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ORIGINAL CONTRIBUTION

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Influence of prepolymers molecular weight on the viscoelastic properties of aqueous HEUR solutions

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Abstract A series of hydrophobically modified ethoxylated urethanes (HEURs) were synthesized by a step growth polymerization of polyethylene glycol with dicyclohexylmethane diisocyanate (H12MDI). The thickeners were produced with different sizes of the hydrophilic section by changing the molar ratios of reactants. The size of the hydrophobic ends was constant for all prepared samples. The changes in hydrophilic lengths were correlated with the rheological properties of HEURs aqueous solutions. The intrinsic viscosity measurements showed that associates are present even at very low concentration. The response of these HEUR systems in aqueous solution to both steady shear and oscillatory shear was determined as a function of hydrophilic chain length and polymer concentration. Dramatic increases in viscosity are observed with decreasing molecular weight of the prepolymer (with a decrease of the hydrophilic components' size and at the same time an increased ratio between hydrophobic and hydrophilic sections of HEURs). Also, a steep increase in viscosity with increasing thickener concentration is obtained. The rheological properties of aqueous solutions of HEUR polymers can be described using a simple Maxwell model with a single relaxation. The dynamic measurements verified the results obtained from the steady state measurements about the hydrophilic section size and its effect on the association phenomenon.

Introduction

The synthesis and properties of hydrophobically modified water-soluble polymers have attracted widespread attention in recent years [1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12]. One class of polymers which has received particular attention is hydrophobically modified ethoxylated urethanes (HEUR). Over the past few years, several rheological studies on HEUR polymers in aqueous solution have been published [13, 14, 15, 16, 17, 18, 19, 20, 21]. These polymers consist of a polyethylene glycol (PEG) backbone chain, extended by diisocyanates and end capped with relatively long chains of hydrophobic alcohols or amines [23]. The effect of these three structural components has been reported by various research teams [7, 24, 25].

HEUR associating thickeners are widely used as rheology modifiers in paints and coatings formulations, and in some other applications, such as oil recovery, cosmetics and aviation antifreeze [22].

In this paper, we focus our interest on the influence of the hydrophilic section's size on aqueous solution rheology. Kaczmarski and Glass have studied solution properties of HEUR with variable PEG spacers [24]. They used monoisocyanate with PEG of varying molecular weight. HEURs synthesized using this method are named Uni-HEUR [23]. In another paper they showed that the internal alkyl groups (the alkyl group of the diisocyanate) do not generate high viscosity through hydrophobic association [26]. Considering this point, we used a step growth polymerization method (S-G HEUR [23]). Using this S-G HEUR polymerization method, the molar ratio of the initial reactants determines the average molecular weight. The molar ratio of polyethylene glycol and diisocyanate for any desirable average molecular weight was selected and applied using a statistical model of step growth polymerization (Carothers' equation):

$$\overline{x_n} = \frac{1+r}{1-r} \qquad (1)$$

where $\overline{x_n}$ is the number average degree of polymerization and r is the molar ratio of OH groups to NCO groups [27].

The prepolymers were synthesized in a wide molecular weight range from 6000 to 50000. The polyurethane thickeners were finally condensed by reaction with cetylalcohol. The solution properties of these materials were investigated.

Experimental

Materials

Polyethylene glycol of molecular weight 6000, cetyl alcohol, toluene and tetrahydrofuran (THF) were supplied by Merck. Dicyclohexylmethane diisocyanate ($H_{12}MDI$, trade name Desmodur^R W) was used as received. Dibutyl tin dilaurate was supplied from Fluka. Petroleum ether with low boiling point was obtained from Pars Chemie.

Synthesis procedure

The thickeners were produced by a step growth polymerization of polyethylene glycol and $H_{12}MDI$, obtaining various molecular weights of the prepolymers. This determines the size of the hydrophilic section in HEUR polymers. All reactants must be dried carefully before polymerization, otherwise the molar ratio will be changed due to reactions of water with isocyanate groups and it would be impossible to control the size of the hydrophilic section. HEUR polymers were produced by end capping of the synthesized prepolymers with cetylalcohol. The details of the synthesis and drying procedure of the reactants were described in a previous work [27].

Molecular weight determination

The molecular weight distribution was determined by gel permeation chromatography (GPC), using a Gynkotek pump, a Phenogel M 5 μm column with 60 cm length and an ERC 7512 (EKMA) refractometer. Chloroform was the mobile phase with a flow rate of 1.0 ml/min. Polyethylene glycols (Polymer Labs) were used as universal calibration standards. The measured molecular weights are shown in Table 1.

Table 1 Molecular weight and polydispersity index PDI (M_w/M_n) of HEUR samples

HEUR sample	M_n	PDI
6-Cet	6410	1.8
15-Cet	8980	1.9
32-Cet	13073	2.5
50-Cet	23577	2.8

Rheological measurements

Intrinsic viscosities were measured at 303 K in THF, using an Ubbelohde capillary viscometer.

The rheological properties of aqueous HEUR solutions were measured using a Paar Physica rheometer UDS 200, with a cone-and-plate geometry of 75 mm diameter and 2°cone angle. The samples were protected from water evaporation by applying a solvent trap during the measurements. Both steady shear and oscillatory measurements were performed in order to obtain the steady shear viscosity and the viscoelastic properties of the polymer solutions. The viscoelastic properties of low viscous HEUR solutions were measured using a dynamic capillary rheometer DCR, manufactured by Paar Physica. All rheological measurements were performed at 293 K.

A standard procedure was used to ensure that all HEUR solutions were subjected to the same shear history. After loading, the sample was pre-sheared at a constant shear rate of 1 s^{-1} for 3 min followed by a 7 min rest period, prior to each experiment. As for the steady shear experiment, we observed that the shear stress increased as a function of time and reached a constant value within 10 s. Therefore at each shear rate the reading was taken after 10 s of constant shear.

The viscoelastic properties were measured in the oscillatory shear mode. The angular frequency range used was 0.1–200 rad s^{-1}. From strain sweep measurements it was determined that the storage and the loss moduli (G', G'') are independent of the applied strain from 0.01 to 0.6. Therefore a shear strain of 0.20 was applied in order to perform all measurement in the linear viscoelastic region.

Aqueous solutions of HEUR polymers with various concentration levels were prepared by directly dissolving a known amount of polymer in 100 ml of triple distilled water. Each solution was gently stirred for 2–6 hours to reach a homogeneous state. The samples were stabilized against degradation, using hydroquinone as an inhibitor at a typical concentration of 10 to15 ppm. The highly viscous samples had to be centrifuged before testing in order to remove residual air bubbles.

Table 2 HEUR solutions in THF: intrinsic viscosity and correlation coefficient R

HEUR sample	η_{spec}	η_{spec}	η_{spec}	$[\eta]$ dl/g	$R\ [\eta]$
c= 0.1 g/dl	c= 0.2 g/dl	c= 0.3 g/dl	c = 0 g/dl		
6- Cet	0.285	0.301	0.306	0.279	0.936
15- Cet	0.271	0.274	0.276	0.279	0.933
32- Cet	0.391	0.461	0.471	0.383	0.927
50- Cet	0.293	0.342	0.346	0.291	0.931

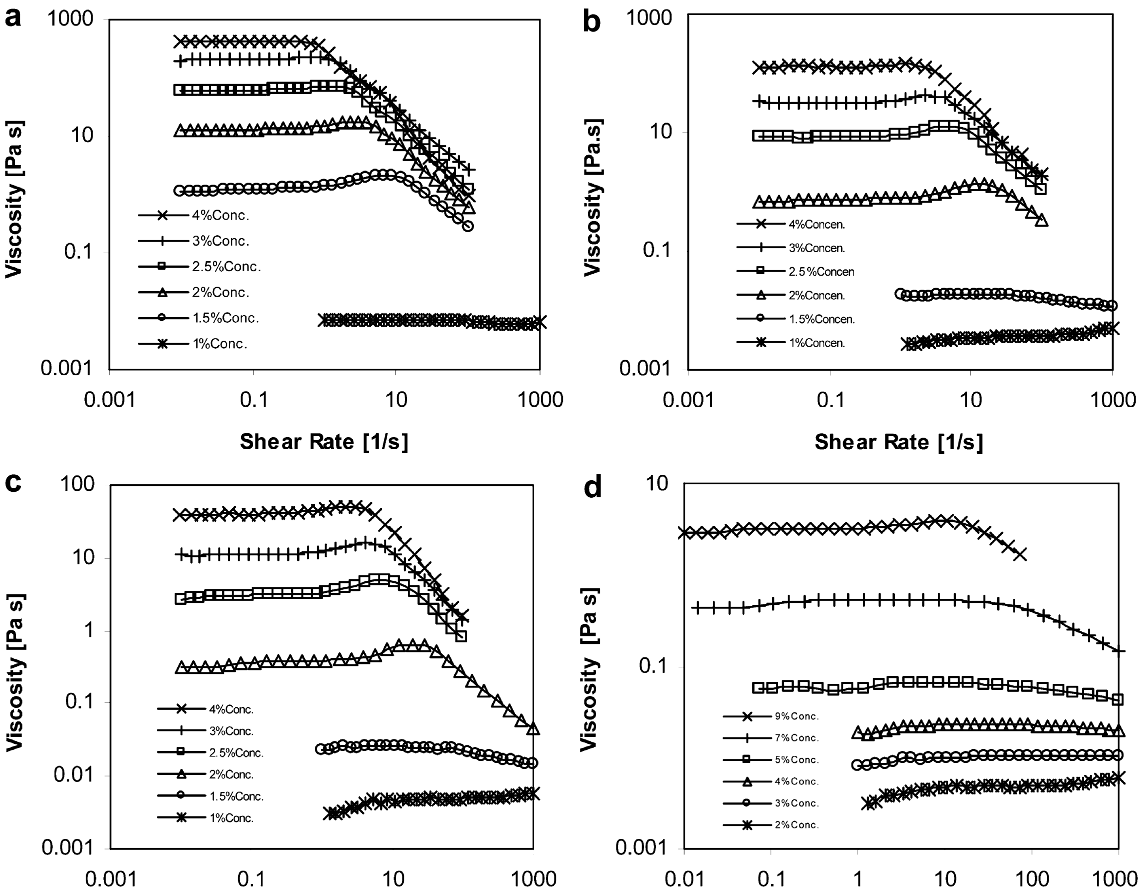

Fig. 1 Steady shear viscosity of (a) 6-Cet, (b) 15-Cet, (c) 32-Cet and (d) 50-Cet solutions in water at 20° C

Results and discussion

Intrinsic viscosity

Intrinsic viscosities [η] were measured in THF. The results are shown in Table 2.

The [η] values were obtained by extrapolation of η_{SP}/c to zero concentration. In view of the molecular weight increase from 6-Cet to 50-Cet, the intrinsic viscosity was expected to increase as well. But this trend was not observed for the 6-Cet and the 50-Cet samples, having the smallest and the largest hydrophilic section, respectively; the length of the hydrophobic section is the same for all samples. It follows that 6-Cet has the most pronounced hydrophobic part which makes association most likely. This association increases the intrinsic viscosity value of 6-Cet to the same value as that of 15-Cet. On the other hand, the 50-Cet sample shows only a weak effect of hydrophobic groups and practically no association. The value of the intrinsic viscosity is lower than that of the 32-Cet sample. The strong and weak association in 6-Cet and 50-Cet samples, respectively, is confirmed by the rheometry results reported below.

Steady shear velocity

The steady shear viscosity as a function of shear rate for various concentrations of HEUR polymers is shown in Fig. 1a–d for 6-Cet, 15-Cet, 32-Cet and 50-Cet, respectively. The flow curves can be assigned to one of three groups of low, medium or highly viscous solutions. All samples show Newtonian behaviour, or shear rate independent viscosity at low shear rates. Samples with a viscosity less than 0.1 Pa.s exhibit Newtonian behaviour until high shear rates. The small deviations from constant viscosity are related to measurement uncertainties in this low viscosity range.

In the medium viscosity group (0.1 to 100 Pa.s) shear thickening was observed at an intermediate shear rate, between the Newtonian and the shear thinning range. Others have reported similar observations for HEUR solutions [13, 18, 28]. They concluded that this effect was due to a rearrangement from intramolecular bridges to intermolecular aggregation when individual polymer chains were stretched under shear (the non-Gaussian stretching of the sample can also be responsible for this effect). In this way, more HEUR chains contribute to the viscosity increase via intermolecular aggregation. However, there are some differences in the medium viscosity groups also. The degree of shear thickening is reduced with increasing viscosity levels. For example, the shear thickening of the samples (6-Cet 2.5%, 15-Cet 4%) is much less than that of samples 15-Cet at 2 and 2.5%.

The high viscosity group (100 to 1000 Pa.s) does not show shear thickening at all. The reason may be that at these concentrations intermolecular bridging is already established and will not be increased by shear orientation and coil deformation. It should be mentioned that with increasing shear rate there is a tendency for air to enter the measuring gap. This happened at the highest shear rates with the sample 6-Cet HEUR at 3 and 4% concentrations, Fig. 1a.

The zero shear viscosity dependence on the concentration of HEUR solutions, as extracted from the Newtonian plateaus, is shown in Fig. 2. The critical association concentration (CAC) is the important and clearly observable deflection point in these curves. The CAC is the concentration where the steep increase of the viscosity occurs. This is a general behaviour associated with all thickeners. It is assumed that network formation starts from the critical association concentration point.

The CAC of 6-Cet HEUR is around 2%, and it is shifted toward higher concentrations with increasing length of the hydrophilic section. The sample 50-Cet HEUR does not show a CAC in the investigated concentration range. This indicates that HEUR with a hydrophilic part long enough to yield a molecular weight between 13.000 and 23.000 are so soluble in water that the hydrophobic sections do not accomplish associations.

Higher concentrations of the thickener are required to obtain elevated viscosity levels. Also the rate of zero viscosity increase with concentration is much steeper in the case of lower molecular weight HEUR polymers (6-Cet) as compared to those with higher molecular weight. The association or the strength of interactions is more pronounced for lower molecular weight HEUR solutions if the size of hydrophobic sections is kept constant.

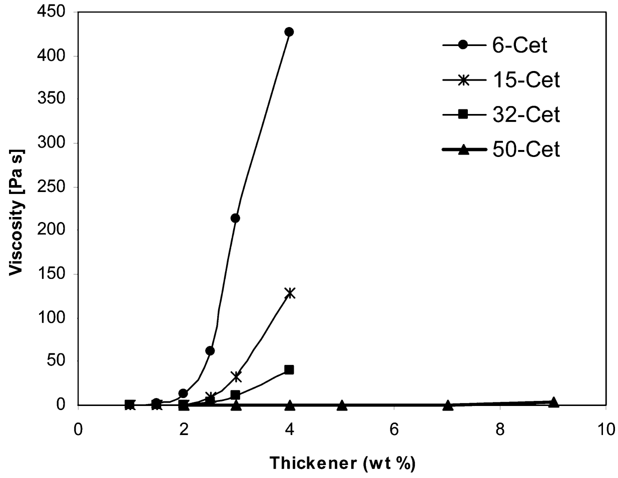

Fig. 2 The comparison of zero steady shear viscosity of HEUR solutions as a function of concentration. T = 20° C

Oscillatory measurements

All aqueous solutions of HEUR show linear viscoelastic behaviour at strains below 1 (Fig. 3). The data presented in Fig. 3 were obtained with the 6-Cet HEUR polymer and a similar behaviour was observed with all samples. The oscillatory shear experiments were carried out at a strain level of 0.2 and below in order to ensure that the experiments were performed in the linear viscoelastic region.

The storage and loss moduli as a function of the frequency are plotted in Fig. 4 for different HEUR polymer solutions of various concentrations. The HEUR solutions that did not have enough association strength to show a crossover of the storage and loss modulus are not shown in this figure. Despite the differences in concentration, the behaviour under oscillatory shear force was similar for all samples.

At low frequencies, the loss modulus increases with a slope of one, the storage modulus with a slope of two. At high frequencies the storage modulus (G') asymptotes to a constant value G_∞. This plateau implies that the solution behaves in this region mainly as an elastic body. The infinite storage modulus G_∞ increases with increasing concentration (Fig. 5). Again, the rate of increase of the 6-Cet HEUR polymer is steeper than that of the other HEUR polymers. The deflection points are similar to those observed with steady shear experiments (Fig. 2).

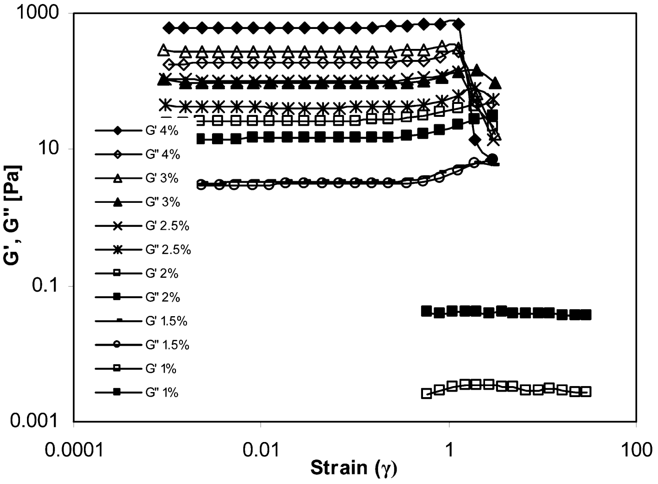

Fig. 3 The storage and loss moduli (G′, G″) as a function of shear strain for 6-Cet HEUR at different concentrations. f = 1 Hz, T = 20 C°

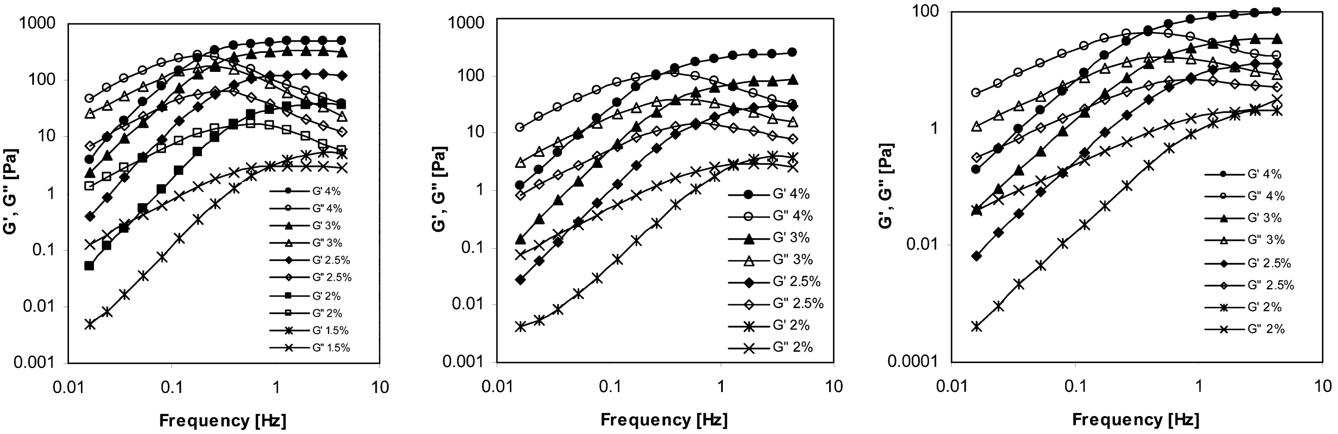

Fig. 4 The storage and loss moduli (G′, G″) versus frequency for Cet HEUR models at $\gamma = 0.2$ and T = 20 C°, for different concentrations, a) 6-Cet b) 15-Cet c) 32-Cet

At low concentrations the solutions (6-Cet 1%, 15-Cet 1.15%, 32-Cet 1.15% and all 50-Cet) behave like Newtonian fluids, as shown in steady shear viscosity measurements.

The storage and loss moduli (G', G'') of these associative thickeners generally follow a single-relaxation Maxwell model. A Maxwell model comprises an elastic component connected in series with a viscous component. In this model G' and G'' are described by the following equations:

$$G' = \frac{G_\infty \omega^2 \lambda^2}{1 + \omega^2 \lambda^2} \tag{2}$$

$$G'' = \frac{G_\infty \omega \lambda}{1 + \omega^2 \lambda^2} \tag{3}$$

where G_∞ represents the plateau value of G' at the highest frequencies, ω is the angular frequency, and λ is the relaxation time.

The number of elastically effective chains (v) is another characteristic parameter used to describe associating systems. The simple theory of rubber elasticity was extended to transient networks by Green and Tobolsky [29], assuming that the cross links in the network are weaker than covalent bonds. They predicted that the magnitude of the plateau modulus G_∞ is related to the number of elastically effective chains per unit volume (v)

$$G_\infty = gvRT \tag{4}$$

where g is a correction factor which is approximately equal to unity [31], v is the number of elastically effective chains per unit volume (mol m^{-3}), R is the universal gas constant and T is the temperature in Kelvin. Later on, some other researchers [25, 30] showed that the expression in Equation 4 could not describe the behaviour of HEUR polymer exactly. However, we used it for the qualitative description of HEUR polymers, due to the simplicity of the expression. The number of elastically effective chains per unit volume of HEURs as a function of concentration is shown in Fig. 5; it increases with increasing concentration. The rate of increase of the 6-Cet HEUR model is steeper than that of the other polymers. The results show, that in the concentration range at hand the hydrophobic intermolecular interactions are responsible for the association and the elastic behavior. The number of the elastically effective polymer chains contributing to the association decreases as soon as the hydrophilic middle section maintains enough solvation. For the 32-Cet HEUR sample the active chains fraction is the smallest.

The fit of the viscoelastic data of 6-Cet HEUR solutions with various concentrations to the Maxwell model is shown in Fig. 6. The single-relaxation Maxwell model fits these data well; the other HEUR polymer solutions showed similar good fitting. The relaxation time of HEUR solutions as a function of thickener concentration is shown in Fig. 7.

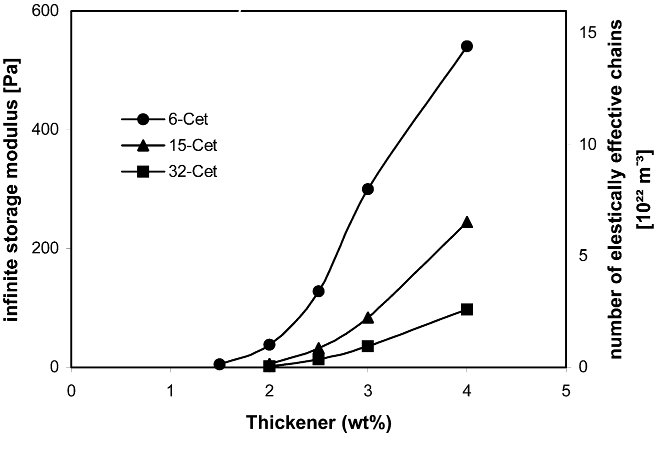

Fig. 5 Infinite storage modulus and the number of elastically effective chains per volume of HEUR solutions as a function of concentration

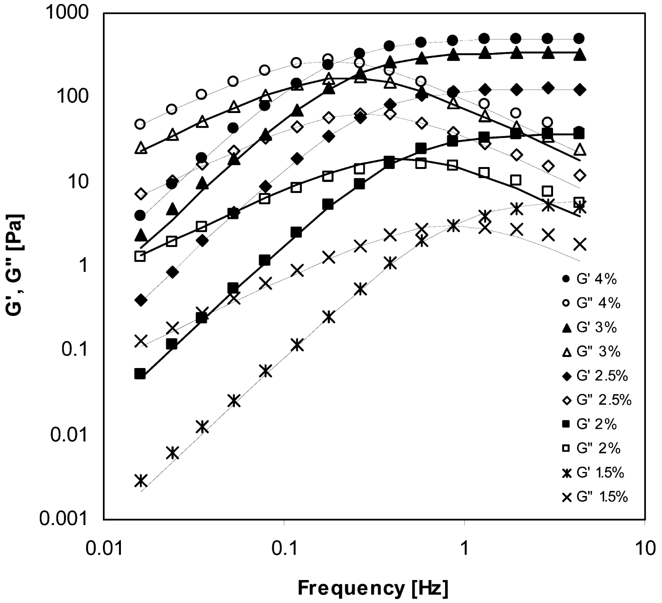

Fig. 6 The storage modulus (closed symbol) and loss modulus (open symbol) of HEUR solutions as a function of frequency for different concentrations. The lines are the fit of the single-mode Maxwell model

Both the 15-Cet and 32-Cet HEUR samples have almost similar relaxation times increasing monotonically with the concentration. The 6-Cet HEUR polymer differs distinctly, exhibiting at least twofold relaxation times. This may be explained by the formation of elastically entangled associations of the molecules' hydrophobic parts.

Conclusions

A series of linear HEUR polymers were synthesized by a step growth polymerization with varying length of the hydrophilic middle section but both hydrophobic ends held constant The intrinsic viscosity of HEUR polymers showed that associations are present even at very low concentrations, but do not contribute much to viscosity. Rheological properties were studied in aqueous solution at concentrations of 1 to 4% by weight. Measurements under steady shear give merely Newtonian behavior for low viscosity solutions, while those with medium or high viscosity are shear thinning at moderate shear rates. Solutions of medium viscosity show three regions, a Newtonian, a shear thickening and a shear thinning one. The onset shear rate and the magnitude of shear thickening decreases, both as the concentration increases and as the length of the hydrophilic section increases. The shear thickening may be caused by an increased coil deformation prior to the loss of entangling interactions.

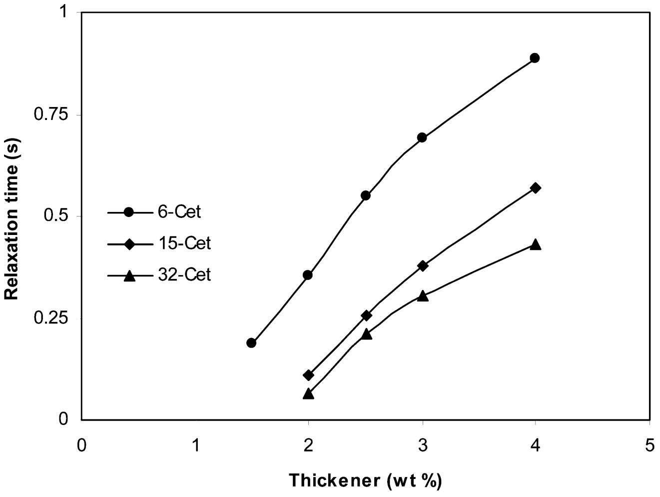

Fig. 7 The relaxation time as a function of HEUR concentration calculated from equation 2

In oscillatory shear experiments these results were confirmed. Interestingly, a single-mode Maxwell model fits the experimental data excellently. The simple theory of rubber elasticity can be applied in order to calculate the number of elastically effective chains, which again shows the enhanced viscous interaction of the shorter molecules.

It was concluded from both steady shear and oscillatory shear results that the association strength can be varied by changing the length of the hydrophilic section. This trend is dominant in the case of HEUR polymers of a molecular mass less than 10,000 (6-Cet HEUR). In the case of a constant length of the hydrophobic end sections a stronger association is achieved with a reduced length of the hydrophilic section. This maintains a good thickener efficacy.

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