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

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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 processes. 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.5,13 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.13

The hydrophilic functional group must be present directly or adjacent to each of the hydrophobic 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 disopropanolamine 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, monoethyleneglycol (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 polyalky(meth)acrylamides.3,5,20 This means that with the use of a VCap-based polymer the...
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 homopolymer21 (Figure 2). This polymer showed some

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 perform-
ance) 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-acryloyloxalkylcaprolactams), prob-
ably 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.

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

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)).
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-methacrylamide 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,19 by dissolving α-amino-γ-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 Na2SO4. The precipitated NEt3HCl(s) was filtered off and solvent was removed in vacuo on a rotary evaporator to yield 2-methacrylamidocaprolactam (2-MACap). 1H 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. 1H NMR showed that all monomer was consumed.

The comonomers used to make copolymers of 2-MACap were N-vinylpyrrolidone (VP), N-vinyl-N-methacrylamide (VIMA), N-methylol methacrylamide (MOIMA), 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 (Tc) 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 Tc 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 Tc temperature. Deposition points (Tdp’s), which are usually a maximum of 5–10 °C above the Tc, 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 (RCS) apparatus supplied by PSL Systemtechnik, Germany. With this apparatus, five high-pressure stainless steel rocking cells, supplied by Sváfas, 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  |
| N2        | 0.10  |
| CO2       | 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:20,21

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...
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.

Figure 6. Graph containing 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.
Table 2. Polymers Synthesized in This Study

| polymer                  | Td (°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 (Teq) 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 (To) and the rapid hydrate formation temperature (Tf) can be observed. Tf 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 Tf has occurred. To 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-vinylcaprolactam (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 KHI.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 1H 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 Mn 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](https://dx.doi.org/10.1021/acs.energyfuels.0c00929)
very active KHI monomer forming a copolymer will usually increase the cloud point. 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. 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).

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

| copolymer        | solvent synergest | polymer concentration (ppm) | $T_o$ (°C) | $T_a$ (°C) |
|------------------|-------------------|----------------------------|------------|------------|
| no additive      |                   | 2500                       | 17.2       | 16.6       |
| PVCap            | 2500              | 4-MePeOl                   | 10.4       | 8.9        |
| PVP K-15         | 2500              | iBGE                       | 8.9        | 7.5        |
| PVIMA            | 2500              | iBGE                       | 8.9        | 7.5        |
| 2-MACap:VP (1:1) | iBGE              | 2500                       | 12.2       | 10.0       |
|                  | iBGE              | 5000                       | 8.9        | 7.5        |
| 2-MACap:VIMA (1:1)| iBGE              | 2500                       | 11.2       | 10.0       |
|                  | iBGE              | 5000                       | 5.4        | 4.6        |
| 2-MACap:VIMA (1:2)| iBGE              | 2500                       | 10.9       | 10.1       |
|                  | iBGE              | 5000                       | 7.6        | 7.2        |
| 2-MACap:VIMA (2:1)| iBGE              | 2500                       | 11.0       | 10.5       |
| 2-MACap:MOlMA (1:1)| iBGE             | 2500                       | 14.7       | 14.5       |
| 2-MACap:MMA (1:1)| iBGE              | 2500                       | 8.8        | 8.1        |
|                  | iBGE              | 5000                       | 6.4        | 5.7        |
| 2-MACap:VIMA (1:2)| iBGE              | 2500                       | 10.9       | 10.1       |
|                  | iBGE              | 5000                       | 7.6        | 7.2        |
| 2-MACap:VIMA (2:1)| iBGE              | 2500                       | 11.0       | 10.5       |
| 2-MACap:MOlMA (1:1)| iBGE             | 2500                       | 14.7       | 14.5       |
| 2-MACap:MMA (1:1)| iBGE              | 2500                       | 8.8        | 8.1        |
|                  | iBGE              | 5000                       | 6.4        | 5.7        |

$^a$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.
$T_s$ value, since the $T_s$ values are not easy to get meaningful comparative data from, unless the $T_s$ 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 ($M_n = 10\,000\,\text{g/mol}$),\textsuperscript{41} PVP K-15 ($M_n = 8000\,\text{g/mol}$),\textsuperscript{42} and PVIMA ($M_n = 12\,401\,\text{g/mol}$)\textsuperscript{33} 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 copolymerization units. Hydrogen bonding can also be observed: between 2-MACap units, between macromolecular 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 $T_n$ and $T_s$ 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 $T_n$ and $T_s$ 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 $T_n$ 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 $T_n$ value was 8.8 °C and the $T_s$ 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 with results for VIMA:VCap copolymers, where it was shown that a 1:1 copolymer had the best KHI performance.\textsuperscript{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.\textsuperscript{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 $T_n$ 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 ppm 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...
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.50 For example, we have shown previously that isobutyl glycol ether (iBGE) had a strong good synergistic effect on PVCap and PNIPMAM. Further, 4-methyl-1-pentanol (4-MePeOl) had a very strong synergistic effect on PVCap.47,48 Therefore, we were interested to see the possible synergistic 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 synergistic 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:MOIMA (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.

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Notes
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