SYNTHESIS AND CHARACTERIZATION OF FLUORINE CONTAINING HYDROPHOBICALLY ASSOCIATING POLYMERS

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INTRODUCTION

Hydrophobically modified ethoxylated urethanes are known as rheology modifiers due to their ability to form temporary hydrophobic association networks in aqueous media. The interest in these materials stems in part from their use as thickening agents in water-borne surface coatings formulations but also as useful model associating polymers for fundamental study.

This work will discuss the rheological behavior of solutions of fluorine containing hydrophobically associative polymers in comparison with more conventional alkyl hydrophobically modified polymers.

1 MODEL ASSOCIATIVE POLYMER SYNTHESIS

The model associative polymers are obtained by condensation of a diisocyanate with a poly(oxyethylene) glycol (POE) and are terminated by an hydrophobic moiety as shown by the following two-step reaction schematic:

$$\text{O=C=N–R'–N=C=O + R OH} \xrightarrow[45°\text{C}]{\text{catalyst, toluene}} \text{R–O–C(O)–NH–R'–N=C=O}$$

then

$$\text{2R–O–C(O)–NH–R'–N=C=O+HO(CH}_2\text{–CH}_2\text{O)}_x\text{–H} \xrightarrow[45°\text{C}]{\text{catalyst, toluene}}$$

$$\text{R–O–C(O)–NH–R'–NH–C(O)–O–(CH}_2\text{–CH}_2\text{O)}_x\text{–C(O)–NH–R'NH–C(O)–O–R}$$

The diisocyanate used is 2.4 diisocyanatoluene and the hydrophobic moieties are fluorinated or hydrogenated alkyl chains.

This two-step addition procedure is used to prevent polymeric chain extension by reaction between the diisocyanate and the POE. Another complicating factor is the reaction of water with the isocyanate groups. So, even trace water must be removed from the reaction vessel prior reactions. This is accomplished through azeotropic distillation of toluene. The samples are characterized by size exclusion chromatography with THF as solvent, i.e. conditions where association does not occur [1]. The chromatograms exhibit only one peak corresponding to that of the unmodified POE. The degree of substitution of the terminal hydroxyl group τ is determined by ^{19}FNMR after a quantitative reaction of the residual hydroxyl groups with trifluoroacetic acid.

The characteristics of the samples are reported in Table 1. The value of τ is found to range from 80 to 100%. The notation XTDUCnF or XTDUCnH where X represents the POE average number molecular weight in thousands Daltons, n represents the number of carbon atoms in the hydrophobic end group, F or H specifies if the hydrophobic moiety is fluorinated or not.

2 VISCOSIMETRY

Steady-flow and dynamic viscoelastic properties are measured by CARRI-MED Rheometer. Dynamic measurements are carried out at low strain amplitude where the storage modulus G' and loss modulus G" show linear viscoelastic responses.

3 STEADY-SHEAR FLOW

In order to determine the rheological difference between alkyl containing polymers and fluorinated alkyl containing

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TABLE 1

Characteristics of the PEO precursors and the related end-capped POE

POE precursor			**Associative polymer**				
Material	M_n	M_w	Material	Hydrophobic end group	τ	M_n	M_w
POE 10.000	11 500	13 000	10TDUC8F	$C_6F_{13}C_2H_4$–			
			10TDUC10F	$C_8F_{17}C_2H_4$–	0.85	13 200	16 500
			10TDUC12H	$C_{12}H_{25}$–	0.98		
			10TDUC16H	$C_{16}H_{33}$–	0.88	15 500	19 700
POE 20.000	18 300	19 800	20TDUC10F	$C_8F_{17}C_2H_4$–			
			20TDUC16H	$C_{16}H_{33}$–			
POE 35.000	34 200	37 500	35TDUC10F	$C_8F_{17}C_2H_4$–		39 800	41 500
			35TDUC16H	$C_{16}H_{33}$–	0.80	41 500	44 500
POE 100.000	–	–	100TDUC10F	$C_8F_{17}C_2H_4$–			
			100TDUC16H	$C_{16}H_{33}$–	0.81		

polymers, the first experiments consist of using the associative polymers to thicken water. The rheological response of associative thickeners is characterized by an extended Newtonian plateau at low shear rates. Viscosity dependence on the associative polymer concentrations at low shear rate ($\dot{\gamma} \rightarrow 0$) is shown in Figure 1 for polymers with M_n equal to 10 000 Daltons. The viscosity differences between modified polymers and POE precursor are especially pronounced at higher concentrations consistent with the pattern expected for associating polymers. Comparison of the viscosity of R_H– and R_F–C_2H_4– modified POE shows much greater hydrophobic association for the fluorine containing polymers in spite of the difference between the hydrophobe lengths. Similar increases in viscosity attributable to stronger hydrophobic association of perfluorocarbon containing polyacrylamide or cellulose derivatives have already been reported [2] and [3]. This result is consistent with the fact that fluorocarbons possess greater effective hydrophobic character than hydrocarbons, as reflected by their lower surface energies and lower cohesive energy density [4]. The greater hydrophobic character of fluorocarbons is also reflected in generally lower critical micelle concentrations of fluorocarbon surfactants compared to hydrocarbon surfactants of a comparable number of carbons [5] and [6]. In fact, for non ionic surfactants, the critical micelle concentration of $C_XF_{2X+1}CH_2(EO)_n$ is roughly equivalent to the critical micelle concentration of $C_YH_{2Y+1}(EO)_n$ where $Y \approx 1.7X$ [6]. Moreover, the presence of hydrocarbon junction between the perfluorocarbon chain and the polyoxyethylene chain (here methylene group) has almost no influence on the CMC [5]. Let us now use the equivalence ratio of 1.7 to compare the fluorocarbon and the hydrocarbon associative polymers. We can foresee, as far as the hydrophobic character is concerned, 10TDUC8F with a C_6 perfluorinated chain (see Table 1) is equivalent to 10TDUC10H and 10TDUC10F with a C_8 perfluorinated chain is equivalent to 10TDUC14H. Within this assumption, Figure 2 shows the effect of hydrophobe length on η ($\dot{\gamma} \rightarrow 0$) at fixed M_n and concentration. We observe an exponential increase of η ($\dot{\gamma} \rightarrow 0$) with the hydrophobe length whatever the nature of the hydrophobe chain, fluorinated or not. Moreover, our results are comparable to previous Annable *et al.* results [7]. From these results, it can be seen that the behaviours of fluorocarbon and hydrocarbon associative polymers in water are quite similar. Like for surfactants, an equivalent ratio of 1.7 must be used to take into account the greater hydrophobic character of fluorocarbons.

Figure 3 allows us to compare the dependence of η ($\dot{\gamma} \rightarrow 0$) with M_n for two associative polymers with hydrocarbon and fluorocarbon hydrophobe chains. A maximum η is found when M_n increases. This phenomenon was already reported by Alami *et al.* [8]. The maximum may be explained by the two opposing effects of a decreased hydrophobicity and an increase in solubility. None difference in their behaviour is noted for the two samples.

4 DYNAMIC VISCOELASTIC FLOW

The viscoelastic response of the 5% wt solutions of 100TDUC10F and 100TDUC16H are shown on Figure 4. The data show that the behaviours of the two polymers are quite similar. For the alkyl containing polymers, the frequency dependence of the dynamic moduli is typical of hydrophobically modified ethoxylated urethanes [7] and [9]; i.e., it is perfectly described by a Maxwell model consisting of an elastic component (spring) connected in series with a viscous component (dashpot). This means that the rheological behavior of these solutions is controlled by a single relaxation process. On the other hand, the fluorinated alkyl containing polymers are not perfectly described by the Maxwell model. Nevertheless we can still define a relaxation time for this polymer. The relaxation time τ is defined as $1/\omega_c$ where ω_c corresponds to the frequency at which

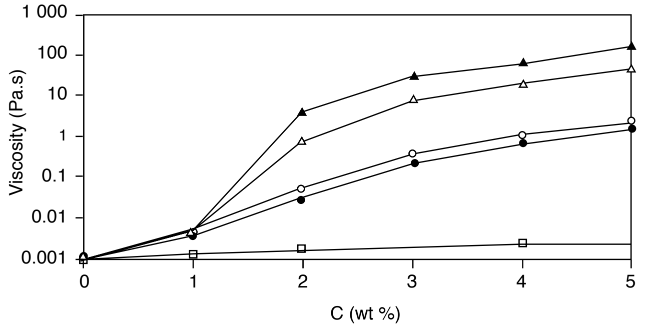

Figure 1

Low shear rate ($\dot{\gamma} \to 0$) viscosity as a function of the aqueous solution concentration of associative polymer, T = 20°C.

☐ POE 10 000 (reference); ● 10TDUC8F; ○ 10TDUC12H;
Δ 10TDUC10F; ▲ 10 TDUC16H.

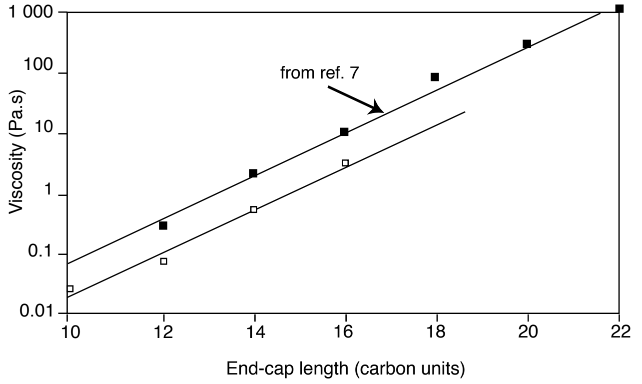

Figure 2

Effect of end-cap chain length at the Newtonian viscosity for M_n = 10 000 at concentration of 2% w/w in water and T = 20°C.
(Results from ref. [7] are given for comparison, they concern polyoxyethylene glycol end-capped by alkyl chains with M_n = 35 000 at concentration of 2% w/w and T = 25°C).

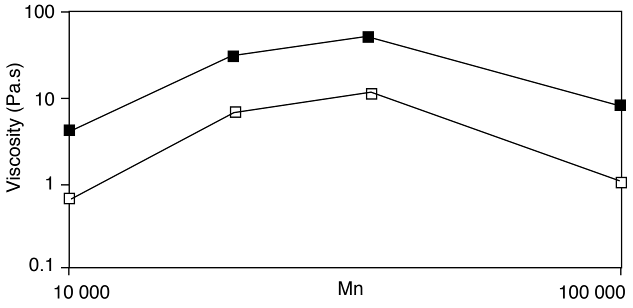

Figure 3

Low shear rate ($\dot{\gamma} \to 0$) viscosity as a function of molecular weight at a concentration of 2% w/w in water and T = 20°C.
■ $C_{16}H_{33}$– modified POE; ☐ $C_8F_{17}C_2H_4$– modified POE.

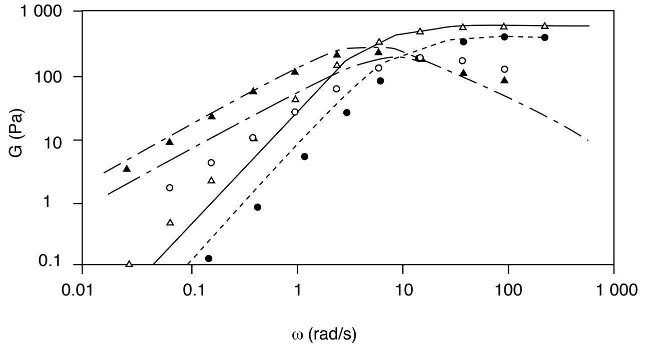

Figure 4

Dynamic moduli of 5% w/w 100TDUC10F and 100TDUC16H solutions, 100TDU16H, G’ (Δ) and G” (▲), 100TDU10F, G’(●) and G” (○). The data are compared to the Maxwell model full line (G’ - 100TDUC16H), dash line (G” - 100TDUC16H), dot line (G’ - 100TDUC10F), dash and dot line (G” - 100TDUC10F).

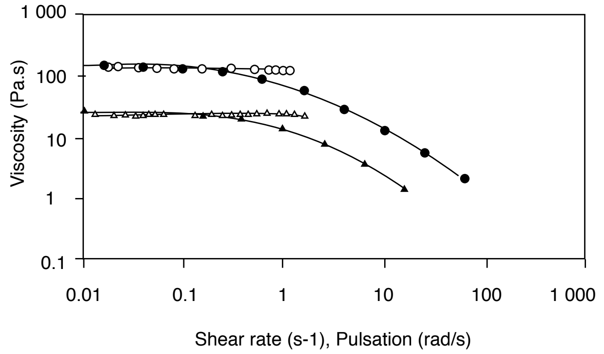

Figure 5

Comparaison between steady-state and dynamic viscosities of 5% w/w solutions.

100TDUC10F: steady-state (Δ) and dynamic (▲)

100TDUC16H: steady-state (○) and dynamic (●).

G' = G". It appears that the relaxation time of the fluorinated thickener is lower than the one of the alkyl modified polymer. This is consistent with the difference in the hydrophobe lengths ($C_8F_{17}– \sim C_{14}H_{29}–$).

The dynamic viscosity is shown to be equal to the steady state viscosity at low shear rates ($\omega.\tau < 1$) while at higher shear rates ($\omega.\tau > 1$) the dynamic viscosity shows a much stronger dependence on frequency than does the steady-shear viscosity on shear rate (Figure 5). This result is consistent with the earlier results of Annable *et al.* [7].

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