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Brine-Soluble Zwitterionic Copolymers with Tunable Adsorption on Rocks

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ABSTRACT: Injection of aqueous fluids into reservoirs as an enhanced oil recovery (EOR) tool has been of great interest in petroleum engineering. EOR using viscous polymer solutions improves the volumetric sweep efficiency. However, significant polymer adsorption on reservoir rock surfaces is one of the greatest challenges in polymer-flooding EOR. We have synthesized and characterized five zwitterionic copolymers and studied their static adsorption on limestone surfaces in seawater at high temperatures and salinities. Our results indicate that polymer adsorption directly correlates to a small percentage of functional co-monomers on the polymer backbone. One particular copolymer shows negligible static adsorption on limestone surfaces.

KEYWORDS: zwitterionic, copolymer, free-radical polymerization, tunable, adsorption

INTRODUCTION

Polymer flooding is widely used in chemical enhanced oil recovery (CEOR) and allows for a more efficient water flood sweep by increasing solution viscosity.1,2 However, retention of polymers is among the biggest challenges when developing applications in this field.3–7 Numerous studies have shown that adsorption of polymers on rock surfaces, mechanical entrapment of polymers in pore matrices, and fluid flow-induced hydrodynamic retention of polymers4,8–10 contribute to the overall polymer loss (polymer retention) in the porous media of rocks. These factors reduce the fluid viscosity and therefore the efficacies of chemicals, requiring the injection of large quantities of chemicals to compensate for the material (viscosity) loss.11 The widely studied polymers for EOR are polyacrylamide (PAM), partially hydrolyzed polyacrylamide (HPAM), and hydrophobically modified polyacrylamide (HMPAM), which is a type of associative polymer.1 PAM and HPAM polymers have limited long-term stability especially in the high-temperature and high-salinity downhole environment, and HMPAM with improved long-term stability in brines has shown high polymer retention.12

Zwitterionics13 containing both anionic and cationic groups can be stable in high salinity fluids at high temperatures as a result of the “anti-polyelectrolyte effect”.14,15 In recent years, polyzwitterions have been used in anti-biofouling coatings, drilling fluids, and EOR, which all rely on their unique surface properties.16,17 For example, Sabhapondit et al. reported the synthesis of N,N-dimethyl-acrylamide-co-Na-2-acrylamido-2-methyl propanesulfonate, which was able to achieve 66% viscosity retention after a month at 120 °C.18 Subsequently, Ye et al. synthesized a novel water-soluble associative polymer by copolymerization and sulfomethylation using acrylamide and N-allyl benzamide with even better salt and temperature tolerance.19 As mentioned previously, the retention of these polymers in porous media is the collective result of adsorption, mechanical entrapment, and flow-induced hydrodynamic retention.4,5,11 On the other hand, the retention of polyzwitterions in porous media is less studied or understood. The competition between attractive forces (e.g., van der Waals interactions, entropic contribution, or specific interactions) and electrostatic forces, which can be either repulsive or attractive, governs polymer adsorption on a charged surface.20,21 Structural modifications on polymers could be used to control polymer adsorption. We intend to study the polymer adsorption on rock surfaces focusing on the contribution of particular functional groups on the side chains of zwitterionic polymers. Furthermore, the potential to finely tune polymer adsorption by varying a small fraction of certain functional groups on the polymers is extremely attractive not only in EOR but also in some other applications22 that prefer polymer adsorption on mineral surfaces.

EXPERIMENTAL SECTION

Materials. All reagent-grade materials were purchased from Sigma-Aldrich and used without further purification unless otherwise
noticed. Crushed, sieved, and hot solvent (toluene and methanol)-
cleaned pieces of Indiana limestone with diameters ranging from 0.5 to
1.41 mm were purchased from Core Laboratories, Houston, TX,
and used as received. The chemical component of Indiana limestone
is 98–99% calcite (CaCO₃).

**Synthesis of the Copolymer of Poly(vinyl imidazole-co-styrene)**

(0.9:0.1) 1’ and Sulfozwitterionic 1. 1-Vinyl imidazole (2 g, 21.25
mmol), styrene (0.2459 g, 2.36 mmol), azobisobutyronitrile (AIBN, 0.03877 g, 0.236 mmol, 1 mol %), and DMSO (5 mL) were
combined in a Schlenk tube with a stir bar. The reaction mixture
was degassed using freeze–pump–thaw (3×) and sealed under a static
inert atmosphere and stirred at 60°C for 4 days. The resulting light
yellow viscous solution was cooled and diluted by the addition of
methanol. The mixture was precipitated into acetone (2×) and then
dried overnight to produce copolymer 1’, which was a clear hard light
yellow solid. 1’ was characterized by ¹H NMR and ¹³C NMR in
deuterated methanol-d₄ (Figure S1). To a solution of copolymer 1’ (1 g, 9.46 mmol of imidazole moieties) in methanol was added 1, 3-propane
sultone (1.386 g, 11.35 mmol, 1.2 equiv). The reaction mixture was
refluxed overnight under an inert atmosphere and the resulting
zwitterionic copolymer 1 precipitated out. Zwitterionic copolymer 1 was filtered out and then washed with a mixture of methanol and diethyl ether (1:1, 2×). Zwitterionic copolymer 1 was characterized by ¹H NMR and ¹³C NMR in
methanol-d₄ (Figure S2).

**Synthesis of Poly(vinyl imidazole-co-4-aminostyrene)**

(0.95:0.05) 2’ and Sulfozwitterionic 2. 1-Vinyl imidazole (5 g, 53.1 mmol), 4-
aminostyrene (0.323 g, 2.796 mmol), azobisobutyronitrile (AIBN, 0.092 g, 0.559 mmol, 1 mol %), and DMSO (5 mL) were combined
in a Schlenk tube with a stir bar. The reaction mixture was degassed
using freeze–pump–thaw (3×) and sealed under a static inert
atmosphere and stirred at 60°C for 4 days. The resulting light yellow
viscous solution was cooled and diluted by the addition of methanol.
The mixture was precipitated into acetone (2×) and then dried overnight
to produce copolymer 2’, which was a clear hard light yellow solid.
To a solution of 2’ (1.085 g, 10.6 mmol imidazole moieties) in methanol was added 1, 3-propane sultone (1.557 g, 12.75 mmol, 1.2
equiv). The reaction mixture was refluxed overnight under an inert
atmosphere and the resulting zwitterionic polymer 4 precipitated out.
Zwitterionic polymer 5 was filtered out and then washed with a mixture of methanol and diethyl ether (1:1, 2×).

**Thermogravimetric Analysis.** Thermogravimetric analysis (TGA) measurements were carried out under a nitrogen
atmosphere (Airgas, ultrahigh purity grade) using a TGA 550 from TA
Instruments. The ramp speed was 20 °C min⁻¹ from room
temperature to 650 °C.

**NMR Spectroscopy.** ¹H and ¹³C NMR spectra for all the
polymers were acquired on a Bruker Advance Spectrometer operating
at 400 MHz. Chemical shifts (δ) are reported in parts per million
(ppm) and referenced with D₂O for ¹H NMR. NMR of polymer 1’, 2’, and 3’ are shown in Figure S1 in the Supporting Information.

**Gel Permeation Chromatography.** The molecular weight
of polymer 4 was determined using a Viscotek GPCmax with a Viscotek
aqueous A6000M (300 × 8.0 mm) column and an Agard guard
column, a Malvern 270 M1 detector and a Viscotek VE 380 RI
detector were used to detect reflective index (RI), viscosity (IV), and
low angle light (LAL) and right angle light (RAL) scattering signals.
The dextran standards with Mₚ 1270, 5220, 11 600, 25 000, and 68
082 g/mol were purchased from Sigma-Aldrich. All the standards and
diluted 0.3 M NaCl solution, and 0.3 M NaCl solution was also used as the eluent at 0.5 mL/min. The retention
volume was selected using the RAL peaks, although other signals
generate the same result. The molecular weight of polymer 1’, 2’, 3’ and 5’ was determined using the same GC/Pmax and
detectors but with Guard-0478 and Malvern CLM1012 (1-MBMMW-3078) columns. The polystyrene
(PS) standards with Mₚ 200, 30 000, 200 000, 400 000, and 900 000 were purchased from Alfa Aesar. The PS standards and polymer 1’, 2’, and 3’ were dissolved in a mixture solvent of 20% methanol in
THF. The same mixed sample was used as the eluent at 0.5 mL/min for the PS standards and the polymer samples.

**pH of the Polymer Solutions in A Brine.** Polymers 1, 2, 3, 4, and 5 completely dissolves in a SW brine (SW, composition shown in
Table S4) at 0.2 wt % after heating at 90°C in a sealed vial for 30–60
min. The pH of the polymer solutions was measured using a pH
meter, Orion Star A111 of Thermo Scientific, at 25°C. The reported
pH is an average after three PMAs.

**Density and Viscosity Measurement of the Polymer Solutions.**
The density (g/cm³) and the dynamic viscosity (mPa·s) of the SW and polymer solutions were determined using an Antare
Paar Stabinger viscometer SVM 3001. The density and viscosity
values were taken at 80–85 °C.
Dynamic Light Scattering. We used a NanoBrook Particle and Zeta potential analyzer (Brookhaven Instruments Corporation) to determine the hydrodynamic diameter ($d_h$) of 0.2 wt % polymers in the SW brine and in NaCl or CaCl₂ solutions at the same ionic strength of 0.115 M as SW. The freshly prepared polymer solutions were first heated at 90 °C in an oven for 30–60 min and then cooled to room temperature before dynamic light scattering (DLS) measurement. All the measurements used a PS cell and 659 nm of laser at 90° angle. The solution was equilibrated at 25 °C for 1 min before the measurement. The reported $d_h$ is an average of three repetitive measurements at 5 min duration for each measurement, and the size distribution was calculated using CONTIN algorithms with an auto (slope analysis) baseline normalization.

Zeta Potential of Limestone Powders. We used a NanoBrook Particle and Zeta potential analyzer (Brookhaven Instruments Corporation) to determine the zeta potential of limestone powders in 1 mM KCl solution at 25 °C. The reported zeta potential is an average of five repeats at 1 min duration.

Scanning Electron Microscopy. Scanning electron microscopy (SEM) images of rock limestone (LS) particles were collected in a JEOL JSM-6010LA in the high vacuum mode using a secondary electron detector. The LS samples were coated with 10 nm of gold in a Quorum SC7640 sputter coater prior to imaging.

Brunauer–Emmett–Teller. The Brunauer–Emmett–Teller (BET) surface area of the LS particles was measured with N₂ sorption at 77 K using a Micromeritics ASAP 2020. Limestone particles were degassed under high vacuum at 150 °C for 6 h prior to the measurement. The analysis of the pore-size distributions was performed using a nonlocal density functional theory model for carbon slit pore geometry provided using ASAP 2020.

RESULTS AND DISCUSSION

Herein, we report the synthesis and static adsorption of four copolymers that share the same zwitterionic backbone with different functional co-monomers. These polymers show excellent solubility and stability in SW brines and not soluble in common organic solvents. 1H NMR in D₂O-containing mixed salts was used for characterizations. The downfield shift of the 1H peak of imidazole groups appear at 2.50, 2.98, and 4.29 ppm on the 1H NMR spectra and at 49.05 and 24.65 ppm on the 13C NMR spectra (Figure S2). We also performed 19F NMR of fluoromethylstyrene (3), and vinyl pyrrolidone (4) to test the “substituent effect” on the polymers’ adsorption properties. For comparison, a pure 1-vinylimidazole-based polyzwitterion (5) is also synthesized. After free-radical polymerization, prezwiterionic polymers 1’, 2’, 3’, 4’, and 5’ were subjected to a postpolymerization functionalization using 1,3-propane sultone to yield their zwitterionic counterparts 1, 2, 3, 4, and 5.

1H and 13C NMR of polymers 1’, 2’, 3’, 4’, and 5’ were performed in methanol-d₄ (Figure S1 in the Supporting Information). The 1H NMR spectra of the five polymers are very similar with aromatic protons of vinylimidazole and styrenic monomers on polymers overlapping in broad peaks at 7.5–6.5 ppm and aliphatic protons at 3.6, 3.2, 2.9, and 2.0 ppm. 1H NMR peaks of vinyl pyrrolidone of 4’ are overlapped with the 1H peaks of the aliphatic backbone. 13C NMR spectra of 1’, 2’, 3’, 4’, and 5’ are also very similar with broad aromatic vinylimidazole and styrenic co-monomers peaks at 136, 129, and 117 ppm (Figure S1) and broad aliphatic carbon peaks at 82 and 41 ppm. The 13C NMR spectra of 4’ show the amide peak (−NC═O) on vinyl pyrrolidone at 176 ppm besides the aromatic vinylimidazole carbon at 136, 129, and 117 ppm. Integration of the carbonyl peak and the vinylimidazole carbon peaks suggest that the vinyl pyrrolidone on 4’ is around 11 mol % (Figure S1 in the Supporting Information). The mol % of co-monomers on 1’, 2’, and 3’ is difficult to determine using NMR data because of their broadly overlapped 1H and 13C peaks. We also performed 19F NMR of 3’ in methanol-d₄ with 4-fluorobenzoic acid as an internal reference. The 19F peak of −CF₃ appears at −63.91 ppm (Figure S1), confirming the formation of a copolymer.

After sulfonation, polymers 1, 2, 3, 4, and 5 are only soluble in brines and not soluble in common organic solvents. 1H NMR in D₂O-containing mixed salts was used for characterizations. The downfield shift of the 1H peak of H₅ on vinylimidazole from 7.34 to 8.97 ppm for each polymer is a clear indication of sulfonating the imidazole groups on the polymers (Figure S2 in the Supporting Information). The broad peaks of propane (H₃₋, H₄, and H₅) protons of sulfone groups appear at 2.50, 2.98, and 4.29 ppm on the 1H NMR spectrum and at 49.05 and 24.65 ppm on the 13C NMR spectrum (Figure S2).

We use pyrolysis-GC/MS (Py-GC/MS) to determine the molar ratios of the comonomer to vinyl imidazole (VIM) for each random copolymer 1’, 2’, 3’, and 4’. Flash thermal depolymerization (pyrolysis) at 550 °C of the copolymers...
generates the molecular ions of VIM, co-monomers, and fragments of the polymer backbone, which are separated by gas chromatography and detected using a mass spectrometer. The chromatogram (total ion count vs retention/acquisition time) of each polymer after pyrolysis shows the elution of the monomers and their derivatives at specific retention times (Figure S3 in the Supporting Information). The area under the polymer solution is in the narrow range of 6.6—6.9 for 1, 2, 3, and 4, and the polymer 5 solution has the lowest pH of 5.7. The viscosity of the polymer 1, 2, 3, 4, and 5 at 80 °C is 0.447, 0.454, 0.436, 0.520, and 0.434 (mPa-s) respectively, which are all higher than 0.425 mPa-s of SW (Table S5 in the Supporting Information). The hydrodynamic diameter $d_h$ of the polymers in SW is measured using DLS. Figure 1 shows the $d_h$ of 0.2 wt % polymers 1, 2, 3, 4, and 5 in SW.

Table 1. Molar Ratio of Co-monomer to VIM via Py-GC/MS

| polymer | comonomer/VIM average | standard deviation | comonomer/VIM stoichiometric |
|---------|------------------------|--------------------|-----------------------------|
| 1′      | 0.111                  | 0.029              | 0.111                       |
| 2′      | 0.034                  | 0.004              | 0.052                       |
| 3′      | 0.082                  | 0.002              | 0.111                       |
| 4′      | 0.114                  | 0.011              | 0.111                       |
| 5′      | 0                     | 0                  | 0                           |

in each copolymer, after three repeats of Py-GC/MS (Table S1 in the Supporting Information). The mol % of vinyl pyrrolidone on 4′ determined by Py-GC/MS is consistent with that determined using the $^{13}$C NMR spectrum.

The intent to determine the molecular weight of polyzwitterions 1, 2, 3, and 5 in 0.3 M NaCl solution using an aqueous column via gel permeation chromatography (GPC) was not successful because of strong polymer retention in the column. Only polymer 4 passed through the column and its molecular weight was determined to be 807 435 g/mol using a calibration curve of dextran in 0.3 M NaCl solution (Figure S4 and Table S2 in the Supporting Information). Alternatively, we measured the molecular weights of the polymers 1′, 2′, 3′, and 5′ using GPC and a polystyrene calibration curve in a mixed solvent of THF (80%) and methanol (20%) (Figure S5 in the Supporting Information).

Interestingly, 4′ is not soluble in the mixed solvent. The number-average molecular weights ($M_n$) of the polymers 1′, 2′, 3′, and 5′ are 483 062, 350 263, 562 385, and 397 289, respectively, which are in the same order of magnitude (Table S3 in the Supporting Information) due to the same loading of the azobisobutyronitrile (AIBN) initiator. $M_n$ of 4 was measured after sulfonation in brine using a different calibration standard, may not be directly compared with that of 1′, 2′, 3′, and 5′.

Polymers 1, 2, 3, and 4 are associative polymers having hydrophobically modified hydrophilic polymers. Previous research has shown that the associative polymers have complicated fluid behaviors in water and especially in brines. We are particularly interested in polymer adsorption in the SW because SW is extensively used in Middle Eastern oil fields.
should be primarily surface-based. For the static adsorption experiments, 2 g of LS particles and 5 mL of 0.2 wt % polymer solution were mixed, sealed, and heated at 80 °C for 3 days (Figure 2a). As a control experiment, 5 mL of 0.2 wt % blank polymer solution without LS particles was also heated at 80 °C for 3 days to quantify the polymer adsorption onto the glass surface of the vial. Total adsorption was calculated by comparing the UV−vis absorbance after heating for 3 days to a predetermined UV−vis calibration curve for each polymer at various concentrations (Figures S10−S14 in the Supporting Information). Subtracting polymer adsorption onto glass surfaces from total adsorption gave the polymer adsorption on LS surfaces (Tables S6−S10 in the Supporting Information).

Figure 2. (a) Experimental procedures for static adsorption using zwitterionic polymers 1, 2, 3, 4, and 5; (b) static adsorption of zwitterionic polymers 1, 2, 3, 4, and 5 using LS particles in SW at 80 °C for 3 days; and (c) schematic representation of interaction between zwitterionic polymers with different co-monomers and LS surfaces.

Figure 2b shows the quantified static adsorption for zwitterionic polymers 1, 2, 3, 4, and 5 as milligrams of the polymer per gram of LS (mg/g) and as mg of polymer $m_p$ per square meter of the rock surface area (mg/m$^2$). The relative adsorption of these zwitterionic polymers follows the order 2 > 4 > 1 > 5 > 3. We also estimate the number density ($N_p$) of the adsorbed polymers per unit rock surface area is calculated according to the following equation

$$N_p(m - 2) = \frac{6m_p}{\pi(d_h)^3\rho_p}$$

where $\rho_p$ is the density of each polymer, assuming the $\rho_p$ of each polymer is the same and is an arbitrary number of 1 mg/m$^3$. The $N_p$ for the polymers follows the order 1 > 5 > 4 > 2 > 3 (Figure S15 in the Supporting Information). It is not surprising that 1 and 5 have the highest $N_p$ because of their smaller hydrodynamic radius than that of 2 and 4. However, the approach to estimate $N_p$ assuming that the polymer is hard, sphere-like nanoparticles and the hydrodynamic radius does not change upon adsorption on the rock surface, is not quite accurate because the polymers could go through conformation change, thus size changes upon binding to the surfaces.

As the LS surface in SW is predominately adsorbed with positive ions,$^{23−25}$ the interactions between the polymers and the LS surfaces include electrostatic attraction through the anionic groups of the zwitterions and the dipole interactions...
through the co-monomers. Polymers 2 and 4 with strong nucleophilic co-monomers have the highest adsorption to LS surfaces. Polymer 1 with styrene as a co-monomer shows 60% less adsorption despite that mol % of styrene is twice as high as that of 4-aminostyrene in the polymer backbone. Pure polyzwitterion 5 exhibits moderately lower rock adsorption compared to that of polymer 1, indicating that styrene moieties may interact with carbonate rock surfaces via potential cation–π interaction. Polymer 3 with 4-trifluoromethylstyrene as a co-monomer has negligible adsorption to LS, probably as a result of the strong repulsion force of −CF3 to most surfaces. The negative adsorption of 3 most likely results from the minor variation of the polymer concentration in SW because of water diffusion (but not polymer) into pores of LS particles. It is worth noting that statistically only one in 10 or 20 repeating units is the functional co-monomer; therefore, it is striking that incorporating only 5–10 mol % of the functional co-monomers into the polymer backbone could greatly change the interaction between the zwitterionic polymers and the carbonate surface (Figure 2c). To the best of our knowledge, this is the first polymer that shows nearly zero static adsorption on limestone in SW. Other polymers such as the family of polyacrylamides typically show static adsorption of a few hundreds of mg/m².

**CONCLUSIONS**

In summary, this paper describes a simple, robust zwitterionic polymer system that exhibits tunable static adsorption to carbonate surfaces. Polymer adsorption can be tuned using different functional co-monomers at low molar percentages during free-radical polymerization. The research presented here represents an attractive and useful approach for the petroleum industry to target different applications from tags for mud logging to tracers for reservoir mapping with tailored polymer adsorption. In addition, the design concept presented here may be extended to other polymer and surfactant systems imparting them with tunable affinities toward mineral surfaces.

**ASSOCIATED CONTENT**

**Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsami.0c02247.

Synthesis and characterization data for polymers; pyrolysis GC/MS data; composition of synthetic SW; DLS results; and limestone particle characterization (PDF)

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**Notes**

The authors declare no competing financial interest.

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