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FIRST STUDY OF POLY(3-METHYLENE-2-PYRROLIDONE) AS A KINETIC HYDRATE INHIBITOR

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ABSTRACT

Formation of gas hydrates is a problem in the petroleum industry where the gas hydrates can cause blockage of the flowlines. Kinetic hydrate inhibitors (KHIs) are water-soluble polymers, sometimes used in combination synergistically or with non-polymeric synergists, that are used to prevent gas hydrate blockages. They have been used in the field successfully since 1995. In this paper, we present the first KHI results for the polymer, poly(3-methylene-

2-pyrrolidone) (P(3M2P)), which is structurally similar to poly(*N*-vinylpyrrolidone) (PVP), one of the first KHIs to be discovered. 3M2P polymers with different molecular weights (5500 and 2500 g/mole) and at different concentrations (2500, 5000 and 7500 ppm) were investigated for their KHI performance on SII hydrates in high-pressure rocking cells. We also investigated the synergistic effect of P(3M2P) with *n*-butyl glycol ether (BGE), a known synergist for some KHI polymers.

At the lower concentrations, P(3M2P) gives a similar performance to PVP (M_w = 8000-9000 g/mole). However, PVP outperforms both samples of P(3M2P) at 7500 ppm, with and without BGE. We suggest that the reasons for the performance level of P(3M2P) are related to greater resonance stabilization of the amide group in P(3M2P) compared to PVP. Also, the pyrrolidone ring of the PVP repeat unit has a larger hydrophobic sequence of three methylene units compared to the two methylene units in the pyrrolidone ring of P(3M2P). This relates well to previous studies where larger hydrophobic groups are preferable in KHI polymers as long as they are water-soluble at hydrate-forming temperatures.

INTRODUCTION

Gas hydrates formed from produced water and natural gas can potentially block production flowlines in the upstream petroleum industry.[1-3] Increased pressure and low temperatures are stable conditions for gas hydrate formation as long as there is free water and smaller hydrocarbons present. Typical hydrocarbons present in natural gas include methane, propane, *iso*-butane as well as carbon dioxide and hydrogen sulfide. [4-6]

Kinetic hydrate inhibitors (KHIs) are a class of low dosage hydrate inhibitor (LDHI) which have been used to mitigate against hydrate plug formation for over 2 decades.[1, 7, 8]

KHIs delay gas hydrate nucleation and/or crystal growth within the thermodynamically stable hydrate region. The mechanisms for inhibition are not fully understood, but include both nucleation and crystal growth inhibition. [9-11] All gas hydrate KHIs are oligomers or polymers with multiple active functional groups. Non-polymeric molecules can be added to the polymers to boost the performance synergistically, but alone these molecules are poor KHIs for gas hydrate inhibition. [12, 13]

One of the very first KHI polymers discovered was poly(N-vinylpyrrolidone) (PVP) (Figure 1). [14, 15] Not only was it found that this polymer delayed hydrate formation, but when the first crystals formed they did not immediately agglomerate. [16-18] However, as water conversion to hydrate progressed a plug was formed as with all KHIs when applied outside their performance window. The subcooling to which you can prevent hydrate formation for a certain time interval is generally used as a measure of the KHI performance. The subcooling to which PVP delays gas hydrate formation is fairly low compared to the best KHI polymers on the market today such as those based on N-vinylcaprolactam (VCap), N-iso-propylmethacrylamide or poly(ester amide)s. However, PVP has a high cloud and deposition point, compared to some KHI polymers, even in high salinity waters and is therefore used in some KHI formulations. [19] The cloud point temperature (T_{Cl}) is important for the production and transport of oil and gas as the production fluids are often very hot. However, will cool down if there is a shut-in of the flow lines, or as the transport lines stretch over longer distances, for example across the seabed offshore. [1, 20]
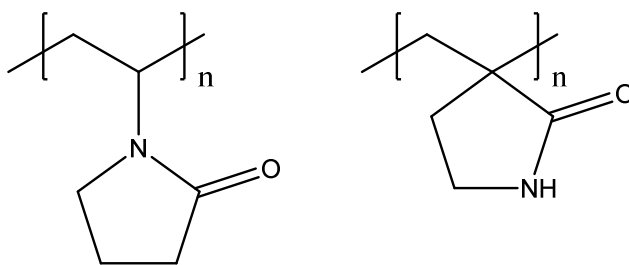
Figure 1. Poly(*N*-vinyl pyrrolidone) (left) and poly(3-methylene-2-pyrrolidone) (right).

Sometimes the solvent used in KHI formulations is a synergist in its own right. *n*-butyl glycol ether (or 2-butoxyethanol, BGE) is a known synergist used with commercial KHIs such as poly(*N*-vinylcaprolactam) (PVCap), PVP and copolymers of VCap and *N*-vinyl pyrrolidone (VP).[12, 21, 22] BGE has negligible KHI effect by itself at typical KHI doses (< 1 wt.%), like other small alcohols and glycols.[23]

Recently, a related class of polymer has been developed based on the 3-methylene-2-pyrrolidone (3M2P) monomer (Figure 1).[24] As with PVP, the 3M2P homopolymer, poly(3-methylene-2-pyrrolidone) P(3M2P), also contains a pendant pyrrolidone ring, however the polyvinyl backbone originates from the conjugated methylene group in the alpha position of the pyrrolidone. In addition, the first reports of this polymer suggest a high cloud point, which as previously discussed is a useful property for injection into hot fluids at the wellhead.

This report describes the first KHI study with P(3M2P) and compares the results to PVP. The synergism of these polymers with added BGE was also investigated.

EXPERIMENTAL METHODS

Chemicals and Polymer Synthesis

PVCap was obtained from BASF as Luvicap EG HM, a 41 wt.% solution of polymer in monoethylene glycol (MEG) with a molecular weight of 7000-12000 g/mole. PVP was obtained from Ashland Chemical as PVP K-15, with a molecular weight of approximately 8000-9000 g/mole and as a pure powder. All chemicals for synthesis and BGE for the KHI studies were purchased from VWR and Sigma-Aldrich. All solvents were used without further purification. ^{1}H and ^{13}C NMR spectra were obtained with a Varian VXR-Unity (300 MHz) spectrometer. Mass Spectrometry (LC-MS) was obtained with a Waters Synapt G2 with Electron Spray Ionization (ESI) in the positive mode. Synthesis of 3M2P was performed by[24,25] the crossed Claisen condensation of *N*-boc-2-pyrrolidone and diethyl oxalate in a basic medium, followed by *β*-elimination with paraformaldehyde, yielding a methylene moiety at the alpha position of the ring. Subsequently the *N*-boc-protecting group was removed with trifluoroacetic acid. *3M2P monomer*: ^{1}H NMR (300 MHz, CDCl$_3$-d$_1$) δ: 7.39 (bs, 1H, -N$\underline{\text{H}}$), 6.06 (t, J = 2.8 Hz, 1H, =C$\underline{\text{H}}_b$), 5.47 (td, J = 2.4, 0.7 Hz, 1H, =C$\underline{\text{H}}_a$), 3.54 – 3.48 (m, 2H, -C$\underline{\text{H}}_2$-NH), 2.93 – 2.85 (m, 2H, -C$\underline{\text{H}}_2$-C=). ^{13}C NMR (300 MHz, DMSO-d$_6$) δ: 175.45, 141.62, 114.47, 38.90, 26.32. MS (ESI): m/z = 98.1 (calculated: 98.06 for [M + H]$^+$). Polymerization of 3M2P was successfully carried out as described earlier[24] by the use of a reversible deactivation radical polymerization technique (RDRP), namely reversible addition fragmentation (chain) transfer (RAFT) polymerization (Figure 2). The M_n of the polymers were determined via NMR spectroscopy (Table 1). *P(3M2P)*: ^{1}H NMR (300 MHz, D$_2$O-d$_2$) δ: 3.4 – 3.3 (broad), 2.4 – 1.3 (broad).
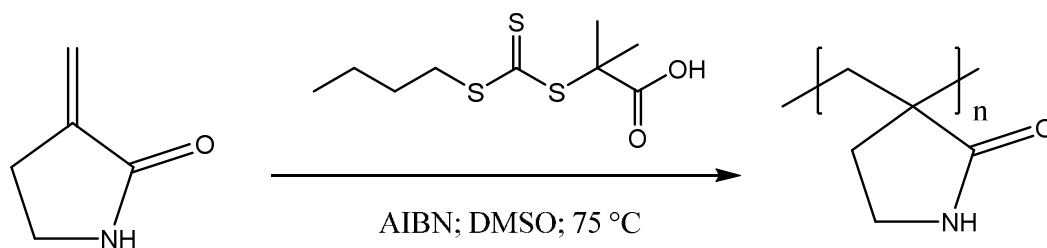
Figure 2. RAFT polymerization of 3M2P.

Table 1. Polymer samples synthesized.

Polymer	M_n [g/mole] (^{1}H NMR)
P(3M2P)-1	5500
P(3M2P)-2	2500

Cloud Point Temperature (T_{Cl}) Measurement

An increase in temperature of the polymer solution causes a phase separation, which can be observed as a cloud or fog appearing in the solution. If the temperature increases, the polymer can eventually precipitate out of solution. The temperature at the first sign of cloudiness gives the cloud point temperature (T_{Cl}). The T_{Cl} was measured by heating the sample approximately 2 °C/min and closely observing phase changes throughout the measurement. The sample was cooled well below the T_{Cl} and the test was repeated for reproducibility.[26, 27]

High Pressure Rocker Rig Tests with Synthetic Natural Gas

The procedure used for the KHI tests is the same as done in previous work by our group, using two steel cell rocker rigs, both supplied by PSL Systemtechnik, Germany.[28, 29] One of the rigs is located in the laboratories at the University of Stavanger (UiS) and one at the Technical University of Denmark (DTU). All the steel cells on both rigs are new and made of

Swagelok high pressure fittings. They are very similar to the original cells used by our group in past work, but are easier to tighten and therefore less prone to leakages. The volume for each cell is approximately 40 mL, where 20 mL of an aqueous sample is added per cell for a test. In addition to the rocking, a steel ball is placed in each cell to agitate the test liquid. The loaded cells are then pressurized with a synthetic natural gas (SNG) mixture that will theoretically form the structure II (SII) hydrate as the most stable hydrate. The components of the SNG mixtures used for these tests are listed in Table 2. For the pressure used in these tests (76 bar), the equilibrium temperature (T_{eq}) has previously been reported to be 20.2 °C ± 0.05 °C. [30-32] This value is similar to 20.5 °C, which is the calculated value at 76 bar using PVTSim from Calsep. The two gases are very similar and give very similar equilibrium curves. Most of the KHI tests were carried out in the one rig (DTU) during an external research stay by the first author. The P(3M2P)-2 with and without BGE was tested with the SNG 2 mixture (UiS).

Table 2. Synthetic natural gas (SNG) mixtures used in the KHI performance tests.

Component	mole %	
	SNG 1	SNG 2
Methane	79.03	80.67
Ethane	10.20	10.20
Propane	5.53	4.90
iso-butane	1.20	1.53
n-butane	2.49	0.76
N_2	0.30	0.10
CO_2	1.24	1.84

The constant cooling KHI test procedure was as follows:

1. The additives were dissolved in distilled water and diluted to desired concentration at least one day before testing.

2. 20 mL sample was added to each cell at 20.5 °C.

3. 3 – 5 bars SNG mixture was used to purge the cells after applying vacuum. This was done to remove the air from the system. After depressurizing the system, vacuum was applied once more before pressurizing to approximately 76 bars.

4. The constant cooling parameters were set to a rocking rate of 20 rocks per minute, rocking angle of 40° and an approximate cooling rate of 1 °C/hour from 20.5 °C to 2 °C.

5. Data logging for each cell on a local computer is possible for both pressure and temperature, as there are sensors connected to each test cell. In addition, there is also a temperature sensor in the cooling bath.

From the pressure and temperature data, we can generate a pressure and temperature graph for each cell as shown in Figures 3 and 4. These are typical plots generated after a constant cooling program. Figure 3 shows a summary chart of all the cells. Here only four cells are used. Figure 4 shows the result of a single cell. As seen from these figures, the pressure in the beginning of the test will decrease by as much as two bars as the gas dissolves in the aqueous phase during initial rocking. Since it is a closed system, the pressure will decrease with a constant rate as the temperature also decreases from 20.5 °C to 2.0 °C. The experiment finishes after about 1230 minutes at which point the cells are warmed to 25 ºC (*i.e.* well outside the hydrate stability region), depressurized, cleaned and made ready for a new experiment.

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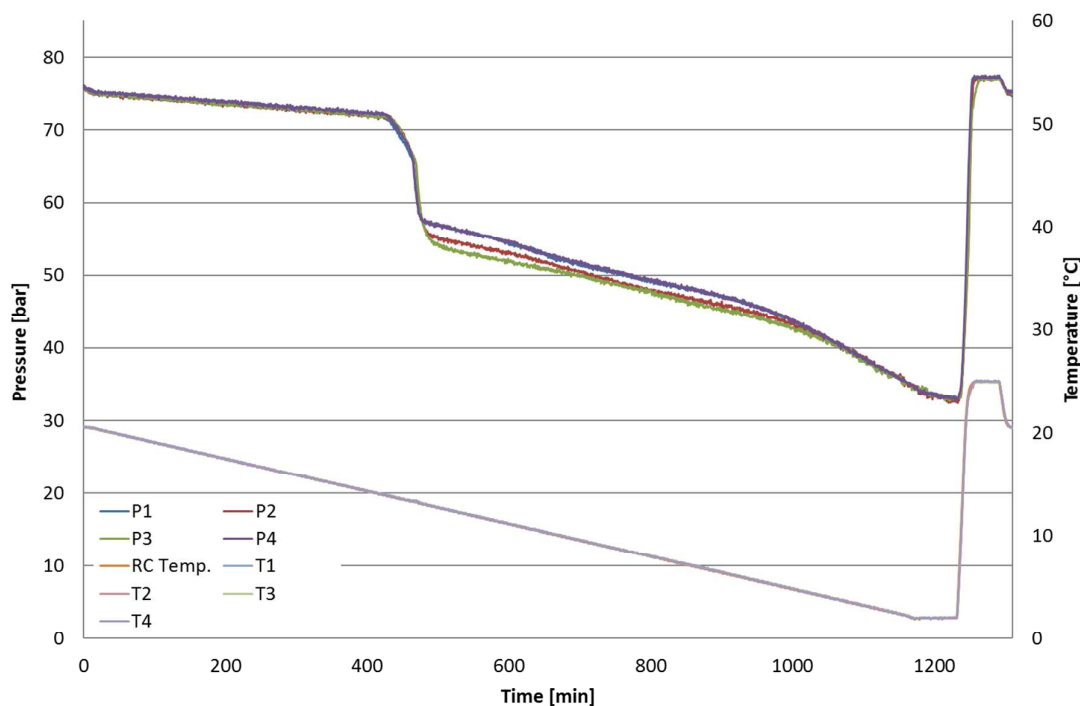21
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Figure 3. Summary of the results from a constant cooling test with 4 cells.

33 Figure 4 shows an example of a plot generated for one of the cells, here the data for cell 1

35 from Figure 3 is shown. P1 shows the pressure and T1 shows the temperature at any given

37 time for cell 1 during the experiment. The hydrate onset temperature (T_o) is the most relevant

39 result, as it indicates the temperature where macroscopic hydrate formation is first detected

41 (increased pressure drop). T_o, as shown in Figure 4, is found after approximately 422 minutes

43 at a temperature of 14.0 °C and T_a, which is the rapid growth temperature, is found after

45 approximately 466 minutes at a temperature of 13.4 °C. The nucleation process is not visible

47 in these graphs and may have started some time before the first pressure drop due to hydrate

49 formation. T_a is the temperature for rapid hydrate formation. The difference in T_o and T_a can

53 give an indication of the KHIs ability to delay the rapid hydrate formation.
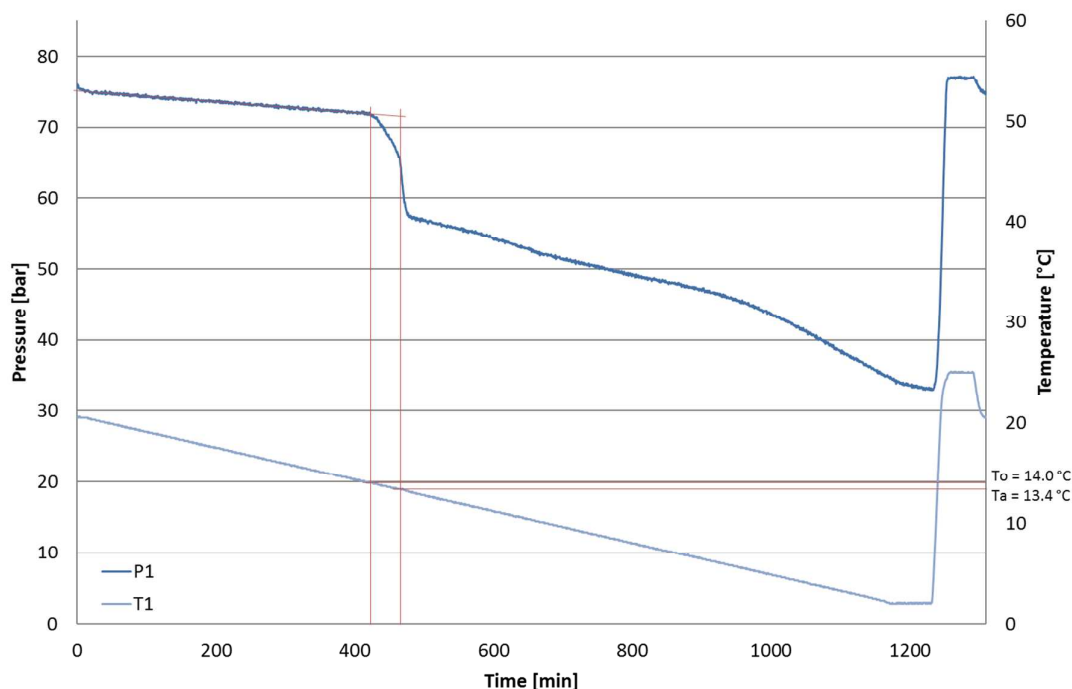
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Figure 4. Determination of T_o and T_a from cell 1 after a constant cooling test.

When using the standard constant cooling test method for screening of KHIs, usually 8-10 experiments are carried out for each polymer to obtain better statistical information. In general, for the results in this paper, we observe a maximum scattering of 15-25% in the T_o data points. This observed maximum percentage may be higher than reported before in our group, possibly due to the use of new rocking cells. The cells were run for a few weeks prior to carrying out this study. However we still observed somewhat larger scattering. The scattering reflects the stochastic nature of hydrate nucleation. However, as the new cells are used even more, the scattering will also be reduced.[29] Another reason for the higher scattering in T_o values is the mediocre performance of the P(3M2P), an effect which has often been observed previously for KHIs with mediocre performance in our research. No systematic error was observed in any of the cells, *i.e.* none of the cells showed consistently better or worse

results for each experiment. All of the samples used are either fresh or heated well above the

equilibrium temperature so there are no residual hydrates in the system at test start.

RESULTS AND DISCUSSION

KHI performance comparison of different concentrations with and without a synergist.

Table 3 lists the results from the KHI tests in addition to the cloud point values. Figure 5

shows the average T_o and T_a values of the different concentrations of all the polymers tested.

Results with two known KHI polymers, PVP, M_w = 8000-9000 g/mole and PVCap, M_w =

7000-12000 g/mole, are also added for comparison. In addition, PVP was also tested at 2500

ppm on both rocker rigs as a reference. For the lower molecular weight sample, P(3M2P)-2,

only 4 tests with a concentration of 2500 ppm and 3 tests with 2500 ppm doped with 1 wt%

BGE were carried out. This is because of the limited amount of polymer available.

Both the 3M2P polymers were initially difficult to dissolve and the solutions were slightly

hazy even when refrigerated at 4 °C. Previously, P(3M2P) has been reported to exhibit no

cloud point in water up to 100 °C.[25] We think the haziness of our solutions could be due to the

RAFT agent used in the RAFT-mediated polymerization of 3M2P. Since our P(3M2P) is a

low molar mass polymer, the RAFT's ω Z-endgroup, which is a *n*-butyl moiety, could

possibly be influencing aqueous solubility.

Table 3. Constant cooling KHI tests, average of 10 tests unless otherwise stated.

Chemical	Synergist [ppm] BGE	2500 ppm		5000 ppm		7500 ppm		
		T_o / °C	T_a / °C	T_o / °C	T_a / °C	T_o / °C	T_a / °C	T_{Cl} / °C
No additive		17.2	16.4					
PVCap		9.9	8.2	7.3	6.4	5.6	5.1	31
PVP		13.8[c]	10.3[c]					
PVP		13.6	10.5	13.7	10.3	10.5	8.9	>95
PVP	10000	13.3	12.6	12.4	11.8	11	10.4	>95
P(3M2P)-1		15.5	15.3	15.2	15	14.8	14.6	*
P(3M2P)-1	10000	14.1	13.4	14.3	13.5	14.4	13.5	*
P(3M2P)-2		15.5[a, c]	15.3[a, c]					*
P(3M2P)-2	10000	15.4[b, c]	14.3[b, c]					*

[a]4 tests, [b]3 tests, [c]result from UiS rocker rig

*Solutions cloudy down to at 4 °C, except P(3M2P)-2 with added BGE.

PVCap is a well-known KHI that delays hydrate nucleation and crystal growth. As seen from the results, PVCap is the best performing KHI of the polymers tested here. Increasing concentration gives increasing performance.

At the lower concentrations, P(3M2P)-1 and P(3M2P)-2 (M_n = 2500-5500 g/mole) perform quite similar to PVP (M_w = 8000-9000 g/mole). However, PVP outperforms P(3M2P) at 7500 ppm, with and without BGE. The addition of BGE to the PVP solutions increases the performance at 5000 ppm. However this glycol does not really change the performance for the sample containing 2500 ppm or 7500 ppm PVP. Carstensen *et al*. also reported no significant synergy with PVP and BGE. However this was in a THF hydrate system.[33]
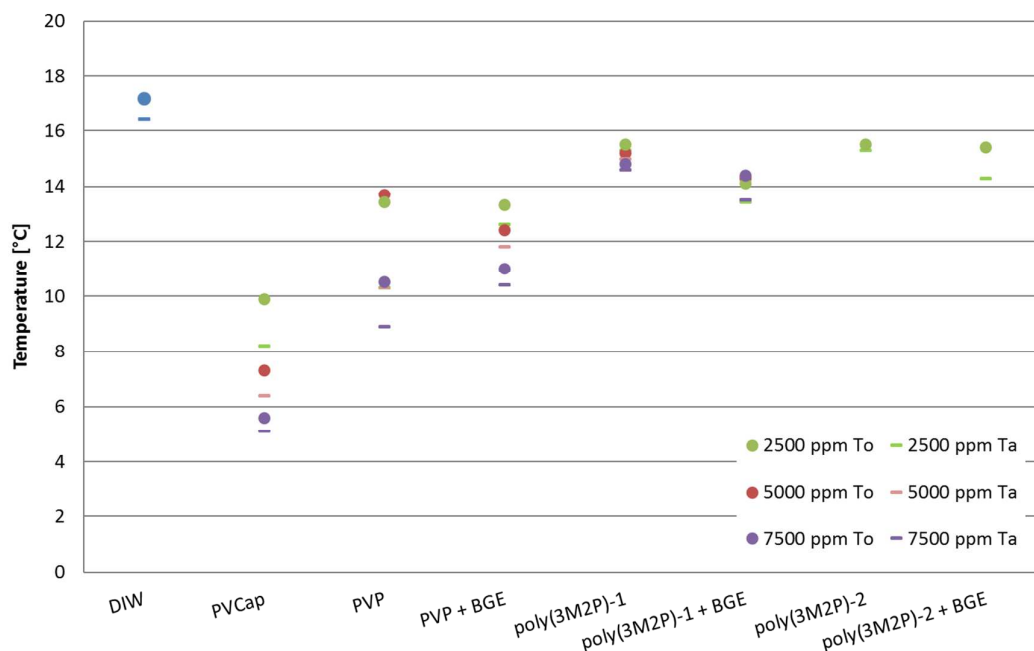
Figure 5. Summary of results found in Table 3.

We carried out t-tests to check for significant difference between two sets of T_o or T_a values.[34] The different P(3M2P)-1 concentrations showed quite similar results over all, where 5000 ppm is not significantly different from either 7500 ppm or 2500 ppm. 2500 ppm is significantly different from 7500 ppm with a P-value of less than 0.05.

There is no statistically significant difference between the T_o values of the P(3M2P)-1 samples without BGE in comparison to the samples with added BGE. Interestingly there is a small but significant difference in these sets of results for the T_a values. This suggests that BGE has some synergistic effect, or that BGE in itself has some inhibiting effect on hydrate crystal growth.

We assumed that the structural similarities of P(3M2P) to PVP would give a similar T_{Cl} and KHI performance. Both polymers contain a nitrogen atom and a carbonyl group (C=O) that

are believed to be a very suitable hydrophilic moiety for the interaction to either free water or

the hydrate surface.[35-37] One possibility for the mediocre performance of P(3M2P) can be that

the structure of the P(3M2P) allows for a possible resonance stabilization of the double bond

from the C=O group to C=N, as shown in Figure 6. This is not possible for PVP as the

nitrogen atom is tertiary. The resonance stabilization in P(3M2P) will energetically lower the

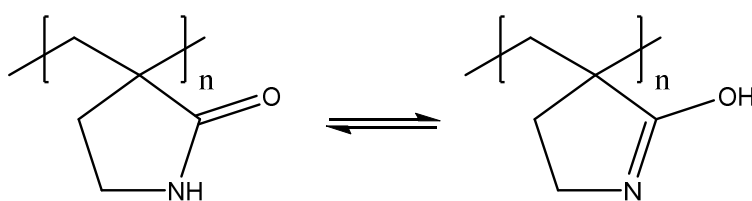bonding preference of the carbonyl group to water molecules compared to PVP.

Figure 6. Resonance stabilization of the amide group in P(3M2P).

Another explanation is related to the size of the hydrophobic area of the pendant groups in

PVP and P(3M2P), as shown in Figure 7. The larger pendant hydrophobic groups generally

give increasing KHI performance, as long as the polymer is kept water-soluble.[31, 38, 39] This

can also explain the slightly better performance of PVP, where the lactam group is not a part

of the polymer backbone, but bound via the nitrogen.

A third explanation can be that since the lactam group is directly bound to the polymer

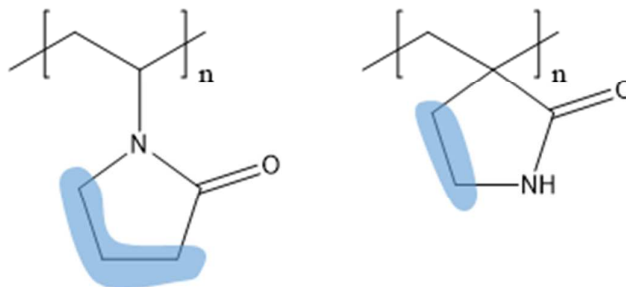backbone, this may cause more sterical hindrance for the pendant group.

Figure 7. PVP (left), P(3M2P) (right). Blue area indicates hydrophobic part of the pendant

groups.

CONCLUSION

The polymer poly(3-methylene-2-pyrrolidone) (P(3M2P)), closely related to PVP, has been

tested for the first time as a KHI. P(3M2P) was reported to have a high cloud point (>90 °C in

aqueous solution) which is useful for high temperature injection of KHIs.

High-pressure rocker rigs with an SNG mixture and the constant cooling program was used

for the experiments. Two samples of P(3M2P) with different molecular weights were tested

with and without BGE (1.0 wt%). In addition, one of the samples was also tested at three

different concentrations (2500, 5000 and 7500 ppm) where all concentrations were also doped

with BGE (1 wt%).

BGE was reported as a synergist by Hu *et al*. for PVP. [22] In our hands, we find that there is

little or no synergy. For both P(3M2P)-1 and P(3M2P)-2, BGE as dopant shows some weak

synergy, however no significant difference. This is in agreement with a report from

Carstensen *et al*. who also found no significant synergy with PVP and BGE. [33]

The KHI performance for P(3M2P) reported in this paper can be explained by a possible

resonance stabilization of the double bond from the oxygen to the nitrogen, which is not

possible for PVP. In addition to this phenomenon, the hydrophobic moiety of P(3M2P) is smaller than that of the hydrophobic pendant moiety of PVP. This can also affect the KHI performance and has been observed before for other KHIs, *i.e.* with increasing hydrophobicity, KHI performance increases, provided that aqueous solubility is maintained.

We hope to investigate variations on P(3M2P) with larger, more hydrophobic rings, as well as copolymers with more hydrophobic monomers and possibly also other synergists in order to improve the performance of this new class of polymer.

ACKNOWLEDGEMENTS

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