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Cationic kinetic hydrate inhibitors and the effect on performance of incorporating cationic monomers into N-vinyl lactam copolymers

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HIGHLIGHTS

- Tributylammoniumethylacrylate bromide (TBAEABr) monomer was prepared.
- Poly(tributylammoniumethylacrylate) bromide (PTBAEABr) performs well as a KHI.
- TBAEABr copolymers with vinyl caprolactam (VCap) are not better KHIs than PVCap.
- PTBAEABr shows good synergy with PVCap.

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ABSTRACT

Kinetic hydrate inhibitors (KHIs) are used in the oil industry to prevent plugging of pipelines by gas hydrates. Cationic molecules with small alkyl groups, such as tetraalkylammonium and alkylimidazolinium salts are known to be synergists for KHI polymers such as N-vinyl lactam polymers. Instead of using separate synergist and polymer molecules, we have investigated the effect on KHI performance of placing the synergist active groups into N-vinyl lactam copolymers. Thus, 3-alkyl-1-vinylimidazolium bromides and tributylammoniumethylacrylate bromide (TBAEABr) monomers and homopolymers and copolymers with N-vinyl lactams were prepared. These were tested for their performance as KHIs with a Structure II-forming gas mixture as well as their ability to prevent tetrahydrofuran hydrate crystal growth inhibition. We conclude that incorporation of the synergist functional groups into N-vinyl lactam polymers does not give a greater benefit as a KHI than using a physical mixture of the synergist molecule and PVCap polymer. However, a cationic TBAEABr homopolymer showed good kinetic inhibition performance when used alone on both THF and SII gas hydrates. This is the first cationic homopolymer KHI with good performance to be reported. Poly(tributylammonium ethylacrylate bromide) (PTBAEABr) was also a better KHI synergist with PVCap than using tetrabutylammonium bromide.

1. Introduction

The main active components in kinetic hydrate inhibitors (KHIs) are water-soluble polymers, which are designed to delay gas hydrate formation in upstream gas and oilfield operations (Kelland, 2009, 2006, 2011; Sloan Jr. and Koh, 2008). Most classes of KHI polymer that have been discovered are vinylic polymers with amide or imide groups. Examples are poly(N-vinyl lactam)s with 5–8 rings (Sloan, 1995a, 1995b; Long et al., 1994; Bakeev et al., 2001; Cohen et al., 1998; Angel et al., 2001; Kolle et al., 1999; Fu et al., 2002; Colle et al., 1996b; Namba et al., 1996), poly(N-N-(di)alkyl(meth)acrylamide)s (Chua et al., 2011a; Chua and Kelland, 2012b; Kelland et al., 2000, 1998), polyvinyloxazolines (not amide-based) (Colle et al., 1996c), polymaleimides (Colle et al., 1996d), polymaleamides (Kelland and Klug, 1998), poly(N-vinylalkanamide)s (Colle et al., 1996e), modified acrylamidopropylsulfonic acid (AMPS) polymers (Pfeiffer et al., 1999) and polyallylamides (Colle et al., 1996a). A variety of small molecule synergists have been designed to improve the performance of the KHI polymer. Most synergist research has been carried out on blends with N-vinyl caprolactam polymers. These synergists include tetraalkylammonium salts, trialkylamine oxides and small ionic or non-ionic amphiphilic molecules (Klomp et al., 1995; Duncum et al., 1996a, 1996b; Chua and Kelland, 2012a; Kelland et al., 2012; Sefidroodi et al., 2011).

We have previously shown that small 1-alkyl-3-methylimidazolinium salts are poor kinetic hydrate inhibitors (KHIs) when used by themselves on a Structure II forming gas hydrate system

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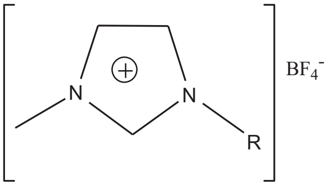

Fig. 1. 1-Alkyl-3-methylimidazolium tetrafluoroborate salts.

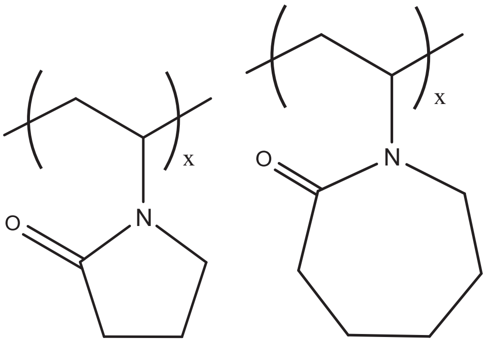

Fig. 2. Poly(N-vinyl pyrrolidone) (PVP, left) and poly(N-vinyl caprolactam) (PVCap, right).

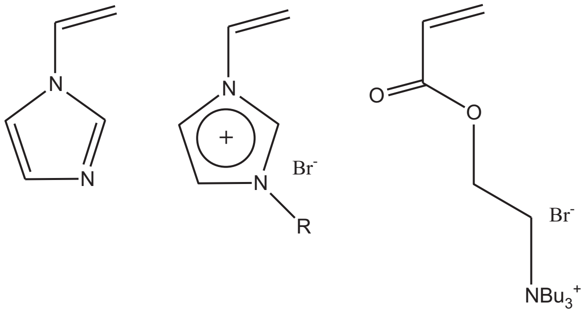

Fig. 3. 1-Vinyl imidazole (VIM), 3-alkyl-1-vinylimidazolium bromides, [RVIM]Br (R=Et or Bu), and tributylammoniumethylacrylate bromide (TBAEABr).

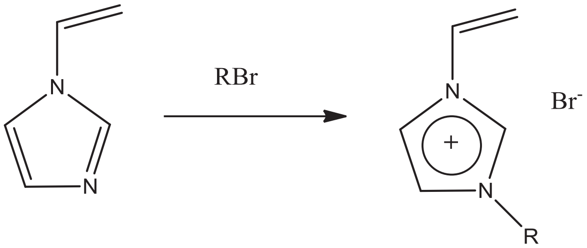

Fig. 4. Synthesis of 3-alkyl-1-vinylimidazolium bromides, [RVIM]Br.

(Fig. 1) (Del Villano and Kelland, 2010b). However, these ionic liquid salts show some synergistic behavior with the known KHI poly (N-vinyl caprolactam) (PVCap), especially when the 1-alkyl group on the imidazolinium ring is n-butyl (Fig. 2). Based on these results, we were interested in determining whether incorporation of the alkylimidazolinium group into N-vinyl lactam copolymers would improve the KHI performance further compared to using the synergistic mixture. At the same time, copolymerization with a cationic monomer would raise the cloud point of the copolymer compared to the poly(N-vinyl lactam) homopolymer. A high cloud point is a useful property for injecting KHIs into hot and/or high salinity well streams to avoid KHI polymer precipitation.

This paper discusses the synthesis and KHI performance of copolymers of N-vinyl lactams with cationic monomers. Both tetrahydrofuran (THF) hydrate crystal growth inhibition and Structure II gas hydrate inhibition experiments were carried out. The THF hydrate crystal growth method gives some indication of the ability of an additive to adsorb to SII hydrate crystal faces and slow the crystal growth, a phenomena which can be observed also in SII gas hydrate tests. This method has been used to great effect to design some classes of LDHIs (Kelland, 2009, 2011, 2006; Sloan Jr. and Koh, 2008). Besides using 3-alkyl-1-vinylimidazolium bromides, which only contain one alkyl group, we also investigated polymers containing a cationic monomer with three alkyl groups in the form of the tributylammoniumethyl acrylate bromide monomer (Fig. 3). This is because the synergistic and crystal growth inhibition performance of butylammonium salts increases with the number of butyl groups. For example, tetrabutylammonium bromide is a good synergist for PVCap polymer. In this work we ask and answer the question, is the KHI performance best using a physical mixture of polymer and synergist, or is it better to incorporate the active functional groups of both molecules into one copolymer?

2. Polymer synthesis and characterization

All syntheses and manipulations of air- and moisture-sensitive materials were carried out in flamed Schlenk-type glassware on a dual-manifold Schlenk line or in an inert gas (Ar or N_2) filled glovebox. 1-Bromoethane, 1-bromobutane, 1-vinylimidazole, acryloyl chloride, dibutylaminoethanol, N-vinylcaprolactam and N-vinylpyrrolidone were purchased from Sigma-Aldrich and used as received. Azobisisobutyronitrile (AIBN) was recrystallized in methanol. Poly(N-vinylpyrrolidone) was obtained from Ashland Chemical. One PVCap sample was made using the method described below. A lower molecular weight PVCap (M_w 2000–4000) in monoethyleneglycol (MEG) was obtained from BASF.

NMR spectra were recorded on a Varian Inova 300 (FT 300 MHz) or a Varian Inova 400 MHz spectrometer. Chemical shifts for ^{1}H NMR spectra were referenced to internal solvent resonances and were reported as parts per million relative to tetramethylsilane. Gel Permeation chromatography (GPC) analyses of polymeric ionic liquids (PILs) were carried out at 40 °C and a flow rate of 1.0 mL/min, with 0.025 M LiBr DMF solution as the eluent, on a Waters University 1500 GPC instrument equipped with two 5 μm PL gel columns (Polymer Laboratories) and calibrated using 10 poly(methyl methacrylate) (PMMA) standards. Chromatograms were processed with Waters Empower software (2002); number–average molecular weight (M_n) and polydispersity index ($PDI=M_w/M_n$) of polymers were given relative to PMMA standards.

Literature procedures were either adopted or modified to prepare water-soluble poly(3-ethyl-1-vinylimidazolium bromide) (poly[EVIM]Br), poly(3-butyl-1-vinylimidazolium bromide) (poly [BVIM]Br), 1:1 3-butyl-1-vinylimidazolium bromide:N-vinylpyrrolidone copolymer (1:1 [BVIM]Br:VP) and 1:1 3-butyl-1-vinylimidazolium bromide:vinyl caprolactam copolymer ([BVIM]Br:VCap) (Figs. 4–6) (Marcilla et al., 2005, 2004; Mu et al., 2005). Described below are typical procedures, using poly[BVIM]Br and [BVIM]Br: VCap copolymer as two examples. Poly[EVIM]Br and [BVIM]Br:VP copolymer were prepared in a similar fashion. 1-Vinyl imidazole polymers were prepared in 2-propanol solvent at 80 °C using AIBN initiator, followed by solvent removal. The synthesis of tributylammonium ethylacrylate bromide monomer and polymers thereof are also described below. The control of the polymerization to give polymers of similar molecular weight proved to be difficult. However, although the KHI performance depends on molecular weight, we were still able to draw conclusions regarding the relative KHI performances of the polymers synthesized.