

## Amphiphilic copolymers based on PEG-acrylate as surface active water viscosifiers: Towards new potential systems for enhanced oil recovery

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**ABSTRACT:** With the purpose of investigating new potential candidates for enhanced oil recovery (EOR), amphiphilic copolymers based on Poly(ethylene glycol) methyl ether acrylate (PEGA) have been prepared by Atom Transfer Radical Polymerization (ATRP). A P(PEGA) homopolymer, a block copolymer with styrene PS-*b*-P(PEGA), and an analogous terpolymer including also sodium methacrylate (MANa) in the poly(PEGA) (PPEGA) block, PS-*b*-P(PEGA-*co*-MANa) have been prepared and characterized. Viscosity and surface activity of solutions of the prepared polymers in pure and salty water have been measured and the results have been interpreted in terms of the chemical structures of the systems. A clear influence of the presence of the charged MANa moieties has been observed in both rheological and interfacial properties. The PS-*b*-P(PEGA-*co*-MANa) terpolymer, being an effective surface active viscosifying agent, is a good candidate as polymeric surfactant for applications in enhanced oil recovery and related. © 2016 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2016**, *133*, 44100.

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### INTRODUCTION

Amphiphilic polymers has been often proposed as potential systems for chemical enhanced oil recovery (EOR).<sup>1–12</sup> Polymer flooding is a common EOR technique, in which solutions of a high molecular weight water soluble polymer is pumped into the reservoir. The purpose of the polymer is to increase the viscosity of the water phase to match as much as possible the one of the oil-in-place, to obtain a favorable mobility and minimize channeling effects, improving sweep, and displacement efficiencies.<sup>13,14</sup> Surfactants can be also used, alone or in combination with the polymers, to decrease the interfacial tension between water and oil and improve the displacement. The balance between viscous and capillary (or interfacial) forces, very important in a EOR process, is generally quantified by a dimensionless parameter, the capillary number ( $Ca$ ). When the oil displacement process is modeled as a droplet of oil being squeezed through a pore throat, the capillary number ( $Ca$ ) can be expressed as:

$$Ca = \frac{v \cdot \eta_c}{\gamma} \quad (1)$$

where  $\eta_c$  is the viscosity of the continuous phase and  $v$  is the fluid velocity, according to Darcy's law. The displaceable oil increases abruptly above a certain critical value of capillary

number, thus in an EOR process the goal is to increase  $Ca$  above this value. From eq. (1), it can be seen that an increase of viscosity and a decrease on interfacial tension should both have a positive effect on oil recovery. This concept is at the basis of surfactant-polymer flooding (SP) and alkaline-surfactant-polymer flooding (ASP), where the polymer act as the viscosifier and the surfactant decreases the interfacial tension. The role of the alkali, when used, is the same as the surfactant: it neutralizes the organic acids present in the oil, forming surfactants *in situ*.<sup>13,14</sup> Typically, SP and ASP processes aim at increasing the  $Ca$  of 2–3 order of magnitude, which translates in interfacial tension values of 0.1–0.01 mN/m.<sup>15</sup>

The main purpose of using polymeric surfactants for EOR applications is to combine the effects of polymers and surfactants in only one component.<sup>12</sup> This approach present potentially the advantage of avoiding unwanted interactions between the different chemicals, chromatographic separation in the porous system, loss of the surfactant by solubilization in the oil or selective adsorption on the rocks.<sup>14</sup>

Actually, many water-soluble polymers containing hydrophobic substitution have been studied and even patented as systems for EOR. Even though the hydrophobic interactions have been introduced with the objective of modifying the solution

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rheology,<sup>16,17</sup> they can also in principle alter the surface behavior. Unfortunately, the surface activity or the emulsification properties of such polymers have been seldom investigated, thus their role in the oil recovery process remains mostly theoretical.

Polymeric surfactants based on hydrophobically modified polyacrylamides (HMPAM) are a logical choice, since they are actually already employed for the same purpose as solution thickeners. Copolymers of acrylamide with 1–6 wt % content of various hydrophobic monomers have been evaluated as polymeric surfactants for EOR. The polymers were prepared by micellar free-radical copolymerization of acrylamide with, respectively, styrene,<sup>6</sup> *N*-Phenethylacrylamide,<sup>18</sup> *N*-Phenylacrylamide,<sup>19</sup> and *N*-benzylacrylamide.<sup>20</sup> All systems proved to be good solution thickeners and showed good surface and interface activities, both in water and in brine, rendering them promising for the intended application. The polymers' structures, however, are not very clearly defined. Since they are prepared by micellar copolymerization, the hydrophobic monomer is distributed in a "multiblocky" way but no information about the block lengths and the overall polymer molecular weight was provided. One important disadvantage in the use of polyacrylamides for EOR is the need to use polymers characterized by very high molecular weights (several millions of Daltons) to achieve sufficiently high viscosities. This increases the extent of unwanted phenomena such as polymer precipitation, shear and thermal degradation, rock adsorption, and pores plugging. The required viscosity values depend strongly on the reservoir characteristics and can vary from 6–10 mPa s for light oils to more than 150 mPa s for heavy oils. Typical ASP formulations include 0.1–0.2 wt % of high molecular weight polyacrylamides.<sup>21</sup>

Other few polymers have been proposed for EOR, prepared, and evaluated from the point of view of surface activity and viscosity, such as polyesters<sup>7</sup> or alkylated polysaccharides.<sup>8</sup> Incorporation of Poly(ethylene glycol) acrylate (PEGA) in the composition of polymeric surfactants for EOR has been recently proposed.<sup>22</sup>

The use of PEGA in the preparations of surface active polymers has recently experienced a great interest.<sup>23–28</sup> These systems are water soluble, salt tolerant and in some cases, they can be thermo-responsive. Taking advantage of controlled radical polymerization methods such as ATRP, several homo- and copolymers of PEGA with well-defined structures have been prepared and characterized in the last 15 years.<sup>23–35</sup> This can be seen as an alternative way to include poly(ethylene glycol) (PEG) moieties in a polymer, avoiding the harsh conditions required by anionic polymerizations and gaining more control on the resulting structure in terms of architecture and molecular weight distribution.

Block polyelectrolytes like Polystyrene-*b*-Poly(methacrylic acid) (PS-*b*-PMAA) or better in their sodium salt form, PS-*b*-PMANa, are known to be efficient water viscosifiers at relatively low molecular weights, due to association into stable micellar aggregates.<sup>36,37</sup> Unfortunately, due to their polyelectrolytic nature, their thickening properties decrease sharply with increasing salinity, which is obviously not desirable for EOR.<sup>36</sup> Moreover, block polyelectrolytes of this kind are known to be poorly or non-surface active.<sup>12</sup>

With the aim of exploring new candidates for EOR, polymeric structures based on PS-*b*-PMAA amphiphilic copolymers, incorporating PEGA have been designed, prepared, and evaluated from the point of view of surface activity and viscosity in water and saline solution.

## EXPERIMENTAL

### Materials

*Tert*-butylmethacrylate (*t*BMA, Aldrich, 98%) was vacuum-distilled over CaH<sub>2</sub> and kept under nitrogen before use. Poly(ethylene glycol) methyl ether acrylate (PEGA, Sigma-Aldrich, Steinheim, Germany,  $M_n = 480$  g/mol) was filtered over basic Alumina to remove the radical inhibitor just before use.

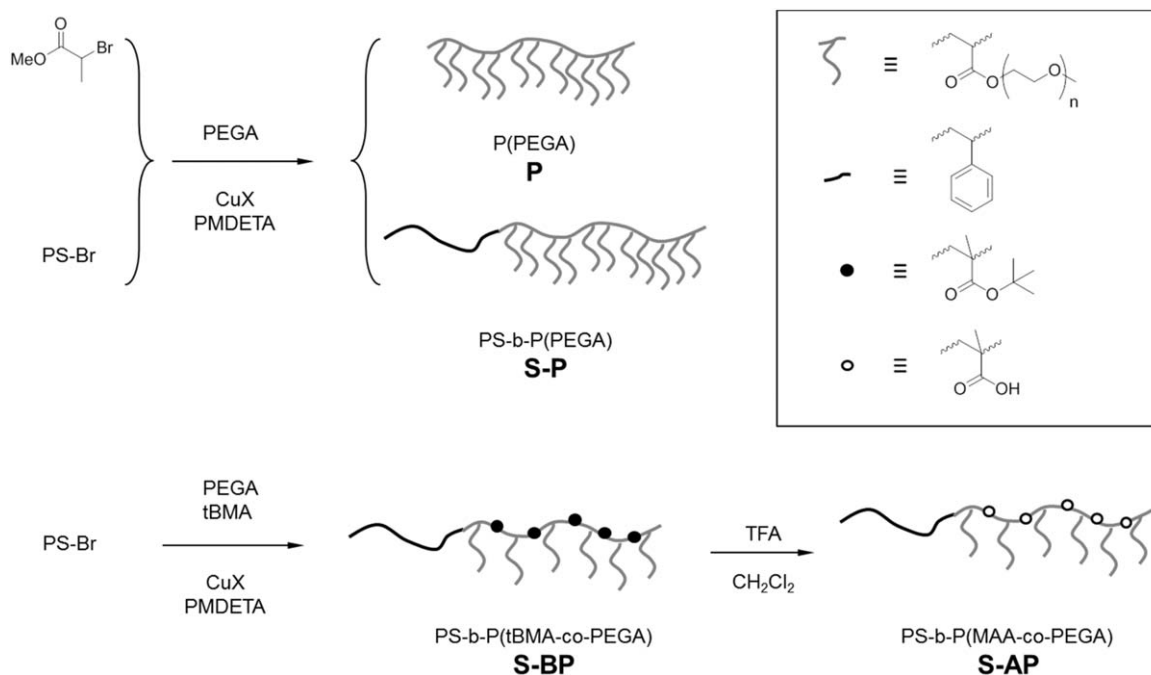
CuCl (Sigma-Aldrich, Steinheim, Germany,  $\geq 99\%$ ) and CuBr (Sigma-Aldrich, Steinheim, Germany,  $\geq 98\%$ ) were stirred in glacial acetic acid for at least 5 h then filtered, washed with acetic acid, ethanol, and ethyl acetate, and dried under vacuum before use. Anisole (Sigma-Aldrich, Steinheim, Germany, anhydrous, 99.7%) was deoxygenated by bubbling nitrogen for at least 30 min before use. tetrahydrofuran (THF) (Acros, Geel, Belgium,  $\geq 99.5\%$ ), trifluoroacetic acid (TFA, 99%, Sigma-Aldrich, Steinheim, Germany), 1-methyl-2-bromopropionate (MBP, Aldrich, 98%), and pentamethyldiethylenetriamine (PMDETA, Aldrich, 99%) were used as received, without further purifications.

### Synthesis

The synthesis of the PS-Br macroinitiator ( $M_n = 4,325$  Da, polydispersity index (PDI) = 1.26) has been previously reported.<sup>36,37</sup>

**General Procedure for the Synthesis of Polymers.** The initiator, (4.6  $\mu$ L of MBP = 0.04 mmol or 0.25 g of PS-Br = 0.06 mmol), the solvent (10 mL anisole), the copper catalyst (2 equivalents with respect to initiator), and the acrylic monomers (PEGA and *t*BMA, in the proportion indicated in the Results and Discussion section) were introduced under nitrogen in a 250 mL round-bottomed flask equipped with magnetic stirring bar and reflux condenser, previously purged with nitrogen. After complete dissolution of the initiator (in case of PS-Br complete dissolution takes few minutes), the flask was put in an oil bath at the chosen temperature and PMDETA (2 equivalents with respect to initiator) was added under nitrogen. After a given interval of time, the reaction was stopped by cooling down, introducing air and diluting with around 50 mL of THF. The THF solution was filtered through a short column of alumina to remove the copper catalyst, then concentrated at the rotavapor, diluted with water (to around 100 mL), and either filtered or dialyzed against milliQ water to remove the excess monomer and solvents, depending on the polymer solubility (see the Results and Discussion section for more details). After filtration or dialysis (performed changing the outer water at least two times every 6–8 h), the solution was dried in the oven at 70 °C overnight to afford the polymers as jelly solids. The polymers were characterized by Gel Permeation Chromatography (GPC) in THF and proton nuclear magnetic resonance (<sup>1</sup>H-NMR) in CDCl<sub>3</sub>.

**Hydrolysis.** The *t*BMA containing polymer was further hydrolyzed as follows: the polymer (around 2.5 g) was dissolved in 30 mL CH<sub>2</sub>Cl<sub>2</sub> and 2 mL TFA were added under nitrogen. The solution was stirred overnight at room temperature. The



**Scheme 1.** Synthesis and structures of the polymers studied in this work.

solution was then concentrated at rotavapor. The sodium salt was prepared by adding an excess of saturated NaHCO<sub>3</sub> solution to the polymer and stirring until complete dissolution. The excess base was removed by dialysis and then the solution was dried in the oven at 70 °C overnight.

#### Characterization

**NMR Spectra.** <sup>1</sup>H-NMR spectra were recorded on a Varian Mercury Plus 400 MHz spectrometer.

**GPC Measurements.** GPC measurements were performed with a HP1100 from Hewlett Packard, equipped with three 300 × 7.5 mm PLgel 3 μm MIXED-E columns in series. Detection was made with a GBC LC 1240 IR detector. The samples were prepared by dissolving the isolated polymers in THF at 10 mg/mL concentrations and using toluene as internal standard. The samples were eluted with THF at a flow rate of 1 mL/min, at a pressure of 140 bar. Molecular weights and PDI were determined using the software PSS WinGPC Unity from Polymer Standard Service. Polystyrene standards ( $M_n = 1,180, 2,360, 4,490, 9,920, 19,720, 46,500, 96,000, \text{ and } 188,700$  Da) were used for calibration.

**Rheology Experiments.** Shear viscosity measurements were performed with a Haake Mars III rotational rheometer at 20 °C, using 2 mL of solution. A trap for the solvent was used to avoid water evaporation during the measurements. Each experiment was performed at least twice for every solution.

**Surface Tension.** Surface tension was measured with an OCA 15EC tensiometer from Dataphysics, using the pendant drop method.

## RESULTS AND DISCUSSION

### Synthesis and Characterization

The synthesis of the polymers was conducted in anisole at 90 °C, based on a procedure reported for PS-*b*-PtBMA block

copolymers.<sup>36,37</sup> The structures of the prepared polymers are shown in Scheme 1 and the results are summarized in Table I.

The obtained polymers present a narrow molecular weight distribution. However, conversions in the used conditions are not very high and S-BP shows a higher incorporation of tBMA, since a 0.45 monomer ratio is obtained starting with a feeding ratio of 1 (last entry of Table I).

The molar ratio between the incorporated monomers was determined by integration of characteristic NMR peaks (Figure 1). The aromatic protons of the polystyrene are in the region between 6.5 and 7 ppm, the methylene protons of the PEG moiety appear in the 3.5–4.5 ppm region of the spectrum, while all the aliphatic protons are included between 1.0 and 2.5 ppm. The sharp signal of the tBu group is easily recognizable at around 1.5 ppm [Figure 1(b)]. It disappears after hydrolysis [Figure 1(c)].

The molecular weights determined by GPC (traces in Figure 2) have to be considered as indicative values, since the calibration was performed with linear Polystyrene (PS) standards. The  $M_n$  measured by GPC are probably underestimated, as it usually happens for graft polymers of the same kind.<sup>31</sup> This is confirmed for the diblock copolymer SP. If the integration of NMR peaks is used to calculate the PEGA/styrene ratio and the GPC value of  $M_n$  for the PS block is accepted, the resulting molecular weight is approximately 38,000 Da. The molecular weight of S-AP has been calculated from the composition of S-BP in Table I, considering complete hydrolysis of the tBuMA units to sodium methacrylate (after neutralization of the carboxylate groups as sodium salt). The obtained value of  $M_n$  is 37,530 Da, which is used for subsequent calculations.

The homopolymer of PEGA can be directly dissolved in water. The block copolymer S-P is water soluble, however, to obtain stable solutions, the polymer has to be first dissolved in a

**Table I.** ATRP Synthesis of PEGA Containing Copolymers

Sample	M1/M2/C/L/I <sup>a</sup>	T (h)	M1/M2 <sup>b</sup>	GPC $M_n$ (PDI)	S units	PEGA units	tBMA units
P	500/-/2/2/1	16	—	24,400 (1.2)	0	51	0
S-P	1,000/-/2/2/1	9	—	23,100 (1.2)	41	39	0
S-BP	500/500/2/2/1	6	0.45	41,270 (1.1)	41	46	103

<sup>a</sup>Molar ratios. M1, PEGA; M2, tBMA; C, CuCl; L, PMDETA; I, PS macroinitiator.

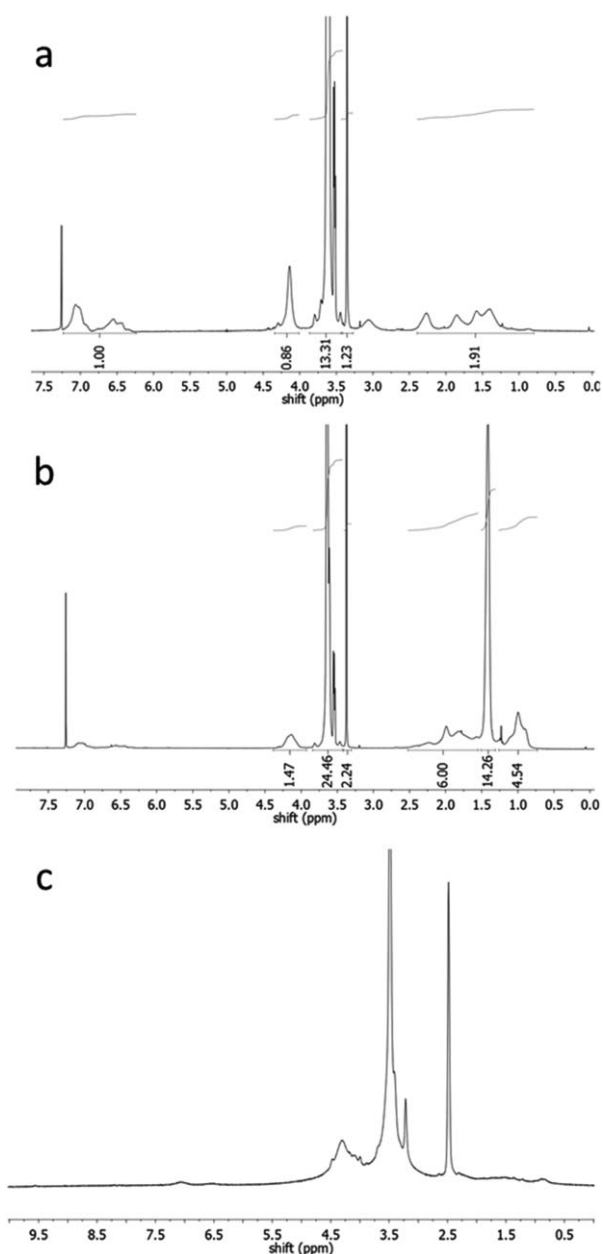
<sup>b</sup>Determined by NMR.

solvent for both blocks and then transferred to pure water.<sup>30,31,33,34</sup> In our case, clear and colorless S-P solutions were obtained in a 1:1 mixture of water with acetone. The

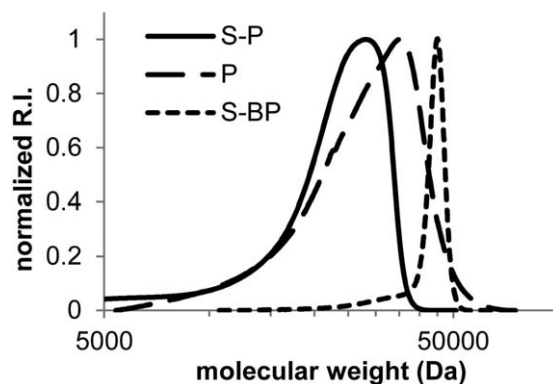
acetone was then almost completely evaporated at the rotavapor. To make sure of the complete removal of acetone, the resulting solution was dialyzed against milliQ water. After dialysis, the volume was adjusted with water to the initial amount. A 5 wt % solution has been prepared this way and used as a stock solution to be diluted to the desired concentrations for the measurements. The stock solution is turbid but no precipitate is observed after two weeks at room temperature. S-BP is insoluble in water. After hydrolysis with TFA in CH<sub>2</sub>Cl<sub>2</sub>, the resulting sticky gum was dissolved in an excess aqueous NaHCO<sub>3</sub> and then dialyzed against milliQ water. The conditions for neutralization of the polymer are very important, because the polymer resulted sensitive to degradation in strongly basic conditions. This is discussed more in detail in a following section. The obtained solution was then dried in the oven (70 °C overnight). The product, S-AP, is completely soluble in water. The disappearance of the tBu peak in the <sup>1</sup>H-NMR confirmed the essentially complete hydrolysis (Figure 1). Again, the solution is turbid but stable for a period of over one month.

#### Surface Activity

The surface tension as a function of concentration in water was measured for the PEGA monomer, the homopolymer P, and the block copolymers S-P and S-AP using the pendant drop method (Figure 3). The measured values are moderate, in line with what usually observed for polymeric surfactants.<sup>12</sup> For EOR applications, these values are usually not considered low enough to have a significant impact on the capillary number and thus on the overall process, but some experiments show that this might not be always the case and non-ultralow values of interfacial tension could still be beneficial.<sup>38</sup>

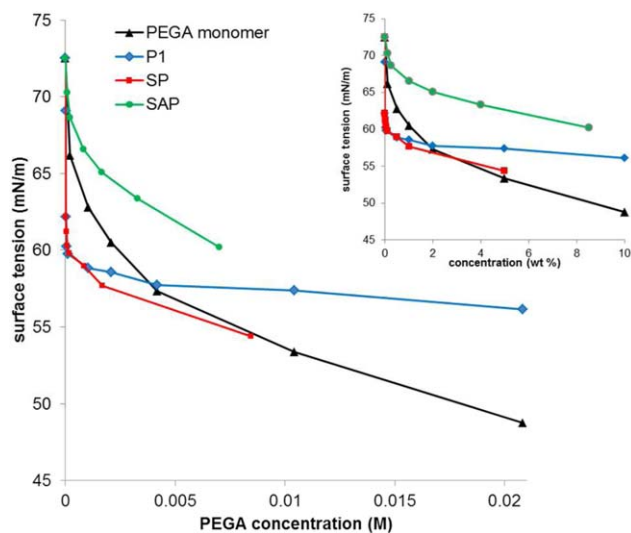


**Figure 1.** <sup>1</sup>H-NMR spectra of: (a) S-P in CDCl<sub>3</sub>; (b) S-BP in CDCl<sub>3</sub>; (c) S-AP in d<sub>6</sub>-DMSO.



**Figure 2.** GPC traces of P1, S-P, and S-BP in THF.

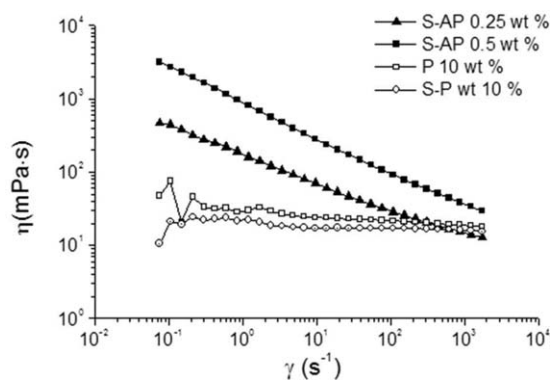




**Figure 3.** Surface tension versus PEGA concentration curves of PEGA monomer, P, S-P, and S-AP. In the insert, the surface tension is plotted against wt % of polymer. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

To have a more meaningful comparison between the prepared systems, the surface tensions as a function of the PEGA monomer content will be considered.

It is possible to observe that the polymer structure influences the surface behavior significantly. First of all, it is very interesting to compare the curve of the PEGA monomer with the one of its homopolymer. At the same amount of PEGA units, the polymer shows a much faster decrease in surface tension, resulting in a sensibly lower apparent Critical Micelle Concentration (CMC). At high concentrations, the monomer reaches a lower



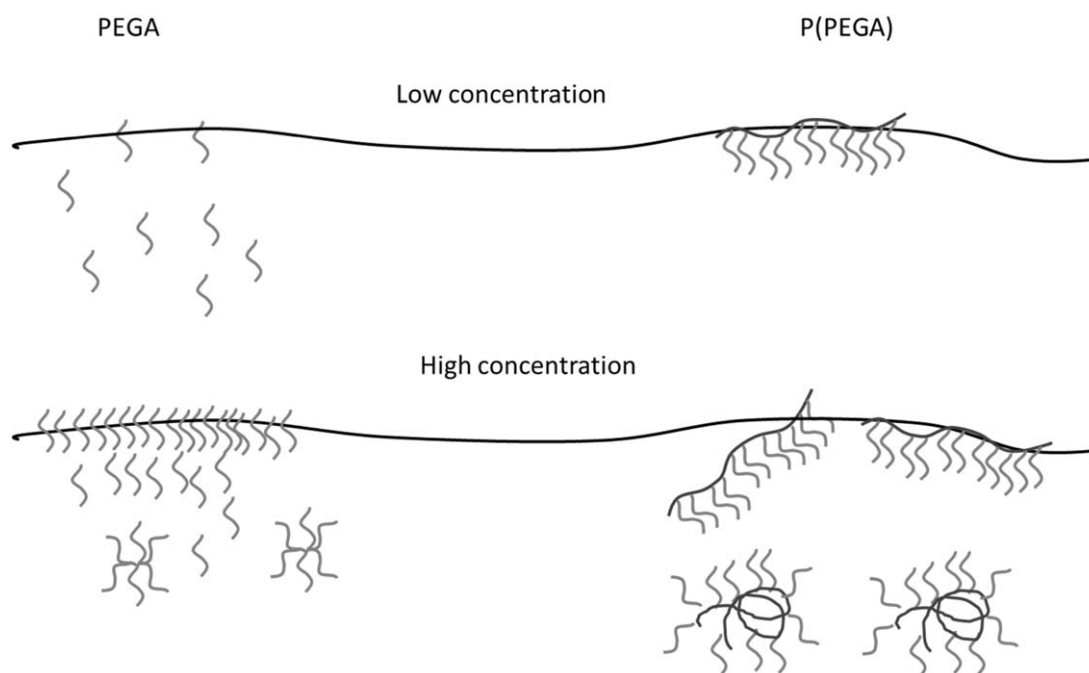
**Figure 4.** Shear viscosity of the synthesized polymers.

absolute value of surface tension. It can be speculated that the polymer has a higher attitude to migrate towards the interface (suggesting that it is more hydrophobic than the monomer), but a surface saturation is reached earlier, possibly because of steric hindrance and reduced mobility of the polymer with respect to the monomer (Scheme 2).

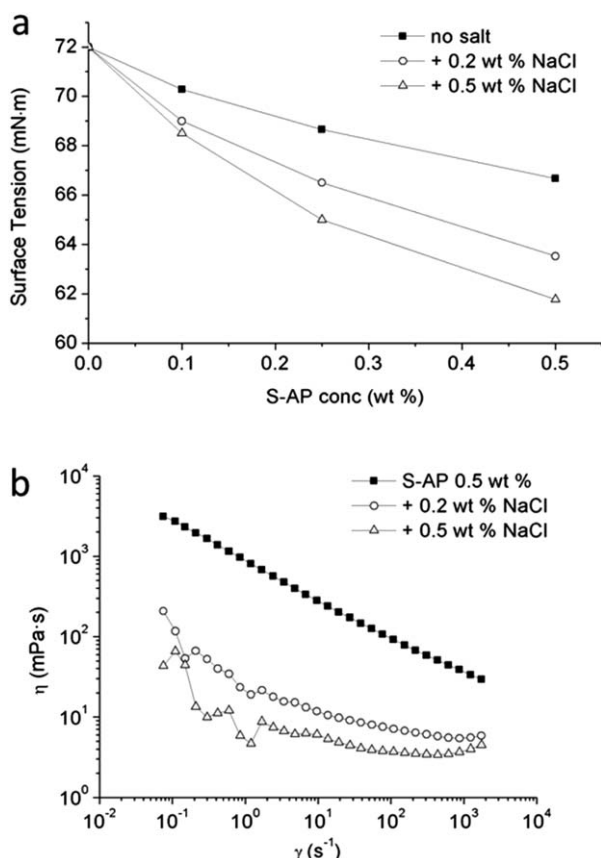
The presence of a PS block in the structure does not affect sensibly the CMC and the behavior at low concentration, but at higher concentrations, the surface tension reaches lower values for the S-P block copolymer. The S-AP terpolymer is the less surface active of the series. In this latter case, the presence of charges in the hydrophilic block might inhibit the migration of the polymer at the interface, analogously to what has been proposed to explain the non-surface activity of other block polyelectrolytes.<sup>39,40</sup>

#### Shear Viscosity

The shear viscosity plays an important role for many applications of water-soluble polymers, and in particular for EOR. As



**Scheme 2.** Proposed explanation for the different surface behavior of PEGA and P(PEGA).



**Figure 5.** Surface tension (a) and shear viscosity (b) of S-AP 0.5 wt % solution in presence of NaCl.

already mentioned in the introduction, the viscosity of the displacing fluid should be close to the one of the resident oil (that is several order of magnitudes higher than that of water). Among the different kind of viscosities, the shear viscosity is the more relevant in this respect, since the displacing fluid experience different shear during the whole process, namely high shear near the injection point and lower shear inside the well. Thus, a shear thinning behavior is preferable.

The shear viscosity of the prepared polymers in water solution has been measured in a cone-plate rheometer. It is evidenced

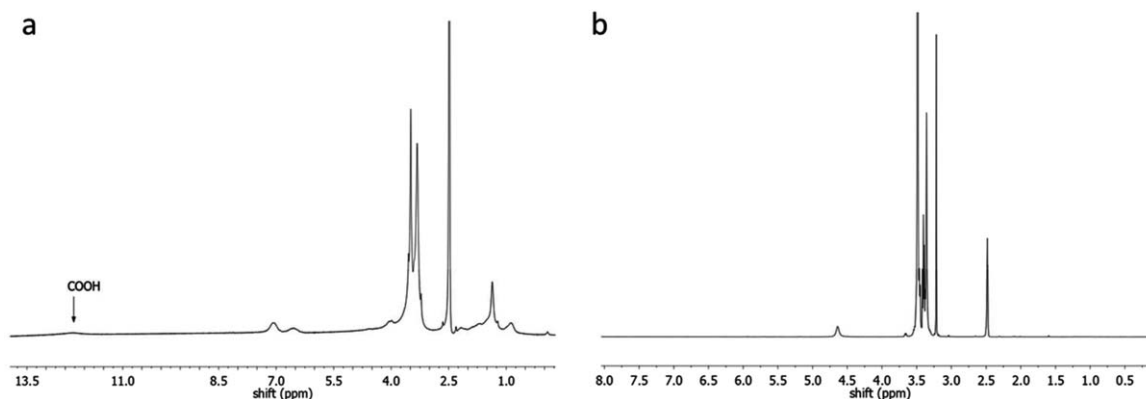
that P and S-P show a viscosity of approximately 10 mPa s with negligible shear thinning at a concentration of 10 wt %, while S-AP is a much more effective viscosifier already at 1/40 of the concentration of the other polymers (0.25 wt %). It also shows a significant shear thinning (Figure 4). Considering the structure of the polymers, it can be concluded that the presence of charges along the polymer backbone has a dramatic effect on the viscosifying properties. This is in line with the known literature about block polyelectrolytes.<sup>41,42</sup> The viscosity values obtained for the tested S-AP solutions are comparable to those of the high molecular weight polymers normally employed in EOR. However, the water salinity plays a very important role in determining the final properties (both rheological and interfacial) of the polymer solutions. Indeed, the salinity is known to decrease the viscosity of solutions of polymers bearing charged moieties along the chain (which includes hydrolyzed polyacrylamides used for EOR).<sup>17</sup> Therefore, the effect of salt must be investigated before drawing any conclusions in this respect.

#### Effect of Salinity on the Properties of S-AP

Among the studied systems, S-AP proved to be the only one possessing both good surface activity and viscosifying properties. Thus, a more detailed investigation about the effect of salinity on the properties of this polymer was performed. As for traditional low-molecular weight surfactants, the presence of increasing concentration of NaCl has a positive effect on the surface activity of S-AP solutions [Figure 5(a)]. However, the viscosity drops of about two order of magnitudes, [Figure 5(b)], i.e. comparable to what happens to analogous PS-*b*-PMAA diblock copolymers.<sup>36</sup> The presence of PEG moieties (that should show a positive salt effect) in the studied polymer clearly does not compensate sufficiently for the presence of the charged ones.

#### Hydrolysis in Strongly Basic Conditions

As anticipated in a previous section, the neutralization step of S-AP after hydrolysis, proved to be more delicate than expected. If the hydrolysis product is left to stir few hours in concentrated NaOH (1 M), the solution, initially yellow, turns dark brown. To further investigate this phenomenon, S-BP (the non-hydrolyzed copolymer) was left to stir overnight in an 1 M solution of NaOH. The polymer was initially insoluble, but a clear



**Figure 6.** <sup>1</sup>H-NMR in d<sub>6</sub>-DMSO of the products of S-BP hydrolysis: fraction insoluble in HCl (a) and fraction soluble in HCl (b).

homogeneous solution was obtained at the end. By neutralization with 1 M HCl a white precipitate was formed. The precipitate was washed with water, dried and a  $^1\text{H-NMR}$  spectrum in  $d_6\text{-DMSO}$  was recorded [Figure 6(a)]. Compared to the starting S-BP [Figure 1(b)], it is evidenced that the peaks corresponding to *t*Bu and PEG were sensibly decreased and a broad peak compatible with the presence of carboxylic group appeared. The remaining solution, after drying, affords a gel that contains the PEG, as evidenced by NMR [Figure 6(b)]. From these observations, it can be concluded that the PEG-acrylate is subject to hydrolysis in strong basic conditions.

## CONCLUSIONS

In this work, different amphiphilic water-soluble polymers were prepared with the aim of finding possible new candidates for enhanced oil recovery. The key parameters are the viscosity and the surface activity in water and salt solutions. To achieve a good control in the polymers compositions, ATRP was used for their synthesis. It was observed that including the PEGA macromonomer in the composition of the polymers has the desired effect of lowering the surface tension of water. However, to observe a relevant effect on the viscosity of the solution, the presence of charged moieties in the hydrophilic block, coming from sodium methacrylate monomers, is required. The viscosity of the prepared polymers compare well with that of traditional polymers employed for EOR, with the advantage of presenting also a non-negligible surface activity. The presence of salt, analogously to commercial polyacrylamides used for EOR, has a negative effect on the viscosity, although it improves the surface activity.

Further studies are in progress to optimize the polymer structure and evaluate the performances in simulated oil recovery experiments.

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## REFERENCES

1. Winnik, M. A.; Yekta, A. *Curr. Opin. Colloid Interface Sci.* **1997**, *2*, 424.
2. McCormick, C. L.; Kirkland, S. E.; York, A. W. *Polym. Rev.* **2006**, *46*, 421.
3. Busse, K.; Kressler, J.; van Eck, D.; Horing, S. *Macromolecules* **2002**, *35*, 178.
4. Fischer, A.; Brembilla, A.; Lochon, P. *Polymer* **2001**, *42*, 1441.
5. Crevecoeur, J. J.; Nelissen, L.; Lemstra, P. J. *Polymer* **1999**, *40*, 3691.
6. Shaikh, S.; Ali, S. A.; Hamad, E. Z.; Abu-Sharkh, B. F. *Polym. Eng. Sci.* **1999**, *39*, 1962.
7. Al-Sabagh, A. M. *Polym. Adv. Technol.* **2000**, *11*, 48.
8. Desbrieres, J.; Babak, V. *Soft Matter* **2010**, *6*, 2358.
9. Ashford, E. J.; Naldi, V.; O'Dell, R.; Billingham, N. C.; Armes, S. P. *Chem. Commun.* **1999**.
10. York, A. W.; Kirkland, S. E.; McCormick, C. L. *Adv. Drug Deliv. Rev.* **2008**, *60*, 1018.
11. Lowe, A. B.; McCormick, C. L. Stimuli Responsive Water-Soluble and Amphiphilic (Co)polymers; ACS Symposium Series: American Chemical Society, Washington, DC, **2001**; Vol. 780, pp 1–13.
12. Raffa, P.; Wever, D. A. Z.; Picchioni, F.; Broekhuis, A. A. *Chem. Rev.* **2015**, *115*, 8504.
13. Lake, L. W. Enhanced Oil recovery; Prentice Hall Inc.: Old Tappan, NJ, **1989**.
14. Sheng, J. J. Modern Chemical Enhanced Oil recovery: Theory and Practice; Elsevier: Burlington, USA, **2010**; pp 648.
15. Iglauer, S.; Wu, Y.; Shuler, P.; Tang, Y.; Goddard, W. A. III. *J. Petrol. Sci. Eng.* **2010**, *71*.
16. Taylor, K. C.; Nasr-El-Din, H. A. *J. Petrol. Sci. Eng.* **1998**, *19*, 265.
17. Wever, D. A. Z.; Picchioni, F.; Broekhuis, A. A. *Progr. Polym. Sci.* **2011**, *36*, 1558.
18. Abu-Sharkh, B. F.; Yahaya, G. O.; Ali, S. A.; Kazi, I. W. *J. Appl. Polym. Sci.* **2001**, *82*, 467.
19. Abu-Sharkh, B. F.; Yahaya, G. O.; Ali, S. A.; Hamad, E. Z.; Abu-Reesh, I. M. *J. Appl. Polym. Sci.* **2003**, *89*, 2290.
20. Yahaya, G. O.; Ahdab, A. A.; Ali, S. A.; Abu-Sharkh, B. F.; Hamad, E. Z. *Polymer* **2001**, *42*, 3363.
21. Olajire, A. A. *Energy* **2014**, *77*, 963.
22. Sun, J.; Xu, X.; Wang, J.; Zhang, W.; Yang, H.; Jing, X.; Shi, X. *J. Dispersion Sci. Technol.* **2010**, *31*, 931.
23. Munoz-Bonilla, A.; Ali, S. I.; del Campo, A.; Fernandez-Garcia, M.; van Herk, A. M.; Heuts, J. P. A. *Macromolecules* **2011**, *44*, 4282.
24. Munoz-Bonilla, A.; van Herk, A. M.; Heuts, J. P. A. *Macromolecules* **2010**, *43*, 2721.
25. Tan, B. H.; Hussain, H.; Liu, Y.; He, C. B.; Davis, T. P. *Langmuir* **2010**, *26*, 2361.
26. Liu, H.; Jiang, X.; Fan, J.; Wang, G.; Liu, S. *Macromolecules* **2007**, *40*, 9074.
27. Cheng, Z. P.; Zhu, X. L.; Kang, E. T.; Neoh, K. G. *Langmuir* **2005**, *21*, 7180.
28. Robinson, K. L.; de Paz-Banez, M. V.; Wang, X. S.; Armes, S. P. *Macromolecules* **2001**, *34*, 5799.
29. Wang, X. S.; Armes, S. P. *Macromolecules* **2000**, *33*, 6640.
30. Bes, L.; Angot, S.; Limer, A.; Haddleton, D. M. *Macromolecules* **2003**, *36*, 2493.
31. Holder, S. J.; Rossi, N. A. A.; Yeoh, C. T.; Durand, G. G.; Boerakker, M. J.; Sommerdijk, N. A. J. M. *J. Mater. Chem.* **2003**, *13*, 2771.
32. Ali, M. M.; Stover, H. D. H. *Macromolecules* **2004**, *37*, 5219.
33. Street, G.; Illsley, D.; Holder, S. J. *J. Polym. Sci. Polym. Chem.* **2005**, *43*, 1129.
34. Holder, S. J.; Durand, G. G.; Yeoh, C.; Illi, E.; Hardy, N. J.; Richardson, T. H. *J. Polym. Sci. Polym. Chem.* **2008**, *46*, 7739.

35. Bergenudd, H.; Coullerez, G.; Jonsson, M.; Malmstrom, E. *Macromolecules* **2009**, *42*, 3302.
36. Raffa, P.; Brandeburg, P.; Wever, D. A. Z.; Picchioni, F.; Broekhuis, A. A. *Macromolecules* **2013**, *46*, 7106.
37. Raffa, P.; Stuart, M. C. A.; Broekhuis, A. A.; Picchioni, F. *J. Colloid Interface Sci.* **2014**, *428*, 152.
38. Zhang, H.; Dong, M.; Zhao, S. *Energy Fuels* **2010**, *24*, 1829.
39. Matsuoka, H.; Maeda, S.; Kaewsaiha, P.; Matsumoto, K. *Langmuir* **2004**, *20*, 7412.
40. Kaewsaiha, P.; Matsumoto, K.; Matsuoka, H. *Langmuir* **2005**, *21*, 9938.
41. Chassenieux, C.; Nicolai, T.; Benyahia, L. *Curr. Opin. Colloid Interface Sci.* **2011**, *16*, 18.
42. Kimerling, A. S.; Rochefort, W. E.; Bhatia, S. R. *Ind. Eng. Chem. Res.* **2006**, *45*, 6885.