Influence of Fluorinated Segments of Variable Length on the Thickening Properties of a Model HASE Skeleton

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ABSTRACT: Introduction of fluorocarbon segments in an associative thickener copolymer (ethyl acrylate (EA)/methacrylic acid/macromonomer) was achieved by the substitution of EA with either trifluoroethyl acrylate, 2-perfluorobutylethyl acrylate, or 2-perfluorooctylethyl acrylate. The thickening properties were evaluated by rheological flow experiments in aqueous medium as well as in 10 wt % of sodium dodecyl sulfate (SDS) aqueous solution. Whereas in the literature no particular attention is devoted to the impact of the ethylene moieties in hydrophobically modified alkali-soluble emulsion (HASE) skeleton, our study reveals they contribute significantly to the performances when modified by an incompatible fluorocarbon segment. Moreover, the synthesis process has a huge influence by inducing a specific distribution of the fluorinated acrylates in the macromolecule. The amount of substitution is also important and even 20 mol % of EA substituted reveals a great impact on the rheological properties of the copolymer solutions. Whereas an SDS aqueous medium generally destroys almost all the hydrocarbon interactions from the macromonomer, the total replacement of ethyl groups by trifluoroethyl groups with a cosolvent process, leads to emulsions with an equivalent thickening effect than the reference hydrocarbon HASE used. This result is quite encouraging for research work on the synthesis of HASE with increased biocompatibility. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 120: 2685–2692, 2011

Key words: associative thickeners; hydrophobically modified polyelectrolyte; semifluorinated acrylates; fluoropolymer; rheology

INTRODUCTION

Physically associating polymers have been the subject of several studies due to their ability to form networked gels. Their associative strength can often be manipulated to modify and control the properties of the physical gel. Among them, hydrophobically modified alkali-soluble emulsion (HASE)[1] are acrylic associative polymers with side groups capable of engendering strong specific interactions. Their backbone consists in a succession of methacrylic acid (MAA) and ethyl acrylate (EA) randomly or bulky distributed with small amounts of a so-called associative macromonomer (AM). AM generally has an amphiphilic structure and is constituted on one hand by a long hydrophilic chain (usually a polyethoxylated group) directly grafted to the polymeric backbone and on the other hand, by a hydrophobic part (mainly an aliphatic chain) situated at the end of the polar segment as shown in Scheme 1.

These copolymers are anionic and thicken at a pH above 7 with an increase of their hydrodynamic volume. Thus, they become soluble in water and expand through repulsions of carboxylate anions[2] while the hydrophobic groups associate to form aggregates inducing a gel-like network, which enhances the solution viscosity.[3–7] They are generally synthesized by direct emulsion polymerization as this result in a water-based medium, and the resulting polymers can even be integrated easily into continuous manufacturing processes.

Optimization of HASE systems for applications in fields as different as cosmetics, paints and anti-icing fluids requires specific studies to determine the main impact of molecular parameters on the rheological properties. Numerous studies have been done on the effect of the methacrylic acid content in the copolymers,[8] on the length and the structure of the macromonomer,[9,10] and on the medium composition (pH, ionic strength...).[11]

In this work, we would like to report the influence of the introduction of a CF_3 fluorinated segment,
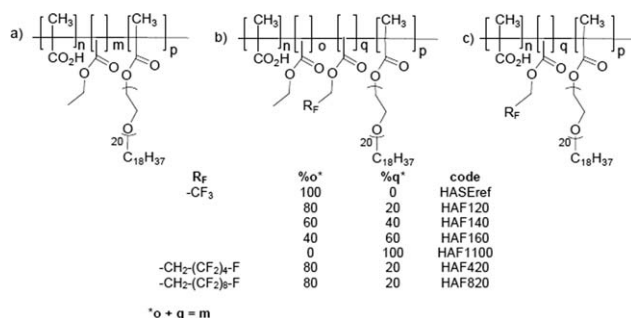
Scheme 1 Basic skeleton of HASE (a); Substitution of a part (b) or the whole EA monomer (c) by a fluorinated acrylate of variable chain length.

indeed such materials might be of great interest because of the very peculiar properties of fluorocarbons such as low surface energies, oleo- and hydrophobic properties,[12,13] high solubilization capacity for gases and more particularly biocompatibility. The fluorination of a simplest model such as hydrophobically modified poly(sodium acrylate) (HMPA) has already been described by Iliopoulos et al.[14] who find that the rheological behavior of a polymer bearing $C_7F_{15}CH_2$ side groups is as associative as a polymer containing the same fraction of $C_{13}H_{27}$ chains. More generally, it is shown that the viscoelasticity of fluorocarbon associative polymer gels is enhanced with respect to that of hydrocarbon analogues.[15,16]

In a HASE model, the system is more complex and no one can predict what will be the contribution of such fluorinated segment on the associative behavior. For this study, EA in the HASE copolymer skeleton was replaced by various amounts of different highly fluorinated monomers and the possible modification of the rheological properties from the corresponding aqueous solutions were evaluated.

In a first part, the substitution of ethylene groups was studied by the introduction of fluorocarbon acrylate monomers of variable length [Scheme 1(b,c)] in a basic HASE skeleton [Scheme 1(a)] using two synthesis processes to study the influence of the number and distribution of the fluorocarbon segments along the polymeric chains. The second part was devoted to rheological studies in the form of flow experiments of aqueous solutions of the copolymers.

MATERIAL AND EXPERIMENTAL METHODS

Materials

Ethyl acrylate, methacrylic acid, sodium dodecyl sulfate (SDS), sodium persulfate, trifluoroethyl acrylate (F1), acetone (>99%), and THF (>99%) were purchased from Sigma-Aldrich. Perfluorobutylethyl acrylate (F4) and perfluorooctylethyl acrylate (F8) were synthesized following a previously described procedure.[17] Stearyl oligooxyethyl methacrylate, the

macromonomer, was obtained from Dow Chemicals France. Water used for the polymerization and the dialysis process was demineralized water (pH 5). The synthesized polymers are coded "HAFxy" where x is the number of fluoromethylene units in the fluorinated monomer (1, 4, or 8) and y is the percentage of EA substituted by a semifluorinated acrylate. The term "cos" can be added to the code in reference to the use of a cosolvent in the synthesis process.

Polymerization in emulsion

Each batch contains: 46 mol % of methacrylic acid, 53 mol % of ethyl acrylate, or/and a fluorinated analog (F1, F4, F8) and 1 mol % of associative macromonomer.

HASEref is the copolymer model; it contains 46 mol % of methacrylic acid (MA), 53 mol % of ethyl acrylate (EA), and 1 mol % of associative macromonomer. The fluorinated monomers used were trifluoroethyl acrylate (F1), 2-perfluorobutylethyl acrylate (F4), and 2-perfluorooctylethyl acrylate (F8). For solubility reasons, only 20 mol % of ethyl acrylate was substituted when F4 and F8 monomers were used. The syntheses were first realized in semicontinuous emulsion process, as this is extensively used for this type of copolymer; then, to optimize the incorporation of the long chain fluorinated acrylates a continuous process with acetone as cosolvent was set up.

Semi continuous emulsion polymerization

Two pre emulsions E1 and E2 (Table I) were prepared independently under vigorous mechanical stirring (1500 rpm) at 5°C. E1 was first placed under inert atmosphere and degassed for 15 min. The bulk was then heated 75°C and when the temperature was stable, E2 was added dropwise over 1 h. The mixture was then heated under an inert atmosphere and with vigorous stirring for a further 5 h until the polymerization was complete. The latex was purified by an extensive dialysis process. The overall composition of the final emulsion is described in Table I.

Continuous process with acetone as cosolvent

The mixture of monomers was added at 0°C to an aqueous solution of SDS and acetone. The

TABLE I
Composition of the Emulsion of the Pre-emulsions E1 and E2 for the Semibatch Process

Products	Total weight (g/100 g)	E1 (wt %)	E2 (wt %)
Monomers	22.6	20	80
SDS	0.375	66	34
Water	76.99	75	25
$Na_2S_2O_8$	0.04	25	75

TABLE II
Composition of the Emulsion for the Synthesis with a Cosolvent

Products	Total weight (g/100 g)
Monomers	22.15
SDS	0.367
Water	76.45
Acetone	1.00
$Na_2S_2O_8$	0.04

composition of the resulting emulsion is summarized in Table II. The system was vigorously shaken (1500 rpm) under nitrogen flux. The initiator was then added and the bulk was heated at 75°C for 5 h.

The latex solution obtained at the end of the reaction was purified by dialysis.

Neutralization of the HASE polymer

Solutions of 1 wt % purified polymer were neutralized with a 10 wt % NaOH aqueous solution up to a pH of 9.5. For all the synthesized copolymers, a transparent and homogenous solution was obtained.

Apparatus

Flow measurements were carried out at 25°C with a Bohlin Gemini rheometer (from Malvern Instruments, France) with a cone-and-plate measuring system having a diameter of 40 mm and a cone angle of 4°. The shear rate range for the steady measurements was from 0.01 to 1000 s^{-1}. Zero shear viscosity was obtained by extrapolation of these curves. Instantaneous viscosity values were obtained with a Brookfield LV-II viscometer (from Brookfield, MA). The molecular weight of the prepared polymers was determined by GPC analysis in THF with an Agilent HP 1100 chromatographic system (from Agilent Technologies, CA) equipped with a PL-GEL Mixed D column using polystyrene standards. The glass transition temperatures were obtained with a Seiko DSC 220C calorimeter (from Seiko Instruments, Japan). The range of temperatures was −40–150°C with a scanning rate of 40°C min^{-1}. The synthesized polymers were characterized by infrared spectroscopy (FT-IR) using a 3100 FTIR microscope (from Perkin–Elmer, France).

RESULTS AND DISCUSSION

Synthesis of the different fluoro-substituted HASE and influence of the emulsion composition on the viscosity

Substitution of progressive amounts of EA by F1 by a semicontinuous procedure

Four different copolymers were synthesized: HAF120 corresponds to 20 mol % substitution of EA by F1,

HAF140 (40 mol % substitution of EA by F1), HAF160 (60 mol % substitution of EA by F1) and HAF1100 (100 mol % substitution of EA by F1). Introduction of the perfluorinated moieties was verified by IR (wide band around 1150 cm^{-1}) for each copolymer. Their conversion yield, molecular weight, and viscosity are summarized in Table III. The main problem encountered is the low level of conversion of the monomers in the emulsion medium: whereas good conversion yields are obtained with the hydrocarbon monomer mixture, when introducing even a slight percent of F1, the yield decreases. With 100 mol % of F1 (HAF1100) in the monomer mixture only 75% conversion yield is obtained against 92% when no fluorocarbon monomer is added (i.e., HASEref).

Table III shows the Brookfield viscosities in water at 14.68 s^{-1} for all the synthesized copolymers.

The measurements were also performed in an aqueous SDS medium as the addition of surfactants to HASE aqueous solutions are well known to induce significant modifications in rheological properties.[18,19] Indeed, in a HASE copolymer, the hydrophobic interaction between the hydrophobic tails of surfactants and the hydrophobic domains of HASE dominates the binding interactions. Moreover, with further increase in surfactant concentration, the network-like cluster can be destroyed leading to a reduction of the solution viscosity. Two types of hydrophobic interactions can be altered by the addition of surfactants: those from the long chain associative macromonomer and those from the ethylene moieties of EA (Scheme 2).[20–23] As hydrocarbon-fluorine interactions are less favored than hydrocarbon hydrophobic ones, the fluorinated copolymer can be expected to be more resistant to the addition of surfactant in the aqueous solution.

In the case of HAF120, HAF140, HAF160, and HAF1100, the viscosities measured (Table III)

TABLE III
Effect of the Introduction of Fluorine on the Instantaneous Viscosity

Sample	Conversion yield (%)	M (g mol^{-1})[a]	H (cPs)[b]	η (cPs)[c]
HASEref	92	600,000	37,000	1600
HAF120	83	400,000	5100	50
HAF140	85	–	2370	60
HAF160	87	–	6800	80
HAF1100	75	340,000	8300	100
HAF420	93	350,000	2920	65
HAF820	67	310,000	7500	80

[a] The molecular mass was obtained with an average polydispersity of 1.5–3.3.
[b] Brookfield instantaneous viscosity of an aqueous neutralised solution of copolymer (1 wt %) at 14.68 s^{-1}.
[c] Brookfield instantaneous viscosity of an aqueous neutralised solution of copolymer (1 wt %) with 10 wt % of SDS at 14.68 s^{-1}.
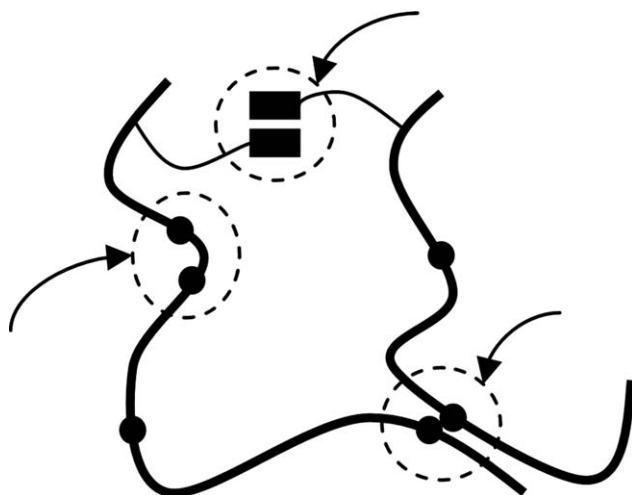
Scheme 2 Different zones of hydrophobic interactions: (●) ethylene moieties, (■) macromonomer hydrophobic endings.

illustrate the dramatic effect of the introduction of the trifluoroethylene unit on the consistency of the corresponding solutions. For a theoretical substitution of 20 wt % of ethyl acrylate, the instantaneous viscosity goes from 37,000 cPs to 5100 cPs in the aqueous medium. The introduction of fluorine appears to disturb the hydrophobic interactions that occurred in the emulsion and it seems that there is no association between the fluorinated moieties. According to the literature,[24] statistical copolymers tend to associate intermolecularly to avoid unfavorable interactions between unlike chains, whereas blocky ones form intramolecular microdomains and provide less consistency in aqueous medium. We certainly are in the second case owing to the small conversion yield. The fluorinated monomer has a poor solubility in the dispersed medium and is probably situated inside the surfactant micelles during the polymerization process. As the initiation phenomenon takes place in the aqueous phase,[25] it is quite evident that a natural segregation occurs between the hydrocarbon and the fluorinated monomers resulting in a blocky macromolecule. As a consequence, when the fluorinated chain length of the acrylate is increased, the destabilization of the medium during the polymerization process induces the creation of shorter polymeric chains, as shown Table III, than for classical emulsion process. The destabilization of the hydrophobic network results in a dramatic decline in the viscosity for the aqueous solution. Moreover, an amplified shear thinning behavior in the surfactant aqueous solution is observed: from 5100 cPs in water to 50 cPs with SDS for HAF120 (respectively, 37,000 cPs to 1600 cPs for HASEref).

In the case of the total substitution (i.e., HAF1100), even with a low conversion yield, we observe a

slight improvement in the viscosity of the aqueous solution as well as for the surfactant aqueous solution. The recovery of consistency is surely due to hydrophobic fluorine interactions as is described in the literature for associative copolymers of a different type.[15] However, only 75% of the total amount of monomers was converted and by enhancing the polymerization yield we can expect to have a better model for rheological properties of the resulting macromolecule in aqueous medium.

Influence of the length of the fluorinated tail: Synthesis and properties of HAF420 and HAF820

To favor interactions between polymeric chains we have introduced longer chain fluorinated acrylates by the same method of synthesis (Scheme 1).

As shown in Table III, when comparing the 20 mol % incorporated emulsions, the best viscosity obtained is with the longer fluorinated chain monomer HAF820 and this is in agreement with results obtained with hydrocarbon hydrophobically-modified polymers.[26] The explanation is probably an easier formation of fluorocarbon microdomains between polymeric chains that reinforce the network in aqueous solution. However, a poor conversion yield occurs for this monomer and only 67% conversion is obtained, even with a substitution of only 20 mol % of EA. The decrease in viscosity compared with the hydrocarbon reference HASEref, is thus not significant for this copolymer and can probably be improved with a better conversion yield. F4 monomer is fairly well incorporated but we do not notice a gain in viscosity of the aqueous solution: 2920 cPs; the introduction of a theoretical amount of 20 mol % of F4 (HAF420 copolymer) does not have the expected effect on the evolution of viscosity in aqueous solution, as it is less effective than F1 in the same proportions (HAF120 copolymer) whereas its incorporation in the copolymer is significantly better than for any other fluorinated acrylate.

Addition of acetone as cosolvent during the polymerization process

The introduction of fluorinated monomers has a major consequence on the stability of the emulsion during the polymerization and an increased phenomenon of coagulation was seen (except for HAF420) when the length and the amount of fluorinated monomers increases, inducing lower conversion yields (Table III). To stabilize the system, acetone was used as co solvent. This solvent is well known to solubilize fluorinated monomers in emulsions.[27,28] To optimize the polymerization process with this cosolvent, the coagulation level versus several amount of acetone were recorded (Fig. 1).
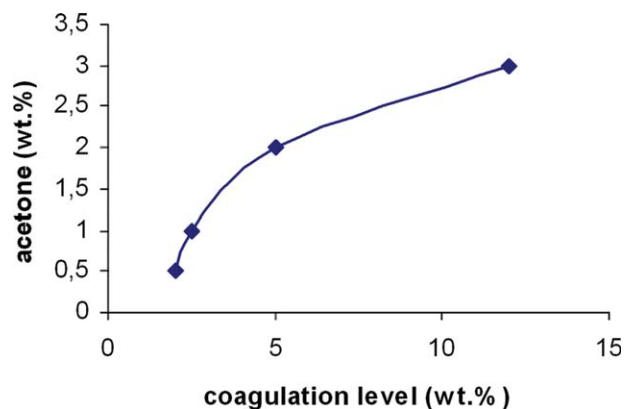
Figure 1 Optimization of the emulsion stability with the addition of different amounts of acetone and correlation with the coagulation level. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

The best compromise is 1% of acetone, which corresponds to a minimum of organic solvent to maintain an environmental safe process, and gives minimum coagulation of the resulting copolymer. This is in agreement with Candau and Selb[29] study that demonstrated even a small amount of organic solvent is sufficient to incorporate fluorinated monomers in the emulsion polymerization. The use of the cosolvent has two potential consequences: firstly, providing of a more fluorinated copolymer and the secondly, giving rise to a different distribution of the fluorinated monomers along the polymeric chain. The recorded conversion yields are now 95% for HAF120cos (against 83% for HAF120), 92% for HAF1100cos (against 75% for HAF1100) and 90% for HAF820cos (against 67% for HAF820).

Table IV summarizes the physicochemical parameters of the different copolymers.

The first main difference between the two synthesis processes is the number and the values of glass transition temperatures of the copolymers: whereas two or three T_g are noticeable for the semicontinuous process, only one is measured when a cosolvent is added. This fact emphasizes the idea of a less segregated skeleton for the copolymers obtained with the cosolvent procedure. If we consider the zero shear viscosity (Table IV) in water, the model HASEref shows the highest value (353 Pa s^{-1}) induced by the strong hydrophobic interactions between the ethylene moieties and the hydrophobic part of the macromonomer. The HAF1100cos copolymer presents an identical zero shear viscosity than the reference HASEref (352 against 353 Pa s^{-1}) and corresponds to the better result compared with all the other copolymers studied. The rather good performance of HAF820 has not been improved by the cosolvent process, whereas better results were expected with an improvement of its introduction

into the HAF820cos copolymer skeleton. In an aqueous solution of surfactant, good results are observed for HAF120cos and HAF1100cos with a zero shear viscosity of 1.0 and 2.2, respectively, against 1.9 for the reference copolymer.

Flow experiments

Figures 2 and 3 correspond to flow experiments in a range of shear rates of (0.01–1000 s^{-1}), in pure aqueous and aqueous surfactant solutions of the copolymers synthesized previously.

The curve obtained for HASEref (+) is represented in each graph for comparison; For this model emulsion, the characteristic behavior of associative polymers is observed, i.e., the occurrence of a Newtonian plateau at low shear rates, followed by a sharp viscosity drop.

Figure 2(a) allows to notice the influence of the replacement of EA by different amounts of F1: the introduction of 20 mol % of trifluoroethylacrylate decreases significantly the zero-shear viscosity and changes the rheological profile for the lower values of shear rate. The HAF1100 copolymer exhibit a noticeable behavior at high shear rates with a regain in viscosity compared with the other copolymers. This reveals that the semicontinuous emulsion process affects the rheological outcomes by favoring blocky fluorinated copolymer as described in the literature.[23] For low shear rate values, the hydrodynamic volume of the chains is increased by the steric hindrance of intramolecular interactions of the blocky fluorinated groups, generating the aqueous solution consistency. By increasing shear rate, tangled polymeric chains are developed and the intramolecular fluorinated interactions modify to give intermolecular interactions, increasing the strength of the physical gel.[30–35] Although rarely observed in common polymer solutions, shear thickening effects have been observed in complex fluids including dense suspensions, wormlike micelles, and associating polymers

TABLE IV
Zero-Shear Viscosity and T_g Values of all the Copolymers Tested in Flowing Experiments

Sample	η_0 (Pa s^{-1}) (water)	η_0 (Pa s^{-1}) (SDS 10 wt %)	T_g (°C)
HASEref	353	1.9	60/62/79
HAF120	8.55	0.06	46/63
HAF1100	13.9	0.07	53/54
HAF420	1.7	–[a]	–
HAF820	47.5	0.07	59/66
HAF120cos	177	1.0	61
HAF1100cos	352	2.2	57
HAF820cos	35	–[a]	59

[a] Viscosity of the aqueous surfactant solution was not measurable.
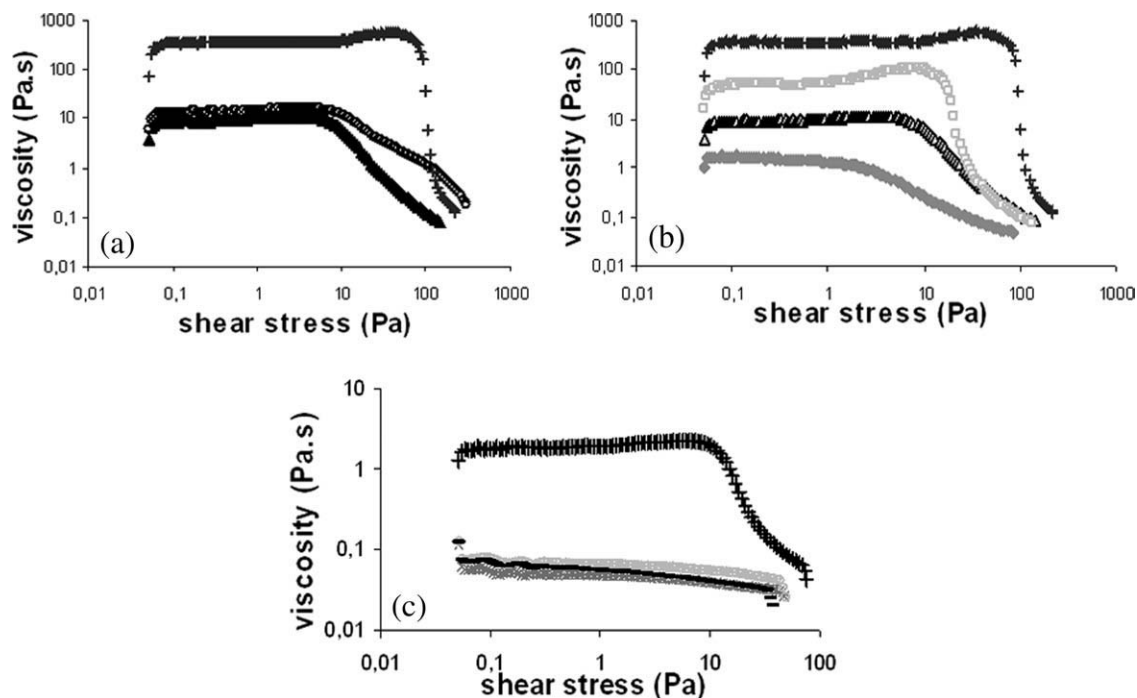
Figure 2 Flow curves for (a) HASEref (+), HAF120 (▲), and HAF1100 (○) in water. (b) HASEref (+), HAF120 (△), HAF420 (◆), and HAF820 (□) in water. (c) HASEref (+), HAF120 (−), HAF420 (×), HAF1100 (○) in a 10 wt % SDS aq. sol.

solutions. The shear thickening seems to be attributed to the shear-induced structural changes throughout the system. Three theories are proposed: shear induced crosslinking, shear induced non-Gaussian chain stretching and network organization.[36]

Figure 2(b) allows to estimate the influence of the fluorinated chain length: introducing 20 mol % of a C_4F_9 tail acrylate disturbs the system as the absolute viscosity measured is very low on the entire range of the flow experiment. Increasing the fluorinated chain length enhances the performances: for the HAF820 copolymer a thickening behavior appeared and it shows a characteristic behavior of associative polymers close to HASEref. This could mean that the longer fluorinated segments allow the polymeric chains to interact through hydrophobic and mixed hydrophobic-fluorinated interactions. HAF120 has an intermediate

behavior; it seems like the trifluoroethyl groups less disturb the system than the perfluorobutyl chains. The best performances of the HAF820 can be attributed to the self assembly properties of the long perfluorinated chains[37] induced by the "fluorophobic effect"[38] [i.e., the strong segregating tendency of fluorocarbon chains (R_f) with hydrocarbons (R_h)].[39]

When testing the rheological properties of an aqueous solution of surfactant containing 2 wt % of polymer, no residual consistency is observed whatever the shear rate applied [Fig. 2(c)]. Apparently, once the intermolecular interactions due to the hydrophobic macromonomer disappear, replaced by surfactant–macromonomer interactions, the network is totally destroyed. A general decrease of viscosity is observed but whereas the hydrocarbon polymer maintains a Newtonian plateau for the lower values
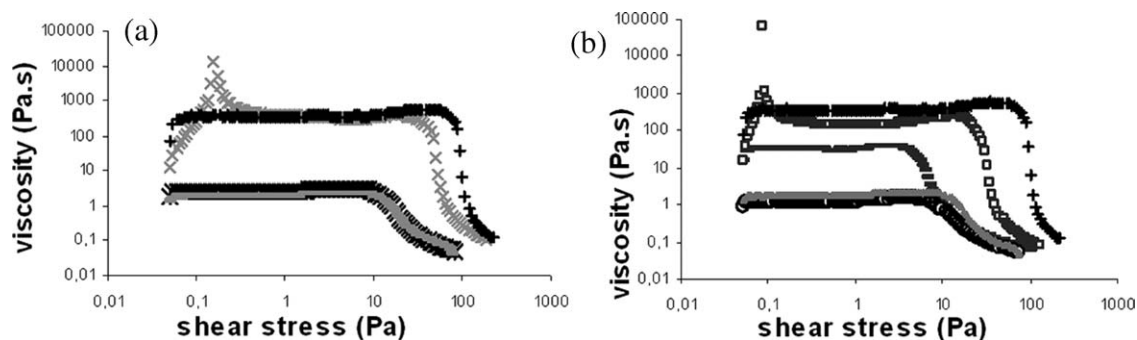
Figure 3 Flow curves for (a) HASEref (+), HAF1100cos (×) in water and HASEref (−), HAF1100cos (×) in a 10 wt % SDS aq. sol. (b) HASEref (+); HAF120cos (□); HAF820cos (−) in water and HAF120cos (○); HASEref (▲) in a 10 wt % SDS aq. sol.

of shear rate, when fluorinated monomers are introduced a Newtonian-like behavior appears for the whole shear rate range.

Figure 3 represents the curves obtained for the copolymer synthesized with the cosolvent process.

Figure 3(a) shows the behavior of the totally substituted HASE with a short *F*-alkyl tail (i.e., CF_3): HAF1100cos. It presents a general behavior very close to HASEref, attesting to a denser network than for the HAF1100 obtained previously. The strength of the network is certainly due to a more regular distribution of each monomer as attested by the variation in the number of glass transition temperatures.

The cosolvent process also improves the properties obtained when only 20 mol % of trifluoroethyl are introduced: HAF120cos presents a characteristic behavior of associative polymers as seen in Figure 3(b). On the other hand, for the longer *F*-alkyl tail containing copolymers HAF820cos, it does not have the expected behavior and its general viscosity profile is close to the profile observed for the previously synthesized HAF820 on the whole range of shear rates. De Crevoisier et al.[27] noted that in emulsion polymerization, even with a large amount of acetone and with a polar comonomer (hydroxymethacrylate), the copolymer obtained with a mixture of hydrocarbon monomers and the F8 presented a blocky structure due to a segregation of the fluorinated monomer.

CONCLUSIONS

A series of fluorinated HASE copolymers by replacing CH_3 of EA by CF_3 or by a long semifluorinated tail, were synthesized and successfully solubilized in an aqueous medium after a neutralization step. In general, the chemical modification of EA generates a dramatic effect: no gain in viscosity for these aqueous solutions was observed compared with the hydrocarbon analog. The amount as well as the distribution (induced by the synthesis process) of modified EA along the polymeric chains have a major influence on the rheological behavior of the copolymer solutions. Each time, when a blocky system is identified, viscosity dramatically decreases. The fact that no difference in rheological behavior was noted between HASEref and HAF1100cos, obtained with the total substitution of EA by its analogous trifluoroethyl acrylate with an experimental process involving the use of acetone as a co solvent, is due to the complete substitution of the hydrocarbon interactions by fluorocarbon ones. This remark emphasizes the need for a controlled amount and distribution of these ethylene or trifluoro ethyl interactions along the copolymer skeleton to obtain the desired thickening properties of the HASE. Although a consequent increase in consistency was revealed in the literature for the introduction of fluorocarbon

segments in thickeners like HEUR (hydrophobic ethoxylated urethane thickeners) or telechelic copolymers,[14,27,28,40,41] in the HASE skeleton, the introduction of fluorocarbon moieties instead of the EA monomers allowed us to illustrate their nonappearance on the copolymers behavior in aqueous and complex media.

By obtaining a fairly similar thickener with fluorocarbon moieties (HAF1100cos) the way is opened for application fields of HASE having improved compatibility with fluorinated molecules in innovative formulations and which will be possible without any change in consistency compared with classical polymers.

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