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To cite this version:

Baptiste Quienne, Julien Pinaud, Jean-Jacques Robin, Sylvain Caillol. From Architectures to Cutting-Edge Properties, the Blooming World of Hydrophobically Modified Ethoxylated Urethanes (HEURs). Macromolecules, 2020, 53 (16), pp.6754-6766. 10.1021/acs.macromol.0c01353 . hal-02924196

HAL Id: hal-02924196

https://hal.science/hal-02924196v1

Submitted on 7 Sep 2020

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From architectures to cutting edge-properties, the blooming world of Hydrophobically modified Ethoxylated Urethanes (HEURs)

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Abstract

Hydrophobically modified ethoxylated urethanes (HEURs) are associative polymers that, compare to others, are far less sensitive to solution parameters, especially pH and ionic strength. Therefore, they are widely used as rheology modifiers in many different waterborne systems such as inks, coatings, emulsions, etc. In solutions, HEURs form transient networks through molecular associations between their hydrophobic groups. The transient network formation and its characteristics are responsible for the rheological properties and depend on the HEUR chains architecture. Many parameters such as molecular weight, size and nature of hydrophobic groups, polymer concentration, etc must be controlled to tune the several physicochemical properties of HEUR solutions. This article aims to give an overview of the HEUR studies reported in the literature in order to highlight the structure/rheological properties relationship. The article also draws attention to new trends in HEURs with innovative architectures and stimuli-responsive properties.

Keywords

Hydrophobically modified Ethoxylated Urethanes; Associative polymers; Telechelic polymers; Thickeners; Thickening performance; Rheology;

I. Introduction

Rheology control is a key point for many applications such as construction, cosmetics, coatings and paints.[1,2,3] Its control over the entire life cycle of the product is essential to guarantee an optimal final application. To achieve this objective, rheology additives are used, representing a constantly growing market of $4.94 billion in 2015, which would reach $6.83 billion by 2024.[4] Moreover, the majority of these additives are used in paint and coating applications that account for more than one third of the market. In these applications, rheology additives represent only a few percentage of the total formulation but they remain the main additive added. With the strict regulatory restrictions of VOC (volatile organic compounds)[5] and the consumer preferences for environmentally friendly products, waterborne technology is in demand nowadays. Associative polymers are among the major rheology additives used in waterborne paints.[6,7,8,9] Their amphiphilic structure allows their solubility in water and the formation of a transient network thanks to interactions of their hydrophobic groups, either with emulsion particles or between themselves.[10] The hydrophobic groups can be randomly attached

to the hydrophilic backbone, leading to comb-like polymers such as hydrophobically modified hydroxyethyl cellulose (HMHEC)[11] and hydrophobically modified alkali soluble emulsion (HASE).[3] The latter are composed of a negative polyelectrolyte backbone therefore, they are sensitive to pH and to the ions present in the solution. Despite their excellent flow properties, their use is limited to alkaline media. On the other hand, the hydrophobic groups can be attached to the chain ends of a hydrophilic backbone, leading to telechelic polymers. These structures are called end-capped polymers. Among them, hydrophobically modified ethoxylated urethanes (HEUR)[12,13,14,15,16] are well known for their good flow properties, high sag-resistance and leveling. Moreover, compared to HASE, they are non-sensitive to pH, which is a strong advantage allowing their use in a wider variety of formulations. Beyond their interest in industry due to their excellent rheological properties, the telechelic structures of HEURs facilitate their modeling by theoreticians. Therefore, they are also studied in depth by chemists and physicists.

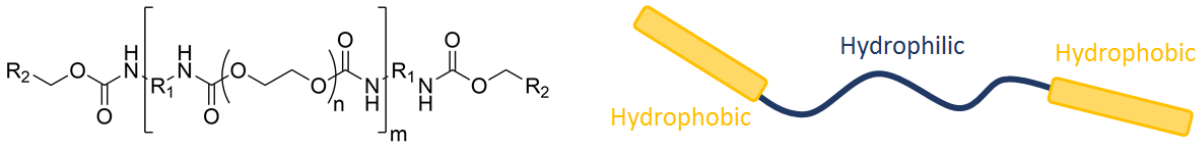

Figure 1: Chemical and schematic HEUR structure (R_1: diisocyanate backbone; R_2: aliphatic alkyl chain)

HEURs are usually composed of a poly(ethylene glycol) (PEG) backbone end-capped with alkyl phenyl,[17] fluorocarbons[18] or typically aliphatic alkyl chains.[14,19] They are obtained by the reaction of hydroxyl PEG end-groups, hydrophobic alcohols and diisocyanates, leading to urethane linkages (Figure 1). Once they are solubilized in aqueous media above the critical aggregation concentration (CAC), intra- and inter-molecular associations of the hydrophobic groups lead to formation of flower-like micelles. The micelles are composed of the associated hydrophobic groups in the core and of hydrophilic chains as flower loops. Once the polymer concentration exceeds the critical percolation concentration (Cp), polymer chains start to link micelles together leading to a physical transient network (Figure 2). The dynamic network formed greatly increases the viscosity and modulus of the solution and is sensitive to shear rate. Thanks to the dynamic interactions of hydrophobic groups, the network can be destroyed under high shear rate and reformed at rest. Hence, the pseudoplastic properties sought in fields of ink, coating and paint are obtained. The high viscosity at low shear rate offered by pseudoplastic properties allows increasing the shelf-life of paint by avoiding sedimentation. Furthermore, the lower viscosity under a high shear rate allows an easy leveling while limiting sagging and spatters. Despite the massive use of HEURs in industry, there is no comparative study in the literature that considers the different aspects of this topic. Hence, in this original perspective paper, we propose to consider the different parameters studied in the literature, from

synthesis to properties and models developed to understand their rheological behavior, in order to give an overview of the HEUR technology.

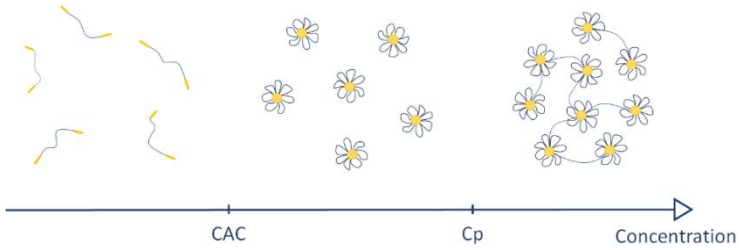

Figure 2 : HEUR solution at different concentrations

II. Synthesis of HEURs

HEURs are low molecular weight polymers, usually inferior to 50,000 g.mol^{-1} compared to HASE (200,000 to 500,000 g.mol^{-1}) and HMHEC (50,000 to 800,000 g.mol^{-1}). They are obtained through the reaction of isocyanates with alcohols leading to urethane linkages; the reaction can be catalyzed with 0.2wt% dibutyltin dilaurate (DBTDL) or tertiary amines. There are three different pathways to obtain these final telechelic structures (Figure 3). One can directly react hydrophobic groups with PEG of desired molecular weight leading to Uni-HEUR.[6,20] These structures can also be prepared by the reaction of PEG with a large excess of diisocyanates (usually isophorone diisocyanate IPDI or hydrogenated methylene diphenyl diisocyanate H_{12}MDI) followed by the reaction of hydrophobic alcohols. On the other hand, HEURs can be prepared by a step-growth polymerization of PEG with diisocyanates, which are then reacted with hydrophobic alcohols. This method leads to higher polydispersity index (PDI) polymers, these structures are called S-G HEURs.[12,14,17] Furthermore, in the 90's, the Glass' group reported the synthesis of particular HEUR structures, containing internal hydrophobic groups from biuret hexamethylene diisocyanate, isocyanurate of isophorone diisocyanate or m-tetramethylxylene diiisocyanate, as well as the synthesis of a comb-like HEUR.[12,14,21]

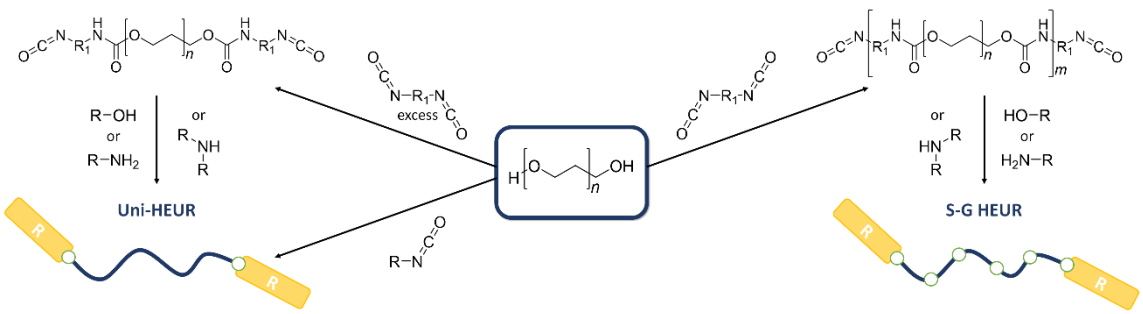

Figure 3: Synthesis pathways to Uni-HEUR and S-G HEUR with ◯ as urethane linkages

Despite their low mass ratio in the HEUR structure, hydrophobic groups are mainly responsible for the final properties obtained. Therefore, many different hydrophobic groups (Figure 4) have been

used to prepare HEURs in order to give a very large panel of rheological properties. The most frequently used are hydrophobic alcohols, or sometime amines, having from 6 to 20 carbons. However, more original structures were studied such as fluorocarbon alkyl chains,[18,22] alkyl phenyl[14,17,23,24] and modified hydrophobic groups containing sensitive or reactive functions. All these structures were mainly synthesized and studied by Tong's group. Mini-dendrons were obtained starting from the methyl gallate, methyl 3,5-dihydroenzoate and methyl paraben modified by the method reported by Percec.[25] Redox and light sensitive hydrophobic groups were as well synthesized with a similar method. In 2016, azobenzene and ferrocene end-functionalized HEURs were described, as Azo-HEUR[26] and Fc-HEUR[27] respectively. The addition of these stimuli-responsive groups to HEURs allowed controlling the rheological properties of the solution by applying external light irradiation or redox reactions. The following year, Tong *et al.* described FcAzo-HEUR[28] combining in a single structure the two sensitive functions using mini-dendron synthesis. This complex structure allowed obtaining four different associative networks depending on the stimuli applied to the solution. In 2017 as well, Ren *et al.* synthesized a novel photosensitive HEUR end-functionalized with spyropyran (SP-HEUR).[29] In 2019, they described a new class of HEURs end-functionalized with benzophenone ($BPC_{11}HEUR$)[30] able to chemically crosslink with acrylic monomers or resin under UV radiations, which can find applications in UV adhesives, coatings or inks…

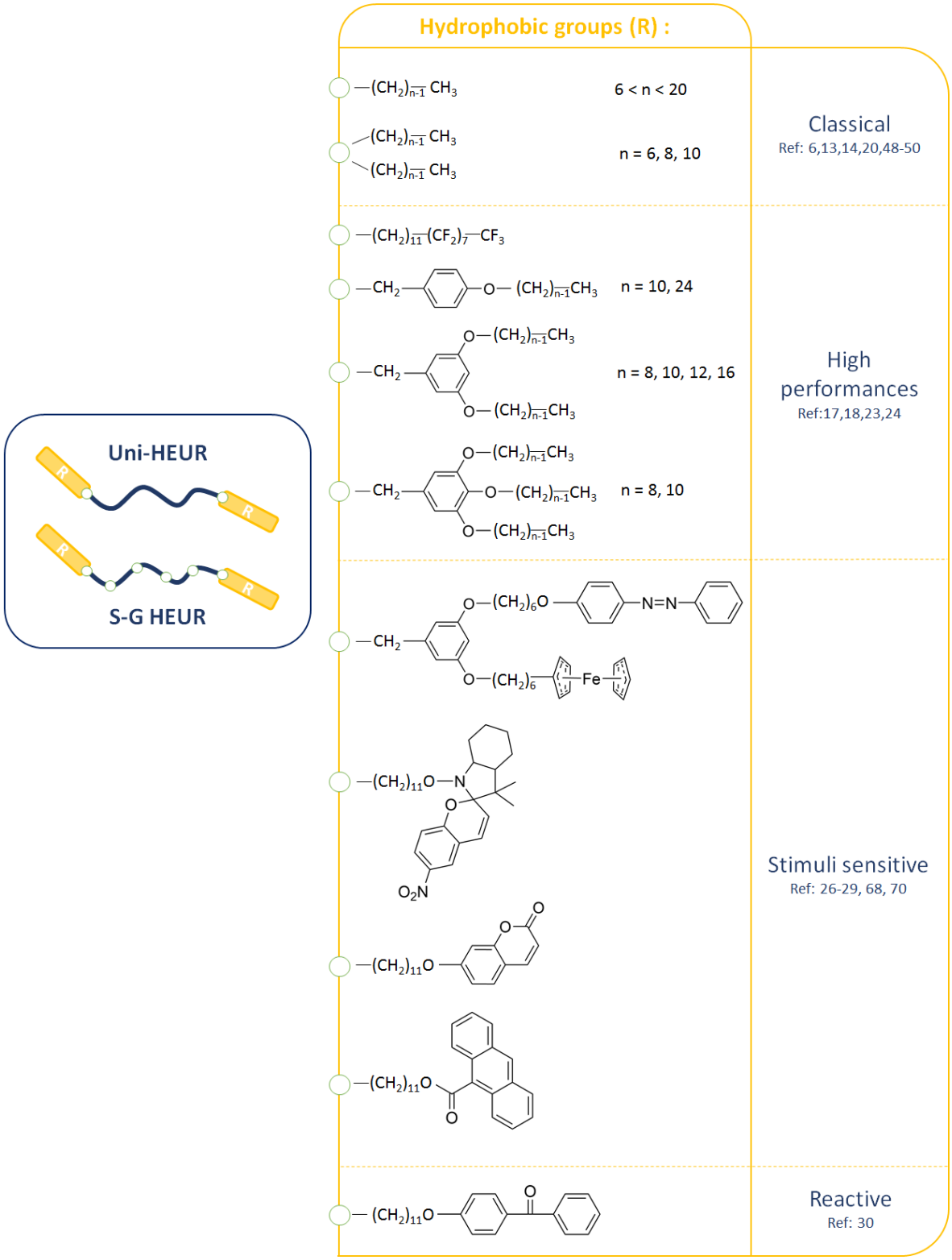

Figure 4: Overview of HEUR structures studied in the literature with ◯ as urethane linkages

III. Structure/rheological properties relationship

HEURs are telechelic polymers which, once in solution, associate *via* intramolecular or intermolecular associations between their hydrophobic groups. Depending on the polymer concentration, flower-

like micelles or a transient network through HEUR chains connecting two different micelles cores, often called super-bridges, are formed. The rheological properties of such associative polymers arise from the formation of this network and its characteristics. Different rheological profiles are obtained depending on the network density, its relaxation time and the polymer concentration. HEUR networks showed the linear viscoelasticity of a Maxwell model,[15,31] but the nonlinear elasticity is much more complex to explain. Indeed, in many systems shear thickening at intermediate shear rate followed by shear thinning at higher shear rate was shown, whereas in others, only shear thinning was observed (Figure 5). The shear-thinning behavior of the transient network was modeled in 1992 by Tanaka and Edwards. The focus on the process of association/dissociation of a polymer chain in solution of this model is well adapted to explain the single-Maxwellian relaxation. Overall, the nonlinear shear thinning behavior of HEUR solutions is explained by the shear induced fragmentation of the transient network, conversion of super-bridges to super-loops,[32] leading to the drop of the solution viscosity. However, the shear thickening behavior is not explained by the Tanaka-Edward model. There have been many attempts to understand and predict the molecular behavior and the nonlinear elasticity of transient networks, especially the shear thickening, but conclusions still remain controversial. Several studies have been performed and explained the appearance of shear thickening because of the finite extensible nonlinear elasticity (FENE) and/or the shear-enhanced formation of network strands.[33,34,35,36,37] On the other hand, Watanabe and co-workers related the thickening to a new approach considering the anisotropy of the transient network.[32,38] Indeed, their model showed that the thickening could arise from the shear enhanced re-association of HEUR strands in the shear gradient direction. This effect was balanced with the dissociation of the network and probably combined to FENE effect and shear induced strand formation. Moreover, they highlighted that HEUR transient networks had two concentration regimes.[39,40] The regime change occurred at a specific concentration called C*. At low concentration (C < C*), under 4wt% for the studied HEUR, sparse network formed by micelles and super-bridges strands was obtained (Figure 5). The rheological properties of such network were strongly influenced by the association/dissociation of hydrophilic blocs in micelles cores and in super-bridges strands formation. Moreover, the network was sensitive to the anisotropy of the spatial distribution of micelle cores, hence, shear thickening and a strong concentration dependence on modulus and on the relaxation time were observed. Whereas above 4wt% (C > C*), a dense, well percolated network was obtained. Micelle cores were connected one to another by a single HEUR chain and it did not contain intra strand association sites. Thus, its modulus and relaxation time were less dependent on polymer concentration. Furthermore, it was less sensitive to the anisotropy of the spatial distribution of cores, therefore, no thickening was observed. All these different models concern pure HEUR aqueous solutions, and it is much more unclear once HEUR are used in latex solutions. Nevertheless in recent years, it has been shown that

for regular HEUR concentrations used in waterborne paints, all or practically all HEUR molecules are adsorbed onto the latex particles surfaces. They form loops or transient network between particles, responsible of the rheological properties, instead of forming micelles and micellar network.[41,42,43,44,45]

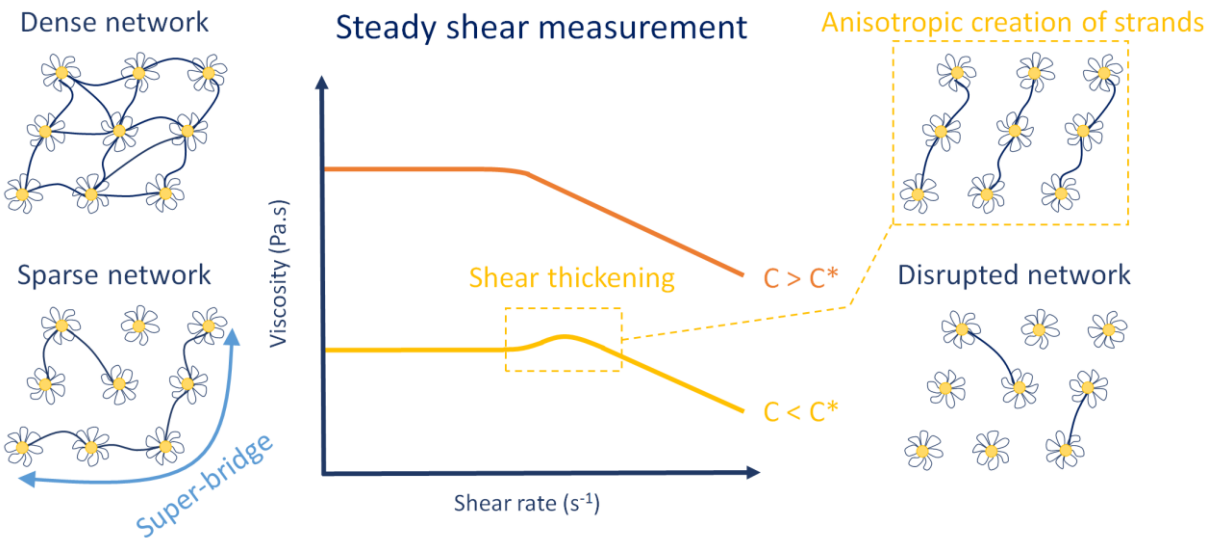

Figure 5 Structure model of the HEUR transient network depending of the concentration and the shear rate

Influence of the hydrophilic group

Despite the numerous HEUR structures described in the literature, the hydrophilic segment is always made of PEG allowing water solubility. One can note that in the industry, copolymers of PEG, poly(propylene glycol) (PPG) or poly(butylene glycol) (PBG) are sometimes used as hydrophilic group.[46,47] Hydrophilic group represents more than 90wt% of the structure, therefore it is mainly responsible of the final HEUR molecular weight. Its length is an important parameter since it determines the hydrophilic/hydrophobic ratio considering a constant hydrophobic group. This ratio is responsible of the network formed by HEUR. With a low molecular weight PEG, intramolecular associations of hydrophobic groups are favored, compared to intermolecular ones, because of their proximity. It leads to a higher aggregation number (N_{agg}) corresponding to the number of looping chains in a micelle.[48] In other words, in low molecular weight HEUR solutions, micelle formation is favored compared to the network formation through intermolecular associations that allow to bridge micelles together. Thus, the network density is low, leading to a low viscosity solution.

By increasing the size of the PEG, the distance between the hydrophobic groups of HEUR chains increases, favoring intermolecular associations. Hence, micelles are composed of less looping chains, N_{agg} decreases, and the network density increases. Therefore, by increasing the PEG molecular weight, the viscosity increases as well.[18,20,49] However, by increasing the PEG length, the hydrophilic/hydrophobic ratio increases up to a point where the hydrophobic groups are too few and their effect is limited in the formation of transient network. To offset this, it is necessary to increase

the HEUR concentration, which is rarely desired. Moreover, the higher is the molecular weight of HEUR, the more chain entanglements occur. It helps to increase the viscosity but at a certain point, it avoids the network formation resulting in the loss of associative polymers properties.[49,50] HEURs between 6,000 and 35,000 $g.mol^{-1}$ have been described but the Glass group reported a HEUR with molecular weight around 23,000 $g.mol^{-1}$ as the most efficient HEUR thickener.[49] However, depending on the final application the objective is not always to have the highest viscosity. Indeed, Reuvers reported the advantages of using 12,000 $g.mol^{-1}$ HEUR in latex solutions to reduce the pseudoplastic degree thus improving the leveling of the paint.[6] Moreover, it also presents a slower increase of viscosity during the curing process, leading to a longer open-time for the coating application. However, by reducing the HEUR molecular weight, one is exposed to undesired phase segregation below a certain molecular weight.[14]

Even though the hydrophilic group is composed of PEG, as previously presented, it can be obtained by two different methods leading to Uni-HEUR or S-G HEUR. The main difference between these two HEURs is their PDI. Indeed, Uni-HEUR are obtained from a narrowly distributed PEG whereas the polyaddition step to obtain S-G HEUR leads to polymer samples with broad PDI. After comparing Uni-HEUR and S-G HEUR end-capped with the same hydrophobic groups and a molecular weight close to 20,000 $g.mol^{-1}$, May *et al.* reported that S-G HEUR needed twice the concentration of Uni-HEUR to obtain the same properties.[51] The main reason is that the small chains present in a broad polydispersed sample associate through intramolecular associations in micelles, rather than contributing to the network formation *via* intermolecular associations.

To resume, the choice of the PEG molecular weight is very important because its length and its polydispersity directly affect the network formation and its density and therefore, the rheological properties of the solution (Figure 6). One should thus choose the hydrophilic group according to the desired rheological properties for the targeted application.

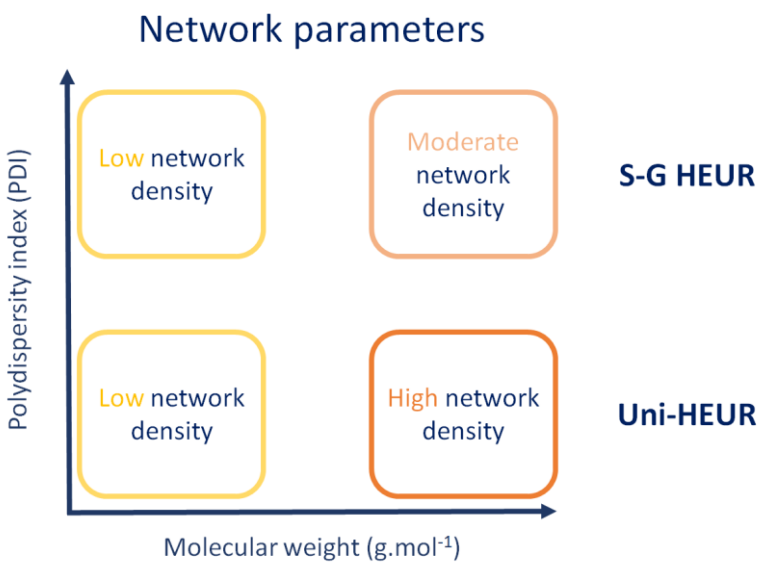

Figure 6: Network parameters depending on the PDI and the molecular weight of the hydrophilic group

Influence of the hydrophobic groups

Even if the hydrophobic groups represent less than 10wt% of the HEUR structure, they are mainly responsible for the rheological properties obtained. Indeed, because they associate *via* intramolecular or intermolecular interactions, they lead to micelle and transient network formation. The rheological properties mainly depend on two parameters: the network density and the relaxation time of the transient network. The aim of this part is to explain the relation between these two important parameters with the structure of the hydrophobic group of HEURs. It is important to note that the lower is the length of the hydrophilic group, the more the rheological properties are different between two hydrophobic groups.[49] Despite the fact that rheological properties of HEURs can be obtained with partially hydrophobically modified chains,[50] in order to understand the relationship between the HEUR structures and the rheological behavior, it is important to make sure that their hydrophobic substitutions are equivalent, usually above 90%. According to the transient network theory, the rheological activation energy (E_m) can be obtained by the following Arrhenius equation[52]:

$$\tau^{-1} = \omega_0 e^{-E_m/RT}$$

With τ the relaxation time of the system, ω_0 the frequency at which G' and G" are equal, T the temperature and R the gas constant. To obtain the E_m of a system, it is therefore necessary to perform oscillatory rheology measurements at different temperatures. Indeed, by increasing the temperature ω_0 is shifted toward higher frequencies, corresponding to a shorter τ. By plotting τ in function of temperature in the Arrhenius form, E_m of the system can be extracted *via* the slope value. This E_m is responsible of the transient network dynamic, and the higher is E_m, the higher is τ, which

means that hydrophobic groups engage and disengage slower in micelles. The increase of τ will reduce the Newtonian behavior at low shear rate and can lead to a pseudoplastic behavior over the whole shear rate range (Figure 7). The E_m is directly dependent on the hydrophobic group structure. Peng *et al.*[23] compared HEUR-1C10, HEUR-2C10 and HEUR-3C10, which are HEURs end-capped with one alkyl chain of ten carbons, two alkyl chains of ten carbons and three alkyl chains of ten carbons respectively. They reported that increasing the number of alkyl chains in hydrophobic groups allows increasing the relaxation time of HEUR solutions. In a same way, Wang *et al.*[17] compared HEUR-2C8, HEUR-2C12 and HEUR-2C16 and concluded that increasing the length of the alkyl chain gave higher relaxation time. Lately, Du *et al.*[24] compared three different HEURs with different hydrophobic parts having a constant carbon number by varying the number of aliphatic chains grafted to a phenyl. They determined E_m for HEUR-3C8, HEUR-2C12 and HEUR-C24 and obtained respectively 91 kJ/mol, 107 kJ/mol and 117 kJ/mol. Hence, one can note that a low E_m corresponds to a higher sensitivity to temperature. From these three studies, it can be concluded that increasing the length of the hydrophobic groups as well as the number of alkyl chains allows directly increasing the relaxation time of a HEUR solution. Moreover, in the specific case of a constant carbon number, the size of the carbon chain has more influence on the E_m than the number of chains. Additionally, the relaxation time is also strongly dependent on the HEUR concentration. Hence, increasing the polymer concentration allows a linear increase of τ.

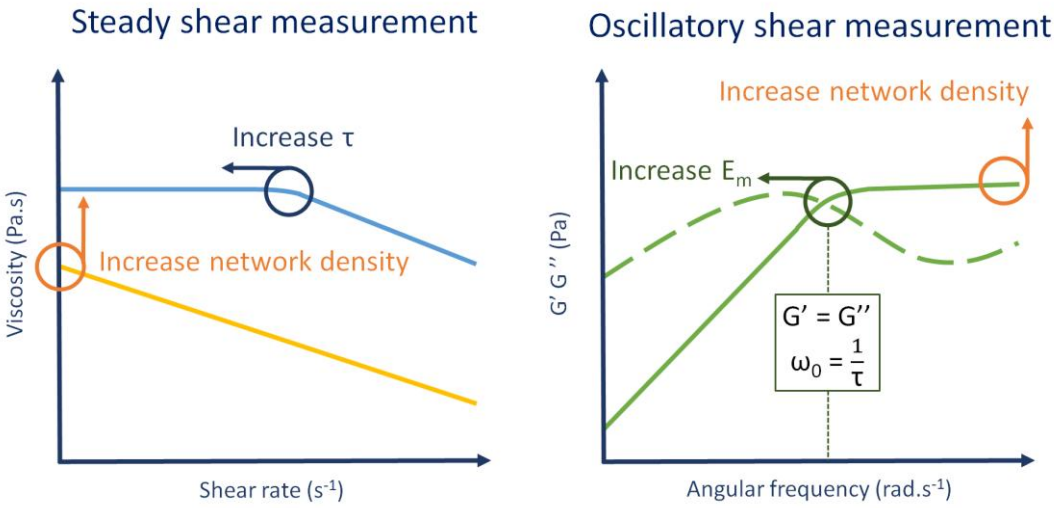

Figure 7: Influence of the network density and relaxation time onto rheological properties in steady shear and oscillatory shear measurements

On the other hand, a particular interest to the transient network density must be paid. Indeed, it is mainly responsible for the final viscosity of the solution. Higher are the number of bridges between micelles, higher is the solution viscosity. The network density mainly depends on three parameters:

the size of the hydrophilic group as explained before, the polymer concentration and the N_{agg}. The effect of the concentration on the density is quite trivial: increasing the polymer concentration entails the increase of the micelle concentration and consequently the density of the network. However, at a given concentration, two different HEURs with the same molecular weight could present a different network density depending on the ability of their hydrophobic groups to associate.[50] Different studies were performed in order to determine the influence of the hydrophobic structure on the ability to form intra or intermolecular associations. Intramolecular associations increase the number of looping chains in micelles, corresponding to a higher N_{agg}, whereas intermolecular associations bridge micelles together, increasing the network density, which corresponds to a lower N_{agg}. Du *et al*.[24] determined the N_{agg} of HEUR-3C8, HEUR-2C12 and HEUR-1C24 by fluorescence quenching measurements and obtained 21, 27 and 31 respectively. As reported before,[53,54] a higher number of hydrophobic groups leads to a smaller N_{agg} and CAC. Indeed, if N_{agg} is low, less polymer chains are involved in the formation of a micelle, thus they are formed at a lower concentration (lower CAC). The other studies of Tong's group did not report N_{agg} and CAC values, however denser networks were observed by increasing the number of C10 chains on HEUR structures comparing HEUR-1C10, HEUR-2C10 and HEUR-3C10.[23] The same trend was observed by increasing the size of hydrophobic groups comparing HEUR-2C8, HEUR-2C12 and HEUR-2C16.[17] To conclude, in order to increase the transient network density, one should increase the size and the number of hydrophobic groups or the polymer concentration. Nevertheless, in the specific case of a constant number of carbon, hydrophobic groups composed of numerous small chains lead to denser network compare to a single long chain systems.

The influence of the diisocyanate structure used for the synthesis of HEURs toward the rheological properties was studied by Kaczmarski *et al*.[50,55] This parameter has a low influence in comparison to the hydrophobic and hydrophilic group structures. Nevertheless, a bulkier diisocyanate such as 4,4'-methylene dicyclohexyl diisocyanate ($H_{12}MDI$) allows an aggregation phenomenon at lower concentration in comparison with hexamethylene diisocyanate (HDI), by increasing the effective size of the hydrophobic group (combination of both diisocyanate and alkyl chain).

Consequently, it is crucial to choose the hydrophobic group of HEURs with a very particular interest. Their association parameters determine the final rheological profile both in term of efficiency, of increasing the viscosity of a solution, as well as in tuning the pseudoplastic behavior to the shear rate range targeted for the application (Figure 8). Hence, a good choice of hydrophobic structure enables to decrease the amount of rheology additive added in a latex solution by a factor of 4 while retaining the same viscosity.[17]

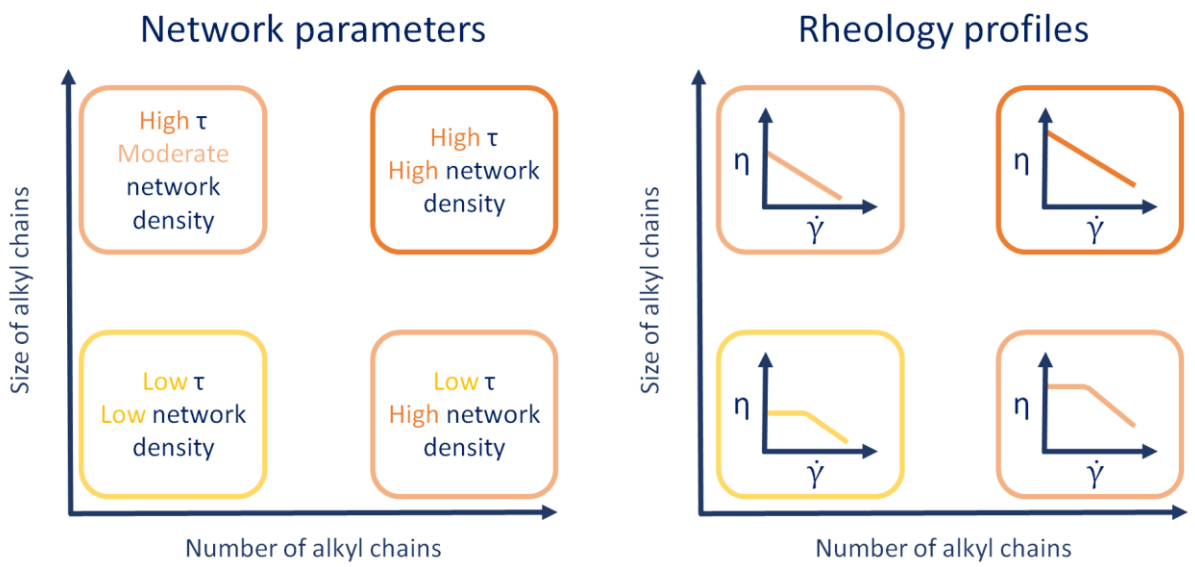

Figure 8: Network parameters and corresponding rheology profiles depending on the size and the number of alkyl chains of hydrophobic groups

Influence of surfactant

HEURs are often used in formulations containing surfactants and both interact strongly together. These interactions directly influence the network formation, the self-diffusion coefficient and the size of aggregates. Therefore, the study of these systems received a particular interest. Generally, the addition of surfactant leads to higher solution viscosity since it helps the micelles formation. Hence, this allows the increase of the transient network density by favoring the intermolecular associations of HEUR chains. However, the viscosity increases up to a maximum value with surfactant concentration. Over this specific concentration, surfactant starts to isolate HEUR chains and a drop of the network density, and therefore of the viscosity, are observed. Sodium dodecyl sulfate (SDS) is widely used as anionic surfactant and known to interact with PEG.[56,57] Consequently, SDS interacts with both hydrophilic and hydrophobic groups of HEURs. The interactions between HEUR and SDS depend on the HEUR structure, and the maximum viscosity is reached at a lower SDS concentration for HEUR composed of longer hydrophilic or hydrophobic groups.[14,49] Zhang *et al.*[58] reported a hydrophobe SDS/HEUR stoichiometry of 4 in their system (HEUR around 50,000 g.mol^{-1} end-capped with C16 alkyl chains) to achieve the maximum viscosity, whereas a hydrophobe stoichiometry of 33 completely dissolved the network, leading to rheological properties similar to a non-modified PEG/SDS solution. The same effects were reported for the cationic surfactant dodecyltrimethylammonium bromide (DTAB), but at higher concentrations. Glass and co-workers[49,55] compared the influence of anionic SDS and non-ionic Triton X-100 ($C_8H_{17}C_6H_4O(EtO)_{10}H$) to HEUR solutions. Higher viscosity and modulus were obtained for the solutions containing Triton X-100. Non-ionic surfactants effectively form larger micelles able to accommodate more hydrophobic HEUR chains than SDS micelles. Therefore, the network density got higher. With the objective to expand

the use of HEUR in food, pharmaceutical and cosmetic applications, requiring safer surfactants, Kim *et al*.[59] studied the influence of a non-ionic surfactant $C_{18}H_{37}(EO)_{20}H$ in HEUR solutions. They compared three Uni-HEUR of 35,000 g.mol^{-1} end-capped with C16, C18 and C22 alkyl chains in solution at 2wt%. For these three structures, the maximum viscosity was obtained with the addition of 0.6wt% of surfactant. However, the increase of viscosity was more important for HEUR with the shortest hydrophobic groups. Afterward, they studied the effect of ionic strength and pH on their optimal surfactant/HEUR-C22 solutions in pure water, in silica suspension and in oil/water emulsion. In the three cases, the solution viscosities were stable from pH 2.5 to 10 and from 0 to 1.2 wt% NaCl, highlighting very stable and versatile networks. Lately, Ibrahim *et al*.[60] reported very interesting results about the interactions occurring between SDS and the urethane linkages of HEURs, a parameter always neglected in HEUR synthesis. They observed a higher viscosity for HEURs with higher urethane linkages content. However, this study compared HEURs with variable molecular weight and hydrophobic groups. Hence, it is essential to compare HEURs with strictly identical structures, except their urethane linkages content to draw clear-cut conclusions about SDS/urethane linkage interactions. The addition of surfactant to HEUR solutions is very beneficial, and both ionic and non-ionic surfactants can be used, extending the possibilities of applications. Usually, other associative polymers (HASE and HMHEC) benefit from this effect only with ionic surfactants.[55] On the other hand, wormlike surfactant micelles were used in the presence of HEURs and yielded the formation of two cooperative transient networks with two distinct nonlinear behaviors with a fast and a slow relaxation time.[61,62] Due to this combination, it might be possible to reduce the necessary amount of rheology additive by using a lower amount of a mixture of the two components to obtain the desired properties.[63]

IV. Original HEURs

Unconventional structures

Even if the majority of HEURs are linear (Figure 1), some research teams have been interested in synthesizing more original structures. In the 90's, Lundberg *et al*.[14] described the synthesis of HEUR with an internal hydrophobic backbone in the structure coming from bi-, tris- or tetra-isocyanates. Then they were reacted with PEG of 50 and 100 oxyethylene units mono-terminated by a methyl (no hydrophobic group) or a nonylphenol group (NP). Therefore, linear, three- and four-arm structures were obtained (Figure 9). The structures with smaller PEG segments and NP presented a phase segregation because of the numerous intra-molecular associations involved due to the hydrophobic groups proximity. To overcome this issue, non-ionic surfactant SDS was added to obtain clear solution showing an increase of the viscosity solution. The study of these structures was not pursued, nevertheless, multi-arm structures as A and B could provide new rheological properties due to the

dense network that they could form. However, the use of longer PEG segment seems essential to avoid the phase segregation of such products.

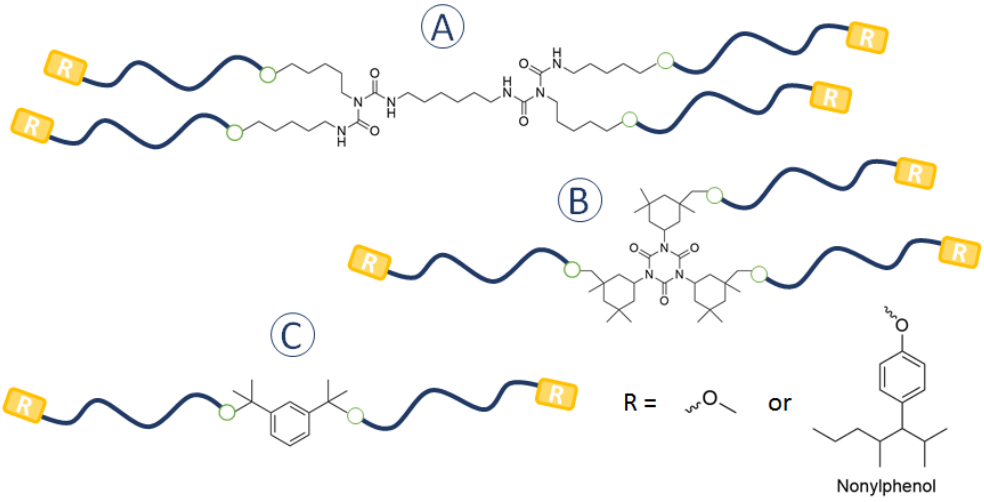

Figure 9: HEUR structures containing internal hydrophobic groups with ◯ as urethane linkages

On the other hand, Elliott *et al.*[48] synthesized a comb-like HEUR (Figure 10) similar to HASE structures. It was composed of polyurethane oligomers containing three pendant hydrophobic groups $C_{14}H_{29}$ spaced by PEG of 270 oxyethylene units and end-capped by $C_{18}H_{37}$ groups. Once in solution, the increase of the viscosity solution was not as high as expected for such a structure. Moreover, without the end-capping of $C_{18}H_{37}$ groups, surprisingly no effect was observed. The synthesized structure was probably not the one expected, no structural analyses being reported. Despite the potential of the multi-arms and comb-like HEURs, the structures studied did not show outstanding performances. However, multi-arms and comb-like HEURs would deserve to be investigated with more reliable synthesis protocols.

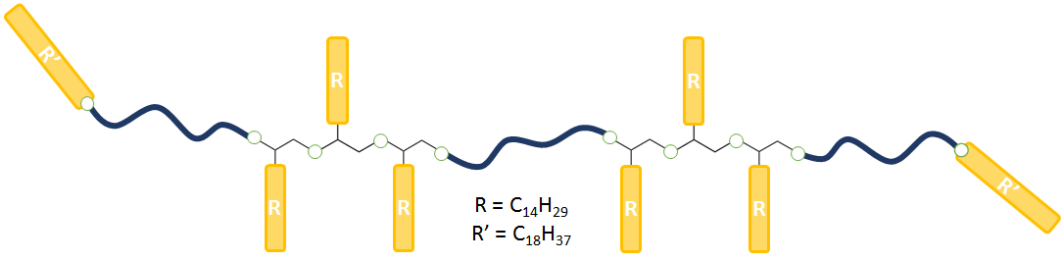

Figure 1: Comb-like HEUR structure with ◯ as urethane linkages

Furthermore, structure with innovative hydrophobic groups were also synthesized (Figure 11). Elliott *et al.*[48] synthesized a Uni-HEUR end-capped with multi-branched hydrophobic segments composed of six $C_{10}H_{21}$ or $C_{12}H_{25}$ chains linked to a polyether backbone. Once again, the increase of the solution viscosity was not as high as it could be expected for this structure. To explain this observation, the polyether backbone probably rendered the hydrophobic block more hydrophilic. Lately, similar multi-branched structures made entirely from carbon were patented by COATEX.[64] Moreover, a multi-

branched structure containing numerous phenyl groups was also described in a patent.[46] This structure would probably combine π-π and hydrophobic interactions to lead to high rheological properties. Numerous structures remain promising, either concerning the HEUR shape or the synthesis of new hydrophobic groups, which could lead to new association behaviors.

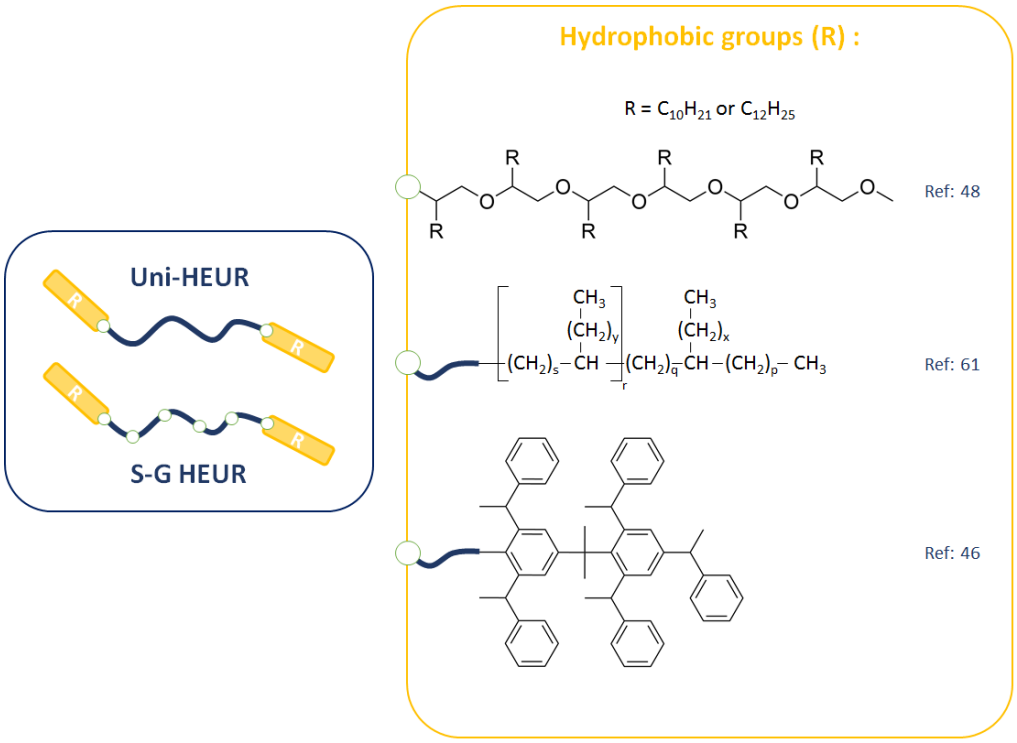

Figure 11: Novel hydrophobic groups used in HEUR synthesis with ◯ as urethane linkages

Sensitive and reactive HEURs

HEURs described until here allow controlling precisely the rheological properties in particular with a well-adapted structures. Nevertheless, in recent years, Tong and co-workers provided a new aspect to the HEUR technology allowing the control of the rheological properties with external stimuli. Therefore, they synthesized HEUR end-functionalized with different stimuli responsive groups.

In one hand, photosensitive groups such as azobenzene[26] and spiropyran,[29] known for their photoisomerisation ability, were grafted to the end of the HEUR hydrophobic groups. These two sensitive groups underwent a quick photoisomerization inducing an amphiphilic change, thus altering the hydrophobic/hydrophilic balance of modified HEUR chains.[65,66] Therefore, the aggregation and the rheological behavior of both photosensitive AzoHEUR and SP-HEUR were controlled by UV irradiation. In both cases, photoisomerization occurred under UV irradiations, resulting in a drop of the solution viscosity by around 10 orders of magnitude (Figure 12). The viscosity change resulted from a rearrangement of the HEUR network because each isomer favored either bridge-loop or loop-bridge transitions. Specifically to AzoHEUR, the initial viscosity value was recovered after 6 min of

irradiation. Many cycles of UV/visible irradiations have been performed, showing the recovery of the viscosity values at each step, supporting the reversibility of the system. Moreover, the *cis*-AzoHEUR obtained under UV irradiation presented a shorter relaxation time in comparison to the *trans*-AzoHEUR, whereas SP-HEUR (visible light) and MC-HEUR (UV-light isomer) had a similar one.

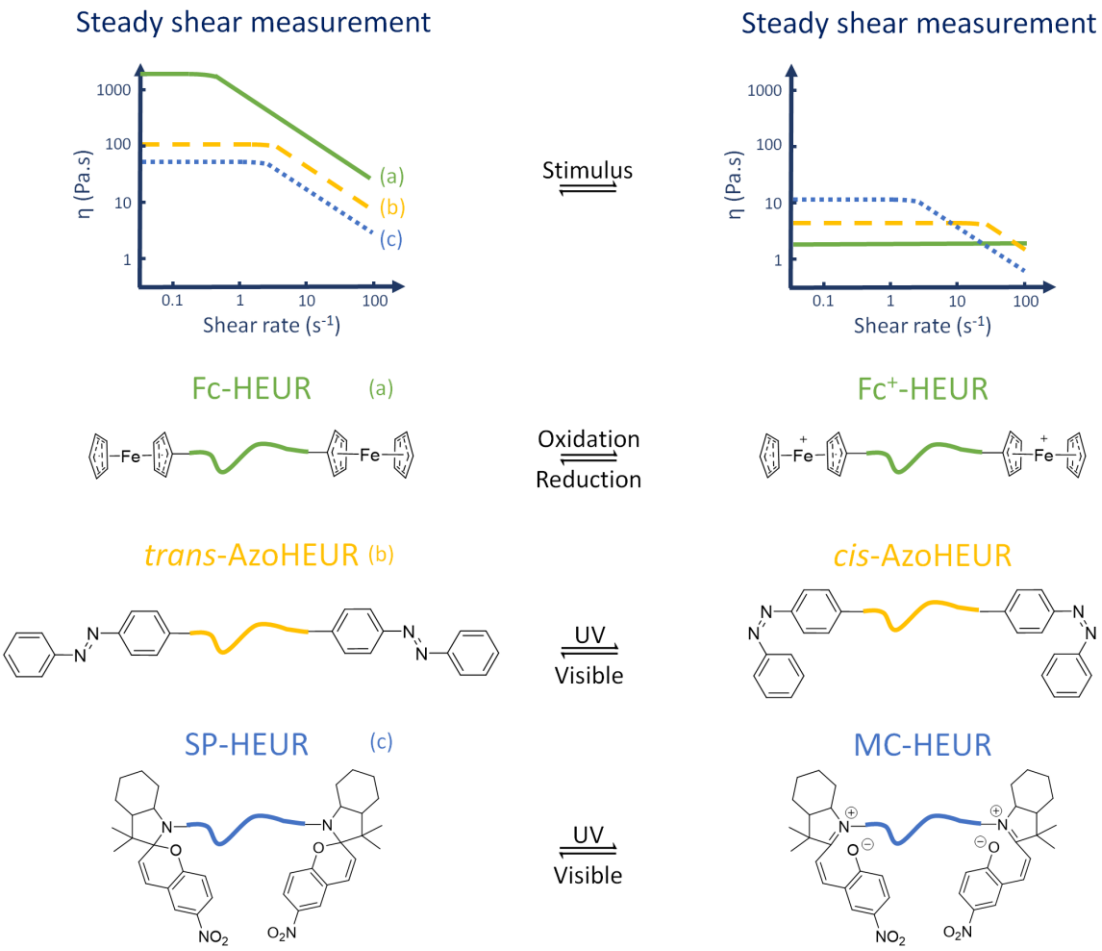

Figure 12: Steady shear measurements and structures of sensitive HEURs under different stimuli

On the other hand, Tong *et al*. synthetized redox sensitive HEUR *via* a ferrocene end-functionalization of HEUR chains.[27] Similarly to photosensitive HEURs, Fc-HEUR presented two rheological profiles depending on the oxidative state of the ferrocene moiety.[67] A strong difference between the CACs of Fc-HEUR and Fc^+-HEUR was observed, of 0.07 g/L and 5.0 g/L respectively, resulting from a strong reduction of the hydrophobic interactions by Fc^+-HEUR. The many redox cycles performed have shown the reversibility of the system and a huge difference in viscosity (of an order of magnitude of 1,000 between the two forms) (Figure 12). Indeed, the Fc^+-HEUR highly favored the bridge-loop transition. Moreover as the *cis*-AzoHEUR and *trans*-AzoHEUR, Fc-HEUR and Fc^+-HEUR presented two different relaxation times. Afterward, Tong's group combined the redox and photosensitive groups into a single AzoFc-HEUR structure (Figure4).[28] Therefore, four different rheological profiles were obtained with a single additive depending on the stimuli applied. The UV

irradiation of the solution led to a slightly lower relaxation time and modulus G_0, whereas under oxidative reaction, a strong drop of both parameters was observed. Combining the two stimuli led to even lower modulus and relaxation time (Figure 13). Thereafter, in 2018, Du *et al*.[68] reported novel sensitive HEURs end-functionalized by coumarin (Cou-HEUR), known for its photo-induced dimerization at 365 nm.[69] Before irradiation, the solution had a Newtonian behavior and was slightly viscous (1.75 Pa.s). After UV-irradiation for 600 s, a maximum degree of dimerization of 82 % was reached and led to shear-thinning properties and a highly viscous solution (around 6,000 Pa.s). Indeed, the dimerization brought to an unusual transient network formed by train loops (end to end linked flower loops) and bridges covalently linked, slowing the system relaxation. The rheological properties of Cou-HEUR were controlled by the degree of dimerization which was influenced by the light irradiation time. However, the dimerization of coumarin is known to be reversible at 254 nm and this aspect was not studied by the authors. Similarly, in 2019, Du *et al*.[70] synthesized anthracene end-functionalized HEUR (An-HEUR) expecting to achieve a higher degree of dimerization than Cou-HEUR. Indeed, anthracene is able to achieve 99% of dimerization in crystal state.[71] After 55 min of UV-irradiation, a dimerization degree of 98.9% was achieved and led to an ultrahigh molecular weight multiblock polymer (850,000 g/mol) from An-HEUR (23,500 g/mol). Once again, the UV-irradiation increased sharply the solution viscosity and shear-thinning properties over the whole range of shear rate were observed. Due to the entanglements and associations, the dynamic of the solution was suppressed because of the train loop and the covalent bridges. However, due to the thermo-reversibility of the dimerization of anthracene, many cycles of UV-irradiation and heating at 150°C were performed to show the reversibility of the network. Indeed, it is possible to return to the initial An-HEUR structure of 23,500 g/mol and its properties by heating it at 150°C for 1 h. The chain extension of HEURs using anthracene dimerization allowed the preparation of ultrahigh molecular weight linear multiblock polymers with well-defined structure and shear-thinning properties.

In conclusion, it is important to select the stimuli sensitive group carefully according to the intensity of desired viscosity change and whether or not the network relaxation time is controlled. The stimuli sensitive HEURs are of interest for the reversible control of their aggregation and rheological behavior which could extend HEURs to specific applications such as smart rheological fluids, sensors or microfluidic devices.

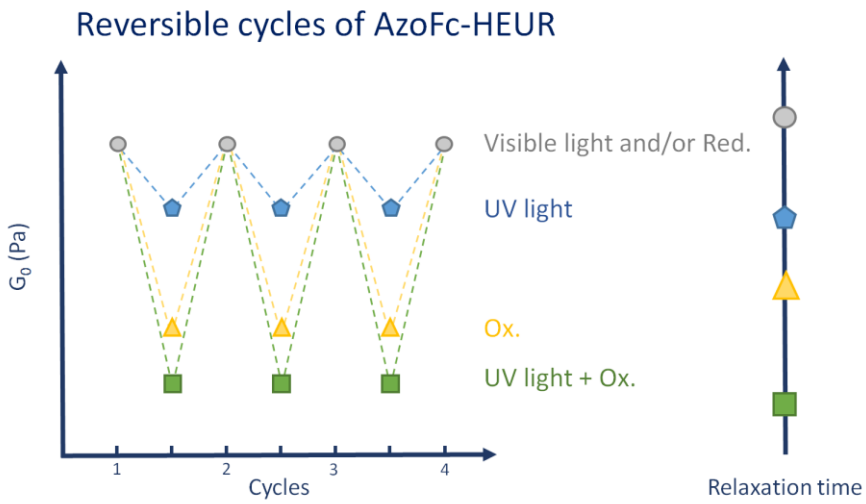

Figure 13: Influence of the different stimulus applied to AzoFc-HEUR solution on G_0 and the relaxation time over many cycles

Later on, Guan *et al.*[30] synthesized a HEUR bearing benzophenone terminal groups, $BPC_{11}HEUR$, to obtain a reactive rheology additive. Benzophenone is effectively known as a hydrogen abstracting type photo-initiator, creating a reactive radical able to initiate polymerization of double bonds, and a non-reactive benzophenone ketyl radical.[72] Therefore, in addition to the typical rheological properties of HEURs, $BPC_{11}HEUR$ acted as a water-soluble macro-initiator for the polymerization of a UV waterborne coating. Finally, non-reactive benzophenone ketyl radicals derived from $BPC_{11}HEUR$ were terminated by other radicals and chemically linked to the resin, limiting its migration in the final cured product. Hence, UV reactive rheological additives could be of interest in many waterborne systems such as cosmetics, inks, coatings or adhesives, etc.

V. Conclusion and outlook

HEURs are used in many waterborne applications due to their wide range of rheological properties, especially because of the multiple possibilities of synthesizable structures. Structural parameters such as molecular weight, dispersity and especially the hydrophobic group structure are decisive to obtain the desired rheological profile. Particularly, they determine the association behavior of the HEUR chains by favoring either intra- or intermolecular interactions. Moreover, these associations lead to a transient network responsible of the rheological properties. Consequently, obtaining the desired rheological properties of a HEUR solution is a complex compromise between the different parameters: HEUR structure, concentration, presence of surfactant, etc. Even if the evolutions of the rheological properties with the HEUR structure are relatively well understood nowadays, some aspects are still controversial in particular the transition from linear to nonlinear viscoelasticity.

Moreover, the synthesis of sensitive or reactive HEURs is a new way to extend the use of HEURs to new application fields. Indeed, the control of the viscosity of a solution under external stimuli would

lead to smart rheological fluids. On the other hand, the development of innovative structures such as multi-arms or the novel hydrophobic or hydrophilic groups would also lead to new rheological properties or more efficient products. However, isocyanate monomers are yet used for HEUR synthesis, which remains a drawback due to toxicity of monomers, hence new routes could be interesting to envisage. These different aspects in combination with the development of waterborne products, in a way to propose more environmentally and health friendly products, promise a flourishing future for the HEUR technology.

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Notes

The authors declare no competing financial interest

Acknowledgement

The authors acknowledge Synthron Company for funding this study and the PhD Thesis of Baptiste Quienne

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