

# High Cloud Point Polyvinylaminals as Non-Amide-Based Kinetic Gas Hydrate Inhibitors

Malcolm A. Kelland,\* Erik Gisle Dirdal, and Qian Zhang



Cite This: *Energy Fuels* 2020, 34, 8301–8307



Read Online

ACCESS |

Metrics & More

Article Recommendations

**ABSTRACT:** In recent years, we have explored non-amide-based classes of kinetic hydrate inhibitor (KHI) polymers to determine if the same level of performance can be achieved as commercial KHI polymers, which all contain amide groups. Here, we have investigated a series of polyvinylaminals as KHIs for the first time. These polymers with pendant alkyl or cycloalkyl groups of varying sizes and shapes were synthesized in a simple one-step procedure from polyvinylamine. Their performance as tetrahydrofuran (THF) hydrate crystal growth inhibitors and as high-pressure KHIs was studied with a structure II-forming natural gas mixture in both sapphire and steel rocking cells. A structure–performance analysis was carried out. The best KHI was obtained with a polyvinylalinal with pendant cyclohexyl groups and gave a similar performance to the well-known KHI poly(*N*-vinyl caprolactam) and without the disadvantage of a low cloud point.

## 1. INTRODUCTION

Plugging of flow lines by gas hydrates is one of the most serious production issues to consider during field development.<sup>1</sup> Various methods are available to avoid this problem, including the use of low-dosage hydrate inhibitors (LDHIs).<sup>2,3</sup> The two main subcategories of LDHIs are antiagglomerants (AAs) and kinetic hydrate inhibitors (KHIs). Both have limitations. KHIs are used to keep a flow line free from any amount of hydrate formation, whereas AAs allow hydrates to form in a controlled manner and keep them dispersed and transportable in the remaining produced fluids. The main limitation of KHIs is the subcooling limit to which they can be used. However, KHI products that can extend this limit would be very welcome as one need not worry about hydrate slurry transportation as with AAs, or melting the hydrates in the processing facilities.

The main constituents in kinetic hydrate inhibitor (KHI) formulations used in the oil and gas industries are water-soluble polymers.<sup>4–8</sup> The great majority of these are polyamides based on vinylic monomers such as *N*-vinyl lactams and *N*-alkyl(meth)acrylamides. Including hyper-branched polyester amides, these three classes represent the majority of all commercially available KHI polymers. Some non-amide-based KHIs have been investigated including poly(amine oxides), polyvinylloxazolines, and polyquaternaries, but as far as we are aware, none of them have been deployed in the field yet. Polyquaternaries based on 3-alkyl-1-vinyl-imidazolium bromide monomers have been reported but only showed good performance when used as synergists with polymers based on an *N*-vinyl caprolactam monomer or when copolymerized with this monomer (Figure 1).<sup>9</sup> 1-Vinyl imidazole and dimethylaminoethylmethacrylate bromide (DMAEMA) have also been used in KHI polymers.<sup>10–12</sup>

In this study, we investigate a new class of nonamide KHI polymer for the first time: polyvinylaminals. They have been

shown to be useful as flocculants and epoxy resin and polyurethane cross-linking agents, and are easily made in one step from commercial polyvinylamine (Figure 2).<sup>13,14</sup> The authors proposed that two amines separated by three carbon atoms (i.e., 1,3-diamines) are involved in the reaction with an aldehyde to give six-ring hexahydropyrimidine groups.<sup>15</sup> Support for this reaction comes from the reaction of 1,3-diaminopropane with alkylamines, which are known to produce hexahydropyrimidines.<sup>16,17</sup> However, if two amines separated by two carbon atoms (i.e., 1,2-diamines) react with an aldehyde, imidazolidine rings can be formed.<sup>18</sup> Polyvinylaminals were not expected to show good biodegradability due to an all-carbon backbone; therefore, this was not investigated. The focus of this study was to determine whether nonamide polymers can perform as well as the classic amide-based polymers.

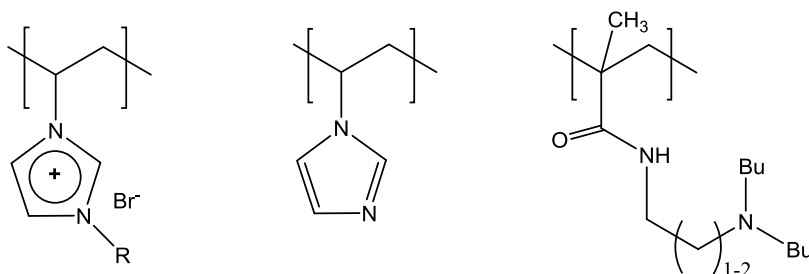
Previously, we have synthesized polyvinylamides from polyvinylamine.<sup>19</sup> However, the size of the pendant alkyl groups for the homopolymer in this class is limited to three carbon atoms (*iso*- or *n*-propyl) due to solubility problems with larger groups. Polyvinylaminals have cyclic aminal (or aminoacetal) groups with two nitrogen atoms and offer the possibility of quaternizing one or both of these atoms to produce cationic groups (Figure 3).<sup>20,21</sup> The charge on the polymer allows for larger pendant alkyl groups. This could be important as studies on other classes of LDHIs have shown that hydrophobic groups larger than propyl can give improved

Received: May 8, 2020

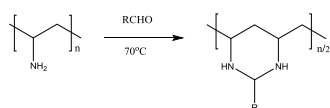
Revised: June 24, 2020

Published: June 26, 2020

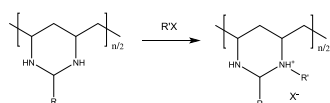




**Figure 1.** Monomer units for 3-alkyl-1-vinylimidazolium bromides, 1-vinyl imidazole (VIM), and *N*-dibutylaminoalkylmethacrylamides.



**Figure 2.** General synthesis of polyvinylaminals.



**Figure 3.** Protonation ( $R = H$ ) or alkyl quaternization of polyvinylaminals.

performance, e.g., pendant dibutylamine groups (or the quaternized versions) in dibutylaminoalkyl(meth)acrylamide-based polymers, butyl, pentyl, *iso*-hexyl, and *t*-heptyl groups in quaternary ammonium salts, and some polyamine oxides (Figure 1).<sup>9,22–26</sup>

## 2. EXPERIMENTAL METHODS

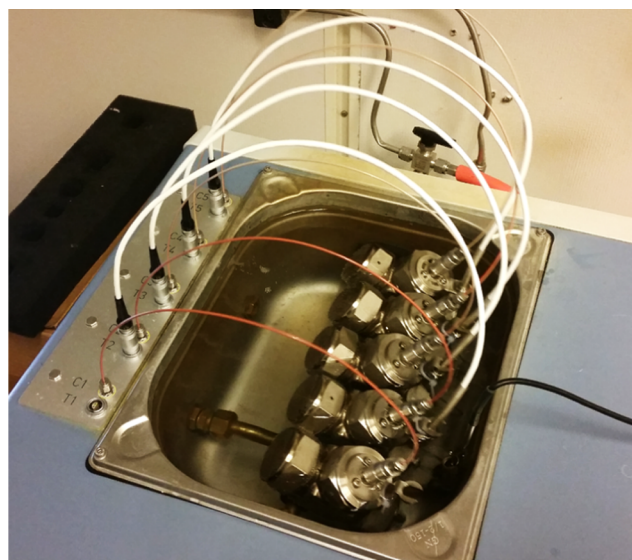
**Materials.** Solvents and commercial aldehyde products (99% pure) were used as received from the suppliers (VWR and Sigma-Aldrich), without any further purifications. 2-Propanol (>99 %) was supplied by VWR. Low-molecular-weight poly(*N*-vinylcaprolactam) (PVCap), 41.1 wt % in monoethyleneglycol, was supplied by Ashland chemical company under the tradename Luvicap EG. Poly(*N*-vinylpyrrolidone) (PVP,  $M_w = 4000$  g/mol) was supplied by BASF. Polyvinylamine was supplied as the hydrochloride salt by BASF under the tradename Lupamin 1595 ( $M_w < 10\,000$  g/mol, pH 7.5) as a 10 wt % aqueous solution. 4-Methylpentanal (*iso*-hexanal) was synthesized by a literature method via reduction of 4-methylpentanitrile with diisobutylaluminum hydride.<sup>27</sup>

**Synthesis of Polyvinylaminals.** To 2.00 g of a solution of 10 wt % polyvinylamine in water were added 0.5 or 1.0 molar equivalents of aldehyde per amine group and 1.00 g of 2-propanol. The flask was sealed and stirred at 70 °C for 18 h. A light orange-brown solution was formed in the normal case, which was used for KHI testing. In some cases with more hydrophobic aldehydes, an orange-brown layer separated from a colorless layer. When these polyvinylalmonal products were diluted with water or tetrahydrofuran (THF)/water to KHI test concentrations (2500–5000 ppm), both layers were found to be fully water soluble, with no cloud point up to 95 °C.

**Tetrahydrofuran Hydrate Crystal Growth Experimental Method.** The tetrahydrofuran (THF) hydrate crystal growth rate experiments were carried out as previously reported.<sup>28–36</sup> An outline of the procedure is as follows: THF and water were mixed in the molar ratio 1:17, and sodium chloride was added and dissolved by stirring to give a final salt concentration of 36 000 ppm (3.6 wt %). This solution (80 mL) was added to a 100 mL glass beaker and placed in a cooling bath (accuracy  $\pm 0.05$  °C) set to  $-0.5$  °C. Taking into account the added salt, this gave a theoretical subcooling for THF hydrate of about 3.4 °C. The solution was stirred every 5 min for 20 min. A hollow glass tube was filled with crushed ice (kept at  $-20$  °C) and the tip of the tube was placed vertically into the THF/salt

solution. The ice initiates nucleation of THF hydrate at the tip. The tube was removed from the solution after 1 h. The THF hydrate crystals growing only from the tube tip were quickly cut off and weighed, having first removed any liquid from the crystals with a dry absorbent cloth or tissue. This gave the rate of growth of THF crystals in grams over 1 h. The average growth rate of 5–8 experiments was recorded, in which the spread in growth rates was about 20–25%. The test requires salt because if no salt is added to the mixture, THF hydrate formation becomes too fast due to high subcooling. This makes it hard to differentiate the ranking of the crystal growth inhibition of the additives. At temperatures above 0 °C, the ice in the glass tube (which we used to initiate THF hydrate formation) melts and falls out of the tube.

**High-Pressure Rocking Cell Kinetic Hydrate Inhibitor (KHI) Performance Tests.** To determine the KHI performance ranking of the additives, we used two different types of rocking cell equipment. One equipment was a set of five high-pressure 40 mL steel rocking cells; the other equipment was a set of six high-pressure 20 mL sapphire rocking cells<sup>37,38</sup> (Figures 4 and 5). All cells contained a steel ball for extra agitation. All equipment was supplied by PSL Systemtechnik GmbH, Germany.



**Figure 4.** RCS rocker rig showing the five steel cells in a cooling bath.

The reason for using two sets of cells was due to maintenance needed on one rig, which meant that we had to move the study to the other rig. To be able to compare the results in the two rigs, we conducted tests on some polymers in both rigs and found that there was general agreement within a 95% confidence limit. We used the same synthetic natural gas mixture that forms structure II hydrate as the thermodynamic stable phase in both sets of equipment. The composition is given in Table 1. We also used our standard slow constant cooling (SCC) test method in both sets of equipment, which we have used in many previous studies, mostly in the steel cells.<sup>39</sup> We



**Figure 5.** RCS20 rocker rig showing hydrate formation in three of the six sapphire cells.

**Table 1. Composition of the Synthetic Natural Gas (SNG) Mixture Used in the KHI Experiments**

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

also used the same gas/water volume ratio, 50:50, in all tests. We have purposely kept to the same method and equipment to allow easy comparison of results from many classes of additives. The cooling rate (1 °C/h) is slower than that observed under real field conditions, but it is not our intention to determine the field KHI performance of the additives but only to provide a ranking in KHI performance. We have found that a series of tests using a slow ramping or cooling method enables better differentiation in performances than using a faster cooling method.<sup>1</sup> Di Profio<sup>40</sup> recently showed that slow ramped cooling experiments gave good reproducibility and recommended lowering the temperature by 0.5 °C every 3 h. However, KHI experiments at this rate could take several days for good additives as the subcooling would be high before hydrates would form. The cooling rate in our method is a good enough compromise to screen new additives to give a rough idea of their KHI performance potential.

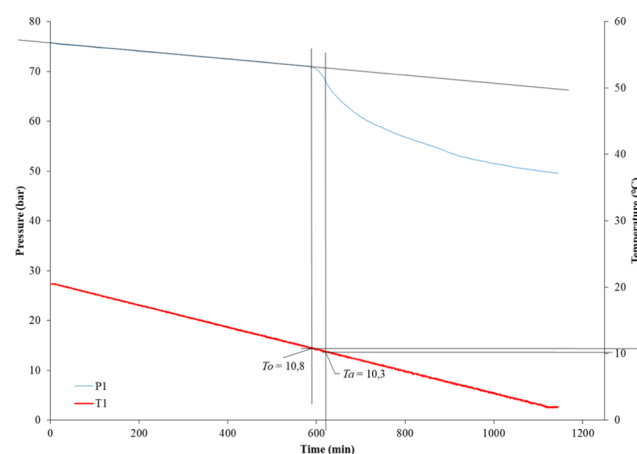
The pressure was approximately 76 bar (accuracy ± 0.1 bar) at the start of each SCC experiment. The hydrate equilibrium temperature (HET) at this pressure was determined by standard laboratory dissociation experiments at a warming rate of 0.025 °C/h for the last 3–4 °C.<sup>41,42</sup> Five repeat tests were carried out, which gave 20.2 ± 0.05 °C as the HET.<sup>39</sup> This value was found in both steel and sapphire cell rocking rigs and agrees very well with a calculated HET value of 20.5 °C at 76 bar using Calsep's PVTsim software.

The constant cooling test procedure was as follows:

- (1) Deionized water (20 mL) containing the chemicals to be tested was added to each cell. If the sample to be tested was in two layers (see the section on [Synthesis of Polyvinylaminals](#)), the sample was vigorously shaken before the correct aliquot was diluted with water to the test concentration.
- (2) Air in the cells was removed using a vacuum pump and refilled with SNG to 2 bar. The procedure was repeated twice.
- (3) The cell was pressurized to 76 bar with the SNG and rocked at 20 rocks/min at a 40° angle.

- (4) The rocked cells were cooled from 20.5 °C at a rate of 1 °C/h down to 2 °C.
- (5) The temperature and pressure for each cell, and the cooling bath temperature, were logged on a computer.

A typical graph of pressure and temperature data versus time for one of the five cells is shown in [Figure 6](#). A thorough explanation of

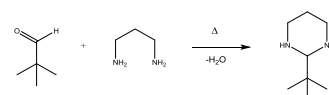


**Figure 6.** Typical pressure and temperature graphical data for a slow constant cooling rocker rig KHI experiment, showing the determination of  $T_o$  and  $T_a$ .

our interpretation of such data has been reported previously.<sup>43</sup> From this data, we determine the onset temperature ( $T_o$ ) (first detection of hydrate formation from the pressure drop) and the temperature at which fast hydrate formation is observed ( $T_a$ ). The  $T_o - T_a$  value gives an indication of the ability of the additive to slow the growth of SII gas hydrate formation but depends on the subcooling at  $T_o$ . Comparisons of  $T_o - T_a$  are only valid between tests when  $T_o$  is similar. [Figure 6](#) illustrates how we determine the  $T_o$  value (here 10.8 °C) and the  $T_a$  value (here 10.3 °C). In this study, at least six identical experiments for any one product were conducted. Due to the stochastic nature of gas hydrate formation, there is some degree of scattering in  $T_o$  and  $T_a$  values, which is never more than 20% for  $T_o$  and 15% for  $T_a$ . A more thorough investigation of the reproducibility under various test conditions in this multicell rocker rig was carried out by Lone et al.<sup>38</sup> *P*-values from statistical *t*-tests lower than 0.05 were considered as an indication of a significant difference in two sets of  $T_o$  or  $T_a$  values.<sup>44</sup>

### 3. RESULTS AND DISCUSSION

A series of polyvinylaminals was synthesized by the reaction of polyvinylamines of varying molecular weights with alkylamines. NMR spectroscopy of the polymers was inconclusive as to the formation of the aminal groups as the lines were very broad, typical for polymers. However, as further proof of the formation of the aminal group, beyond the references given in the Introduction section, we carried out the reaction of pivaldehyde with 1,3-diaminopropane and obtained 2-tert-butylhexahydropyrimidine in quantitative yield as judged by comparison of our <sup>1</sup>H and <sup>13</sup>C NMR spectroscopic analyses with the reported values ([Figure 7](#)).<sup>17</sup>



**Figure 7.** Synthesis of 2-tert-butylhexahydropyrimidine.

Table 2. THF Hydrate Crystal Growth Results<sup>a</sup>

polyvinylaminal	concn. (ppm)	pH	g/h	crystal shape
no additive		7	1.59	rhombic
		3	1.30	rhombic
tetrabutylammonium bromide	4000	7	0.45	distorted rhombic
tetrapentylammonium bromide	4000	7	0.04	very distorted
polyvinylamine, $M_w$ 10 000 g/mol	4000	7	1.81	rhombic
polyvinylaminal/ <i>n</i> -butanal	4000	6.5	0.72	rhombic
polyvinylaminal/ <i>n</i> -pentanal	2000	3	0.80	mostly rhombic
		4000	7	0.34
polyvinylaminal/ <i>n</i> -hexanal	2000	3	0.23	hexagonal plates
		3	1.25	rhombic crystals + hexagonal plates
		7	0.65	rhombic crystals + hexagonal plates
polyvinylaminal/cyclopentanecarboxaldehyde	4000	3	0.38	hexagonal plates
		7	0.58	rhombic crystals + hexagonal plates
polyvinylaminal/cyclohexanecarboxaldehyde	4000	7	0.39	hexagonal plates
		3	0.33	hexagonal plates

<sup>a</sup>Average of minimum six tests per chemical.

### THF Hydrate Crystal Growth-Inhibition Experiments.

Due to the possibility of quaternization of the amine groups, we reasoned that the polyvinylaminals may be good hydrate crystal growth inhibitors like some of the tetraalkylammonium salts.<sup>28,45</sup> THF hydrate is an easy medium on which to test the crystal growth-inhibition ability at atmospheric pressure. It was originally used by Shell energy company to determine the optimum quaternary ammonium groups for surfactant antiagglomerants (AAs).<sup>46,47</sup> A summary of the THF hydrate crystal growth inhibition experiments is given in Table 2. The use of no additive gave an average growth rate of 1.75 g/h, forming a cluster of regular rhombic pyramidal crystals at the end of the tube. The pH of this solution was about 7, but since we were investigating protonated polyvinylaminals, we also carried out tests at pH 3. The growth of THF hydrate crystals was still high but a little less than that at pH 7. Presumably, a higher concentration of hydronium ions ( $H_3O^+$ ) and larger protonated water clusters found in the acidic solution slow the hydrate growth rate, possibly also by protonating the water molecules at the THF hydrate crystal surface. Under the same conditions, PVCap at 4000 ppm gives no THF hydrate growth at all.<sup>36</sup>

For the polyvinylaminals at pH 7, some gave similar performance to tetrabutylammonium bromide (TBAB) but none of them performed as well as tetrapentylammonium bromide (TPAB), which is one of the best quaternary ammonium salt THF hydrate growth inhibitors.<sup>28,46</sup> The best results were obtained with the *n*-pentanal and cyclohexanecarboxyaldehyde derivatives. As far as we know, cyclopentyl and cyclohexyl groups in nonpolymeric quaternary ammonium salts have not been investigated as hydrate growth inhibitors. Some of the polyvinylaminals were also tested at pH 3 and most gave a small but not dramatic improvement in performance. Presumably, protonation of some of the amine groups to give quaternary ammonium groups is only a minor advantage for hydrate growth inhibition with this class of polymers.

Often, both rhombic crystals (with no additive) as well as hexagonal plates showing preferential crystal facial inhibition were obtained. In general, as the concentration increased with the best inhibitors, we observed more and thinner hexagonal plates. An example of hexagonal plates is shown in Figure 8 for the cyclohexanecarboxyaldehyde derivative at pH 3. Aqueous



Figure 8. Hexagonal THF hydrate plates from a test with 4000 ppm of polyvinylaminal/*n*-hexanal at pH 3.

solutions of this polymer at 4000 ppm polymer were a little cloudy at pH 7, but solubility increases at pH 3, again indicating quaternization of at least some of the polymer amine groups.

**High-Pressure Slow Constant Cooling Gas Hydrate KHI Experiments.** The high-pressure KHI test results are summarized in Table 3. As explained earlier, we conducted tests in both steel and sapphire rocking cells. The results in this table for PVP 15K ( $M_w$  8000 g/mol) and PVCap ( $M_w$  10000 g/mol), with similar molecular weights to the polyvinylaminals, are taken from previous work.<sup>48–50</sup> In general, there was good agreement for the polymers tested in both sets of equipment. The variation in the  $T_o$  values in our rocking cell equipment has been reported many times before as about  $\pm 10$ –15% and this study was no exception.<sup>36–38</sup>

Table 3. Constant Cooling Test Results<sup>a</sup>

polyvinylaminal	test concn. (ppm)	pH	$T_o$ (°C)	$T_a$ (°C)	cell type
no additive		7.0	17.1	16.6	steel
		7.0	16.8	16.4	sapphire
PVP-K15 $M_w$ 8000 g/mol	2500	7.0	11.6	10.9	sapphire
		7.0	11.1	9.9	steel
PVCap, $M_w$ 10 000 g/mol	2500	7.0	9.6	9.2	steel
			9.9	8.9	sapphire
polyvinylamine, $M_w$ 10 000 g/mol	2500		16.9	16.8	sapphire
polyvinylaminal/butanal	2500	6.5	15.1	15.0	sapphire
polyvinylaminal/ <i>iso</i> -pentanal (3-methylbutanal)	2500	6.5	11.6	11.2	steel
			11.8	11.5	sapphire
	5000	6.5	10.0	9.7	sapphire
polyvinylaminal/pivaldehyde (2,2-dimethylpropanal)	2500	6.5	15.2	15.1	sapphire
polyvinylaminal/ <i>n</i> -pentanal	2500	6.5	11.8	11.7	sapphire
		2.9	11.5	11.4	sapphire
polyvinylaminal/ <i>n</i> -hexanal	2500	6.5	11.9	11.8	sapphire
polyvinylaminal/ <i>iso</i> -hexanal (4-methylpentanal) in <i>i</i> PrOH (8 tests)	2500	6.5	10.3	10.0	steel
polyvinylaminal/cyclopentanecarboxaldehyde	2500	6.5	11.6	11.5	sapphire
polyvinylaminal/cyclohexanecarboxaldehyde	2500	6.5	9.8	9.4	steel
			10.4	10.2	sapphire
		3.1	11.2	10.8	sapphire
	5000	6.5	7.0	6.5	steel
			7.6	7.1	sapphire

<sup>a</sup>Average of six tests. All samples were made with polyvinylamine ( $M_w$  10 000 g/mol) in  $H_2O$ /*i*PrOH unless otherwise stated.

Polyvinylamine ( $M_w$  10 000 g/mol), the starting material for making the polyvinylaminals, showed no KHI effect as was expected for a very hydrophilic polymer with no pendant hydrophobic groups. As many previous studies have shown, an effective KHI polymer requires pendant hydrophobic groups of a certain size (preferably containing three to six carbon atoms) and neighboring hydrophilic groups to maintain water solubility.<sup>51</sup> All commercial KHI polymers have these structural properties.

All of the polyvinylaminals derived from polyvinylamine showed some KHI activity, which increased with the size of the pendant alkyl or cycloalkyl groups as long as water solubility was not lost. Thus, the butanal ( $R = n$ -propyl in Figure 2) and pivaldehyde ( $R = t$ -butyl in Figure 2) polyvinylaminals gave the poorest KHI performance, with average  $T_o$  values of 15.0 and 15.1 °C, respectively. Branching the end of the butanal derivative using 3-methylbutanal (*iso*-pentanal) gave a more hydrophobic group and better kinetic inhibition efficacy. The average  $T_o$  value dropped to 11.6 °C in the steel rocking cells and 11.8 °C in the sapphire cells. The same trend was seen for polymers made using pentanal and 4-methylpentanal (*iso*-hexanal), with the latter giving the lowest average  $T_o$  values of the polymers with acyclic groups. We believe that the reason for these observations is that the alkyl branching gives an end group that gives a better van der Waals interaction with open hydrate cavities than the straight-chain alkyl group, which has been seen in previous studies.<sup>28,50</sup> These cavities can be formed on the hydrate particle surface, causing growth inhibition, or a hydrate cavity could be created around the alkyl group by free water molecules, leading to nucleation inhibition. Either way, this leads to better kinetic inhibition.

Another class of hydrocarbyl fragments with good van der Waals interactions either with hydrate cavities or creating cavities in the water solution are cycloalkyl groups. We know that cyclopentane forms structure II hydrates, as can cyclohexane with the help of a gas like methane.<sup>52</sup> Therefore,

we also investigated two polymers with cycloalkyl groups made by reacting the base polyvinylamine with cyclopentanecarboxaldehyde or cyclohexanecarboxaldehyde. The five-ring polyvinylaminal gave a similar performance to the pentanal derivative, but the six-ring polyvinylaminal with pendant cyclohexyl groups gave the best performance of all of the new polymers tested. At 2500 ppm and pH 6.5 (initial pH before pressurizing the cells), the average  $T_o$  values were 9.8 °C in the steel rocking cells and 10.4 °C in the sapphire rocking cells. There was no statistically significant difference between these results. The actual pH under pressure during the test was probably a little lower due to the dissolution of the acid gas  $CO_2$ . When the solution was adjusted to pH 3.1 (by addition of aq. HCl) and retested in the sapphire cells, the average  $T_o$  value increased to 11.2 °C, which was significant ( $p = 0.03$  in the *t*-test). We speculate that the slightly poorer performance might be attributed to increased protonation of the amine groups at the lower pH, making the polymer less hydrophobic. Previous results from our group suggest that increased hydrophobicity with hydrocarbyl groups of the correct size and shape can improve KHI performance as long as water solubility is not lost.<sup>51</sup> When the cyclohexanecarboxaldehyde polyvinylaminal derivative was tested at 5000 ppm and pH 6.5, the average  $T_o$  values decreased significantly to 7.0 °C (steel cells) and 7.6 °C (sapphire cells). An increase in performance with an increase in concentration for KHI polymers is a typical occurrence.<sup>23,44,53</sup>

There are some previous studies on KHIs showing the usefulness of the cyclohexyl group. For example, the best KHI performance for a series of poly(ethylene citramide)s was found for the polymer with pendant cyclohexyl groups.<sup>53</sup> Related polytartramides also perform well with cyclohexyl groups.<sup>54</sup> The six-ring cyclohexyl group is also present in hyperbranched poly(ester amide) KHIs.<sup>55</sup> However, only four carbon atoms in the ring are available for hydrophobic interactions as the polymer is made using hexahydrophthalic

anhydrides. Cyclohexyl groups are also useful in solvent synergists for *N*-vinyl caprolactam or isopropylmethacrylamide polymers.<sup>56</sup>

## CONCLUSIONS

A series of water-soluble polyvinylaminals with pendant alkyl and cycloalkyl groups were prepared. Under acidic conditions, the amines can be protonated to give quaternary groups. The best polyvinylaminals functioned as THF hydrate crystal growth inhibitors, but not as powerfully as poly(*N*-vinylcaprolactam) (PVCap). The best results were observed for the pentanal and cyclohexanecarboxyaldehyde derivatives. In gas hydrate experiments with a gas that preferentially forms structure II hydrate, several polyvinylaminals gave good KHI performance. Branching of the end of the pendant alkyl groups improved the inhibition performance. As with the THF hydrate tests, the polyvinylalinal with pendant cyclohexyl groups gave good results, but now, the performance was similar to PVCap. The contrasting results of these polymers on the two clathrate hydrate systems indicate that nucleation inhibition is probably also taking place in the gas hydrate system with the polyvinylalinal derivative for this polymer to surpass the performance of PVCap.

## AUTHOR INFORMATION

### Corresponding Author

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

### Authors

Erik Gisle 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

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

Complete contact information is available at:  
<https://pubs.acs.org/10.1021/acs.energyfuels.0c01473>

### Notes

The authors declare no competing financial interest.

## ACKNOWLEDGMENTS

We thank Ayesha Akhtar for some of the preliminary THF hydrate work in this study.

## REFERENCES

- (1) Sloan, E. D., Jr.; Koh, C. A. *Clathrate Hydrates of Natural Gases*, 3rd ed.; CRC Press, Taylor & Francis Group: Boca Raton, FL, 2008.
- (2) Kelland, M. A. *Production Chemicals for the Oil and Gas Industry*; CRC Press, Taylor & Francis Group: Boca Raton, Florida, 2009.
- (3) Kelland, M. A. History of the development of low dosage hydrate inhibitors. *Energy Fuels* **2006**, *20*, 825.
- (4) Kelland, M. A. A Review of Kinetic Hydrate Inhibitors—Tailor-Made Water-Soluble Polymers for Oil and Gas Industry Applications. In *Advances in Materials Science Research*; Wytherst, M. C., Ed.; Nova Science Publishers Inc.: New York, 2011; Chapter 5, Vol. 8.

- (5) Perrin, A.; Musa, O. M.; Steed, J. W. The chemistry of low dosage clathrate hydrate inhibitors. *Chem. Soc. Rev.* **2013**, *42*, 1996–2015.

- (6) Kamal, M. S.; Hussein, I. A.; Sultan, A. S.; von Solms, N. Application of various water soluble polymers in gas hydrate inhibition. *Renewable Sustainable Energy Rev.* **2016**, *60*, 206–225.

- (7) Zhukov, A. Y.; Stolov, M. A.; Varfolomeev, M. A. Use of Kinetic Inhibitors of Gas Hydrate Formation in Oil and Gas Production Processes: Current State and Prospects of Development. *Chem. Technol. Fuels Oils* **2017**, *53*, 377–381.

- (8) Shahnazar, S.; Bagheri, S.; TermehYousefi, A.; Mehrmashhadi, J.; Karim, M. S. A.; Kadri, N. A. Structure, mechanism, and performance evaluation of natural gas hydrate kinetic inhibitors. *Rev. Inorg. Chem.* **2018**, *38*, 1–19.

- (9) Nakarit, C.; Kelland, M. A.; Liu, D.; Chen, E. Y.-X. Cationic kinetic hydrate inhibitors and the effect on performance of incorporating cationic monomers into *N*-vinyl lactam copolymers. *Chem. Eng. Sci.* **2013**, *102*, 424–431.

- (10) Sheng, Q.; da Silveira, K. C.; Tian, W.; Fong, C.; Maeda, N.; Gubner, R.; Wood, C. D. Simultaneous Hydrate and Corrosion Inhibition with Modified Poly(vinyl caprolactam) Polymers. *Energy Fuels* **2017**, *31*, 6724–6731.

- (11) Park, J.; Kim, H.; Sheng, Q.; Wood, C. D.; Seo, Y. Kinetic Hydrate Inhibition Performance of Poly(vinyl caprolactam) Modified with Corrosion Inhibitor Groups. *Energy Fuels* **2017**, *31*, 9363–9373.

- (12) Spencer, H. J.; Virdee, R.; Squicciarini, M. P.; Rivers, G. T.; Lehmann, M. N. Low Dosage Kinetic Hydrate Inhibitors for Natural Gas Production Systems. U.S. Patent US9,145,4652015.

- (13) Badesso, R. J.; Pinschmidt, R. K.; Sagl, D. Polyvinylamine at last. *J. Proc. Am. Chem. Soc. Div. Polym. Mat. Sci. Eng.* **1993**, *69*, 251–252.

- (14) Pinschmidt, R. K. Polyvinylamine at last. *J. Polym. Sci., Part A: Polym. Chem.* **2010**, *48*, 2257–2283.

- (15) Titherley, A. W.; Branch, G. E. K. XLI.—Hexahydropyrimidine and its benzoyl derivatives. *J. Chem. Soc. Trans.* **1913**, *103*, 330–340.

- (16) Evans, R. F. Hydroypyrimidines. V. Hexahydropyrimidines. The Reaction of Aldehydes and Ketones with 1,3-Diaminopropanes. *Aust. J. Chem.* **1967**, *20*, 1643–1661.

- (17) Zelenin, K. N.; Alekseyev, V. V.; Ukraintsev, I. V.; Tselinsky, I. V. 2-Substituted hexahydropyrimidines and their tautomerism. *Org. Prep. Proced. Int.* **1998**, *30*, 53–61.

- (18) Riebsomer, J. L. A Study of the Reaction Products of 1,2-Diamines with Aldehydes. *J. Org. Chem.* **1950**, *152*, 237–240.

- (19) Chua, P. C.; Kelland, M. A.; Ajiro, H.; Sugihara, F.; Akashi, M. Poly(vinylalkanamide)s as Kinetic Hydrate Inhibitors: Comparison of Poly(*N*-vinylisobutyramide) with Poly(*N*-isopropylacrylamide). *Energy Fuels* **2013**, *27*, 183–188.

- (20) Pinschmidt, R. K., Jr.; Lai, T.-W. Amine Functional Polymers Containing Acetal Groups. U.S. Patent US5,086,1111992.

- (21) McAndrew, T. P.; Nordquist, A. F.; Pinschmidt, R. K., Jr.; Eichelberger, D. P. Amine Functional Polymers as Thickening agents. U.S. Patent US5,270,3791992.

- (22) Conrad, P. G.; Acosta, E. J.; McNamee, K. P.; Bennett, B.; Lindeman, O. E. S.; Carlise, J. R. Method of Controlling Gas Hydrates in Fluid Systems. U.S. Patent US9,550,9352017.

- (23) Magnusson, C. D.; Kelland, M. A. Nonpolymeric Kinetic Hydrate Inhibitors: Alkylated Ethyleneamine Oxides. *Energy Fuels* **2015**, *29*, 6347–6354.

- (24) Kelland, M. A.; Magnusson, C.; Lin, H.; Abrahamsen, E.; Mady, M. F. Acylamide and Amine Oxide Derivatives of Linear and Hyperbranched Polyethyleneimine. Part 2: Comparison of Gas Kinetic Hydrate Inhibition Performance. *Energy Fuels* **2016**, *30*, 5665–5671.

- (25) Kelland, M. A.; Moi, N.; Howarth, M. Breakthrough in Synergists for Kinetic Hydrate Inhibitor Polymers, Hexaalkylguanidinium Salts: Tetrahydrofuran Hydrate Crystal Growth Inhibition and Synergism with Polyvinylcaprolactam. *Energy Fuels* **2013**, *27*, 711–716.

- (26) Bartels, J. W.; Jones, R. A.; Servesko, J. M. Kinetic Hydrate Inhibitors for Controlling Gas Hydrate Formation in Wet Gas Systems. International Patent Application, WO20190366712019.
- (27) Clemens, J. J.; Abela, A. R.; Anderson, C. D.; Busch, B. B.; Chen, W. G.; Cleveland, T.; Coon, T. R.; Frieman, B.; Ghirmai, S. G.; Grootenhuis, P.; Gulevich, A. V.; Hadida Ruah, S. S.; Hsia, C. K.-J.; Kang, P.; Khatuya, H.; McCartney, J.; Miller, M. T.; Paraselli, P.; Fabrice; Swift, S. E.; Termin, A.; Uy, J.; Vogel, C. V.; Zhou, J. Modulators of Cystic Fibrosis Transmembrane Conductance Regulator, Pharmaceutical Compositions, Methods of Treatment, and Process for Making the Modulators. U.S. Patent US20,190,248,8092019.
- (28) Chua, P. C.; Kelland, M. A. Tetra(iso-hexyl)ammonium Bromide; The most powerful quaternary ammonium-based tetrahydrofuran crystal growth inhibitor and synergist with polyvinylcaprolactam kinetic gas hydrate inhibitor. *Energy Fuels* **2012**, *26*, 1160.
- (29) Anselme, M. J.; Muijs, H. M.; Klomp, U. C. Method for Inhibiting the Plugging of Conduits by Gas Hydrates. International Patent Application, WO93/257981993.
- (30) Larsen, R.; Knight, C. A.; Sloan, E. D. Clathrate hydrate growth and inhibition. *Fluid Phase Equilib.* **1998**, *150–151*, 353–360.
- (31) Makogon, T. Y.; Larsen, R.; Knight, C. A.; Sloan, E. D., Jr. Melt growth of tetrahydrofuran clathrate hydrate and its inhibition: method and first results. *J. Cryst. Growth* **1997**, *179*, 258.
- (32) Del Villano, L.; Kelland, M. A. An investigation into the kinetic hydrate inhibitor properties of two imidazolium-based ionic liquids on Structure II gas hydrate. *Chem. Eng. Sci.* **2010**, *65*, 5366.
- (33) Norland, A. K.; Kelland, M. A. Crystal growth inhibition of tetrahydrofuran hydrate with bis- and polyquaternary ammonium salts. *Chem. Eng. Sci.* **2012**, *69*, 483–489.
- (34) Del Villano, L.; Kelland, M. A. Tetrahydrofuran hydrate crystal growth inhibition by hyperbranched poly(ester amide)s. *Chem. Eng. Sci.* **2009**, *64*, 3197–3200.
- (35) Del Villano, L.; Kommedal, R.; Fijten, M. W. M.; Schubert, U. S.; Hoogenboom, R.; Kelland, M. A. A study of the kinetic hydrate inhibitor performance and seawater biodegradability of a series of poly(alkyloxazoline)s. *Energy Fuels* **2009**, *23*, 3665.
- (36) O'Reilly, R.; Leong, N. S.; Chua, P. C.; Kelland, M. A. Crystal growth inhibition of tetrahydrofuran hydrate with poly(N-vinyl piperidone) and other poly(N-vinyl lactam) homopolymers. *Chem. Eng. Sci.* **2011**, *66*, 6555–6560.
- (37) Chua, P. C.; Kelland, M. A. Study of the Gas Hydrate Anti-agglomerant Performance of a Series of n-Alkyl-tri(n-butyl)-ammonium Bromides. *Energy Fuels* **2013**, *27*, 1285–1292.
- (38) Lone, A.; Kelland, M. A. Exploring Kinetic Hydrate Inhibitor Test Methods and Conditions Using a Multicell Steel Rocker Rig. *Energy Fuels* **2013**, *27*, 2536–2547.
- (39) Chua, P. C.; Kelland, M. A. Poly(N-vinyl azacyclooctanone): A More Powerful Structure II Kinetic Hydrate Inhibitor than Poly(N-vinylcaprolactam). *Energy Fuels* **2012**, *26*, 4481–4485.
- (40) Canale, V.; Fontana, A.; Siani, G.; Di Profio, P. Hydrate Induction Time With Temperature Steps: A Less Stochastic Procedure For The Determination Of Kinetic Parameters. *Energy Fuels* **2019**, *33*, 6113–6118.
- (41) Gjertsen, L. H.; Fadnes, F. H. Measurements and predictions of hydrate equilibrium conditions, Gas Hydrates: Challenges for the future. *Ann. N. Y. Acad. Sci.* **2006**, *912*, 722–734.
- (42) Tohidi, B.; Burgass, R. W.; Danesh, A.; Ostergaard, K. K.; Todd, A. C. Improving the Accuracy of Gas Hydrate Dissociation Point Measurements. *Ann. N. Y. Acad. Sci.* **2006**, *912*, 924–931.
- (43) O'Reilly, R.; Leong, N. S.; Chua, P. C.; Kelland, M. A. Missing poly(n-vinyl lactam) kinetic hydrate inhibitor: high-pressure kinetic hydrate inhibition of structure II gas hydrates with poly(N-vinyl piperidone) and other poly(N-vinyl lactam) homopolymers. *Energy Fuels* **2011**, *25*, 4595–4599.
- (44) Myers, R. H.; Myers, S. L.; Walpole, R. E.; Ye, K. *Probability & Statistics for Engineers & Scientists*; Pearson Education Int.: New Jersey, U.S.A., 2007.
- (45) Mady, M. F.; Kelland, M. A. Tris(tert-heptyl)-N-alkyl-1-ammoniumbromides -Powerful THF hydrate crystal growth inhibitors and their synergism with poly-vinylcaprolactam kinetic gas hydrate inhibitor. *Chem. Eng. Sci.* **2016**, *144*, 275.
- (46) Klomp, U. C.; Kruka, V. C.; Reijndhart, R. International Patent Application, WO95/175791995.
- (47) Klomp, U. C.; Reijndhart, R. Method for Inhibiting the Plugging of Conduits by Gas Hydrates. International Patent Application, WO96/341771996.
- (48) Magnusson, C.; Abrahamsen, E.; Kelland, M. A.; Cely, A.; Kinnari, K.; Li, X.; Askvik, K. M. As Green As It Gets: An Abundant Kinetic Hydrate Inhibitor from Nature. *Energy Fuels* **2018**, *32*, 5772–5778.
- (49) Abrahamsen, E.; Kelland, M. A. Comparison of Kinetic Hydrate Inhibitor Performance on Structure I and Structure II Hydrate-Forming Gases for a Range of Polymer Classes. *Energy Fuels* **2018**, *32*, 342–351.
- (50) Kelland, M. A.; Dirdal, E. G.; Ree, L. H. S. Solvent Synergists for Improved Kinetic Hydrate Inhibitor Performance of Poly(N-vinylcaprolactam). *Energy Fuels* **2020**, *34*, 1653–1663.
- (51) Dirdal, E. G.; Kelland, M. A. Does the Cloud Point Temperature of a Polymer Correlate with Its Kinetic Hydrate Inhibitor Performance? *Energy Fuels* **2019**, *33*, 7127–7137.
- (52) Sun, Z.-G.; Fan, S.-S.; Guo, K.-H.; Shi, L.; Guo, Y.-K.; Wang, R.-Z. Gas Hydrate Phase Equilibrium Data of Cyclohexane and Cyclopentane. *J. Chem. Eng. Data* **2002**, *47*, 313–315.
- (53) Reyes, F. T.; Kelland, M. A.; Sun, L.; Dong, J. Kinetic Hydrate Inhibitors: Structure–Activity Relationship Studies on a Series of Branched Poly(ethylene citramide)s with Varying Lipophilic Groups. *Energy Fuels* **2015**, *29*, 4774–4782.
- (54) Li, D.; Ma, S.; Laroui, A.; Zhang, Y.; Wang, J.; Lu, P.; Dong, J. Controlling water dynamics for kinetic inhibition of clathrate hydrate. *Fuel* **2020**, *271*, No. 117588.
- (55) Klomp, U. C. Method for Inhibiting the Plugging of Conduits by Gas Hydrates. US Patent US6,905,6052005.
- (56) Ree, L. H. S.; Kelland, M. A. Investigation of Solvent Synergists for Improved Kinetic Hydrate Inhibitor Performance of Poly(N-isopropyl methacrylamide). *Energy Fuels* **2019**, *33*, 8231–8240.