Synthesis and Linear Viscoelasticity of Fluorinated Hydrophobically Modified Ethoxylated Urethanes (F-HEUR)

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Received June 20, 1997; Revised Manuscript Received December 8, 1997

ABSTRACT: The influence of the terminal segment of hydrophobically modified ethoxylated urethane (HEUR) on the linear mechanical behavior is examined through the synthesis of perfluoroalkyl telechelic HEUR (defined as F-HEUR). A series of perfluoroalkyl-modified poly(oxyethylene) (POE) of molecular weight $M_n = 6000$, 10 000, and 20 000 with a well-defined structure has been synthesized by reacting POE with a large excess of isophorone diisocyanate (IDPI) to produce an isocyanato functional precursor, followed by the reaction of the terminal isocyanato group with a perfluoroalkyl alcohol ($C_8F_{17}(CH_2)_{11}$-OH). The linear viscoelasticity of aqueous solutions has been investigated as a function of the polymer concentration (noted c_{pol}, in weight percent), temperature, and intermediate chain length. For the $M_n =$ 10 000 chains as c_{pol} is raised from 0.1% to 5%, an increase of more than 6 decades is observed in the static viscosity around $c^*_{pol} \sim 1.5\%$. This increase coincides very precisely with the onset of viscoelasticity of the solutions. Moreover, the linear mechanical responses exhibit striking features: In all experiments performed, the stress relaxation function $G(t)$ decreases as a stretched exponential of the form $G(t) = G_0 \exp[-(t/\tau)^{\alpha}]$ with $\alpha = 0.8 \pm 0.05$. Here, G_0 denotes the plateau modulus and τ the macroscopic relaxation time of the transient network. Compared with already published data [Annable *et al.*, *J. Rheol.* **1993**, *37*, 695−726], τ is found to be nearly 3 decades larger than for fully hydrogenated end caps, and the associated activation energy is twice the one previously reported (53 k_BT against ∼25 k_BT). These data are actually remarkable since they provide the opportunity to probe the dynamics of the transient network in the time scale of minutes.

1. Introduction

The synthesis and properties of hydrophobically modified water-soluble polymers have attracted widespread attention in recent years.[1−11] Modifications of polymer solution behaviors are ascribed to physical cross-links arising from associations of hydrophobic groups in aqueous medium. These associations can be intramolecular, intermolecular, or both. Such polymers referred to as associative thickeners (AT) have generated interest in rheology modifiers for coating applications.[12] The efficiency in modifying the rheological properties for such polymers strongly depends on the chemical structure of the water-soluble polymeric chain, the size and the nature of the hydrophobic segments, and their location along the polymer backbone.

Polymers of this type can be prepared by grafting hydrophobic segments onto a water-soluble polymeric chain (e.g., hydroxyethylcellulose[13,14]), through copolymerization of water-soluble monomers (as for acrylamide or *N*,*N*-dimethylacrylamide) with small amount of hydrophobe-containing comonomers.[15] AT's obtained by chemical modifications (such as grafting) or copolymerization present a random distribution of hydrophobic pendent groups along the chain. The chemical structures of these polymers are not well-defined with regard to both content and location of the hydrophobic segments.

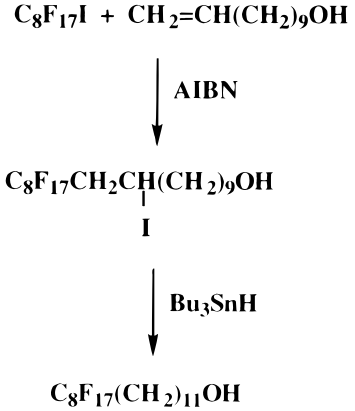
Hydrophobically modified ethoxylated urethanes (HEUR) have recently received attention because of their relatively well-defined architecture with telechelic groups. Hydrophobic groups introduced in the polymer chain are typically a nonylphenol[3,11,16] or a linear hydrocarbon segment containing at least 12 or 14 carbon atoms.[3,5,7,11,16,17] The efficiency of HEUR to increase the low shear viscosity depends on both the hydrophobicity of the end group and the length of the POE chains. A maximum of efficiency was observed with POE with a degree of polymerization close to 500 ($M_n = 20\,000$).[16]

Hogen-Esch *et al.* have reported that perfluoroalkyl-modified water-soluble polymers (hydroxyethylcellulose,[14] polyacrylamides,[8,18] or POE[19]) are much more effective thickeners compared to the corresponding hydrocarbon derivatives. The enhanced viscosity can be explained by the clustering and self-assembling of the perfluorinated groups. Fluorinated end-capped POE synthesized by Hogen-Esch *et al.*[19] contain a hydrocarbon spacer linking the perfluoroalkyl group to the hydrophilic chain reduced to two CH_2. The present paper aims to determine the influence of the length of the hydrocarbon spacer on the rheological properties of the perfluoroalkylated HEUR, referred to as to F-HEUR in the following.

In order to establish correlations between the enhanced rheological properties and the chemical structure, it was necessary to synthesize a linear perfluoroalkyl telechelic HEUR with low polydispersity. The usual step growth polymerization process leads to a broad molecular weight distribution.[11,20] In order to reduce polydispersity, model F-HEURs were prepared by stepwise addition of a large excess of diisocyanate to poly(oxyethylene)diol, followed by the reaction of the

S0024-9297(97)00901-7 CCC: $15.00

Scheme 1. Synthesis of (Perfluoroalkyl)undecanol



isocyanate-ended POE with perfluoroalkyl alcohols.[21] In the present paper, we focus on telechelic polymers where the central chain is the water-soluble poly(oxyethylene) ($M_n = 6000-20\,000$) and the hydrophobic end caps are $F(CF_2)_8(CH_2)_{11}$ alkane chains. We have investigated the linear viscoelasticity of solutions as a function of F-HEUR concentration at ambient temperature. For the $M_n = 10\,000$ intermediate POE chains, as the polymer concentration c_{pol} is raised from 0.1% to 5% (in weight percent), an increase of more than 6 decades is observed in the static viscosity around $c^*_{pol} \sim 1.5\%$. This increase coincides very precisely with the onset of viscoelasticity of the solution. In addition, the linear mechanical susceptibility $G(t)$ has been measured as a function of temperature and concentration. The main feature is that the stress relaxation function decreases in all experiments performed as a stretched exponential of the form: $G(t) = G_0 \exp[-(t/\tau)^\alpha]$ with $\alpha = 0.8$. Here, G_0 denotes the plateau modulus whereas τ is the macroscopic relaxation time of the transient network. Compared with already published data,[1,2,9] τ is found to be 2 decades larger than for fully hydrogenated end caps, and the associated activation energy twice the one reported in ref 1 (53 k_BT against $\sim$25 k_BT). These data are actually remarkable since they provide the opportunity to probe the dynamics of a transient network in the time scale of minutes. They are compared to the rheology of fully hydrogenated end caps.

2. Experimental Section

2.1. Materials. Poly(oxyethylene)s of molecular weights 6000, 10 000, and 20 000 (Merck), dibutyltin dilaurate (Merck), and isophorone diisocyanate (IPDI, Hüls) were used as received. Perfluorooctyl iodide and 10-undecen-1-ol provided by Atochem were used as received. Water used in viscometric analysis was distilled and passed trough a Milli-Q (Millipore) ion exchange column.

2.2. Synthesis. Synthesis of 11-(Perfluorooctyl)-1-undecanol. 11-(Perfluorooctyl)-1-undecanol was prepared in two reaction steps (Scheme 1).

(i) A 0.03 mol sample of perfluorooctyl iodide and 0.045 mol of 10-undecen-1-ol were placed in a three-necked round bottom flask equipped with a reflux condenser, a nitrogen inlet tube, and a magnetic stirrer. The mixture was homogenized by heating to 80 °C, and then 75 mg of azobis(isobutyronitrile) (AIBN) was added in small portions and the reaction mixture was stirred for 5 h at 80 °C.

(ii) 11-(Perfluoroctyl)-10-iodo-1-undecanol was not isolated and directly reduced by tri-*n*-butyltin hydride. A 0.06 mol sample of tributyltin hydride and 0.003 mol of AIBN dissolved in 30 mL of absolute toluene were added with a syringe via a rubber septum, and the solution was stirred for 18 h at 80 °C under nitrogen. After solvent evaporation by reduced pressure distillation, the solid obtained was purified by recrystallization from toluene.

Synthesis of Isocyanato Telechelic POE Prepolymers. A three-neck 250 mL round bottom flask was equipped with a nitrogen inlet tube, a reflux condenser, a magnetic stirrer and a thermometer. A 15 g sample of POE ($M_n = 6000$, 10 000, and 20 000) was weighted into the reaction flask and 150 mL of 1,1,1-trichloroethane was added. The solvent was heated to reflux (75 °C), and water was removed by azeotropic distillation. The flask was cooled and then purged with nitrogen. A large excess of isophorone diisocyanate (IPDI, 50 equiv of NCO to 1 equiv of OH) and tin catalyst (0.1 wt % based on POE) was added with a syringe. The reaction was stirred for 2 h at 75 °C. After cooling at room temperature, the prepolymer was filtrated before being precipitated into petroleum ether, collected on a sintered glass Büchner funnel, and dried under reduced pressure. Purification of prepolymer was performed by dissolution in hot CH_3CCl_3 and reprecipitated into petroleum ether. These prepolymers were stored under nitrogen.

Synthesis of F-HEUR. In a three-neck round bottom flask as described before, 5 g of prepolymer was dissolved into 100 mL of CH_3CCl_3. The flask was purged with nitrogen, and dibutyltin dilaurate (0.1% by weight of POE) was added. An excess of 11-(perfluorooctyl)-1-undecanol (2 equiv of OH to 1 equiv of NCO) dissolved into CH_3CCl_3 (5×10^{-2} to 10^{-1} mol/L CH_3CCl_3) was injected in the flask and the reaction was stirred for 3 hours at 75 °C. The solution was cooled at room temperature, filtrated and precipitated into petroleum ether, dried and purified as for prepolymer. The F-HEUR were collected on a Büchner and dried under vacuum at 40 °C for 2 hours.

2.3. Characterization of the Thickeners. FT-IR spectra of prepolymers and F-HEUR recorded on a Perkin-Elmer 1420 spectrophotometer were compared in order to check the disappearance of the isocyanate band (2250−2300 cm^{-1}). After each step of the synthesis, prepolymer and thickener were analyzed with respect to their molecular weight distribution by size exclusion chromatography using a Shimadzu differential refractometer and tetrahydrofuran as the mobile phase (flow rate 1 mL·mn^{-1}). A set of three PL gel columns was used with the following pore sizes: 500, 10^3, and 10^4 Å. A calibration curve was established from poly(ethylene oxide) standards. Size exclusion chromatography confirms that the molecular weight distribution of the modified polymer is not drastically changed compared to the initial product (Figure 1). However, some polycondensation has been evidenced which consists essentially in telechelic chains with twice the initial molecular weight. As evidenced in Figure 1 for the $M_n = 10\,000$ POE chains, the proportions of both species (10 000 *versus* 20 000, indicated by arrows) are about 80%/20%, respectively.

2.4. Linear Rheology. The low-concentrated solutions ($c_{pol} < 1\%$) were studied using a Ubbelohde capillary viscometer with diameter of 0.56 mm (at ambient temperature, $T = 25$ °C). The capillary viscometer was restricted to the investigations of Newtonian solutions with a typical viscosity of water. As a result, the reduced viscosity η_{red} was obtained according to

$$\eta_{red} = \frac{\eta - \eta_s}{\eta_s c_{pol}} \tag{1}$$

where η and η_s denote the viscosities of the solution investigated and of water, respectively, and c_{pol} is the weight percent concentration.

Above $c_{pol} \sim 1\%$, the F-HEUR telechelics solutions become viscoelastic and so, a standard rotational rheometer is of appropriate use. The linear viscoelasticity was obtained on a Rheometrics fluid spectrometer (RFS II) working either in a Couette geometry for viscosity lower than 1 Pa·s or in a cone-and-plate geometry for higher static viscosity η_0. The Couette gap is of 1 mm (mean radius 16.5 mm) whereas the cone dimensions are 30 and 50 mm with an angle of 0.02 rad. Two

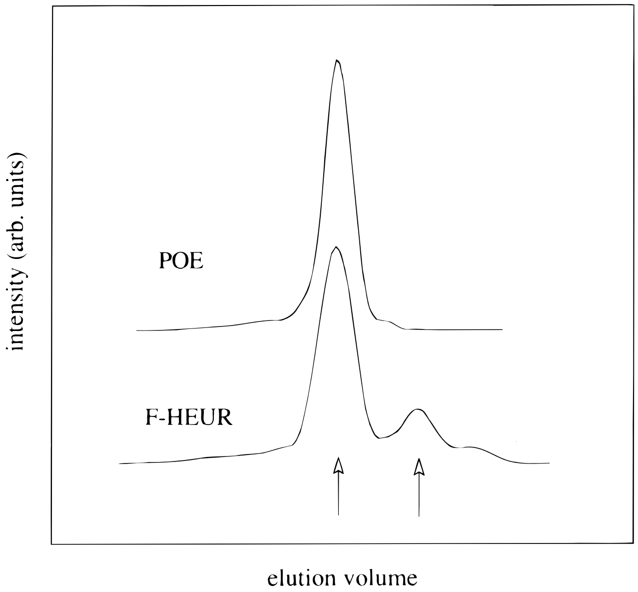


Figure 1. Size exclusion chromatograms obtained for the ploy(oxyethylene) with molecular weight $M_n = 10\,000$ (upper curve) and for the perfluoroalkyl telechelics F-HEUR (low curve) in tetrahydrofuran. The small peak right of the main contribution is attributed to telechelic chains with molecular weights of 20 000.

types of measurements were performed with the RFS II. In the low-concentration limit, which necessitates the use of the couette geometry, steady shear rate measurements were carried out. The resulting shear stress σ or viscosity $\eta = \sigma/\dot{\gamma}$ was plotted *versus* the shear rate $\dot{\gamma}$. This enables a clear identification of Newtonian and shear-thinning behaviors. Above $c_{pol} \sim 1.2\%$, the linear viscoelasticity was investigated using step−strain experiments, and the stress relaxation function $G(t)$ was determined. In these experiments, a deformation γ_0 is applied to the sample and the resulting stress $\sigma(t)$ developed in the material is recorded as function of time. Measurements were carried out for deformation amplitudes $\gamma_0 = 1{-}40\%$ (linear response) and temperatures ranging between $T = 15$ °C and $T = 30$ °C. The stress relaxation function $G(t)$ is calculated according to

$$G(t) = \frac{\sigma(t)}{\gamma_0} \tag{2}$$

From the relaxation spectra, the static viscosity can be computed since it equals the integral over time of the $G(t)$ function during the step−strain experiment, *i.e.*

$$\eta_0 = \int_0^{\infty} G(t)\, \mathrm{d}t \tag{3}$$

3. Experimental Results and Analysis

3.1. Influence of the Middle POE Chain Length. At low concentration, e.g., for $c_{pol} < 1\%$, the telechelic solutions behave as Newtonian fluids. Figure 2 displays the reduced viscosity of the telechelic solutions, as defined by eq 1, as a function of the weight percent concentration c_{pol}. Three intermediate chain lengths have been investigated for the POE polymers, namely, polymeric chains with 136, 227, and 454 ethylene oxide units. Also in Figure 2, the reduced viscosities of the unmodified POE homologue are shown for comparison. For the sake of clarity, the $M_n = 10\,000$ data have been omitted, but an arrow indicates the extrapolation of the viscosity at zero concentration. For the unmodified polymeric solutions, we have checked that the extrapolation to zero concentration of the reduced viscosity scales as $\eta_{red} \sim N^{0.8}$, with a prefactor in agreement with the good solvent conditions for the POE coils.[22] First, for the three telechelics solutions, η_{red} extrapolated at zero concentration is systematically higher than that in the unmodified homologue (in a ratio 60%). With increasing concentration, η_{red} is found to increase drastically for the two longest middle chains, $N = 227$ ($M_n = 10\,000$) and $N = 454$ ($M_n = 20\,000$). For the 6000 solution, the increase is much more modest and, as for the unmodified species the reduced viscosity varies here linearly with the concentration in the range of interest. Note that the increase in η_{red} observed in Figure 2 coincides with the onset of viscoelasticity of the solution, that is for $c_{pol} > 1\%$ (see below).

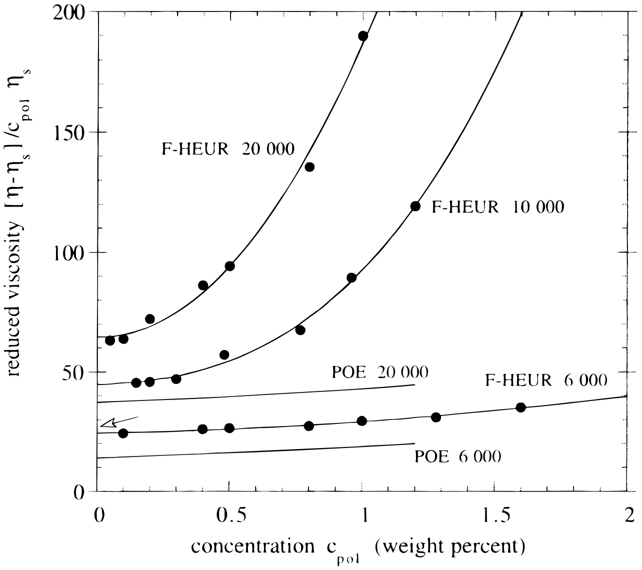


Figure 2. Variation of the reduced viscosity η_{red} as a function of the F-HEUR telechelic concentration c_{pol} for POE molecular weights $M_n = 6000$, 10 000, and 20 000. The reduced viscosities of the unmodified POE homologue are shown for comparison ($M_n = 6000$ and 20 000). The arrow indicates the extrapolation of the viscosity at zero concentration for the $M_n = 10\,000$ unmodified polymer. Continuous lines are guides for the eyes only.

3.2. Effect of Concentration on the Viscoelasticty of the Fluorinated HEUR. In the following sections, we focus on the concentration and temperature dependencies of the rheological properties for a unique middle chain length, $M_n = 10\,000$.

Figure 3 displays the static viscosity η_0 as received from rotational rheometry at room temperature ($T = 20$ °C). The low-c_{pol} solutions were investigated with the Couette cell in steady shear conditions, whereas the highest concentrated samples were using a cone and plate geometry. The three first samples at $c_{pol} = 0.2$, 0.4, and 0.8 were perfectly Newtonian fluid up to 1750 s^{-1}. The 1% solution, on the contrary first exhibits a shear thinning effect with increasing shear rate. Above 1%, the static viscosity exhibits a huge increase, which represents one of the major findings of this paper. Going from $c_{pol} = 1\%$ to $c_{pol} = 2\%$, the viscosity as expressed in units of the viscosity of water passes from ~1 to more than 10^6. Around 3%, η_0 seems to saturate around 2000 Pa·s.

As already mentioned, the increase in the static viscosity of the fluid corresponds to the onset of viscoelasticity. Usually, the viscoelasticity of a solution is tested using oscillatory strains at various frequencies, and the response is expressed in terms of the complex

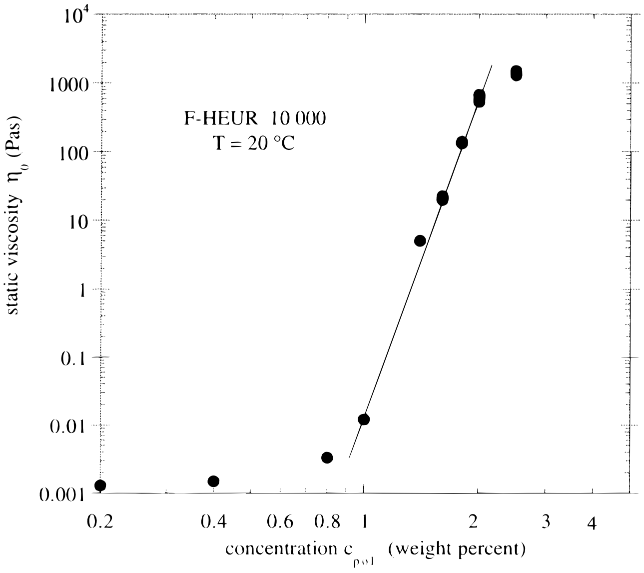


Figure 3. Concentration dependence of the static zero-shear viscosity η_0 of the F-HEUR telechelic aqueous solutions (M_n = 10 000) as obtained from rotational rheometry at room temperature (T = 20 °C). The low-c_{pol} solutions were investigated with the Couette cell in steady shear conditions, whereas the highest concentrated samples were using a cone and plate geometry. Note the huge $\eta_0(c_{pol})$ increase at $c^*_{pol} \sim 1.5\%$.

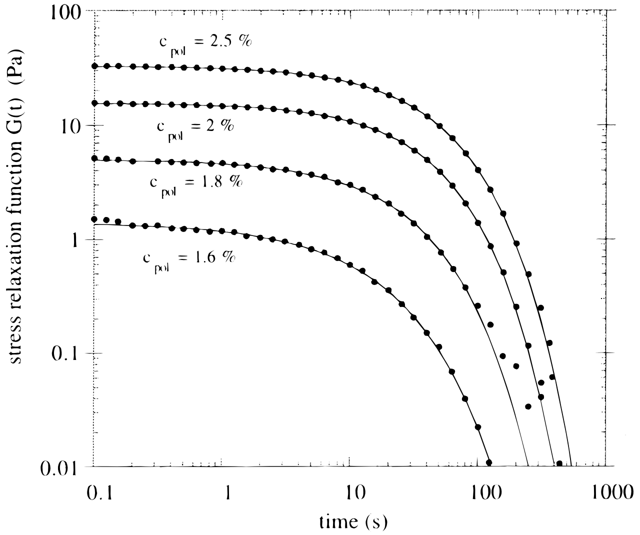


Figure 4. Time dependencies of the stress relaxation functions $G(t)$ obtained in step−strain experiments for c_{pol} = 1.6%, 1.8%, 2%, and 2.5% (M_n = 10 000, T = 20 °C). After the elastic plateau at short times, $G(t)$ decreases to zero in a total time that can reach several minutes (c_{pol} = 2.5%). The static viscosity is deduced from these mechanical responses through eq 3. The continuous lines are best fit calculations using a stretched exponential decrease (eq 4). The adjustable parameters, G_0, τ, and α, are listed in Table 1.

elastic modulus $G^*(\omega)$.[1,2,9] This approach was first attempted but ruled out very quickly. Instead, we chose step-strain experiments for the systems exhibiting the highest viscoelasticity. Here, a shear deformation is applied to the sample comprised between a cone and a plate and the response is recorded as a torque as a function of time. Initial strains of 1% to 40% (linear regime) were needed to obtained a satisfactory signal-to-noise ratios.

The stress relaxation function $G(t) = \sigma(t)/\gamma_0$ obtained in step−strain experiments are shown in Figure 4 for c_{pol} = 1.6%, 1.8%, 2%, and 2.5% (T = 20 °C). A double logarithmic representation has been used to emphasize the huge variations of the stress response. For the four solutions investigated, a typical behavior is observed. At short time (t < 1 s), $G(t)$ remains almost constant and above 1−10 s starts to decrease. Note that this decrease is fully completed after a given time, which can exceed 10 min for the c_{pol} = 2.5% solutions. This is of the utmost importance since it means that the static viscosity η_0 as given in eq 3 is a finite quantity. The values of the static viscosity shown in Figure 3 were calculated according to this technique.

Table 1. List of the Viscoelastic Quantities Retrieved from the Analysis of the Stress Relaxation Function $G(t)$ in Terms of Stretched Exponential, $G(t) = G_0 \exp(-(t/\tau)^a$

x (%)	G_0 (Pa)	τ (s)	α	η_0 (Pa·s)
1.6	1.4	12.2	0.68	22.5
1.8	5.0	22.6	0.76	134
2	15.6	33.6	0.80	591
2.5	32.0	39.1	0.79	1474

[a] Here, G_0 is the elastic plateau modulus, τ is the relaxation time of the stress decrease, α is the exponent of the stretched exponential, and η_0 is the static viscosity as obtained from the integral of $G(t)$ for t = 0 to ∞ (see eq 3). Data are obtained at T = 20 °C.

The relaxation spectra displayed in Figure 4 are characterized by at least two quantities. These are the extrapolation at $t = 0$ of the stress relaxation function that we call the elastic plateau modulus G_0 (sometimes referred to as G'_∞) and the typical time τ of the $G(t)$ decrease. If one does not know a priori the kind of relaxation one is facing, the time τ determined through the relation $G(\tau) = G_0/e$ is an approximation of an average relaxation time. More refined treatments have been conducted using the relaxation distribution function $H(\tau)^2$. Instead of these qualitative arguments and after having checked the inadequacy of the monoexponential decrease (Maxwell model), we choose here to approximate the $G(t)$ functions by the stretched exponential:

$$G(t) = G_0 \exp\left[-\left(\frac{t}{\tau}\right)^{\alpha}\right] \tag{4}$$

In eq 4, G_0 and τ have the same definitions as above and α is the exponent of the order of unity. One can then compute the static viscosity η_0 which reads $\eta_0 = A(\alpha)\, G_0\tau$, where $A(\alpha)$ is a decreasing function of α for α > 0. Stretched exponentials as provided by eq 4 have been suggested to describe the phenomenology of relaxations in complex, slowly relaxing and strongly interacting materials.[23] The continuous lines through the data points in Figure 3 arise from best fit calculations according to eq 4. The agreement is excellent. The three fitting constants G_0, τ, and α are listed in Table 1 to enable comparison. With increasing c_{pol}, both G_0 and τ, and so the static viscosity, are found to increase; however, the coefficient α remains surprisingly constant for the four solutions investigated, around α = 0.8.

3.3. Temperature Dependence of the Linear Viscoelasticity. The effect of temperature on the viscoelastic response of the F-HEUR solutions has been investigated at c_{pol} = 2%. Results of step−strain experiments similar to those detailed in the preceding section are displayed in Figure 4 from T = 15 °C to T = 29.4 °C. The overall evolution of the stress relaxation function $G(t)$ reminds us of Figure 4. With increasing T, Figure 5 reveals that both elastic modulus G_0 and

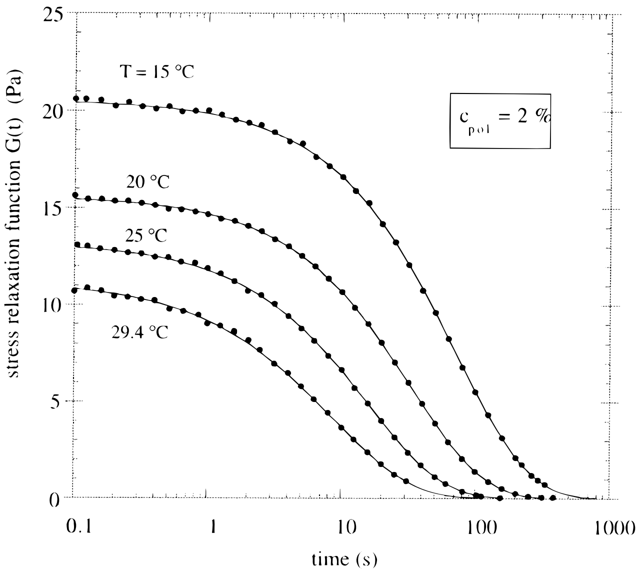


Figure 5. Stress relaxation functions $G(t)$ for the $M_n = 10\,000$ telechelics aqueous solution at $c_{pol} = 2\%$ for $T = 15-30$ ° C. Data at $T = 20$ °C are identical to those of Figure 4 but here displayed using semilogarithmic scales. As for Figure 4, the continuous lines are best fit calculations using a stretched exponential decrease (eq 4). The adjustable parameters, G_0, τ, and α, are listed in Table 2.

Table 2. Viscoelastic Parameters Determined at c_{pol} = 2% (M_n = 10 000) from the Analysis of the Stress Relaxation Function $G(t)$ in Terms of Stretched Exponential[a]

T (°C)	G_0 (Pa)	τ (s)	α	η_0 (Pa·s)
15	20.5	71.3	0.79	1676
20	15.6	33.6	0.80	591
25	13.2	16.0	0.79	242
29.4	11.2	8.7	0.74	118

[a] Definitions are identical to those of Table 1.

the relaxation time τ decrease. Moreover, each set of data could be fitted successfully using again the stretched exponential function (eq 4). The viscoelastic parameters received from this fitting procedure are listed in Table 2 for comparison. At 15 °C, the relaxation time exceeds 1 min, indicating that once a deformation is applied to the sample, at least 5 min is necessary to return to an undeformed state (equilibrium). More interestingly, the exponent α of the stretched function is found again to be around $\alpha = 0.8$. Figure 6 summarizes the different α values, as obtained when both concentration and temperature are varied. Although the use of a stretched exponential is not fully founded on the theoretical side, the observation of a unique form for the stress function is an appealing result.

Finally, we have also checked that the relaxation time and static viscosity are thermally activated. In Figure 7, both quantities are plotted against the inverse temperature, yielding straight lines in the T range investigated. The activation energies associated with the decrease of η_0 and τ are 53.2 and 42.9 in units of k_BT (132.6 and 107 kJ/mol, respectively).

4. Discussion

The aim of the present paper is to demonstrate that aqueous solutions of associating polymers of the HEUR family, for which the hydrophobic end caps are partially fluorinated, are forming a transient network. This statement is based on mechanical analogies with the

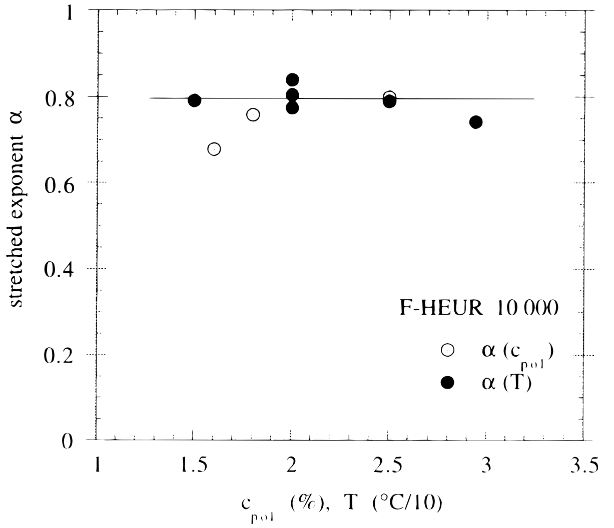


Figure 6. Evolution of the exponent α entering the stretched exponential decay (eq 4) as a function of the concentration c_{pol} (data from Figure 4) and temperature T(°C)/10 (data from Figure 5). For both sets of data, the stretched coefficient remains unchanged around $\alpha = 0.8$.

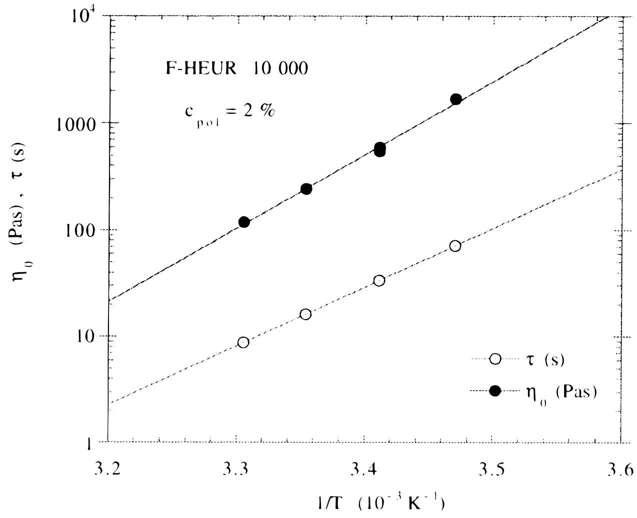


Figure 7. Arrhenius plots of the static viscosity η_0 and of the relaxation time τ deduced from best fit calculations of the stress relaxation function $G(t)$ at $c_{pol} = 2\%$ ($M_n = 10\,000$, Table 2). The straight lines correspond to activation energies 53.2 (η_0) and 42.9 (τ) in units of k_BT (132.6 and 107 kJ/mol, respectively).

model HEUR associative thickeners, widely investigated during the last years.[1-7,9] Rheology has been used as a characterization technique to probe the linear response of the F-HEUR solutions. As a transient network, we have to imagine a dispersion of aggregates consisting in the self-assembled hydrophobic end caps. These aggregates are assumed to be (multi-)connected through reversible junctions. One of the most fundamental challenges is to determine the morphology (shape, size, aggregation number, stretching state of the POE chains, etc.) of the hydrophobic entities.

As far as the F-HEURs are concerned, the identification in terms of transient network results from the following observations:

(i) A very sharp increase of the static viscosity at the F-HEUR concentration, $c^*_{pol} \sim 1.5\%$ (see Figure 3, for $M_n = 10\,000$ middle chain of POE). For the unmodified analogues (that is without hydrophobic end caps) at comparable concentrations, the rheology is that of a Newtonian fluid (dilute regime). This rise in the zero-shear viscosity is at most pronounced with long middle-POE chains (as shown in Figure 2 for M_n = 6000, 10 000, and 20 000).

(ii) The highly viscoelastic solutions are almost perfect Maxwellian fluids. The linear mechanical response is entirely governed by two parameters, an elastic plateau modulus denoted G_0 and a relaxation time τ. Slight deviations to the Maxwellian behaviors have been accounted for by modifications in the stress relaxation function. $G(t)$ is found to be at best fitted by a stretched exponential with exponents $\alpha = 0.8$.

(iii) Both the static viscosity η_0 and the relaxation time $\tau = \eta_0/G_0$ obey Arrhenius dependencies. Activation energies are for the present compounds of the order of 50 k_BT (T = 300 K is the ambient temperature).

Points i−iii are in close agreement with the conclusions derived by Annable *et al.* on the HEUR solutions with fully hydrogenated paraffinic chains.[1,2] However, since the hydrophobicity of the end-capped groups are so different, it is not surprising that the detailed mechanical properties exhibit profound discrepancies.

In the paper by Annable *et al.*[1] an increase of the Maxwell static viscosity η_0 is observed too (at slightly higher c_{pol} than for the fluorinated system), but it is clearly related to a huge increase of the elastic plateau modulus G_0 with concentration. G_0 characterizes the degree of entanglement of the resulting network, in the sense that it depends linearly on the density of elastically effective chains (connecting aggregates). On the other hand, the relaxation time for the polymers with end-capped hydrophobic groups remains almost unchanged as c_{pol} varies (around 0.1 s for C_{16} species).

For the F-HEUR, the situation is rather different: already at the onset of viscoelasticity ($G_0 \sim 0$, $c_{pol} = c^*_{pol}$), τ is several seconds long and with increasing telechelic concentration, both τ and G_0 grow (see Table 1). Below ambient temperature, several minutes are needed for the stress to relax after a solution has been subjected to a constant strain (see Tables 1 and 2). This long relaxation time is associated with the high activation energy deduced from $\eta_0(1/T)$ and $\tau(1/T)$ Arrhenius plots. So, the noticeable increase in η_0 is mainly due to the existence of a very long relaxation time at c^*_{pol}. This effect is moreover reinforced by the strong enhancement of the elastic plateau modulus observed as c_{pol} is increased. There is also another difference with the conventional HEUR that we have not commented on, so far. In Figure 2, we mentioned that the reduced viscosity η_{red} extrapolated at zero concentration is systematically higher than that in the unmodified homologue (by a factor 1.6). This is clearly an unusual property that could be due to interaggregate interactions (bridging) efficient at concentrations as low as 0.1%. The species with twice the initial molecular weight ($M_n \sim$ 20 000) resulting from the polycondensation and evidenced in Figure 1 might also play a role in the overestimation of the reduced viscosity.

As far as the plateau modulus is concerned, a simple estimate of the elastically active chains can be made to emphasize the deviations with respect to the HEUR systems end capped with fully hydrogenated groups. As in previous reports,[1,2,9] we assume that the elastic modulus G_0 at the plateau scales with the number density of elastically active chains ν through the relation $G_0 = \nu k_BT$. The proportion of bridging chains between hydrophobic clusters (neglecting functionality coefficients) can thus be estimated according to

$$\frac{\nu}{n} = \frac{G_0}{nk_BT} \tag{5}$$

where n denotes the number density of total chains in the solution. For the 2% solution, G_0 = 15 Pa (Table 1) is obtained for the ratio $G_0/nk_BT = 3.7 \times 10^{-3}$. Expressed differently, for this F-HEUR telechelic system, such a low value of ν/n implies that 1 chain over 270 acts as a connecting cross-link between aggregates. This rough estimate should not be overestimated. However, we interpret such a low modulus as an indication of large aggregation numbers for the hydrophobic clusters in F-HEUR. As a comparison, Annable *et al.*[1] and Xu *et al.*[9] have found values for G_0/nk_BT in the range 0.1−0.5, depending on c_{pol}. Their model assumes for the hydrophobic clusters aggregation numbers of the order of 10[1] to 20[9]. For the model associative polymers polyethylene didodecyl ether (slightly different from the present HEUR compounds), aggregation numbers between 15 and 30 have been obtained from fluorescence and light scattering experiments.[10]

Considering the above arguments, the long relaxation time and high activation energy as well as the low amount of elastically active chains, we conclude that for the F-HEUR associating polymers, the elementary aggregates are large bodies and the aggregation number should be large too (50−100). This statement will be experimentally demonstrated in our forthcoming publication.

5. Concluding Remarks

We have synthesized associative polymers belonging to the class of hydrophobically modified ethoxylated urethane, for which both end caps are perfluorinated. The linear mechanical responses of aqueous solutions of these perfluoroalkyl telechelic HEUR have revealed similar qualitative behaviors, compared to the conventional HEUR with fully hydrogenated terminal segments.[1,9] We thus confirm the existence of a very sharp increase of the static viscosity at the F-HEUR concentration, $c^*_{pol} \sim 1.5\%$. In addition, the highly viscoelastic solutions are almost perfect Maxwellian fluids and, when studied with respect to temperature, both the static viscosity η_0 and the relaxation time $\tau = \eta_0/G_0$ obey Arrhenius dependencies with activation energies of the order of 50 k_BT. These findings are interpreted in terms of a transient network made of hydrophobic clusters (star micelles) connected through reversible junctions ($c_{pol} > c^*_{pol}$). From the strength of the elastic modulus G_0, as well as the activation energy associated with the disengagement of one end cap, we suggest that the aggregation number might be higher than in the hydrogenated homologues. In this respect, the transient network we have in mind should correspond more closely to the modeling proposed by Semenov *et al.*,[24] rather than the one imagined by Tanaka and Edwards.[25]

Clearly, the anomalous enhanced viscoelasticity of the perfluoroalkyl telechelic HEUR compared to parent species arise from the fluorinated spacer of eight carbon atoms. Attempts have been made with different perfluoroalkyl end groups containing six carbon atoms, and the results were less impressive than the ones shown here. For these latter systems, no dramatic viscoelastic effects were observed at polymer concentrations $c_{pol} \sim 1-5\%$. We are also aware that the polycondensation occurring during the synthesis and giving rise to telechelic chains with twice the initial molecular weight might play an important role at the crossover concentration and below. This point will be clarified in our forthcoming report.

Acknowledgment. We acknowledge VITAL PEGOT (Colomiers, France) for the financial support provided to one of us (N.C.) in the course of the Thèse de Doctorat. We are also grateful to Elf-Athochem for providing the perfluoroiodoalkanes and the undecanol used as starting compounds.

Note Added in Revision. Subsequent to the submission of this article, a contribution has appeared by B. Xu, L. Li, A. Yekta, Z. Masoumi, S. Kanagalingam, M. A. Winnick, K. Zhang, and P. M. Macdonald (*Langmuir* **1997**, *13*, 2447-2456) reporting rheological experiments on associative thickeners with fluorocarbon hydrophobes. There is a small difference, however, between the present F-HEUR and those from Xu *et al.* The hydrophobic end cap contains here a $F(CF_2)_8(CH_2)_{11}$ alkane chain, whereas it is replaced by $F(CF_2)_8(CH_2)_2$ in Xu's report. This subtle difference has a considerable effect on the viscoelasticity of these telechelics.

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MA9709011