetic resonance (nmr), varying both associative polymer and surfactant concentration.[86] Compared to the parent homopolymer, the associative French HEUR, $H_{25}C_{12}(EO)_{460}C_{12}H_{25}$, exhibited a much wider distribution of self-diffusion coefficients, which narrows with surfactant concentration (with both SDS and $C_{12}H_{25}EO_{23}H$ surfactants). When the surfactant concentration reaches the saturation level for the polymer, the width of the distributions of the parent homopolymer and associative polymer become identical. In an earlier study of this thickener but with a shorter $–(EO)_{200}–$ spacer link, Persson and co-workers also observed[87] that HEURs of this short chain length when saturated with SDS accommodate only one SDS aggregate, and they concluded that both chain ends are then associated with the same SDS aggregate. We have found it difficult to solubilize such short chain HEURs with nonionic surfactants, which would account for the absence of such polymer studies with nonionics in their study.

The larger EO spacer HEUR, $H_{25}C_{12}(EO)_{460}C_{12}H_{25}$, was also examined with a more hydrophobic nonionic surfactant, $C_{12}H_{25}EO_8H$, and this study also noted the high viscosity promoted by nonionics with narrow molecular weight HEURs. Much of this study related the interactions with the substantial depression of the cloud point temperature[88] among ethoxylated derivatives. As in the study described previously, a decrease in the diffusion coefficient and an increase in the solution viscosity were observed. At concentrations where the surfactant structure dominates, the HEUR was concluded to associate with the existing domains rather than forming new ones.

The remarkable synergy between a narrow molecular weight HEUR and a nonionic surfactant is reflected in the magnitude of the viscosity maximum that can be achieved (*Figure* 12). As the terminal hydrophobe size of the model HEUR is increased the viscosity achieved relative to SDS is dramatic.[85] Conventional nonionic surfactants, however, do not viscosify HMHEC[89] containing a mixture of $C_{12}H_{25}–$ and $C_{16}H_{33}–$ hydrophobes or HASE[90] thickeners containing nonylphenol hydrophobes.

In view of the strong synergy noted with large hydrophobe model HEURs, the very large hydrophobe modified guaran discussed earlier might be expected to show a significant viscosity increase with nonionic surfactants, even though guaran is a segmentally rigid polymer. Thickening by nonionic surfactant at a very low concentration[91] was observed, but in comparison to HEURs, the viscosity increase is trivial. As the nonionic surfactant at low concentrations is increased slightly, the guaran solution viscosity drops below that observed in the absence of nonionic surfactant. A similar minimum thickening at a very low nonionic surfactant also is observed by Khan and co-workers in Chapter 23 of reference 118. One parameter that influences the viscosity of associative thickeners is the EO spacer distance between the hydrophobe and the mainchain.[92,93] We have attempted to increase the EO spacing between the hydrophobe and the HEC mainchain and thereby promote thickening by nonionic surfactants, but with only limited success.[94] A more diligent effort is required in this area.

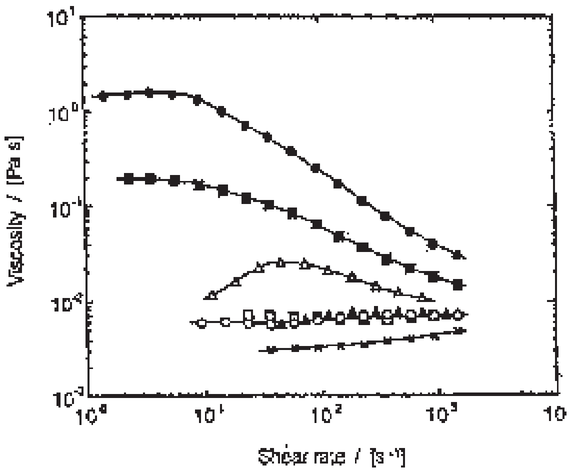
One can enhance the viscosity of HMHEC or HASE solutions with a nonionic surfactant of marginal solubility (i.e., one with a very short oxyethylene chain). This was first reported for HMHEC solutions.[95] A synergistic increase in solution viscosities has also been observed with large hydrophobe HASE thickeners when the $C_{12}EO_4H$ concentration is increased to 0.1 M.[96] In the intermediate range of surfactant concentrations (0.001-0.01 M), the parallel superposition of steady shear and dynamic testing reveal that the microstructure of the network is affected by stress even in the low-shear plateau region of the flow curves. At very high surfactant concentrations (>0.01 M), HASE hydrophobes interact with the surfactant to form a stiff gel-like structure. This limited solubility surfactant is reported to form a mired bilayer structure with the polymer hydrophobes. A marginally soluble nonionic surfactant influence on building viscosity also is reported for a HASE thickener in Chapters 22 and 23 of reference 118. It also has been reported to alter the viscosity profile, in a coating formulation[97] of the too surfactant sensitive (i.e., in a formulation with a nonionic surfactant with reasonable water solubility) comb-HEUR, discussed in an earlier subsection.

ADSORPTION AND STABILIZATION

Over the past two decades, a great deal has been published on the viscosity of aqueous thickener solutions. If this were all that associative polymers provided, the interest in such products would be mostly academic. An important role of associative thickeners is their ability to stabilize disperse phases.

Liquid Interfaces

In 1996, researchers in Iliopoulos' labs studied the effects of an adsorbing hydrophobically-modified sodium polyacrylate on the phase behavior of a nonionic surfactant-water-oil system. With increasing polymer concentration, the middle phase microemulsion first increases its water-to-oil ratio, but above a certain polymer concentration the trend reversed.[98] The reversal was attributed to saturation of the interface by polymer adsorption. Following these observations, Perrin examined the variation in hydrophobically-modified polyelectrolytes on microemulsion and emulsion stability. Low dodecylacrylamide-modified poly(acrylic acid), sodium salt, of various degrees of modification and molecular weights, were used as emulsifiers of n-dodecane/water ($NaNO_3$ 10^{-3} M) systems. Stability of the resulting n-dodecane in water emulsions (dispersed phase volume fraction = 0.5) were investigated as a function of the extent of modification (0 to 10%), molecular weight (5,000, 50,000, and 150,000 g/mol), and concentration (0 to 10%) of polymer. Viscosity build occurs via an associating mechanism of the external phase of emulsions. In recent studies,[99] the length (n) and type (single-versus twin-tailed) of the hydrophobic moiety were examined, along with the extent of hydrophobe modification and salinity. Inverse dispersions were preferentially formed with twin-tailed rather than single-tailed copolymers. Moreover, the types of emulsions stabilized with hydrophobically-modified polyelectrolytes can be flipped from O/W to W/O with increasing salt concentration. Stabilization of emulsions



Latex	Dz (nm)	Surface Acids (µmol m^{-2})	At the Particle Surface (µmol m^{-2}) SDS	NPE$_{10}$
B2 (■)	197±5	0.03	0.87	0.98
B3 (•)	127±1	0.03	0.59	0.66
B5 (x)	120±1	0.10	2.3	2.3
B7 (❑)	220±4	0.08	0.4	1.5
B8 (▲)	425±7	0.14	0.2	2.6
B((Δ)	536±8	0.39	0.3	3.6
B10 (❍)	373±10	0.13	0.2	2.7

Figure 13A—Viscosity dependence on shear rate of latex dispersions (in descending order: B3 (127 nm), B2 (197 nm), B9 (536 nm), B7 (220 nm), B10 (373 nm), B8 (425 (nm)) thickened witha S-G HEUR of 31,000 average mole wt. containing octadecyl end groups. Hexamethylene diisocyanate was the coupler used in the step-growth synthesis.

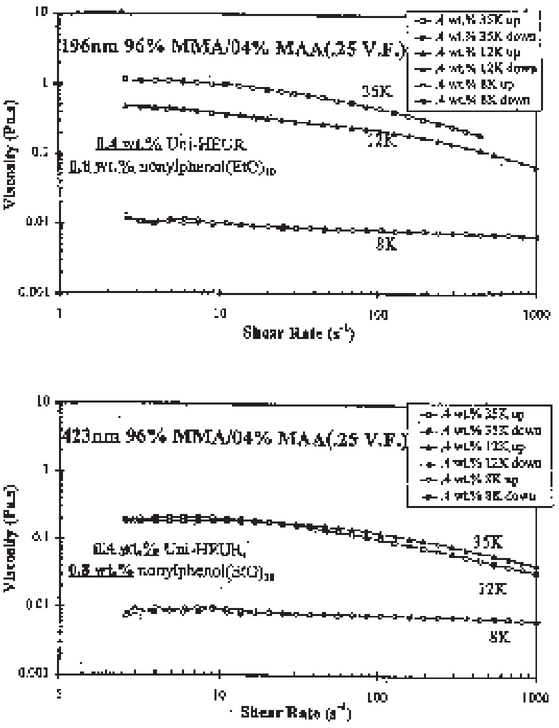
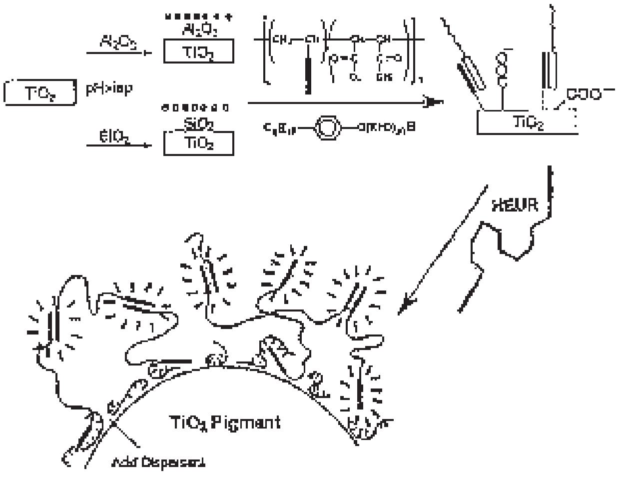


Figure 13B—Viscosity (Pa.s) dependence on shear rate (s^{-1}) for two model methylmethacrylate latices with 4% methacrylic acid. Monodisperse particle sizes are 196 and 423 nm, respectively. Both latices are thickened with model HEURs containing $H_{12}MDI-C_{12}H_{25}$ terminal end groups and 8,000, 12,000 and 35,000 EO spacer links. In addition to latex diameter, changes in HEUR and $NPEO_{10}$ concentrations and latex surface acid content influence non-Newtonian flow behavior.



Scheme 1—Treatment and adsorption sequences in a pigment grind preparation.

has been of interest in cosmetic applications for several decades, and these types of materials may prove beneficial in this area.

There are many studies bordering on the stability of liquid drops that involve two polymers and possibly surfactant combinations. They generally involve materials of opposite charge and are referred to as coacervates. The polymers involved generally do not contain hydrophobes and will not be discussed in this review.

Solid Substrates

Clays: Hydrophobe-modified water-soluble polymers also adsorb on solid substrates in an applications formulation. In petroleum applications, such substrates are primarily high surface area clays, such as montmorillonite. The most recent studies have involved HMPAM, discussed in the first section. Contrary to polyacrylamides that present a classical high affinity adsorption isotherm on montmorillonite surfaces, the adsorption of HMPAM continues to increase with polymer concentration.[100] The effect is observed even if no intermolecular associations are evident in solution. Some modified polymers almost completely replace the bound water (determined by ^{1}H-NMR), forming a quasi impenetrable adsorbed layer.

Latices: Associative polymers adsorb on polymer latices via hydrophobic interactions to generate dense layers that increase the hydrodynamic size of the particles and increase the stability of the latex. This inhibits depletion flocculation[101] and provides better coating film properties. It is surprising that so few adsorption studies have been conducted. Recently, the adsorption behavior of a well-defined $C_{16}H_{37}(EO)_{750}C_{16}H_{33}$ was studied. At low concentrations both hydrophobes were noted to adsorb on the surface; at higher concentrations one of the hydrophobes is free to couple with micelles in solution and adsorbed layers on other particles.[102] The adsorbed amounts and layer thickness of this model HEURs on poly(methylmethacrylate) particles suggest a dense layer of moderately stretched chains in very dilute dispersions. At higher concentrations, adsorption increases the intrinsic viscosity, by an amount consistent with the measured layer thickness of 26 nm. The details of this work with other data from Russel's group are presented in Chapter 14 of reference 118. Others have conducted similar studies with the marketing HEUR[103] and with a step-growth HEUR containing pyrene terminal groups connected to the POE chain via H_{12}MDI urethane linkages.[104]

To address the importance of adsorption in coating formulations, adsorption studies must be conducted in the presence of surfactant. There have been only three studies of this nature. The first was by the original Rohm and Haas group that examined the adsorption of S-G HEUR and HASE thickeners as a function of latex particle size at a given solid level.[105] Small particle latices adsorbed more thickener than the larger particle size latices due to their greater surface area. Addition of SDS, the classical anionic surfactant, was effective in displacing the thickeners from the latex surface. Hulden

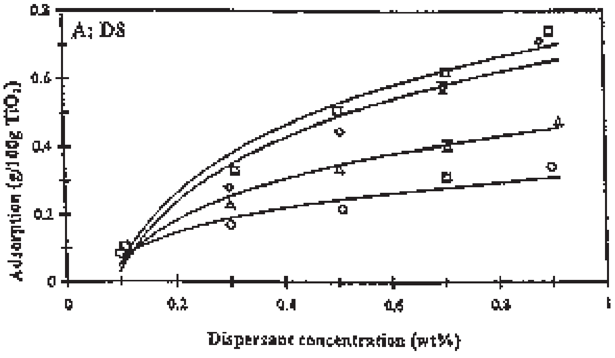


Figure 14—Adsorption of α-olefin/maleic acid co-oligomer dispersants (D8/MA) on titanium dioxide pigments surface treated with mixed inorganic oxides. Symbols: (❑) IEP=9.49, (◊) IEP=8.28, (Δ) IEP=6.36, (o) IEP=4.51.

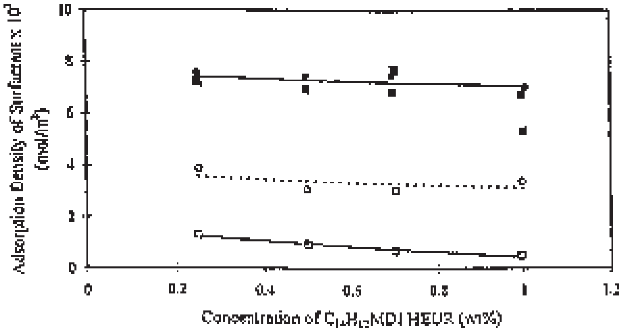


Figure 15—Adsorption density (mol/m^2) of 0.8 wt% C_8H_{17}-$C_6H_4O(EtO)_{10}H$ nonionic surfactant on Al_2O_3/TiO_2 (❑) and SiO_2/TiO_2 (o) in the presence of $C_{14}H_{29}$-H_{12}MDI-$C_{14}H_{29}$ HEUR associative thickener. Closed symbol pigment pretreated by D8/MA dispersant; open symbol pigment pretreated by D4/Maleic acid dispersant.

broadened the study and made it more realistic by examining conventional nonionic surfactants.[106] This investigation was marred by the study of S-G HEURs synthesized with toluene diisocyanate (that hydrolyzes in alkaline media) and the use of acrylic acid (that polymerizes mostly in the aqueous phase) in preparing the latex, but the study in total (e.g., the HDI coupled HEUR with octadecyl hydrophobes) highlights the complexity (*Figure* 13A) observed in the responses of a complex fluid to shear deformation. Model latex interactions with model HEURs of variable spacer links have also been studied[107] (*Figure* 13B). Both studies encompass a matrix of variables that would bring up the usual stabilization, interbridging, and aggregation concepts of classical colloid chemistry. No one to date has quantified a before-the-fact predictive mechanism because of all of the complexities in experimental design in such studies. A recent review[108] of the adsorption of HEURs on latices has been published and will not be reemphasized here.

What is known from studies using variable terminal size S-G HEURs (C_6H_{13}– to $C_{18}H_{37}$–) is that the competitive adsorption of HEURs and nonionic surfactants is an equilibrium process depending upon the relative sizes and concentration of the associative thickener and surfactant hydrophobes.[109] However, a coating formulation is a complex fluid that contains many components, particularly surfactant types. Hulden addresses[110] the problem in a realistic way by studying the complexity in competitive adsorption of SDS and $NPEO_{10}$H on latices in the presence of coalescing aids. The preferential adsorption of the more surface active $NPEO_{10}$ is greatest at the onset of micellization and diminishes as the total surfactant concentration increases. The addition of a small amount of coalescing aid decreases the CMC of SDS but increases the CMC of $NPEO_{10}$. The decrease in the difference of the respective CMC of the nonionic and anionic surfactants is paralleled by the reduction in the preferential adsorption of the nonionic surfactant in the presence of coalescence aids. Those not knowledgeable about the type of coalescing aids used in coatings, their solubility in various latex compositions and influence on HEUR rheology are referred to a prior publication.[111] Such complex adsorption behaviors including associative thickeners have not been reported. Competitive adsorption studies require more diligence to obtain meaningful data. This area is in need of more detailed research.

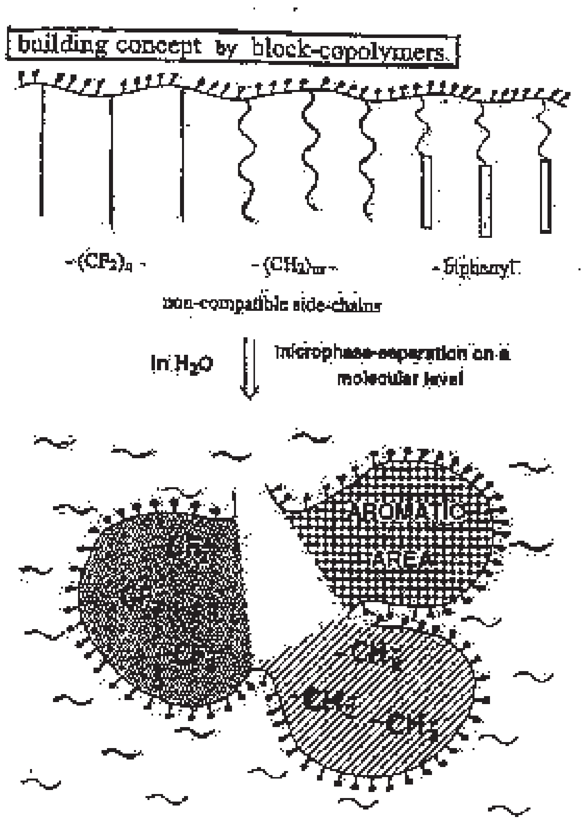


Figure 16—Ringsdorf's vision of the future.

Adsorption on Treated TiO_2 Dispersions: The dispersion of pigments also is an important factor in application formulations. Titanium dioxide, the hiding pigment in a coating, is easily flocculated in aqueous solutions below its isoelectric point (IEP). Above the IEP, low salinity levels may flocculate it. In addition, titanium dioxide, by electron transfer reactions, reacts with organic materials. To protect the coating from degradation, it is a common practice for the manufacturer to pretreat TiO_2 with either Al_2O_3 or SiO_2 or both. It is the IEP of these metal oxides that is important to the stabilization of the pigment. To stabilize such a high energy disperse phase, the metal oxide is treated with surfactant and an oligomeric polyacid dispersant. The adsorption of surfactant and dispersant (e.g., an acrylic (PAA) or methacrylic acid oligomer or an alpha-olefin/maleic acid co-oligomer) increases the stability of the dispersion by increasing the electrosteric repulsion between particles, but in the presence of a non-adsorbing thickener and salinity, TiO_2 is often not stable enough to ensure good applied film gloss.

Hulden and Sjoblom noted many of these observations in 1990.[112] The anionic surfactant SDS, and polyacrylic acid and EHEC adsorb on the Al_2O_3 treated TiO_2,, but not on the SiO_2 treated pigment. The nonionic surfactant, $NPEO_{10}$ does not adsorb on PAA pretreated TiO_2 pigments. It was also observed that EHEC adsorbed on Al_2O_3 treated TiO_2 is displaced by PAA. In other studies, a maleic acid co-oligomer was noted to adsorb[113] significantly more than the oligomeric methacrylic acid dispersant because it contains more unneutralized acid to hydrogen bond or acid-base interact with the pigment surface. The co-oligomer also possesses alternating hydrophobic units of four or eight carbon atoms next to each maleic acid unit (referred to here as D4/MA and D8/MA) to interact and "adsorb" the conventional surfactant and HEUR associative thickeners on the TiO_2 surface. HEUR thickeners and nonionic surfactants did not adsorb on TiO_2 surfaces without this interaction from an alkaline media, typical of an exterior latex coating. Nonionic surfactants will adsorb on TiO_2 if its surface has been treated with SiO_2. A graphic of these separate steps is illustrated in *Scheme* 1. Most of these observations were reported earlier, and have been reviewed.[114]

In more recent studies,[115] the nature of the inorganic treatment has been extended to cover multilayers of aluminum, silicon, and zirconium oxides. The IEP of the metal oxide determines the amount of organic dispersant adsorbed (*Figure* 14). The different IEP treatments were achieved by varying the amount and type of metal oxide applied to the TiO_2 surface. The individual metal oxide IEP used in this study were: 9, Al_2O_3; 6-7, ZrO_2; and 3-4, SiO_2. It would be expected that at a pH of 9.3, the higher IEP surfaces with remaining hydroxyl groups would more readily participate in reverse hydrogen bonding or acid-base interact with the maleic acid dispersant, also not fully ionized, and this would promote greater adsorption. This is observed.

The surfactant, $C_8H_{17}–C_6H_4O(EO)_{10}H$, concentration used in the competitive adsorption studies is 0.8 wt%, well into the adsorption plateau. The available adsorption sites on the pretreated TiO_2 should be occupied, and the hydrophobes of the HEURs would be expected to displace the surfactant, as was observed in the latex study. The adsorption of the surfactant, however, can be independent of the amount of dispersant adsorbed, unlike the conventional HEUR thickener. When the dispersant alpha-olefin size is $–C_8H_{17}$, the surfactant is not displaced by the adsorbing HEUR, in contrast to that observed in the latex studies. When the repeating alpha-olefin size is $–C_4H_9$, the HEUR thickener (*Figure* 15) displaces part of the nonionic surfactant.

There are additional surprises when the comb type architecture (*Figure* 4D) is examined[52]; greater amounts of adsorption occur than are observed with the traditional terminal hydrophobe HEUR. This is in part due to the higher molecular weight of the comb polymers and possibly a result of its lower solubility. Due to the length of this article we will conclude by noting that such architectures provide higher film gloss to pigmented coatings, but they appear to flocculate small particle latices.[114]

FUTURE AREAS OF STUDY

The advent of surfactant-modified, water-soluble polymers from industrial laboratories, almost 30 years ago, has provided academic investigators an interesting area to apply their skills and information has been gained from their studies. Although interesting, little of this understanding has been of value in real applications areas. The have been two investigators whose efforts standout: (1) Candau in chain-growth associative thickeners, and (2) Hulden in understanding the application of associative thickeners in the coatings area. Although Hulden's studies have often used less than model HEURs, the details in her work demonstrate the complexity needed to really address application technology.

Ringsdorf entered the area of polymer synthesis at the prompting of one of his German associates, who was tired of studying poorly defined industrial products. Someone like Ringsdorf, who is willing to be the synthetic source, is needed in this area. Advancement in the areas that have been published will be slow in the future due to the lack of well-defined products. With the individual need to publish and journal needs for manuscripts there will be a continuum in the publication of studies on poorly defined materials.

The initial academic contributor[116] in this area, Strauss, began his study of hydrophobically-modified, water-soluble polymers as a means of understanding protein interactions. This is an area that is being re-addressed now and promises to show the greatest contribution. Ringsdorf and co-workers capture a preview of what is to come in a recent short article.[117] It is a vision of liposomes and cell simulations via compartmental micelles from surfactant-modified, water-soluble polymers (*Figure* 16), with potential in drug release and disease control. It is an admirable goal.

SUMMARY AND CONCLUSIONS

In this extended review, an effort has been made to detail the numerous contributions that many have made to the area of hydrophobically-modified water-soluble polymers. The understanding obtained and the areas where future research would be most meaningful are summarized in the following paragraphs.

The attachment of surfactant hydrophobes to a low molecular weight water-soluble polymer permits the achievement of minimum elastic response at high deformation rates with a low molecular weight thickener that is capable of building a significant viscosity at low shear rates through hydrophobic bonding. Such materials also are capable of stabilizing disperse phases and these influences have been key assets in the acceptance of "associative thickeners" in commercial formulations. For simplistic studies and for optimum quality coatings the attachment of hydrophobes to the ends of a polyoxyethylene chain (generically referred to as HEUR) provides the only model from which to initiate fundamental studies. This is not to be confused with the mixture of products generated from the step-growth addition of diisocyanates to polyetherdiols.

Model HEURs in aqueous solutions provide rheological responses in which stress relaxation occurs via disengagement of chain ends from associations followed by rapid Rouse relaxation of the stressed chains. In the associative state, their state of aggregation is a function of their concentration and hydrophobe size. Distributions of self-diffusion coefficients are observed. In the dilute region, faster diffusion coefficients are attributed to unimers or small oligomeric aggregates. At concentrations near the point where the viscosity rises, an intermediate mode appears. This mode is considered to reflect the cooperative motions of the formed network. A general model of this behavior is illustrated in *Figure* 6 of this article. When the EO spacer length is small (ca. 200 units), a two-step association model is proposed. In the first association, well-defined small clusters are identified; however, these units have a tendency to aggregate. It has been observed recently that the two steps occur simultaneously for model HEURs with larger EO spacers, as would have been expected from pyrene labeled POE studies of the 1980s. At low concentrations, the aggregates of HEURs with shorter spacer lengths and $C_{12}H_{25}$–termini consist of five macromolecules, whereas the aggregates of larger EO spacer HEURs consist of three macromolecules. This of course varies with terminal hydrophobe size.

When this model thickener in aqueous solution is placed under deformation, the solutions can exhibit Newtonian, shear-thickening and shear-thinning behaviors as a function of shear rate. The exact response will again depend on concentration, EO spacer length between the hydrophobes, and hydrophobe size. Phase separation is observed during the shear-thinning step. Although the shear viscosity is not notably influenced by low rates of deformation, recent flow birefringence studies of model HEURs have observed orientation and alignment at low deformation rates. This has also been observed in step-growth HEUR mixtures, in transient flow studies in carbohydrate associative polymers, and in oscillatory rheometry of ASE that have been hydrophobically-modified.

The most efficient viscosifiers among model HEUR polymers are those with POEs in the 12,000-20,000 molecular weight range. Such narrow molecular weight HEURs do not provide a desired coating rheology profile because of their thickening efficiency. To obtain coating formulations with viscosities that are higher at higher shear rates, a step-growth synthesis is used to produce HEURs that contain enough ineffective low viscosity components to promote higher viscosities at high shear rates (10^4 s^{-1}). To obtain enough of the 11–20K materials that are effective viscosifiers at low shear rates, the step-growth HEUR is generally prepared in the molecular weight range of 35,000.

Due to a number of economic factors and lower performance criteria in a number of applications, hydrophobe modification of other polymer structures has a place in the technology. This has included carbohydrate polymers, the first being HMHEC. In common with the guaran and chitosan-modified carbohydrate polymers discussed in this article, placement of the hydrophobes along the segmentally rigid chain is random and unknown. Their diffusion modes are similar to that observed in model HEURs, but their influence on coatings rheology is more limited. Hydrophobes properly spaced from the rigid chain with oxyethylene units should broaden the influence of carbohydrate polymers on coatings rheology, but this has not been delineated clearly to date.

In the polymerization of chain growth monomers (i.e., HMPAM and HASE) there will be variations in composition with conversion. In the copolymerization of unmodified and hydrophobically-modified monomers, this will be exaggerated in aqueous solution due to the micelle forming character of the hydrophobically-modified monomers. These problems have been beautifully by passed with disubstituted acrylamides, but in the synthesis of HASE thickeners, the ambiguity of old emulsion synthesis techniques has muddied the scientific waters. The lack of acknowledgment of the crosslinking monomers added to increase the shear viscosity and to decrease the extensional viscosity of aqueous solutions of HASE thickeners, and the lack of acknowledgment of the generation of small particle size latex particles with high hydrophobe monomer content has been a discredit to the HASE thickener area studies.

The addition of an anionic surfactant results in thickening of all associative polymers by promoting hydrophobe associations. A greater distribution of self-diffusion coefficients is observed in HEURs without surfactant than is observed in the presence of both SDS and traditional water-soluble nonionic (e.g., $C_{12}H_{25}(EO)_{23}H$) surfactants, until the surfactant concentration reaches the saturation level for the polymer where a viscosity maximum is observed. Conventional nonionic surfactants do not viscosify HMHEC containing a mixture of $C_{12}H_{25}$–and $C_{16}H_{33}$– hydrophobes or HASE thickeners containing nonylphenol hydrophobes. Viscosity increases in HMHEC or HASE solutions have been observed with a nonionic surfactant of marginal solubility (i.e., one with a very short oxyethylene chain, e.g., $C_{12}EO_4H$), but in comparison to HEURs, the viscosity increase is trivial.

The most remarkable synergies influencing viscosity increases occur in model HEUR and conventional nonionic surfactant systems. At surfactant concentrations well above their critical micelle concentration (CMC), viscosities equivalent to the anionic SDS surfactant/model HEUR combination are observed. As the hydrophobe size of the model HEUR is increased, the viscosity of the conventional nonionic/HEUR combination dramatically dwarfs the SDS/HEUR combinations.

In the stabilization of disperse phases, dodecylamide-modified polyelectrolytes of various degrees of modification and molecular weights have been used effectively as emulsifiers of n-dodecane/water ($NaNO_3$ 10^{-3} M) systems. Inverse dispersions were preferentially formed with twin-tailed rather than single-tailed copolymers. The types of emulsions stabilized with hydrophobically-modified polyelectrolytes can be flipped from O/W to W/O with increasing salt concentration. Hydrophobe-modified polyelectrolytes also adsorb on solid substrates in an applications formulation. Contrary to polyacrylamide, which has a classical high affinity adsorption isotherm on aluminosilicate surfaces, the adsorption of hydrophobically-modified polymers increases with polymer concentration. Some modified polymers almost completely replace the bound water, forming a quasi-impenetrable adsorbed layer.

Associative polymers also adsorb on polymer latices via hydrophobic interactions to generate dense layers that increase the hydrodynamic size of the particles and increase the stability of the latex. In the adsorption behavior of a well-defined $C_{16}H_{33}NCOO(EO)_{750}CONC_{16}H_{33}$ at low surface coverages, both hydrophobes adsorb on the surface; at higher concentrations one of the hydrophobes is free to couple with micelles in solution and adsorbed layers on other particles. At higher concentrations, a layer thickness is estimated to be 26 nm. In the presence of surfactant the adsorption process will change. Addition of SDS, the classical anionic surfactant is very effective in displacing the thickeners from the latex surface. Higher concentrations of nonionic surfactants are required to displace HEUR thickeners from the latex interface. Both surfactant types are present in a coating formulation and this adds significant complexity to analyzing component influences. For example, the adsorption of the more surface active $NP(EO)_{10}H$ nonionic surfactant is greatest at the onset of micellization and diminishes in competition with SDS as the total surfactant concentration increases. Competitive adsorption of associative polymers in this type of complexity is needed. Studies of HEURs with variable terminal sizes (C_6H_{13}– to $C_{18}H_{37}$–) indicate that the competitive adsorption of HEURs and nonionic surfactants is an equilibrium process depending upon the relative sizes and concentration of the associative thickener and surfactant hydrophobes. The studies to date encompass a matrix of variables that would bring up the usual stabilization, interbridging, and aggregation concepts of classical colloid chemistry, but no one thus far has quantified a before-the-fact predictive mechanism because of all of the complexities in experimental design in such studies. This is an area that demands additional research.

With regard to adsorption and stabilization of pigments, the IEP of the dominant metal oxide determines the stabilization of inorganic oxide treated titanium dioxide in aqueous dispersions. The IEP defines the amount of organic dispersant adsorbed. An acid-base or hydrogen-bonding interaction between the dispersant and the metal oxide surface is the parameter being reflected. The acid groups in a HASE thickener compete with the adsorption of the dispersant and this destabilizes the pigment, irrespective of the metal oxide treatment. With HEUR thickeners, stabilization is achieved if the acid dispersant also contains hydrophobic units to attract the HEUR to the metal oxide surface. This is also true in HMHEC thickened coatings. Adsorption of the nonionic surfactant can be independent of the amount of dispersant adsorbed on the metal oxide, in contrast to the behavior in latex dispersions if the TiO_2 is treated with $Si0_2$.

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