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Baptiste Quienne, Julien Pinaud, Sylvain Caillol. Synthesis of Hydrophobically modified ethoxylated non-isocyanate urethanes (HENIURs) and their use as rheology additives. *European Polymer Journal*, 2022, 175, pp.111384. 10.1016/j.eurpolymj.2022.111384 . hal-03706671

**HAL Id: hal-03706671**

**<https://hal.science/hal-03706671>**

Submitted on 27 Jun 2022

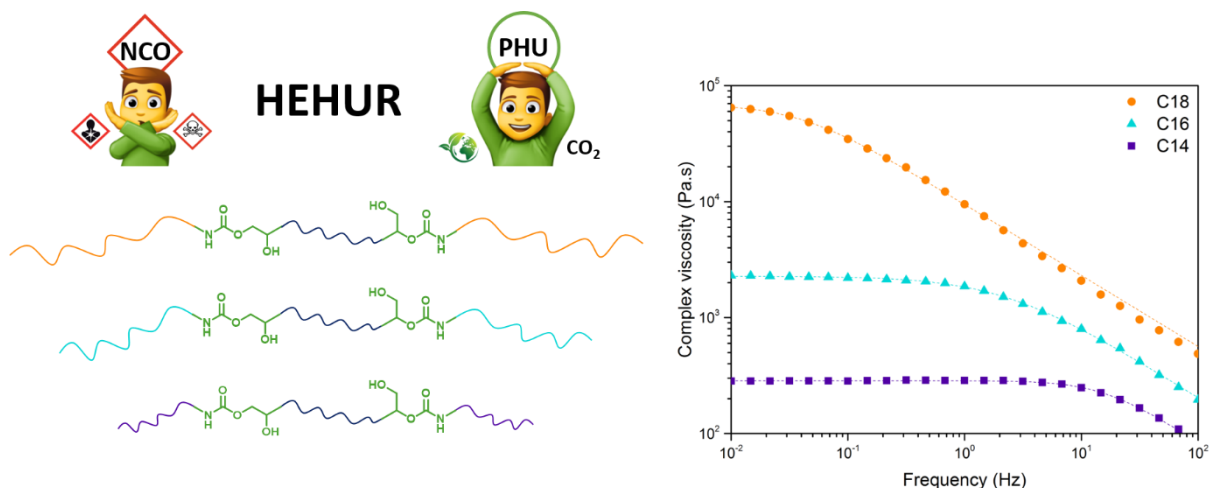
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# Synthesis of Hydrophobically modified ethoxylated non-isocyanate urethanes (HENIURs) and their use as rheology additives

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## Abstract

Telechelic associative polymers such as Hydrophobically modified ethoxylated urethanes (HEURs) are an important class of rheology additives used in many industrial fields allowing a precise control of the rheology. To avoid the use of toxic isocyanates, more eco-friendly HEURs were synthesized based on the cyclo-carbonate/amine addition reaction. Hydrophobically modified ethoxylated hydroxyurethanes (HEHURs) were thus obtained by the aminolysis of telechelic 5-membered cyclic carbonates functionalized PEG in the presence of hydrophobic amines of 14, 16 and 18 carbons. The rheological properties ( $G'$ ,  $G''$  and  $\eta^*$ ) of these amphiphilic structures were investigated, as well as the influence of different parameters such as: temperature (5 to 25 °C), concentration (10 to 20 wt%) and hydrophobic chain length. Their rheological properties were also compared to isocyanate-based equivalent structures (HEURs). Finally, HEHURs were used in latex solution to illustrate their potential use as rheology additives and their thickening efficiency at 0.25 wt%. Mainly Newtonian to fully pseudoplastic profiles were obtained depending on the variation of the hydrophobic chain length.

## Keywords

Polyhydroxyurethanes, viscosity, waterborne, eco-friendly, thickening

## Introduction

Hydrophobically modified ethoxylated urethanes (HEURs) are widely used as rheology additives in many waterborne systems for various applications such as coatings, emulsions, ink...<sup>1-5</sup> They are telechelic polymers composed of a hydrophilic main chain of poly(ethylene glycol) (PEG) that is end-functionalized with hydrophobic groups attached through urethane linkages. HEURs are associative polymers, which through molecular association of their hydrophobic groups, form flower-like micelles above their critical micelle concentration (CMC).<sup>6-10</sup> The hydrophilic chains form the flower loops and the hydrophobic groups the micelle cores. Above the critical percolation concentration ( $C_p$ ), polymer chains start to bridge neighboring micelles together and lead to a transient network.<sup>11</sup> The dynamic physical network formed leads to a sharp increase of the modulus and of the viscosity of the solution. Due to the dynamic interactions of hydrophobic groups, the system can relax in a finite time and is sensitive to shear rate. Indeed, under a high shear rate, the transient network is destroyed but is reformed at rest, therefore, pseudoplastic properties are obtained.<sup>12</sup> The rheological properties of HEURs depend strongly on the network formation and its characteristics such as its relaxation time and its density. Lately, Ginzburg *et al.* discussed the structure, the rheology and the models of HEUR aqueous solutions and model paints containing HEURs.<sup>13</sup> Our team has also recently published a perspective article focusing on the structure/rheological properties relationship of HEURs, highlighting the influence of the different structural parameters and the new trends of architectures and innovative HEURs.<sup>14</sup> We also put our interest to the synthesis pathways reported in the literature to obtain HEURs and mentioned the possibility to develop less toxic and more eco-friendly routes. Indeed, HEURs are usually synthesized by reacting the terminal hydroxyl groups of PEG with diisocyanates and hydrophobic mono-alcohols.<sup>15,16</sup> However, isocyanates are harmful for health and environment,<sup>17,18</sup> and during the last decade, their substitution has become a major concern.<sup>19-21</sup> Intensive research about non-isocyanate polyurethanes (NIPUs) has thus been carried out and the synthesis of polyhydroxyurethanes (PHUs) seems to be the most promising and practical solution.<sup>22-25</sup> PHUs are obtained through aminolysis reaction of cyclic carbonates that leads to an urethane linkage and a pendant hydroxyl group. Five-membered cyclic carbonates are particularly interesting because they can be synthesized *via* carbonation of epoxides with carbon dioxide. Due to the valorization of carbon dioxide known as: a renewable, cheap and nontoxic resource, this synthesis pathway is the less toxic and one of the most eco-friendly for the synthesis of PHUs.<sup>26-32</sup>

The development of water-based PHUs is currently gaining increasing interest to extend their scope of applications to more specific markets and performances and proposes greener processes. With this keen interest, Bizet *et al.*<sup>33</sup> discussed about the achievements and the remaining challenges of water-based non-isocyanate polyurethane-ureas (NIPUUs). Water-based PHUs are mainly

waterborne dispersions of PHUs and there are only few studies about water soluble PHUs. In 2016, Gennen *et al.*<sup>34</sup> reported the first PHU hydrogels based on poly(ethylene glycol) dicyclic carbonate crosslinked with different amines. Moreover, they recently published novel PHU hydrogels with adaptable functionalities and properties using a copolymerization strategy, or for formaldehyde capture.<sup>35,36</sup> Bossion *et al.*<sup>37</sup> synthesized water-dispersible PHUs for the formation of self-healable supramolecular networks using ionic interactions. On the other hand, Matsukizono *et al.*<sup>38</sup> synthesized linear PHUs from 6-membered dicyclic carbonates and diamines, prior functionalizing their OH groups with succinic anhydride to obtain pendant carboxylates and afford water-soluble PHUs.

In the present work, we synthesized, to our knowledge, the first amphiphilic PHUs through the aminolysis of poly(ethylene glycol) dicyclic carbonate (PEG6000-DC<sub>5</sub>) with hydrophobic amines. These are the first non-isocyanate HEURs (HENIURs) ever reported, that are more precisely called hydrophobically modified ethoxylated hydroxyurethanes (HEHURs), in reference to NIPU and PHU respectively. By combining PEG of 6,000 g/mol and hydrophobic chains from 14 to 18 carbons of length, three innovative structures were designed and prepared. A comparative study of their rheological properties were performed in water and in a latex solution to highlight their use as rheology modifiers. Moreover, they were compared to two isocyanate-based equivalent structures.

## Materials & Methods:

### Materials

Poly(ethylene glycol) 6,000 g/mol was purchased from Alfa Aesar (Kandel, Germany). Poly(ethylene glycol) diglycidyl ether 6,000 g/mol, tetradecylamine, tetradecyl isocyanate, hexadecylamine, octadecylamine, octadecyl isocyanate, triazabicyclodecene (TBD), tetra-butylammonium bromide (TBABr), ethyl acetate, diethyl ether, toluene, ethanol and dibutyltin dilaurate (DBTDL) were purchased from Sigma-Aldrich Merck (Darmstadt, Germany). Pure acrylic emulsion (50 wt%, pH 5.2) was purchased from Synthomer. Carbon dioxide was purchased from Air Liquide (Vitrolles, France). All materials were used as received. The NMR solvent CDCl<sub>3</sub> was purchased from Eurisotop (Saint-Aubin, France).

### Characterizations

#### Nuclear Magnetic Resonance

Proton Nuclear Magnetic Resonance (<sup>1</sup>H NMR) analyses were performed in deuterated chloroform (CDCl<sub>3</sub>, 99.50% isotopic purity) using Bruker Advance 400 MHz NMR spectrometer at a temperature of 25 °C.

## Size Exclusion Chromatography

Molar masses and polydispersity were measured by Size Exclusion Chromatography (SEC) using two Resipore 300 x 7.5 mm columns from Agilent as stationary phase and DMF with 0.1 wt% LiBr as eluent at 70 °C and 0.8 mL/min. Narrow PEG standards were used for calibration.

## Rheology

Rheological properties were measured using a Thermo Fisher HAAKE MARS rheometer with a cone-plate geometry with a diameter of 35 mm and 2° cone angle.

## Synthetic protocols

### Synthesis of PEG-dicyclic carbonate (PEG6000-DC<sub>5</sub>)

Poly(ethylene glycol) diglycidyl ether of 6,000 g/mol (PEG6000-DGE) was solubilized in ethyl acetate and poured in an autoclave reactor with 3 wt% of tetra-butylammonium bromide (TBABr). The reaction was conducted at 80 °C under CO<sub>2</sub> pressure of 20 bar for 3 days. The polymer was then precipitated in diethyl ether and washed with cold diethyl ether before drying under vacuum. The epoxides were fully converted into cyclic carbonates, as shown by <sup>1</sup>H NMR (Figure S1). PEG6000-DC<sub>5</sub> was recovered as a white powder with a yield of 94 %.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ/ppm = 3.63 (s, CH<sub>2</sub>), 3.61–3.72 (m, CH<sub>2</sub>), 4.35-4.51 (m, CH<sub>2</sub>), 4.82 (m, CH).

### Synthesis of HEHURs

2 g (1 eq.) of PEG6000-DC<sub>5</sub>, 0.285 g (2 eq.) of tetradecylamine and 0.005 g (0.05 eq.) of TBD were reacted in bulk at 80 °C for 12 h. Then, 20 mL of ethanol were added and heating of the reaction media was stopped. Once the solution was back to room temperature, the polymer was precipitated in diethyl ether to remove the remaining amines and catalyst. The polymer obtained HEHUR-2C14 was then washed with diethyl ether before drying under vacuum. A white powder was obtained with a yield of 85 %. The same procedure was performed with hexadecylamine and octadecylamine and led respectively to HEHUR-2C16 (yield = 86 %) and HEHUR-2C18 (yield = 90 %).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ/ppm = 0.86 (t, CH<sub>3</sub>), 1.24 (s, CH<sub>2</sub>), 1.47 (t, CH<sub>2</sub>), 3.14 (q, CH<sub>2</sub>), 3.63 (s, CH<sub>2</sub>), 3.97 (m, CH), 4.05-4.16 (m, CH<sub>2</sub>), 4.93 (m, CH).

### Synthesis of HEURs

3 g (1 eq.) of Poly(ethylene glycol) 6 000 g/mol and 0.0065 g of DBTDL (0.2 wt% of the total mass) were solubilized in 6 mL of dried toluene. The mixture was then freeze-dried to remove any trace of water. Then, under argon atmosphere, 0.251 g of tetradecyl isocyanate (1.05 eq.) were added to the mixture at 80 °C under stirring. After 2 h of reaction, 10 mL of toluene were added and the heating

was stopped. Once the solution was back to room temperature, the polymer was precipitated in diethyl ether to remove the remaining isocyanates and catalyst. The polymer obtained, HEUR-2C14, was then washed with diethyl ether before drying under vacuum. A white powder was obtained with a yield of 92 %. The same procedure was performed with octadecyl isocyanate and led to HEUR-2C18 (yield = 94 %).

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta/\text{ppm}$  = 0.86 (t,  $\text{CH}_3$ ), 1.24 (s,  $\text{CH}_2$ ), 1.47 (t,  $\text{CH}_2$ ), 3.14 (q,  $\text{CH}_2$ ), 3.63 (s,  $\text{CH}_2$ ), 4.19 (t,  $\text{CH}_2$ ).

### Determination of end-capping functionality

The end-capping functionality of the HEHURs and HEURs were calculated using  $^1\text{H}$  NMR spectroscopy. In theory, for a PEG of 6 000 g/mol, the integration of the  $\text{CH}_2$  protons of the polymer chain ( $nH_{\text{theo}}$ ) should integrate for:

$$nH_{\text{theo}} = \int 3.63 \text{ ppm} = \frac{M_n \times nH_0}{M_0} \quad (1)$$

With  $M_n$  the PEG molar mass,  $M_0$  the molar mass of the ethylene glycol repetition unit and  $nH_0$  the number of H of the ethylene glycol repetition unit.

Therefore, the end-capping functionality (ECF) was calculated with the following equation:

$$ECF (\%) = \frac{nH_{\text{theo}}}{nH_{\text{synth}}} \quad (2)$$

With  $nH_{\text{synth}} = \int 3.63 \text{ ppm}$ , when the spectrum is calibrated at 6 H for the peak of the terminal alkyl chains groups  $\text{CH}_3$  (0.86 ppm).

### Preparation of samples for rheology measurements

Weighted amount of rheology additives were solubilized in deionized water and stirred at room temperature overnight before analyses. For analyses in latex (pure acrylic emulsion, solid content of 50 %, pH 5.2), rheology additives were first solubilized at 25 wt% in ethanol. The rheology additive solution was then added to latex under stirring. Latex solutions were analyzed after 45 min of equilibrium.

### Maxwell model

The relaxation behavior of HEURs and HEHURs aqueous solutions can be described by the single Maxwell model. All the plots were fitted ( $R^2 > 0.99$ ) with the following equations:

$$G'(f) = \frac{G_0(2\pi f)^2\tau^2}{1 + (2\pi f)^2\tau^2} \quad G''(f) = \frac{G_0(2\pi f)^2\tau^2}{1 + (2\pi f)^2\tau^2} \quad (3)$$

With  $f$  the frequency,  $G_0$  the plateau modulus and  $\tau$  the relaxation time.

## Carreau-Yasuda model

The complex viscosity measurements were fitted with the Carreau-Yasuda model ( $R^2 > 0.99$ ) known to study shear thinning behaviors through complex viscosity. Curves were fitted with the following equation<sup>50</sup>:

$$\eta^*(f) = \eta_0^* \left[ 1 + \left( \frac{\eta_0^*}{\tau^*} 2\pi f \right)^a \right]^{\frac{n-1}{a}} \quad (4)$$

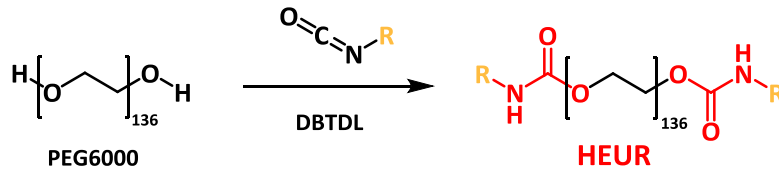
With  $f$  the frequency,  $\eta^*$  the complex viscosity,  $\eta_0^*$  the zero-frequency complex viscosity,  $\tau^*$  the shear stress at the transition between Newtonian and power law regions,  $a$  the width of the transition region between Newtonian and power law behavior and  $n$  the power law index.

Moreover, the relaxation time  $\tau$  can be presented as:

$$\tau = \frac{\eta_0^*}{\tau^*} \quad (5)$$

## Results & discussion:

### HEUR synthesis:



### HEHUR synthesis:

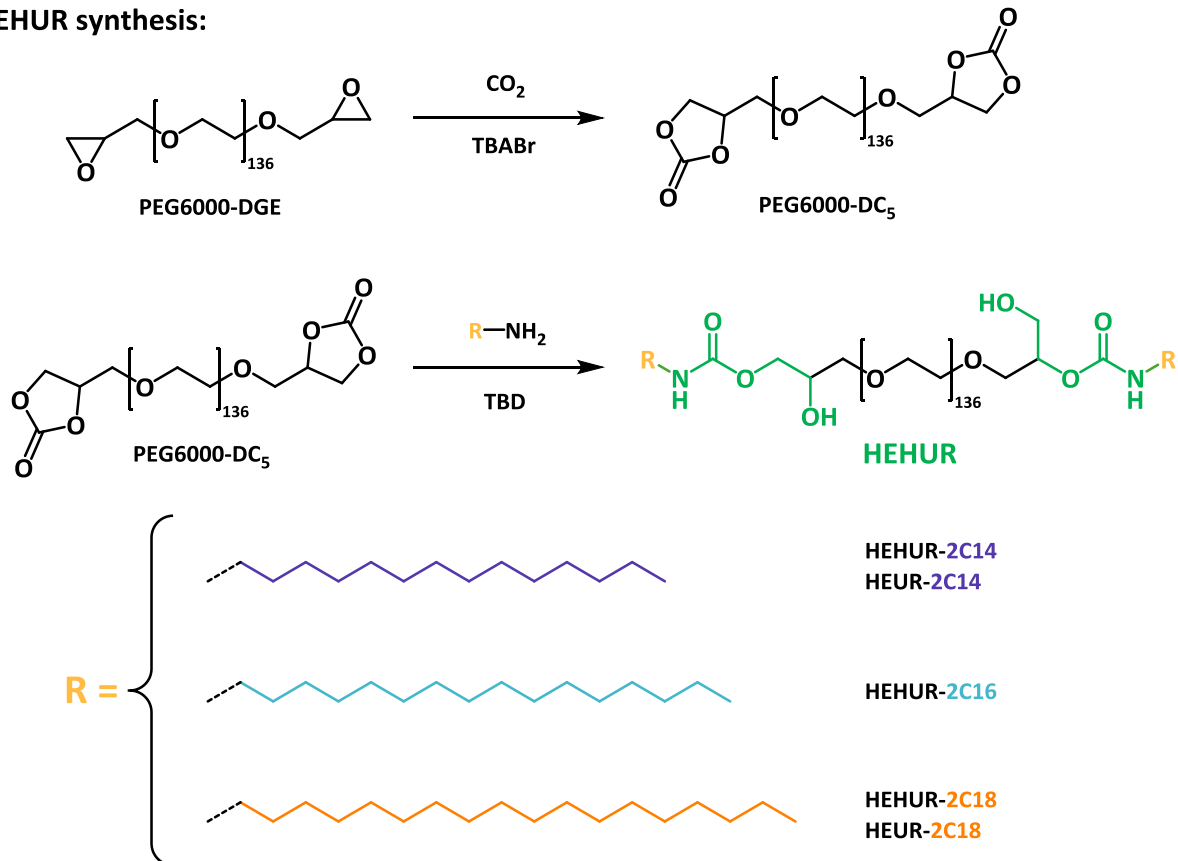


Figure 1: Synthesis pathways of HEURs and HEHURs.

## Synthesis and structural characterizations

The HEHURs structures were synthesized from commercially available PEG6000-DGE. After its carbonation with CO<sub>2</sub>, the aminolysis of the PEG6000-DC<sub>5</sub> with alkylamines of 14, 16 and 18 carbons were performed and HEHUR-2C14, HEHUR-2C16 and HEHUR-2C18 were respectively obtained with 85 % to 90 % yield. On the other hand, in order to compare their rheological properties, two isocyanate-based equivalent HEUR structures were synthesized in a single step. Alkyl isocyanates of 14 and 18 carbons were reacted with PEG6000 in presence of 0.2 wt% DBTDL and yielded HEUR-2C14 and HEUR-2C18 respectively (Figure 1). A molar mass of 6,000 g/mol is quite low compared to HEURs described in the literature which are usually between 10,000 and 25,000 g/mol. Indeed, this is the highest molar mass of PEG-DGE commercially available. Low molar masses HEURs usually leads to



low CMC and high aggregation numbers ( $N_{agg}$ ). Furthermore, the influence of the hydrophobic groups on the network formation and rheological properties is increased as it represents a larger part of the HEUR structure.<sup>14,39</sup>

The structure of the five pure HEHURs and HEURs synthesized were characterized by SEC and  $^1\text{H}$  NMR (Figure S2). All the HEHURs and HEURs have an identical dispersity ( $\mathcal{D}$ ) of 1.1 as their initial PEG. It is an important parameter since it influences the transient network formation responsible of the thickening properties. A high  $\mathcal{D}$ , usually found with S-G HEURs obtained by a step growth polymerization, leads to lower rheological properties in comparison with Uni-HEURs (monodispersed HEURs) at the same concentration.<sup>40</sup> Indeed, the residual lower masses of a step growth polymerization preferentially form micelles rather than the transient network responsible of the final shear-thinning properties. With a similar  $\mathcal{D}$ , the rheological properties of different structures are comparable.

The  $^1\text{H}$  NMR spectra of the HEHURs and HEURs in  $\text{CDCl}_3$  (Figure 2) allow to clearly identify the urethane and the hydroxyurethane linkages in the structures. Indeed, the aminolysis of cyclic carbonates leads to the formation of primary and secondary hydroxyl groups that can be identified by  $^1\text{H}$  NMR signals. Indeed, the signal displayed at 3.97 ppm corresponds to the proton in  $\alpha$  position of the secondary alcohol, and the two signals between 4.03 and 4.22 ppm to the diastereoisotopic protons close to it, whereas the signal at 4.93 ppm corresponds to the proton in  $\beta$  position of the primary alcohol (Figure 2a). In the case of HEURs, a single signal is observed at 4.19 ppm, which corresponds to protons in  $\alpha$  position of the urethane linkage (Figure 2b). For both HEHURs and HEURs, the protons in  $\alpha$  position of the NH form a quadruplet at 3.13 ppm.

In order to make sure that the PEG was well end-functionalized, the end-capping functionality (ECF) was determined by  $^1\text{H}$  NMR. In order to form a strong transient network, it is imperative that a maximum of chain-ends are functionalized with hydrophobic chains. HEURs were obtained with more than 96 % of their chain-ends functionalized with a hydrophobic group. On the other hand, HEHURs were obtained with a slightly lower functionality since the starting PEG6000-DC<sub>5</sub> had 92 % of cyclic carbonates chain-ends. The use of tetradecylamine led to the full conversion of the cyclic carbonates to obtain HEHUR-2C14. A functionality of 90 % and 82 % was obtained for HEHUR-2C16 and HEHUR-2C18 respectively. These high values of ECF confirmed that the expected structures were successfully obtained.

Table 1: Structural and solution characteristics of HEURs and HEHURs

$M_n$ (g/mol) <sup>a</sup>	$\mathcal{D}$ <sup>a</sup>	ECF <sup>b</sup>
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PEG6000-DC <sub>5</sub>	6,200	1.1	92 %
HEHUR-2C14	6,600	1.1	92 %
HEUR-2C14	5,800	1.1	99 %
HEHUR-2C16	6,600	1.1	90 %
HEHUR-2C18	6,700	1.1	82 %
HEUR-2C18	5,800	1.1	96 %

<sup>a</sup>: determined by SEC in DMF; <sup>b</sup>: determined by <sup>1</sup>H NMR.

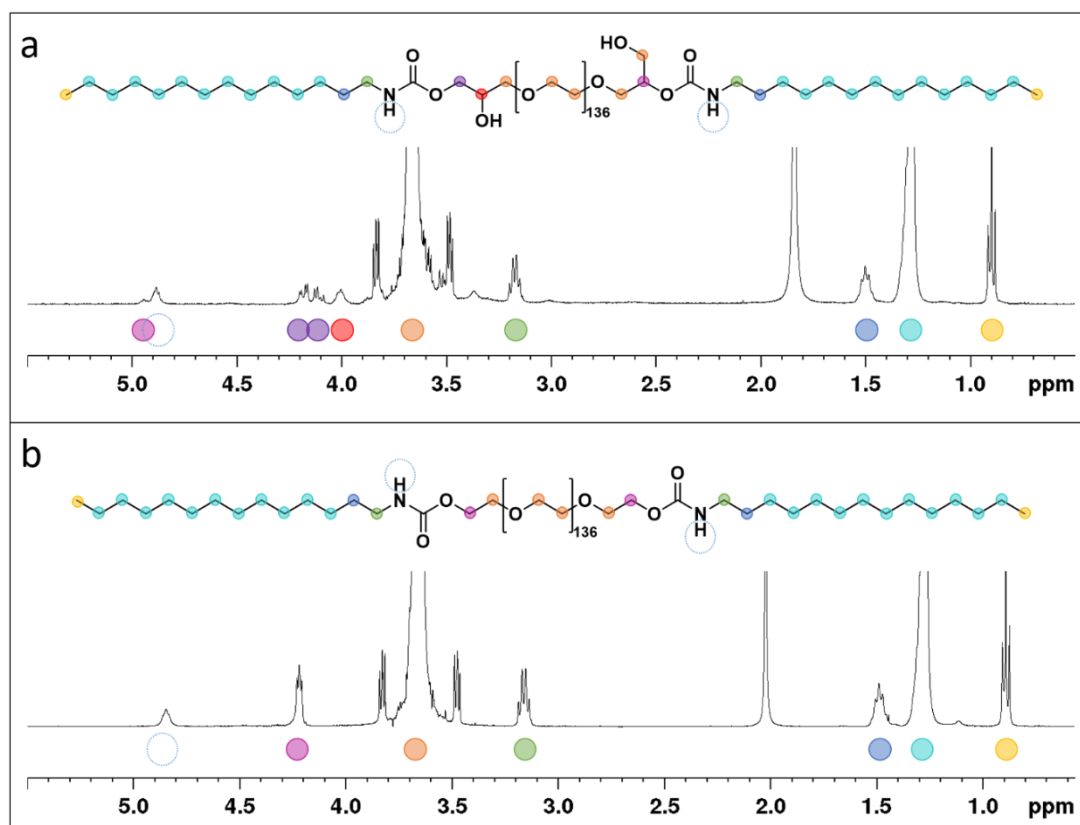


Figure 2: <sup>1</sup>H NMR spectrum of (a) HEHUR-2C14 and (b) HEUR-2C14 in CDCl<sub>3</sub> at 25 °C.

## Rheological properties

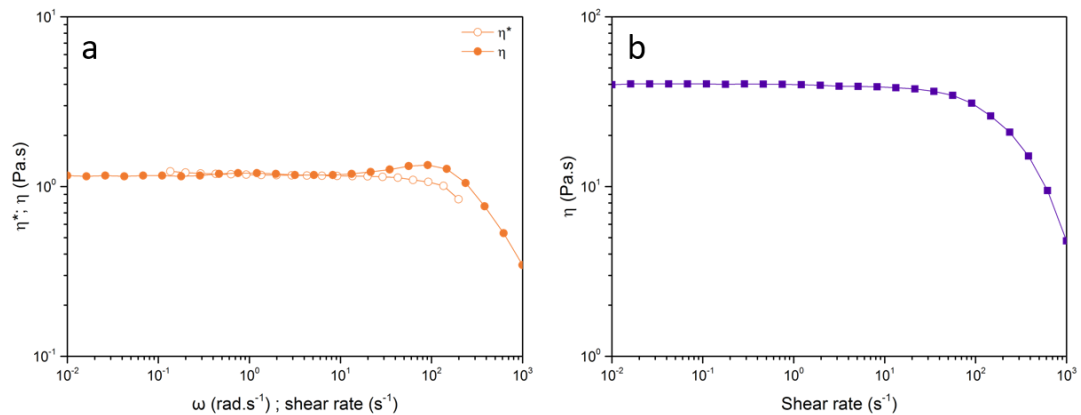


Figure 3: (a) Comparison of steady state viscosity and complex viscosity of 5 wt% HEHUR-2C18 aqueous solution at 25 °C. (b) Steady state viscosity of 20 wt% HEHUR-2C14 aqueous solution at 25 °C.

Steady state shear measurements were first performed on 5 wt% HEHUR-2C18 solution (Figure 3a). Shear thinning properties preceded by shear thickening were observed at high shear rate. Moreover, the deviation of the steady state viscosity ( $\eta$ ) compared to the complex viscosity ( $\eta^*$ ) at high shear rate indicates that dilute HEHUR solutions do not obey to the Cox-Merz ( $\eta(\dot{\gamma}) = \eta^*(\omega)$ ) empirical rule as already described for sparse HEUR networks and complex structured fluids.<sup>41–43</sup> The shear thickening highlights that a sparse network is obtained and is composed of linear sequences of HEHUR chains (superbridges) that connect micelles together. The dissociation/association of these anisotropic superbridges was already described by Watanabe *et al.* for low HEUR concentrations.<sup>44</sup> Conversely, at higher concentration, a denser network is formed and micelles are connected by individual HEUR chains, less affected by the creation of strands. Indeed, the concentration needed to be increased up to 20 wt% for HEHUR-2C14 to observe pseudoplastic properties (Figure 3b) due to the shorter hydrophobic groups that lead to a weaker transient network. Moreover, in comparison to 5 wt% HEHUR-2C18 solution, no shear thickening was observed. Indeed as discussed previously, at high concentration, a dense network composed of micelles connected by single HEUR chains are usually obtained for HEURs. These first results demonstrate that similarly to HEUR, nonlinear rheological properties of HEHURs are also concentration dependent.

However, as some of the HEUR and HEHUR solutions studied were extremely viscous when the concentration was increased above 5 wt%, the analyses were limited to very low shear rates. Therefore, the nonlinear rheological properties of HEHURs could not be further studied. To this aim, HEHUR networks that relax more slowly are required, for instance by increasing the size of the PEG hydrophilic chain. Nevertheless, PEG-DGE of higher molar mass than 6,000 g/mol is not commercially available and, despite all our attempts, very difficult to synthesize with a good functionality. Hence,

to study and compare the thickening properties of the different additives synthesized, HEUR and HEHUR aqueous solutions were analyzed exclusively by oscillatory shear measurements measuring storage  $G'$  and loss  $G''$  moduli and the complex viscosity from 100 to 0.01 Hz in their linear domain. The influence of different parameters such as concentration, temperature and additives structures was investigated. HEHUR-2C18 was mainly used to illustrate the different effects of these parameters on the rheological properties, nevertheless, the same conclusions can be made with HEHUR-2C16 and HEHUR-2C14 (Figure S4 & S5)

The relaxation behavior of HEUR aqueous solutions in their linear domain can be described by the single Maxwell model. It is also the case for the HEHUR aqueous solutions studied, therefore, all the plots were fitted (dashing lines) with the Equation 3. Moreover, the complex viscosity measurements were fitted with the Carreau-Yasuda model (dashing lines) known to study shear thinning behaviors through complex viscosity. Curves were fitted with the Equation 4.<sup>45</sup>

### a. Influence of the concentration

First, the influence of the polymer concentration was studied. Measurements were performed with aqueous solutions of 10, 15 and 20 wt% of polymer. In this conditions, HEHUR-2C18 was the most suitable HEHUR to observe the different behaviors induced by the increase of the concentration (Figure 4). At low frequencies,  $G'' > G'$  and  $G'$  increased with a slope of one and  $G''$  with a slope of two, characteristic of a viscous liquid. At high frequencies,  $G' > G''$  and  $G'$  reached a plateau while  $G''$  started to decrease. Between the two frequency regimes,  $G'$  and  $G''$  crossed at a point, indicating that the solutions were viscoelastic. With the increase of the concentration from 10 to 20 wt%, the plateau modulus  $G_0$  increased while the  $G'-G''$  cross point gradually shifted to lower frequencies, indicating a network with a longer relaxation time  $\tau$ , as usually observed with HEURs.

On the other hand, as can be seen with the complex viscosity measurements (Figure 4b), the HEHUR solutions showed a Newtonian plateau at low frequencies and a decrease of the complex viscosity at higher frequencies corresponding to the thermal reorganization of the transient network through dissociation/association of hydrophobic chains. By increasing the concentration, the zero-frequency complex viscosity  $\eta_0^*$  is increased from 110 Pa.s at 10 wt%, 765 Pa.s at 15 wt% to 3,500 Pa.s at 20 wt%. Moreover, at higher concentrations the Newtonian plateau at low frequencies is reduced, in accordance with the shift of the  $G'-G''$  cross point. Indeed, at higher concentration, the transient network is denser and displays a higher relaxation time as indicated by the calculated  $\tau$  using the Carreau-Yasuda model (Table 2). Indeed, the latter goes from 0.01 to 0.14 s for 10 and 20 wt% respectively. Moreover the decrease of the  $a$  parameter with the increase of the concentration is in accordance with the reduction of the Newtonian plateau.<sup>50</sup> Furthermore, the  $n$  values comprised between 0 and 1 confirmed the pseudoplastic properties of the HEHUR solutions.

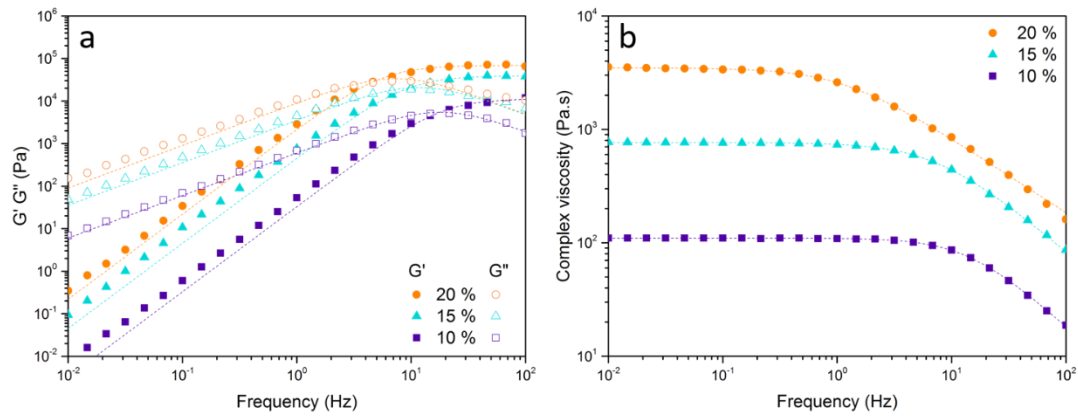


Figure 4: Plots of storage modulus  $G'$  and loss modulus  $G''$  (a) and complex viscosity (b) vs frequency for HEHUR-2C18 aqueous solutions at 25 °C and indicated concentrations.

Table 2: Calculated Carreau-Yasuda parameters for HEHUR-2C18 aqueous solutions at 25°C.

Concentration	$\eta_0^*$ (Pa.s)	$\tau^*$ (Pa)	a	n	$\tau$ (s)
10 %	110 ± 1	9,700 ± 390	1.65 ± 0.03	0.10 ± 0.02	0.01
15 %	765 ± 1	36,900 ± 2,200	1.39 ± 0.04	0.13 ± 0.03	0.02
20 %	3,500 ± 13	24,900 ± 2,000	1.26 ± 0.06	0.39 ± 0.02	0.14

## b. Influence of the hydrophobic chain length

The hydrophobic chain length is known to modify the aggregation behavior and rheological properties of HEURs. Therefore, HEHUR-2C14, HEHUR-2C16 and HEHUR-2C18 were analyzed at 20 wt% and 5 °C, allowing to highlight the influence of the hydrophobic chain length on the rheological properties (Figure 5).

HEHUR-2C14 shows a viscous liquid behavior above almost the whole range of frequency studied with  $G'' > G'$ , which is well corresponding with a single Maxwellian relaxation. It indicates that the transient network formed is very sparse and with a very low relaxation time. Indeed, HEURs with shorter hydrophobic chains are known to form low density networks with very fast exchanges favoring a low relaxation time.<sup>46</sup> On the other hand, longer hydrophobic chains form denser network with higher relaxation time. This is in perfect accordance with HEHUR-2C16 which presents higher  $G_0$  and higher relaxation time than HEHUR-2C14. With a shift of  $G'-G''$  cross point to lower frequencies, HEHUR-2C16 shows viscoelastic properties over the range of frequencies studied. The trend is confirmed with the HEHUR-2C18 solution that has even higher  $G_0$  and a cross point at even lower frequencies (Figure 5a). At low frequencies, HEHUR-2C18 shows a single Maxwellian relaxation,

whereas at high frequencies it starts to deviate from the model, indicating another relaxation mode. This relaxation mode corresponds to the formation of a dense network as described by Uneyama *et al.*<sup>47</sup> Similarly to HEURs, HEHURs are able to self-associate to sparse and dense networks. Moreover, denser networks are obtained with longer hydrophobic chains.

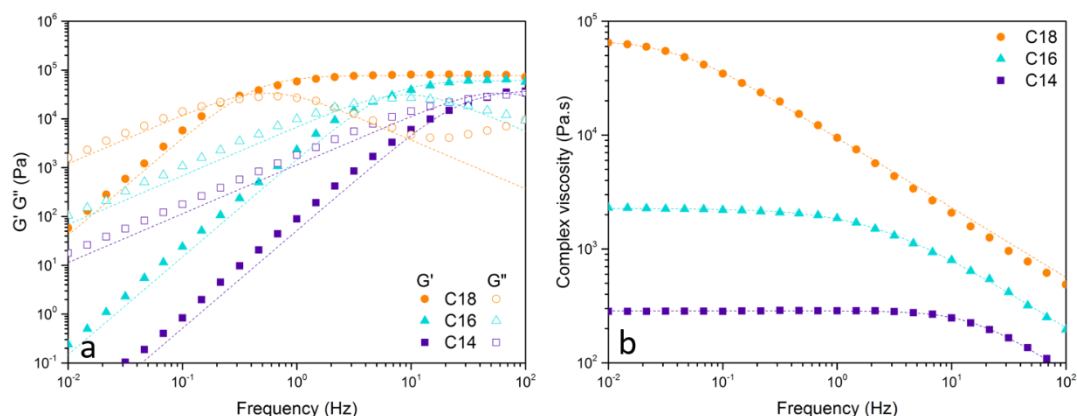


Figure 5: Plots of storage modulus  $G'$  and loss modulus  $G''$  (a) and complex viscosity (b) vs frequency of HEHUR aqueous solutions with indicated hydrophobic chain length at 20 wt% and 5 °C.

Concerning the complex viscosity (Figure 5b), HEHUR-2C14 shows a large Newtonian plateau whereas, HEHUR-2C18 viscosity almost drop over the whole frequency range. Nevertheless, they both perfectly fit with the Carreau-Yasuda model. As seen before, the increase of the network relaxation time from 0.01 to 4.06 s induced by longer hydrophobic chains leads to a reduction of the Newtonian plateau to lower frequencies (Table 3). Moreover, the higher network density produced with longer hydrophobic chain associations strongly increases the complex viscosity from 285 to 68,900 Pa.s for HEHUR-2C14 and HEHUR-2C18 respectively.

Table 3: Calculated Carreau-Yasuda parameters for HEHUR aqueous solutions at 20 wt% and 5°C.

	$\eta_0^*$ (Pa.s)	$\tau^*$ (Pa)	a	n	$\tau$ (s)
HEHUR-2C14	285 ± 1	27,400 ± 1,800	1.83 ± 0.15	0.36 ± 0.03	0.01
HEHUR-2C16	2,300 ± 9	31,900 ± 1,300	1.43 ± 0.13	0.37 ± 0.04	0.07
HEHUR-2C18	68,900 ± 15	17,000 ± 1,100	1.05 ± 0.10	0.39 ± 0.04	4.06

To highlight both effects of concentration and hydrophobic chain length, the zero-frequency ( $10^{-2}$  Hz) complex viscosity  $\eta_0^*$  was represented as a function of HEHUR concentration (Figure 6). For HEHUR-2C14,  $\eta_0^*$  is very low, the increase of the concentration from 10 to 20 wt% only increasing the  $\eta_0^*$  by a factor of 12. HEHUR-2C16 shows higher  $\eta_0^*$  with a stronger increase particularly above 15 wt%,

since between 10 and 20 wt%,  $\eta_0^*$  is multiplied by a factor of 17. In the case of HEHUR-2C18, a sharp increase of  $\eta_0^*$  is observed above 15 wt% and  $\eta_0^*$  is multiplied by a factor of 32 between the two extreme concentrations. Concentration and the hydrophobic structures have strong impacts to  $\eta_0^*$  values. The rise in concentration densifies the transient network allowing to reach higher viscosities. Additionally, the length of the hydrophobic chain can strengthen this effect by favoring strong network associations. Therefore, the hydrophobic chains play a key role in the final HEHUR rheological properties.

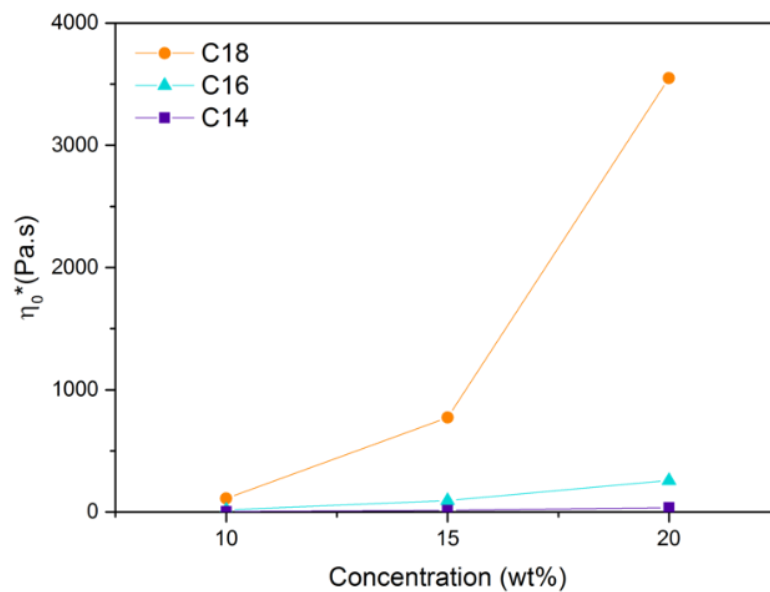


Figure 6: Zero-frequency complex viscosity  $\eta_0^*$  as a function of HEHUR concentration at 25 °C.

### c. Comparison to HEURs

In order to compare the rheological properties of HEHURs and HEURs, HEUR-2C14 and HEUR-2C18 were analyzed in the same conditions than HEHURs, in aqueous solutions of different concentrations. Concerning C18 hydrophobic chains, for both HEHUR and HEUR, the rheological properties at 10 wt% are extremely similar. They both present the same short relaxation time, with a  $G'$ - $G''$  cross point at high frequencies and a single Maxwellian relaxation at lower frequencies (Figure 7). Moreover,  $\eta_0^*$  are identical as well as their rheological profiles with a long Newtonian plateau and a drop of complex viscosity at high frequencies. This similarity indicates that both HEHUR-2C18 and HEUR-2C18 form similar transient networks. With the increase of concentration to 20 wt%, HEHUR-2C18 starts to present slightly higher  $G_0$  and  $\eta_0^*$  compared to its isocyanate-based equivalent, which indicates the formation of a bit stronger network with a longer relaxation time (Table 4).

Table 4: Calculated Carreau-Yasuda parameters for HEHUR-2C18 and HEUR-2C18 aqueous solutions at 10 and 20 wt% at 25°C.

	Concentration	$\eta_0^*$ (Pa.s)	$\tau^*$ (Pa)	a	n	$\tau$ (s)
HEUR-2C18	10 %	110 ± 1	11,300 ± 700	1,67 ± 0.05	0.06 ± 0.03	0.01
HEHUR-2C18	10 %	110 ± 1	15,700 ± 400	1.67 ± 0.03	0.01 ± 0.02	0.01
HEUR-2C18	20 %	1,500 ± 7	61,600 ± 4,50	1.02 ± 0.06	0.03 ± 0.01	0.02
HEHUR-2C18	20 %	3,500 ± 13	24,900 ± 2,000	1.39 ± 0.06	0.36 ± 0.02	0.14

In the case of C14 hydrophobic chains, the rheological properties of HEURs and HEHURs are different. Indeed, HEHUR-2C14 presents reduced properties compared to HEUR-2C14 at 20 wt% with Newtonian properties, whereas HEUR-2C14 is mainly pseudoplastic. The 20 wt% HEHUR-2C14 solution presents similar properties than the 10 wt% HEHUR-2C14 solution (Figure S3).

To conclude, HEHUR-2C14 has reduced properties compared to its isocyanate-based equivalent, whereas, HEHUR-2C18 and HEUR-2C18, present similar rheological properties. With shorter hydrophobic chains, the pendant hydroxyl groups of the hydroxyurethane linkages may reduce the aggregation behavior of HEHUR-14. Indeed, by increasing the hydrophilicity of the structure, the hydrophilic/lipophilic (HLB) may increase, therefore the ability of HEHURs to self-aggregate may vary. Nevertheless, with longer hydrophobic chains, the possible influence of the pendant hydroxyl groups on the HEHUR self-association seems to be suppressed as HEHUR-2C18 and HEUR-2C18 have similar rheological properties. Indeed, the longer C18 hydrophobic chains could neutralize the hydroxyl effect more easily.

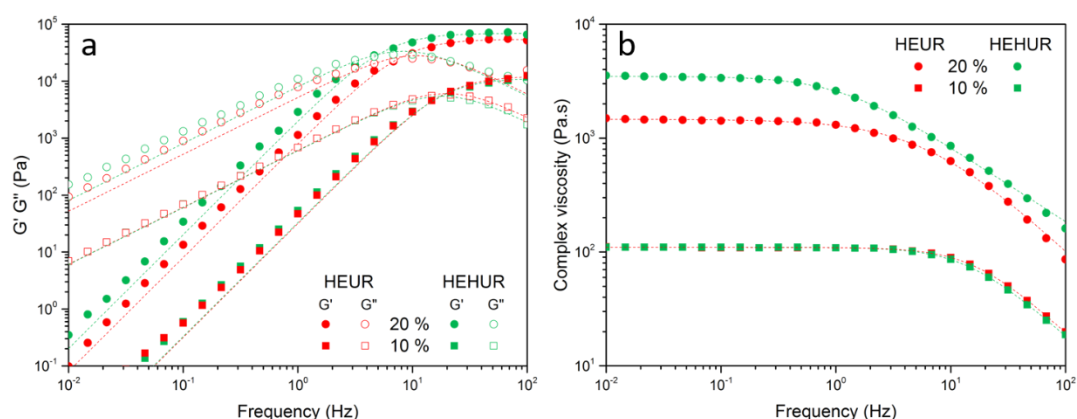


Figure 7: Plots of storage modulus  $G'$  and loss modulus  $G''$  (a) and complex viscosity (b) vs frequency of HEHUR-2C18 aqueous solutions at 25 °C and indicated concentrations.



#### d. Influence of temperature

The last parameter studied was the temperature, able to favor or not the association in the transient network and modify the final rheological properties. Therefore, HEURs and HEHURs were investigated at three temperatures 5, 10 and 25 °C.

The effect of temperature was clearly observed with the HEHUR-2C18 aqueous solutions at 10 wt% (Figure 8). Indeed, with the reduction of the temperature from 25 to 5 °C,  $G_0$  increased and the  $G'$ - $G''$  cross point shifted to lower frequencies. At low temperature, the engaging/disengaging mechanism of the polymer chains in the transient network is reduced. Therefore, the relaxation time is increased from 0.01 to 0.1 s and the viscosity from 100 to 1,600 Pa.s at 25 and 5 °C respectively (Table 5). Moreover, the Newtonian plateau were reduced to lower frequencies.

Table 5: Calculated Carreau-Yasuda parameters for HEHUR-2C18 aqueous solutions at 10 wt%.

Temperature	$\eta_0^*$ (Pa.s)	$\tau^*$ (Pa)	a	n	$\tau$ (s)
25 °C	110 ± 1	15,700 ± 400	1.67 ± 0.03	0.01 ± 0.02	0.01
10 °C	650 ± 1	13,900 ± 400	1.66 ± 0.03	0.03 ± 0.01	0.05
5 °C	1,600 ± 1	9,700 ± 300	1.65 ± 0.02	0.1 ± 0.01	0.10

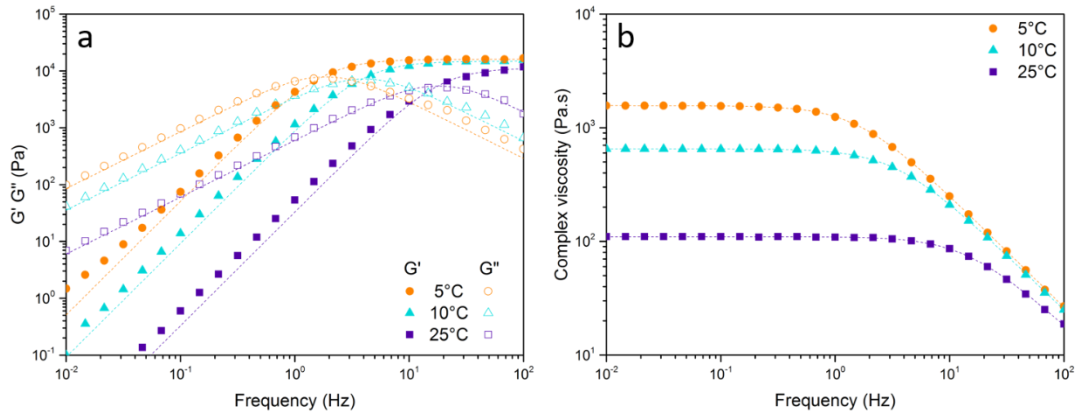


Figure 8: Plots of storage modulus  $G'$  and loss modulus  $G''$  (a) and complex viscosity (b) vs frequency for HEHUR-2C18 aqueous solutions at a concentration of 10 wt% at indicated temperatures.

Furthermore, the study at different temperatures allowed to determine the rheological activation energy ( $E_m$ ) of the associative polymer solutions. It represents the potential energy barrier of hydrophobic chains disengaging in micellar associations. According to the transient network theory,  $E_m$  can be obtained with the temperature dependence of the zero-frequency viscosity  $\eta_0^*$  in the following Arrhenius form:<sup>46</sup>

$$\eta_0^*(T) = Ae^{E_m/RT} \quad (6)$$

Where A is a pre-exponential constant,  $E_m$  is the rheological activation energy (J/mol), T is the thermodynamic temperature (K) and R the gas constant (8.314 J.mol<sup>-1</sup>.K<sup>-1</sup>). Experimental complex viscosity values, measured at a frequency of 0.01 Hz in the Newtonian region were used as  $\eta_0^*$ , where the transient network is not affected by the frequency and viscosity is constant.

The plot of  $\eta_0^*$  as a function of temperature in Arrhenius form is illustrated in Figure 9. The  $E_m$  of each HEUR and HEHUR was extracted from the slope of the linear fitting (Table 6). Surprisingly, despite the different rheological behaviors of the HEUR and HEHUR solutions observed previously, HEHUR-2C14 and HEUR-2C14 have an identical  $E_m$  of 65 kJ/mol. In the case of C18 hydrophobic chains, once again, similar  $E_m$  values were obtained for HEHUR and HEUR (90 kJ/mol). Between the two, HEHUR-2C16 have an intermediate  $E_m$  of 70 kJ/mol.

To conclude, the activation energy for disengagement of polymers chains  $E_m$  increases with the size of the hydrophobic chain of the synthesized associative polymers.  $E_m$  is correlated to the number of elastically effective chains  $\nu$  in the network. Their number in Newtonian plateau is given by<sup>27</sup>:

$$\nu = n \left( \frac{\omega(M)^2 e^{\frac{E_m}{kT}}}{1 + \omega(M)^2 e^{\frac{E_m}{kT}}} \right) \quad (7)$$

With M the molar mass, n the number of chains,  $\omega(M)$  a weak function of molar mass. As mentioned before, the five associative polymers synthesized have similar molar masses and polydispersities and differ only by the length of their hydrophobic chains and the nature of the urethane linkages. As  $\nu$  is a unique function of  $E_m$ , a larger  $E_m$  means a higher number of elastically effective chains and a higher relaxation time. This is in accordance with the rheological investigations, HEHUR-2C18 has the highest  $E_m$ ,  $\eta_0^*$  and  $\tau$  and forms a transient network with more elastically effective chains.

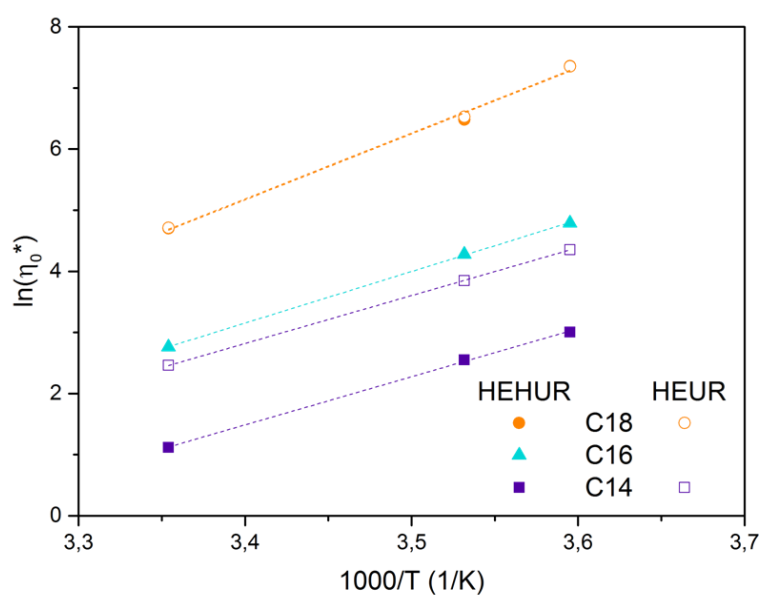


Figure 9: Plots of  $\eta_0^*$  as a function of temperature in Arrhenius form for 10 wt% HEHUR and HEUR aqueous solutions.

Table 6: Rheological activation energy of HEHURs and HEURs.

	$E_m$ (kJ/mol)
HEHUR-2C14	$65 \pm 1$
HEUR-2C14	$65 \pm 1$
HEHUR-2C16	$70 \pm 1$
HEHUR-2C18	$90 \pm 6$
HEUR-2C18	$90 \pm 5$

### Thickening performances in latex solution

The aggregation behavior of HEHURs was demonstrated in aqueous solutions. In order to illustrate their potential use as rheology additives in industrial fields such as inks, coatings, emulsions, foods or cosmetics, HEHURs properties were investigated in BA/MMA/MAA copolymer latex solutions. Steady state shear and oscillatory measurements were performed at 25 °C with a latex solution and 0.25 wt% of HEUR or HEHUR. With oscillatory measurements, the influence of the hydrophobic chain length was observed (Figure 10). In the same manner than in water, HEHUR-2C18 and HEUR-2C18 presented a  $G'-G''$  cross point at lower frequencies characteristic to a longer relaxation time. By reducing the hydrophobic chains to 16 carbons, the relaxation time was reduced and even more with

14 carbons as presumed by the  $G'$ - $G''$  cross point at higher frequencies, almost out of the range studied. The similarity between HEHURs and HEURs analyses is clear, and the differences previously described between HEHURs and HEURs functionalized with C14 hydrophobic chains are no longer observed. Indeed, in latex solutions, the hydrophobic chains of HEURs adsorb onto the latex particles surfaces and form a transient network instead of micelles and micellar network.<sup>48</sup> Therefore, the rheological properties depend less on their ability to self-associate but more on their ability to interact with latexes particles. It seems that hydroxyl pendant groups of HEHURs that could reduce their self-association ability in water did not affect their interactions with latex particles.

With the addition of 0.25 wt% of rheology additives to the latex solution, its viscosity was increased by a factor of 41, 145 and 1383 for HEHUR-2C14, HEHUR-2C16 and HEHUR-2C18 respectively. Same orders of magnitude were obtained for HEUR-2C14 and HEUR-2C18 with factors of 39 and 2785 respectively. These results confirm the high thickening efficiency of the synthesized additives. Moreover, these experiments highlight the similar properties between HEHURs and their isocyanate-based equivalents once added in latex solutions. HEHUR-2C14 and HEUR-2C14 presented mainly Newtonian properties over the shear rate range studied as supposed by their low relaxation time. They formed low density network only sensitive to high shear rate. On the other hand, fully pseudoplastic properties were obtained with HEHUR-2C18 and HEUR-2C18, as expected with their long relaxation time observed with oscillatory measurements. The long hydrophobic chains formed a dense network that got destroyed even at very low shear rate inducing a drop of viscosity and the absence of Newtonian properties. HEHUR-2C16 had an intermediate profile with a Newtonian plateau at lower shear rate and shear thinning properties at higher shear rate. These results highlight once again the importance of the hydrophobic chain length of HEHURs and HEURs to obtain the desired and adapted rheological profile to the targeted application. Moreover, it demonstrates the ability of HEHURs to thicken latex solutions with an efficiency similar to their isocyanate-based equivalents.

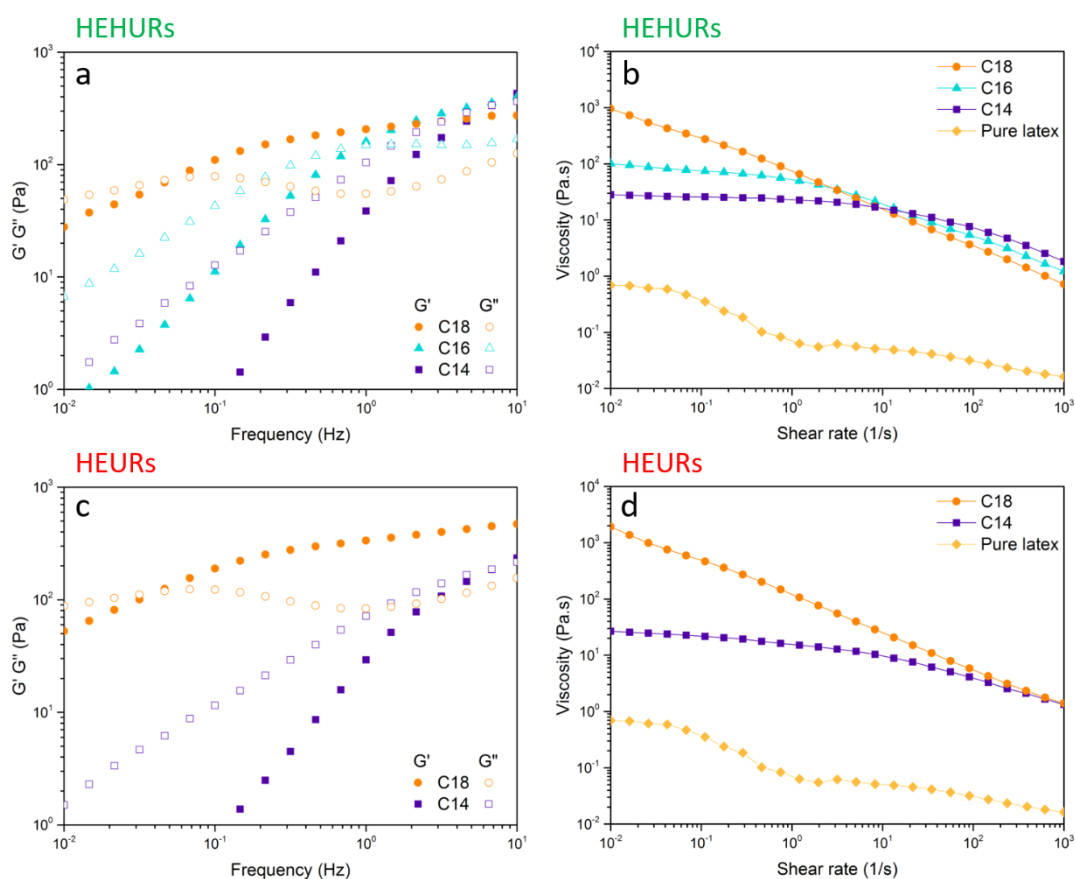


Figure 10: Plots of storage modulus  $G'$  and loss modulus  $G''$  vs frequency (a,c) and plots of viscosity vs shear rate (b,d) of 0.25 wt% HEHURs (a,b) and HEURs (c,d) in latex solutions at 25 °C.

## Conclusion

The synthesis and the characterization of three amphiphilic PHU structures and HENIURs were described for the first time, to the best of our knowledge. The three isocyanate-free HEHURs designed with hydrophobic aliphatic chains composed of 14, 16 or 18 carbons were used as rheology additives. Their rheological properties in water were investigated and compared to two equivalent isocyanate-based HEUR structures. HEHUR-2C14 presented reduced rheological properties in water in comparison to HEUR-2C14, whereas HEHUR-2C18 and HEUR-2C18 demonstrated very similar properties. The additional hydroxyl pendant groups of HEHURs inducing higher hydrophilicity of the structure could be responsible of this observations, while C18 hydrophobic chains could be hydrophobic enough to limit their effect. Linear viscoelastic behavior of aqueous solutions of these additives were studied by oscillatory measurements where  $G'$  and  $G''$  were fitted with the single Maxwell model and the complex viscosity with the Carreau-Yasuda model. Influence of the temperature, the concentration and the length of the hydrophobic chains was investigated and revealed that the relaxation time of the transient network were reduced with longer hydrophobic chains, higher concentration and low temperature. By reducing the network relaxation time, the

Newtonian plateau were reduced and a drop of the complex viscosity was observed at lower frequencies. Moreover, the rheological activation energy of each network were determined, allowing to conclude that longer hydrophobic chains granted higher energy and elastically effective chains improving the rheological properties. Finally, HEHURs were used as rheology additives in latex solution. The influence of the hydrophobic chain length was demonstrated with a fully pseudoplastic profile obtained after the addition of HEHUR-2C18, while a mainly Newtonian profile was obtained with HEHUR-2C14. HEHUR-2C16 had an intermediate profile confirming the versatility of HEHURs and the possibility to tune the chemical structure to obtain the desired rheological properties. The HEHUR properties were compared to their HEUR equivalents and demonstrated a similar thickening efficiency. In this study, we highlighted the potential of HEHURs to be used as rheological additives. Their preparation without toxic isocyanates is very promising to obtain safer and more eco-friendly additives for waterborne systems. It offers a novel approach to reduce the environmental impact of synthetic rheology additives in many fields such as coatings, paints, inks, cosmetics and so on.

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### Notes

The authors declare no competing financial interest

### Acknowledgements

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

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