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

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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 polyvinylaminal 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. Various methods are available to avoid this problem, including the use of low-dosage hydrate inhibitors (LDHIs). The two main subcategories of LDHIs are antiagglomeration (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. The great majority of these are polyanilides based on vinylic monomers such as N-vinyl lactams and N-alkyl(meth)acrylamides. Including hyperbranched 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), polyvinyloxazolines, 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-imidazolidine 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). 1-Vinyl imidazole and dimethylaminomethylacrylate bromide (DMAEMA) have also been used in KHI polymers.

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). 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. Support for this reaction comes from the reaction of 1,3-diaminopropane with alkylamines, which are known to produce hexahydropyrimidines. However, if two amines separated by two carbon atoms (i.e., 1,2-diamines) react with an aldehyde, imidazolidine rings can be formed. 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. 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 aminocetal) groups with two nitrogen atoms and offer the possibility of quaternizing one or both of these atoms to produce cationic groups (Figure 3). 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
A chemical company under the tradename Luvicap EG. Poly-(PVCap), 41.1 wt % in monoethyleneglycol, was supplied by Ashland vinylpyrrolidone (PVP, in a cooling bath (accuracy ±0.05 °C) set to -0.5 °C. Taking into account the added salt, this gave a theoretical subcooling for 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.

**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, MW = 4000 g/mol) was supplied by BASF. Polyvinylamine was supplied as the hydrochloride salt by BASF under the tradename Lupamin 1595 (MW < 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-methylpentanal with diso-butylaluminum hydride.27

**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 polyvinylaminal 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.28–30 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 ±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 (Figures 4 and 5). All cells contained a steel ball for extra agitation. All equipment was supplied by PSL Systemtechnik GmbH, Germany.

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.31 We

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**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 quaternionization of polyvinylaminals.

**Figure 4.** RC5 rocker rig showing the five steel cells in a cooling bath.
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. Di Profo 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. Five repeat tests were carried out, which gave 20.2 ± 0.05 °C as the HET. This value was found in both steel and sapphire cell rocking rigs and agrees very well with a calculated HET of 20.5 ± 0.5 °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 our interpretation of such data has been reported previously. 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 ($T_{fs}$). The $T_o-T_{fs}$ 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 $T_o-T_{fs}$ 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 $T_{fs}$ 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 $T_{fs}$ values, which is never more than 20% for $T_o$ and 15% for $T_{fs}$. A more thorough investigation of the reproducibility under various test conditions in this multicell rocker rig was carried out by Lone et al. $P$-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 $T_{fs}$ values.

### 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 $^1$H and $^{13}$C NMR spectroscopic analyses with the reported values (Figure 7).

![Figure 5. RCS20 rocker rig showing hydrate formation in three of the six sapphire cells.](image)

![Figure 6. Typical pressure and temperature graphical data for a slow constant cooling rocker rig KHI experiment, showing the determination of $T_o$ and $T_{fs}$](image)

![Figure 7. Synthesis of 2-tert-butylhexahydropyrimidine.](image)
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.28,45 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).46,47 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 (H₃O⁺) 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.36

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.28,46 The best results were obtained with the n-pentanal and cyclohexanecarboxaldehyde 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 cyclohexanecarboxaldehyde derivative at pH 3. Aqueous 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 (Mₚ 8000 g/mol) and PVCap (Mₚ 10000 g/mol), with similar molecular weights to the polyvinylaminals, are taken from previous work.48−50 In general, there was good agreement for the polymers tested in both sets of equipment. The variation in the Tₒ values in our rocking cell equipment has been reported many times before as about ±10−15% and this study was no exception.36−38

### Table 2. THF Hydrate Crystal Growth Results

| 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, Mₚ 10 000 g/mol        | 4000         | 7   | 1.81    | rhombic              |
| polyvinylaminol/n-butanal              | 4000         | 6.5 | 0.72    | rhombic              |
| polyvinylaminol/n-pentanal             | 2000         | 3   | 0.80    | mostly rhombic       |
|                                        | 4000         | 7   | 0.34    | hexagonal plates     |
|                                        |              | 3   | 0.23    | hexagonal plates     |
| polyvinylaminol/n-hexanal              | 2000         | 3   | 1.25    | rhombic crystals + hexagonal plates |
|                                        | 4000         | 7   | 0.65    | rhombic crystals + hexagonal plates |
|                                        |              | 3   | 0.38    | hexagonal plates     |
| polyvinylaminol/cyclopentanecarboxaldehyde | 4000     | 7   | 0.58    | rhombic crystals + hexagonal plates |
| polyvinylaminol/cyclohexanecarboxaldehyde | 4000   | 7   | 0.39    | hexagonal plates     |
|                                        |              | 3   | 0.33    | hexagonal plates     |

*a Average of minimum six tests per chemical.

Figure 8. Hexagonal THF hydrate plates from a test with 4000 ppm of polyvinylaminol/n-hexanal at pH 3.
Table 3. Constant Cooling Test Results

| polyvinylaminal                              | test concn. (ppm) | pH  | T°c (°C) | T°n (°C) | cell type |
|----------------------------------------------|-------------------|-----|----------|----------|-----------|
| no additive                                  | 7.0               | 17.1| 16.6     |          | steel     |
| PVP:K15 Mw 8000 g/mol                       | 7.0               | 16.8| 16.4     |          | sapphire  |
| PVCap, Mw 10 000 g/mol                      | 7.0               | 11.6| 10.9     |          | sapphire  |
| PVCap, Mw 10 000 g/mol                      | 7.0               | 11.1| 9.9      |          | steel     |
| polyvinylamine, Mw 10 000 g/mol             | 2500              | 7.0 | 9.6      | 9.2      | steel     |
| polyvinylaminal/butanal                     | 2500              | 6.5 | 15.1     | 15.0     | sapphire  |
| polyvinylaminal/isoo-pentanal (3-methylbutanal) | 2500       | 6.5 | 11.6     | 11.2     | steel     |
| polyvinylaminal/isoo-pentanal (4-methylpentanal) in iPrOH (8 tests) | 2500       | 6.5 | 11.8     | 11.5     | sapphire  |
| polyvinylaminal/isoo-hexanal                | 5000              | 6.5 | 10.0     | 9.7      | sapphire  |
| polyvinylaminal/isoo-hexanal (4-methylpentanal) | 2500       | 6.5 | 15.2     | 15.1     | sapphire  |
| polyvinylaminal/cyclopentancarboxaldehyde   | 2500              | 6.5 | 11.8     | 11.7     | sapphire  |
| polyvinylaminal/cyclohexanecarboxaldehyde   | 2500              | 6.5 | 9.8      | 9.4      | steel     |
| polyvinylaminal/pivaldehyde (2,2-dimethylpropanal) | 2500       | 6.5 | 11.9     | 11.8     | sapphire  |
| polyvinylaminal/n-pentanal                  | 2500              | 6.5 | 11.5     | 11.4     | sapphire  |
| polyvinylaminal/n-hexanal                   | 2500              | 6.5 | 11.9     | 11.8     | sapphire  |
| polyvinylaminal/cyclohexanecarboxaldehyde   | 2500              | 6.5 | 10.3     | 10.0     | steel     |
| polyvinylaminal/cyclohexanecarboxaldehyde   | 2500              | 6.5 | 11.6     | 11.5     | sapphire  |
| polyvinylaminal/cyclohexanecarboxaldehyde   | 2500              | 6.5 | 9.8      | 9.4      | steel     |
| polyvinylaminal/cyclohexanecarboxaldehyde   | 2500              | 6.5 | 10.4     | 10.2     | sapphire  |
| iso-pentanal                                 | 5000              | 6.5 | 7.0      | 6.5      | steel     |
| iso-pentanal                                 | 5000              | 6.5 | 7.6      | 7.1      | sapphire  |

*Average of six tests. All samples were made with polyvinylamine (Mw 10 000 g/mol) in H2O/iPrOH unless otherwise stated.*

Polyvinylamine (Mw 10 000 g/mol), the starting material for making the polychlorocarboxyl groups, showed no KHI activity 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. Polychlorocarboxyls are derived from polychlorocarboxylic acids and neighboring hydrophilic groups to maintain water solubility. Polychlorocarboxyls have been seen in previous studies. 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. Therefore, we also investigated two polymers with cycloalkyl groups made by reacting the base polyvinylamine with cyclopentancarboxaldehyde 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°c values were 9.8 °C in the steel rocking cells and 10.4 °C in the sapphire rocking cells. There was not 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 CO2. When the solution was adjusted to pH 3.1 (by addition ofaq. HCl) and retested in the sapphire cells, the average T°c value increased to 11.2 °C, which was significant (p = 0.03 in the t-test). We speculate that the slightly poorer performance may 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. When the cyclohexanecarboxaldehyde polyvinylaminal derivative was tested at 3000 ppm and pH 6.5, the average T°c value 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.

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. Related polytartramides also perform well with cyclohexyl groups. The six-ring cyclohexyl group is also present in 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. Related polytartramides also perform well with cyclohexyl groups.
anhydrides. Cyclohexyl groups are also useful in solvent synergists for N-vinyl caprolactam or isopropylmethacrylamide polymers.  

**CONCLUSIONS**

A series of water-soluble polyvinylaminals with pendant alkyl and cycoalkyl 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-vinyl-caprolactam) (PVCap). The best results were observed for the pentan-1-ol and cyclohexanecarboxaldehyde 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 experiments, the polyvinylaminal 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 polyvinylaminal derivative for this polymer to surpass the performance of PVCap.

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**Notes**

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