Asymmetric End-Capped Poly(ethylene oxide). Synthesis and Rheological Behavior in Aqueous Solution

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ABSTRACT: A method was developed to prepare asymmetric end-capped poly(ethylene oxide)s (PEOs), containing an alkyl group on one chain end and a perfluoroalkyl group on the other one ($C_{18}H_{37}-PEO-C_2H_4-C_8F_{17}$ and $C_{18}H_{37}-PEO-C_{10}H_{20}-C_8F_{17}$). These new telechelic associative polymers (APs) were synthesized by anionic polymerization of ethylene oxide initiated by an alkoxide ($C_{18}H_{37}-O^-K^+$) followed by esterification. The rheological behavior of asymmetric and analogous symmetric APs in aqueous solutions has been investigated as a function of polymer concentration (C), hydrophobic end-cap and surfactant used to homogenize the system: sodium dodecyl sulfate (SDS) or lithium perfluorooctyl sulfonate (LiFOS). A steep increase of the static viscosity η, attributed to the formation of a multiconnected network, is observed for $C \approx 1$ wt %. Semidilute solutions present a Maxwellian rheological behavior with only one relaxation time τ associated with the least hydrophobic end group. The viscoelastic response is modified by the interactions between hydrophobic end groups and surfactant inside mixed aggregates.

1. Introduction

Associative polymers (APs) have received considerable interest because of their unusual rheological properties in water.[1−3] They are used in a wide range of applications as rheology modifiers. APs are hydrophobically modified water-soluble polymers. These amphiphilic polymers have a strong tendency to undergo intra and intermolecular associations. The viscosifying properties of APs originate from the formation of a transient network. Interest raised by fluorocarbon APs comes from the low surface energy and hydrophobic properties of fluorinated substituents but also from the considerably enhanced viscosifying properties.[4] The degree of substitution has to stay low (a few units per chain) in order to maintain solubility of fluorinated APs in water.[4,5] Among the various classes of APs, hydrophobically end-capped poly(ethylene oxide) (PEO) present a well-defined architecture. Because of the known position of hydrophobic groups at each end of the polymer chain, these telechelic APs can be used as model systems for fundamental and systematic studies.[6]

Due to the mode of synthesis involving hydroxytelechelic PEO as starting polymer, end-capped APs present a symmetrical structure with the same hydrophobic groups. Fluorocarbon telechelics PEO are obtained by different methods including various linkers connecting the hydrophobic segment with the hydrophilic main chain.[2] The synthesis of modified PEO with linkers such as ethers,[7] esters,[8,9] urethanes,[10,11] or diurethanes[12,13] were reported. It was clearly established that the solution behavior is sensitive to any subtle changes in the chemical structure of the linker[11] and the hydrophobic group.[6] These telechelic APs self-assemble into starlike flowers in dilute regime and develop a fully connected network of flowers above some threshold concentration.[14]

In order to improve our understanding of hydrophobic segment influence on rheological behavior, we have developed a method to prepare asymmetric functional (PEOs) by taking advantage of living anionic polymerization of ethylene oxide (EO)[15−21] initiated by alkoxides. The hydroxy telechelic one-ended PEO is then modified by esterification. By this method, hydrophobic groups are connected to PEO by ether and ester groups, so as to limit the influence of the linker. Solution behavior of these new compounds is compared with analogous symmetric telechelic APs. Rheological properties of asymmetric APs were also compared with mixture of analogous symmetric polymers. We have investigated the linear viscoelasticity of solution at 25 °C, as a function of AP concentration (C), and surfactant nature.

2. Experimental Part

2.1. Materials. Octadecanol, dodecanol, and 1,1,1-trichloroethane provided by Aldrich and potassium, diphenylmethane, and naphthalene provided by Fluka were used as received. Dicyclohexylcarbodiimide (DCC) and dimethylaminopyridine (DMAP) from Accros, perfluorooctyliodide and undecylenic acid from Atochem and allyl alcohol from Avocado were used as received too.

11-Perfluorooctyl-1-undecanoic acid was obtained by addition of perfluorooctyliodide to undecylenic acid followed by reduction of the iodo intermediate.[8] 3-perfluorooctyl-1-propanol was obtained by the same way. Oxidation with Jone's agent leads to the 3-pefluorooctyl-1-propanoic acid. Tetrahydrofuran (THF) was stood over granulated potassium hydroxide to remove stabilizer, dried over $CaCl_2$ and finally distilled under nitrogen from potassium. THF was then degassed under vacuum and stored over calcium hydride. Crown ether, 18-crown-6, from Accros was recrystallized in petroleum ether.

2.2. Polymerization of Ethylene Oxide. The vacuum techniques employed for anionic polymerization have been fully described previously.[22−24] Reactions were carried out under high vacuum (10^{-7} bar). A typical experiment was conducted as follows. Initiator was first prepared by reaction of potassium 58.5 mg (1.5×10^{-3} mol) with naphthalene 220 mg (1.72×10^{-3} mol) into 50 mL of THF for 15 h. Diphenyl methane 289 mg (1.72×10^{-3} mol) was injected into the reaction vessel (flask 2 in Figure 1) containing the dark green colored-solution via the septum cap. The mixture was left to react for 8 h at room temperature under stirring. A quantity of alkyl alcohol (ROH) in slight excess, in order to obtain a molar ratio K diphenyl methane/alcohol = 0.85, was introduced

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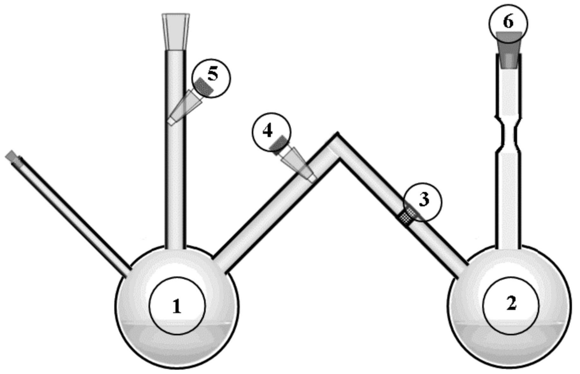

Figure 1. Apparatus for ethylene oxide polymerization. Key: (1) polymerization flask; (2) flask for initiator synthesis; (3) sintered glass filter; (4 and 5) vacuum valves; (6) septum cap.

in flask 1 (Figure 1) closely separated by a vacuum valve and connected to the vacuum line. THF (100 mL) was distilled and the red-colored solution of K diphenyl methane is transferred through a sintered glass filter. Red color immediately disappears and potassium alkoxide precipitates.

At this point 20 g (0.45 mol) of ethylene oxide were distilled into the reaction flask and the system is allowed to polymerize at 40 °C for 24 h. To obtain a PEO with molecular weight 20 000 g/mol, another quantity (20 g) of ethylene oxide was distilled and the system is allowed to react for additional 24 h. Polymerization was terminated with small amounts of acidified water. Finally polymer was precipitated from petroleum ether three times and vacuum-dried before analysis.

2.3. Modification of Poly(ethylene oxide). Poly(ethylene glycol) and one-ended PEO obtained by anionic polymerization were modified by esterification of hydroxy end groups with carboxylic acid, in presence of *N*,*N*-dicyclohexylcarbodiimide (DCC) and (dimethylamino)pyridine (DMAP) as described by Hartmann et al.[8]

2.4. Purification of Associative Polymers. The mode of synthesis using DCC and DMAP leads to complete esterification of hydroxy end groups but dicyclohexylurea (DCU), byproduct of the reaction, is particularly difficult to remove by conventional techniques such as repeated precipitations into petroleum ether. A strategy involving molecularly imprinted polymer (MIP) has been tested to purify APs. Molecular imprinting is a process by which polymeric materials are synthesized with highly specific binding sites for small molecules.[25,26] MIPs are cross-linked polymeric matrices formed in the presence of template molecule. Upon removal of the template, a binding cavity is formed with functional groups (carboxylic acids) accessible to specific guest molecule. The MIP's synthesis, developed by Rushton et al.,[27] based on methacrylic acid and ethylene glycol dimethacrylate copolymer matrix with DCU as initial template molecule, was successfully used to eliminate DCU.

2.5. Characterization. The degree of substitution is determined by titration of residual hydroxy groups by ^{19}F NMR, on a Bruker 300 NMR according to the method previously described.[8]

Molecular weight distribution of polymer was determined by size exclusion chromatography (SEC) using a Shimadzu differential refractometer. To prevent polar interactions between APs and the gel phase, a solution of tetrabutylammonium bromide in tetrahydrofuran (10^{-2} mol·L^{-1}) is used as eluent (flow rate 1 mL·mn^{-1}). A set of two PLgel columns was used with pore sizes 10^3 and 10^4 Å. A calibration curve was established from poly(ethylene oxide) standards.

2.6. Linear Rheology. Dilute solutions were studied using a Ubbelohde capillary viscometer with diameter of 0.56 mm (at constant temperature, $T = 25$ °C). The capillary viscometer is restricted to the investigation of Newtonian solutions. The static viscosity (η) was obtained according to $\eta = Kt_f$, where t_f is the solution flow time in seconds. The instrument constant K has been determined from the pure water flow time for which $\eta = 0.8904 \times 10^{-3}$ Pa·s at 25 °C. For higher polymer concentrations (typically $C > 0.8$ wt %), AP solutions become viscoelastic, and so, a standard rotational rheometer is used. The mechanical properties were obtained on a Rheometrics fluid spectrometer (RFS II) working either in Couette geometry (gap 1 mm) for viscosity lower than 50 Pa·s or in a cone-and-plate geometry (diameter 30 mm, gap 50 μm, angle 0.02 rad) for higher static viscosity. Some results were also obtained on a rheometer MCR 301 from Physica, working in strain controlled with a cone and plate geometry (diameter 50 mm, gap 51 μm, angle 0.0175 rad).

3. Results

3.1. Synthesis of Asymmetric Fluorinated APs. Synthesis of asymmetric functional poly(ethylene oxide) involves as a first step an anionic polymerization initiated by alkoxide, and as a second step an esterification of hydroxy group with fluorinated carboxylic acid. Alkoxides used as polymerization initiators are synthesized in situ by reaction of potassium diphenyl methane and alcohol according to Scheme 1.

The anionic polymerization involves a ring opening of ethylene oxide (EO) with an oxanion as propagating specie. Shen et al.[19] have shown that propagation will continue without termination even in the presence of free alcohol. As long as the equilibrium between alcohol and alkoxide (eq 1) is much faster than the propagation step (eq 2), the system is terminationless and can be considered as a living process.

$$R'OK + ROH \rightleftarrows R'OH + ROK \qquad (1)$$

$$RO^{-}K^{+} + EO \rightarrow RO{-}CH_2CH_2O^{-}K^{+} \qquad (2)$$

Shen et al. showed the influence of degree of alkoxidation $x = [(C_6H_5)_2CH^{-}K^{+}]/[C_pH_{2p+1}OH]_0$ on polymerization kinetics. The ratio x must be both smaller than 1 (which means an excess of alcohol) and as high as possible to increase the rate of propagation. Polymers were characterized by SEC and NMR.

Table 1 summarizes characterization data of polymers with different theoretical molecular weights (M_n(th)) obtained under various conditions. These results underline the influence of polymerization conditions (ratio x, time, initiator structure) on polymer molecular weights.

Results of polymerizations initiated by 1-decanol clearly show that polymer molecular weights can be controlled by initial conditions. Polymers present narrow molecular weight distributions with polydispersity index $I \le 1.1$. Alkyl alcohols, with hydrogenated chain length up to 18 carbons, are efficient initiators. On the other hand perfluoroalkyl alcohols do not initiate the anionic polymerization of EO. That could be explained by side reactions probably due to hydrogen abstraction on the methylene group close to the perfluorinated group.

Polymerization was followed by SEC with samples isolated from time to time. The unimodal distribution of chromatograms (Figure 2) proves that the equilibrium between alcohol and alkoxide (eq 1) is much faster than the propagation. Thus all the alcohol molecules charged in the feed can be initiator fragments to form the PEO whose number-average degree of polymerization (DP$_n$) is given by:

$$DP_n = n = \frac{[M]_0\theta}{[A]_0} \qquad (3)$$

where $[M]_0$ and $[A]_0$ are respectively the initial molar concentration of EO and alcohol and θ is the conversion of EO polymerized.

It has been shown that complexing agents of alkali metals increase the reactivity of active centers in anionic polymerization[20,22,28] and allow the initiation of heterocyclic monomers.[23] In order to increase the propagation rate, polymerizations were performed in presence of 18-crown-6. In fact, due to the

Scheme 1. Anionic Polymerization of EO Initiated by Potassium Alkoxides

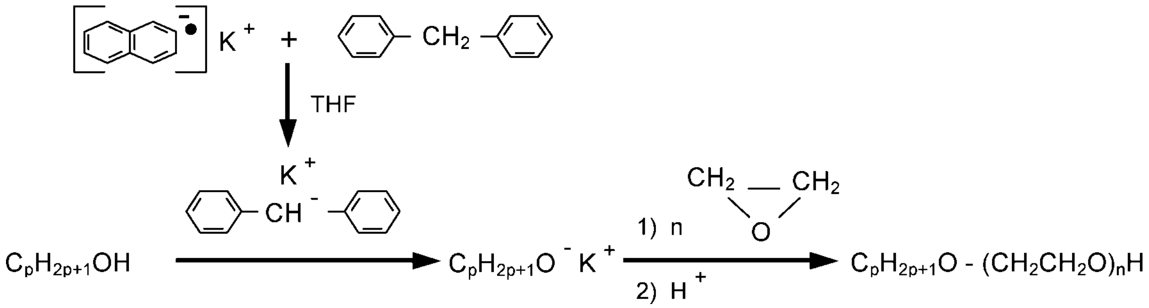

Table 1. Characterization of Polymers Synthesized[a]

initiator	x	time (h)	M_n(th) (g/mol)	M_n(NMR) (g/mol)	M_n (g/mol)	I
$C_{10}H_{21}-O^-K^+$	0.61	15	800	900	1100	1.03
$C_{10}H_{21}-O^-K^+$	0.89	65	1200	1100	1300	1.07
$C_{10}H_{21}-O^-K^+$	0.80	89	2300	1800	1900	1.07
$C_{12}H_{25}-O^-K^+$	0.89	46	20000	14900	13800	1.04
$C_{18}H_{37}-O^-K^+$	0.89	115	20000	17900	18700	1.07
$C_{18}H_{37}-O^-K^+$	0.92	111	5300	5000	5600	1.13
$C_8F_{17}-C_2H_4-O^-K^+$	0.90	116	2800	0	0	0
$C_8F_{17}-C_{11}H_{22}-O^-K^+$	0.92	116	2900	0	0	0

[a] x is the degree of alkoxydation; M_n(th) is the theoretical molecular weight calculated from the initial ratio of EO/alcohol; M_n(NMR) is the molecular weight determined by ^{1}H NMR; M_n is the molecular weight determined by SEC; I is the polydispersity index obtained by SEC.

complexing agent the conversion and the propagation rates are markedly decreased. After 24 h of polymerization, the conversion rates are lower than 65%.

Similar results were observed by Sigwalt and Boileau for the anionic polymerization of EO in presence of cryptand.[21] To explain such behavior, the authors suggest that the ionic dissociation of the living propagating chain is modified by the complexing agent and free ions are more reactive than cryptated ion pairs. Whatever the complexing agent, cryptand or crown ether, the EO polymerization rate cannot be increased by this way.

To prove the living character of the anionic polymerization of EO initiated by alkoxides in presence of a slight excess of alcohol, aliquots of monomers were added successively with an interval of 24 or 48 h. The evolution of the molecular weight is reported in Figure 3. After 24 h of reaction Mn values were stabilized. Addition of a second amount of monomers is followed by a new increase of the molecular weights. This procedure, involving two steps, was used to synthesize asymmetric APs with molecular weights up to 20 000 g/mol (cf. Figure 3).

3.2. Phase Behavior. In aqueous media, at low polymer concentrations but above the critical aggregation concentration (cac) ($C \geq 0.1$ wt %), symmetric polymer with strong hydrophobic groups $F_8H_{10}-H_{10}F_8$ and fluorinated asymmetric APs $H_{18}-H_2F_8$ and $H_{18}-H_{10}F_8$ exhibit a macroscopic phase separation. A dilute phase, with a low viscosity like water, coexists with a viscous gel-like condensed phase. A similar behavior was already reported.[6,10,29,30] This phenomenon can be explained by the theory developed by Semenov et al.[31] Due to the attractive energy, increasing with the aggregation number, the aggregates have a tendency to stick together leading to a phase segregation. The phase separation can occur even in dilute solution if the forces of interaction are strong enough. Borisov and Halperin showed that the attraction is due to chains bridging two micelles.[32,33]

All experimental results provide evidence that phase separation depends on the degree of functionalization, hydrophobic strength of the end group that is reinforced by a perfluorinated segment, and PEO molecular weight. In other words, it is governed by the hydrophobic−hydrophilic balance of APs. Macroscopic phase separation of aqueous solutions of telechelic hydrophobically modified PEO occurs when the ratio of hydrophobic length to backbone length exceeds a critical value. For solutions of fully end-capped PEO 20 kg/mol, the critical hydrophobic length was estimated close to 18 CH_2. In order to evaluate the hydrophobic equivalent length of fluorinated end groups, we assume that one CF_2 is equivalent to 1.5 CH_2.[34] Thus the equivalent length of semifluorinated end groups are 22 CH_2 for $(CH_2)_{10}C_8F_{17}$ and 14 CH_2 for $(CH_2)_2C_8F_{17}$. The phase separation observed for asymmetric APs could be explained, for the asymmetric $H_{18}-H_{10}F_8$, by the strong hydrophobic character of $(CH_2)_{10}C_8F_{17}$ end group. But this explanation is not valid for the asymmetric polymer $H_{18}-H_2F_8$. The phase separation occurring with asymmetric APs is probably in relation with the increase of the density of elastically active chains due to the asymmetric structure of these polymers. This point will be developed in the discussion section.

Addition of surfactant improves the homogenization of strong associated polymers and prevents phase segregation. To compare our results with previous works reported elsewhere,[6] the same surfactant sodium dodecyl sulfate (SDS) was used. In order to improve our understanding of the influence of surfactant on rheological behavior a fluorinated surfactant, lithium perfluorooctyl sulfonate (LiFOS) was tested. The minimal quantity of SDS to obtain homogenization of dilute solutions was determined. Phase diagrams are reported in Figure 4 with respect to polymer weight concentration (C) and molar ratio between surfactant and polymer (C_{SDS}/C_{Pol}). When the molar ratio C_{SDS}/C_{Pol} is equal to 0.3, the system is homogeneous whatever the polymer concentration. This means that a very small amount of surfactant is sufficient to prevent phase segregation.

Previous studies showed that viscosity of AP−surfactant mixtures reach a maximum when the surfactant concentration is close to its critical micellar concentration (cmc).[6,14] Therefore the surfactants SDS and LiFOS were added at concentrations of 8 and 4 mmol/L, respectively. In these conditions the molar ratio surfactant/AP is much higher than that required for homogenization of studied solutions with polymer concentrations ranging from 0.5 to 5 wt %.

Table 2. Telechelic Associative Polymers Synthesized

symmetric APs	asymmetric APs
$C_{17}H_{35}-CO-PEO(20K)-CO-C_{17}H_{35}(H_{17}-H_{17})$	$C_{18}H_{37}-O-PEO(20K)-CO-C_{10}H_{20}-C_8F_{17}$ ($H_{18}-H_{10}F_8$)
$C_8F_{17}-C_{10}H_{20}-CO-PEO(20K)-CO-C_{10}H_{20}-C_8F_{17}$ ($F_8H_{10}-H_{10}F_8$)	$C_{18}H_{37}-O-PEO(20K)-CO-C_2H_4-C_8F_{17}$ ($H_{18}-H_2F_8$)
$C_8F_{17}-C_2H_4-CO-PEO(20K)-CO-C_2H_4-C_8F_{17}$ ($F_8H_2-H_2F_8$)	

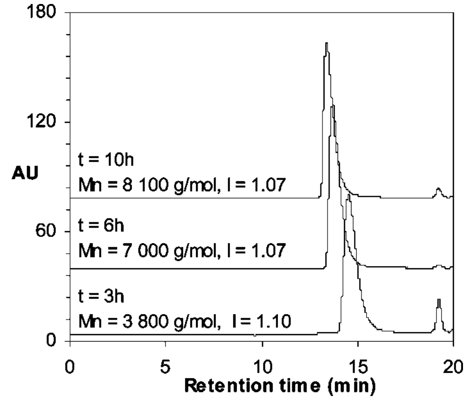

Figure 2. SEC traces that illustrate the evolution of PEO molecular weight, initiated by $C_{12}H_{25}-O^{-}K^{+}$, as a function of reaction time.

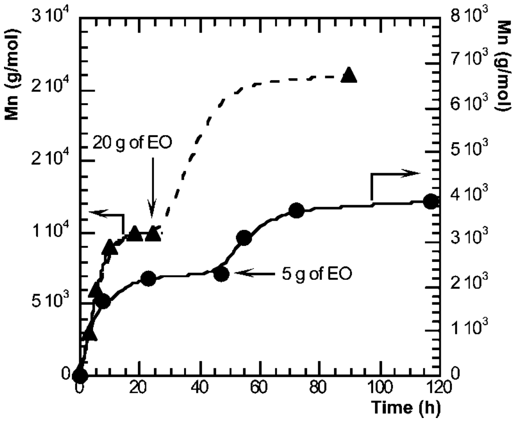

Figure 3. Evolution of PEO molecular weight following successive addition of monomer as a proof of the living character of the polymerization. The final M_n values of one ended PEO are 20 000 g/mol. (▲) and 4 000 g/mol. (●). The dashed line is only a guide for the eyes, the number of experimental data being limited by the conditions of synthesis under high vacuum.

3.3. Aggregate Structure. Aggregate structure in ternary mixtures (AP−surfactant−water) was determined by small angle neutron scattering (SANS) and ^{13}C NMR. Conclusive results of these studies will be presented and discussed in detail elsewhere.[35] These experiments prove the formation of mixed aggregates in spite of the low affinity between hydrogenated and fluorinated chains. The aggregate structure is a core containing hydrophobic groups of surfactants and APs surrounded by the hydrophilic corona of hydrated polymer chains. One of the most important results of SANS study emphasizes the evolution of mixed aggregate structure with AP and surfactant concentrations.

3.4. Viscoelastic Behavior. Viscosity of dilute APs solutions was investigated using a capillary viscometer and semidilute solutions were studied by rheometry. Static viscosities of semidilute solutions were obtained from steady shear experiments. At low shear rate, viscoelastic fluids show linear response i.e. Newtonian behavior. The stress relaxation function G(t) is independent of strain γ, and stress σ is proportional to shear rate $\dot{\gamma}$ ($\sigma = \eta\dot{\gamma}$). Evolution of static viscosity (η) for the different systems, reported in Figure 5, is a typical feature of the viscoelastic behavior of telechelic APs, with a huge increase of viscosity at the percolation threshold between the sol and the physical gel. The rapid rise of viscosity at the threshold concentration denoted C^* is interpreted as a sol−viscoelastic transition between the dilute solution of small aggregates and the infinite interconnected network of flowers. Static viscosities start rising rapidly at a concentration of the order of 1 wt % whatever the chemical structure of AP chain end. It is interesting to note that the steep increase of viscosity for asymmetric polymers occurs in the same range of concentration than that observed for symmetric APs. Nevertheless, static viscosities above C^* depend on the hydrophobic character of the polymer end-cap. Due to the higher hydrophobicity of perfluorinated groups, in many cases the static viscosity of fluorinated APs is enhanced. The asymmetric APs static viscosity is located between the viscosities of the homologous symmetric APs. The influence of end cap chemical structure on rheological parameters will be discussed later.

The viscosities of polymer solutions, above C^*, are high enough to allow the study of rheological behavior. The linear viscoelasticity was investigated using dynamic frequency experiments and steady shear rate measurements. In dynamic frequency experiments, the strain depends sinusoidally on frequency ω ($\gamma(t) = \gamma_0 \sin(\omega t)$). From stress measurements, storage modulus G' and loss modulus G'' were determined using the following equation:

$$\sigma(t) = \gamma_0[G'(\omega)\sin(\omega t) + G''(\omega)\cos(\omega t)] \tag{4}$$

When the fluid follows the Maxwell model, the moduli G' and G'' can be expressed in terms of the elastic plateau modulus G_0 and the relaxation time τ:

$$G'(\omega) = G_0\frac{\omega^2\tau^2}{1+\omega^2\tau^2} \tag{5}$$

and

$$G''(\omega) = G_0\frac{\omega\tau}{1+\omega^2\tau^2} \tag{6}$$

Figure 6 shows G' and G'' of 3 wt % asymmetric polymer solutions. The average relaxation time τ can be determined from the intersection point of G' and G'' curves corresponding to $1/\tau$. The elastic modulus G_0 is obtained from the plateau of the G' curve. Values of parameters τ and G_0 for the different systems are reported in Table 3. Experimental data are correctly fitted by eq 5 and eq 6 derived from the Maxwell model. G' and G'' curves (Figure 6) illustrate the Maxwellian viscoelastic behavior of asymmetric APs. As reported elsewhere,[2,6,36−38] the rheological behavior of telechelic APs can be described with a good approximation by the Maxwell model. It must be noted also that asymmetric APs behavior can be described, following the Maxwell model, by a single relaxation time.

Another method to examine the suitability of the Maxwell model is to present the data in the alternative form of a Cole−Cole plot, G'' versus G'. From eq 5 and 6 of the Maxwell model with only one relaxation time, the plot can be described by: $G'' = [G_0G' - G'^2]^{1/2}$.

This relationship can be extended in the following form:

$$G'' = [G_0G' - G'^2]^a \tag{7}$$

where the exponent a is related to the relaxation time distribution. The radius of Cole−Cole curve is one-half of the elastic modulus G_0. In Figure 7 are reported experimental data, for asymmetric APs, in the Cole−Cole form using eq 7. Data fitted by the Maxwell model yield a semicircle pointing out a narrow distribution of τ. The best fit is obtained when the exponent a = 0.5 for $H_{18}-H_2F_8$ and a = 0.494 for $H_{18}-H_{10}F_8$. The rheological behavior of these systems can be described by only one set of parameters (τ and G_0). Therefore we can compare rheological characteristics of asymmetric polymers with symmetric polymers.

The concentration dependence of τ and G_0 for $H_{18}-H_{10}F_8$ asymmetric polymer and the two homologous symmetric polymers ($H_{17}-H_{17}$ and $F_8H_{10}-H_{10}F_8$) are shown in Figure 8. The evolution of τ with polymer concentration, for the different

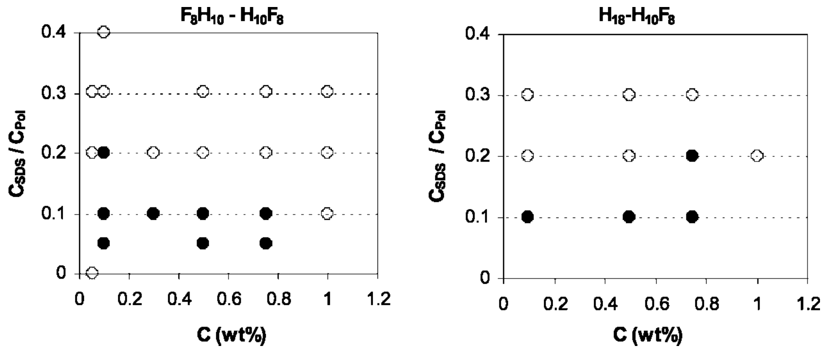

Figure 4. $F_8H_{10}-H_{10}F_8$ and $H_{18}-H_{10}F_8$ phase diagrams with respect of polymer weight concentration C in aqueous solution, and molar ratio between SDS and polymer C_{SDS}/C_{Pol}, at 25 °C. Key: (●) heterogeneous system; (○) homogeneous system.

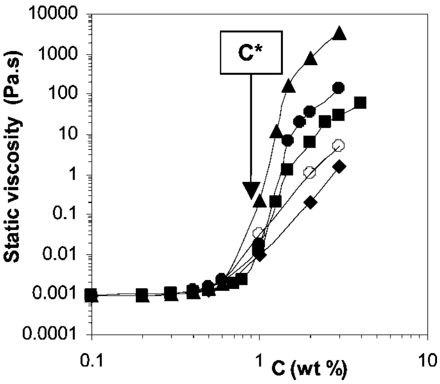

Figure 5. Concentration dependence of the static viscosity η of aqueous solution of symmetric APs $F_8H_{10}-H_{10}F_8$ (▲), $H_{17}-H_{17}$ (■), $F_8H_2-H_2F_8$ (◆) and asymmetric APs $H_{18}-H_{10}F_8$ (●), $H_{18}-H_2F_8$ (○) in the presence of SDS (8 mmol L^{-1}) at 25 °C.

systems, depends on the chemical structure of polymer end group. The increase in relaxation time is enhanced by the presence of fluorinated end-caps. The values of τ for fluorinated symmetric AP are higher, by an order of magnitude, than those observed for asymmetric AP. The elastic modulus G_0 is the second parameter characterizing the structure of the transient network. As expected, G_0 increases sharply with the polymer concentration above C^* (cf. Figure 8 B). Solutions at the same concentration, up to 3 wt %, are characterized by similar values of G_0, whatever the AP. Within this domain of concentrations (1 wt % < C < 3 wt %) the network seems independent of the end group structure. For higher concentrations ($C \geq 3$ wt %) the asymmetric structure of polymer $H_{18}-H_{10}F_8$ leads to increased values of G_0. The rheological characteristics of 3 wt % polymer solutions, summarized in Table 3, show that asymmetric polymers have higher elastic plateau modulus than homologous symmetric APs. This observation leads to an important result which will be developed below.

According to the theory of rubber elasticity extended to transient networks, the magnitude of the plateau modulus G_0 can be related to the density of elastically active chains ν. To calculate the number of bridging chains we assume that the elasticity in the system is due to bridging chains which are the active components of the system. By analogy with the theory of rubber elasticity, G_0 can be expressed by: $G_0 = \nu k_B T$ where ν is the number of elastically active chains per unit volume (molecules/m^3), k_B the Boltzmann constant, and T the temperature.[39] The proportion of mechanically active chains (ν/n) between hydrophobic clusters can be estimated by the relationship

$$\frac{\nu}{n} = \frac{G_0}{n k_B T} \tag{8}$$

where n is the total number of polymer chains per unit volume. This expression is only an estimate, but it gives a concrete idea of the network structure. Results reported in Table 3 show that more than 30% of chains are acting as bridges to form the network of symmetric polymers solutions. At the same polymer concentration ($C = 3$ wt %) asymmetric APs form networks with a more important density of elastically active chains than homologous symmetric polymers. The particular behavior of asymmetric APs could be a consequence of the poor affinity between fluorinated and hydrogenated end groups. So the different end groups (fluorinated and hydrogenated) of the asymmetric APs have a more marked tendency to form bridges between aggregates than loops in mixed aggregates. The network topology of asymmetric APs is determined by the non equivalent structure of end groups.

Viscoelastic behavior and mechanical response of transient network are governed by two parameters, the elastic plateau modulus G_0 and the relaxation time τ. On the one hand, transient network of asymmetric APs presents a higher value of G_0 and a larger density of bridging chains than the conventional symmetric APs. On the other hand, comparable relaxation times are observed for asymmetric APs and analogous symmetric systems containing the less hydrophobic end groups. As a consequence the static viscosity of asymmetric APs is intermediate between viscosities of their symmetric analogues as reported in Figure 5.

Another characteristic of transient network is that viscosity and relaxation time are thermally activated. Both relaxation time and viscosity obey Arrhenius dependencies. The activation energy (E_a) was obtained from the variation of relaxation time versus $1/T$, yielding a straight line in the temperature range between 5 and 40 °C, according to the relationship

$$\tau(T) = \tau' e^{E_a/(RT)} \tag{9}$$

In terms of the transient network theory proposed by Tanaka and Edwards,[37] E_a is the potential barrier to disengagement of the end group from the aggregate core. The values of activation energy, reported in Table 3, are consistent with the tendency observed for relaxation time with respect to the chain end. From temperature dependence of the solution viscosity, Annable et al.[40] determined a value of $E_a \approx 70$ kJ/mol for HEUR polymers. The greater activation energy of HEUR polymers reveals the contribution of the isophorone diurethane spacer to the hydrophobicity of polymer end group.

3.5. Influence of Surfactant. Addition of surfactant to AP solutions has a great influence on their properties. As reported in the literature,[1,41] the initial AP viscosity increases in presence of growing concentrations of surfactant, passes through a

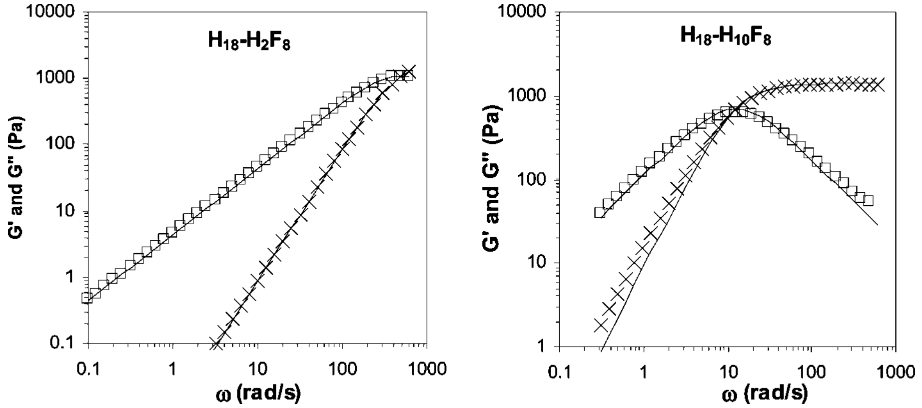

Figure 6. Frequency dependence of the storage modulus G' (×) and the loss modulus G'' (□), for 3 wt % asymmetric polymer solutions, in presence of SDS (8 mmol/L), at 25 °C. Solid lines are Maxwell model fits.

Table 3. Rheological Parameters of 3 wt % Polymer Solutions with SDS (8 mmol/L) or LiFOS (4 mmol/L)

polymer	surfactant	η (Pa·s)	G_0 (Pa)	τ (s)	E_a (kJ/mol)	ν/n (%)	one bridging chain for...
$H_{18}-H_2F_8$	SDS	5	2200	0.002	53	58.9	1.7 chains
$H_{18}-H_{10}F_8$	SDS	140	1400	0.08	66	32.3	3.1 chains
$F_8H_2-H_2F_8$	SDS	1.5	950	0.0014	55	29.4	3.4 chains
$H_{17}-H_{17}$	SDS	30	1080	0.026	59	25.6	3.9 chains
$F_8H_{10}-H_{10}F_8$	SDS	3300	1030	3.2	76	27.8	3.6 chains
$H_{18}-H_2F_8$	LiFOS	11	2700	0.0038	55	72.7	1.4 chains
$H_{18}-H_{10}F_8$	LiFOS	40	1150	0.025	45	31.0	3.2 chains
$F_8H_2-H_2F_8$	LiFOS	3	1200	0.0025	51	32.3	3.1 chains
$H_{17}-H_{17}$	LiFOS	20	1200	0.015	53	32.3	3.1 chains
$F_8H_{10}-H_{10}F_8$	LiFOS	3000	1070	2.8	65	28.8	3.5 chains

maximum and then decreases. The rheological response in presence of anionic surfactant is complex because surfactant can interact with hydrophobic polymer end groups (inside mixed aggregates) as well as with the PEO chain. The onset of the cooperative binding between SDS and PEO chains of telechelic APs, was clearly established, at a critical aggregation concentration (cac) of SDS lower than the cmc. The cac was found to be close to 3 mmol/L for hydrophobic ethoxylated urethane (HEUR)[42] and 4 mmol/L for telechelic APs[35] studied in the present paper. At the cmc, with semidilute solutions, surfactant molecules are in cooperative association with APs in mixed aggregates. In order to better understand the surfactant/APs interactions, the viscoelastic behavior of semidilute solutions was investigated in presence of hydrogenated (SDS) and fluorinated (LiFOS) surfactants. The rheological characteristics of 3 wt % APs solutions with the both surfactants are summarized in Table 3. The topology of the network, evaluated from G_0 values, is not drastically modified by the surfactant structure. The effect of surfactant on the relaxation time and thus on the viscosity is more complex. The surfactant can change the nature of the system through the structure of mixed aggregates and the compatibility (or affinity) between hydrophobic groups. As shown in Table 3, the values of τ are significantly modified according to surfactant (SDS or LiFOS). The relaxation times of APs with highly fluorinated end-caps ($-(CH_2)_2C_8F_{17}$), including symmetric ($F_8H_2-H_2F_8$) and asymmetric ($H_{18}-H_2F_8$) polymers, are increased by the presence of perfluorinated surfactant. Inversely, the relaxation time of polymers with hydrogenated end-caps ($H_{17}-H_{17}$ and $H_{18}-H_{10}F_8$) increases in presence of SDS. Surfactant/AP interactions are even more complex for telechelic polymers containing semifluorinated end groups ($F_8H_{10}-H_{10}F_8$) with comparable lengths of hydrogenated and fluorinated segments.

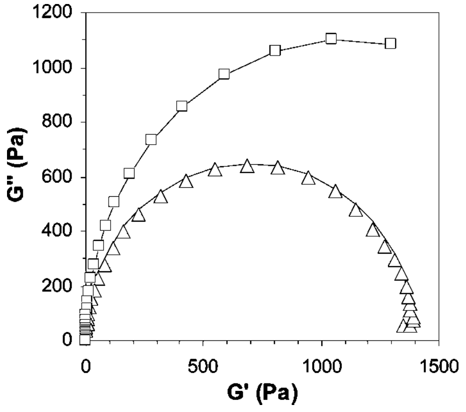

Figure 7. Cole−Cole plot of 3 wt % solutions of asymmetric polymers $H_{18}-H_2F_8$ (□) and $H_{18}-H_{10}F_8$ (Δ), in presence of SDS (8 mmol/L), at 25 °C. Solid lines are Maxwell model fits.

In the first analysis, it seems that the main influence of the surfactant nature comes from interaction, inside mixed aggregates, between the hydrophobic end groups of polymer and the hydrophobic tail of surfactant. The higher compatibility between hydrophobic groups leads to stronger interactions. As a consequence, the relaxation time and the viscosity are increased.

3.6. Mixture of Hydrogenated and Fluorinated Polymers. To emphasize the specific behavior of asymmetric telechelic polymers, their rheological properties were compared with that of symmetric APs analogue end-capped by alkylated and semifluorinated hydrophobic groups. With this aim, aqueous solutions of asymmetric AP ($H_{18}-H_{10}F_8$) and 50:50 mixture of symmetric analogues ($H_{17}-H_{17}/F_8H_{10}-H_{10}F_8$) were investigated and compared at an overall polymer concentration of 3 wt %. The viscosity of the 50:50 mixture solution of $H_{17}-H_{17}/F_8H_{10}-H_{10}F_8$, in presence of SDS, is comparable with that of asymmetric polymer $H_{18}-H_{10}F_8$ (200 and 140 Pa·s respectively). Nevertheless dynamic frequency experiments reveal the different behavior of the two systems. As can be seen in Figure 12, the G' and G'' variations present significant deviation from Maxwellian response and eq 5 and 6 are no longer valid. The G'' loss modulus curve of symmetric APs mixture shows two maxima, meaning that this system has at least two relaxation times. In such a case the modulus can be obtained by fitting a sum of Maxwell elements, where f_i is a participation factor:

$$G'(\omega) = G_0 \sum_i \left(f_i \frac{\omega^2 \tau_i^2}{1 + \omega^2 \tau_i^2} \right) \quad (10)$$

$$G''(\omega) = G_0 \sum_i \left(f_i \frac{\omega \tau_i}{1 + \omega^2 \tau_i^2} \right) \quad (11)$$

The number of elements was kept to the minimum required to fit the data. In Figure 9 the data are fitted, using eq 10 and 11, with two relaxation times $\tau_1 = 0.04$ s and $\tau_2 = 0.9$ s and the corresponding participation factors ($f_1 = 0.8$, $f_2 = 0.2$). In this way, $G'(\omega)$ and $G''(\omega)$ data are correctly fitted (cf. Figure 9A), yielding a value of the elastic plateau modulus, $G_0 = 970$ Pa. As can be seen in Figure 9B, from the Cole−Cole curve, experimental data are somewhat less well fitted than pure APs. Nevertheless, it can be considered that G' and G'' moduli are roughly described by two Maxwell elements. This is consistent with the conclusion reported by Annable et al.[40] for mixed solutions of PEO with different hydrogenated end-cap lengths. The formation of mixed aggregates, with both hydrogenated and fluorinated end-caps, would lead, to some extend, to a mean relaxation time with a value intermediate to pure components. The correspondence between the relaxation times in pure and mixed solutions proves that, in mixed solutions, polymer chains with different end groups relax independently.

4. Discussion

The aim of the present paper is to investigate the rheological behavior of asymmetric APs by comparison with symmetric analogues. The chemical structure of asymmetric APs with different end-caps constrains the system to form mixed aggregates in aqueous phase with a core containing both hydrogenated and semifluorinated groups. As a result these systems offer the possibility to analyze the interactions between hydrophobic groups and their role in modifying the transient network.

The macroscopic phase separation occurring with symmetric telechelic APs was correlated with the hydrophobicity of polymer chain ends, with a critical chain length around 18 CH_2 for PEO with molecular weight 20 kg/mol. With asymmetric APs, the low affinity between hydrogenated and semifluorinated end groups, inside mixed aggregates, promotes bridges compared to loops. The chains bridging two aggregates are more numerous, as a consequence the attraction between aggregates is increased leading to phase separation.

In semidilute regime, in presence of surfactant, the viscoelastic properties of asymmetric associating polymer solutions can be described by the Maxwell model. The system is characterized by the elastic modulus G_0 that provides information about the network structure. The G_0 of asymmetric polymer solutions are higher than that observed for analogous symmetric polymers. The magnitude of G_0 can be related to the number density of elastically active chains, so asymmetric polymers form a network with higher density of bridging chains. This result confirms our explanation of the phase separation. The second rheological characteristic parameter of transient network is the relaxation time. The relaxation times of symmetric polymers are largely determined by the end group length and hydrophobicity. Perfluorinated segments can produce a large increase of τ by several orders of magnitude.[2] An exponential relationship between relaxation time and hydrogenated end group length was originally proposed by Annable et al.[40] Figure 10 illustrates the

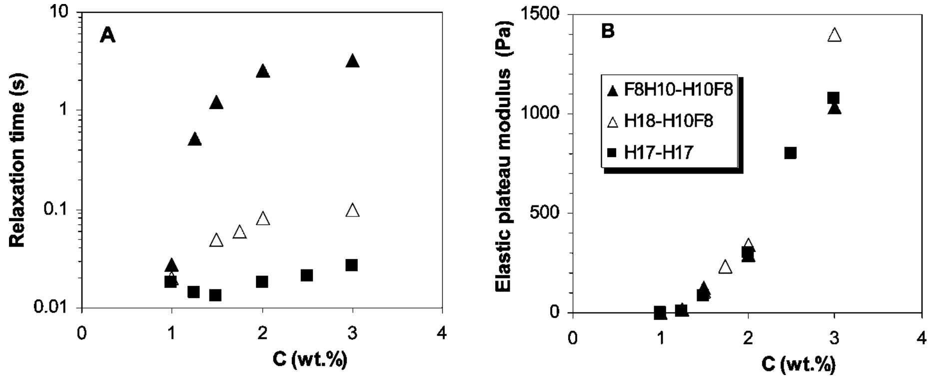

Figure 8. Polymer concentration dependence on the relaxation time τ (A) and the elastic plateau modulus G_0 (B) for aqueous solutions of $F_8H_{10}-H_{10}F_8$ (▲), $H_{18}-H_{10}F_8$ (△), and $H_{17}-H_{17}$ (■) in the presence of SDS (8 mmol L^{-1}) at 25 °C.

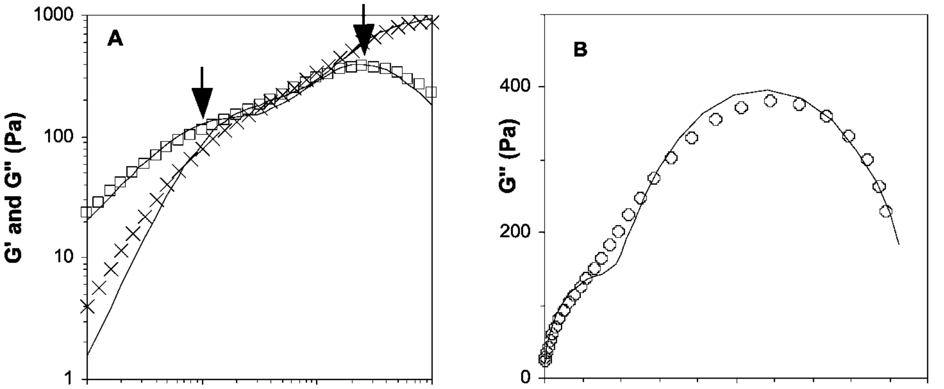

Figure 9. (A) Storage modulus G' (cross) and loss modulus G'' (square) in dynamic frequency experiments. (B) Cole−Cole curve of 3 wt % solutions of 50:50 mixture $H_{17}-H_{17}/F_8H_{10}-H_{10}F_8$, in the presence of SDS (8 mmol/L), at 25 °C. Solid lines show the best fit to a sum of two Maxwell elements.

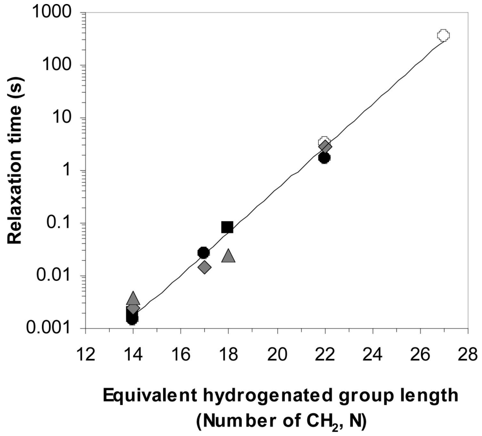

Figure 10. Relaxation time τ vs number N of equivalent CH_2 end group. Data are from our own work (full symbols) and from the literature[6] (open symbols). The values of relaxation times are determined in the physical gel phase (C = 3 wt %) at 25 °C, in presence of surfactant. The different systems reported are symmetric APs in presence of SDS (●) or LiFOS (♦) and asymmetric APs in presence of SDS (■) or LiFOS (▲). Data from the literature (○) concern telechelic HEUR, and the isophorone diurethane spacer equals 4 CH_2. The straight line through the data points corresponds to eq 12.

exponential increase of the relaxation time with the number N of equivalent CH_2. The equation of the straight line

$$\tau(N) = 6\times10^{-9}e^{0.907N} \qquad (12)$$

corresponds to the best fit of experimental data obtained with symmetric and asymmetric APs in presence of surfactant (SDS and LiFOS).

The eq 12 confirms the relationship established by Berret et al.[2] with fluorinated telechelic polymers using the convention 1 CF_2 = 1.5 CH_2. In addition, results reported in Figure 10 demonstrate that (i) the relaxation time is mainly governed by the polymer end group hydrophobicity and to a lesser extent by the interactions stickers/surfactant inside mixed aggregates and that (ii) the behavior of asymmetric APs is determined by the less hydrophobic polymer end-cap. The determination of equivalent length of hydrophobes associated with asymmetric polymers $H_{18}-H_2F_8$ and $H_{18}-H_{10}F_8$ was respectively based on $C_8F_{17}C_2H_4$ (N = 14) and $C_{18}H_{37}$ (N = 18) end groups. Following this assumption, data points corresponding to asymmetric APs/SDS systems are correctly fitted by eq 12. On the contrary, in the presence of fluorinated surfactant, asymmetric APs slightly deviate from the straight line. The compatibility between the hydrophobic end groups and the surfactants influences the relaxation time. The symmetric APs relaxation time is higher when hydrophobic end group and surfactant are similar. So the evolution of asymmetric AP relaxation times gives information on the nature of the relaxing end group. The relaxation time of the polymer $H_{18}-H_2F_8$ increases with the fluorinated surfactant, thus the relaxing end group is the fluorinated one ($C_8F_{17}C_2H_4$). Inversely the $H_{18}-H_{10}F_8$ relaxation time is lower with the LiFOS so the relaxing end group is hydrogenated ($C_{18}H_{37}$). These evolutions confirm that the rheological behavior of asymmetric APs is governed by the less hydrophobic end group.

According to the transient network model the relaxation time is the average lifetime of a link. The lifetime of a bridging chain is in turn related to the kinetics of the end-cap detachment from the aggregate core. The results developed here demonstrate the role of the end group environment, inside the mixed aggregates, on the kinetics.

5. Conclusion

We have synthesized PEO end-capped by hydrophobic hydrogenated and fluorinated groups. These telechelic polymers, denoted asymmetric associative polymers, present a well defined architecture with a complete chain end modification.

In aqueous solution the asymmetric polymers induce phase separation. As a consequence linear rheology study was made in presence of surfactant. The steep increase of the static viscosity observed at polymer concentrations of about 1 wt % is comparable to that observed for symmetric associative polymers. In the semidilute regime, the values of the static viscosity are located between those of symmetric analogues. The asymmetric polymers present a rheological behavior slightly different from symmetric analogues. The transient network formed by these polymers is characterized by an increased elastic plateau modulus G_0 with a higher density of elastically active chains. The bridging tendency is probably favored by the nonequivalent chemical structure of end groups. The asymmetric AP solutions behave as nearly perfect Maxwell fluids with only one relaxation time which is governed by the less hydrophobic chain end. The lifetime of polymer end group into the aggregate core and the kinetics of detachment are influenced by the environment of the mixed aggregate constituted by hydrogenated (SDS) or fluorinated (LiFOS) surfactant. The relaxation time is enhanced when surfactant and hydrophobic group are similar. Relaxation time and viscosity are thermally activated and follow an Arrhenius law.

The asymmetric polymers have a specific behavior which is not equivalent to the mixture of the analogous symmetric polymers.

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