

Reliability and Performance of Vinyl Lactam-Based Kinetic Hydrate Inhibitor Polymers after Treatment under a Range of Conditions

Malcolm A. Kelland,* Qian Zhang, Erik G. Dirdal, and Mohamed F. Mady

Cite This: *Energy Fuels* 2021, 35, 1273–1280

Read Online

ACCESS |

Metrics & More

Article Recommendations

ABSTRACT: Well-known kinetic hydrate inhibitors (KHIs) such as poly(*N*-vinylcaprolactam) (PVCap), poly(*N*-vinylpyrrolidone) (PVP), and 1:1 *N*-vinylcaprolactam:*N*-vinylpyrrolidone (VCap:VP) copolymer have been subjected to a range of treatments to determine their reliability and whether the treatment conditions could affect the KHI performance, both positively or negatively. This included thermal aging (at varying temperatures, at varying pH, and in monoethylene glycol (MEG) solvent), treatment with microwaves or ultrasound, ball-milling, and oxidizing agents (household bleach or hydrogen peroxide, also with heat). In addition, samples of commercial polymer solutions kept for up to 15 years were also tested for KHI performance to determine their long-term reliability. Testing was carried out using a synthetic natural gas mixture in steel rocking cells using slow constant cooling starting at ca. 76 bar. All samples of PVCap and 1:1 VP:VCap showed good KHI performance to the first sign of hydrate formation, but older samples showed a better ability to inhibit crystal growth. KHI polymer testing after treatment with microwaves or ultrasound, or thermal aging (at varying temperatures, varying field pH, and in MEG solvent up to 160 °C) showed little loss of performance. Oxidizing agents, particularly sodium hypochlorite solution, worsened the KHI performance.

1. INTRODUCTION

One of the chemical methods used to prevent gas hydrate formation in oil and gas field production flow lines is injection of kinetic hydrate inhibitors (KHIs).^{1–7} The main active ingredient in KHIs is a water-soluble polymer, but deployed formulations usually contain organic solvents or other molecules that can act as synergists. KHI polymers usually contain amphiphilic groups. The mechanism of KHIs is still the subject of debate, but it appears several of these amphiphilic groups (i.e., in oligomers or polymers) are needed to prevent gas hydrate nuclei and/or crystals from growing into macroscopic size and subsequently blocking flow lines.^{8–10}

Well-known classes of KHI polymers that have been applied in the field include various *N*-vinyl lactam homopolymers and copolymers and poly(*N*-alkyl(meth)acrylamides) (Figure 1).⁷ KHI polymers may be subjected to a range of field conditions. First, before injection they may be stored in tanks for long periods at temperatures up to 40 °C. Later, the polymer will be

injected into a hot well stream usually at the well head, where the fluids may reach 80–100 °C. Some polymers may thermally degrade at these temperatures.^{11–13}

In addition, the pH of the produced water (i.e., aqueous phase from an unprocessed well stream) under pressure will be quite acidic due to dissolved carbon dioxide and often hydrogen sulfide, as well as organic acids from the liquid hydrocarbon phase. The pH is usually around 4–6 but can occasionally be even lower. Thus, the KHI polymer must be able to survive hot acidic conditions for a time and still inhibit hydrate formation when the fluids cool inside the hydrate-forming region.

The KHI may also be injected along with a thermodynamic inhibitor (THIs) to boost the hydrate inhibition.^{14–17} The commonest THIs used in production flow lines are methanol and monoethylene glycol (MEG), but ethanol is also sometimes used. Due to the volumes and costs, methanol and MEG are often regenerated and reused. If the THI is injected with KHI and is regenerated on site, the KHI polymer will be subjected to elevated temperatures; this can be up to 160 °C if the THI is MEG.^{18,19} It is important that the KHI polymer in the MEG does not cause fouling and is not degraded by this thermal treatment as the whole formulation is to be reinjected.

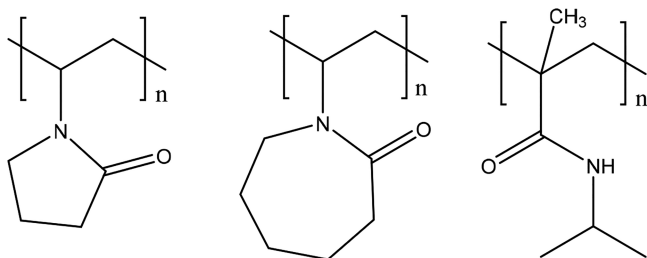
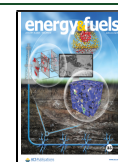


Figure 1. KHI polymers, left to right: poly(*N*-vinylpyrrolidone) (PVP), poly(*N*-vinylcaprolactam) (PVCap), and poly(*N*-isopropylmethacrylamide) (PNIPMAm).

Received: October 20, 2020
Revised: December 11, 2020
Published: January 7, 2021



If the KHI polymer is not to be recycled, it may be preferable in some regions if the polymer is destroyed before it is discharged in the produced water into the environment. Several methods have been proposed recently.^{20–22} One method to destroy the polymer is oxidation with common oxidizing agents such as bleach solution (aqueous sodium hypochlorite) or hydrogen peroxide. In the field, this oxidation treatment may be the last one to be encountered by the KHI polymer but, in this case, it is preferable if the polymer is not preserved but is degraded as much as possible.

In this report we have investigated typical conditions encountered by the KHI polymer as well as some other nonfield conditions simply to observe the effect on the polymer. These include

1. aging for up to 15 years
2. thermal treatment—at varying temperatures, varying pH, and in MEG solvent
3. microwave treatment
4. ultrasound
5. ball-milling
6. oxidizing agents with or without heat treatment—household bleach or hydrogen peroxide

The KHI polymer was tested before and after these different treatment conditions.

2. EXPERIMENTAL METHODS

2.1. Chemicals Used and KHI Polymer Treatment Equipment. Batches of poly(*N*-vinylcaprolactam) (PVCap; M_w 3000–4000 and 7000–12000 g/mol) and 1:1 *N*-vinylcaprolactam:*N*-vinylpyrrolidone (VCap:VP; M_w 2000–4000 g/mol) were supplied by BASF, Germany between 2004 and 2016. PVCap samples were approximately 41 wt % solution in MEG. For all experiments except the long-term stability study, the MEG was removed by triple precipitation of the polymer, followed by removal of residual solvents under vacuum. The VCap:VP copolymer was 53.8 wt % in water and was used as supplied. Poly(*N*-vinylpyrrolidones) (PVP K15, 8000 g/mol; PVP 120k, M_w 3×10^6 g/mol) pure powders were obtained from Ashland Chemical Co. All of these lactam-based KHI polymers had pH about 7–8 as 2500 ppm aqueous solutions. MEG solvent (99%) and acetic acid (99+%), aqueous hydrogen peroxide (30 vol %), and aqueous hydrochloric acid (37 wt %) were supplied by VWR (Avantor). Sodium hypochlorite (“Klor” bleach solution, approximately 5 wt % NaOCl) was supplied by Coop Mega, Norway.

Microwaving of polymer solutions was carried out using a Miele microwave oven. A 100 mL aliquot of a 2500 ppm solution of KHI polymer was placed in the oven in a glass vessel and subjected to microwaves at 780 W until the solution boiled (4–5 min). Ball-milling on solid KHI polymer samples was carried out using a Pulverisette 7, from Fritsch GmbH, Germany. Zirconium(IV) oxide balls were used in containers of the same material. Solids were milled for 10 min periods (with 2 min cooling periods in-between) at 700 rpm.

Ultrasound treatment of KHI polymer solutions was carried out using a Branson 2510 ultrasonic cleaner at 40 kHz with 2.8 L bath from Emerson, USA. A 2500 ppm solution of KHI polymer was placed in the sonic bath and subjected to ultrasound for 5 min at ca. 20.5 °C.

2.2. KHI Equipment and Experimental Methods. We carried out high-pressure KHI performance tests using a multisteel rocking cell apparatus, supplied by PSL Systemtechnik, Germany (Figure 2). The cells themselves were made by Svafas, Norway, and each has an internal volume of 40 mL. Five cells were used for our study placed in a water bath. A steel ball is placed in each cell which runs smoothly back and forth when the cells are rocked. Each cell was filled with 20 mL of aqueous KHI solution.

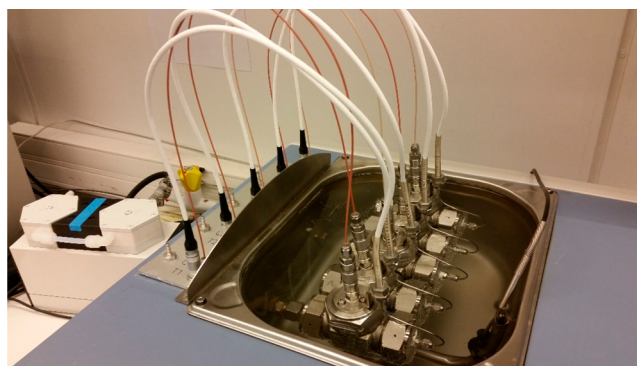


Figure 2. Rocking cell rig showing the five steel cells in upright position.

The test method in both rigs was our standard “slow constant cooling” test method described previously.^{23,24} The rest of the test method was as follows: Air in the sapphire or steel cells was removed using a vacuum pump, and then the cells were filled with 2–3 bar of synthetic natural gas (SNG; Table 1). The cells were briefly rocked,

Table 1. Composition of Synthetic Natural Gas

component	mol %
methane	80.67
ethane	10.20
propane	4.90
isobutane	1.53
<i>n</i> -butane	0.76
N ₂	0.10
CO ₂	1.84

and the procedure pump–fill was repeated twice except on the last fill the cells were then charged with 79 bar of SNG. This gas mixture preferentially forms structure II hydrates as the most thermodynamically stable phase. A computer logged the pressure, and temperature for each cell as well as the temperature in the cooling bath. The cells were cooled at a rate of 1.0 °C/h from 20.5 to 2.0 °C while rocking at 15 rocks per minute at an angle of 40°.

In this type of test, we first observe a pressure drop of 1.5–2 bar due to gas dissolution in the aqueous phase. Thereafter a linear pressure decrease is observed as the temperature decreases in a closed system. The first deviation from this linear pressure decrease is taken as the first sign of hydrate formation in the system. We call this the onset temperature (T_o) although true nucleation could have taken place at an earlier stage. The second parameter obtained from these experiments is the temperature for rapid hydrate formation (T_a), which is found where the pressure drop is at its steepest (meaning the inflection point of the pressure curve). This gives an indication of when the KHI is no longer able to confine the growth of hydrates. Some KHIs give very rapid hydrate growth once nucleation has begun while others, such as many *N*-vinylcaprolactam-based polymers, are able to slow the crystal growth process for long periods.

At the end of the slow constant cooling experiment, we plot a graph of pressure and temperature vs time for each cell. These graphs are essentially identical in form for both the steel and sapphire cells. Up to 10 individual tests were carried out on each sample. An example of a typical set of pressure and temperature vs time data for one sample is given in Figure 3. This is a graph from two sets of five tests giving a total of 10 tests. The closeness of the pressure and temperature traces gives some visual idea of the reproducibility of the test. In Figure 4 we show a graphical example, demonstrating how we determine T_o and T_a . The test is for PVCap (2020 sample). In this test, T_o was found to be 10.3 °C and T_a is found to be 8.6 °C. Due to the stochastic nature of hydrate formation, the data scattering is 10–15%.^{25,26} A full set of T_o and T_a values from eight blank tests and 10 tests on a

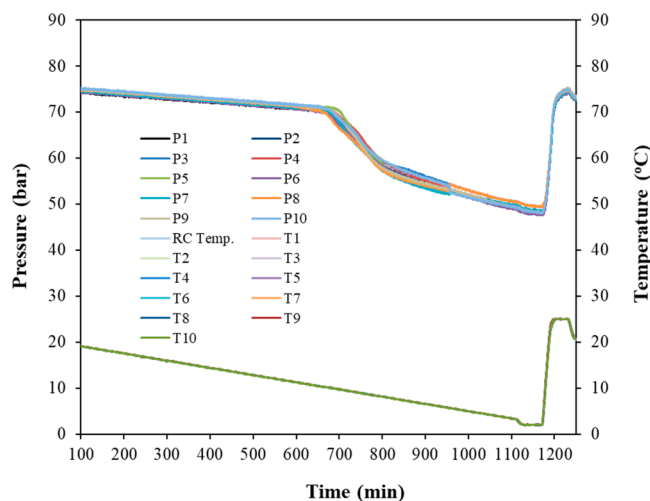


Figure 3. Example of pressure and temperature vs time graph for a set of 10 slow constant cooling tests. (RC Temp. is the temperature given on the cooling bath display.)

PVCap sample are given in Table 2. In addition, we give the average and standard deviations (population type). No systematic errors leading to consistently better or worse results for any of the cells were observed. Temperatures in the cells and the water bath were observed to be homogeneous. The two methods that we used to determine the hydrate equilibrium temperature (HET) for high-pressure gas hydrate systems are calculations using Calsep's PVTsim and laboratory experiments by standard slow hydrate dissociation.^{27,28} Previous experiments conducted by our group using a SNG–water system agreed very well with the calculated value (accuracy within 1 °C).²⁹

2.3. Results and Discussion. **2.3.1. Long-Term Aging.** All polymer solutions were tested 8–10 times to get reasonably reliable T_o and T_a values. Standard deviations were no more than 0.7 °C. Each solution was prepared the day before testing unless otherwise stated. The first part of the study was to check the long-term reliability of commercial KHIs. We had obtained samples of PVCap (ca. 41 wt % in MEG) and 1:1 VP:VCap copolymer (53.8 wt % in water) from the supplier at four times, in 2004, 2010, 2016, and 2020. All samples were kept at the laboratory temperature of 20.5 °C the whole time in screw-lid-sealed plastic bottles which were only opened occasionally

and briefly. Thus, the samples were stored aerobically but without loss of solvent. Both types of these VCap-based polymers are known to be very poorly biodegraded in the OECD306 seawater test over 28 days.^{2,7} Samples were used as received; no solvents were removed for these long-term aging studies.

The KHI performance results for tests at 2500 ppm active polymer were carried out in the steel multicell rocking equipment and are summarized in Table 3. 8–10 tests were conducted on each polymer solution. Tests were carried out in 2019 so that the oldest samples were approximately 15 years old at that time. Although the lowest average T_o value (7.3 °C) was found for the oldest batch (2004), at the 95% confidence level ($p > 0.05$ from statistical t test), there was no significant difference between the T_o values performances of each group of polymers supplied at the three dates. However, there is a trend to higher T_a values as the polymers get older. This is for both PVCap and 1:1 VP:VCap copolymer. We are not sure of the reason for this trend. Since operators wish to keep their flow lines completely hydrate free, the time to first hydrate crystal formation is usually regarded as the more important parameter. Therefore, we conclude that on the basis of T_o values both polymers give reliable KHI performance even after a 15 year storage period. Other commercial KHI polymers such as hyperbranched poly(esteramide)s or poly(*N*-alkylmethacrylamide)s were not investigated as we had not stored them for such a long time.

Usually, we make up 2500 ppm polymer aqueous solutions the day before the test to allow the polymer chains to be fully hydrated by the water and come to their equilibrium structure.^{9,23,24,26} To check if this is necessary, we prepared solutions of 1:1 VP:VCap copolymer (2004 batch) at 2500 ppm and tested them immediately as well as after stirring overnight at 20.5 °C. Both solutions gave almost identical average T_o and T_a values, indicating that there was no difference in waiting approximately 24 h before testing the polymer solution. We also carried out the same procedure with this polymer but with added 2500 ppm MEG, i.e., immediate testing with a freshly made solution and testing after stirring 24 h. The results are summarized in Table 4 but discussed later in this study.

2.3.2. Thermal Aging at Normal pH. Some KHI storage facilities, for example in the Middle East, might keep concentrated KHI solutions for many months at up to 40+ °C, especially during the summer. We have not kept any of our laboratory samples at these temperatures for long periods, so instead we decided to investigate heating the samples to even higher temperatures for short periods, which might be typical of well head temperatures. The PVCap used in this study had a higher molecular weight range (7–12 kg/mol) than

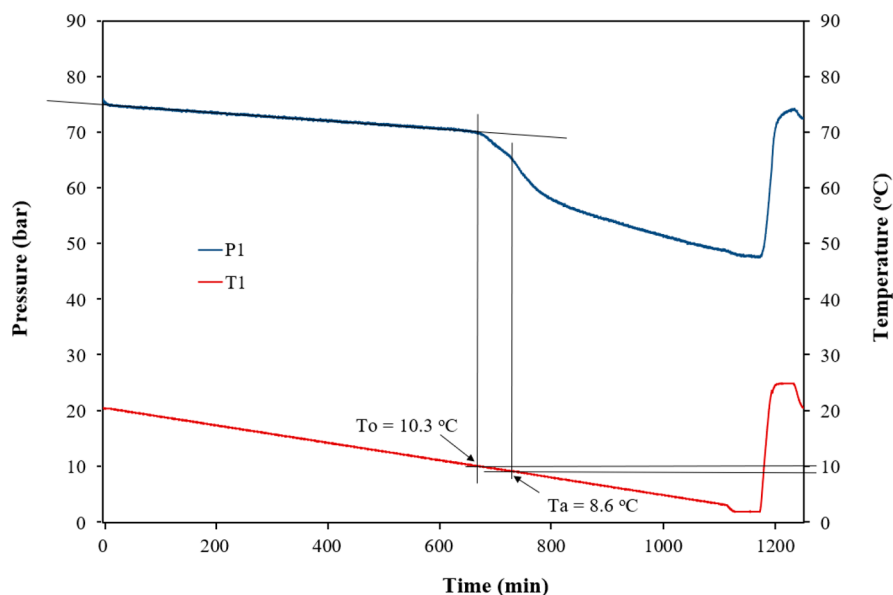


Figure 4. Example of T_o and T_a determination for one of the steel rocking cells in a slow constant cooling test.

Table 2. Examples of the Range of T_o and T_a Values for Blank Tests and PVCap ($M_w = 7\text{--}12k$)

	T_o values, °C	T_a values, °C	$T_o(\text{av})$, °C	SD, °C	$T_a(\text{av})$, °C	SD, °C
blank test	16.8, 17.2, 17.3, 17.0, 16.0, 17.1, 17.8, 16.7	16.8, 17.1, 17.1, 17.0, 15.9, 16.9, 17.6, 16.7	17.0	0.49	16.9	0.45
PVCap(7–12k)	10.3, 10.3, 10.5, 10.3, 9.8, 10.6, 10.2, 11.2, 10.4, 10.3	9.9, 9.9, 10.1, 9.8, 9.6, 10.1, 9.9, 10.0, 9.8, 9.9	10.4	0.34	9.9	0.14

Table 3. Slow Constant Cooling Tests on 2500 ppm Active Polymer^a

polymer	$T_o(\text{av})$, °C	$T_a(\text{av})$, °C
no additive	16.8 (0.5)	16.7 (0.4)
PVCap 2004	10.0 (0.3)	7.9 (0.2)
PVCap 2010	9.7 (0.4)	7.8 (0.5)
PVCap 2016	10.2 (0.2)	7.5 (0.4)
1:1 VP:VCap copolymer 2004 (immediate testing)	7.3 (0.5)	6.0 (0.5)
1:1 VP:VCap copolymer 2004	7.4 (0.6)	6.5 (0.4)
1:1 VP:VCap copolymer 2010	8.5 (0.7)	5.8 (0.7)
1:1 VP:VCap copolymer 2016	8.2 (0.6)	5.8 (0.3)
1:1 VP:VCap copolymer 2020	8.1 (0.4)	5.4 (0.4)

^a T_o and T_a are the average of 8–10 individual experiments. Standard deviations are given in parentheses.

those used in Table 2. The MEG solvent was removed before testing. PVCap homopolymer is less likely to be injected at high well head temperatures as it has a cloud and deposition point of about 30–40 °C as a 2500 ppm solution in deionized water. Therefore, we concentrated on heating the 1:1 VP:VCap copolymer in aqueous solution, which has cloud and deposition points of about 70 and 85 °C, respectively.³⁰ We found that heating a 2500 ppm aqueous solution of this polymer to 80 °C for 20 h gave no visual change in the solution, when cooled back to room temperature, and no significant change in the KHI performance (Table 4). Photographs of the 2500 ppm solution of this copolymer at 20 °C (after heating) and at 80 °C are given in Figure 5.

2.3.3. Thermal Aging with MEG. KHIs can be used as a retrofit solution, to replace some or all of the injected thermodynamic hydrate inhibitor (THI), in a field application.³¹ MEG is often regenerated and reinjected. Therefore, it is important to know if the KHI would survive the MEG regeneration processing where the temperature of the fluids can reach as high as 160 °C.^{32–36}

First, we checked if MEG was a synergist for the 1:1 VP:VCap copolymer 2004 batch. A mixture of 2500 ppm of both chemicals gave average T_o and T_a values (10 tests) of 7.1 and 5.7 °C, respectively (Table 4). The T_o value is a little lower but is not statistically

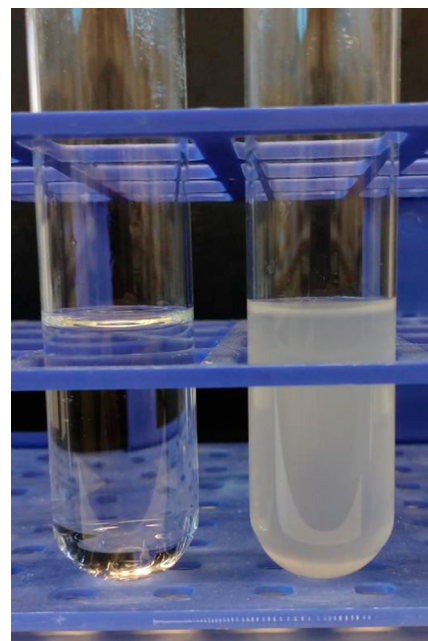


Figure 5. 2500 ppm solutions of 1:1 VP:VCap copolymer at 20 °C after first heating to 80 °C (left) and at 80 °C (right).

significantly different from the copolymer alone ($p < 0.05$ for statistical t test). MEG has been reported to be a weak synergist with PVCap.³⁷ Sometimes synergy is reported between KHI and THI, but often this is just an additional effect and not true synergy; i.e., the KHI gives extra inhibition on top of the THI inhibition but not more than the full effect of each when mixed.^{38–40} At best, MEG is a poor synergist. Etherification (ethoxylation) of alcohols to form alkyl glycol ethers produces much more powerful synergists.⁴¹

Next, we heated a solution of 1:1 VP:VCap copolymer (2004 batch) with an equivalent weight (based on active copolymer) of MEG to 160 °C for 1 h under an anaerobic atmosphere in a sealed stirred vessel. The pH was still about 7 after this treatment. When we

Table 4. Effect of Thermal Aging in MEG, pH, Ultrasonic and Microwave Treatment^a

polymer	$T_o(\text{av})$, °C	$T_a(\text{av})$, °C
no additive	16.8 (0.5)	16.7 (0.4)
PVCap ($M_w = 7\text{--}12$ kg/mol)	10.4 (0.3)	8.9 (0.3)
PVCap + MEG	9.2 (0.4)	8.8 (0.3)
PVCap (pH 3.9)	10.2 (0.2)	9.6 (0.2)
PVCap (pH 3.9, heat 90 °C for 20 h)	10.6 (0.3)	9.8 (0.3)
1:1 VP:VCap copolymer 2004	7.4 (0.6)	5.6 (0.4)
1:1 VP:VCap copolymer 2004 (heat 80 °C for 20 h)	7.5 (0.4)	5.6 (0.3)
1:1 VP:VCap copolymer 2004 + MEG	7.1 (0.5)	5.7 (0.3)
1:1 VP:VCap copolymer 2004 + MEG (immediate testing)	7.0 (0.5)	5.5 (0.4)
1:1 VP:VCap copolymer 2004 + MEG (after 160 °C for 1 h)	7.4 (0.6)	6.3 (0.5)
1:1 VP:VCap copolymer 2004 (pH 3.9)	7.8 (0.5)	5.5 (0.4)
1:1 VP:VCap copolymer 2004 (pH 3.9, heat 80 °C for 20 h)	8.0 (0.4)	5.6 (0.4)
1:1 VP:VCap copolymer 2004 (microwave treatment)	7.1 (0.4)	5.9 (0.4)
1:1 VP:VCap copolymer 2004 (ultrasonic treatment)	7.3 (0.5)	5.7 (0.5)

^a2500 ppm KHI polymer used in all tests. MEG concentration was 2500 ppm. Average of 5–10 tests.

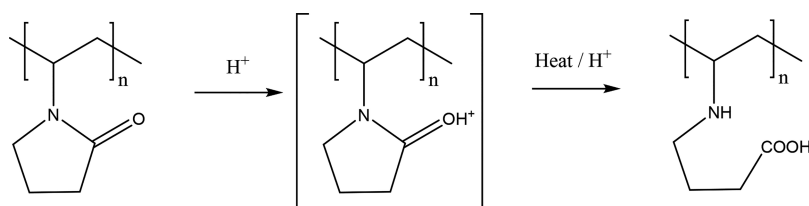


Figure 6. Hydrolysis of *N*-vinylpyrrolidone monomer units.

retested the solution at 2500 ppm active polymer, we observed an average T_o of 7.4 °C and T_a of 6.3 °C, i.e., the same KHI performance as before heat treatment at the 95% confidence level (Table 4). Therefore, since MEG was shown earlier to give no synergy, it appears this copolymer is able to survive the temperature and residence time experienced in MEG regeneration equipment.

2.3.4. Effect of pH. The motivation for this part of the study is unofficial reports from service companies that some KHI polymers perform differently at low produced water pH values. In this study we only investigated *N*-vinylactam-based polymers. The pyrrolidone rings in PVP are reported to slowly ring-open hydrolyze under acidic conditions and elevated temperatures⁴² (Figure 6). This may occur via the protonated monomer species, $[VP-H^+]$, which will exist in solution at low pH before hydrolysis and could also affect the KHI performance. If these reactions also occur for caprolactam rings in VCap-containing polymers, it could also cause loss of KHI performance but might raise the polymer cloud point. Basic conditions can also cause hydrolysis of lactam rings, but alkyl substitution on the lactam nitrogen (as in VP or VCap-based polymers) makes the lactam more resistant against hydrolysis.⁴³ Degradation of *N*-vinylactam polymers under basic conditions may be a relevant issue for their use in water-based drilling fluids which often have pH of 10–11.³⁰

As explained earlier, the pH of the aqueous produced fluids from a gas or oilfield under pressure could be quite acidic due to the presence of dissolved CO_2 and H_2S , with the pH occasionally dropping below 4 for some fields. Although the CO_2 in our natural gas mixture would be expected to lower the pH of the KHI aqueous solution to about 5, we deliberately acidified a solution of 1:1 VP:VCap copolymer (2004 batch) to pH 3.9 by addition of hydrochloric acid. (A weak acid was not used as the amount needed for this pH could have an effect on the hydrate equilibrium temperature.)⁴⁴ Although we preacidified to pH 3.9, the actual pH at 70–80 bar from the partial pressure of CO_2 in the gas mixture, and its buffering effect, may raise the pH somewhat higher than 3.9 during the test.

The effect of preacidification (protonation) of KHI polymers has been reported previously, but usually in connection with quaternization of amine monomer units.^{45,46} We maintained the final acidified VP:VCap polymer concentration at 2500 ppm. When this was tested the next day with no heating above room temperature, we obtained an average T_o of 7.8 ± 0.4 °C (Table 4). Then we heated an identical sample at pH 3.9 and 80 °C anaerobically for 20 h in a sealed tube. No deposition during the heating process was observed, and the sample was clear when cooled to room temperature. When we carried out new KHI tests, we observed an average T_o value of 8.0 ± 0.5 °C (10 tests), indicating no loss of performance at the 95% confidence level.

We also investigated a commercial PVCap under more acidic conditions with added hydrochloric acid. A 2500 ppm solution of this polymer at pH 3.9 gave the same KHI performance as the pure PVCap. We then heated an identical acidified polymer solution at pH 3.9 and 90 °C anaerobically for 20 h in a sealed tube. Surprisingly, this also did not affect the KHI performance (Table 4). This “stability” may be due to polymer precipitation above the cloud and deposition point of about 40 °C and therefore being less accessible for aqueous hydrolysis.

2.3.5. Mechanochemical Treatment. KHI polymers must survive rapid injection, movement through valves and the harsh physical flow environment in a multiphase flow line. To push this environment to

an even more extreme physical condition, we investigated ball-milling of KHI polymers as powders using zirconium(IV) oxide balls. We wondered if this mechanical strain could cause cleavage of side groups on the polymer backbone or even the backbone itself. Mechanochemical solvent-free reactions by milling or grinding are becoming more popular as methods to do solvent-free reaction chemistry.⁴⁷ Mechanochemistry can even accomplish reactions and access molecules previously not accessible by solution chemistry. Ball-milling can also affect the microscopic and macroscopic properties of a material such as structure, morphology, crystallinity, and thermal stability.^{48,49}

First, we presumed ball-milling might be able to break long polymer chains to shorter chains which would give improved KHI performance. Several studies suggest that very low molecular weight ranges (down to as little as 6–8 monomer units) give the best performance for KHI polymers when the distribution is monomodal.^{2,8,50–52}

Some reports indicate substantial polymer degradation from ball-milling, e.g., for poly(methyl methacrylate).⁵³ However, other polymers such as polypropylene-ethylene copolymer or polyethylene homopolymer show a much slower degradation effect.⁵⁴ In addition, ball-milling of solutions of polymers are expected to give less chain breakage than powdered solids, so we used powdered polymers to ensure we would see an effect. For these reasons, we tested a high molecular weight polymer powder, PVP 120k ($M_w = 3 \times 10^6$ g/mol given by the manufacturer; PDI not given), as VP monomer is known to polymerize to much higher molecular weights compared to VCap forming PVCap for example. We also knew that the KHI performance of PVP on our structure II hydrate-forming synthetic natural gas increases with decreasing molecular weight.⁵⁵

We ball-milled PVP 120k powder for 60 min. The temperature during this type of milling can reach up to 70 °C.⁵⁶ GPC analysis of the milled polymer indicated a lower and broad molecular weight distribution (M_n now 10000 g/mol with PDI = 12.1), so we expected a higher KHI performance, i.e., lower T_o value. We found that the average T_o value (six tests) of the PVP dropped from 13.7 °C before ball-milling to 12.8 °C after ball-milling, but the drop was only statistically significant at the 90% confidence level, giving $p = 0.09$ in a t test (Table 5).

We then ball-milled a sample of poly(*N*-isopropylmethacrylamide) (PNIPMAM) which had a much lower molecular weight (M_n of 19000 g/mol (PDI = 2.6). After 60 min ball-milling the average T_o value had dropped from 10.5 to 9.8 °C but this was not statistically significantly different at the 95 or even 90% confidence level (Table

Table 5. KHI Test Results for Ball-Milled Polymers (5–6 Tests on Each Polymer)

polymer	M_n (g/mol)/PDI	T_o (av), °C	T_a (av), °C
no additive		16.8 (0.5)	16.7 (0.5)
PVP 120k (M_w , 3×10^6 g/mol)	<i>a</i>	13.7 (0.4)	11.2 (0.3)
PVP 120k after 60 min ball-milling	10000/2.57	12.8 (0.5)	10.5 (0.5)
PNIPMAM	19000/12.1	10.5 (0.5)	10.1 (0.4)
PNIPMAM after 60 min ball-milling	7000/1.47	9.8 (0.4)	9.4 (0.3)

^aInsoluble in DMF. Manufacturer gives M_w as 3×10^6 g/mol.

5). GPC analysis indicated a decrease in M_n after ball-milling, dropping from 19000 to 7000 g/mol. These two results with PVP and PNIPMAM indicate that KHI polymers may degrade to some degree under very harsh mechanical conditions. However, this could improve the KHI performance if the molecular weight range is reduced to shorter, *but not too short*, polymer chains. Thus, ball-milling or some other kind of mechanical strain degradation might be a way to produce shorter and more optimal KHI polymers from larger polymer chains if they were not easily available by other means. An example might be natural polymers such as proteins and polysaccharides.

Ball-milling has recently been shown to convert monomers into polymers. This was demonstrated first for the conversion of phenylenevinylenes using a butoxide-based catalyst and ball-milling to poly(phenylenevinylenes) (PPVs).⁵⁷ Other polymers have been made, but as far as we know, classic radical polymerization has not been carried out for polyvinylation.⁵⁸ Therefore, we decided to try using ball-milling to form a polymer via vinyl polymerization of classic monomers found in KHIs with a radical initiator. We ball-milled both VCap and NIPMAM separately with 1% AIBN for 3×10 min periods. The resulting solid was analyzed by ¹H NMR and shown to be monomer only with no broad peaks indicating polymer formation. The milling was repeated, this time with added 2-propanol as solvent. Again, no polymerization appeared to have taken place by NMR analysis.

2.3.6. Treatment with Oxidizing Agents. The final chemical treatment we investigated was oxidation. Oxidation processes have been proposed as a method to eliminate or reduce a KHI polymer in the produced water prior to discharge to an environmentally sensitive body of water.⁵⁹ There may also be a need to use an oxidizing biocide to treat injected water containing a KHI to prevent gas hydrate formation, for example in WAG or CO₂ injection. We have previously attempted to partially oxidize PVCap to convert the seven-ring caprolactam to a seven-ring adipimide (Figure 7).⁶⁰ We tried a variety

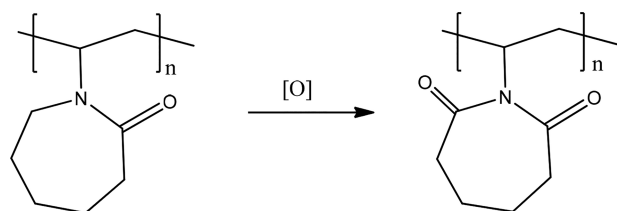


Figure 7. Oxidation of poly(*N*-vinylcaprolactam) to poly(*N*-vinyladipimide).

of oxidizing agents, but none were able to accomplish the required oxidation, probably due to steric problems. (We are currently investigating oxidation of the caprolactam ring from the monomer, and we will report on this in a later study.) However, in that study we did not attempt the oxidation with the two biocides, sodium hypochlorite or hydrogen peroxide solution. Here we report these experiments for the first time.

Addition of 1 mol equiv of sodium hypochlorite to a solution of PVCap ($M_w = 7\text{--}12$ kg/mol; MEG removed), so that the polymer

concentration was 2500 ppm, raised the pH to 9. This solution gave the same KHI performance as the untreated polymer (Table 6). However, when we heated the sodium hypochlorite/PVCap solution to 90 °C for 20 h (above the deposition point of PVCap) and cooled to room temperature, we observed a small amount of solid that would not dissolve, less than 10% of the polymer weight. After filtering, the filtrate was retested and the average T_o value had increased from 10.0 to 13.0 °C. This is obviously due to a lower concentration of polymer, but some of the remaining PVCap may have oxidized also, including degradation of the polymer chain, but remained water-soluble. The bleach-induced decomposition of other water-soluble polymers has been reported previously. For example, the molecular weight of poly(*N*-vinylpyrrolidone) decreased by a factor of 5 when exposed to sodium hypochlorite at pH 11.5.⁶¹ The authors proposed that scission was initiated by free radical induced hydrogen abstraction of the proton α to the carbonyl. The polymer chain of poly(*N*-isopropylacrylamide) is degraded by sodium hypochlorite at pH 7–9 but the side chains are chlorinated to form a stable *N*-chloramide copolymer at higher pH.⁶²

Attempted oxidation of VP:VCap copolymer with aqueous NaOCl (bleach) was also carried out for 20 h at 80 °C, just below the cloud point of the copolymer. This polymer appears to be quite robust. No visual change in the solution was observed, and as the results in the last two entries in Table 5 show, there was no significant change in the KHI performance of the polymer, assuming the small amount of bleach in solution did not interfere with the hydrate equilibrium temperature.

Hydrogen peroxide is a cheap oxidizing biocide which is known to form a solid 1:1 adduct with PVP.^{63,64} However, we are unable to find a report of an adduct with PVCap. To a solution of PVCap we added 1 molar equiv (per VCap monomer) of 30 wt % hydrogen peroxide solution so the polymer concentration was 2500 ppm. The solution was stirred at 20.5 °C for 20 h with no sign of precipitation. We did not heat the solution as this would decompose the peroxide. When we tested the solution for KHI performance, we obtained an average T_o of 8.3 °C, which was significantly lower than the 10.2 °C value for the untreated polymer (statistically, p value in t test was <0.05). Interestingly, the cloud point was measured and it was found to have dropped by about 1 °C from about 39 to 38 °C (repeat tests). This seems to rule out oxidation to the adipimide ring as this is more hydrophilic than the caprolactam ring. We also found a 2 wt % solution of hydrogen peroxide decreased the cloud point to about 36 °C. Therefore, it seems the hydrogen peroxide is able to affect the solubility of PVCap. We can only speculate on the apparent synergistic effect of hydrogen peroxide on the PVCap KHI performance. For example, it is known that hydrogen bonds in pure hydrogen peroxide are weaker than those in water.⁶⁵ The presence of hydrogen peroxide in the PVCap solution may affect the rate of hydrate formation by weakening hydrogen bonding, or possibly the hydrogen bonding to PVCap is weakened allowing for better inhibition of growing hydrate clusters. Finally, since PVP·H₂O₂ is known, the formation of a PVCap·H₂O₂ adduct in solution cannot be ruled out.⁶⁴

2.4. Conclusion. *N*-Vinylactam-based kinetic hydrate inhibitor polymers (KHIs) such as poly(*N*-vinylcaprolactam) (PVCap),

Table 6. KHI Performance after Treatment with Oxidizing Agents^a

polymer	T_o (av), °C	T_a (av), °C
no additive	16.8 (0.5)	16.7 (0.5)
PVCap ($M_w = 7\text{--}12$ kg/mol)	10.2 (0.5)	9.0 (0.3)
PVCap +2500 ppm bleach (pH 9)	10.0 (0.3)	9.4 (0.3)
PVCap +2500 pm bleach (heat 90 °C for 20 h) ^b	13.0 (0.4)	9.5 (0.3)
PVCap + 10000 ppm H ₂ O ₂ (20 °C for 20 h, pH 4.5)	8.3 (0.3)	7.6 (0.3)
PVCap + 20000 ppm H ₂ O ₂ (immediate test, pH 4.3)	9.5 (0.3)	8.9 (0.2)
1:1 VP:VCap copolymer 2016	8.2 (0.4)	5.8 (0.3)
1:1 VP:VCap copolymer 2016 + 2500 ppm NaOCl (pH 10.8, heat 80 °C for 20 h)	8.1 (0.3)	6.4 (0.3)

^aAll KHI polymer concentrations are 2500 ppm. ^bSome precipitate in the sample, removed before KHI performance testing.

poly(*N*-vinylpyrrolidone) (PVP), and 1:1 *N*-vinylcaprolactam:*N*-vinylpyrrolidone (VCap:VP) copolymer were subjected to a range of treatments to determine their reliability and whether the treatment conditions could affect the KHI performance. Samples of PVCap and 1:1 VP:VCap up to 15 years old showed good performance regarding the onset of hydrate formation, but older samples showed a better ability to inhibit crystal growth. Various samples of VP:VCap copolymer of up to 15 years old showed no loss of performance after aerobic storage in plastic bottles at room temperature. KHI testing after thermal aging of PVCap or VP:VCap (at varying temperatures, at varying field pH, and in MEG solvent) showed little loss of performance, indicating good robustness for these polymers. Treatment with microwaves or ultrasound showed little change in the polymer performance. Harsh mechanical stress from ball-milling can reduce the polymer molecular weight to shorter chain lengths but might serve to improve the performance since it is known that low molecular weight polymers are most effective as KHIs. Oxidizing agents did affect the KHI performance. Bleach (aqueous sodium hypochlorite) worsened the performance of PVCap but only at elevated temperatures and in basic solution. The performance of PVCap improved upon addition of hydrogen peroxide. This may be due to formation of a PVCap·H₂O₂ adduct or a synergistic effect.

AUTHOR INFORMATION

Corresponding Author

Malcolm A. Kelland – Department of Chemistry, Bioscience and Environmental Engineering, Faculty of Science and Technology, University of Stavanger, N-4036 Stavanger, Norway; orcid.org/0000-0003-2295-5804; Email: malcolm.kelland@uis.no

Authors

Qian Zhang – Department of Chemistry, Bioscience and Environmental Engineering, Faculty of Science and Technology, University of Stavanger, N-4036 Stavanger, Norway; orcid.org/0000-0002-9137-1821

Erik G. Dirdal – Department of Chemistry, Bioscience and Environmental Engineering, Faculty of Science and Technology, University of Stavanger, N-4036 Stavanger, Norway; orcid.org/0000-0002-1634-9907

Mohamed F. Mady – Department of Chemistry, Bioscience and Environmental Engineering, Faculty of Science and Technology, University of Stavanger, N-4036 Stavanger, Norway; orcid.org/0000-0002-4636-0066

Complete contact information is available at:
<https://pubs.acs.org/10.1021/acs.energyfuels.0c03519>

Notes

The authors declare no competing financial interest.

NOMENCLATURE

AIBN = azobisisobutyronitrile
GPC = gel permeation chromatography
HET = hydrate equilibrium temperature
KHIs = kinetic hydrate inhibitors
MEG = monoethylene glycol
 M_n = number-average molecular weight
 M_w = weight-average molecular weight
NMR = nuclear magnetic resonance
PDI = polydispersity index
PNIPMAm = poly(*N*-isopropylmethacrylamide)

THI = thermodynamic inhibitor

T_{onset} = temperature for first detection of hydrate formation

VCap:VP = *N*-vinylcaprolactam:*N*-vinylpyrrolidone

WAG injection = water and gas injection

REFERENCES

- (1) Kelland, M. A. *Energy Fuels* **2006**, *20*, 825–847.
- (2) Kelland, M. A. A Review of Kinetic Hydrate Inhibitors: Tailor-Made Water-Soluble Polymers for Oil and Gas Industry Applications. In *Advances in Materials Science Research*; Wytherst, M. C., Ed.; Advances in Materials Science Research, Vol. 8; Nova Science: New York, 2011; Chapter 5.
- (3) Sloan, E. D., Jr.; Koh, C. A. *Clathrate Hydrates of Natural Gases*, 3rd ed.; CRC Press (Taylor & Francis Group): Boca Raton, FL, USA, 2008.
- (4) Perrin, A.; Musa, O. M.; Steed, J. W. *Chem. Soc. Rev.* **2013**, *42*, 1996–2015.
- (5) Kamal, M. S.; Hussein, I. A.; Sultan, A. S.; von Solms, N. Application of various water soluble polymers in gas hydrate inhibition. *Renewable Sustainable Energy Rev.* **2016**, *60*, 206–225.
- (6) Ke, W.; Kelland, M. A. *Energy Fuels* **2016**, *30*, 10015–10028.
- (7) Kelland, M. A. *Production Chemicals for the Oil and Gas Industry*, 2nd ed.; CRC Press, Taylor & Francis: Boca Raton, FL, USA, 2014; Chapter 9.
- (8) Yagasaki, T.; Matsumoto, M.; Tanaka, H. Molecular Dynamics Study of Kinetic Hydrate Inhibitors: The Optimal Inhibitor Size and Effect of Guest Species. *J. Phys. Chem. C* **2019**, *123* (3), 1806–1816.
- (9) Dirdal, E. G.; Kelland, M. A. Does the Cloud Point Temperature of a Polymer Correlate with Its Kinetic Hydrate Inhibitor Performance? *Energy Fuels* **2019**, *33*, 7127–7137.
- (10) Varma-Nair, M.; Costello, C. A.; Colle, K. S.; King, H. E. Thermal Analysis of Polymer-Water Interactions and Their Relation to Gas Hydrate Inhibition. *J. Appl. Polym. Sci.* **2007**, *103* (4), 2642–2653.
- (11) Ree, L. H. S.; Sirianni, Q. E. A.; Gillies, E. R.; Kelland, M. A. Systematic Study of Polyglyoxylamides as Powerful, High-Cloud-Point Kinetic Hydrate Inhibitors. *Energy Fuels* **2019**, *33*, 2067–2075.
- (12) Wang, W.; Kan, A.; Yan, C.; Tomson, M., The Use of Inhibition Kinetics and NMR Spectroscopy in Thermal Stability Study of Scale Inhibitors. *SPE International Symposium on Oilfield Chemistry*, SPE 164047, The Woodlands, TX, USA, Apr. 8–10, 2013; Society of Petroleum Engineers, 2013; DOI: 10.2118/164047-MS.
- (13) Glibowski, P.; Bukowska, A. The Effect of pH, Temperature and Heating Time on Inulin Chemical Stability. *Acta Sci. Pol., Technol. Aliment.* **2011**, *10* (2), 189–196.
- (14) Talley, L. D.; Colle, K. Int. Pat. Appl. WO 2006/110192, 2006.
- (15) Kaasa, B.; Hemmingsen, P. V. Int. Pat. Appl. WO 2013/041143, 2013.
- (16) Moen, K.; Calvo, A. S. Int. Pat. Appl. WO 2013/093789, 2013.
- (17) Xu, S. R.; Fan, S. S.; Wang, Y. H.; Lang, X. M. *Chem. Eng. Sci.* **2017**, *171*, 293–302.
- (18) Xu, S.; Fan, S.; Wang, Y.; Lang, X. Recovery of monoethylene glycol combined with kinetic hydrate inhibitor. *Chem. Eng. Sci.* **2017**, *171*, 293–302.
- (19) Othman, A.; Al-Sobhi, S. A.; Almomani, F.; Khraisheh, M.; AlNouss, A.; Adham, S.; Qiblawey, A. Systematic Approach for the Design and Simulation of Monoethylene Glycol (MEG) Recovery in Oil and Gas Industry. *Int. J. Energy Res.* **2020**, *44*, 12363–12375.
- (20) Hussain, A.; Gharfeh, S.; Adham, S. Study of Kinetic Hydrate Inhibitor Removal Efficiency by Physical and Chemical Processes. *SPE International Production and Operations Conference & Exhibition*, SPE-157146, Doha, Qatar, May 14–16, 2012; Society of Petroleum Engineers, 2012; DOI: 10.2118/157146-MS.
- (21) Minier-Matar, J.; Gharfeh, S.; Hussain, A.; Adham, S. U.S. Pat. Appl. US 20160376171, 2016.
- (22) Kelland, M. A. A Review of Kinetic Hydrate Inhibitors from an Environmental Perspective. *Energy Fuels* **2018**, *32*, 12001–12012.

- (23) Zhang, Q.; Heyns, I. M.; Pfkwa, R.; Klumperman, B.; Kelland, M. A. Improving the Kinetic Hydrate Inhibition Performance of 3-Methylene-2-pyrrolidone Polymers by N-Alkylation, Ring Expansion, and Copolymerization. *Energy Fuels* **2018**, *32*, 12337–12344.
- (24) Zhang, Q.; Kelland, M. A. Study of the Kinetic Hydrate Inhibitor Performance of Poly(N-vinylcaprolactam) and poly(N-isopropylmethacrylamide) with Varying End Caps. *Energy Fuels* **2018**, *32*, 9211–9219.
- (25) Koh, C. A. Towards a fundamental understanding of natural gas hydrates. *Chem. Soc. Rev.* **2002**, *31* (3), 157–167.
- (26) Kelland, M. A.; Abrahamsen, E.; Ajiro, H.; Akashi, M. Kinetic Hydrate Inhibition with N-Alkyl-N-vinylformamide Polymers: Comparison of Polymers to n-Propyl and Isopropyl Groups. *Energy Fuels* **2015**, *29* (8), 4941–4946.
- (27) Gjertsen, L. H.; Fadnes, F. H. *Ann. N. Y. Acad. Sci.* **2000**, *912*, 722–734.
- (28) Tohidi, B.; Burgass, R. W.; Danesh, A.; Ostergaard, K. K.; Todd, A. C. *Ann. N. Y. Acad. Sci.* **2000**, *912*, 924–931.
- (29) Chua, P. C.; Kelland, M. A. *Energy Fuels* **2013**, *27* (3), 1285–1292.
- (30) Kelland, M. A.; Mønig, K.; Iversen, J. E.; Lekvam, K. Feasibility Study for the Use of Kinetic Hydrate Inhibitors in Deep-Water Drilling Fluids. *Energy Fuels* **2008**, *22* (4), 2405–2410.
- (31) AlHarooni, K.; Gubner, R.; Iglauer, S.; Pack, D.; Barifcani, A. Influence of Regenerated Monoethylene Glycol on Natural Gas Hydrate Formation. *Energy Fuels* **2017**, *31*, 12914–12931.
- (32) Alef, K.; Smith, C.; Iglauer, S.; Gubner, R.; Barifcani, A. MEG on hydrate inhibition performance over multiple regeneration cycles. *Fuel* **2018**, *222*, 638–647.
- (33) Alef, K.; Gubner, R.; Iglauer, S.; Barifcani, A. Evaluation of MEG reclamation and natural gas hydrate inhibition during corrosion control switchover. *J. Pet. Sci. Eng.* **2019**, *176*, 1175–1186.
- (34) Magnusson, C.; Abrahamsen, E.; Kelland, M. A.; Cely, A.; Kinnari, K.; Li, X.; Askvik, K. M. As Green As It Gets: An Abundant Kinetic Hydrate Inhibitor from Nature. *Energy Fuels* **2018**, *32*, 5772–5778.
- (35) Tohidi, B.; Anderson, R.; Mozaffar, H.; Tohidi, F. The Return of Kinetic Hydrate Inhibitors. *Energy Fuels* **2015**, *29* (12), 8254–8260.
- (36) Xu, S.; Fan, S.; Wang, Y.; Lang, X. Recovery of monoethylene glycol combined with kinetic hydrate inhibitor. *Chem. Eng. Sci.* **2017**, *171*, 293–302.
- (37) Kelland, M. A.; Dirdal, E. G.; Ree, L. H. S. Solvent Synergists for Improved Kinetic Hydrate Inhibitor Performance of Poly(N-vinyl caprolactam). *Energy Fuels* **2020**, *34*, 1653–1663.
- (38) Kim, M.; Bae, Y. W.; Lee, B.; Cheong, I. W. M.; Shin, K. LCST-Modulated Polymers for Synergistic Hydrate Inhibition in Methane Gas Flowlines. *Energy Fuels* **2018**, *32*, 3013–3021.
- (39) Shin, K. J.; Chang, D.; Seo, Y.; Chang, P. K.; Kinetic Hydrate Inhibition Performance of MEG in Under-Inhibition System: Reduction Opportunities of MEG Injection for Offshore Gas Field Developments, OTC-24961. *Offshore Technology Conference-Asia*, Kuala Lumpur, Malaysia, Mar. 25–28, 2014.
- (40) Semenov, A. P.; Medvedev, V. I.; Gushchin, P. A.; Yakushev, V. S.; Vinokurov, V. A. Inhibiting Gas Hydrate Formation by Polymer-Monoethylene Glycol Mixture. *Chem. Technol. Fuels Oils* **2016**, *52* (1), 43–51.
- (41) Cohen, J. M.; Wolf, P. F.; Young, W. D. Enhanced Hydrate Inhibitors: Powerful Synergism with Glycol Ethers. *Energy Fuels* **1998**, *12*, 216–218.
- (42) Reppe, W. *Polyvinylpyrrolidone*; Verlag Chemie: Weinheim/Bergstrasse, Germany, 1954; p 72.
- (43) Conix, A.; Smets, G. *J. Polym. Sci.* **1955**, *15* (79), 221–229.
- (44) Peng, C.; Crawshaw, J. P.; Maitland, G. C.; Trusler, J. P. M.; Vega-Maza, D. The pH of CO₂-saturated water at temperatures between 308 and 423 K at pressures up to 15 MPa. *J. Supercrit. Fluids* **2013**, *82*, 129–137.
- (45) Bartels, J. W.; Jones, R. A.; Servesko, J. W. Int. Pat. Appl. WO 2019/036671.
- (46) Ree, L. H. S.; Mady, M. F.; Kelland, M. A. N,N-Dimethylhydrazidoacrylamides. Part 3: Improving Kinetic Hydrate Inhibitor Performance Using Polymers of N,N-Dimethylhydrazido-methacrylamide. *Energy Fuels* **2015**, *29*, 7923–7930.
- (47) Friščić, T.; Mottillo, C.; Titi, H. M. Mechanochemistry for Synthesis. *Angew. Chem., Int. Ed.* **2020**, *59* (3), 1018–1029.
- (48) Ago, M.; Endo, T.; Okajima, K. Effect of solvent on morphological and structural change of cellulose under ball-milling. *Polym. J.* **2007**, *39* (5), 435–441.
- (49) Zheng, Y.; Fu, Z.; Li, D.; Wu, M. Effects of Ball Milling Processes on the Microstructure and Rheological Properties of Microcrystalline Cellulose as a Sustainable Polymer Additive. *Materials* **2018**, *11* (7), 1057.
- (50) Sloan, E. D.; Subramanian, S.; Matthews, P. N.; Lederhos, J. P.; Khokhar, A. A. Quantifying Hydrate Formation and Kinetic Inhibition. *Ind. Eng. Chem. Res.* **1998**, *37* (8), 3124–3132.
- (51) Clements, J.; Pakulski, M. K.; Riethmeyer, J.; Lewis, D. C.; Improved Poly(Vinyl Caprolactam) Kinetic Gas Hydrate Inhibitor And Method For Preparing The Same. Int. Pat. Appl. WO 2017048424, 2017.
- (52) Kelland, M. A.; Svartaas, T. M.; Øvsthus, J.; Namba, T. A new class of kinetic hydrate inhibitor. *Ann. N. Y. Acad. Sci.* **2000**, *912* (1), 281–293.
- (53) Smith, A. P.; Shay, J. S.; Spontak, R. J.; Balik, C. M.; Ade, H. M.; Smith, S. D.; Koch, C. C. High-energy mechanical milling of poly(methyl methacrylate), polyisoprene and poly(ethylene-alt-propylene). *Polymer* **2000**, *41*, 6271–6283.
- (54) Castricum, H. L.; Yang, H.; Bakker, H.; Van Deursen, J. H. A Study of Milling of Pure Polymers and A Structural Transformation of Polyethylene. *Mater. Sci. Forum* **1996**, *235–238*, 211–216.
- (55) O'Reilly, R.; Jeong, N. S.; Chua, P. C.; Kelland, M. A. Missing Poly(N-vinyl lactam) Kinetic Hydrate Inhibitor: High-Pressure Kinetic Hydrate Inhibition of Structure II Gas Hydrates with Poly(N-vinyl piperidone) and Other Poly(N-vinyl lactam) Homopolymers. *Energy Fuels* **2011**, *25*, 4595–4599.
- (56) Schmidt, R.; Scholze, H. M.; Stolle, A. Temperature progression in a mixer ball mill. *Int. J. Ind. Chem.* **2016**, *7* (2), 181–186.
- (57) Ravnsbæk, J. B.; Swager, T. M. Mechanochemical Synthesis of Poly(phenylene vinylenes). *ACS Macro Lett.* **2014**, *3* (4), 305–309.
- (58) Park, S.; Kim, J. G. Mechanochemical synthesis of poly(trimethylene carbonate)s: an example of rate acceleration. *Beilstein J. Org. Chem.* **2019**, *15*, 963–970.
- (59) Hussain, A.; Gharfeh, S.; Adham, S. Study of Kinetic Hydrate Inhibitor Removal Efficiency by Physical and Chemical Processes. *SPE International Production and Operations Conference & Exhibition*, SPE-157146-MS, Doha, Qatar, May 14–16, 2012; Society of Petroleum Engineers, 2012; DOI: 10.2118/157146-MS.
- (60) Kelland, M. A. Designing Kinetic Hydrate Inhibitors - Eight Projects With Only Partial Success, But Some Lessons Learnt. *Energy Fuels* **2017**, *31*, 5046–5054.
- (61) Wienk, I. M.; Meuleman, E. E. B.; Borneman, Z.; Vandenboomgaard, T.; Smolders, C. A. Chemical treatment of membranes of a polymer blend - mechanism of the reaction of hypochlorite with poly(vinyl pyrrolidone). *J. Polym. Sci., Part A: Polym. Chem.* **1995**, *33*, 49–54.
- (62) Wang, Z.; Pelton, R. Chloramide copolymers from reacting poly(N-isopropylacrylamide) with bleach. *Eur. Polym. J.* **2013**, *49*, 2196–2201.
- (63) Breitenbach, J.; Sanner, A.; Preparation of hydrogen peroxide/polymer complexes in powder form. Can. Pat. CA 2163928 A1.
- (64) Panarin, E. F.; Kalninsk, K. K.; Pestov, D. V. Complexation of hydrogen peroxide with polyvinylpyrrolidone: ab initio calculations. *Eur. Polym. J.* **2001**, *37* (2), 375–379.
- (65) Giguère, P. A.; Chen, H. Hydrogen bonding in hydrogen peroxide and water. A Raman study of the liquid state. *J. Raman Spectrosc.* **1984**, *15* (3), 199–204.