

First investigation of modified poly(2-vinyl-4,4-dimethylazlactone)s as kinetic hydrate inhibitors



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HIGHLIGHTS

- A series of amine derivatives of poly(2-vinyl-4,4-dimethylazlactone)s has been synthesized.
- The polymers have been investigated as kinetic hydrate inhibitors for the first time.
- Performance increased with decreasing molecular weight down to 1845 mol/g.
- The best performance was for the *n*-propylamine derivative.

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ABSTRACT

A series of polymers of 2-vinyl-4,4-dimethylazlactone (VDMA) of varying molecular weights modified with small organic amines have been synthesized. Their performance as kinetic hydrate inhibitors (KHIs) has been investigated in high pressure steel rocking cells using a Structure II-forming synthetic hydrocarbon gas mixture. It was found that the PVDMA polymer with the lowest molecular weight ($M_n = 1845$ g/mole by ¹H NMR) performed the best. It was also found that the *n*-propylamine derivative performed the best of the amine derivatives. The cloud point of this polymer derivative was found to be lower than ambient temperature, which is considered too low for practical oilfield applications. However, high cloud point PVDMA derivatives such as the ethylamine or pyrrolidine derivatives still gave reasonable KHI performance. The KHI performance of the *n*-propylamine derivative of PVDMA-I was tested at different concentrations in the range 1000–7000 ppm. It was found that the performance improved as the polymer concentration was increased.

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1. Introduction

Gas hydrate plugging is a major flow assurance issue to consider in the oil and gas industry, particularly for flow lines in subsea and cold climate situations (Carroll, 2009; Makogon, 1997; Sloan and Koh, 2008). One of the methods to combat this problem is the use of kinetic hydrate inhibitors (KHIs) (Kelland, 2006; Kelland, 2011; Perrin et al., 2013). KHIs are one class of low dosage hydrate inhibitors (LDHIs) which, as the name implies, are added at low concentrations in the order of 0.5–2 wt.% as formulations in solvents. KHIs are often a mixture of chemicals but always with one or more water-soluble polymers as the main active ingredients. Synergists may be added, which may include other polymers or non-polymeric chemicals including the solvent (s) used in the formulation. Many polymers have been investigated

for their efficacy as KHIs but only a few have been commercialized. This includes polymers based on the monomers *N*-vinyl pyrrolidone, *N*-vinyl caprolactam (VCap) and *N*-isopropylmethacrylamide (NIPMAM) as well as hyperbranched poly(ester amide)s. One of the field compatibility issues with KHI polymers is that they often have limited solubility in produced water especially at high temperatures and salinities (Kelland, 2014). Above a certain temperature called the cloud point (T_{Cl}) the polymer will often phase separate, giving a cloudy solution. Further heating to usually an incrementally higher temperature (T_{Dp}) can lead to precipitation of the polymer, which may then deposit and build up in the flow line near the injector site. Operator and service companies would consider this detrimental as the polymer is then apparently unavailable in the water phase for carrying out kinetic hydrate inhibition. Although field cases exist where a KHI polymer has been injected into well stream temperatures above the cloud and deposition point, and successfully used to prevent hydrate formation, most operators prefer to avoid this complication by using a

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product that will remain water-soluble or at worst water-dispersible at the well head temperature.

Poly(*N*-vinyl caprolactam) (PVCap) and poly(*N*-isopropylmetacrylamide) (PNIPMAM) have cloud points around 30–45 °C depending on the method of manufacture. This is often too low for injection at the well head temperature. One way to overcome this problem is to add chemicals that often also act as synergists, to raise the deposition point of the KHI formulation when injected (Kelland, 2014). Another method is to copolymerize the active monomers with a more hydrophilic comonomer. For example, VCap or NIPMAM copolymerize in a 1:1 M ratio with *N*-methyl-*N*-vinyl acetamide (VIMA) with optimized molecular weight distributions have been shown to give similar or superior performance KHIs to the homopolymers but with significantly higher cloud and deposition point temperatures (Colle et al., 1999; Talley and Mitchell, 1998). Another method is to build into the active monomer a more hydrophilic functional group so that the new homopolymer will be water-soluble at higher temperatures than the unmodified polymer. An example of this is the use of dimethylhydrazido groups instead of isopropylamido groups in substituted acrylamide monomers (Fig. 1) (Mady and Kelland, 2014). The extra nitrogen atom in the hydrazido group confers a greater hydrophilicity on the monomer than just one nitrogen atom from an amide group. Thus, poly(dimethylhydrazidoacrylamide) has no cloud point in water as a 1 wt.% aqueous solution at any temperature up to 100 °C. This homopolymer or copolymers with NIPMAM or VCap are still very active KHIs with improved cloud points compared to PVCap or PNIPMAM (Mady and Kelland, 2015).

A related example of modifying a monomer to raise the cloud point of its polymers is the alkylated polyacrylamidopropylsulfonates (alkylated polyAMPS) (Fig. 2). (Peiffer et al., 1999) A hydrophobic pendant alkyl group alone would not give a water-soluble polymer but incorporation of a hydrophilic sulfonate group made this polymer class water-soluble as long as the alkyl chains R_1 and R_2 were not too large. Conversely, the AMPS homopolymer alone is a poor KHI, but it was found that the addition of a hydrophobic tail between the amide and the sulfonic acid group increased the performance of the polymer. The optimum size of the tail R_1 was 5 carbon atoms long. A homopolymer of this monomer gave a KHI performance similar to PVCap in a high pressure natural gas mini-loop.

We were initially interested in poly(2-vinyl-4,4-dimethylazlactone) (PVDMA) as the azlactone pendant ring resembled the oxazoline ring that had been investigated earlier as a functional groups for KHI polymers in polyvinylloxazolines (Fig. 3) (Reyes et al., 2013; Colle et al., 1996). The monomer 2-vinyl-4,4-dimethylazlactone is commercially available but not on an industrial scale.

However, PVDMA is not water-soluble as the homopolymer, although it was known that PVDMA hydrolyzes to give poly(*N*-acryloyl-2-methylalanine) (PAMA) with both pendant dimethyl groups and a carboxylate group (Fig. 4) (Gardner et al., 2012). The resemblance of PAMA to the alkylated AMPS polymers described earlier is

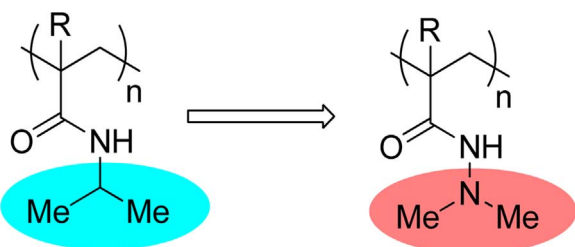


Fig. 1. Structures of polyIPAM, polyIPMAM and the hydrazine-based analogs poly(*N,N*-dimethylhydrazidoacrylamide derivatives $R=H$ or CH_3).

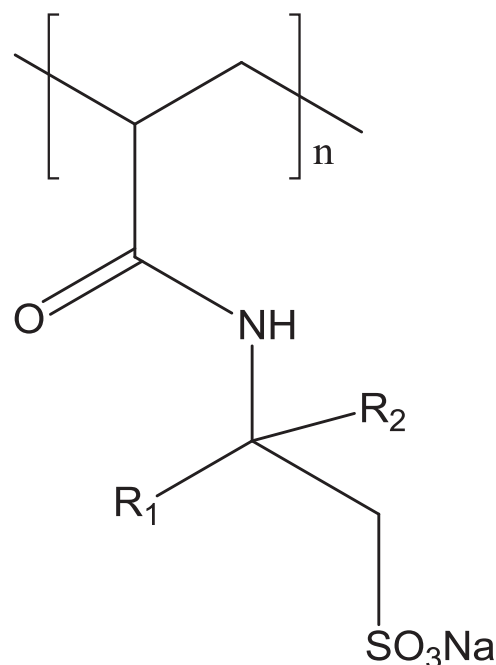


Fig. 2. Alkylated AMPS polymers, where R_1 is an alkyl tail of 1–6 carbon atoms and R_2 is H or CH_3 .

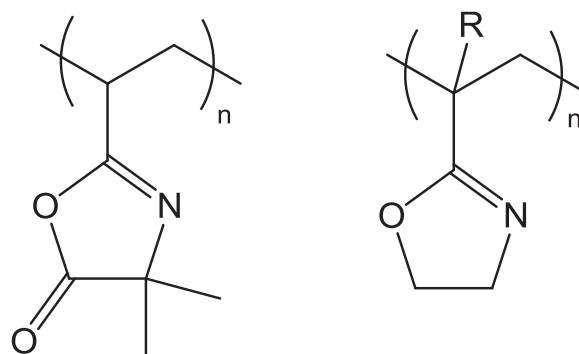


Fig. 3. Poly(2-vinyl-4,4-dimethylazlactone) (PVDMA) (left) and ring-closed polyvinylloxazolines, $R=H$ or CH_3 (right).

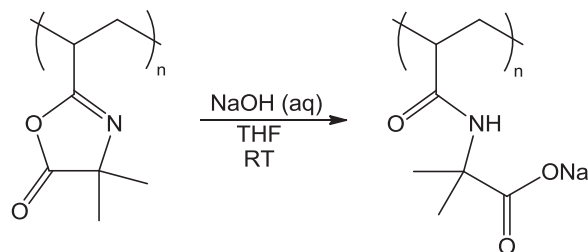


Fig. 4. Reaction scheme for hydrolysis of poly(2-vinyl-4,4-dimethylazlactone) (PVDMA) to the sodium salt of poly(*N*-acryloyl-2-methylalanine) (PAMA).

apparent. Therefore, we were interested in investigating PAMA as a KHI. Since the size of the 2,2-dimethyl hydrophobic group was relatively small we expected the KHI performance to be low, and so we sought ways to incorporate larger hydrophobic groups into the polymer. One method is to begin with a 2-vinyl-4,4-dialkylazlactone monomer where the alkyl groups are larger than methyl. However, so far we have not explored this route. Instead, we chose a route explored already by some of us by incorporating hydrophobic pendant groups through postpolymerization modification of PVDMA with primary or secondary amines (Fig. 5). This ring-opening addition reaction proceeds quantitatively under mild

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