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Published in:
Journal of Applied Polymer Science

DOI:
[10.1002/app.50366](https://doi.org/10.1002/app.50366)

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Document Version
Publisher's PDF, also known as Version of record

Publication date:
2021

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Citation for published version (APA):

Boulif, N., Sebakhy, K. O., Joosten, H., & Raffa, P. (2021). Design and synthesis of novel di- and triblock amphiphilic polyelectrolytes: Improving salt-induced viscosity reduction of water solutions for potential application in enhanced oil recovery. *Journal of Applied Polymer Science*, 138(19), [50366].
<https://doi.org/10.1002/app.50366>

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ARTICLE

Design and synthesis of novel di- and triblock amphiphilic polyelectrolytes: Improving salt-induced viscosity reduction of water solutions for potential application in enhanced oil recovery

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Abstract

In the present study, three different block copolymers based on styrene, tert-butyl methacrylate, and glycidyl methacrylate (GMA) were synthesized via sequential atom transfer radical polymerization. The addition of the GMA block was found to be best performed at 60°C. The polymers were then hydrolyzed and neutralized, to afford amphiphilic block copolymers, and the rheological properties of their aqueous solutions were measured, in order to investigate solution properties relevant for enhanced oil recovery, as a function of the polymer structure. It was observed that these polymers behave as thickening agents with shear thinning behavior. As expected, the polymers were sensitive to the presence of salt, as lower viscosities were recorded in saline water. However, the viscosity is less affected by high salinity, when compared to previously studied analogous diblock systems. In the best case, the viscosity only decreased by a factor of 1.8 upon salt addition whereas it decreased by a factor of 10 in previously reported non-GMA containing polymers. Finally, thermo-responsive behavior was found for one of the synthesized polymers. In particular, a hydrolyzed triblock poly[styrene-*b*-tert-butyl methacrylate-*b*-glycidyl methacrylate], which synthesis is reported here for the first time, showed a thermothickening behavior, promising for the intended application in oil recovery.

KEYWORDS

hydrophilic polymers, oil and gas, polyelectrolytes, rheology, stimuli-sensitive polymers

1 | INTRODUCTION

The physical properties of polymers have valued them a lot of interest in the past years, especially thanks to the gained ability to fine-tune their composition and chain length. Among all the different types of polymers, an

interesting category is constituted by amphiphilic polymers, also known as polymeric surfactants, which are typically macromolecules containing simultaneously hydrophobic part and hydrophilic parts.^{1–3} Most of the studies on synthetic polymeric surfactants concern diblock polymers that contain two blocks (A and B) with

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different solvent affinities.^{1,2} Those A-B type structures are able to form micelles when dissolved, where the solvophobic blocks aggregate to form an insoluble core, and the solvophilic blocks form a “protective” shell (the corona) on the outside. Changing the chemical structure of the monomers, the polymer size and architecture, and the relative length of the blocks, can greatly alter the physical properties of the material. This array of possibilities becomes even greater upon the addition of a third monomer C in the polymer structure, yielding A-B-C polymer types.⁴ This has become especially possible since discoveries and advances were made in controlled radical polymerization.^{1,2,4} Among these methods, atom transfer radical polymerization (ATRP) has quickly reached maturity.⁵ With the proper choice of initiator, copper complex, and solvent, block copolymers with well-defined structures and narrow molecular weight distributions can be obtained.

The properties originating from the behavior of amphiphilic block copolymers in solution, in addition to the possibility to fine tune them, has valued them a lot of interest in many fields, ranging from bio-medical applications to engineering applications, such as, chemical enhanced oil recovery (cEOR).^{2-4,6-12} cEOR techniques rely on the injection of chemicals, which are able to mobilize the residual oil after water flooding, due to a decrease of the interfacial tension and/or the increase of the viscosity of the water solution used to sweep the oil.¹⁰ These two objectives can be achieved by adding surfactants and/or high molecular weight molecules (e.g., polymers), respectively. For cEOR applications, polymeric surfactants are therefore unique since they allow the combinations of these two functions into a single molecule.^{3,10}

In previous studies carried out by our research group, the synthesis via ATRP of diblock, triblock and star block polystyrene-*b*-poly(sodium methacrylate) PS-*b*-PMAA have been reported, together with their rheological characterization in water solution.¹²⁻¹⁴ These polymers showed good thickening ability at relatively low concentrations, which makes them potential candidates for cEOR applications.²⁴ Moreover, these studies also showed that the gel properties could be tuned by changing the length of the hydrophilic block. However, one limitation of such polymers was found to be a sharp decrease in the viscosity of the solution upon addition of salts due to shrinking of the coronae due to electrostatic interactions and osmotic effects involving the PMAA polyelectrolytic block.¹³

Building up on those findings, further studies have been carried out in order to investigate the effect of the incorporation of hydrophilic non-charged monomers,

such as polyethylene glycol (PEG)-acrylate and glycidyl methacrylate (GMA) to the diblock copolymers of poly(styrene-*b*-tert-butyl methacrylate).^{15,16} The addition of GMA to the polymer allowed to explore new opportunities for functionalizing the macromolecules with fluorophores and carbon nanotubes thanks to the reactive epoxide rings contained in the polymer.¹⁶ Moreover, neutral hydrophilic moiety can be obtained upon hydrolysis of the polymer. In the present paper, a study of the effect of the presence of GMA on the rheological properties of the hydrolyzed polymer in water was carried out. It was found that the ratio of GMA units to tert-butyl methacrylate groups had a larger effect on the rheological properties rather than the molecular weight of the polymer itself.

Following up on the previous work, the main aim of this paper is to take a deeper insight into the effect of neutral monomers in the chemical composition of the hydrophilic block of analogous amphiphilic block copolymers. In order to achieve this goal, different polymers based on styrene (S), tert-butyl methacrylate (tBMA) and glycidyl methacrylate (GMA) have been synthesized, hydrolyzed and their rheology in aqueous solutions have been investigated. In particular, three block copolymers have been prepared: a triblock PS-*b*-PtBMA-*b*-PGMA, a triblock PS-*b*-PGMA-*b*-PtBMA, and a diblock with a random hydrophilic block PS-*b*-P(GMA-*r*-tBMA), according to Figure 1.

The main objective of this work is to study the effect of the introduction of the GMA units in the PS-*b*-PMAA amphiphilic structures on solution viscosity. For the first time, the effect of the structure of the hydrophilic segment (random or ordered structure) and of the sequence of the GMA and tBMA blocks on the water solution rheology will be investigated, which pinpoints the novelty and originality of this study. It is expected that the polymer will be less sensitive to the presence of salts in the solution, compared to analogous PS-*b*-PMAA diblock copolymers, due to a lower charge density present in the polyelectrolyte block.¹⁶ Similar to the previous works, ATRP has been employed for the synthesis of the polymers. As anticipated, this should in principle allow for the preparation of nearly monodisperse systems with a fine-tuning of block length, and this was the initial scope of this research. However, due to the very reactive nature of the epoxide group of the GMA, it was not possible to find optimal conditions for the polymerization to be controlled; therefore, this was not entirely possible. Nonetheless, the desired block structures have been successfully synthesized, and the solution properties could be measured and compared, providing very interesting findings that will be described in the results and discussion section.

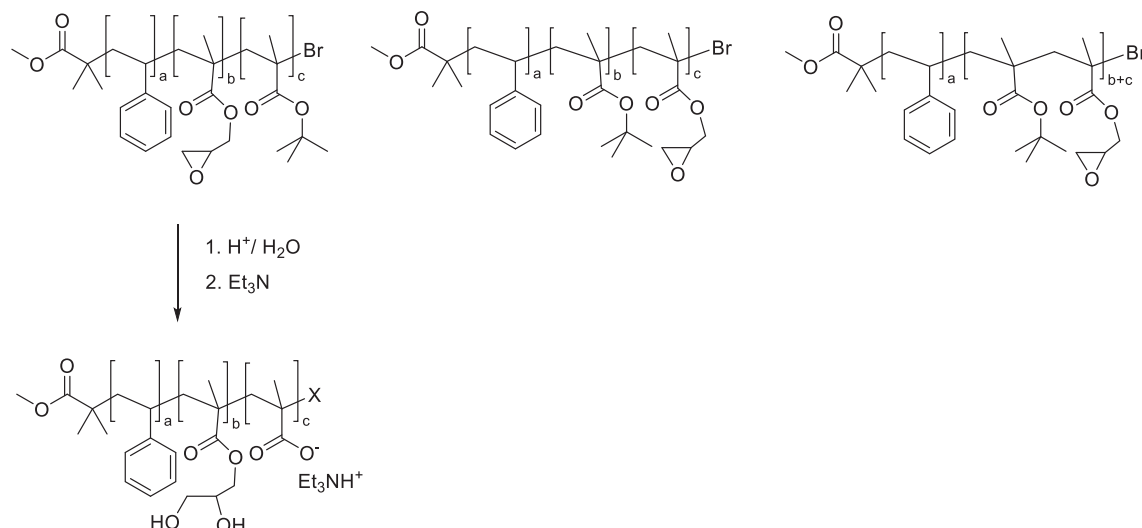


FIGURE 1 Structure of the prepared polymers and example of hydrolyzed product

2 | MATERIALS AND METHODS

2.1 | Materials

The monomers used during this synthesis (Styrene (Sigma-Aldrich, 99.9%, CAS Number 100-42-5), tert-butylmethacrylate (tBMA, Sigma-Aldrich, 98%, CAS Number 585-70-9), and glycidyl methacrylate (GMA, Sigma-Aldrich, 97%, CAS Number 106-91-2)) were purified over a short basic alumina column right before use to remove inhibitor. The catalysts (copper (I) chloride (CuCl, Sigma-Aldrich, $\geq 99\%$, CAS Number 7758-89-6) and copper (I) bromide (CuBr, Sigma-Aldrich, $\geq 98\%$, CAS Number 7787-70-4)) were regenerated before use by stirring them for at least 5 h in acetic acid to reduce the copper that has oxidized to Cu(II) back to Cu(I). After filtering, the catalysts were washed with acetic acid, ethanol, and ethyl acetate and stored in a freezer at -17°C . *N,N,N',N'',N''* pentamethyldiethylenetriamine (PMDETA, Sigma-Aldrich, 99%, CAS Number 3030-47-5), methyl- α -bromoisobutyrate (Sigma-Aldrich, $\geq 99\%$, CAS Number 23426-63-3), anisole (Sigma-Aldrich, anhydrous, 99.7%, CAS number 100-66-3), dioxane (Sigma-Aldrich, anhydrous, 99.8%, CAS Number 123-91-1), 37 wt% hydrochloric acid (HCl, Sigma-Aldrich, 37%) and triethylamine (Et_3N , Sigma-Aldrich, $\geq 99.5\%$, CAS Number 121-44-8) were used as received. Tetrahydrofuran (THF, Sigma-Aldrich, 99.9%, stabilized over BHT, CAS Number 109-99-9) was used as a solvent and for gel permeation chromatography (GPC) analysis. Deuterated dimethylsulfoxide (d_6 -DMSO, Sigma-Aldrich, anhydrous, 99.8%, CAS Number 2206-27-1) and deuterated chloroform ($CDCl_3$, Sigma-Aldrich,

anhydrous, 99.9%) were used as solvents for ^1H -nuclear magnetic resonance ($^1\text{H-NMR}$) analysis.

2.2 | Characterization techniques

2.2.1 | ^1H -Nuclear magnetic resonance

A Varian Mercury 300 MHz spectrometer was used in order to record the NMR spectra, which were then analyzed in MestReNova (V10.0.2). The samples were prepared by dissolving 5–20 mg polymer in the desired $^1\text{H-NMR}$ solvent ($CDCl_3$ or d_6 -DMSO).

2.2.2 | Fourier transform infrared

The Fourier transform infrared (FTIR) spectra were recorded using a Perkin Elmer Spectrum 2000 machine. Five milligrams of sample were mixed with 500 mg of KBr, ground in an agate mortar and the entire mixture was spread over the DRIFTS sample holder. The spectra were recorded from 400 to 4000 cm^{-1} with a resolution of 4 cm^{-1} , being these spectra the average output from 64 scans.

2.2.3 | Gel permeation chromatography

A HP1100 instrument from Hewlett-Packard was used. For samples with molecular weights lower than 25,000 g/mol, three $300 \times 7.5\text{ mm}$ PLgel $3\text{ }\mu\text{m}$ MIXED-E columns in series were used. The elution rate was

1 ml/min at a pressure of 125 bar. For samples with a molecular weight higher than 25,000 g/mol, a single 300 × 7.5 mm PLGEL 10 μm MIXED-B column, operating with a pressure drop of 22 bar and an elution rate of 1 ml/min was used. In both cases, the detector was a GBC LC 1240 RI detector. The obtained chromatograms were analyzed using the PSS WinGPC Unity software from Polymer Standard Service. The samples were prepared by dissolving 5 mg of the polymer in 1 ml THF and adding one drop toluene as an internal standard.

2.2.4 | Rheology

A Haake Mars III rheometer was used for the viscosity measurements. The software used was the Haake RheoWin Job Manager and Data Manager for performing the experiments and analyzing the results, respectively. The samples were prepared at 1 and 2.5 wt% concentration of polymer in water and were stirred for at least 16 h prior to the measurement. For the samples dissolved in saline water, the solution used had a 16 wt% NaCl concentration. The volume used for each experiment was 2 ml.

2.3 | Polymers synthesis and hydrolysis

2.3.1 | Synthesis of the polystyrene macroinitiator (PS-Br)

0.8010 g (5.58 mmol) purified Cu(I)Br were weighed and added to a three-neck round bottom flask. The system was purged with ultra-high purity nitrogen, after which 19 ml styrene (0.17 mol) and 0.71 ml (5.49 mmol) methyl- α -bromoisobutyrate were added to the flask and bubbled with nitrogen for 30 min. The reaction was started by addition of 1.2 ml (5.75 mmol) PMDETA, and the mixture was left to react at 100°C until it became so viscous that the stirring (set between 300 and 400 rpm) stopped (after about 1.5 h). The polymerization was stopped by cooling the flask in an ice bath followed by introduction of air and addition of 10 ml THF. This mixture was then passed over neutral alumina column in order to remove the copper catalyst from the polymer. The polymer was then recovered by precipitation in a 20-fold excess 2:1 methanol/water mixture and vacuum filtration over Buchner funnel. It was then re-dissolved in THF and re-precipitated in a 20-fold excess 2:1 methanol/water solution twice. After recovery by filtration and drying overnight in a vacuum

oven at 60°C, 9.936 g (yield = 57%) of the polystyrene macroinitiator (PS-Br) were obtained as a white-yellowish powder. The product was characterized by FTIR, ¹H-NMR and GPC.

2.3.2 | Synthesis of the polymers PS-b-PtBMA-b-PGMA, PS-b-PGMA-b-PtBMA, and PS-b-P(GMA-r-tBMA)

CuCl or CuBr and the PS-Br, PS-b-PtBMA, or PS-b-PGMA macro-initiators were put in a three-neck round bottom flask. The flask was purged with nitrogen, and anisole was added. Once the polymer was dissolved in anisole, GMA, tBMA, or a mixture of both were added and the reaction mixture was bubbled with nitrogen for 30 min. The reaction was started by addition of PMDETA. The mixture was reacted at the desired temperature until it became viscous, after which the reaction was stopped by cooling down in an ice bath and addition of THF. Removal of the copper catalyst was done by adding neutral aluminum oxide into the mixture under stirring until the solution turned from blue/green to very pale yellow. This mixture was then filtered and precipitated in a 20-fold excess 2:1 methanol/water solution. After filtration over a Buchner funnel, the polymer was further purified by re-dissolution in THF and re-precipitation in a 20-fold 2:1 methanol/water mixture. The polymer was recovered by filtration and dried overnight in a vacuum oven at 40°C. The yields were determined by gravimetric analysis in wt% and the products were characterized using ¹H-NMR, FTIR, and GPC. Monomer conversion could not be determined. All the reaction conditions are reported in Table 1 for the diblock polymers and in Table 2 for the triblock polymers.

2.3.3 | Hydrolysis of the PS-b-PGMA-b-PtBMA, PS-b-PtBMA-b-PGMA, and PS-b-P(GMA-r-tBMA)

0.3–1.5 g polymer were added to a round bottom flask and 10–25 ml dioxane were added in order to dissolve the polymer. The reaction was started by addition of 0.6–3 ml of 37 wt% hydrochloric acid, and the mixture was refluxed at 100°C for 4–6 h (Table 3 gives an overview of the reaction conditions). The products were recovered by precipitation in a 20-fold excess acetone or pentane followed by filtration over a Buchner funnel. The hydrolyzed polymers were left to dry overnight in a vacuum oven at 40°C and afforded a white powder. The products were characterized using FTIR and ¹H-NMR.

TABLE 1 Reaction conditions for the synthesis of the diblock polymers

Macroinitiator (mmol)	Copper catalyst ^a (mmol)	PMDETA ligand (mmol)	Monomer (mmol)	Anisole (ml)	Reaction time and temperature	Yield
0.36	0.38	0.38	tBMA 71	6	2 h 90°C	37%
0.36	0.37	0.36	GMA 71	4	1.5 h 60°C	X ^b
0.45	0.37	0.38	GMA 71	10	50 min 60°C	X ^b
0.29	0.28	0.29	GMA 53	8	4 h 25°C	22%
0.27	0.28	0.29	GMA 53	10	2.5 h 60°C	12%
0.18	0.18	0.19	GMA 38	7	1.5 h 60°C	X ^b

^aCuBr was only used for the reactions carried out at 25°C, all the other reactions were performed using CuCl.

^bThe yield was not determined due to the formation of crosslinked products.

TABLE 2 Reaction conditions for the synthesis of the triblock polymers

Macroinitiator (mmol)	Copper catalyst (mmol)	PMDETA ligand (mmol)	Monomer (mmol)	Anisole (ml)	Reaction time and reaction temperature	Yield (%)
PS-Br 0.18	CuCl 0.20	0.19	tBMA 28 GMA 19	8	6 h 60°C	28
PS-b-PGMA 0.06	CuCl 0.08	0.05	tBMA 28	5	6 h 60°C	10
PS-b-tBMA 0.03	CuBr 0.04	0.05	GMA 26	5	22 h 60°C	46

TABLE 3 Reaction conditions for the hydrolysis reactions

Polymer	Amount of polymer (μmol)	Solvent (dioxane) (ml)	Amount of 37 wt% HCl (mmol)	Reaction time (h)	Yield (%)
PS-b-PGMA-b-PtBMA	7	10	7	5.5	68
PS-b-PtBMA-b-PGMA	19	24	28	5	88
PS-b-P(GMA-r-tBMA)	50	20	24	5.25	87

2.3.4 | Neutralization of the hydrolyzed polymers

0.04–0.3 g of the hydrolyzed polymers were suspended in 1–15 ml distilled water. Triethylamine was added dropwise until the solution became neutral or slightly basic (the pH varied from 7 to 9). Once the solutions became homogeneous, the excess base was removed with an air flow and the samples were dried by putting them in an oven at 60°C for 48 h.

3 | RESULTS

3.1 | Polymer synthesis

The synthesis of the PS-Br macroinitiator and t-BMA polymers were successfully carried out as reported in previous works.^{12,13} Chain extensions were then conducted as described in the experimental section, to afford the desired polymers. Their molecular weights and compositions are reported in Table 4. The polydispersity indexes

TABLE 4 Summary of the composition of the synthesized polymers

Polymer	\bar{M}_n from $^1\text{H-NMR}$ (g/mol)	\bar{M}_n GPC (g/mol)	Polydispersity index (PDI)	Number of styrene units	Number of GMA units	Number of tBMA units
PS-b-tBMA	26,387	25,900	2.0	25	0	166
PS-b-PGMA	12,045	8534	1.61	25	40	0
PS-b-PtBMA-b-PGMA ^a	—	50,422	1.75	25	172	166
PS-b-PGMA-b-PtBMA	—	52,371	1.1	25	40	310
PS-b-PGMA-b-PtBMA ^a	—	35,746	2.09	27	30	201
PS-b-P(tBMA-r-GMA) ^a	19,678	20,320	1.87	25	45	70

^aThe rheological properties of these polymers will be reported later.

(PDI) of the obtained polymers are quite large for ATRP, suggesting that the initiation step was not fast enough in these conditions. PS-b-PGMA-b-PtBMA is the only polymer with a reasonable PDI for a polymer synthesized through ATRP, meaning that low PDI are achievable. Although the polymerization of methacrylates on a PS macroinitiator by ATRP is usually not an ideal choice⁵, in our previous work it proved it to be the most successful approach to make block copolymers with a long methacrylate block and a short PS block.¹³ The halogen exchange technique can be used in order to ensure better control via fast initiation and slow propagation.¹⁷

Polymerization conditions have not been optimized, as the main focus of this study was on the study of solution properties. The use of ATRP is still justified as one powerful and mild method to obtain block copolymers, although we acknowledge that the broad dispersity and the low control do not allow for more insight into structure-properties relationships.

The polymers were characterized using $^1\text{H-NMR}$, FTIR, and GPC. Full results and spectra are included in the Supporting Information.

As it can be seen from Table 4, the PDI is generally not satisfactory for an ATRP process. For example, the GPC of the diblock PS-b-tBMA present a narrow peak, but with pronounced tailing (Figure S6), showing that the conditions employed are not optimal. The most challenging step of the synthesis, which did not allow for good control over the process, proved to be the polymerization of GMA, due to the formation of insoluble products. Tuning the reaction time (and hence conversion of the monomer) to achieve the highest possible yield was rather tricky as the solutions went from very low viscosity solution to completely crosslinked gel in a matter of min. This might be due to high reactivity of the epoxide ring, which causes crosslinking between the different polymer chains.¹⁸ The epoxide ring, in fact, can be easily opened by action of an electrophile or a nucleophile, due to high strain, causing the initiation of ring opening polymerization. This crosslinking can be due to several factors. It is

possible that the copper catalyst used promotes gelation as discussed in previous studies on the ARGET ATRP of GMA, which showed that using lower copper concentrations suppresses crosslinking of the product.¹⁸ In addition, the presence of a tertiary amine in the mixture (PMDETA ligand) can also contribute to the crosslinking mechanisms of well-known epoxide ring curing using amines.¹⁹ Finally, thermal instability of the epoxide ring could also be another factor contributing to crosslinking. Some previous studies report that drying the products in an oven at 60°C might promote crosslinking between the chains.²⁰ Only conversions below 15% could be achieved at a reaction temperature of 60°C, as longer reaction times resulted in the formation of a crosslinked gel that could not be further processed. As such, Hansson et al. suggested that the conversion should not exceed 40% as it was observed that gelation starts to occur at this conversion value.²⁰

The maximum yield achieved in the polymerization of GMA, was of 22% when performing the reactions at room temperature with CuBr as a catalyst (0.035 mmol/ml) and monomer concentration of 6.63 mmol/ml (Table 1). However, the GPC chromatogram of the obtained polymer displayed a multimodal distribution of molecular weight (see Figure 2), which indicates that the polymerization did not proceed in a controlled fashion. The polydispersity of this polymer was of 1.76. This was most likely due to the very slow initiation step resulting from the reaction being done at room temperature. Therefore, a higher reaction temperature (60°C) was found to be more suitable for the reaction with a GMA concentration of 5.3 mmol/ml and a copper catalyst concentration of 0.028 mmol/ml. However, the yield achieved in this case was only 12%. In that case, the polydispersity was of 1.61, which is still quite high for ATRP but better than the one obtained from the room temperature reaction, and the GPC shows one single peak (Figure 2b). For this reason, a reaction temperature of 60°C was adopted throughout all this work for incorporation of GMA.

Further investigation would be required to achieve better control in the synthesis of these kind of ter-

FIGURE 2 Gel permeation chromatography chromatograms of the PS-*b*-PGMA obtained from the reactions at: (a) room temperature; (b) 60°C

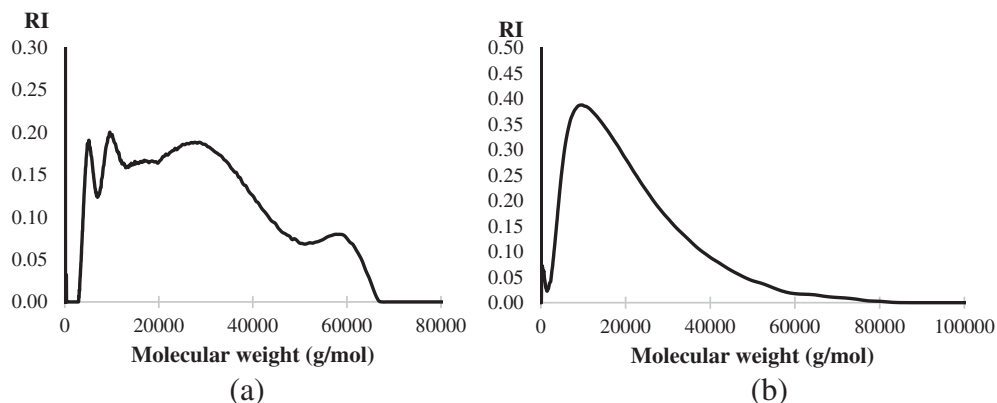
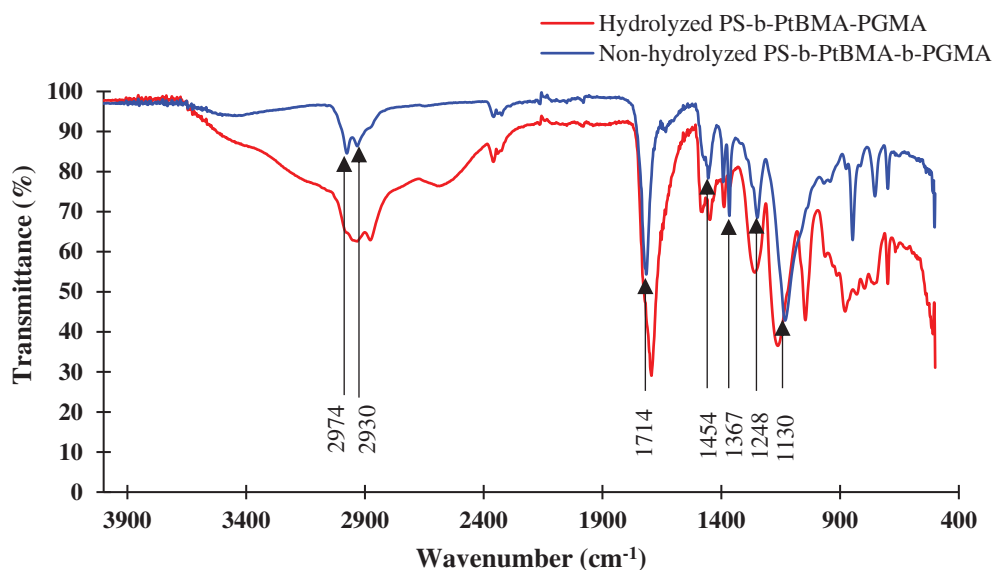


FIGURE 3 Comparison of the Fourier transform infrared (FTIR) spectrum of hydrolyzed and non-hydrolyzed polymers [Color figure can be viewed at wileyonlinelibrary.com]



polymers with ATRP. Other controlled radical polymerization techniques, such as the ARGET variant of ATRP or RAFT, might prove to be more suitable. As the main goal of this work was the study of solution properties, and not optimization of reaction conditions, we did not further investigate the polymerization.

The obtained polymers were then hydrolyzed. All hydrolyzed polymers were characterized by FT-IR. Comparison of the FTIR spectra before and after hydrolysis showed that a broad peak at about 3000 cm^{-1} appeared due to the formation of —OH groups (see Figure 3). The polymer PS-*b*-PGMA-*b*-PtBMA with low polydispersity ($\text{PDI} = 1.1$, Table 4) produced insoluble material after hydrolysis, possibly because of cross-linking, therefore its solution properties could not be investigated. The other ter-polymers were soluble, and their $^1\text{H-NMR}$ spectra showed that full hydrolysis was reached. Indeed, the two characteristic peaks of the epoxide protons at 3.8 and 4.2 completely disappeared, leading to a peak for the alcohol protons at 5.53. The large peak of the 9 tert-butyl

methacrylate moiety is also not to be found in the hydrolyzed polymer. An example $^1\text{H-NMR}$ of a hydrolyzed polymer, showing complete conversion, is displayed in Figure 4. The $^1\text{H-NMR}$ is similar to that reported in a previous study.¹⁶ In the FTIR spectra of PS-*b*-PtBMA-*b*-PGMA the peaks wavenumber values are corresponding to the spectrum of the non-hydrolyzed polymer. The peaks are associated to the following signals.¹⁶ FT-IR (wavenumber in cm^{-1}): 2974 and 2930 cm^{-1} (C—H stretching); 1714 cm^{-1} (C=O stretching of the ester); 1454 and 1367 cm^{-1} (C—H bending); 1248 and 1130 cm^{-1} (C—O stretching). The hydrolyzed polymer displays the same peaks, with the addition of a broad peak between 2233 and 3605 cm^{-1} , which corresponds to the O—H stretching.

3.2 | Rheology experiments

After neutralization with Et_3N , polymer solutions of 1 and 0.5 wt% were made both in distilled water and in

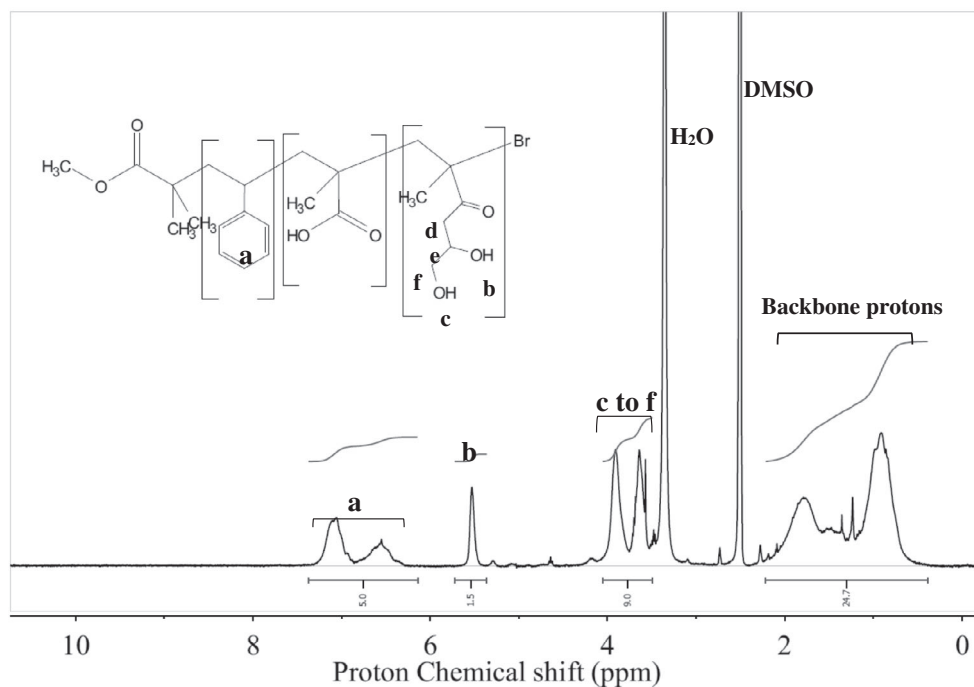


FIGURE 4 ^1H -nuclear magnetic resonance (^1H -NMR) of a hydrolyzed polymer in d_6 -DMSO

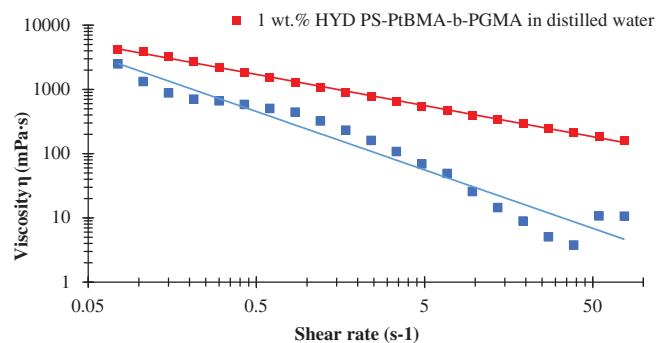


FIGURE 5 Viscosity of the hydrolyzed PS-*b*-PtBMA-*b*-PGMA as function of the shear rate [Color figure can be viewed at wileyonlinelibrary.com]

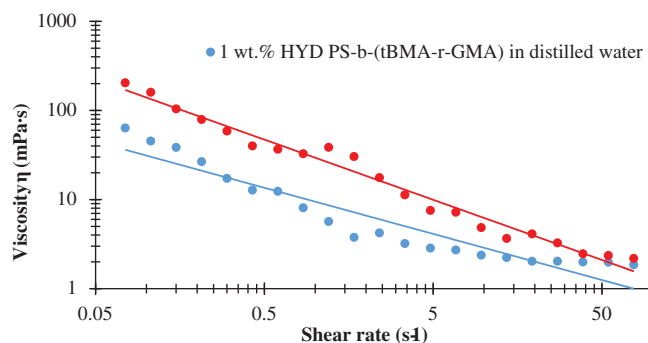


FIGURE 6 Viscosity of the hydrolyzed PS-*b*-(PtBMA-*r*-GMA) as function of the shear rate [Color figure can be viewed at wileyonlinelibrary.com]

1.6 or 1 wt% saltwater. These concentrations were chosen to be able to compare directly the salinity effect on these polymers with diblock PS-*b*-PMAA previously reported.¹³ All the polymers were well soluble in both saline and distilled water, except for one of the hydrolyzed PS-*b*-PGMA-*b*-PtBMA, which showed limited solubility in both distilled and saltwater. This might be attributed to incomplete hydrolysis, or to irreversible crosslinking between neighboring GMA units upon addition of the tBMA block or during storage of the product.²⁰ Indeed, previous studies have shown that even storing the polymer for a long period of time at room temperature was already enough for the polymer to crosslink due to the humidity present in the air.²⁰

In line with analogous systems, all the polymers were found to be good viscosifiers and display shear-thinning behavior, as depicted in Figures 5–7. The reduction in viscosity at higher shear rates is due to the loss of connectivity between the micelles in solution, making it easier for the solution to flow at higher shear rates. Nevertheless, the viscosity remains always remarkably higher than that of water, indicating that the polymers behave as good thickening agents. Since all the polymers have different molecular weights, their thickening abilities cannot be easily compared to one another.

All the polymers were fully soluble in water, except for the hydrolyzed PS-*b*-PGMA-*b*-PtBMA which had a lower solubility in water and was therefore only tested at

a polymer concentration of 0.5 wt%. It was found that all three polymers were still sensitive to the presence of salts due to the corona shrinking caused by the higher salt concentration, as shown in Figures 5–7. However, these

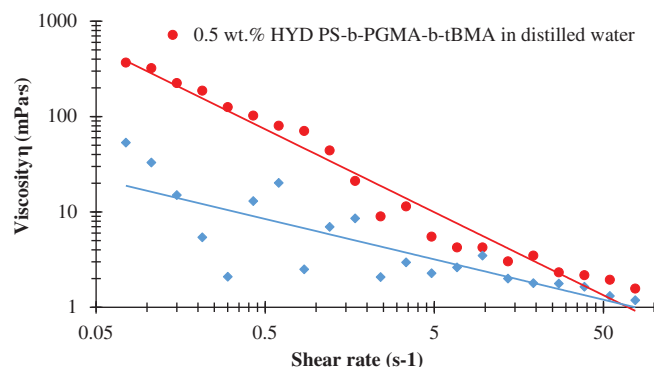


FIGURE 7 Viscosity of the hydrolyzed PS-*b*-PGMA-*b*-PtBMA as a function of the shear rate [Color figure can be viewed at wileyonlinelibrary.com]

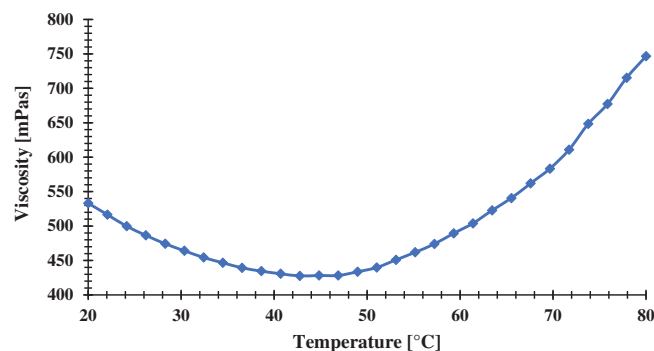


FIGURE 8 Viscosity versus temperature for the PS-*b*-PtBMA-*b*-PGMA polymer at a constant shear rate 5 s^{-1} [Color figure can be viewed at wileyonlinelibrary.com]

polymers still perform better than PS-*b*-PMAA reported in previous works,¹³ as those had a viscosity, which was 10 times lower at a salt concentration of 1.6 wt% and shear rate of 0.1 s^{-1} . Here, the PS-*b*-PtBMA-*b*-PGMA polymer showed only a viscosity 1.8 times lower in the presence of salt and the random polymer had a viscosity only 3 times lower than in demineralized water. The PS-*b*-PGMA-*b*-PtBMA does not show an improvement of the polymer behavior in the salt solution. However, it should be noted that the polymer concentration is half that of the other samples, which also affects the results, as the ratio polymer/salt is different.

In the context of EOR, the solution viscosity is of importance since solution with increased viscosity have a lower mobility ratio, and thus, have an improved sweep efficiency.¹⁹ Hence, this lower sensitivity to the presence of salt in the water is of importance for the desired cEOR application as the water injected in the wells to displace the oil typically comes from abundant sources of water that are typically salty, such as, seawater (notably offshore) or produced water.

Measurements of viscosity at constant shear rate of 5 s^{-1} , but increasing temperature, were also performed and are shown in Figure 8. This is relevant for EOR application, as reservoir temperatures are notoriously high.^{3,11}

It was found that the PS-*b*-PtBMA-*b*-PGMA polymer also exhibited a thermal-thickening behavior at temperatures above 45°C , as depicted in Figure 8. A plausible explanation for this behavior is that as the polymer chains gain thermal energy, the hydrogen bonds formed by the hydrolyzed GMA block become weaker, increasing the hydrophobicity of the outer shell, and causing formation of a network, responsible for increased viscosity. This structural change upon temperature increase has been already observed for other systems, such as

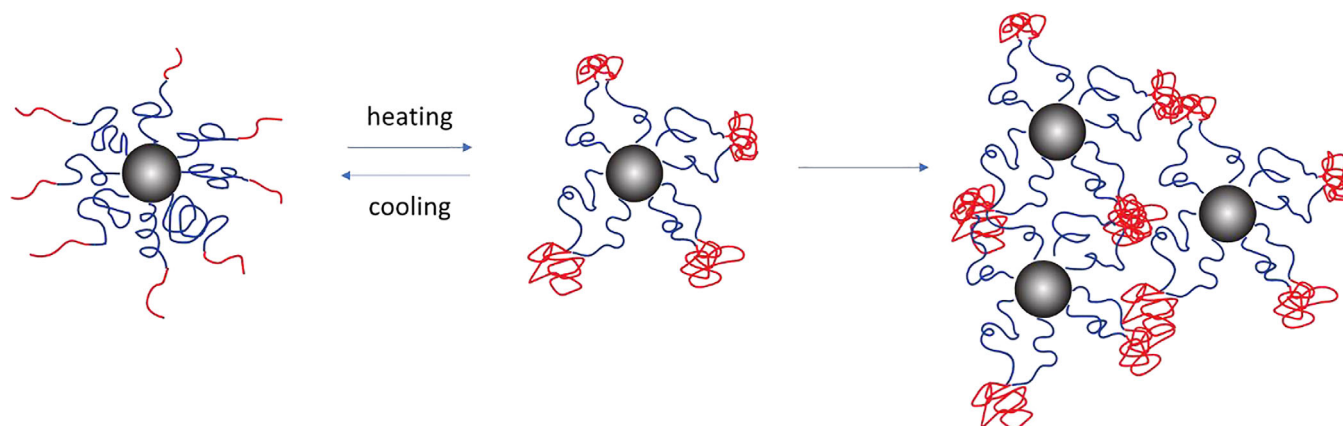


FIGURE 9 Aggregation of the micelles upon heating. Redrawn from Zhou et al.²¹ [Color figure can be viewed at wileyonlinelibrary.com]

poly(ethylene-alt-propylene)-b-poly(ethylene oxide)-b-poly(N-isopropylacrylamide) terpolymers, as depicted in Figure 9.²¹

To the best of the authors knowledge, it is the first time that this effect was investigated and found in a PS-b-PtBMA-b-PGMA polymer. This thermal-thickening behavior is of interest for EOR applications as the extracting solution can easily be pumped at high shear rates and low temperatures, which can be found in the wellbore. However, as the solution goes deeper in the oil well, its viscosity will increase due to the lower shear rates caused by the porous structure of the native rocks and the higher temperatures.²² Therefore, this effect could potentially increase oil recovery while keeping low operational costs. To further investigate the potential of this polymer for EOR applications, the surface properties of the polymers should also be investigated as those are also of importance when it comes to EOR. Indeed, the surfactant should also be able to reduce the surface tension between the oil-rock-water interface.²³ It is expected that those surfactants would also greatly lower the surface tension as foaming was observed in some samples.

4 | CONCLUSIONS

In this work, three different amphiphilic block copolymers consisting of styrene, glycidyl methacrylate, and tert-butyl methacrylate, characterized by a different distribution of monomers, were synthesized using ATRP polymerization. Di- and triblock copolymers were successfully prepared, although the very reactive nature of GMA did not allow to obtain structures with low PDIs, typical of controlled radical polymerizations. It was found that the polymerization of glycidyl methacrylate works best at 60°C with low copolymer concentrations. The obtained polymers were then hydrolyzed, to render them water soluble, and the rheology of the water solutions was studied in demineralized and saline water. It was found that all the solutions were remarkably viscous at relatively low concentration, and shear-thinning. The viscosity was lower when salt was present in the solution, as expected from polyelectrolytes, due to corona shrinking of the micelles; however, when compared with analogous diblock PS-b-PMAA, the drop in viscosity due to the presence of salt is less dramatic in relative value. We attributed this behavior to the presence of neutral GMA groups, which, while still maintaining good viscosifying properties, are not affected by the increased ionic strength of the solution.

Additionally, in this study a thermo-thickening response of poly(styrene)-*block*-poly(tert-butyl methacrylate)-*block*-poly(glycidyl methacrylate) polymer was

recorded, for the first time to our knowledge. This makes this polymer even more attractive for enhanced oil recovery, as reservoir temperatures are usually high, or for other applications in smart materials.

In future work, we plan to optimize the polymers synthesis, in order to enable a better structure-properties relationship study, and investigate more in detail rheological behavior, especially as a function of the temperature. Moreover, surface/interfacial tension will be measured, as foaming of the samples in water indicated that the polymers are surface active. Finally, the most promising systems in terms of rheology and surface tension, will be evaluated in simulated oil recovery experiments, such as core flood tests.

CONFLICT OF INTEREST

The authors declare no potential conflict of interest.

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REFERENCES

- [1] S. Liu, S. P. Armes, *Curr. Opin. Colloid Interface Sci.* **2001**, *6*, 249. [https://doi.org/10.1016/S1359-0294\(01\)00090-5](https://doi.org/10.1016/S1359-0294(01)00090-5).
- [2] T. Tadros, *Adv. Colloid Interface Sci.* **2009**, *147–148*, 281. <https://doi.org/10.1016/j.cis.2008.10.005>.
- [3] P. Raffa, D. A. Z. Wever, F. Picchioni, A. A. Broekhuis, *Chem. Rev.* **2015**, *115*, 8504. <https://doi.org/10.1021/cr500129h>.
- [4] I. W. Wyman, G. Liu, *Polymer* **1950–1978**, *2013*, *54*. <https://doi.org/10.1016/j.polymer.2012.12.079>.
- [5] K. Matyjaszewski, *Macromolecules* **2012**, *45*, 4015. <https://doi.org/10.1021/ma3001719>.
- [6] A. Blanz, S. P. Armes, A. J. Ryan, *Macromol. Rapid Commun.* **2009**, *30*, 267. <https://doi.org/10.1002/marc.200800713>.
- [7] T. F. Tadros, A. Vandamme, B. Leveck, K. Booten, C. V. Stevens, *Adv. Colloid Interface Sci.* **2004**, *108–109*, 207. <https://doi.org/10.1016/j.cis.2003.10.024>.
- [8] G. Riess, *Colloids Surf. Physicochem. Eng. Asp.* **1999**, *153*, 99. [https://doi.org/10.1016/S0927-7757\(98\)00429-4](https://doi.org/10.1016/S0927-7757(98)00429-4).
- [9] M. A. C. Stuart, W. T. S. Huck, J. Genzer, M. Müller, C. Ober, M. Stamm, G. B. Sukhorukov, I. Szleifer, V. V. Tsukruk, M. Urban, F. Winnik, S. Zauscher, I. Luzinov, S. Minko, *Nat. Mater.* **2010**, *9*, 101. <https://doi.org/10.1038/nmat2614>.
- [10] P. Raffa, A. A. Broekhuis, F. Picchioni, *J. Pet. Sci. Eng.* **2016**, *145*, 723. <https://doi.org/10.1016/j.petrol.2016.07.007>.
- [11] P. Raffa, P. Druetta, *Chemical Enhanced Oil Recovery: Advances in Polymer Flooding and Nanotechnology*, De Gruyter, Berlin **2019**.
- [12] P. Raffa, M. C. A. Stuart, A. A. Broekhuis, F. Picchioni, *J. Colloid Interface Sci.* **2014**, *428*, 152. <https://doi.org/10.1016/j.jcis.2014.04.047>.
- [13] P. Raffa, P. Brandenburg, D. A. Z. Wever, A. A. Broekhuis, F. Picchioni, *Macromolecules* **2013**, *46*, 7106. <https://doi.org/10.1021/ma401453j>.
- [14] M. Meijerink, F. van Mastrigt, L. E. Franken, M. C. A. Stuart, F. Picchioni, P. Raffa, *Pure Appl. Chem.* **2017**, *89*, 1641. <https://doi.org/10.1515/pac-2016-1021>.

- [15] P. Raffa, A. A. Broekhuis, F. Picchioni, *J. Appl. Polym. Sci.* **2016**, *133*, 44100. <https://doi.org/10.1002/app.44100>.
- [16] F. Di Sacco, A. Pucci, P. Raffa, *Nanomaterials* **2019**, *9*, 458. <https://doi.org/10.3390/nano9030458>.
- [17] K. Matyjaszewski, D. A. Shipp, J.-L. Wang, T. Grimaud, T. E. Patten, *Macromolecules* **1998**, *31*, 6836. <https://doi.org/10.1021/ma980476r>.
- [18] M. Jonsson, D. Nyström, O. Nordin, E. Malmström, *Eur. Polym. J.* **2009**, *45*, 2374. <https://doi.org/10.1016/j.eurpolymj.2009.05.002>.
- [19] I. T. Smith, *Polymer* **1961**, *2*, 95. [https://doi.org/10.1016/0032-3861\(61\)90010-6](https://doi.org/10.1016/0032-3861(61)90010-6).
- [20] S. Hansson, E. Östmark, A. Carlmark, E. Malmström, *ACS Appl. Mater. Interfaces* **2009**, *1*, 2651. <https://doi.org/10.1021/am900547g>.
- [21] C. Zhou, M. A. Hillmyer, T. P. Lodge, *Macromolecules* **2011**, *44*, 1635. <https://doi.org/10.1021/ma102786q>.
- [22] Y. Fan, N. Boulif, F. Picchioni, *Polymer* **2018**, *10*, 92. <https://doi.org/10.3390/polym10010092>.
- [23] L. Torres, A. Moctezuma, J. R. Avendaño, A. Muñoz, J. Gracida, *J. Pet. Sci. Eng.* **2011**, *76*, 6. <https://doi.org/10.1016/j.petrol.2010.11.022>.
- [24] P. Raffa, F. Picchioni, *J. Pet. Sci. Eng.* **2020**, in press. <https://doi.org/10.1016/j.petrol.2020.108181>

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How to cite this article: Boulif N, Sebakhy KO, Joosten H, Raffa P. Design and synthesis of novel di- and triblock amphiphilic polyelectrolytes: Improving salt-induced viscosity reduction of water solutions for potential application in enhanced oil recovery. *J Appl Polym Sci.* 2021;138:e50366. <https://doi.org/10.1002/app.50366>