energy&fuels

Article

Synthesis and Investigation of Polymers of 2-Methacrylamido-caprolactam as Kinetic Hydrate Inhibitors

Erik G. Dirdal* and Malcolm A. Kelland

Cite This: *Energy Fuels* 2020, 34, 6981−6990

Read Online

ACCESS | Metrics & More | Article Recommendations

ABSTRACT: Poly(N-vinylcaprolactam) (PVCap) and related copolymers have been used as kinetic hydrate inhibitors (KHIs) for over 25 years to combat gas hydrate formation in oil and gas field production flow lines. The caprolactam groups in this polymer class have been shown previously to have a particularly strong interaction with hydrate surfaces, inhibiting crystal growth but probably also gas hydrate nucleation. We report here a study on an alternate class of copolymers with pendant caprolactam groups from the 2-methacrylamido-caprolactam (2-MACap) monomer. KHI experiments were carried out in high pressure steel rocking cells using a structure-II-forming natural gas mixture. The KHI performance of some of these copolymers exceeded that of PVCap of similar molecular weight, with further performance enhancement provided by solvent synergists.

1. INTRODUCTION

Gas hydrates are nonstoichiometric crystalline solids where gases of certain molecular weights stabilize the hydrogen-bonded molecular water cages. Thus, if suitable low-molecular-weight hydrocarbon gases combine with water under specific conditions of temperature and pressure, typical favoring conditions will be temperature and pressure in the ranges of <25 °C and >30 bar, respectively, and gas hydrates will form.[1−4]

It is not uncommon to encounter such conditions when producing or transporting oil and gas, and if it is left untreated formation of gas hydrate plugs can occur, potentially jeopardizing the operation.[4−12] There exist multiple measures to handle and treat gas hydrate: one of them is the utilization of low dosage hydrate inhibitors (LDHIs) and the subgroup kinetic hydrate inhibitors (KHIs).[5]

The main active compound of a KHI formulation is the water-soluble polymer, which typically makes up 10−30 wt %, with the remainder being carrier solvent.[13] Regarding the polymers, it appears that they need two structural features in order to perform well as hydrate inhibitors, namely, to be able to have both hydrophilic and hydrophobic capabilities. It is usually amide, imide, or amine oxide groups that make up the hydrophilic functional groups of the polymer.[5,14,15] The hydrophobic functional group must be present directly or adjacent to each of the hydrophilic functional groups.[16] Polymers and copolymers based on the monomers N-vinylcaprolactam (VCap), N-vinylpyrrolidone (VP), and N-isopropylmethacrylamide, as well as hyperbranched poly(ester amide)s based on diisopropanolamine and various cyclic anhydrides, make up the bulk of commercially available KHIs.[5] The other part of the KHI formulation, the carrier solvent, is often a low-molecular-weight alcohol, glycol, or glycol ether, such as methanol, ethanol, monoethylene glycol (MEG), and 2-n-butoxyethanol (nBGE).[12] In addition to easing the pumping of the KHI formula, the carrier solvent also

can act as a synergist with the KHI polymer, thus enhancing the hydrate inhibiting properties of the polymer.[13]

The mechanism behind the inhibition properties of these KHI polymers is not fully understood, but the KHIs kinetically interact with the hydrate formation process. They are assumed to interfere with the hydrate nucleation and crystal growth processes.[17,18]

Poly(N-vinylcaprolactam) (PVCap) is one of the best KHIs currently available (Figure 1). Several copolymers of VCap have also been applied in the field.[19] Therefore, we were interested in investigating other polymers containing the caprolactam ring.

VCap-based KHI polymers are known to be particularly good at inhibiting hydrate crystal growth compared to other KHI polymer classes such as polyalkyl(meth)acrylamides.[1,5,20] This means that with the use of a VCap-based polymer the
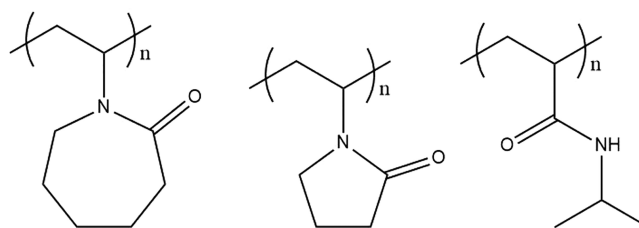

Figure 1. Structures of common polyvinylic KHIs. From left to right: poly(N-vinylcaprolactam) (PVCap), poly(N-vinylpyrrolidone) (PVP), and poly(N-isopropyl methacrylamide) (PNIPMAM).

time before enough hydrate crystals have formed to cause catastrophic hydrate growth is prolonged. Therefore, this can give the field operator a better opportunity to avoid plugging of the flow line completely once hydrates are first suspected to be formed. This also gave us incentive to explore alternate caprolactam-based polymers.

Very few studies on polymers (other than VCap-based polymers) containing caprolactam rings as KHIs have been reported. In an earlier attempt in our research group, 2-aminocaprolactam was reacted with poly-(dichlorophosphazene) (PDCP) in order to make poly-(caprolactam-2-amino)phosphazene, which was water-soluble as a homopolymer[21] (Figure 2). This polymer showed some

Figure 3. Structures of polyacryloalkylenecaprolactams with one (left) and two (right) carbon atoms in the chain connecting the caprolactam ring, respectively.

Figure 4. Structure of poly(2-methacrylamido-caprolactam) (poly(2-MACap)).
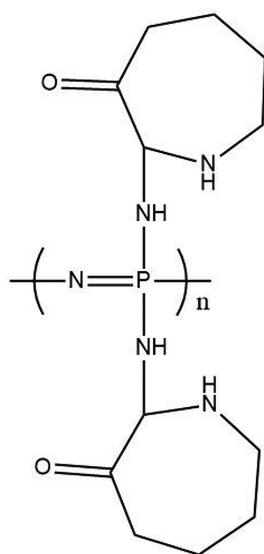

Figure 2. Structure of poly(caprolactam-2-amino)phosphazene.

KHI effect, but it had two major drawbacks: First, the water solubility for even ethyl derivative was low; increasing the hydrophobicity (thereby probably increasing the KHI performance) by using pendant propyl groups would have been futile as the polymer became insoluble in water. Second, especially at the pH of produced oilfield water, the polymer has limited stability in water. The water-soluble polyphosphazenes are proven to be biodegradable, which is of interest when they are considered as KHIs.[22] The making of these polymers was challenging, and in general the trend was that the longer the pendant alkyl group the more hydrolytically stable was the polymer, with the result of being less water soluble.[21] In one patent a research group reported that caprolactam groups can be attached to amines and polyamines via a Mannich reaction with formaldehyde.[23] In our hands, this reaction does not work and was unofficially confirmed by contact with the patent owners.

We previously synthesized acryloyloxyethylcaprolactam and acryloyloxymethylcaprolactam, but it proved surprisingly difficult to make poly(N-acryloyloxyalkylcaprolactams), probably due to steric problems during the polymerization procedure (Figure 3). We presume the methacryloyl polymers, with extra methyl groups in the backbone, would also be difficult to make by radical polymerization.[21]

In this study, we have synthesized a new class of caprolactam-containing polymers. They are based on 2-methacrylamido-caprolactam (Figure 4). In these polymers
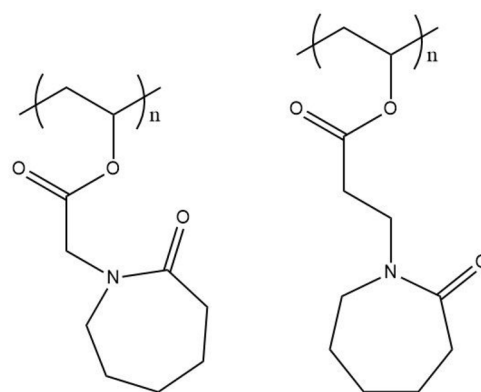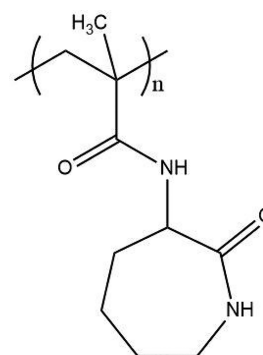
the caprolactam ring will be two atoms further from the backbone than is the case for PVCap. We chose to use the methacrylamido monomer unit as previous work has shown that an extra methyl group in the polyvinyl backbone is favorable for KHI performance of N-alkyl acrylamide polymers.[24] The beneficial extra methyl group in the polyvinyl backbone has also been recently demonstrated for poly(N,N-dimethylhydrazido methacrylamide) compared to poly(N,N-dimethylhydrazido acrylamide).[25,26] The improved KHI effect given by this extra methyl group in the polyvinyl backbone is presumed to be due to the steric effect of the methyl group, opening the polymer structure and increasing its surface-to-volume ratio. One other important aspect of having the methyl group in the polyvinyl backbone is the potential to keep the molecular weight of the polymer or copolymer low. This is particularly useful for the efficacy of a KHI. In radical polymerization or copolymerization, an acrylamide forms secondary radicals as the propagating end group, while methacrylamide forms tertiary radicals.[27] Tertiary radicals are more stable than secondary radicals, and they are thus thought to decrease the reactivity of the propagating end for further polymerization. In addition, with methacryl, there is always a greater steric effect of approach than with acryl monomer to monomer radical. This effect is more pronounced for methacrylamides, and therefore they polymerize more slowly.

2. EXPERIMENTAL SECTION

2.1. Chemicals. α-Amino-ε-caprolactam was obtained from ABCR, Germany. Triethylamine and solvents used in this study
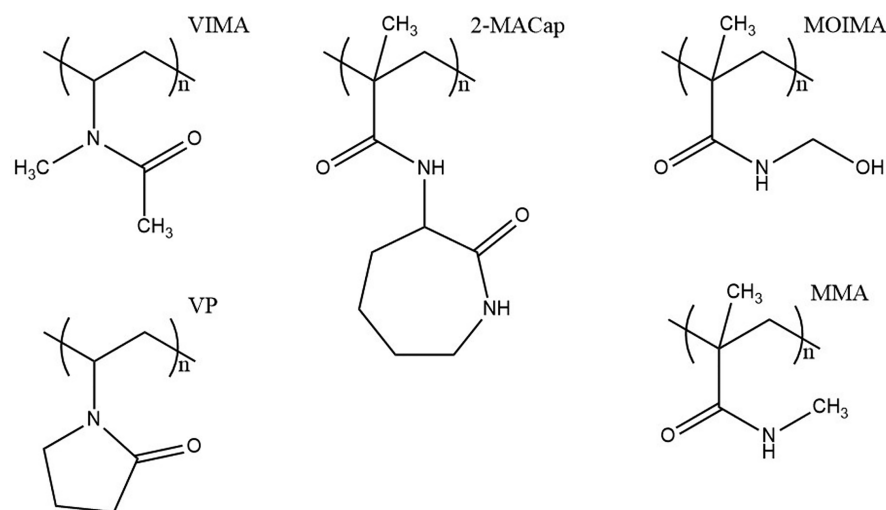
Figure 5. Structure of comonomer units used with 2-MACap copolymers: *N*-vinyl-*N*-methylacetamide (VIMA), *N*-vinylpyrrolidone (VP), *N*-methylol methacrylamide (MOlMA), and *N*-methylmethacrylamide (MMA). Poly(2-MACap) is shown in the center.

were obtained from Merck. *N*-Methylol methacrylamide was obtained from Evonik, Germany. *N*-Methylmethacrylamide was obtained from Tokyo Chemical Industry (TCL). Methacryloyl chloride, *N*-vinyl-2-pyrrolidone, and *N*-vinyl-*N*-methylacetamide were obtained from Sigma-Aldrich. All chemicals were commercially available and used without further purification. NMR spectra were recorded on a Bruker Ascend NMR 400 MHz spectrometer at ambient temperature unless otherwise stated.

2.2. Synthesis of 2-Methacrylamido-caprolactam (2-MACap). The synthesis was based on the described method,[28] by dissolving *α*-amino-*ε*-caprolactam (1 g, 7.8 mmol) in dichloromethane (20 mL) in a 100 mL round-bottom flask. Then triethylamine (0.789 g, 7.8 mmol) was added and the mixture was cooled to 0 °C in an ice bath. Methacryloyl chloride (0.816 g, 7.8 mmol) dissolved in dichloromethane (10 mL) was added dropwise to the solution in the round-bottom flask with vigorous stirring. The mixture was slowly heated to room temperature and stirred overnight. The reaction mixture was washed with NaCl brine. Then the organic phase was extracted, washed with DI water, and dried with Na_2SO_4. The precipitated $NEt_3HCl(s)$ was filtered off and solvent was removed *in vacuo* on a rotary evaporator to yield 2-methacrylamido-caprolactam (2-MACap). ^{1}H NMR confirmed that the resulting product was pure, and it was thus used without further purification steps.

2.3. Poly(2-methacrylamido-caprolactam) (Poly(2-MACap)) Synthesis. The polymerization synthesis was done in the same general manner for all homopolymers and copolymers. 2-MACap did not polymerize in 2-propanol, so the solvent used in the following polymer synthesis was DMSO. 2-MACap (0.5 g, 2.5 mmol) was dissolved in DMSO (2 g) in a Schlenk flask with a magnet. AIBN (1 wt %, 0.005 g) was added, and the solution was flushed with nitrogen using the standard pump-fill technique. While the solution was stirring, it was heated to 70 °C and left to react under the protection of nitrogen overnight. Then the poly(2-MACap) solution was cooled to room temperature and the product was left in solution. ^{1}H NMR showed that all monomer was consumed.

The comonomers used to make copolymers of 2-MACap were *N*-vinylpyrrolidone (VP), *N*-vinyl-*N*-methylacetamide (VIMA), *N*-methylol methacrylamide (MOlMA), and *N*-methylmethacrylamide (MMA) (Figure 5). The copolymerizations followed the same steps as for the 2-MACap homopolymer, except that the comonomer was added in the first step.

2.4. GPC Analysis. In order to determine the molecular weight as well as the polydispersity index (DPI) of the polymers made, a GPC analysis was conducted. The apparatus used was a JASCO Chem NAV size exclusion chromatography (SEC) system. This system was equipped with PU-2080, AS-2055, CO-2065 RI-2031, and two commercial columns (TSKgel SuperH4000 and TSKgel GMHXL). The testing was done at 40 °C with dimethylformamide (DMF) as eluent. Polystyrene standards were used for calibrating the molecular weights of the polymers.

2.5. Cloud Point (Tcl) Measurements. A sample of the polymer was dissolved in deionized water, making a concentration of 1.0 wt %. This solution was then heated at approximately 2 °C/min, during heating visual observation was continuously done, and the Tcl was determined at the temperature where the first sign of haze was observed. This was repeated at a minimum one more time for each polymer for verification of the Tcl temperature. Deposition points (Tdp's), which are usually a maximum of 5−10 °C above the Tcl, were not measured.

2.6. Gas Hydrate Performance Testing in High-Pressure Apparatus. The apparatus used for conducting the performance testing was The Rocking Cell 5 (RC5) apparatus supplied by PSL Systemtechnik, Germany. With this apparatus, five high-pressure stainless steel rocking cells, supplied by Svafas, Norway, are rocked in a cooling bath. The cells have an internal volume of 40 mL and are equipped with a stainless steel ball for agitating the test solution. The gas used in these tests was a standard natural gas mixture (SNG), which preferentially forms a structure II gas hydrate. The composition of the gas mixture is provided in Table 1.

Table 1. Composition of the Synthetic Natural Gas Mixture Used in the Performance Testing

component	mol %
methane	80.67
ethane	10.20
propane	4.90
isobutane	1.53
n-butane	0.76
N_2	0.10
CO_2	1.84

In the following, the procedure for high-pressure kinetic hydrate inhibition testing by the use of constant cooling is summarized and it has been described previously:[29,30]

1. The polymer, and if applicable the synergist, was dissolved to the desired concentration in deionized water at least 1 day in advance before initialization of the test.

2. The test solution consisted of various additives dissolved in distilled water, and 20 mL was added to each of five cells.

3. A sequence of vacuum and pressurizing with SNG was applied: first vacuum and then pressurizing with SNG to 3−5 bar; then
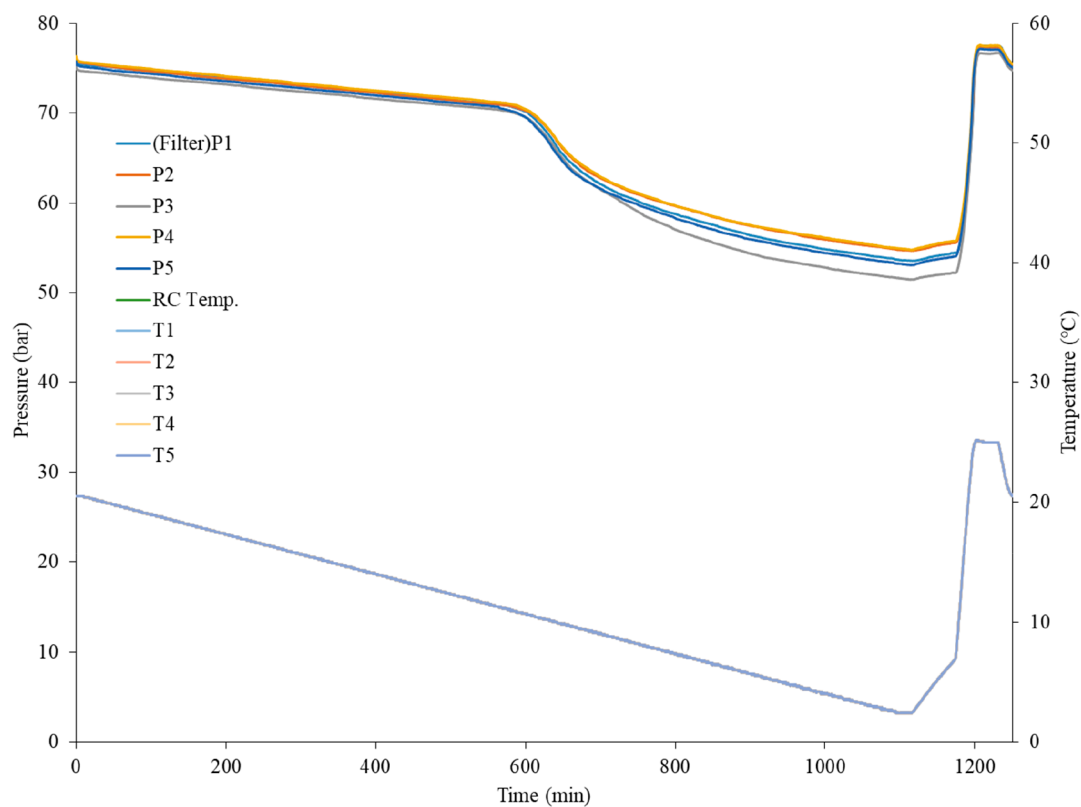
Figure 6. Graph containig the results from all five cells during a standard constant cooling experiment. In this example, each cell contained 2-MACap:VP (1:1) copolymer in DMSO.
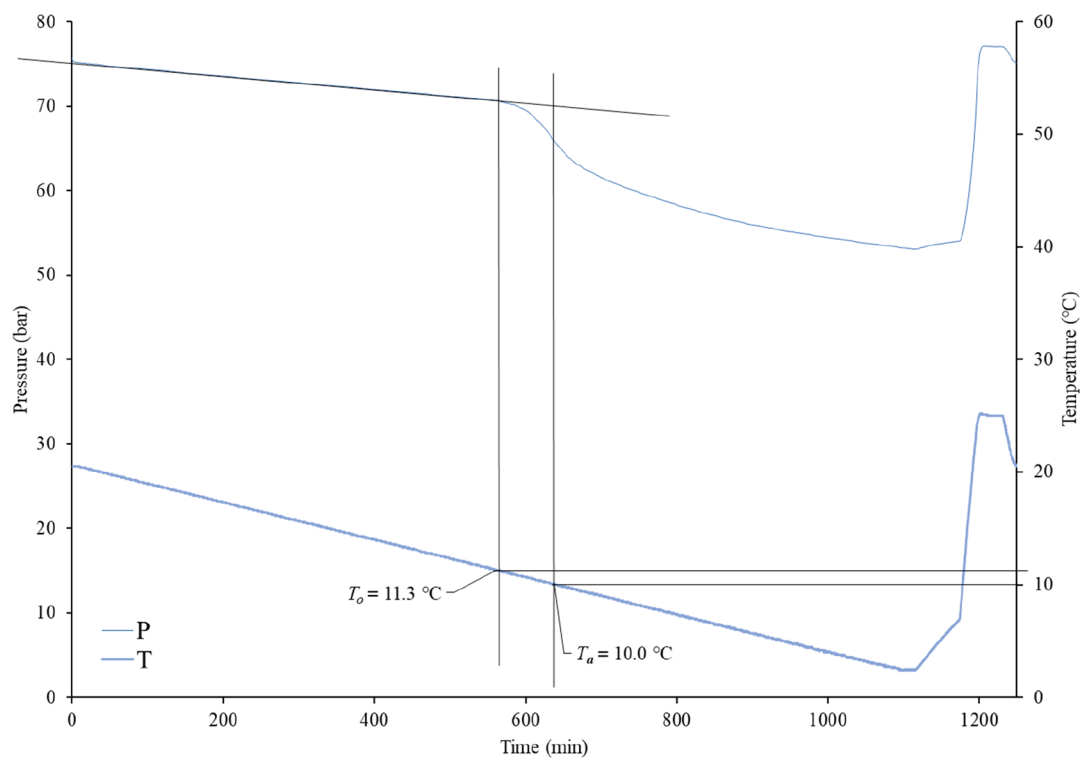

Figure 7. Graph from cell 5 containing 2-MACap:VP (1:1) in DMSO during a standard constant cooling experiment. Both T_o and T_a are determined in the graph.

depressurizing before another round with vacuum. This was done in order to replace the air with SNG in the cells.

4. The system was then pressurized with SNG to the experimental pressure of 76 bar.

Table 2. Polymers Synthesized in This Study

polymer	Tcl (°C)	mol wt (g/mol)	PDI
poly(2-MACap)	<0	12 600	5.42
2-MACap:VP 1:1 copolymer	27	99 400	2.67
2-MACap:VIMA 1:1 copolymer	28	61 500	2.93
2-MACap:VIMA 1:2 copolymer	35	aggregated	
2-MACap:VIMA 2:1 copolymer	43	aggregated	
2-MACap:MOlMA 1:1 copolymer	>95	not soluble in DMF	
2-MACap:MMA 1:1 copolymer	58	2 100 (major), 120 800 (broad minor)	1.16, 12.21

5. While the cells were rocking at a rate of 20 rocks/min at an angle of 40°, the cells were cooled at a cooling rate of 1.0 °C/h from 20.5 to 2.0 °C.

In standard laboratory dissociation experiments warming at 0.025 °C/h for the last 3–4 °C, the hydrate equilibrium temperature (T_{eq}) at 76 bar has previously been determined to be 20.2 ± 0.05 °C. This correlated well with calculations done by the Calsep PVTSim software.[31,32]

[Figure 6](#) shows an example of a constant cooling experiment with results from all five cells. In this particular experiment all five cells contain 2-MACap copolymerized 1:1 with VP. The initial pressure is 76 bar and the temperature is decreased from 20.5 to 2.0 °C during testing. There will be a linear pressure decrease since each cell is a closed system. From this linear pressure decrease both the onset temperature for hydrate formation (T_o) and the rapid hydrate formation temperature (T_a) can be observed. T_o is defined as the temperature at which the first observable deviation from the linear pressure decrease is observed. It is however possible that the hydrate nucleation initiated at a molecular level is not detected by the test equipment. Instead, the deviation from the pressure trend corresponding to the first macroscopic observation of hydrate formation is measured. A rapid pressure decrease can be observed with varying interval after the T_o has occurred. T_a is defined as the temperature at which the pressure decrease is at its steepest, in other words, where the hydrate formation is at its fastest. An example of how these values are determined from one of the cells can be found in [Figure 7](#).

3. RESULTS AND DISCUSSION

In our first attempts at polymerizing 2-MACap the solvent used was 2-propanol, with the result that the monomer did not polymerize. When we switched to DMSO as solvent, we managed to polymerize 2-MACap to form poly(2-MACap). However, this homopolymer was not soluble in water. Considering that the side groups are more hydrophilic than caprolactam in PVCap, we were initially surprised by this result. We suspect that considerable internal hydrogen bonding might be present in the homopolymer.[33]

Therefore, in order to obtain water-soluble polymers containing the 2-MACap monomer, we had to make copolymers. The majority of KHI polymers are based upon free radical polymerization of vinylic monomers, thus making the backbone polyvinyl. Formation of statistical copolymers with no particular order of the comonomers is the result of free radical polymerization of two or more vinylic comonomers.[34,35] Polymers and copolymers based on N-vinyl-caprolactam (VCap) are the most commonly used. Comonomers such as N-vinylpyrrolidone (VP), N-vinylpyridine, N-methyl-N-vinylacetamide, vinyl acetate, (acrylamide)-propanesulfonic acid (AMPS), and (dimethylamino)-ethyl methacrylate (DMAEMA) have been investigated as KHIs.[18,36−39]

The monomers used to copolymerize with 2-MACap were N-vinyl-2-pyrrolidone (VP), N-vinyl-N-methylacetamide (VIMA), N-methylol methacrylamide (MOlMA), and N-

methylmethacrylamide (MMA). The reason for choosing these is that they are hydrophilic and it was hoped they would not diminish the performance of poly-2-MACap assuming it had been water-soluble. It is also possible that the KHI performance could be increased by copolymerization, e.g., for VIMA as reported for its VCap copolymers.[19,20] [Table 2](#) summarizes all the polymers and copolymers made in this study, with Tcl, molecular weight, and PDI where available. We assume the molar ratio of the two comonomers in the copolymer end product is approximately the same as the molar ratio before the start of polymerization since there were negligible protons on a C=C double bond by ^{1}H NMR spectroscopic analysis.

[Table 2](#) indicates that we encountered aggregation problems with the GPC analysis for two of the polymer samples, 2-MACap:VIMA (2:1) and 2-MACap:VIMA (1:2). We were able to see broad peaks for the nonaggregated state for 2-MACap, 2-MACap:VP (1:1), and 2-MACap:VIMA (1:1) at M_n values of 12 600, 99 400, and 61 500 respectively. The GPC trace was too broad to see the unaggregated state for polymers 2-MACap:VIMA (2:1) and 2-MACap:VIMA (1:2). The reason for the bimodal distribution of 2-MACap:MMA (1:1) is not known but may be due to very uneven polymerization rates of the monomers. Some of the polymer molecular weights were not ideal for optimal performance or comparison. However, this was our first foray into 2-MACap polymer chemistry and the results discussed below still give a good indication of the potential of this new KHI technology.

Besides [Table 2](#), the cloud points for the 2-MACap polymers are graphically represented in [Figure 8](#). It can be observed that, of the water-soluble copolymers, 2-MACap:VP (1:1) had the lowest cloud point and the 2-MACap:MOlMA (1:1) had the highest. The VIMA copolymers had an increase in cloud point from 2-MACap:VIMA (1:1) to 2-MACap:VIMA (1:2) and 2-MACap:VIMA (2:1). Adding a hydrophilic comonomer to a
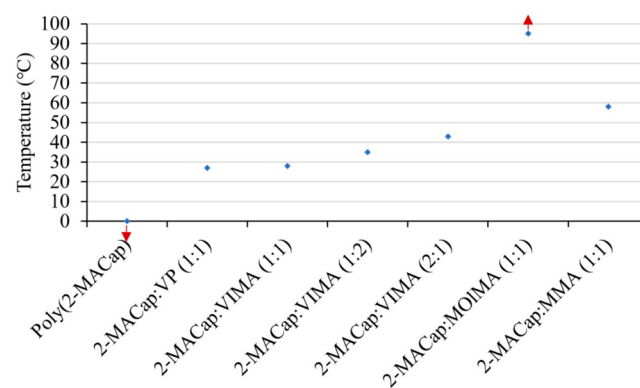

Figure 8. Graphical presentation of cloud points for water-soluble copolymers together with the homopolymer.

Table 3. Summarized KHI Test Results for the Water-Soluble Polymers, Also with Synergist Solvents[a]

| copolymer | solvent synergist | concentration (ppm) | | T_o (°C) | T_a (°C) |
		polymer	synergist		
no additive				17.2	16.6
PVCap		2500		10.4	8.9
PVP K-15		2500		13.3	9.1
PVIMA		2500		14.2	13.2
2-MACap:VP (1:1)		2500		11.2	10.0
		5000		8.9	7.5
	iBGE	2500	5000	8.3	6.7
	4-MePeOl	2500	5000	6.7	5.4
2-MACap:VIMA (1:1)		2500		8.8	7.7
		5000[b]		9.2	8.2
	iBGE	2500	5000	7.4	6.3
	4-MePeOl	2500	5000	5.7	4.6
2-MACap:VIMA (1:2)		2500		10.9	10.1
		5000		7.6	7.2
2-MACap:VIMA (2:1)		2500		11.0	10.5
2-MACap:MOlMA (1:1)		2500		14.7	14.5
2-MACap:MMA (1:1)		2500		8.8	8.1
		5000		6.4	5.7
	iBGE	2500	5000	6.2	5.4
	4-MePeOl	2500	5000	4.6	3.8

[a]iBGE = isobutyl glycol ether; 4-MePeOl = 4-methyl-1-pentanol. [b]97+% soluble.
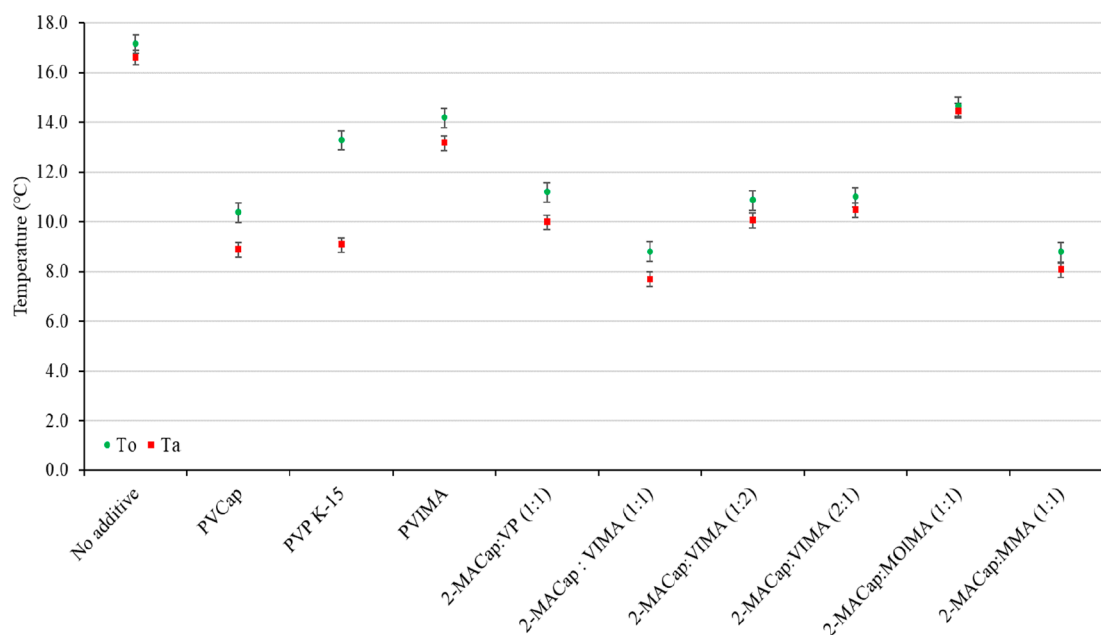

Figure 9. Graphical summary of polymers and copolymer KHI test results at 2500 ppm.

very active KHI monomer forming a copolymer will usually increase the cloud point.[19] This is also demonstrated by the cloud point of 2-MACap:MMA (1:1). The addition of the synergist solvents 4-methyl-1-pentanol (4-MePeOl) and isobutyl glycol ether (iBGE), used and discussed later in this study, had a negligible effect on the cloud point of this copolymer at the concentrations tested.

The benefit of low cloud point for high KHI performance, given the correct size functional groups, has been investigated previously.[40] This advantage has been suggested as being due to maximizing the KHI polymer surface area/hydrodynamic volume ratio. For example, copolymers of VIMA:VCap have better performance than PVCap homopolymer despite a higher

cloud point, which is assumed to be due to a greater surface area/hydrodynamic volume (SA/HV) ratio for the copolymers. Further, copolymers of N-vinylazacyclooctanone (VACO) with N-vinyl-N-methylacetamide (VIMA) perform better than PVACO (due to higher SA/HV factor) or VIMA:VCap (due to SA/HV and lower cloud point).[19]

Only the polymers that were water-soluble were tested for their inhibition performance in KHI tests. The KHI test results are summarized in Table 3. For each copolymer, a minimum of five tests were done. The maximum number of tests for a copolymer was 14, where we needed more tests for a statistically significant result. Thus, both the T_o and T_a values reported in the following are averages. The focus will be on the

T_o value, since the T_a values are not easy to get meaningful comparative data from, unless the T_o values are similar. When synergist was added, the concentration was always 2500 ppm for the copolymer and 5000 ppm for the synergist. Also included in Table 3 are results for PVCap (M_w = 10 000 g/mol),[41] PVP K-15 (M_w = 8000 g/mol),[42] and PVIMA (M_w = 12 401 g/mol)[43] from previous studies using the same equipment and test method.

From Table 3 one can observe that all the copolymers gave some KHI effect compared to no additive. The solubility for the copolymers differed. Interestingly, not all of them showed complete solubility at 5000 ppm. Those that were completely soluble, plus 2-MACap:VIMA (1:1) with <3% insoluble material, were tested at 5000 ppm. We speculate that there may be considerable internal hydrogen bonding, making the pendant groups less available for hindering gas hydrate nucleation or crystal growth. In the polymer and in the copolymers there exist many options where this type of bonding can take place: between 2-MACap units, between copolymerization units, and between 2-MACap units and copolymerization units. Hydrogen bonding can also occur between polymer strands. In addition, polymerization rates of the monomers were different, and this could possibly make blocks of each monomer rather than an even distribution throughout the copolymer, causing some of the copolymer strands to exhibit low water solubility or even surfactant properties. For example, 2-MACap:VIMA (1:1) at 2500 ppm gave a foamy solution, and at a concentration of 5000 ppm a very small amount of the copolymer was not soluble (<3%). Since all the copolymers were water-soluble at 2500 ppm, we present results from their KHI performance tests graphically in Figure 9 together with PVCap, PVP-K15, and PVIMA for comparison. For those copolymers that were completely water-soluble, i.e., 2-MACap:VP (1:1), 2-MACap:VIMA (1:1), 2-MACap:VIMA (1:2), and 2-MACap:N-methylmethacrylamide (1:1), their performances as KHIs are compared for 2500 and 5000 ppm in Figure 10.

Beginning with the first copolymer made, 2-MACap:VP (1:1), at 2500 ppm we obtained T_o and T_a values of 11.2 and 10.0 °C, respectively. This copolymer was also the copolymer
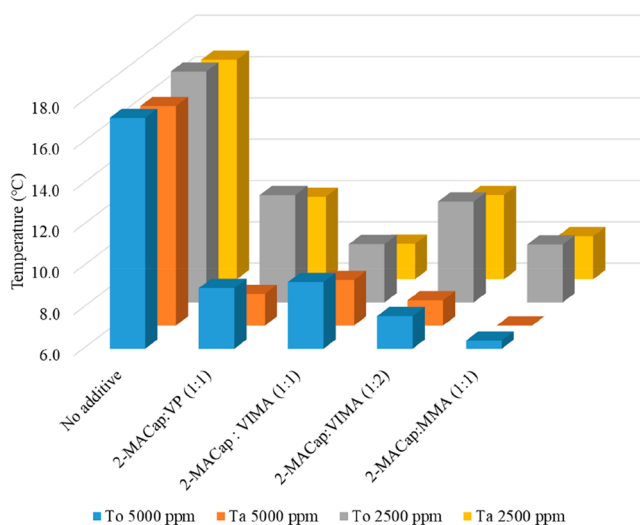
in this study with the lowest cloud point (27 °C). The performance was a little bit poorer than that of pure PVCap, but significantly better than that of PVP K-15 which had T_o and T_a values of 13.3 and 9.1 °C, respectively. This indicates that the caprolactam group in the 2-MACap monomer is a more effective monomer for KHI polymers than the VP monomer. This is further underlined by the nonoptimal high molecular weight of 2-MACap:VP (1:1) copolymer (99 400 g/mol) compared to the relatively low value for PVP-K15 (8000 g/mol). When the concentration of 2-MACap:VP (1:1) was increased to 5000 ppm, the T_o value dropped to 8.9 °C, showing a clear improvement in the KHI performance of the copolymer compared to that at 2500 ppm.

For 2-MACap:VIMA (1:1) the T_o value was 8.8 °C and the T_a value was 7.7 °C when the concentration was 2500 ppm. This copolymer had a low cloud point (28 °C) similar to 2-MACap:VP (1:1). This copolymer had a better performance than pure PVCap had at the same concentration. Copolymers with other ratios of these monomers (1:2 and 2:1) had poorer performances at 2500 ppm (Figure 11). This correlates well
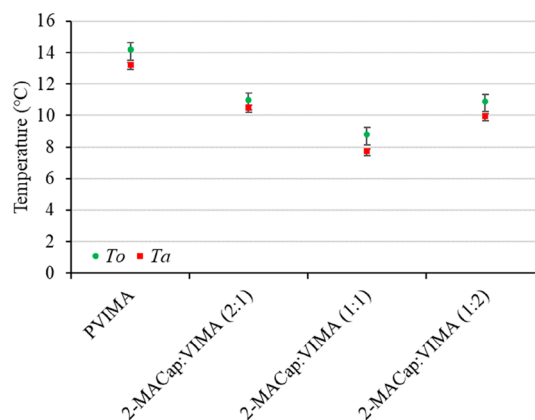
Figure 11. 2-MACap:VIMA in the ratios 1:1, 1:2, and 2:1 compared with PVIMA, all with 2500 ppm concentration.

with results for VIMA:VCap copolymers, where it was shown that a 1:1 copolymer had the best KHI performance.[19,20] One possible reason for this beneficial KHI effect of the VIMA in the copolymers of VIMA:VCap is that it causes a greater surface area/hydrodynamic volume ratio compared to PVCap homopolymer, thus allowing caprolactam groups more interaction with the water phase and hydrate particle surfaces.[20,40]

When the concentration of 2-MACap:VIMA (1:1) was increased to 5000 ppm, it was expected that there would be a clear improvement in the performance as KHI, but this was not the case. The T_o value between 2-MACap:VP (1:1) at 5000 ppm and at 2500 ppm was not found to be significantly different ($p > 0.05$ in a statistical t-test). This was most likely caused by the solubility issue at the higher concentration. This fits with the even poorer solubility of 2-MACap:VIMA (2:1) copolymer at 5000 pm and the KHI results with 2-MACap:VIMA (1:2) copolymer. This 1:2 copolymer, which is more hydrophilic and fully soluble at 5000 ppm, showed a marked improvement in KHI performance when the concentration was increased from 2500 to 5000 ppm.

Because of solubility issues and surfactant properties of some of the 2-MACap:VIMA copolymers, we therefore tried acrylamide monomers. We hoped these conjugated vinyl
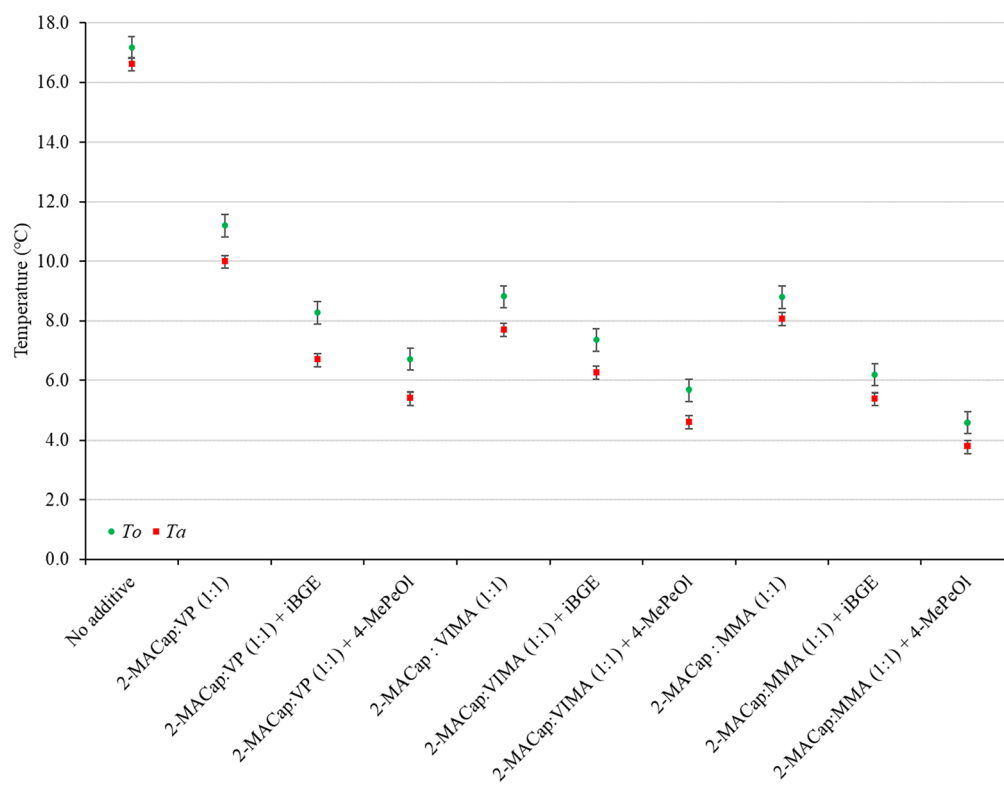
Figure 10. Comparison of T_o and T_a values at concentrations of 2500 and 5000 ppm for copolymers that were water-soluble at both concentrations.

Figure 12. KHI synergetic effect of 5000 ppm iBGE or 4-MePeOl added to 2500 ppm 1:1 2-MACap copolymers with VP, VIMA, and MMA.

monomers would have a polymerization rate fairly similar to that of 2-MACap, which hopefully would diminish the solubility and surfactant issues. 2-MACap:MOlMA (1:1) copolymer had a T_o value of 14.7 °C and a T_a value of 14.5 °C at a concentration of 2500 ppm. Do to the poor result, this copolymer was not tested at a concentration of 5000 ppm. The poor result may be due to being overly hydrophilic causing a lack of cloud point up to 95 °C as discussed earlier.

2-MACap:MMA (1:1) had a much better KHI performance, with T_o and T_a values of 8.8 and 8.1 °C, respectively, at a concentration of 2500 ppm. This is better than PVCap and with a more useful cloud point (58 °C) for field use. The T_o value of 2-MACap:MMA (1:1) at 2500 ppm was in the same range as the T_o value for both 2-MACap:VP (1:1) at 5000 ppm and 2-MACap:VIMA (1:1) at 2500 ppm. The average T_o and T_a values between 2-MACap:MMA (1:1) at 2500 ppm and 2-MACap:VIMA (1:1) at 2500 ppm were not found to be significantly different ($p > 0.05$). This indicates that the performances of these copolymers are similar although the molecular weights are clearly different.

2-MACap:MMA (1:1) copolymer, which was fully soluble at a concentration of 5000 ppm, gave an average T_o value of 6.4 °C and a T_a value of 5.7 °C. This shows the same trend as for the other fully water-soluble copolymers, i.e., that higher concentration of copolymer results in better KHI performance, which is typically seen within this concentration range. In addition, 2-MACap:MMA (1:1) has a bimodal molecular weight distribution with most of the polymer being of low molecular weight. This could be an advantage compared to a monomodal distribution of only low molecular weight, as was found for PNIPMAM.[44,45]

From previous research it is well-known that certain solvents can act as synergists with the KHI polymer.[20] For example, we have shown previously that isobutyl glycol ether (iBGE) had a

strong good synergetic effect on PVCap and PNIPMAM. Further, 4-methyl-1-pentanol (4-MePeOl) had a very strong synergetic effect on PVCap.[41,46] Therefore, we were interested to see the possible synergetic effect of these two solvents with 2-MACap copolymers. Results with 2500 ppm 1:1 copolymers of VP, VIMA, and MMA with 5000 ppm solvent are given in Table 3 and graphically in Figure 12.

All three of the copolymers had an improved KHI performance when synergists iBGE and 4-MePeOl were added. The effect of 4-MePeOl was larger for all copolymers. The best result was obtained for 2-MACap:MMA (1:1) copolymer with added 4-MeHexOl, resulting in a T_o value of 4.6 °C and a T_a value of 3.8 °C. Looking back over the past 10 years of work from our research group with the same test method, this represents one of the best results for polymers with reasonably high cloud points, useful for many field applications.

The mechanisms behind the synergetic effect of alcohols or glycol ethers on KHI polymers are not well-established. One reported hypothesis is that alcohols or glycol ethers increase the ability of the KHI polymers to adsorb on nucleation and/or growth sites.[47,48] The reason that 4-MePeOl worked so well as synergist with PVCap is thought to be because both the size and shape of the alkyl group are important for the synergy, but also the fact that the alcohol is close to the solubility limit may also be a factor.[40] We suspect that this is also the case for the good synergy between 2-MACap copolymers and 4-MePeOl.

4. CONCLUSION

We have synthesized and investigated the KHI properties of polymers of 2-methacrylamido-caprolactam (2-MACap) for the first time. Poly(2-MACap) homopolymer was found to be insoluble in water; therefore, a range of copolymers were made. The solubility and molecular weights of the copolymers varied

and may be due to significantly different polymerization rates of 2-MACap and the other comonomers. All the copolymers showed KHI effects compared to no additive. The 2-MACap:MOlMA (1:1) copolymer, which was the most hydrophilic copolymer with no cloud point, gave the poorest result. Of the copolymers investigated, several had better KHI performances than PVCap, with 2-MACap:MMA (1:1) copolymer giving outstanding results as well as possessing a fairly high cloud point for a wide range of field applications. However, comparisons of performances are hampered by the variation in molecular weights of the copolymers. Several 2-MACap copolymers performed significantly better when blended with synergist solvents, iBGE and 4-MePeOl, with the latter giving the more powerful effect.

Although this study is the first time that polymers of 2-MACap have been synthesized and tested as KHIs, the results are very promising. Further optimizing of the polymers should be possible for improved KHI performance. Both 2-MACap:VIMA (1:1) and 2-MACap:MMA (1:1) show the potential to be further optimized, with the latter probably having the greater potential. Further synthesis work will focus on investigating other comonomers, optimizing the molecular weight of the copolymers, adjusting the polymerization procedure, and the monomer feed ratio. Other KHI test methods and test conditions will also be investigated for the best polymers.

■ AUTHOR INFORMATION

Corresponding Author

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; Email: erik.g.dirdal@uis.no

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

Complete contact information is available at:
https://pubs.acs.org/10.1021/acs.energyfuels.0c00929

Notes

The authors declare no competing financial interest.

■ REFERENCES

(1) Sloan, E. D., Jr.; Koh, C. A. *Clathrate Hydrates of Natural Gases,* 3rd ed.; CRC Press: Boca Raton, FL, 2008.

(2) Koh, C. A.; Sum, A. K.; Sloan, E. D. Gas hydrates: Unlocking the energy from icy cages. *J. Appl. Phys.* **2009**, *106*, 061101.

(3) Talley, L. D.; Mitchell, G. F. Application of Proprietary Kinetic Hydrate Inhibitors in Gas Flowlines. *Proceedings of the 1999 Offshore Technology Conference, Houston, TX, May 3−6, 1999;* Offshore Technology Conference: 1999; OTC 11036.

(4) Koh, C. A. Towards a fundamental understanding of natural gas hydrates. *Chem. Soc. Rev.* **2002**, *31* (3), 157−167.

(5) Kelland, M. A. *Production Chemicals for the Oil and Gas Industry,* 2nd ed.; CRC Press: Boca Raton, FL, 2014.

(6) Carroll, J. J. *Natural Gas Hydrates: A Guide for Engineers,* 2nd ed.; Elsevier Gulf Professional: Amsterdam, 2009.

(7) Sloan, E. D., Jr. Natural gas hydrates. *JPT, J. Pet. Technol.* **1991**, *43* (12), 1414−1417.

(8) Alapati, R.; Sanford, E.; Kiihne, E.; Vita, E. Proper Selection of LDHI for Gas Condensate Systems, in the Presence of Corrosion Inhibitors. *Proceedings of the Offshore Technology Conference, Houston, TX, May 3−6, 2010;* Offshore Technology Conference: 2010; OTC 20896.

(9) Davies, S. R.; Boxall, J. A.; Koh, C. A.; Sloan, E. D.; Hemmingsen, P. V.; Kinnari, K. J; Xu, Z. G. Predicting Hydrate-Plug Formation in a Subsea Tieback. *Proceedings of the SPE Annual Technical Conference and Exhibition, Denver, CO, Sept 21−24, 2008;* Society of Petroleum Engineers: 2008; SPE 115763.

(10) Lavallie, O.; Al Ansari, A.; O'Neill, S.; Chazelas, O.; Glénat, P.; Tohidi, B. Successful Field Application of an Inhibitor Concentration Detection System in Optimising the Kinetic Hydrate Inhibitor (KHI) Injection Rates and Reducing the Risks Associated with Hydrate Blockage. *Proceedings of the International Petroleum Technology Conference, Doha, Qatar, Dec 7−9, 2009;* International Petroleum Technology Conference: 2009; IPTC 13765.

(11) Davalath, J.; Barker, J. W. Hydrate Inhibition Design for Deepwater Completions. *SPE 26532. SPE Drill. Completion.* **1995**, *10*, 115.

(12) Mehta, A. P.; Herbert, P. B.; Cadena, E. R.; Weatherman, J. P. Fulfilling the Promise of Low-Dosage Hydrate Inhibitors: Journey From Academic Curiosity to Successful Field Implementation. *Proceedings of the 2002 Offshore Technology Conference, Houston, TX, May 6−9, 2002;* Offshore Technology Conference: 2002; OTC 14057.

(13) Anderson, R.; Tohidi, B. WO 2015/022480, 2015.

(14) Kelland, M. A. History of the development of low dosage hydrate inhibitors. *Energy Fuels* **2006**, *20* (3), 825−847.

(15) Yousif, M. H. The Kinetics of Hydrate Formation. *Proceedings of the SPE 69th Annual Technical Conference and Exhibition, New Orleans, LA, Sept 25−28, 1994;* Society of Petroleum Engineers: 1994; SPE 28479.

(16) 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.

(17) Kelland, M. A.; Svartaas, T. M.; Dypvik, L. Studies on New Gas Hydrate Inhibitors. *Proceedings of the SPE Offshore Europe Conference, Aberdeen, U.K., Sept 5−8, 1995;* Society of Petroleum Engineers: 1995; SPE 30420.

(18) Ke, W.; Chen, D. A short review on natural gas hydrate, kinetic hydrate inhibitors and inhibitor synergists. *Chin. J. Chem. Eng.* **2019**, *27* (9), 2049−2061.

(19) Colle, K. S.; Oelfke, R. H.; Kelland, M. A. US 5874660, 1999.

(20) Kelland, M. A. A review of kinetic hydrate inhibitors: Tailormade water-soluble polymers for oil and gas industry applications. In *Advances in Materials Science Research*; Wytherst, M. C., Ed.; Nova Science Publishers, Inc.: New York, 2011; Vol. 8.

(21) Kelland, M. A. Designing Kinetic Hydrate Inhibitors- Eight Projects With Only Partial Success, But Some Lessons Learnt. *Energy Fuels* **2017**, *31* (5), 5046−5054.

(22) Linhardt, A.; Konig, M.; Schofberger, W.; Bruggemann, O.; Andrianov, A. K.; Teasdale, I. Biodegradable Polyphosphazene Based Peptide-Polymer Hybrids. *Polymers* **2016**, *8* (4), 161.

(23) Rivers, G. T.; Crosby, D. L. Gas hydrate inhibitors. WO 2004/022910 A1, 2004.

(24) Colle, K. S.; Costello, C. A.; Talley, L. D.; Oelfke, R. H.; Berluche, E. WO 96/41786, 1996.

(25) Mady, M. F.; Kelland, M. A. N, N-Dimethylhydrazidoacrylamides. Part 1: Copolymers with N-Isopropylacrylamide as Novel High-Cloud-Point Kinetic Hydrate Inhibitors. *Energy Fuels* **2014**, *28* (9), 5714−5720.

(26) 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* (12), 7923−7930.

(27) Doetschman, D. C.; Mehlenbacher, R. C.; Cywar, D. Stable free radicals produced in acrylate and methacrylate free radical polymer-

ization: Comparative EPR studies of structure and the effects of cross-linking. *Macromolecules* **1996**, *29* (5), 1807−1816.

(28) Burkhart, A.; Ritter, H. Influence of cyclodextrin on the UCST- and LCST-behavior of poly (2-methacrylamido-caprolactam)-co-(N, N-dimethylacrylamide). *Beilstein J. Org. Chem.* **2014**, *10* (1), 1951−1958.

(29) Ree, L.; Kelland, M. A.; Haddleton, D.; Alsubaie, F. Comparison of the kinetic hydrate inhibition performance of block and statistical *N*-alkylacrylamide copolymers. *Energy Fuels* **2017**, *31* (2), 1355−1361.

(30) Mady, M. F.; Kelland, M. A. N, N-Dimethylhydrazidoacrylamides. Part 2: High-Cloud-Point Kinetic Hydrate Inhibitor Copolymers with N-Vinylcaprolactam and Effect of pH on Performance. *Energy Fuels* **2015**, *29* (2), 678−685.

(31) Gjertsen, L. H.; Fadnes, F. H. Measurements and predictions of hydrate equilibrium conditions. In *Gas Hydrates: Challenges for the Future*; Holder, G. D., Bishnoi, P. R., Eds.; New York Academy of Sciences: New York, 2000; Vol. *912*, pp 722−734.

(32) Tohidi, B.; Burgass, R. W.; Danesh, A.; Østergaard, K. K.; Todd, A. C. Improving the accuracy of gas hydrate dissociation point measurements. In *Gas Hydrates: Challenges for the Future*; Holder, G. D., Bishnoi, P. R., Eds.; New York Academy of Sciences: New York, 2000; Vol. *912*, pp 924−931.

(33) Wijaya, A. W.; Nguyen, A. I.; Roe, L. T.; Butterfoss, G. L.; Spencer, R. K.; Li, N. K.; Zuckermann, R. N. Cooperative Intramolecular Hydrogen Bonding Strongly Enforces cis-Peptoid Folding. *J. Am. Chem. Soc.* **2019**, *141* (49), 19436−19447.

(34) *Alternating Copolymers*; Cowie, J. M. G., Ed.; Plenum Press: New York, 1985.

(35) *Controlled/Living Radical Polymerization*; Matyjaszewski, K., Ed.; ACS Symposium Series 768; American Chemical Society: Washington, DC, 2000. DOI: 10.1021/bk-2000-0768.

(36) Thieu, V.; Bakeev, K. N.; Shih, J. S. US 6359047. 2002.

(37) Hu, J.; Li, S.; Wang, Y.; Lang, X.; Li, Q.; Fan, S. Kinetic hydrate inhibitor performance of new copolymer poly (N-vinyl-2-pyrrolidone-co-2-vinyl pyridine)s with TBAB. *J. Nat. Gas Chem.* **2012**, *21* (2), 126−131.

(38) Musa, O. M.; Cuiyue, L. WO 2010/114761, 2010.

(39) Musa, O. M.; Cuiyue, L.; Zheng, J.; Alexandre, M. M. Advances in Kinetic Gas Hydrate Inhibitors. *Chemistry in the Oil Industry XI: Regulation Meets Innnovation-Moving Forward, Manchester, U.K., Nov 2−4, 2009*; Specialty Chemicals Sector, Royal Society of Chemistry: Leek, U.K., 2009.

(40) 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* (8), 7127−7137.

(41) Kelland, M. A.; Dirdal, E. G.; Ree, L. S. Solvent Synergists for Improved Kinetic Hydrate Inhibitor Performance of Poly (N-vinyl caprolactam). *Energy Fuels* **2020**, *34* (2), 1653−1663.

(42) Zhang, Q.; Heyns, I. M.; Pfukwa, 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* (12), 12337−12344.

(43) Reyes, F. T.; Kelland, M. A. Investigation of the kinetic hydrate inhibitor performance of a series of copolymers of N-vinyl azacyclooctanone on structure II gas hydrate. *Energy Fuels* **2013**, *27* (3), 1314−1320.

(44) Colle, K. S.; Talley, L. D.; Longo, J. M. WO 2005/05567, 2005.

(45) 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*, 1806−1816.

(46) Ree, L. H.; Kelland, M. A. Investigation of Solvent Synergists for Improved Kinetic Hydrate Inhibitor Performance of Poly (N-isopropyl methacrylamide). *Energy Fuels* **2019**, *33* (9), 8231−8240.

(47) Yang, J.; Tohidi, B. Characterization of inhibition mechanisms of kinetic hydrate inhibitors using ultrasonic test technique. *Chem. Eng. Sci.* **2011**, *66*, 278−283.

(48) Fu, B. The development of advanced kinetic hydrate inhibitors. In *Chemistry in the Oil Industry VII: Performance in a Challenging Environment*; Frampton, H., Craddock, H. A., Eds.; Royal Society of Chemistry, ACS: Cambridge, U.K., 2002; pp 264−276.