



Synthesis and Characterization of Acrylamide-Based Homo- and Copolymers and Their Application in Water-Based Drilling Fluid

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INTRODUCTION

Water-based drilling fluid (WBDF) is a colloidal dispersion containing matrix, solid and chemical phases, and its roles in during drilling process are transferring drilled cutting to surface, forming filter cake on the well, cooling and bit lubricating [1]. Hydrophilic polymers are one of the most important polymers used in drilling fluid (DF), controlling the fluid viscosity and reducing the fluid loss. Among other hydrophilic polymers, partially hydrolyzed polyacrylamide (PHPA) is able to increase fluid viscosity at low concentrations due to its high hydrophilicity and high molecular weight. However, this polymer has not a good resistant against harsh operation conditions such as high salinity and temperature. It has been shown in the previous works that incorporating a small amount of hydrophobic monomers into the hydrophilic acrylamide (AM) chains results in the three-dimensional physical networks via

hydrophobic associations, leading to significant increase in the aqueous solution viscosity [2].

In the present study, polyacrylamide homopolymer and acrylamide/styrene (AM/St) copolymer were synthesized via micellar copolymerization method and then characterized. Based on the literature, copolymers synthesized via this method have a multiblock structure as a hydrophobic blocks incorporated into the hydrophilic chains. Finally, effect of presence of synthesized polymers in the WBDF was investigated.

EXPERIMENTAL PROCEDURE

SYNTHESIS OF ACRYLAMIDE-BASED HOMO- AND COPOLYMERS

First, 1.2 g AM, for synthesis of homopolymer (P1), and 1.1702 g AM and 0.0298 g St, for synthesis of copolymer (P2), were added to 40 ml distilled water. After dissolution, 20 mg ammonium persulfate as an initiator was added

under magnet stirring. After sealing the reaction ampule, the solution was purged with N_2 gas for 30 min and then immersed in water bath at 60 °C for 8 h. Finally, reaction was terminated with adding small amount of hydroquinone, washed two times with excess acetone and dried under vacuum at 60 °C for 24 h.

CHARACTERIZATION

Monomer conversion was determined via gravimetric method using corresponding equation [3]. Length of St blocks in the copolymer chains was also calculated via an equation reported in the literature [4]. FT-IR spectroscopy was used to characterize functional groups of the synthesized polymers. Also, viscosity method was used to measure intrinsic viscosity in 0.1 M NaCl aqueous solution, from which viscosity-average molecular weight was estimated using Mark-Houwink equation with corresponding constants reported for 0.1 M NaCl aqueous solution in the literature [5]. Intrinsic viscosity was measured to be 215.69 and 122.67 ml/g for homo- and copolymer respectively. To investigate the effect of polymer concentration on the aqueous solution viscosity, Brookfield viscometer was used under room temperature at a shear rate of 2.55 s^{-1} .

Three different concentrations of polymers P_1 and P_2 were used in the WBDF recipe. Corresponding fluids were subjected to the viscometry and fluid loss tests. WBDF contains 350 ml tap water, 0.5 g sodium carbonate, 15 g bentonite and given amount of synthesized polymer. To investigate salt effect, above- mentioned fluid was also prepared with a water having 4 wt.% NaCl salt (namely sea water). Thermal stability of WBDFs was evaluated via hot rolling at 120 °C for 4 h and measuring properties of aged fluids.

RESULTS AND DISCUSSION PHASE COMPOSITION ANALYSIS

Conversion of monomer to polymer was obtained to be 94 and 89 wt.% for reactions P_1 and P_2 respectively. Also, viscosity-average molecular weight was estimated to be 6.6×10^5 and $3.1 \times 10^5 \text{ g/mol}$ for homo- and copolymer respectively. Higher conversion and molecular weight of homopolymer can be attributed to presence of transfer reaction in the micellar copolymerization resulted from emulsified used in this reaction [3]. Moreover, length of St blocks in the AM/St copolymer (P_2) was estimated to be 3.

FT-IR spectra of polymers are shown in Fig. 1. Due to low amount of St incorporated into the copolymer, there is no distinguishable absorption band for St (Presence of St in the copolymer was verified by NMR). Absorption bands appeared at 3180 and 3350 cm^{-1} can be assigned to amine stretching vibrations while that appeared at 1680 cm^{-1} is related to the amide carbonyl group. Also, peaks appeared at 1550, 2940 and 1460 can be assigned to the amine group bending vibration and C-H stretching and bending vibrations respectively [5]. Based on the appeared peaks, it seems that polymerization has been performed successfully in both reactions.

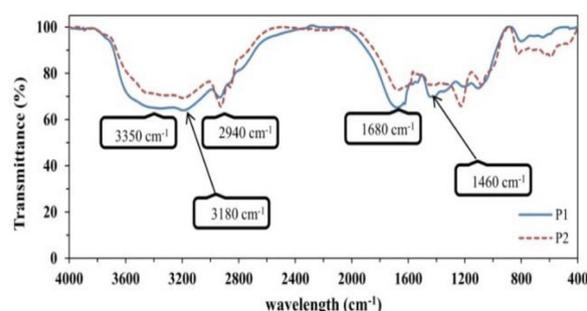


Figure 1: FT-IR spectra of homo- and copolymer.

Results of apparent viscosity of aqueous solution versus polymer concentration are shown in Fig. 2, showing an increase in the apparent viscos

ity by increasing the polymer concentration. It means that added polymers had a positive effect in the aqueous medium. Fig. 2 shows clearly that apparent viscosity of P2 solution is much higher than that of P2 solution. In spite of lower molecular weight of P2, higher viscosity for copolymer P2 can be attributed to hydrophobic association between styrene block units in the copolymer chains [3].

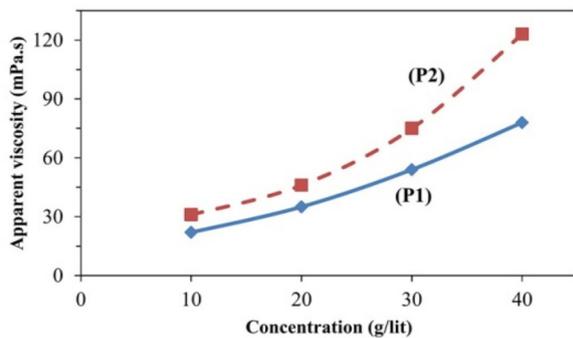


Figure 2: Changes in aqueous solution apparent viscosity as a function of polymer concentration at room temp. and shear rate of 2.55 s^{-1} . Effect of homo- (P1) and copolymer (P2) on the properties of the tap water and sea water WBDFs is given in Table 1 before (BHR) and after hot rolling (AHR). Moreover, it is clear from this table

that rheology parameters and fluid loss have been improved in the presence of polymers. In the tap water, homopolymer P1 resulted in more improvements in comparison with the copolymer P2. It means that in tap water, effect of molecular weight of the polymers is more than that of the hydrophobic associations [2]. On the other hand, when sea water was used, ability of the copolymer P2 to maintain rheological properties and fluid loss against salt and temperature was observed to be much higher than that of homopolymer P1. These results show that WBDF prepared with AM/St copolymer has a higher resistance against operating conditions such as salt and temperature. It can be attributed to formation of stronger hydrophobic physical networks in the presence of salt via a phenomenon so called “Salting effect” [6]. In the presence of salt, water molecules available for dissolving copolymer chains decrease; hence, hydrophobic blocks phase separate from water medium and form hydrophobic associations.

Table 1: Effect of polymers P1 and P2 on the apparent viscosity, plastic viscosity, yield point and fluid loss of tap and sea waters- based WBDFs before (BHR) and after hot rolling (AHR).

Fluid type	Apparent Viscosity (cP)		Plastic Viscosity (cP)		Yield Point (lbf/100ft ²)		Fluid Loss (ml)	
	BHR	AHR	BHR	AHR	BHR	AHR	BHR	AHR
Tap Water	8	12	4	8	8	8	18.5	48
Tap Water + 0.21 wt.% P1	28.5	10.5	7	7	43	7	14.5	15
Tap Water + 0.4 wt.% P1	118	15.5	73	10	90	11	11.5	10.2
Tap Water + 0.7 wt.% P1	100	17	65	9	70	16	11.7	12.5
Tap Water + 0.21 wt.% P2	15.5	9.5	5	6	21	7	19	16.5
Tap Water + 0.4 wt.% P2	28.5	12.5	10	9	37	7	13.8	13.3
Tap Water + 0.7 wt.% P2	69.5	11	24	6	91	10	13.7	14.5
Sea Water	15.5	11	5	5	21	12	188	-
Sea Water + 0.21 wt.% P1	7	9	7	9	0	0	70	57
Sea Water + 0.4 wt.% P1	16	26.5	22	16	0	21	19	23.5
Sea Water + 0.7 wt.% P1	47.5	18	18	13	59	10	13.5	16.2
Sea Water + 0.21 wt.% P2	14	4.5	13	3	2	3	103	45
Sea Water + 0.4 wt.% P2	16	5.5	18	4	0	3	24.5	27
Sea Water + 0.7 wt.% P2	18.5	8	16	7	5	2	11.5	23.5

CONCLUSIONS

Polyacrylamide homopolymer P1 and AM/St copolymer P2 were successfully synthesized and characterized. Conversion of monomers was obtained to be 94 and 89 wt.% and viscosity-average molecular weight was estimated to be 6.6×10^5 and 3.1×10^5 g/mol for homo- and copolymer respectively. Decreased conversion and molecular weight of copolymer P2 relative to homopolymer P1 was attributed to occurrence of transfer reactions to emulsifier in the micellar copolymerization of AM and St. Apparent viscosity measurements showed higher thickening capability of the copolymer P2. It was attributed to intermolecular interactions via hydrophobic associations, resulting in the three dimensional physical network. Finally, synthesized polymers were used to prepare tap and sea water-based drilling fluid. Although homopolymer P1 performed more effective in the tap water-based fluid; however, copolymer P2 showed high performance against salinity and high temperature where rheological properties and fluid loss remained high enough under salinity and high temperature conditions

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