



Examination of zwitterionic polymers and gels subjected to mechanical constraints

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ABSTRACT

The effect of mechanical constraints on the anti-polyelectrolyte behavior of zwitterionic polymers was studied systematically in this work via viscosity examination of uncross-linked polymer solutions, swelling of cross-linked polymer gels and swelling of elastomers compounded with these gels. Zwitterionic polymers, poly(sulfobetaine methacrylate) (polySBMA), poly(2-methacryloyloxyethyl phosphorylcholine) (polyMPC) and copolymers of polySBMA with a polyelectrolyte, poly(sodium methacrylate) (polyNaMA) were used in this study. Anti-polyelectrolyte effects were observed both in solution and as gels. However, when the zwitterionic gels were compounded with hydrogenated acrylonitrile butadiene rubber (HNBR), the anti-polyelectrolyte behavior of the native polymer was lost. This is attributed to mechanical constraints imposed by the elastomeric HNBR matrix that dominate Coulombic interactions. Without the manifestation of chain relaxation and extension afforded by the charge screening, the zwitterionic polymers serve as hydrophilic agents that facilitate water diffusion into rubber.

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1. Introduction

Superabsorbent polymers (SAPs) are lightly cross-linked hydrogels capable of absorbing and retaining water up to 2000 times their original weight [1,2]. SAP applications range from pharmaceuticals [3] and biomaterials [4] to soil additives [5] and petroleum recovery systems [6,7]. SAPs are typically composed of polyelectrolytes, which contain either cationic or anionic groups, or of polyampholytes, which contain both cationic and anionic species [8–14]. Polyzwitterions, having positive and negative charge on each monomer, are gaining interest as SAPs for their superior salt tolerance relative to conventional polyelectrolytes [15,16].

In pure water, polyelectrolytes exhibit an extended conformation due to repulsion between like charges on the backbone. However, addition of salt, such as sodium chloride, partially or completely shields electrostatic repulsion [16], resulting in chain collapse to random coils [17]. This is generally referred to as the polyelectrolyte effect. Polymers bearing zwitterionic sulfobetaine

groups behave differently, adopting a more collapsed state in pure water as a result of Coulombic attraction between dipoles along the chain. Addition of salt screens this inter-zwitterionic attraction, allowing the polymers to expand into random coils; this is often referred to as the anti-polyelectrolyte effect [18,19]. This solution behavior extends to cross-linked polymers, in which polyelectrolyte gels de-swell with increasing salt concentration, and polyampholyte gels maintain their swollen state despite the presence of salt [13,20,21]. In the case of anionic–zwitterionic copolymer gels, the solution behavior depends greatly on the ratio of anionic to cationic species [8,9,11,16]. As this ratio approaches unity, polymer behavior is dominated by the anti-polyelectrolyte effect [11].

A water-swellaable packer is a self-actuating oilfield sealing device enabled by water-absorbing elastomers. It is conveyed downhole on a production tubing and usually used during well completions to isolate the annulus from the production conduit, enabling controlled production, injection or treatment. A water-swellaable packer typically employs elastomers highly loaded with SAPs and is often placed in groundwater with salt concentrations as high as 3 M [22,23]. Similar to polyelectrolyte SAPs, salt adversely affects the swelling of these systems [23,24]. However, the effect of mechanical constraints on SAP swelling, particularly on those confined within a stiff rubber matrix, has

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not been studied, despite the relevance of such systems to practical materials performance.

Here we describe the solution behavior of zwitterionic polymers and gels subjected to salt concentrations similar to those encountered in some oil wells. Polymer solutions, cross-linked gels, and SAP-compounded elastomers represent increasing extents of mechanical restriction to swelling of SAPs. Therefore, we report a thorough study correlating polymer rheology, swelling of cross-linked gels, and swelling of elastomers compounded with SAP gels as a function of salt concentration, which to the best of our knowledge has not yet been described.

2. Experimental methods

2.1. Materials

[2-(Methacryloyloxy)ethyl]dimethyl-(3-sulfopropyl)ammonium hydroxide (sulfobetaine methacrylate, SBMA, 97%), methacrylic acid (MAA, 99%), potassium persulfate (KPS, $\geq 99\%$), 4-cyano-4-(phenylcarbonothioylthio)pentanoic acid ($>97\%$), and 4,4'-azobis(4-cyanovaleic acid) ($\geq 98\%$) were purchased from Aldrich. Water (Optima[®]), sodium chloride (granulated) and dialysis tubing (Spectra/Por[®], regenerated cellulose membranes with a molecular weight cutoff of 6000–8000 g/mol) were purchased from Fisher Scientific. PEG 1000 dimethacrylate ($>99\%$, stabilized with 90 ppm MEHQ and 250 ppm BHT) was purchased from Polysciences, Inc. Sodium hydrogen carbonate (99%) was purchased from Alfa Aesar. KPS was recrystallized from water. 2-Methacryloyloxyethyl phosphorylcholine (MPC) was prepared according to a literature report [25,26]. Hydrogenated acrylonitrile butadiene rubber (HNBR) was purchased from LANXESS. The cross-linking co-agent, triallyl isocyanurate (TAIC) was purchased from Natrochem. Zinc oxide and Trigonox were purchased from AkzoNobel. All other materials were used as received.

2.2. Characterization

¹H and ¹³C nuclear magnetic resonance (NMR) spectroscopy was recorded on a Bruker 300 or Bruker Avance 400 spectrometer. Size exclusion chromatography (SEC) was performed at 0.75 mL/min, using 0.2 M sodium nitrate with 0.01 wt% sodium azide, using an Agilent series 1100 pump, two Waters ultrahydrogel linear columns (10 μ m, 300 nm \times 7.5 mm), a Wyatt DAWN EOS multi angle light scattering (MALLS) detector operating at 690 nm and a Wyatt Optilab[®] refractive index (RI) detector operating at 685 nm. A Wyatt Optilab[®] refractive index detector was used to measure dn/dc values for poly(sodium methacrylate) (polyNaMA) and poly(-sulfobetaine methacrylate) (polySBMA) (0.175 mL/g and 0.140 mL/g, respectively). The dn/dc values of the copolymers were calculated according to the additivity rule [27]:

$$(dn/dc)_C = x(dn/dc)_A + (1-x)(dn/dc)_B$$

where A, B, and C refer to homopolymer A, homopolymer B, and the copolymer poly(A-co-B), respectively. x is the average copolymer composition, determined by ¹H NMR spectroscopy, expressed by the weight fraction of monomer A in the copolymer. The scattering intensity as a function of scattering angle data generated from the MALLS detector was fit to an order 1 Zimm model.

2.3. Synthesis

2.3.1. Conventional radical polymerization procedure

SBMA, MAA, KPS, and water were combined in a 250-mL two-neck round-bottom flask equipped with a septum and a gas inlet,

using amounts of reagents as given in Table 1. The solution was degassed with bubbling N₂ for 30 min, and the flask was then placed in an oil bath heated to 65 °C. The reaction mixture was stirred at this temperature under N₂. Polymer solutions containing MAA were treated with NaHCO₃ (aq) and stirred for 2 h at room temperature. The polymerization mixtures were dialyzed against water, then lyophilized. The polymers were isolated as white powders. PolySBMA was fractionated after dialysis. Solutions of polyNaMA were precipitated into ethanol and dried under vacuum at room temperature to yield the solid polymer and excess salt.

2.3.2. Fractionation and isolation of polySBMA

PolySBMA was dialyzed in water, lyophilized, and isolated in 95% yield as a white solid in two fractions. The first fraction (3.4 g, 26% total mass) was a soft powder and the second (9.5 g, 74% total mass) was a porous solid. The polymer structure of both fractions was confirmed by ¹H NMR in 0.2 M NaNO₃ in D₂O and the molecular weight was characterized by SEC (MALLS + RI): Fraction 1: $M_n = 76,000$ g/mol, PDI = 2.03, Fraction 2: $M_n = 560,000$ g/mol, PDI = 1.08. The higher molecular weight Fraction 2 was used for compounding experiments. ¹H NMR of Fraction 2: δ (0.2 M NaNO₃ in D₂O, 4.79 ppm) 4.56 (2H), 3.88 (2H), 3.65 (2H), 3.28 (6H), 3.03 (2H), 2.34 (2H), 1.69–2.21 (2H), 0.57–1.60 (3H).

2.3.3. PolySBMA-co-NaMA

Representative ¹H NMR: δ (D₂O, 4.79 ppm) 4.50 (2H from SBMA), 3.81 (2H from SBMA), 3.60 (2H from SBMA), 3.23 (6H from SBMA), 2.99 (2H from SBMA), 2.28 (2H from SBMA), 1.53–2.16 (2H from SBMA + 2H from NaMA), 0.47–1.53 (3H from SBMA + 3H from NaMA).

2.3.4. PolySBMA70-co-NaMA30

8.09 g (81% yield). SEC (MALLS + RI): $M_n = 348,000$ g/mol, PDI = 1.87, dn/dc = 0.144 mL/g.

2.3.5. PolySBMA33-co-NaMA67

6.36 g (97% yield). SEC (MALLS + RI): $M_n = 46,000$ g/mol, PDI = 1.17, dn/dc = 0.153 mL/g.

2.3.6. PolyNaMA

15 g (243% yield) of salt and polymer. After dialysis against water and lyophilization of 53.2 mg salt and polymer, 18.9 mg polymer remains (35.5% of the original mass). Therefore, yield can be recalculated as 5.32 g (81% yield). SEC (MALLS + RI): $M_n = 31,900$ g/mol, PDI = 1.20, dn/dc = 0.175 mL/g. ¹H NMR: δ (D₂O, 4.79 ppm) 1.45–2.30 (2H), 0.62–1.39 (3H).

2.3.7. RAFT polymerization of SBMA

Following a prior report [28], SBMA (42.9 mmol), 4-cyano-4-(phenylcarbonothioylthio)pentanoic acid (0.09 mmol), ACVA (0.0046 mmol), and 0.5 M NaBr (aq) (60 mL) were added to a 250 mL two-neck round-bottom flask equipped with a septum and a gas inlet. The solution was degassed by bubbling N₂ for 1 h, then immersed in an oil bath thermostated at 70 °C and stirred for 12 h under N₂. The

Table 1
Conventional radical polymerizations.

Polymer	SBMA (mmol)	MAA (mmol)	KPS (mmol)	Water (mL)	Reaction time (h)	NaHCO ₃ (g)
PolySBMA	48.0	0	0.45	180	6	0
PolySBMA70-co-NaMA30	31.7	13.6	0.44	150	6	2
PolySBMA33-co-NaMA67	13.6	31.9	0.44	150	6	5
PolyNaMA	0	69.6	0.70	70	4	15

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