Alternative Lactam-Based Kinetic Hydrate Inhibitors—Investigation of Polymers of 2-Methacrylamido-caprolactam

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ABSTRACT: Kinetic hydrate inhibitors (KHIs), such as poly(*N*-vinylcaprolactam) (PVCap) and related copolymers, are a well-known method to help 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. In an earlier study, we reported on the first alternate KHI polymer class with pendant caprolactam groups based on the 2-methacrylamido-caprolactam (2-MACap) monomer. This report builds on that study, by optimizing the best copolymers from that study and copolymerizing 2-MACap with other comonomers. 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. In addition, the importance of the methyl group in 2-MACap for enhanced KHI performance was confirmed by making and testing polymers with 2-acrylamido-caprolactam, which has no methylated backbone. Further confirmation from 2-MACap copolymers with 1-acryloylpyrrolidine and *N*-methacryloylpyrrolidine, for which the latter copolymer performed best. Finally, it was shown that a series of well-known synergists for PVCap were able to give excellent KHI performance enhancement of the selected 2-MACap copolymers, although some molecules showed antagonistic effects. This could be due to unhelpful polymer−synergistic interactions or both molecules competing in the same KHI mechanistic processes.
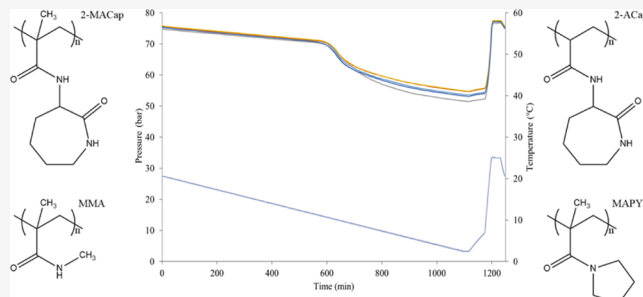
1. INTRODUCTION

Gas hydrates are non-stoichiometric crystalline solids that have many similarities with ice. Gases of certain molecular-weight stabilize the hydrogen-bounded molecular water cages. These relatively low-molecular-weight gases are entrapped within the cavities of the lattice of solid water molecules. Thus, gas hydrates will form if suitable low-molecular-weight hydrocarbon gases combine with water under specific favoring conditions of temperature (<25 °C) and pressure (>30 bar).[1−4] The formation of the gas hydrate is an energetically (enthalpy) favored process because of the extraordinary amount of energy that is released as heat as additional hydrogen bonds form. Gas hydrate formation is thus an exothermal process. Because of these additional hydrogen bonds formed, a more ordered structure is formed. Therefore, the formation of the gas hydrate is not favored by entropy.[5,6]

These gas hydrate favorable conditions are not uncommon to encounter when producing or transporting oil and gas. If the situation is left unattended, then gas hydrate plugs can occur, potentially jeopardizing the operation.[4,7−14] There exist multiple measures to handle and treat gas hydrates, with one of them being the utilization of chemicals. More specifically, low-dosage hydrate inhibitors and the sub-group kinetic hydrate inhibitors

(KHIs).[7] The concentration range, in which these KHIs are added is 0.1−1.0 wt %.[10,15−19]

The KHI formulation consists of two parts, the water-soluble polymer and the carrier solvent.[20]

Regarding the carrier solvent, it typically makes up 70−90 wt % of the KHI formulation. This is often a low-molecular-weight alcohol, glycol, or glycol ether, like methanol, ethanol, monoethylene glycol, and 2-*n*-butoxyethanol (BGE).[14] The viscosity of the KHI polymer solution is diluted sufficiently to enable it to be injected and pumped over long distances in umbilical flow lines. The carrier solvent can enhance the hydrate inhibiting properties of the polymer, and thus act as a synergist with the KHI polymer. The solvent synergism is therefore able to increase the application performance window of the pure KHI polymer or reduce the total polymer dosage.[20]
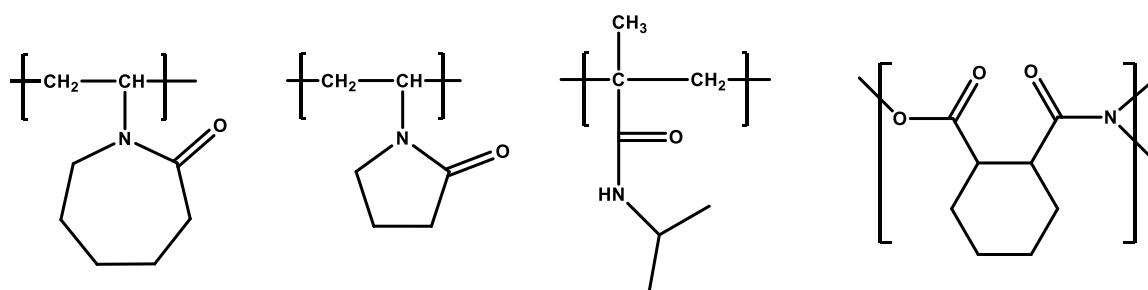
Figure 1. Structures of common KHIs, from left to right: PVCap, PVP, poly(*N-iso*-propylmethacrylamide) (PNIPMAM) (polyvinylic KHIs), and the esteramide unit in hyperbranched poly(ester amide)s.

Regarding the polymers, this is the main active compound and typically makes up 10−30 wt % of the KHI formulation.[20] Further, the polymer needs two structural features in order to perform good as hydrate inhibitors. This is achieved by incorporating hydrophilic and hydrophobic moieties into the polymer. The hydrophilic functional groups of the polymer consists usually of amide, imide, or amine oxide groups, moieties that are capable of making strong hydrogen bonds.[7,21,22] For the best performance of the polymer, the hydrophilic functional groups must be accompanied either directly or adjacent by a hydrophobic functional group.[23] These features consist of enabling the polymer to have both hydrophilic and hydrophobic capabilities making the polymer amphiphilic. The molecular weight of the polymer also determines how good it will perform as KHI, with a bimodal distribution of the molecular weight giving better nucleation inhibition.[24] However, it is beneficial that the majority of the polymer is of low-molecular weight, with a smaller portion being of higher molecular weight.[21] The bulk of commercially available KHI polymers and copolymers are 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 (Figure 1).[7]

The mechanism behind the inhibition properties of these KHI polymers as well as the synergetic mechanism is not fully understood and highly debatable. The performance of KHI polymers have been ascribed to different mechanisms because there is no consensus within the hydrate community and ranges from labile cluster hypothesis, nucleation at interface hypothesis, local structuring mechanism, and the blob mechanism.[22,25] However, the KHI polymers are believed to kinetically interact with the hydrate formation process and are able to interfere with the hydrate nucleation step and/or the crystal growth process. Further, the KHI polymers are assumed to prevent the hydrate particles from reaching the critical size for continuous growth by binding onto the surface of hydrate particles at an early stage of nucleation and growth.[15,16] Hence, any nuclei with a radius smaller than the critical radius will re-dissolve in the liquid medium.[16,25,26] Thus, clusters of these molecules can either grow or shrink until they reach the critical size. Until they exceed the critical size, the agglomerates are in quasi equilibrium with each other and the labile clusters.[27] When clusters possessing the critical size, monotonic growth occurs. This phenomenon can also be interpreted as an excess in Gibbs free energy, ΔG, between the small dissolved solid particles and the solvent in the solution.[28] ΔG becomes negative and the growth becomes spontaneous or catastrophic.[1] The hypothetical mechanisms behind the synergetic performance of the solvents, especially glycol ethers and alcohols, range from co-operative adsorption on the hydrate particles and/or water perturbation together with

the KHI polymer, as well as giving a stronger adsorption of the KHI polymer on the surface of the aqueous phase where nucleation is expected to first occur by lowering the gas/liquid interfacial tension.[29−36]

One of the best KHIs currently available is poly(*N*-vinylcaprolactam) (PVCap), and several copolymers of VCap have also been applied in the field.[37] The majority of KHI polymers are based upon free radical polymerization of vinylic monomers, thus making the backbone polyvinyl. Free radical polymerization of two or more vinylic comonomers will cause the formation of statistical copolymers with no particular order of the comonomers.[38,39] Polymers and copolymers based on VCap are the most commonly used. Comonomers such as VP, *N*-vinylpyridine, *N*-methyl-*N*-vinyl acetamide, vinyl acetate, (acrylamide)propanesulfonic acid and (dimethylamino)-ethyl methacrylate have been investigated as KHIs.[16,40−43] Compared to other KHI polymer classes such as poly(alkyl methacrylamide)s, VCap-based KHI polymers are known to be particularly good at inhibiting hydrate crystal growth.[1,7,17] This means that once hydrate nucleation has started it may still be a long time before enough hydrate crystals have formed before catastrophic hydrate growth occurs using a VCap-based polymer. This can give the field operator a better opportunity to avoid completely plugging the flow line once hydrates are first suspected to be formed.

This gave us the incentive to investigate alternate caprolactam-based polymers. Interestingly, there exist very few reported studies on polymers containing caprolactam rings as KHIs, except for the VCap-based polymers. Our research group have previously attempted to react 2-aminocaprolactam with poly(dichlorophosphazene) in order to make poly(caprolactam-2-amino)phosphazene, which was water soluble as a homopolymer.[44] Another attempt was made by synthesizing acryloyloxyethylcaprolactam and acryloyloxymethylcaprolactam but it proved surprisingly difficult to make poly(*N*-acryloyloxyalkyl-caprolactams), probably due to steric problems during the polymerization procedure (Figure 2).[44]

Both of the poly(caprolactam-2-amino)phosphazene and polyacryloalkylenecaprolactams had their drawbacks. Therefore, in the previous research, we synthesized 2-methacrylamido-caprolactam (2-MACap) from α-amino-ε-caprolactam reacted with methacryloyl chloride, which was not water soluble as a homopolymer and needed to be copolymerized.[45] 2-MACap was copolymerized with the more hydrophilic monomers, *N*-methylmethacrylamide (MMA), *N*-methylol methacrylamide (MOIMA), VP, and *N*-vinyl-*N*-methylacetamide (VIMA) (Figure 3). Of these copolymers, 2-MACap/MMA (1:1) showed the best potential KHI potential. In addition, it had a fairly high cloud point at 1 wt % in deionized water (58 °C) and the KHI performance was improved with two solvent synergists.
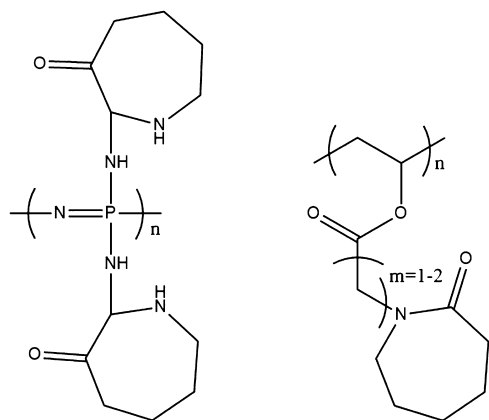
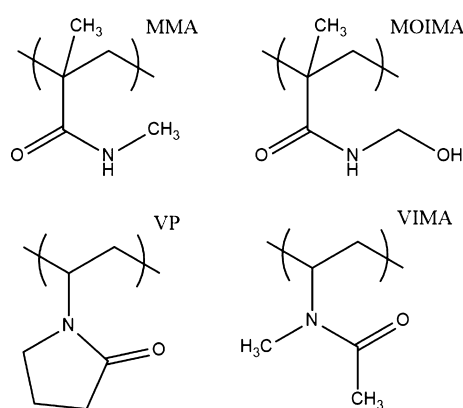**Figure 2.** Poly(caprolactam-2-amino)phosphazene (left) and poly-acryloalkylenecaprolactams (right).

Figure 3. Hydrophilic comonomer units polymerized with 2-MACap from the previously study:[45] MMA, MOIMA, VIMA, and VP.

In this study, we continued our research on the new class of caprolactam-containing polymers to understand the structure–performance relationship better and find further improvements. We chose some new comonomers to copolymerize with 2-MACap that we postulated could either enhance the performance or raise the cloud point to more useful levels. We also investigated polymers with a new monomer 2-acrylamido-caprolactam (2-ACap) to determine if an extra methyl group in the polyvinyl backbone is favorable for KHI performance, as seen for *N*-alkyl methacrylamide polymers and poly(*N*,*N*-dimethylhydrazido methacrylamide)[46–48] (Figure 4). In addition, we have also investigated the synergetic properties of 2-MACap polymers with some molecules that are well-known
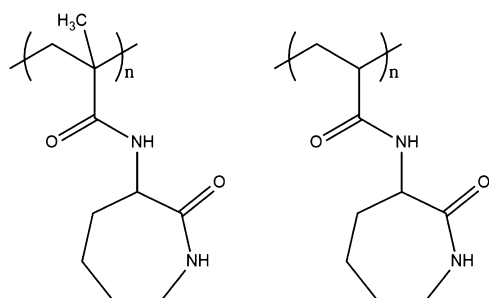

Figure 4. Poly(2-methacrylamido-caprolactam) [poly(2-MACap)] (left) and poly(2-acrylamido-caprolactam) [poly(2-ACap)] (right).

synergists for PVCap to see if the performance improvements are similar with our new class of caprolactam-based polymers.

2. EXPERIMENTAL SECTION

2.1. Chemicals. α-Amino-ε-caprolactam was obtained from ABCR, Germany. Triethylamine and solvents used in this study were obtained from Merck. MOIMA was obtained from Evonik, Germany. MMA was obtained from Tokyo Chemical Industry (TCL). Methacryloyl chloride, *N*-vinyl-2-pyrrolidone, and VIMA were obtained from Sigma-Aldrich. All chemicals were commercially available and used without further purification. 1-Acryloylpyrrolidine (APYD),[49] *N*-methacryloylpyrrolidine (MAPYD),[50] and *N*-(pyrrolidine-1-yl)-methacrylamide (NPyMA)[51] were synthesized previously. Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker Ascend NMR 400 MHz spectrometer at ambient temperature unless otherwise stated.

2.2. Synthesis of 2-MACap. The synthesis was based on the described method,[52] by dissolving α-amino-ε-caprolactam (1 g, 7.80 mmol) in dichloromethane (20 mL) in a 100 mL round-bottomed flask. Triethylamine (0.79 g, 7.80 mmol) was then added and the solution was cooled to 0 °C in an ice bath. Methacryloyl chloride (0.82 g, 7.80 mmol) dissolved in dichloromethane (10 mL) was added dropwise to the solution in the round-bottomed 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 d. i. 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-MACap. ^1H NMR confirmed that the resulting product was pure and was used for polymerizations without further purification.

2.3. Synthesis of 2-ACap. This synthesis was also based on the described method,[52] by dissolving α-amino-ε-caprolactam (5 g, 39.01 mmol) in dichloromethane (20 mL) in a 100 mL round-bottomed flask. Then, triethylamine (3.95 g, 39.01 mmol) was added and the solution was cooled to 0 °C in an ice bath. Acryloyl chloride (3.53 g, 39.01 mmol) dissolved in dichloromethane (5 mL) was added dropwise to the solution in the round-bottomed flask with vigorous stirring. The mixture was slowly heated to room temperature and stirred overnight. The resulting white precipitate was filtered off and washed with dichloromethane. The combined solvents were then removed in vacuo on a rotary evaporator to yield 2-ACap. ^1H NMR confirmed that the resulting product was pure and was used for polymerizations without further purification.

2.4. Poly(2-MACap), Poly(2-ACap), and Copolymer Synthesis Thereof. From the first study, we found out that 2-MACap would not polymerize in 2-propanol, so dimethylsulfoxide (DMSO) was the preferred solvent used.[45] The resulting homopolymer was, however, not water soluble, as was also the case for 2-ACap. Therefore, copolymers were made for both these monomers. The polymerization synthesis was done in the same general manner for all copolymers. 2-MACap or 2-ACap (0.50 g, 2.50 mmol) was dissolved in DMSO (2 g) in a Schlenk flask with a magnet. The desired amount of the comonomer was added depending on the monomer ratio in the copolymer required. Then, AIBN (1 wt %) was added and the solution was flushed with dinitrogen using a standard pump-fill technique. While the solution was stirring, it was heated to 70 °C and left to react under the protection of dinitrogen overnight. Then, the copolymer solution was cooled to room temperature and the product was left in the solution. ^1H NMR showed that all the monomer was consumed.

The comonomers used to make copolymers of 2-MACap were methacrylamide (MAm), MMA, *N*,*N*-dimethylmethacrylamide (DMMAm), *N*-isopropylmethacrylamide (NIPMAm), *N*,*N*-dimethyl-hydrazidomethacrylamide (NDMHMAm), APYD, MAPYD, NPyMA, poly(ethylene glycol)monoethyl methacrylate (PEGMA-9), and VIMA (Figure 5).

2.5. Gel Permeation Chromatography/Size Exclusion Chromatography Analysis. Gel permeation chromatography/size exclusion chromatography (GPC/SEC) analysis was conducted in order to determine the molecular weight as well as the polydispersity index of
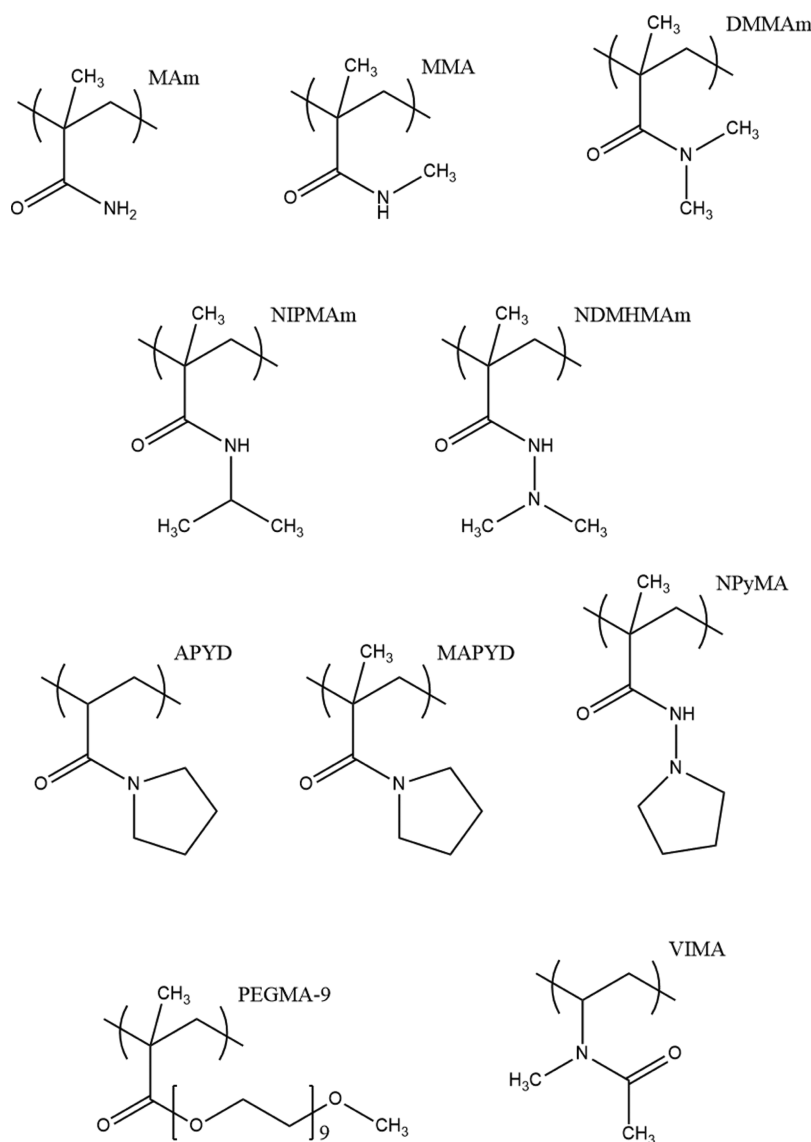
Figure 5. Structure of comonomer units used with 2-MACap copolymers: MAm, MMA, DMMAm, NIPMAm, NDMHMAm, APYD, MAPYD, NPyMA, PEGMA-9, and *N*-methyl-*N*-vinylacetamide (VIMA).

the polymers made. The apparatus used was a JASCO Chem NAV size-exclusion chromatography 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 an eluent. Polystyrene standards were used for calibrating the molecular weights of the polymers.

2.6. Cloud Point (T_{cl}) Measurements. A sample of the polymer was dissolved in deionized water making a 2500 ppm concentration. This solution was then heated at approximately 2 °C/min. A visual observation was continuously done during heating, and the cloud point (T_{cl}) was determined at the temperature where the first sign of haze was observed. This was repeated minimum one more time for each polymer for the verification of the T_{cl} temperature and to show reproducibility.

2.7. Gas Hydrate KHI Performance Testing Using High-Pressure Apparatus. The KHI performance testing was conducted in a multi-rocking cell apparatus, the Rocking Cell 5 (RC5) apparatus supplied by PSL Systemtechnik, Germany. This apparatus contains a cooling bath where five high-pressure stainless steel rocking cells, supplied by Svafas, Norway, are rocked. Both the cooling bath and the cells are equipped with temperature sensors in addition to each cell having pressure sensors. The cells have an internal volume of 40 mL and a stainless-steel ball inside each cell is used for agitating the test solution.

A standard natural gas mixture (SNG), which preferentially forms a structure II gas hydrate as the most thermodynamically stable phase, was the gas used in these tests (Table 1).

The procedure for high-pressure KHI testing by the use of slow constant cooling (SCC), described previously, is summarized in the following:[53,54]

1. At least 1 day before initializing the test, the polymer, and if applicable the synergist, was dissolved to the desired concentration in deionized water.

Table 1. Composition of the Synthetic Natural Gas Mixture (SNG) Used in the High-Pressure KHI Performance Testing

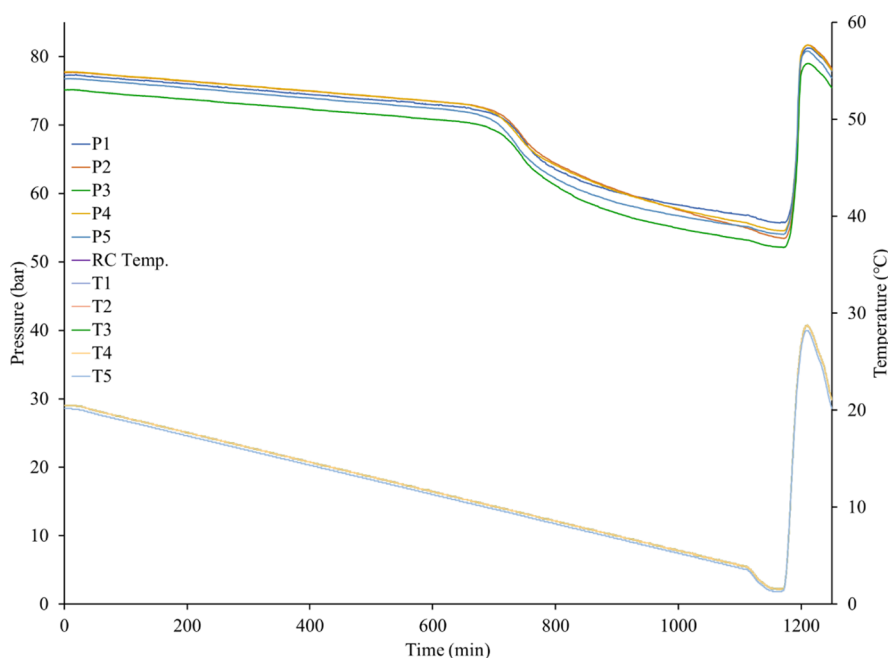| component	mol %
methane	80.67
ethane	10.20
propane	4.90
iso-butane	1.53
n-butane	0.76
N_2	0.10
CO_2	1.84

Figure 6. Graph containing the results from all five cells during a SCC experiment. In this example, each cell contained 2-MACap/MMA (1:2) copolymer in DMSO. RC temp. is the temperature recorded in the cooling bath.
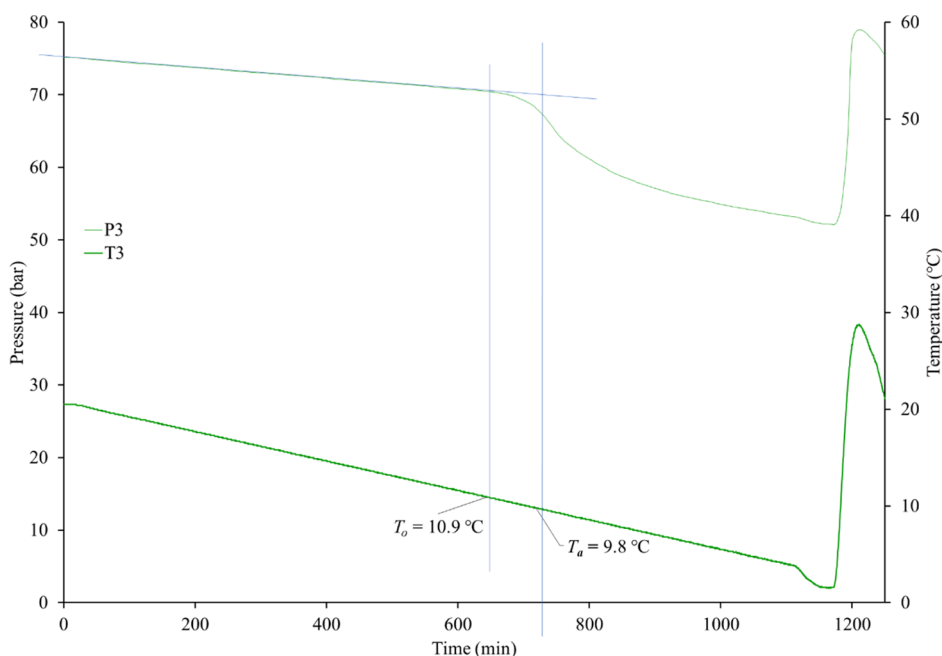

Figure 7. Graph from cell three during a SCC experiment with both T_o and T_a is determined. In this example, the cell contained 2-MACap/MMA (1:2) copolymer in DMSO.

2. Usually 20 mL of solution was added to each of the five cells, with the solution consisting of various additives dissolved in distilled water.

3. A sequence of vacuum and pressurizing with SNG was applied in order to replace the air with SNG in the cells. First, vacuum then pressurizing with SNG to 3−5 bar, and then depressurizing before a final round with vacuum.

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

5. The cells were cooled down and rocked with a cooling rate of 1.0 °C/h from 20.5 to 2.0 °C, and a rocking rate of 20 rocks per minute at an angle of 40°, respectively.

The hydrate equilibrium temperature (T_{eq}) at 76 bar have previously been determined to be 20.2 ± 0.05 °C by standard laboratory dissociation experiments warming at 0.025 °C/h for the last 3−4 °C. This correlated well with calculations done by Calsep PVTSim software.[55,56]

The initial pressure was 76 bar and the temperature were decreased from 20.5 to 2 °C during a SCC experiment (Figure 6). Because each cell is being a closed system, there will be a linear pressure decrease from which both the onset temperature for hydrate formation (T_o) and the rapid hydrate formation temperature (T_a) can be observed.

From this linear pressure decrease, T_o is defined as the temperature at the first observable deviation from the linear pressure decrease. It is quite possible that the hydrate nucleation initiated at a molecular level

Table 2. Summarized SCC KHI Test Results for the Copolymers with Cloud Points and GPC/SEC Data[a]

copolymer	T_{cl} (°C)	molecular weight (g/mol)	PDI	concentration (ppm)	T_o (°C)	T_a (°C)
poly(2-ACap)	<0	9600	1.94			
poly(2-MACap)	<0	12 600	5.42			
no additive					17.2	16.6
PVCap		10 000		2500	10.4	8.9
2-MACap/MAm (1:1)	33	not soluble in DMF		2500	10.3	9.0
2-MACap/MMA (1:1)	58	2100 (major), 120 800 (broad minor)	1.16, 12.21	2500	8.8	8.1
				5000	6.4	5.7
2-MACap/MMA (1:2)	85	not soluble in DMF		2500	10.8	9.6
2-MACap/DMMAm (1:1)	<2	2000	3.11	2500	10.7	9.9
2-MACap/NIPMAm (1:1)	24	3200	5.01	2500	8.0	7.4
2-MACap/NDMHMAm (1:1)	>100	500	1.25	2500	12.0	11.8
				5000	10.1	9.9
2-MACap/APYD (1:1)	28	3300	4.39	2500	9.2	8.6
				5000	6.7	5.8
2-MACap/MAPYD (1:1)	24	1300	2.42	2500	8.4	8.1
2-MACap/MAPYD (1:2)	20	2500	3.25	2500	10.8	10.3
2-MACap/NPyMA (1:1)	>100	800	1.25	2500	11.8	10.8
				5000	9.4	8.3
2-MACap/PEGMA-9 (4:1)	54	15 900	8.74	2500	10.3	9.0
				5000	7.8	6.8
2-MACap/VIMA (1:1)	28	61 500	2.93	2500	8.8	7.7
2-MACap/NIPMAm/VIMA (1:1:0.5)	30	7800	4.37	2500	9.4	8.5
2-ACap/MMA (1:1)	60	22 600	38.2	2500	9.7	8.8
2-ACap/MAPYD (1:1)	24	4700	2.25	2500	10.4	10.0

[a]From the previous publications no additive, PVCap, 2-MACap/MMA (1:1) and 2-MACap/VIMA (1:1) are added for comparison.[45,58]

prior to this because this is the first macroscopic observation of hydrate formation done by an observation on a linear pressure decrease. However, these experiments are not capable of detecting nucleation, which possibly happens earlier. A rapid pressure decrease can be observed with varying intervals after T_o have occurred. The temperature when the pressure decrease is at its steepest, that is, when the hydrate formation is at its fastest is defined as T_a (Figure 7).

3. RESULTS AND DISCUSSION

3.1. KHI Results from New Copolymers Based on 2-MACap and 2-ACap. A series of new copolymers of 2-MACap were synthesized as well as the structurally similar 2-ACap. These copolymers gave a wide range in molecular weights. This meant that KHI performance comparison was not always easy to carry out because molecular weight is one of the structural parameters that affects the performance. Therefore, we have been cautious to only compare the performance of polymers with fairly similar molecular weight values. Past studies suggest that the majority of the polymers should have a low-molecular weight for optimal performance, perhaps only 8−10 repeat units and a molecular weight of 1200−2000 g/mol for most of the well-known KHI classes.[17,21]

To validate the KHI potential of the copolymers, they were evaluated using SCC tests (Table 2, Figure 8). Both the T_o and T_a values reported in the following are averages. The focus in this discussion will be on the T_o value because this parameter refers to the first detection of hydrate formation after which crystal growth can potentially cause hydrate plugging irrespective of the growth rate. Therefore, the T_a values, and the difference to the T_o value can be used as an indicator of fast or slow hydrate growth in the system. Figure 8 gives average T_o or T_a values as well as the maximum spread in results obtained for each series. The standard deviation (assuming a normal distribution) for a set of T_o or T_a values is no more than 0.6 °C and usually less than 0.3 °C. Independent sample t-tests with equal variances for each
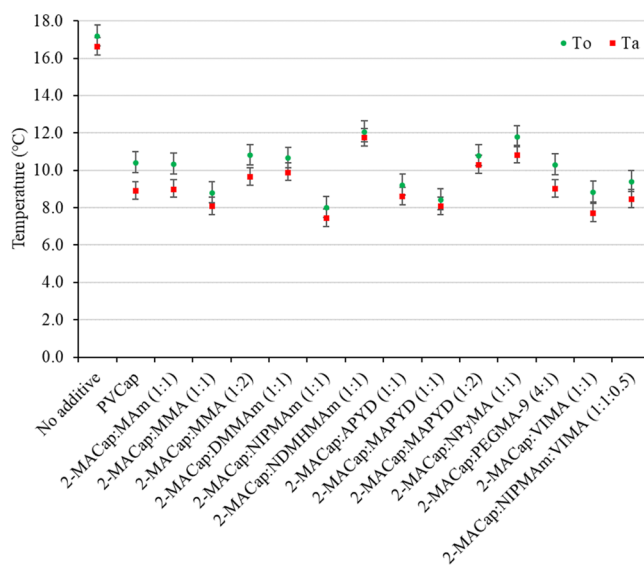

Figure 8. Graphical summary of SCC test results for 2-MACap copolymers at 2500 ppm. Both T_o and T_a values are given.

polymer were used to identify statistical differences in the performance between T_o and T_a values of the different polymers. The predetermined significant level is often 0.05 and when the p value is less, this indicates that the observed result would be statistically significant.[57]

The results for no additive and PVCap are added to Table 2 and Figure 8 as comparisons for KHI performance. Only a few copolymers of 2-MACap were synthesized and tested as KHIs in the first study.[45] In this present discussion of the new copolymers tested, we take 2-MACap/MMA (1:1) from the previous study as the starting point as this gave the best performance. The first structural aspect investigated was the

importance of the backbone methyl group coming from both comonomers. Therefore, one or both methyl groups needed to be removed from the two monomers and their relative performances compared.

The comonomers APYD and MAPYD were copolymerized with 2-MACap. Both comonomers have a pyrrolidine ring attached to the acrylamide. These cyclic structures have been reported to be beneficial for the KHI effect.[59,60] Further, this heterocyclic five-membered ring could potentially fit into the $5^{12}6^4$ cages of structure II gas hydrate. In addition, this ring is a common feature in a number of known KHI polymers, including poly(N-vinyl-pyrrolidone) (PVP) and poly(meth)-acryloylpyrrolidine.[51,61] We begin by discussing results with the simplest of them, APYD, which is an acrylamide with a pyrrolidine ring. Copolymerized with 2-MACap, making 2-MACap/APYD (1:1), the performance was adequate, giving T_o value and T_a value of 9.2 and 8.6 °C, respectively. We then investigated the methylated version, MAPYD. The copolymer 2-MACap/MAPYD (1:1) had an excellent KHI performance, resulting in a T_o value of 8.4 °C and a T_a value of 8.1 °C. Not only did this copolymer perform better than the non-methylated comonomer, but it had a performance among the best of the comonomers tested. However, both the T_o value and the T_a value between 2-MACap/MAPYD (1:1) and 2-MACap/MMA (1:1) was not found to be significantly different ($p > 0.05$ in a statistical t-test). The cloud point between the copolymers was different, with the MAPYD-containing copolymers having the lower value. The cloud point between MAPYD and APYD copolymers were more or less the same but perhaps slightly higher for the copolymer containing APYD.

Because both 2-MACap/MMA (1:1) and 2-MACap/MAPYD (1:1) had such a good KHI performance, we wanted to test them in a different ratio to see if this could possibly further enhance their performance and increase their cloud point. Because of the fact that poly(2-MACap) was not water soluble, the only way to change the ratio would be to increase the amount of MMA and MAPYD, respectively. 2-MACap/MMA (1:2) and 2-MACap/MAPYD (1:2) copolymers were synthesized and the results from both were clearly worse than the 1:1 ratio copolymers with the same monomers, and now on the same performance level with PVCap. Here, the ratio between the monomers were not optimal, and the hydrophilic to hydro-phobic moiety of the copolymer was imbalanced. As it is for copolymers, in general, it is important to find the right ratio between the monomers used in order to obtain optimal results.[62] The cloud point for 2-MACap/MMA (1:2) had a profound increase compared to the 1:1 copolymer, but for 2-MACap/MAPYD (1:2), the cloud point had a slight decrease, compared to the 1:1 ratio of the same monomers (Table 2).

Continuing our investigation of the importance of a backbone methyl group, we synthesized 2-ACap, which when polymerized will be structurally the same as 2-MACap polymers but now without the methyl in the backbone (Figure 4). Poly(2-ACap) was insoluble as also found for poly(2-MACap), so copolymers were synthesized. There may be increased solubility at lower molecular weights as seen for some polymer classes with hydrophilic monomers. As comonomers with 2-ACap we used MMA and MAPYD because both of these gave excellent KHI performance results when copolymerized with 2-MACap (Table 2). Both 2-ACap/MMA (1:1) and 2-ACap/MAPYD (1:1) had a poorer result than their methylated counterparts indicating that adding a methyl group improved the inhibition performance. In addition, the cloud points of the 2-MACap and 2-ACap

copolymers were virtually identical. Both the inhibition and cloud point trends correlate well with the findings for N-alkyl acrylamide polymers.[46] 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).[47,48] The steric effect of the methyl group opens the polymer structure and increases the surface-to-volume ratio, which is presumed to be the cause of the improved KHI effect. Further, it is essential for a good functionality of a KHI polymer that the bulk of the polymer has a low molecular weight. One possible way to achieve this is to polymerize monomers with the methyl group in the backbone. In radical polymerization or copolymerization, the acrylamide will form secondary radicals as the propagating end group, while methacrylamide form tertiary radicals as the propagating end group.[63] By nature, tertiary radicals are more stable than secondary radicals so they are thought to decrease the reactivity of the propagating end resulting in the polymerization rate to decrease. Moreover, the steric effect of approach of the monomer radical to monomer radical is always greater with regard to methacryl then acryl. This is in keeping with the fact that 2-ACap/MMA (1:1) and 2-ACap/MAPYD (1:1) had a higher molecular weight than the corresponding 2-MACap backbone-methylated copolymers.

From Table 2 and Figure 8, we can observe that all copolymers had an inhibition effect compared to PVCap, except when DMMMAm and NPyMA were used as the comonomers. 2-MACap copolymerized with the simplest acrylamide-based comonomer, namely, MAm, making 2-MACap/MAm (1:1), had almost identical inhibition efficacy as PVCap. Both the T_o value and the T_a value between 2-MACap/MAm (1:1) and PVCap were not found to be significantly different ($p > 0.05$ in a statistical t-test). This copolymer was not totally dissolved (<95%) at a concentration of 2500 ppm. This could be caused by internal hydrogen bonding that might take place, polymer cross-linking, or some of the copolymers may have such a high percentage of the 2-MACap comonomer that it renders it water insoluble.

In the next part of our inquiry, we investigated other comonomers copolymerized together with 2-MACap to see if they could improve the KHI effect and increase the cloud point beyond 2-MACap/MMA (1:1) from the previous study. We selected the comonomers as they are hydrophilic and it was hoped they would not diminish the performance of poly-2-MACap, assuming it had been water soluble. Copolymerization could also possibly increase the KHI performance of homopolymers, as has been reported for VIMA/VCap copolymers.[17,37,64,65] Other vinyl lactam monomers have been copolymerized with amine-based monomers in order to obtain better KHI performance and potentially increase the cloud point.[41] The comonomers used with 2-MACap were all acrylamide based, with PEGMA-9 (an acrylate ester) and VIMA (a vinyl amide) as the only exceptions. This was done in the hope that these conjugated acrylamide monomers would have a polymerization rate fairly similar to that of 2-MACap, also an acrylamide.

Extending the complexity of the comonomer beyond MMA to introduce DMMMAm results in the branching of the nitrogen on the amide, making 2-MACap/DMMMAm (1:1). The resulting copolymer had limited solubility in water, which would explain why it gave lower performance compared to the 1:1 copolymer with MMA as the comonomer. Interestingly, increasing the hydrophobicity of the comonomer by using NIPMAm, gave the

Table 3. SCC Test Results with 2-MACap/MMA (1:1) and 2-MACap/MAPYD (1:1) with Different Synergists[a]

copolymer	solvent synergist	concentration (ppm)		T_o (°C)	T_a (°C)
		polymer	synergist		
2-MACap/MMA (1:1)		2500		8.8	8.1
	TBAB	2500	5000	7.8	6.6
	TPAB	2500	5000	9.7	7.0
	TBPB	2500	5000	8.8	7.3
	HBuGCl	2500	5000	6.4	4.5
	*i*BGE	2500	5000	6.2	5.4
	4-MePeOl	2500	5000	4.6	3.8
	iPeCOOH	2500	5000	7.3	6.2
	iPeCOONa	2500	5000	6.9	5.9
2-MACap/MAPYD (1:1)		2500		8.4	8.1
	TBAB	2500	5000	6.4	5.2
	TPAB	2500	5000	3.4	2.0
	TBPB	2500	5000	4.8	3.0
	HBuGCl	2500	5000	3.1	2.0
	iPeCOOH	2500	5000	11.9	11.2
	iPeCOONa	2500	5000	8.1	7.3

[a]Results with 2-MACap/MMA (1:1) with *iso*-butyl glycol ether (*i*BGE) and 4-MePeOl taken from the first study are added for comparison.[45]

copolymer 2-MACap/NIPMAm (1:1) with a higher cloud point of 24 °C. We assume there must be more going than just a straightforward increase in hydrophobicity compared to 2-MACap/DMMAm (1:1) for this cloud point increase to occur. For 2-MACap/NIPMAm (1:1), the impact was a clear improvement in the KHI properties, resulting in the T_o value and T_a value of 8.0 and 7.4 °C, respectively. The good performance is not only due to the 2-MACap monomer units but also NIPMAm, the homopolymer of which is known as a powerful inhibitor in its own right.[46,66,67] This result is in accordance with the good performing copolymers of MMA and MAPYD. The results for 2-MACap/NIPMAm (1:1) and 2-MACap/MMA (1:1) both the T_o value and the T_a value were found to be significantly different ($p < 0.05$ in a statistical *t*-test). However, for 2-MACap/NIPMAm (1:1) and 2-MACap/MAPYD (1:1) only, the T_a value between them was found to be significantly different ($p < 0.05$ in a statistical *t*-test).

A cloud point of 24 °C for the 2-MACap/NIPMAm (1:1) copolymer was still too low for practical application. Therefore, a terpolymer, containing 2-MACap, NIPMAm, and VIMA as the monomers, was made in order to see if this could raise the cloud point without losing performance. VIMA was used because in the previous publication it was one of the copolymers that gave the best performance, in addition to reports that VIMA copolymerized with VCap increased the performance.[17,37,45] The resulting terpolymer was 2-MACap/NIPMAm/VIMA (1:1:0.5). The terpolymer had a slight increase in a cloud point to 30 °C, but the KHI effect for the terpolymer was less than the copolymers 2-MACap/NIPMAm (1:1) and 2-MACap/VIMA (1:1).

To avoid the low polymer cloud point using NIPMAm as a comonomer with 2-MACap, we investigated using a comonomer NDMHMAm. This comonomer has a hydrazide-bond where a carbon atom in the alkyl is replaced with a nitrogen atom. Homopolymers of this monomer were previously investigated as an alternative to PNIPMAm as well as copolymers with VCap.[47,54] A second hydrazide comonomer NPyMA, which contain a pyrrolidine ring, was also used to make a 2-MACap copolymer. The homopolymer PNPyMA has been reported to give good KHI results and no cloud point up to 95 °C in deionized water at 1 wt %.[51] Both 2-MACap/

NDMHMAm (1:1) and 2-MACap/NPyMA (1:1) gave no cloud point even in boiling deionized water, which was a great improvement over 2-MACap/NIPMAm (1:1). However, although both copolymers gave a similar and reasonable performance (average T_o 11.8 and 12.0 °C), the results were clearly worse than PVCap. The low performance could be related to the molecular weight being too low (500 and 800 g/mol), although it has been shown that PVCap with a molecular weight as low as these values can still give good KHI performance. A second reason for the mediocre performance of 2-MACap/NDMHMAm (1:1) and 2-MACap/NPyMA (1:1) may be the increased hydrophilicity of these hydrazide-based polymers. The past work has shown that many classes of KHI polymers perform the best when the cloud point is low, as long as the size and shape of the alkyl substituents are optimized.[64]

The last copolymer made with 2-MACap in this inquiry was by using PEGMA-9 as a large but hydrophilic comonomer. Under the test conditions, 2-MACap/PEGMA-9 (4:1) showed an inhibition effect similar to PVCap and 2-MACap/MAm (1:1). In fact, both the T_o value and the T_a values between 2-MACap/PEGMA-9 (4:1), PVCap and 2-MACap/MAm (1:1) were not found to be significantly different ($p > 0.05$ in a statistical *t*-test). The PEGMA comonomer had a strong effect on the hydrophilicity of the copolymer with 2-MACap. Just 20 mol % PEGMA turned an insoluble homopolymer into a water-soluble copolymer with cloud point 54 °C, also considerably higher than PVCap.

All of the above copolymers and the terpolymers were all sufficiently water soluble at 2500 ppm, and the results at this concentration are given. 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 exists numerous options where internal hydrogen bonding can take place, between 2-MACap/2-ACap units, between copolymerization units, and between 2-MACap/2-ACap units and copolymerization units. In addition, hydrogen bonding can also occur between polymer strands. Moreover, 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. This could also explain the solubility issues with some of the copolymers going from 2500 to 5000 ppm. Those copolymers that did show a sufficient solubility at 5000 ppm were also tested at this higher concentration, including 2-MACap/MMA (1:1), 2-MACap/NDMHMAm (1:1), 2-MACap/APYD (1:1), 2-MACap/NPyMA (1:1), and 2-MACap/PEGMA-9 (4:1). All copolymers had an improved inhibition effect at the higher concentration (Table 2).

3.2. Synergists for 2-MACap Copolymers. From the previous publication and other research, it is known that by adding certain solvents, it is possible that they can act as synergists with the KHI polymer, thereby improving the kinetic inhibition capabilities.[16,17,32,33,45,58,68−70] Knowing PVCap has many synergists, we wanted to investigate if 2-MACap copolymers, which also contain caprolactam rings, would show similar synergism. From the previous publications, we have shown that the acyclic aliphatic alcohol 4-methyl-1-pentanol (4-MePeOl) gave a good synergetic performance with the caprolactam-based KHI polymers PVCap and 2-MACap.[45,58,70] Here, we have broadened the field of the potential synergist using mixtures with 2-MACap/MMA (1:1) and 2-MACap/MAPYD (1:1). The synergists investigated were hexabutylguanidinium chloride (HBuGCl), tetrabutylphosphonium bromide (TBPB), tetrabutylammonium bromide (TBAB), tetrapentylammonium bromide (TPAB), sodium 4-methyl pentanoate (iPeCOONa), and 4-methylvaleric acid (iPeCOOH) (Table 3).

From Table 3, it can be observed that with the exception of iPeCOOH with 2-MACap/MAPYD (1:1), all synergists made this copolymer's KHI performance better than compared to PVCap. However, not all synergists improved the performance of the copolymers themselves.

Three of the synergists are onium salts (quaternary ammonium or phosphonium salts), which have good synergy with PVCap.[71−73] Interestingly, these synergists gave little performance enhancement to the 2-MACap/MMA (1:1) copolymer with only TBAB giving a significant improvement despite it being the least hydrophobic and weakest tetrahydrofuran hydrate crystal growth inhibitor of the three onium salts. In fact, the addition of TPAB worsened the average T_o value relative to the copolymer alone. This behavior is more reminiscent of some corrosion inhibitors, which are known to be antagonistic to VCap-based KHI polymers.[74−78] The average T_a value decreased for 2-the MACap/MMA (1:1) copolymer with all three synergists, which reflects their hydrate crystal growth inhibition abilities.

In contrast, the copolymer 2-MACap/MAPYD (1:1) gave a good synergetic effect with all three onium salts, significantly decreasing both the average T_o and T_a values. The addition of TPAB gave the best results, decreasing the average T_o and T_a from 8.8 to 8.1 °C for the polymer alone to 4.8 and 3.0 °C, respectively.

The onium salts are thought to exhibit good synergy with PVCap because of their different geometries (alkyl vs ring structure, respectively). Therefore, the onium salts and PVCap should attach to different sites on the hydrate crystal surface. This has been shown in molecular modeling by TBAB or TPAB penetrating $5^{12}6^4$ cavity on the 1,1,1 structure II hydrate surface.[14] The channels on the hydrate surface, where new $5^{12}6^4$ cages would normally form, are now occupied by two of the other butyl or pentyl groups. The possibility arises that these cages could partially form, trapping or imbedding the butyl or

pentyl groups in the hydrate surface. TBAB or TPAB will not be able to embed themselves in the surface of the hydrate crystal as long as the critical nuclear size is not reached, and thus the growth of the nuclei is energetically unfavorable (ΔG is positive). In this case, the likelihood is toward the detachment of the onium salts. When the growth of the nuclei is energetically favorable (ΔG is negative), TBAB or TPAB can become embedded in the hydrate surface as partial hydrate cages form around the butyl or pentyl groups but further structure II growth is prevented by the remaining butyl or pentyl groups.[79] While the onium salts start to work after the growth of the nuclei is energetically favorable (ΔG is negative), PVCap attaches to several sites on the hydrate surface via caprolactam rings and prevents the declustering of subcritical nuclei. Crystal growth will become favorable once these nuclei reach a critical size, and at this stage the onium salts can embed on the hydrate surface and prevent further growth.[36] Based on this, we speculate that the reason for this surprising result was potentially caused by the pyrrolidine ring on the methacrylamide incorporating into the growing hydrate together with the caprolactam ring before the hydrate nuclei reach a critical size. After reaching critical size, TPAB embeds on the hydrate surface and prevents further growth. This means that the copolymer and the synergist operate on different aspects on the hydrate formation, thereby optimizing their combined inhibition. 2-MACap/MMA (1:1) does not have the extra pyrrolidine ring, so its mode of action might be too similar to TPAB and they end up outcompeting themselves for the same $5^{12}6^4$ cavity on the 1,1,1 structure II hydrate surface.

These multiple alkyl group in these quaternary ammonium or phosphonium salts could be increased by introducing them on guanidinium salts, which have three nitrogen atoms in the cationic center. The guanidinium salt HBuGCl also contains the butyl group so we wanted to see how this compound worked as a synergist with the copolymers, as it has been reported to give good synergy with PVCap.[80] The performance increased for both copolymers, with the most pronounced improvement for 2-MACap/MAPYD (1:1). For 2-MACap/MMA (1:1), the synergetic effect gave a T_o value of 6.4 °C and T_a value of 4.5 °C. The butyl groups have also performed well as a synergist when they are on a monoglycol ether, like iBGE. Together with PVCap, it has a good synergetic effect.[58] From the previous publication, we also observed this synergetic effect with 2-MACap/MMA (1:1).[45] When iBGE was added, it improved the performance of 2-MACap/MMA (1:1) resulting in the T_o value and T_a value of 6.2 and 5.4 °C, respectively. The T_o value between 2-MACap/MMA (1:1) with iBGE and with HBuGCl was not found to be significantly different ($p > 0.05$ in a statistical t-test). The T_a value between them indicates that the HBuGCl could be better at delaying catastrophic hydrate growth. HBuGCl with 2-MACap/MAPYD (1:1) had a much stronger synergy, with a T_o value of 3.1 °C and T_a value of 2.0 °C, similar values as those obtained with TPAB.

Previous works with alcohols has shown that branching of an acyclic aliphatic hydrocarbon "tail" can lead to better synergy than an unbranched tail. Thus, 4-MePeOl was tested with PVCap and 2-MACap/MMA (1:1) and gave excellent synergy for both polymers. For 2-MACap/MMA (1:1) with 4-MePeOl, an average T_o value of 4.6 °C and T_a value of 3.8 °C was the result.[45,58,70] To get a better understanding of the role the of the functional group, we changed the functional group from alcohol to a carboxylic acid in the compound iPeCOOH and tested it with the same copolymers. We also used the carboxylate form

iPeCOONa, although the CO_2 in the gas mixture will buffer the effect of the higher pH.[51,54] Compared to the hydroxyl group in 4-MePeOl, the synergy was less pronounced for 2-MACap/MMA (1:1), with average T_o value and T_a values of 7.3 and 6.2 °C, respectively. A similar result was also found for iPeCOONa. Interestingly, both iPeCOOH and iPeCOONa were antagonistic with 2-MACap/MAPYD (1:1).

The synergy KHI test results highlight the difficulty in predetermining, which molecules will enhance the performance of a given KHI polymer. Thus, while the onium salts gave good synergy with 2-MACap/MAPYD (1:1), they had only a weak effect on 2-MACap/MMA (1:1) and sometimes even antagonistic (e.g., TPAB). In contrast, iPeCOOH gave some synergy with 2-MACap/MMA (1:1) but was antagonistic with 2-MACap/MAPYD (1:1). Exactly what is happening in solution to cause these differences is hard to say, but it may be a combination of polymer−synergist interactions as well as competitive interactions to prevent hydrate nucleation and crystal growth.

4. CONCLUSIONS

2-ACap was synthesized for the first time and its homopolymer poly(2-ACap) was found to be insoluble in water. The KHI properties of a series of water-soluble 2-MACap and 2-ACap copolymers were investigated. All the copolymers showed KHI effects compared to no additive. The KHI performance of some of these copolymers exceeded that of PVCap of similar molecular weight. The copolymers that gave the poorest results were also the most hydrophilic with no cloud point, 2-MACap/NDMHMAm (1:1) and 2-MACap/NPyMA (1:1). Of the copolymers investigated, several gave a better KHI performance than PVCap, with the best results for 2-MACap/MMA (1:1), 2-MACap/NIPMAm (1:1), and 2-MACap/MAPYD (1:1). The performance also increased with increasing polymer concentration. As has been seen in previous methacrylamido-based polymers, a high percentage of backbone methyl groups led to improved performance. This was seen for 2-MACap/MAPYD (1:1) versus 2-MACap/APYD (1:1), as well as for 2-MACap/MAPYD (1:1) versus 2-ACap/MAPYD (1:1) and 2-MACap/MMA (1:1) versus 2-ACap/MMA (1:1).

Several known synergists for PVCap were investigated with two of the best 2-MACap copolymers, 2-MACap/MMA (1:1) and 2-MACap/MAPYD (1:1). Excellent synergy was obtained with 2-MACap/MAPYD (1:1) for several synergists but the effect on average T_o values was sometimes quite different for 2-MACap/MMA (1:1), with TPAB even being antagonistic. Conversely, iPeCOOH gave some synergy with 2-MACap/MMA (1:1) but was antagonistic with 2-MACap/MAPYD (1:1). HBuGCl gave the most consistent synergetic effect for both copolymers. These results highlight the difficulty in predetermining, which molecules will enhance the performance of a given KHI polymer, without doing the necessary experimental work.

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Notes

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