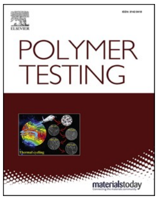
Polymer Testing 82 (2020) 106332

Contents lists available at ScienceDirect

Polymer Testing

journal homepage: http://www.elsevier.com/locate/polytest



Material Properties

High-molar mass acrylamide-co-diacetoneacrylamide graft copolymers as viscosity enhancer for polymer flooding oil recovery

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ARTICLE INFO

Keywords:
High temperature and high salinity oil reservoirs
Thermoassociating copolymer
Rheological properties
Inverse-miniemulsion polymerization
Semi-batch process

ABSTRACT

One of the most widely applied enhanced oil recovery processes is the polymer flooding, in which aqueous solution of polymer viscosifier is introduced in oil reservoirs to increase the recuperation of the remaining oil. From the current challenges of this process, it can be referred to a high cost of materials regarding their substantially required amount and the low impact on the mobility ratio during the process due to the reduction of solution viscosity at high temperatures and high salinity environments. The purpose of this study is to investigate the concept of acrylamide-based thermosassociating copolymer (TAP), with a specific morphology and chemistry (hydrophilic main backbone made of polyacrylamide with grafted amide functionalized pending chains) as viscosity enhancer at harsh conditions of high temperature and salinity. For that aim, a specific TAP microstructure was targeted (very high molar mass linear polymer chains with improved copolymer homogeneity). It is achieved in this study throughout applying the reaction engineering approach, such as synthesis in semi-batch mode or/and in heterogeneous dispersed media. As a result, the synthesized TAP presented excellent behavior as viscosity enhancer especially under high temperature and salinity conditions with improved performance in comparison to TAP synthesized by a conventional solution polymerization approach and to actual commercial high molar mass acrylamide-based polymer.

1. Introduction

Polymer flooding is one of the chemical enhanced oil recovery (EOR) processes for the oil production, in which water-soluble polymers are used to modify the rheological properties of the displacing fluid, improve the water-to-oil mobility ratio, and thus enhance the displacement efficiency. Such a technique has been recognized as the most efficient and most widely applied EOR method for mature oil fields, such as Daqing and Shengli in China [1,2]. Primarily because of its low cost, polymer flooding has been performed more than any other types of EOR processes. The collapse of the oil price in the mid-1980s caused that polymer EOR developing projects virtually disappeared, giving way to a variation of the processes based on polymer gels. Returning the oil price, attention to polymer EOR has risen again in relation to its good achievements in the Chinese Daqing Field. Polymer processes have historically recovered about 5% of the original oil in place and taken about 1 lbm of polymer to produce an incremental barrel [3].

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https://doi.org/10.1016/j.polymertesting.2020.106332
Received 8 November 2019; Accepted 2 January 2020

Partially hydrolyzed polyacrylamide (HPAM) is the most commonly used polymer to alter the viscosity of the pushing water in the polymer flooding EOR process in order to recover immobile, trapped oil, and improve the sweep efficiency [4]. However, in conditions of high salinity (TDS) (above 30,000 mg L^{-1}) and high temperature (>60 °C) characteristic for many oil reservoirs, side amide groups of HPAM extensively hydrolyzed, which decreases the viscosifying effect [5]. Besides, the electrostatic repulsion between the HPAM chains becomes screened by the presence of cations in the high salinity waters, resulting in collapsing of the polymer coils, decreasing the hydrodynamic volume and finally lowering the solution viscosity [6]. Under such harsh condition, the efficiency of the HPAM aqueous solution becomes weak and it is required to use higher polymer concentrations to improve the performance, leading to increase the project costs.

To develop a resistant polymer to apply in the high temperature and salinity environment, a number of researches have tried to alter the chemical structure of polyacrylamide [7–10]. To overcome the HPAM constraints, Hourdet et al. [11–19] proposed the concept of thermoassociating polymer (TAP). Aqueous solution of such TAP is characterized by temperature and salinity dependent viscosity that is reversibly increased upon heating and/or increasing salinity. Afterwards, Wang et al. [20–22] synthesized a novel TAP for the EOR process. Recently, pilot commercial TAP product was developed by Beijing Hengju Polymer Co., Ltd [23,24]. The success of these TAP copolymers is based on precise control of the chemical structure via the grafting method, and control of the length and the molar mass distribution of the backbone, as well as the placement of grafts along the main chain. The grafted side chains onto the hydro-soluble main chain are usually thermosensitive and introduce a property of lower critical solution temperature (LCST). Surpassing this temperature, water becomes a poor solvent for the thermosensitive grafts, resulting in formation of self-aggregated hydrophobic microdomains, forming a network by physical junction and a macroscopic viscosity enhancement.

Basically, two types of PEO- or NIPAM-based thermosensitive functionalities were introduced into main polymer backbones via the grafting technique. Within the first type, either poly(ethylene oxide) (PEO), poly(propylene oxide) (PPO) or PEO/PPO copolymer were grafted via a coupling reaction into the main chains of a low molar mass hydrosoluble parent polymer, such as poly(acrylic acid) (PAA) [11,17], PAM [14], copolymer of AA and 2-acrylamido-2-methyl propanefulfonic acid (AMPS) [12], terpolymer of AM, AMPS, and N-ethyl vinyl acrylamide [13,14], carboxymethylcellulose, aliginate, and carboxylated dextran [19], or PPO-based macromonomers were copolymerized with acrylamide [25,26]. Secondly, N-isopropylacrylamide (NIPAM)-based amino-end functionalized macromonomer [15] or oligomer of NIPAM and other comonomers such as AM, AMPS, or butyl methacrylate [16] were grafted onto low molar mass PAA backbone through a two-step process. Such TAP polymers applied in the EOR process through reservoirs at high salinity and temperature will not overcome some common problems of traditional polymers such as PAM, since they have a low viscosity at the beginning of the process (when injected into the well). On the other hand, due to the type of the viscosity enhancement mechanism in the aqueous phase, these polymers are more effective than other polymers used for similar aims.

Moreover, the preparation of thermoviscosifying water-soluble polymers with such a ‘‘grafting onto’’ procedure using PEO- and NIPAM-based thermosensitive stickers presented several disadvantages. Beside that the presence of carboxylic groups in polymeric precursor is required to couple the amino-terminated groups in most of the cases [11–15,18,19], the grafting process always has to be done at low polymer concentration to avoid the formation of gels resulting in molar mass reduction. For example, for polymer loading in the reaction system below 4%, the molar mass of PAA was generally less than half million [14]. Furthermore, use of relatively expensive materials for the coupling reaction, including NIPAM, dicyclohexylcarbodiimide and N-(3-dimethylaminopropyl)-N′-ethylcarbodiimide hydrochloride (EDC), and certain non-organic salts such as K_2CO_3 are required to reduce the critical temperature of the PEO-based polymers [12,14,18,19]. Finally, molar mass of the most synthesized polymers is lower than commercial ones, which generally cannot provide a corresponding increase in the viscosity at a required concentration and a higher polymer concentration is needed to achieve the targeted viscosity increase. These limitations may impede large-scale manufacturing of the polymers and acceptance of petroleum engineers.

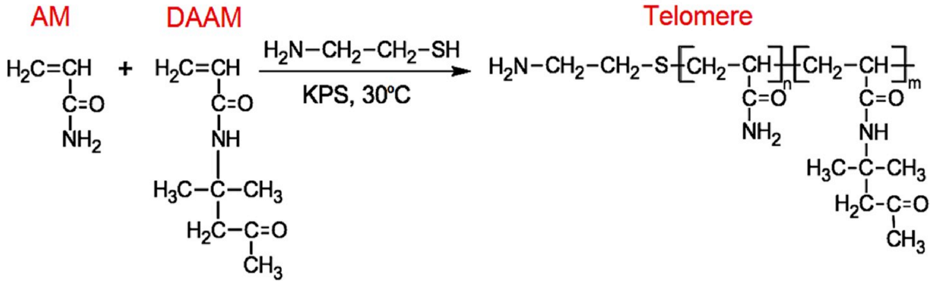
Wang et al. [20–22] tried to overcome the above limitations. They increased the molar mass of TVPs and finely tuned the LCST by copolymerization of acrylamide with a newly developed thermosensitive comonomer (MPAD) based on N-(1,1-dimethyl-3- oxobutyl)-acrylamide (DAAM) [20–22]. They provided the rheological behavior investigation and preliminary core flooding results under simulated high temperature and salinity oil reservoirs conditions, demonstrating the efficiency of the new TAP polymers that had recovery factor of 13.5% versus only 2.1% for the HPAM. However, beside the excellent performance reported, the main drawback of the new TAP polymers is their medium molar mass polymer chains that finally may compromise the aging behavior in the reservoirs. Moreover, the synthesis strategy used in these studies (solution batch polymerization) [20–22] resulted in low functional monomer incorporation in the copolymer that decrease the viscosifying performance. In such conditions, the final copolymer composition that is determined by reactivity ratios of both monomers was not controlled, thus, low incorporation of functional monomer into the AM-based backbone was obtained. Up to the best knowledge of the authors, there is no report so far concerning an approach for synthesizing a TAP with higher molar mass and better control of the copolymer composition.

Therefore, in the present work by use of polymerization reaction engineering strategies, high molar mass DAAM-modified TAPs with improved copolymer composition were targeted. The TAP was synthesized in three steps throughout the synthesis of telomere, macromonomer, and TAP copolymer. In the telomere synthesis, semi-batch mode was applied by feeding one of the components of redox pair initiator system to keep low the radicals concentration in the solution. In such conditions mutual radical termination is decreased and possibility to obtain higher molar masses increased. In TAP synthesis, inverse miniemulsion polymerization strategy was applied. This heterogeneous colloidal system allows polymerization of monomer aqueous solution dispersed in the solvent continuous media, providing few advantages for the TAP synthesis. In such conditions, the monomer droplets containing high concentration of monomer and low concentration of growing radicals are the main polymerization loci. These conditions are well suited to grow high kinetic chain lengths polymers at relatively high polymerization rates, taking advantage of the radical compartmentalization effect. On the other hand, the heterogeneous system, where the both comonomers are distributed between the aqueous and organic phases, may contribute importantly to the copolymer composition and final incorporation of the functional macromonomer into the PAM backbone leading toward improved performance as rheological modifiers. Finally, the performance of the synthetic copolymers as a viscosity enhancer was compared with the same TAP synthesized in solution and with the latest AM-based commercial polymer, presenting significantly improved enhancing behavior especially at high temperature, salt concentrations and shear rate with decreased amount of polymer, which from an industrial point of view seems to be very promising.

2. Materials and methods

2.1. Materials

In this study, acrylamide monomers (AM, ≥99.9%) and diacetoneacrylamide (DAAM, ≥99.9%), potassium persulfate initiator (KPS, ≥99.9%), 2,2′-Azobis(isobutyronitrile) initiator (AIBN, ≥99.9%), 2-aminoethanethiol hydrochloride (AET.HCl, ≥99.9%), acryloyl chloride



Scheme 1. Telomerization reaction of acrylamide and diacetoneacrylamide monomers in the presence of KPS and AET.HCl redox initiator.

Table 1
Conditions employed for telomeres synthesis.

Sample (synthesis method)	Amount of Raw Materials					
	AM (wbt %)	DAAM (wbt%)	Water (wbt%)	KPS (wtm %)	AET.HCl	
					(wtm %)	Feeding rate
T-B	7.74	22.54	69.72	0.8	1.09	–
T-SB	7.74	22.54	69.72	0.8	1.09	2 g/min for 50 min

wbt%: weight percent based on total weight of solution.
wbm%: weight percent based on total weight of monomer.

(ACH, $\geq$99.9%), chloroform solvent (ChF, $\geq$99.9%), cyclohexane solvent (CyH, $\geq$99.9%), Span80 (SP80, $\geq$99.9%, HLB = 4.3), Tween85 (TW85, $\geq$99.9%, HLB = 8.6), and Toluene solvent (Tol, HPLC grade) were purchased from Sigmma Aldrich Company, Madrid, Spain, and Disulfine Blue (DB, 99%) from Merck Company, Darmstadt, Germany, and were used without any purification. Acetone and methanol solvents from Acros Organics Company, New Jersey, USA, were used to purify the prepared polymers. Water was purified with a Millipore system combining inverse osmosis membrane (MilliRO) and ion exchange resins (MilliQ). Double distillated water was deoxygenated by heating to boiling point and cooling under the nitrogen purge system and finally used for the preparation of all solutions. Because of negative role of oxygen as an inhibiting agent in the polymerization efficiency, nitrogen gas with a high purity (99.9%) was used to remove oxygen from the reaction system.

Besides, for the sake of comparison, the newest commercial copolymer based on PAM with a high stability under harsh conditions, high salinity and high temperature (up to 80 °C) were used.

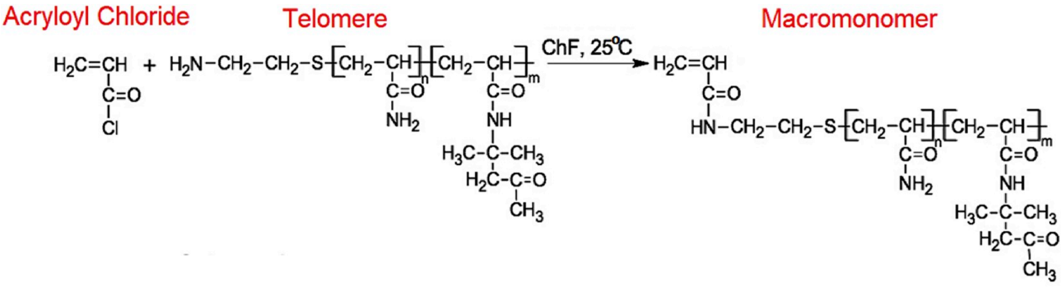
2.2. *Recipe and polymerization procedure*

For TAP synthesis, the procedures reported by Wang et al. [20–22], originated from the protocol mentioned in Chen and Hoffman study [27], composed of three successive steps were pursued, including synthesis of amine-terminated telomere, macromonomer, and TAP. Differently than reported procedures, which were performed exclusively by the batch solution method, we optimized individual steps in order to increase the final molar mass and to improve the final properties. Therefore, the telomere was synthesized by semi-batch solution in order to improve the chemical homogeneity of the resulting polymer chains, by eliminating the influence of the reactivity ratios on the copolymer composition. The batch-based synthesis was applied as well with the aim of the comparison. On the other hand, the TAP was synthesized by inverse miniemulsion polymerization to take advantage of the radical compartmentalization effect, characteristic for polymerization in dispersed media processes, expecting to reach higher molar masses.

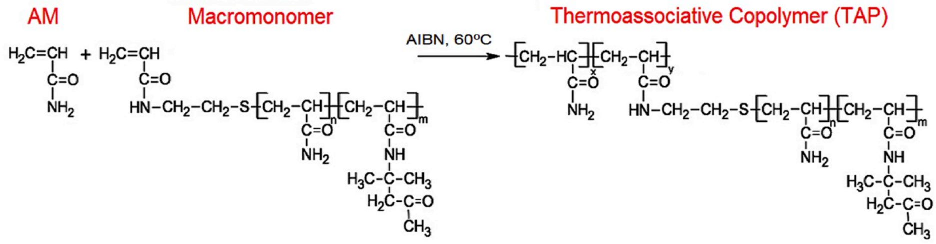
2.2.1. *Telomere synthesis*

To synthesize the telomere, AM and DAAM were copolymerized according to Reaction Scheme 1 by the batch (T-B) and semi-batch (T-SB) solution (water) method for 72 h under constant mixing and different reaction conditions, as shown in Table 1. The reaction was performed at 30 °C and a redox pair initiator based on KPS and AET.HCl was used at two different concentrations (in the case of semi-batch) of AET.HCl (1.09 wbm% and 0.75 wbm%). In the semi-batch solution method, the AET.HCl was fed at constant feeding rate into the reactor to keep the amount of free radical at low values, which will be prosperous to form long chain lengths. The effect of different flow rates (0.8 g min^{-1} and 2 g min^{-1}) on the molar mass was studied. In addition, AET.HCl acted as chain transfer agent and controlled the final functional groups, in this case amine group-terminated oligomer, but as well the molar mass of the chains. Therefore, decreasing the content of AET.HCl at minimum necessary will be favorable for the longer chains formation.

To obtain dry powder of amine-terminated telomere, tel(AM-co-DAAM)-NH$_2$, the following procedure was applied. Telomeres were frozen dried and then dissolved in methanol, after which they were precipitated in diethylether and washed several times. The final precipitation was dissolved in water and re-frozen dried. The yield of purified telomeres was above 90%.



Scheme 2. Reaction scheme of macromonomer synthesis.



Scheme 3. Copolymerization reaction of acrylamide and macromonomer for preparation of thermoassociating copolymer.

2.2.2. *Macromonomer synthesis*

Macromonomers were synthesized in chloroform (ChF) solution following the reaction presented in Scheme 2, showing the reaction of the synthetic telomeres with acryloyl chloride. Two macromonomers were obtained, M-B based on telomere obtained by batch reaction and M-SB based on telomere obtained by semi-batch reaction. In both cases the same amount of telomere (17.86 wbt%), acryloyl chloride (3.57 wbt%) and chloroform (71.43 wbt% for dissolving the telomere and 7.14 wbt% for dissolving the acryloyl chloride) were used. The purified telomeres were dissolved in chloroform and its temperature was reduced to −5 °C under the nitrogen purging. The dissolved acryloyl chloride in chloroform was then continuously added to the telomere solution for 60 min. After the feeding of the solution, the reaction was performed at 25 °C for 24 h under the nitrogen purge. The reaction product was precipitated in acetone at a ratio of 1:5 and then washed by this solvent. Finally, the obtained macromonomer was dissolved in water and after freeze drying at −46 °C and 0.02 mbar for 24 h, white granules with a yield of above 85% were obtained.

2.2.3. *Thermoassociating copolymer synthesis*

The TAP copolymer was synthesized by copolymerizing the macromonomers from the previous step and AM monomer following the reaction in Scheme 3. The reaction was performed in inverse miniemulsion polymerization, where the organic continuous phase was composed by a cyclohexane solution of a mixture of Span80 and Tween85 surfactants. The aqueous dispersed phase consisting of acrylamide monomer, diacetoneacrylamide-based macromonomer, and deionized water was initially prepared in a different beaker under a gentle mixing for 10 min. For preparing the inverse miniemulsion, the aqueous phase was then injected with a micron syringe into the organic phase under a probe sonication (Branson Sonifier W450, 90%, 0.8:0.2) for 30 min. The obtained milky emulsion was transferred to the reactor at 30 °C under the nitrogen purging and the mechanical stirring of 400 rpm, afterwards the temperature was increased to 60 °C. AIBN initiator was then injected to the reaction mixture and the polymerization process was carried out for 10 h. The reaction product was obtained with 96% yield after freeze-drying process and precipitation in acetone (a ratio of 1:5, TAP to acetone). The solution-based copolymerization of macromonomer and AM was performed for the comparison. The recipes employed in both processes are shown in Table 2.

2.3. *Analytical method*

2.3.1. *Chemical structure of telomere, macromonomer and thermoassociating copolymer and their conversion*

^{1}HNMR and DEPT spectra were used for the characterization of the chemical structure of the telomeres, macromonomers, and copolymers as well as the conversion along the reactions. The telomere samples were dissolved in DMSO-d_6 and macromonomer and copolymer samples were dissolved in D_2O and all of them were measured in a Bruker 400 MHz spectrometer. The calculation of the conversion along the reactions was done by sampling 65.0 mg in 1.0 mL of the NMR solvent during a defined time period.

2.3.2. *Molar mass of telomere, macromonomer and thermoassociating copolymer*

Once the samples were dried, aqueous solutions at the required concentrations (2.5–5 mg mL^{-1}) were prepared for the molar mass determination. The molar mass of the polymers was analyzed by SEC/MALS/RI equipment, composed of a LC20 pump (Shimadzu) coupled to 3 columns in series (2 PL-Aquagel-OH-MIXED-H (Agilent) and Ultrahydrogel 120 (Waters)), a miniDAWN TREOS multiangle (3 angles) light scattering laser photometer equipped with an He–Ne laser ($\lambda = 658$ nm) and an Optilab T-Rex differential refractometer ($\lambda = 658$ nm) (both from Wyatt Technology Corp., Santa Barbara, CA, USA).

The SEC/MALS/RI data were analyzed using the ASTRA software version 6.1 (Wyatt technology Corp., Santa Barbara, CA, USA). The absolute molar masses were calculated from the MALS/RI data using the Debye plot (with first-order Zimm formalism). The analyses were performed at 35 °C and DDI water (stabilized with sodium azide) was used as mobile phase at a flow rate of 0.6 mL min^{-1}. The samples were injected without filtering. The $dn.dc^{-1}$ used for the calculation of the absolute molar mass was 0.15 mL g^{-1} (M-SB and TAP-E-SB) and 0.139 mL g^{-1} (M-B and TAP-S-B), which were previously measured for M-SB and M-B as follows.

The refractive index increment ($dn.dc^{-1}$) was measured by means of an Optilab T-Rex differential refractometer ($\lambda = 658$ nm) (Wyatt Technology Corp., Santa Barbara, CA, USA) at 35 °C. The equipment consisted of a LC20 pump (Shimadzu, Izasa S.A., Barcelona, Spain) and a Rheodyne manual injector coupled with a 2 mL sample loop.

The experiment was carried out by injecting six samples (in 0.5–5.0 or 2.5 mg mL^{-1} concentration range) of the same batch of polymer. The samples were prepared as follows. First, the main solution was prepared

Table 2
Synthesis method and required amount of raw materials for preparation of thermoassociating copolymers.

Synthetic Material	Synthesis Method	Amount of Raw Materials					
TAP-S-B	batch solution	**AM** (wbt%)	**Macro** (wbt%)	**Water** (wbt%)	**KPS** (wbm%)	–	–
		7.00	3.00	90.00	5.00		
TAP-E-SB	inverse miniemulsion	**AM**	**Macro**	**Water**	**AIBN**	**CyH** (wbt%)	**SP80-TW85** (wbt%)[a]
		7.00	3.00	13.00	1.00	76	1.0

wbt%: weight percent based on total weight of dispersion.
wbm%: weight percent based on total weight of monomers.
[a] weight percent of surfactant mixtures based on total weight of raw materials for HLB = 6.5.

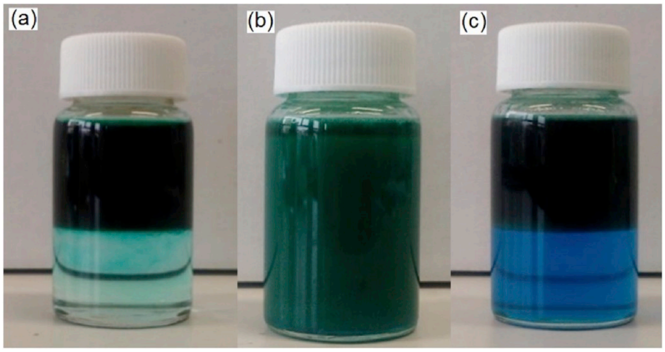


Fig. 1. Solution of amine-terminated telomere (T-SB): a) before, b) during, and c) after mixing of both organic and aqueous phases.

by dissolving the dried polymer in DDI water (Milli-Q, Millipore Ibérica S.A.U, Madrid, Spain) (5.0 or 2.5 mg mL^{-1}). From the mother solution, five solutions with concentrations 4.0, 3.0, 2.0, 1.0, and 0.5 mg mL^{-1} were prepared by dilution.

The analysis was performed at 35 °C in DDI water (stabilized with sodium azide) at a flow rate of 1 mL min^{-1}. The dn.dc^{-1} was calculated from the slope obtained from the plot of the refractive index against concentration.

2.3.3. *Identification of the presence of amine groups in telomere chains*

Qualitative analysis of amine groups at the end of the telomeric chain was accomplished by analyzing disulfine blue [28,29]. In this analysis, two different solutions were prepared, disulfine blue VN150 aqueous solution with a concentration of 800 mg L^{-1} in 0.01 M hydrochloric and 0.3 mol L^{-1} sodium sulfate and organic solution made of 20 mg telomere in 10 mL of chloroform. The both solutions were then mixed for 2 h to complete the pigmentation process, in which amine-dye complexes were formed. The formation of the complexes is demonstrated by the change in the color of chloroform from transparent to blue, which confirms the presence of amine in the polymer chain. It is noteworthy to mention that since this analysis requires soluble telomeres in the organic phase and insoluble one in the aqueous phase, sodium sulfate was added to the colored solution in order to ensure the insolubility of telomeres in the aqueous solution.

2.3.4. *Phase separation temperature of telomere*

The determination of phase separation temperature (T_p) of the telomeric aqueous solutions (100 mg L^{-1} and 5% KCl) was performed by analyzing their turbidity variation with the temperature. The aqueous solution was equilibrated in a 50 mL round-bottom flask containing a magnetic stirrer at room temperature and immersed in a cell equipped with a temperature controller. The heating rate was 1 °C.min^{-1} and T_p was defined as the temperature at which the samples start becoming cloudy. Furthermore, these results were compared with the temperatures obtained from the slope of viscosity versus temperature graph during the rheological experiments.

2.3.5. *Fraction of macromonomer in thermoassociating copolymer*

Elemental analysis of the macromonomer and copolymer was conducted using Carlo Erba 1160 elemental analyzer (Italy) and the presence of macromonomer and acrylamide in the final copolymer (w_m and w_a) was determined by Equations (1) and (2).

$$\frac{c_m w_m + c_a w_a}{w_m + w_a} \times 100\% = c_{co}\% \tag{1}$$

$$\frac{n_m w_m + n_a w_a}{w_m + w_a} \times 100\% = n_{co}\% \tag{2}$$

In above equations, c_m, c_a, c_{co}, n_m, n_a, n_{co}, w_m, and w_a represent the carbon content in macromonomer, acrylamide and copolymer, nitrogen content in macromonomer, acrylamide and copolymer and the weight of macromonomer and acrylamide units in the final copolymer, respectively.

2.3.6. *Thermal and salinity stability of thermoassociating copolymer*

Polymeric solutions were prepared by dissolving the desired amount of copolymer powder in deionized water under gentle mixing. Then in order to remove the formed bubbles, the samples were left without any agitation for one day. For the samples prepared in saline medium, potassium chloride was added directly to the already prepared polymeric aqueous solutions and left stirring for one day. Afterwards, the samples were left without agitation for one more day prior to be analyzed. In addition, to study the effect of potassium chloride, the behavior of the copolymers under different saline conditions was also investigated.

Static rheology measurements were carried out in a Physica MCR301 rheometer (Anto-Paar, Germany), equipped with a Pelletier system for heating and cooling at a temperature range of 20–80 °C. The measurements were carried out with the geometry of CC27 conical plate (radius of 13.33 mm and an ending radius of 46.44 mm) at a heating rate of 2 °C. min^{-1} and at constant shear rate of 10 s^{-1}. In order to prevent evaporation of the solution, a special cap was used on the sample container. Thermoassociating behavior was evaluated from the images of the telomere and copolymer solutions which were taken by a Cryo-TEM equipped with an environmental temperature controller system. In the case of high temperature analysis, the temperature of the samples was first increased up to 80 °C and relative humidity was maintained in saturated state to prevent evaporation. Then, the polymer solution was placed on a carbon-coated film and copper mesh. The aforementioned mesh was rapidly cooled down to −180 °C by immersing it in liquefied nitrogen at −196 °C. The frozen sample was transferred to the JEM2010 Cryomicroscope. The accelerator voltage was set on 200 kV at a temperature of −170 °C.

3. Results and discussion

3.1. *Characterization of telomeres, macromonomers and thermoassociating copolymers*

The presence of amine terminal groups in telomeres' chains was qualitatively investigated by dye-partition test (DB test) with disulfine blue. Fig. 1 shows the images of the solution containing amine group-terminated telomere before, during and after the mixing of the two phases. As it may be observed in Fig. 1c, after completing the partitioning process, the color of chloroform phase is changed from green to blue, showing that distribution of amine-dye complex between the water and the solvent occurred, which demonstrates the presence of ending amine groups in the telomere chains.

To further confirm this, the chemical composition of the obtained products was investigated by ^{1}HNMR and FTIR spectroscopy. ^{1}HNMR spectra of raw materials used for the telomere synthesis are shown in Fig. S1 and ^{1}HNMR spectra of telomere, macromonomer, and synthesized copolymer are shown in Fig. 2. The characteristic peaks of the functional groups of the obtained materials by ^{1}HNMR and DEPT methods with detailed assignment information are listed in Table 3. The results from Table 4 demonstrates clearly that the chemical structure of telomere includes AM and DAAM monomer units; the structure of macromonomer includes amine group-terminated telomere and vinyl groups, and the structure of TAP copolymer includes macromonomer and AM units. These results are supported by FTIR spectra, presented in Fig. S2, Table S1 and the discussion in Supporting Information, demonstrating successful synthesis of the telomere, macromonomer, and TAP.

The evolution of conversion of the telomerization reactions T-B and T-SB is presented in Fig. S3, Supporting information. High conversion rates were obtained for both reactions, achieving almost full conversion

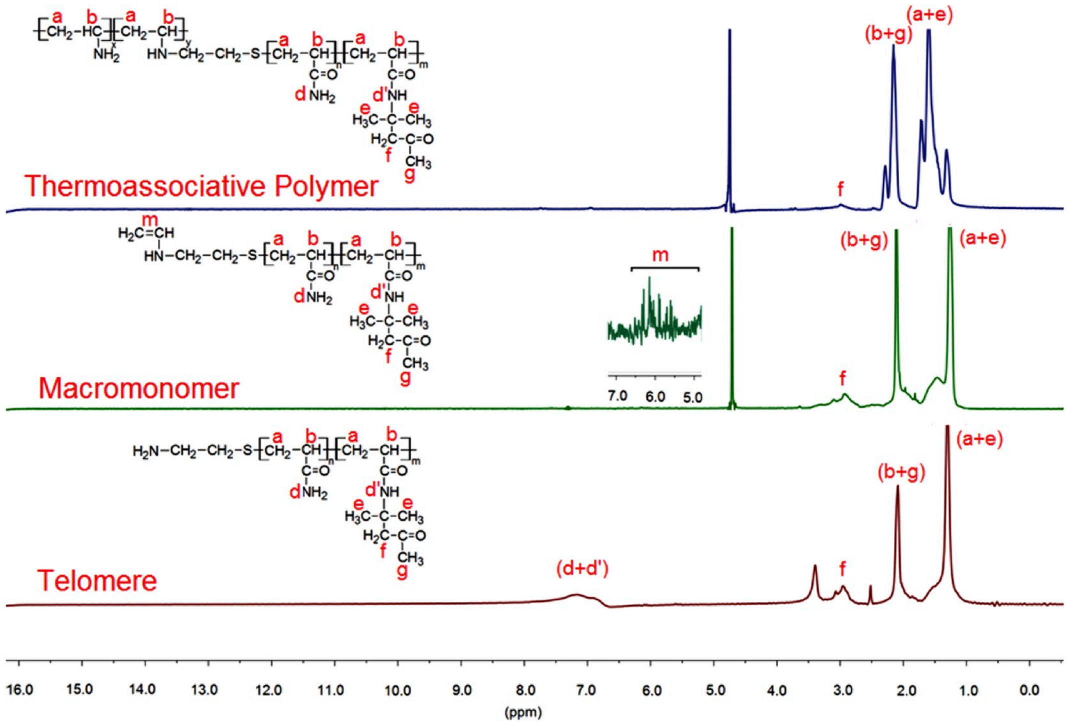


Fig. 2. ^{1}HNMR spectra of telomere, macromonomer and thermoassociating copolymer.

in the semi-batch reaction. The characteristics of all the telomeres obtained under different conditions are presented in Table 4. The mode of performing the reactions influences the kinetics and the properties of the telomeres. The reaction is faster in case of batch mode (T-B) because all the initiator was added as a shot since the reaction start. As a result, large number of radicals are formed, a great part of which started growing new polymer chains. In such conditions the rate of termination is high, resulting in medium ranged average molar masses with the wide distribution ($Đ = 1.6$). In the corresponding semi-batch reaction (T-SB), the AET.HCl was continuously fed, keeping the number of radicals low and so the termination rate, resulting initially in slower kinetics and almost double higher average molar mass than in the batch with much narrow distribution ($Đ = 1.1$).

Following the Reaction Scheme 2 the telomeres synthesized in the first step were converted into macromonomers. Both resulting macromonomers, M-B and M-SB, were completely soluble in aqueous media; therefore, they were successfully converted into respective TAP copolymers by both inverse miniemulsion polymerization (TAP-E-SB) and solution polymerization (TAP-S-B).

The weight and number average molar masses and dispersity index, Đ, for macromonomers and corresponding TAPs synthesized according to the reaction in Scheme 3 and conditions presented in Table 2 are summarized in Table 5. The molar masses of the macromonomer are similar to these of the telomeres (Table 4), as it may be expected, and the difference observed especially for $\overline{Mn}$ is likely due to the lack of MALS signal at long elution times. For the analysis of the RI/MALS signals, it is well known that in order to calculate the molar mass properly, MALS and RI signals, should be high enough in the whole elution range. This is particularly important at short elution times where MALS is more sensitive than RI and the opposite happens at long elution times. Therefore, even at long elution times there is still good enough RI signal, the MALS signal can be not sufficient resulting in a narrower integrated peak. As a consequence, the obtained $\overline{Mn}$ is higher and the dispersity index narrower. Moreover, M-SB presents higher average molar mass than that of M-B, because the former one is based on the semi-batch telomere with higher molar mass.

The TAPs were synthesized by two routes solution and inverse miniemulsion polymerization in order to compare the both routes. The former one is similar to already published synthetic route [20–22], where all the reactions were performed in the batch solution. According to Table 5, TAP-E-SB copolymer prepared by the inverse miniemulsion method has significantly higher molar mass and much narrower molar mass distribution than that of the TAP-S-B sample solution. This result is because of low radical's content due to the initiator feeding during reactions and the radical compartmentalization effect characteristic for the polymerization in dispersed media techniques, according to which the individual growing radical is enclosed within the polymer particle contributing towards decreasing the termination rate and growing of larger polymer chains [30,31], effect that cannot be achieved in the solution polymerization.

In Table 6 the elemental analysis of macromonomers and TAPs are presented, on the base of which, using Equations (1) and (2), the weight fraction of AM and macromonomer in the TAPs were calculated and shown in Table 7. The fraction of macromonomer in TAPs is 13.2 wt% and 23.9 wt%, respectively for solution and inverse miniemulsion-prepared TAPs. When compared with the initial fraction of macromonomer for the synthesis (30 wt%), obviously not all the macromonomer was incorporated within final TAPs. The lower incorporation of the macromonomer is probably due to the different reactivity ratios of both monomers in the copolymerization process. Nevertheless, the incorporation of macromonomer increased significantly in the process of inverse miniemulsion polymerization. Inverse miniemulsion is heterogeneous system, where aqueous solution of both monomers is dispersed in cyclohexane continuous phase. Under such conditions, the partitioning coefficients of both monomers between aqueous and cyclohexane phase influences the copolymerization and copolymer composition. Taking into account that AM monomer molecules are much smaller than the macromonomer, the possibility to diffuse towards the continuous phase is important. Thus, as the present results indicate, partitioning of AM between water and cyclohexane is higher than the partitioning of macromonomer, resulting in increasing fraction of macromonomer in the dispersed phase, which is the reaction locus. As a result, the incorporation of macromonomer is higher. This result is in agreement with similar published works [15,20].

Table 3
Characteristic peaks of telomere, macromonomer, and thermosassociating copolymer in ^{1}HNMR and DEPT.

Analysis	Functional group	ppm
	Telomere	
^{1}HNMR	Methylene ($-CH_2$) in the main chain and methyl ($-CH_3$) in the side chain of diacetoneacrylamide	a+e @ 1.31
	Methyne (–CH) in the main chain and methyl ($-CH_3$) at the end of the diacetoneacrylamide side chain	b + g @ 2.15
	Methylene in the diacetoneacrylamide side chain between carboxyl group and 4th type carbon	f @ 2.94
	Amide in the acrylamide side chain ($-NH_2-$) and diacetoneacrylamide (–NH–)	d + d' @ 6.68–7.33
	Macromonomer	
	Methylene ($-CH_2$) in the main chain and methyl ($-CH_3$) in the side chain of diacetoneacrylamide	a+e @ 1.26
	Methyne (–CH) in the main chain and methyl ($-CH_3$) at the end of the diacetoneacrylamide side chain	b + g @ 2.11
	Methylene in the diacetoneacrylamide side chain between carboxyl group and 4th type carbon	f @ 2.93
	Double bond carbon containing methyne and methylene	d + d' @ 5.50–6.67
	Copolymer	
	Methylene ($-CH_2$) in the main chain and methyl ($-CH_3$) in the side chain of diacetoneacrylamide	a+e @ 1.60
	Methyne (–CH) in the main chain and methyl ($-CH_3$) at the end of diacetoneacrylamide side chain	b + g @ 2.15
	Methylene in the diacetoneacrylamide side chain between carboxyl group and 4th type carbon	f @ 2.96
DEPT	**Telomere**	
	Methyl ($-CH_3$) in the diacetoneacrylamide side chain	e @ 27.57
	Methylene ($-CH_2$) along the main chain	a @ 31.15
	Methyne (–CH–) along the main chain	b @ 40.38
	Methyl ($-CH_3$) at the end of diacetoneacrylamide side chain	g @ 50.80
	Methylene in the diacetoneacrylamide side chain between carboxyl group and 4th type carbon	f @ 60.63
	Macromonomer	
	Methyl ($-CH_3$) in diacetoneacrylamide side chain	e @ 28.98
	Methylene ($-CH_2$) along the main chain	a @ 36.99
	Mathyne (–CH) along the main chain	b @ 42.98
	Methyl ($-CH_3$) at the end of diacetoneacrylamide side chain	g @ 53.27
	Methylene in the diacetoneacrylamide side chain between carboxyl group and 4th type carbon	f @ 59.71
	Methyl ($-CH_3$) in diacetoneacrylamide side chain	m @ 125.02–133.05
	Copolymer	
	Methyl ($-CH_3$) in diacetoneacrylamide side chain	e @ 27.96
	Methylene ($-CH_2$) along the main chain	a @ 34.79
	Mathyne (–CH) along the main chain	b @ 43.90
	Methyl ($-CH_3$) at the end of diacetoneacrylamide side chain	g @ 50.26
	Methylene in the diacetoneacrylamide side chain between carboxyl group and 4th type carbon	f @ 61.01

Table 4
Number average molar mass and dispersity index measured for synthesized telomeres.

Telomere type	AET.HCl concentration (mol/L)	KPS concentration (mol/L)	$\overline{\mathbf{Mn}}$(kDa)	(Đ)
T-B	0.0096	0.0030	21.3	1.6
T-SB	0.0096	0.0030	38.6	1.1

Table 5
Weight and number average molar mass of macromonomers and thermoassociating copolymers.

Sample	$\overline{\mathbf{Mn}}$(kDa)	$\overline{\mathbf{Mw}}$ (kDa)	Đ
M-B	23.5	29.0	1.2
M-SB	43.8	46.0	1.0
TAP-S-B	4000	6200	1.5
TAP-E-SB	7700	10,300	1.3

Table 6
Elemental Analysis of nitrogen and carbon contents of macromonomers and thermoassociating copolymers.

Elements	AM	M-B	TAP-S-B	M-SB	TAP-E-SB
Carbon (wt%)	0.5	43.0 ± 8.2	49.0 ± 8.1	73.0 ± 3.2	56.0 ± 1.1
Nitrogen (wt%)	0.2	15.0 ± 7.1	19.0 ± 2.3	13.0 ± 9.3	18.0 ± 3.2

Table 7
Weight percent of acrylamide and macromonomer in feed and thermoassociating copolymers.

Polymer	Feed composition (wt%)		Copolymer composition (wt%)	
	Acrylamide	macromonomer	acrylamide	macromonomer
TAP-S-B	70.0	30.0	86.8	13.2
TAP-E-SB	70.0	30.0	76.1	23.9

Table 8
Comparison between T_{ass} of copolymers and T_p of their telomeres for different polymer concentrations and 5% KCl aqueous solution.

Copolymer	C_p (ppm)	T_{ass} (°C)	T_p (°C)
TAP-S-B	1000	62 ± 2	68 ± 2
TAP-S-B	1500	55 ± 2	64 ± 1
TAP-S-B	2000	49 ± 1	54 ± 2
TAP-E-SB	1000	56 ± 1	56 ± 1
TAP-E-SB	1500	50 ± 2	48 ± 1
TAP-E-SB	2000	47 ± 1	48 ± 2

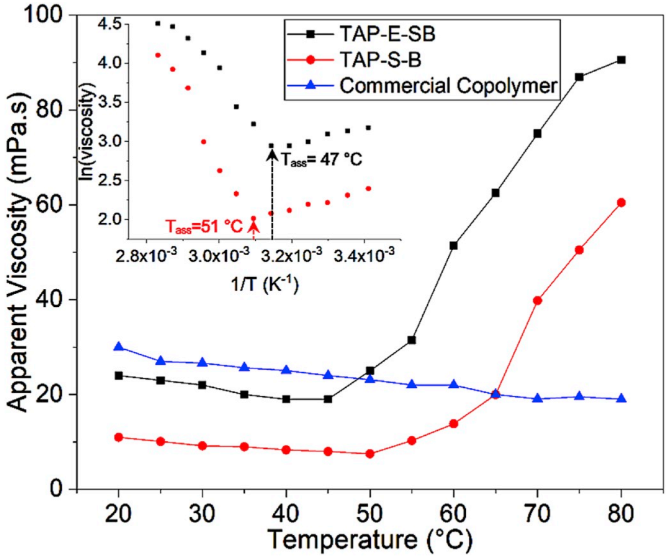


Fig. 3. Viscosity behavior versus temperature for TAP-E-SB, TAP-S-B and commercial AM-based copolymer at a concentration of 2000 ppm in a 5% KCl aqueous solution (In the inset: Arrhenius correlation for two TAPs).

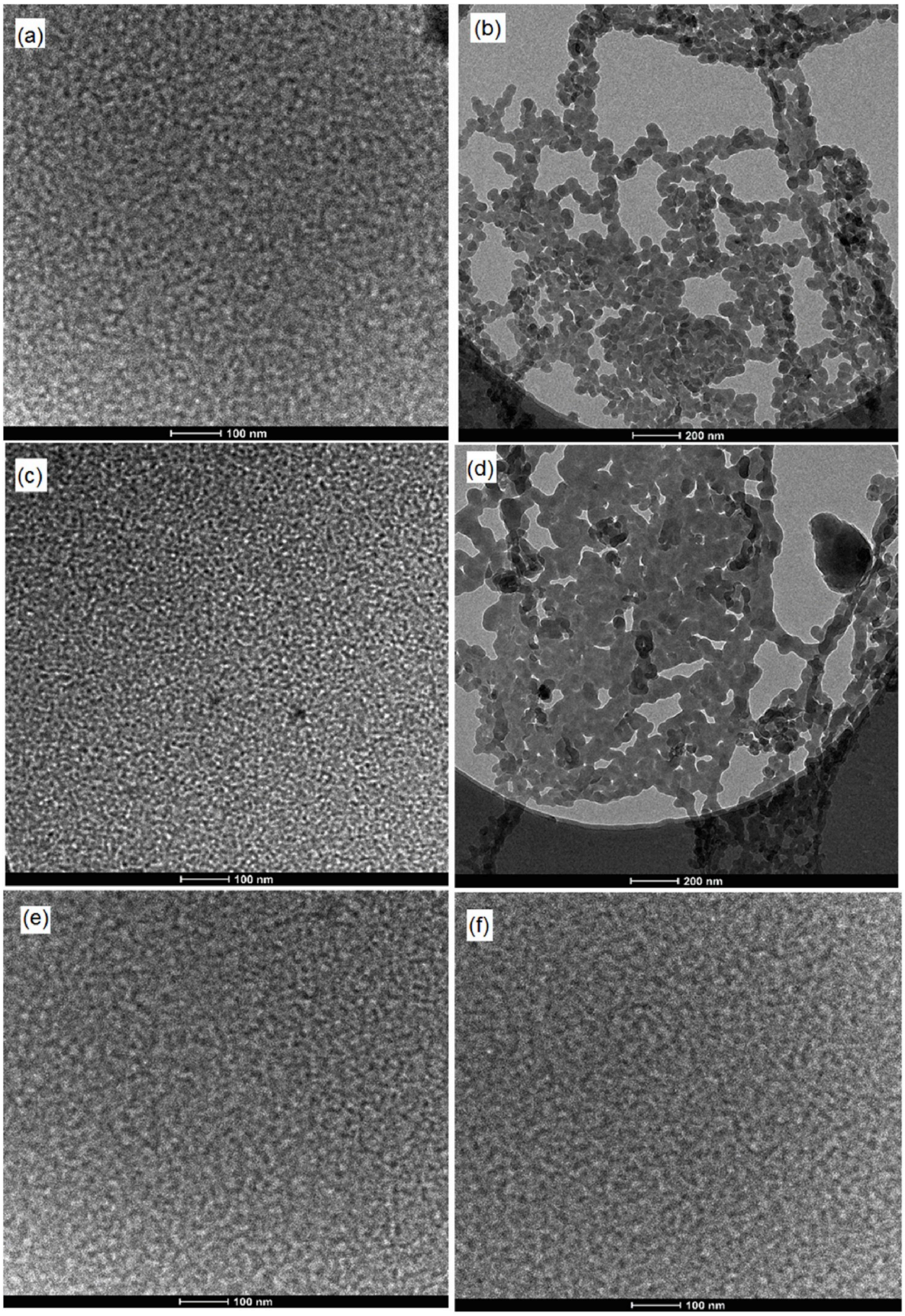


Fig. 4. Cryo-TEM images of TAP-E-SB at 30 °C (a) and 80 °C (b); TAP-S-B at 30 °C (c) and 80 °C (d); and commercial AM-based copolymer at 30 °C (e) and 80 °C (f), under the same conditions (concentration of 2000 ppm in a 5% KCl aqueous solution).

Table 8 presents the thermal associative temperature (T_{ass}) of the two TAPs at three different concentrations (similar to the concentration used in polymer flooding procedures), and the phase separation temperature of the respective telomere (T_P) at constant KCl concentration of 5%. These results illustrate that the long length of the side chains present similar behavior in both free and grafted state. In case of TAP-S-B the differences between the T_P and T_{ass} are much more important than in case of TAP-E-SB. We hypothesize that these differences arise from the presence of telomere chains with different compositions in T-B and subsequently in M-B and TAP-S-B. In such case, the results in Table 6 indicate that telomeres synthesized by semi-batch method (and subsequently the macromonomer) likely have much more homogeneous composition. This hypothesis is based on the synthesis method: by producing the telomere in semi-batch, the effect of the monomers reactivity ratios onto copolymer chain composition was eliminated. Subsequently, in the TAP-E-SB more amide functionalities are incorporated within the grafted pending chains (as it will be shown latter). On the other hand, the results in Table 8 indicate that by increasing the TAP concentration in the aqueous solution the T_{ass} dropped importantly. This behavior is due to the easier association of the polymer chains at higher content in the solution, which may be used to vary T_{ass} with respect to individual properties of different reservoirs.

3.2. Rheological analysis of thermoassociating behavior of copolymers

The main feature of the synthesized copolymer is the capability of

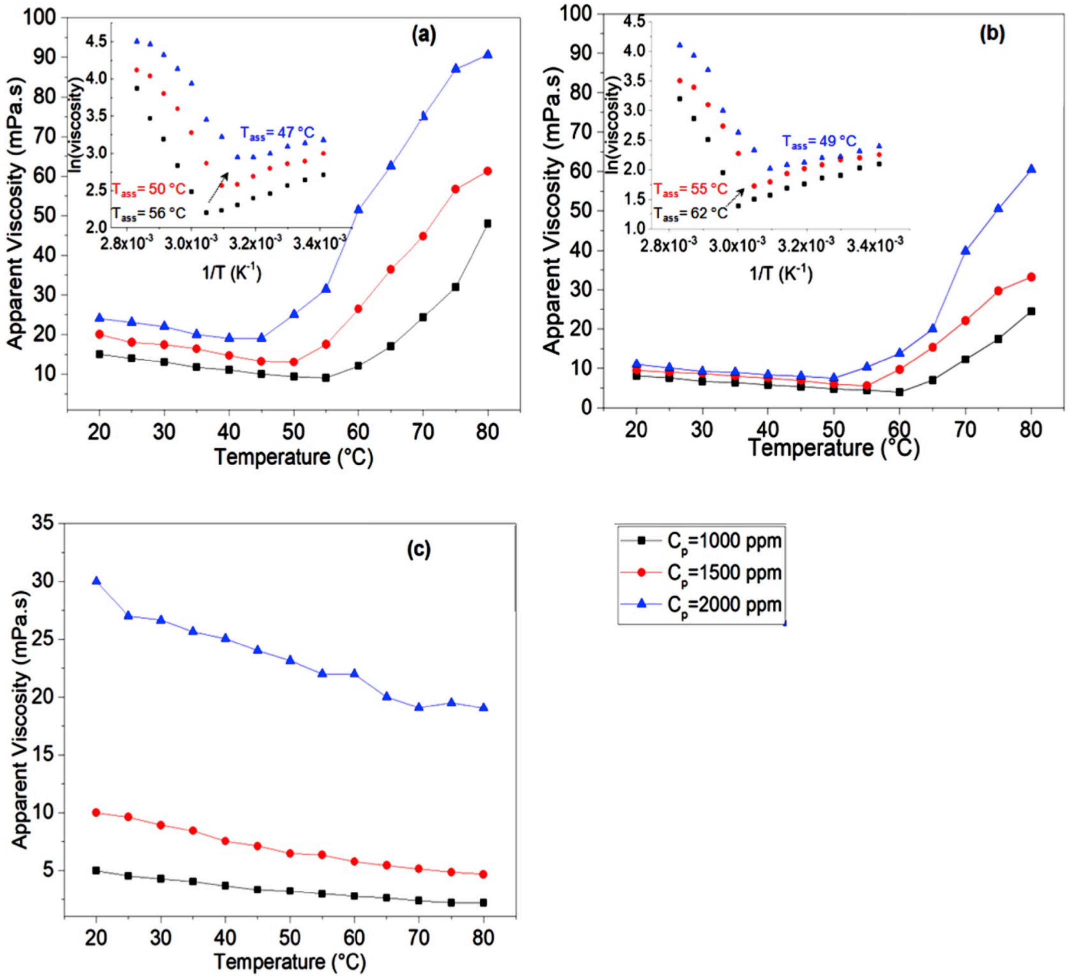


Fig. 5. Viscosity behavior versus temperature for a) TAP-E-SB, b) TAP-S -B and c) commercial AM-based copolymer at different concentrations in a 5% KCl aqueous solution (In the inset: Arrhenius correlation for two TAPs).

rheological modification of the pushing water added to the oil reservoirs with aim of enhancement of the oil displacement efficiency. To accomplish it, the TAPs must have thickening rheological behavior, especially under increased temperature and salinity. To check this, the temperature dependence of the apparent viscosity of both TAP-S-B and TAP-E-SB was investigated and compared to that of commercial AM-based copolymer (Fig. 3), under a similar concentration and conditions (2000 ppm in a 5% KCl aqueous solution). Fig. 3 presents that in the case of TAPs aqueous solutions (TAP-S-B and TAP-E-SB), the viscosity behavior is divided into two regions. Below the copolymer's T_{ass}, both TAPs behave similarly to the commercial AM-based copolymer (the viscosity slowly decreased with temperature, probably due to the polyelectrolyte effect arising from a partial hydrolysis of acrylamide units [32]). At T_{ass}, the side chains' behavior suddenly changed and the viscosity started growing with temperature. At T_{ass} the solubility of the short side thermoresponsive chains in the aqueous media dropped, introducing hydrophobicity in the hydrophilic main backbone. These amphiphilic structures assembled between themselves causing transient network formation that leads to important increase in the solution viscosity.

The inverse miniemulsion TAP-E-SB provides much higher viscosity at the same concentration in the whole temperature range, which likely is due to the higher molar masses of these polymer chains and better incorporation of the macromonomer that provides more amide functionalities. In the case of commercial sample, the viscosity continuously decreased with temperature in whole range investigated.

By drawing Arrhenius curve that is shown in inset of Fig. 3, the start of the association process (T_{ass}) may be predicted, which is equal to 51 and 47 °C for the samples prepared by solution and inverse miniemulsion methods, respectively. The determined values from the graphs correspond well with the experimentally determined in Table 8. The reason of temperature differences between two TAPs is likely because of the different incorporation of macromonomer with different molar mass in the TAP chains. The weight fraction of macromonomer in TAP synthesized by inverse miniemulsion polymerization is 23.9 wt% with molar mass of 48 kDa versus 13.2 wt% for solution polymerization TAP with molar mass of 29 kDa. As the macromonomer is the thermoassociating component within the copolymer, all of this led to higher thermal sensitivity of the inverse miniemulsion TAP, which formed the physical networks earlier than solution-based TAP, resulting in a 4 °C drop in the associating temperature.

Evidence of the difference in the copolymer structure at temperatures lower and higher than T_{ass} was obtained by analyzing the telomeres and TAPs at concentration of 2000 ppm in a 5% KCl aqueous solution by Cryo-TEM. For the sake of comparison, the commercial copolymer was analyzed, too. The results of copolymers and telomeres are presented in Fig. 4, Fig. S4 and Fig. S5, respectively.

All three polymers behave similarly at low temperature (30 °C), representing the small telomere chains solubilized in water and completely stretched (Fig. 4a, c, e). By increasing the temperature to 80 °C (Fig. 4b and d), the TAPs are organized in particulate structures interconnected in a network, likely responsible for the viscosity increment. As explained, this network is an assembled of the hydrophilic AM-based backbones with the grafted telomere chains that form the

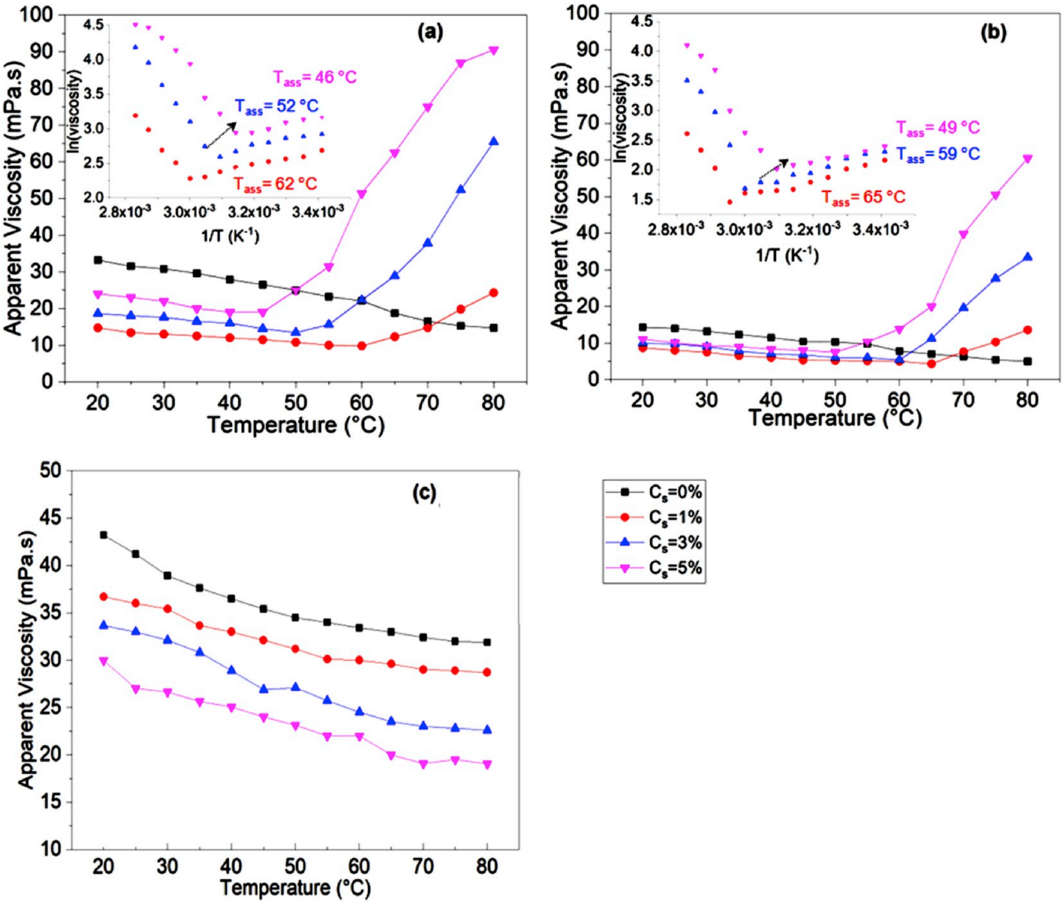


Fig. 6. Viscosity behavior versus temperature for a) TAP-E-SB, b) TAP-SB and c) commercial AM-based copolymer at a concentration of 2000 ppm and in an aqueous solution with different KCl concentrations (In the inset: Arrhenius correlation for two TAPs).

hydrophobic microdomains. Such amphiphilic structures will not precipitate, but rather will cause the viscosity enhancement of the polymer solution. Comparing the TAP-E-SB and TAP-S-B (Fig. 4b and d, respectively) the entanglements in inverse miniemulsion-based TAP are smaller (10–20 nm) than in solution-based TAP (~50 nm), giving rise to less compact network formed of higher number of structures within it. In solution-based TAP even aggregated structures may be noticed. This is likely due to the higher incorporation of macromonomorer in the inverse miniemulsion process that improve the performance at the same polymer concentration. It should be noted that, the commercial sample behaves equally at low and high temperatures (Fig. 4f).

The polymer concentration is an important parameter that influences the viscosity behavior of the polymer solution. Fig. 5 presents the apparent viscosity versus temperature for 5% KCl aqueous solutions of TAP-S-B, TAP-E-SB and commercial AM-based copolymer at different polymer concentrations. It may be observed in Fig. 5a and b for both TAPs that by increasing their concentration, T_{ass} decreased (inset in Fig. 5a and b). In more concentrated solutions due to the improved interaction between the chains in more concentrated solution, the coil to coil connection of the chains occurs at lower temperature. The 3D network formation depends on the number of physical connections and this number rises by increasing copolymer concentration, which additionally caused that the thickening effect augmented strongly with the concentration. All these effects are more significant for inverse miniemulsion TAP-E-SB. The comparison between the TAPs indicates that similar viscosity may be achieved by using much less amount of inverse miniemulsion TAP than solution one (similar viscosity was obtained with 1500 ppm miniemulsion TAP and 2000 ppm solution TAP). Furthermore, in Fig. 5a and b a possible trend to reach a plateau at higher temperatures and at higher polymer concentrations can be observed, this indicates that further augmentation of temperature (>80 °C) will not have an effect on the viscosity. Likely, under these conditions all the TAP chains are already associated; therefore, the viscosity cannot be furthermore improved.

Apparently, the commercial AM-based copolymer behaves differently (Fig. 5c). The viscosity of commercial polymer solution increases with its concentration, whereas the drop of the viscosity due to the temperature rise in the solutions is less apparent at higher concentration.

It is well known that the behavior of the TAPs is strongly influenced by salt concentration in the solution [21,33]. Having in mind that most of the oil reservoirs are characterized by high salinity conditions, it is important to determine the thickening activity of the TAPs synthesized here at different salt concentrations. In Fig. 6 the apparent viscosity as a function of temperature is presented at four different KCl concentrations (0–5 wt%) for aqueous solution of TAP-S-B, TAP-E-SB and commercial AM-based copolymer with a concentration of 2000 ppm. If there is no salt in the solutions, the polymer solution lacks the thermoassociating behavior, even more it shows thermothinning behavior. This means no association of chains occurs in salt-free water, the solubility remains unaffected by the temperature in such conditions. However, temperature increase induces intra-chain an interaction, shrinkage of the individual chains happens resulting in the viscosity decrease. Addition of salt into the solution induce the thermothickening behavior, inter-chains interactions, developing of the network as seen in TEM images (Fig. 4) and viscosity increase. Increasing salt concentration promotes further the thermothickening behavior of the TAPs and decrease T_{ass}, due to the salting out phenomenon, according to which the polymer chains associate earlier due to decreased polymer–water interactions and increased polymer–polymer interactions. For instance, by increasing KCl concentration from 1 to 5% at 40 °C, the viscosity of TAP-E-SB and TAP-S-B copolymer solutions increased from 12.1 to 19.5 and from 6.2 to 8.3 mPa s, respectively, (Fig. 5a and b). This demonstrates again the better performance of inverse miniemulsion TAP than the solution one. Regarding the commercial AM-based copolymer (Fig. 6c), the addition of salt does not influence the behavior. However, at high salinity conditions no thermothickening behavior was noticed and the viscosity of the solutions dropped significantly likely due to the important electrostatic repulsion between the polymer chains that prevent association to occur.

4. Conclusions

In this work high molar mass thermoassociating copolymers were synthesized in three steps. First of all, telomeres were synthesized by solution copolymerization of acrylamide and diacetoneacrylamide monomers, from which by addition of vinyl double bond in the chain by acryloyl chloride reaction with the telomere in solution, macromonomers were synthesized. Keeping the radical's concentration in the solution at low level by slow feeding of one component of the redox pair initiator in the semi-batch process, high molar mass telomere and subsequently macromonomer were obtained. In comparison to the batch process, in which macromonomer with 29 kDa average molar mass was produced, the semi-batch process resulted in 46 kDa M mass macromonomer. The semi-batch macromonomer was polymerized by inverse miniemulsion method, taking advantages of lower average concentration of radicals per particle to grow large kinetic chain lengths. Indeed, very high molar mass thermoassociating copolymers were obtained by copolymerizing the macromonomer and acrylamide, with average molar mass of 10,300 kDa versus 6200 kDa produced in the similar solution polymerization.

The selected chemistry of the components used in these processes provided thermoassociating behavior to the aqueous polymer solutions. As one of the projected applications of these copolymer solutions is the enhanced oil recovery, in which they serve as viscosity enhancers. Their performance was investigated by rheological analysis performed at different temperatures, different polymer concentrations and varying the ionic strength in the polymer solution, as well as by TEM imaging. The idea was to have improved performance under high temperature and salinity, common conditions in oil reservoirs. The performance of thermoassociating copolymers synthesized with inverse miniemulsion was compared with the similar thermoassociating copolymers synthesized in solution, and with the actual commercial acrylamide-based copolymer with very high molar mass.

The commercial acrylamide-based copolymer showed thermothinning behavior in the whole range of temperatures, polymer concentrations and ionic strengths studied. Both copolymers synthesized in the solution and inverse miniemulsion polymerization presented thermoassociating behavior, characteristic associating temperature at which thermothickening behavior started to occur. However, inverse minimeulsion copolymer demonstrated a lower temperature of association, achieving much higher viscosity values at increased temperatures likely due to the much higher molar mass achieved and higher incorporation of macromonomer units within the copolymer. This allows decreasing of the polymer concentration in the thickening solution, which on large scale brings important cost reduction. Furthermore, due to the tailored morphology and chemistry of the polymer chains (rich in amide functionalities in the pending chains) at conditions of increased salt concentration, the thermothickening behavior was even further promoted.

Data availability

The raw/processed data required to reproduce these findings cannot be shared at this time as the data also forms part of an ongoing study.

Acknowledgement

The authors gratefully acknowledge the financial support by Spanish Government (CTQ2016-80886-R) and Basque Government (GV IT999-16).

It would be also appreciated the instruments and faculty member's grant supports by Shahid Chamran University of Ahvaz, Grant No. SCU.EC98.33983, Contract No. 98/3/05/14909.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.polymertesting.2020.106332.

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