

# 5-Methyl-3-vinyl-2-oxazolidinone—Investigations of a New Monomer for Kinetic Hydrate Inhibitor Polymers

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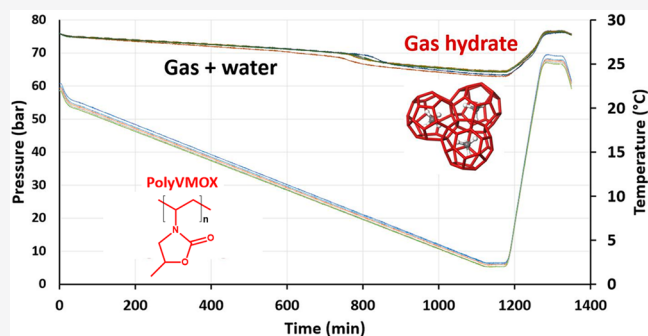


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**ABSTRACT:** Kinetic hydrate inhibitors (KHIs) are polymers used in a chemical method to prevent gas hydrate plugging of oil and gas production flow lines. The main ingredient in a KHI formulation is one or more water-soluble amphiphilic polymers. Several classes of KHI polymers contain pendant heterocyclic 5-rings including poly(*N*-vinylpyrrolidone) (PVP) and poly(2-isopropenyl-2-oxazoline) (PiPOx). Here, we present a KHI performance study on polymers based on the 5-ring vinylic monomer 5-methyl-3-vinyl-2-oxazolidinone (VMOX), which has only recently been manufactured in large quantities. Low molecular weight PVMOX homopolymers were produced in quantitative yield using radical polymerization, with or without a chain transfer agent. For example, PVMOX-2.4k ( $M_n = 2400$  g/mol) had a cloud point at 2500 ppm of 73 °C in deionized water. The polymers were screened for KHI performance using slow constant cooling tests (1.0 °C/h) in high-pressure rocking cells with a synthetic natural gas blend. At 2500 ppm, PVMOX-2.4k gave a better performance than PVP or PiPOx at a similar molecular weight but not as good as poly(*N*-vinylcaprolactam) (PVCap). Isobutyl glycol ether was shown to enhance the KHI performance of PVMOX. PVMOX gave improved performance with increasing concentration but not as steep of an improvement as some of the best amide-based KHI polymers. A 1:1 copolymer of VMOX with *N*-vinylcaprolactam gave improved performance compared to the PVMOX homopolymer.



## INTRODUCTION

Gas hydrate plugging of flow lines from gas or oil fields is one of the most serious production issues to manage.<sup>1–5</sup> There are several chemical methods to use to avoid this problem, and one of them is the deployment of kinetic hydrate inhibitors (KHIs) which are a subgroup of low dosage hydrate inhibitors (LDHIs).<sup>6–17</sup> KHIs delay particle growth whether as subcritical size particles (nucleation inhibition) or as crystal growth inhibition.<sup>18</sup> KHIs are liquid formulations containing one or more water-soluble polymers plus solvents and synergists. The solvent system is often synergetic also. Low molecular weight (MW) and amphiphilic side groups are typical features of KHI polymers. Typical reported MW values that give the best KHI performance are usually in the range of about 1000–5000 g/mol.<sup>6,8,13</sup> Since most monomer units used in KHI polymers (see examples in Figure 1) have a weight of about 120–140 Da, the optimum MW does not vary much between polymer classes. The hydrophilic group is often a strong hydrogen-bonding group such as amide, imide, or amine oxide groups, and the hydrophobic group is usually a hydrocarbon fragment with 3–6 carbon atoms. Typical linear KHI polymers are based on the monomers *N*-vinylcaprolactam (VCap), *N*-vinylpyrrolidone (VP), and *N*-isopropylmethacrylamide (NIPMAm), as well as hyperbranched poly(ester

amide)s based on diisopropanolamine and various cyclic anhydrides (Figure 1).

5-Methyl-3-vinyl-2-oxazolidinone (VMOX) is a relatively new commercial monomer used as a reactive diluent in UV curing products such as adhesives, coatings, and inks (Figure 1). It contains a 5-ring as also seen in pyrrolidone but now with an extra ring oxygen atom and a methyl group. Therefore, we were interested in determining the KHI performance of the VMOX homopolymer and comparing it with PVP and 3-alkylated derivatives thereof as well as poly(2-isopropenyl-2-oxazoline) (PiPOx).<sup>19–22</sup> (Figure 2). Here, we report the first KHI performance study on the PVMOX homopolymer as well as the VMOX statistical copolymer with VCap.

## EXPERIMENTAL SECTION

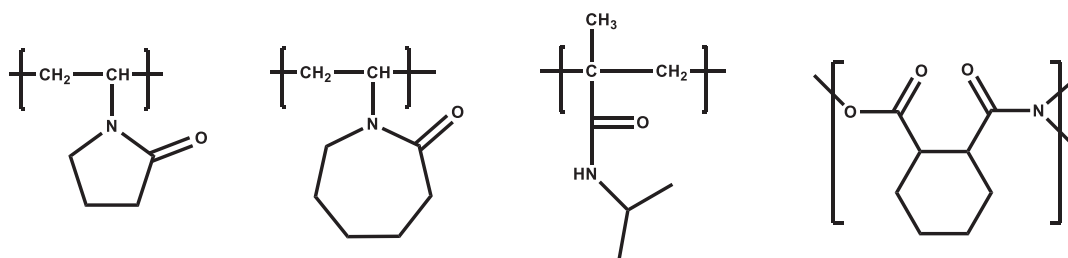
**Materials.** *N*-Vinyl caprolactam (VCap), *N*-isopropylmethacrylamide (NIPMAm), bisazoisobutyronitrile (AIBN), and 2-propanol

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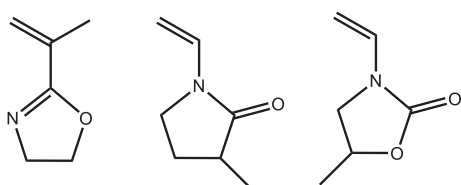
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**Figure 1.** Common amphiphilic amide-based monomer units in commercial KHI polymers. From left to right, poly(*N*-vinylpyrrolidone) (PVP), poly(*N*-vinylcaprolactam) (PVCap), poly(*N*-isopropylmethacrylamide) (PNIPMAm), and hyperbranched poly(ester amide)s.



**Figure 2.** 2-Isopropenyl-2-oxazoline (iPOx) (left), 3-alkyl-*N*-vinylpyrrolidone (middle), and 5-methyl-3-vinyl-2-oxazolidinone (VMOX) (right).

(iPrOH) were purchased from VWR (Avantor) and used as-received. A sample of 5-methyl-3-vinyl-2-oxazolidinone (VMOX) was kindly donated by BASF, Norway. The PVCap homopolymer ( $M_n = 2600$  g/mol, 41.1 wt % in MEG) and the vinylpyrrolidone:VCap 1:1 copolymer (VP:VCap 1:1) ( $M_n = 2000$ – $4000$  g/mol, 53.8 wt % in water) were obtained from BASF.

**Synthesis of PVMOX Homopolymer and VMOX:VCap 1:1 Copolymer and Attempted Synthesis of VMOX:NIPMAm 1:1 Copolymer.** The polymerization synthesis was done in the same general manner for both the homopolymer and copolymers. VMOX (5 g, 39.32 mmol) was dissolved in 2-propanol (10 g) in a Schlenk flask with a magnet. AIBN (1.0 w%, 0.05 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 80 °C and left to react under the protection of nitrogen overnight. The PVMOX polymerized out of the solution, so the remaining solvent was removed *in vacuo* on a rotary evaporator, leaving the white solid PVMOX-5.4k. The comonomers *N*-vinyl caprolactam (VCap) (1.12 g, 7.86 mmol) and *N*-isopropylmethacrylamide (NIPMAm) (1.00 g, 7.86 mmol) were added to VMOX (1 g, 7.86 mmol) with AIBN (1 w %) and dissolved in 2-propanol (5 g), respectively. Then, the copolymerization followed the same procedure as for the homopolymerization. Both copolymers were left in the solution. For  $^1\text{H}$  NMR spectroscopy characterization, the solvent was removed. The

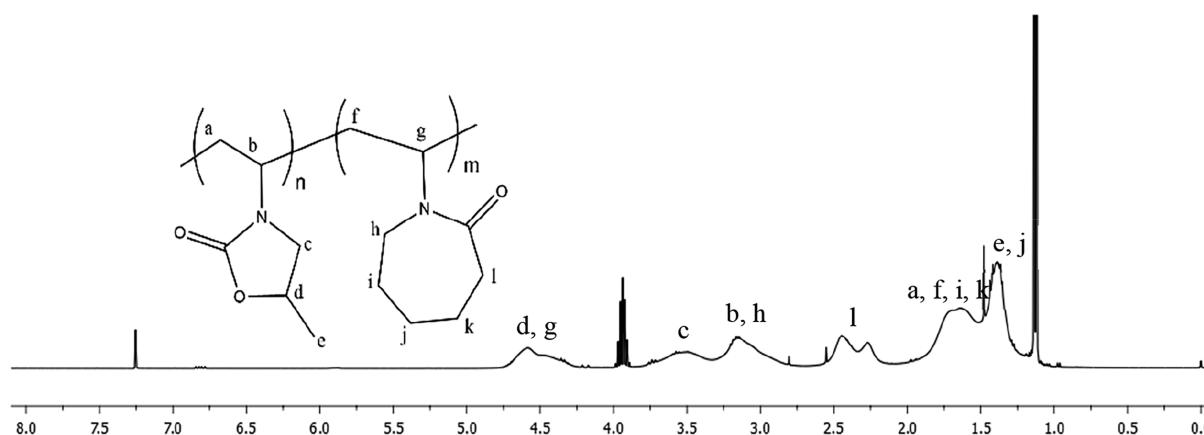
spectrum for VMOX:VCap is given in Figure 3 and shows complete polymerization with a small amount of residual 2-propanol. For the attempted formation of the copolymer VMOX:NIPMAm, the  $^1\text{H}$  NMR spectrum showed no sign of polymerization of VMOX at all, just broad peaks for the PNIPMAm homopolymer and sharp peaks for the unreacted VMOX monomer.

**Homopolymerization with a Chain Transfer Agent (CTA).** In a Schlenk flask were added VMOX (5 g, 39.32 mmol), 1 wt % of AIBN (0.05 g, 0.304 mmol), 3-mercaptopropionic acid (413.9 mg, 3.9 mmol), and finally 2-propanol (10 g).  $\text{N}_2$  purging and vacuum were applied at least 5 times. The mixture was kept stirring for 5 h at 80 degrees under  $\text{N}_2$ . When cooled to room temperature, a precipitate of the synthesized polymer is formed which was washed twice with 2-propanol and dried under reduced pressure to get a white powder of PVMOX-2.4k as the final product.  $^1\text{H}$  NMR spectra are given in Figure 4. Both the CTA 3-mercaptopropionic acid and 2-propanol can be seen as impurities in the spectrum.

**Cloud Point ( $T_{cl}$ ) Measurement.** The polymer was dissolved in deionized water to 2500 ppm and heated slowly with shaking. The temperature at which clouding of the solution was first observed was taken as the cloud point ( $T_{cl}$ ). The test was repeated to check for reproducibility.

**Kinetic Hydrate Inhibitor (KHI) Performance Tests.** These were carried out in five parallel high-pressure rocking cells placed in a thermally controlled water bath, part of a rig supplied by PSL Systemtechnik, Germany (Figure 5).<sup>23–25</sup> A synthetic natural gas (SNG) blend was used (Table 1). This gas blend was made by Yara Praxair, Norway, and the composition was analyzed to be within  $\pm 0.1\%$  of all the required concentrations. The equilibrium temperature ( $T_{eq}$ ) for sII gas hydrate at 76 bar of SNG was predicted to be 20.5 °C by PVTsim software, Calsep.

Slow constant cooling (SCC) tests were carried out to evaluate the KHI performance of all polymers. This method has been used by our group for many years using the same equipment and SNG which enables us to compare the performance of new KHIs to a plethora of previously tested KHIs.<sup>26</sup> This was particularly useful for this study for



**Figure 3.**  $^1\text{H}$  NMR spectra for PVMOX-*co*-PVCap (1:1) with residual iPrOH in  $\text{CDCl}_3$ .

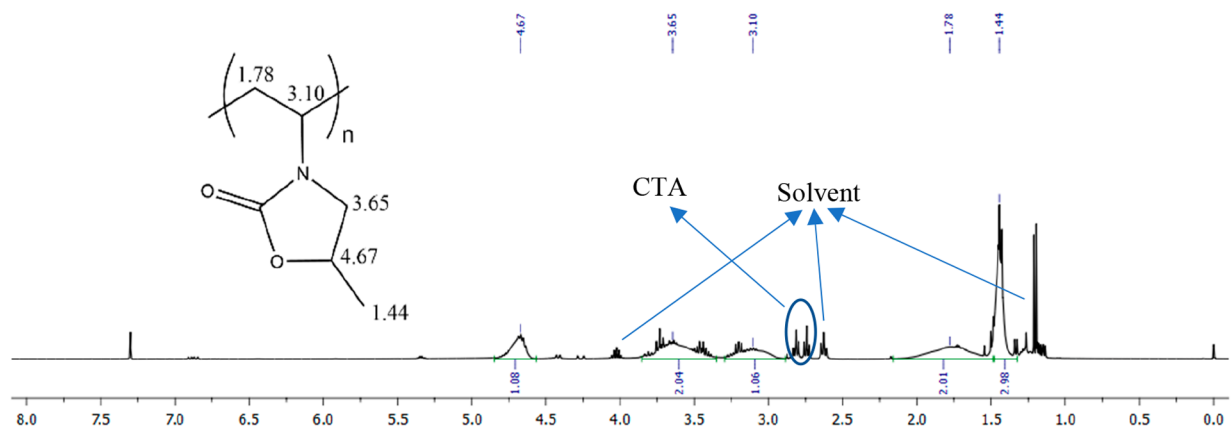


Figure 4.  $^1\text{H}$  NMR spectrum for PVMOX-2.4k with residual *i*PrOH and 3-mercaptopropionic acid in  $\text{CDCl}_3$ .

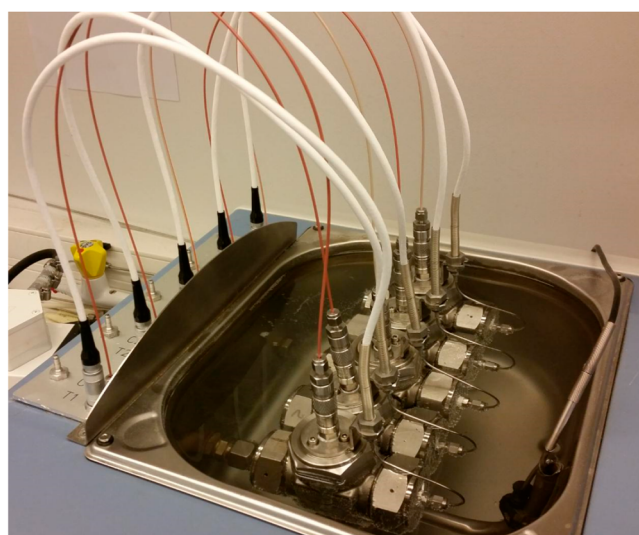


Figure 5. High-pressure steel multicell rocking in a temperature-controlled bath.

Table 1. Composition of the Synthetic Natural Gas (SNG) Mixture

component	mol %
nitrogen	0.11
<i>n</i> -butane	0.72
isobutane	1.65
propane	5.00
$\text{CO}_2$	1.82
ethane	10.3
methane	80.4

comparison of PVMOX with the structurally related polymers PVP, alkylated PVPs, and PiPrOX. The standard procedure for SCC tests was as follows:

1. The test polymer was dissolved in 105 mL of deionized water. Preparation was done 24 h prior to the KHI test. Twenty milliliters of this test solution was added to each cell.
2. Each cell was purged with SNG, and then vacuum was applied to remove the air in the system. This was then repeated.
3. Approximately 76 bar of SNG was loaded to each cell at 20.5  $^\circ\text{C}$ , and each cell was shut individually at the gas inlet/outlet valves.
4. The cells were rocked and slowly cooled at a rate of 1  $^\circ\text{C}/\text{h}$ . Pressure and temperature data were recorded by sensors.

An example of the data obtained (pressure and temperature versus time) from a set of five experiments on the same polymer is shown in Figure 6.

Two parameters were determined from the data obtained, the hydrate onset temperature ( $T_o$ ) and rapid hydrate formation temperature ( $T_a$ ) (Figure 7). In the closed system, the pressure decreased linearly due to the constant temperature decrease. Once gas hydrates begin to form, the pressure deviates from the original linear track, and this first pressure drop point was marked as  $P_o$ . The corresponding temperature at  $P_o$  is  $T_o$ . The first fastest pressure drop point was marked as  $P_a$  and its corresponding temperature is  $T_a$ . Generally, 5–6 individual experiments were carried out for each polymer sample. For a set of 5–6 experiments, we typically observe a 10–15% margin of error in  $T_o$  and  $T_a$  values which was also the case in this study. This is due to the stochastic nature of the hydrate nucleation process. No bias was observed between any of the five cells, such as one cell regularly giving higher or lower  $T_o$  and  $T_a$  values than the other four. Standard deviations (assuming normal distribution) were calculated for all sets of  $T_o$  data. The  $T_o$  value is a more important parameter than  $T_a$  for determining the KHI performance since operators preferably want to completely stop macroscopic hydrate formation in flow lines. To evaluate if there is a significant difference between sets of  $T_o$  values for two polymers, we carried out statistical  $t$  tests and determined the  $p$ -value. The  $t$  test is a well-known statistical method to evaluate if there is a significant difference between two sets of data, which, in our case, can help rank the KHIs.<sup>27</sup> A  $p$ -value is calculated, usually by software (e.g., add-on in Excel), and if the  $p$ -value is less than 0.05, it is considered that there is a significant difference between the two sets of data at the 95% confidence level. Thus, a  $p$ -value of less than 0.05, between two sets of  $T_o$  values, indicates a 95% confidence that the performance of one KHI is better than another.

## RESULTS AND DISCUSSION

The VMOX monomer polymerized easily with a 1 wt % AIBN radical initiator in 2-propanol to form the homopolymer PVMOX. This PVMOX-5.4k homopolymer had  $M_n = 5400$  g/mol (PDI = 3.8) and a cloud point ( $T_{Cl}$ ) in DI water at 2500 ppm of 45  $^\circ\text{C}$ . We also carried out the same reaction but with added chain transfer agent (CTA) 3-mercaptopropionic acid to give a lower molecular homopolymer (PMVOX-2.4k) that analyzed as  $M_n = 2400$  g/mol (PDI = 2.9). Interestingly, this homopolymer had a cloud point of 73  $^\circ\text{C}$  at 2500 ppm, considerably higher than the higher molecular weight PVMOX-5.4k. The cloud point in varying sodium chloride salinities was also investigated for PVMOX-2.4k (Figure 8). Even in 15 wt % NaCl, the cloud point only dropped to 43  $^\circ\text{C}$ , which gives some indication of the compatibility range for

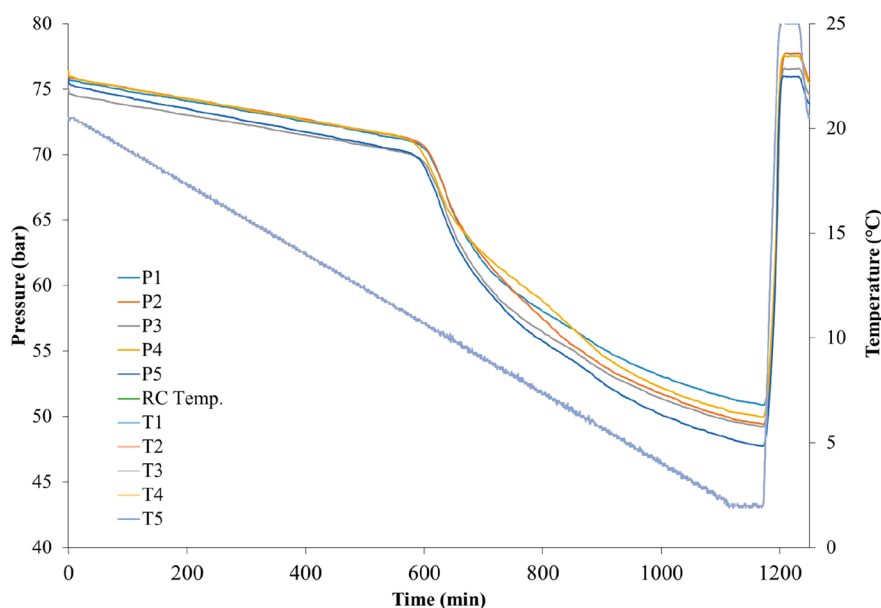


Figure 6. Pressure–time and temperature–time curves obtained for a set of five SCC tests.

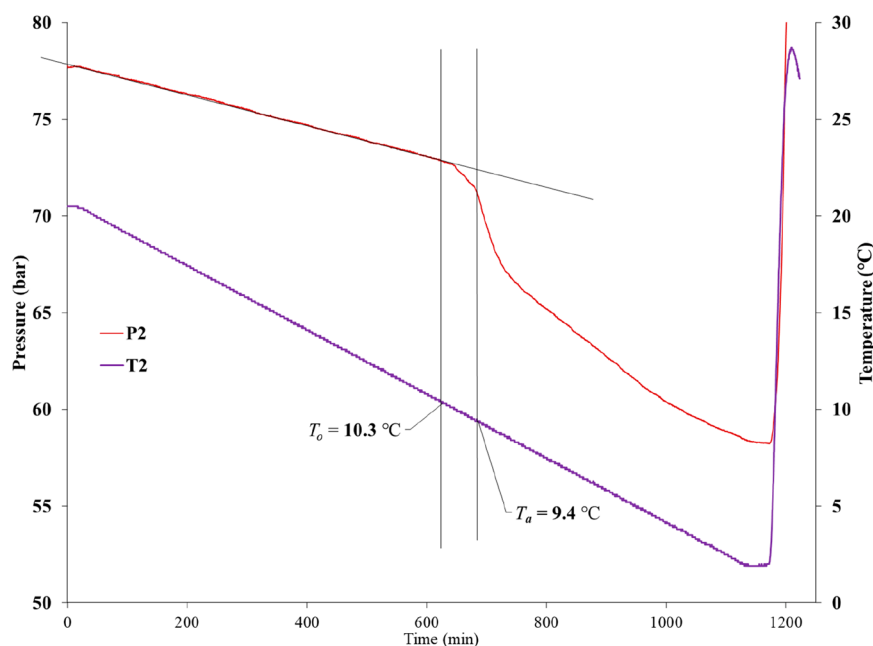


Figure 7. Determination of  $T_o$  and  $T_a$  values from PT data vs time for an SCC screening test.

injection into the produced water at wellhead temperatures. The compatibility with respect to the cloud point is fairly similar over the 0–15 wt % salinity range to a commercial VP:VCap 1:1 copolymer KHI.<sup>28</sup> We are currently exploring the KHI performance of PVMOX in high salinity brines and will report on this later.

Table 2 gives a summary of the molecular weight, cloud point ( $T_{cl}$ ), and KHI performance data (average  $T_o$  and  $T_a$  values, plus standard deviation for  $T_o$ ) for all polymers tested plus some data from past studies for comparison. For the high-pressure SCC rocking cell tests, the onset temperature  $T_o$  is considered the most valuable parameter, as this represents the first detection of gas hydrate formation. The  $T_o$ - $T_a$  value can also be useful to gauge the ability of the polymer to arrest hydrate growth. However, caution must be used in comparing

data between polymers if the  $T_o$  values are considerably different since the driving force at hydrate onset will not be the same.

As Table 2 shows, at 2500 ppm, both samples of the PVMOX homopolymer (Entries 13 and 14) gave much lower  $T_o$  values than DI water (Entry 1) showing good KHI ability. PVMOX also gave a worse performance than the caprolactam-based polymers PVCap and VP:VCap 1:1 (Entries 2 and 3) but gave a better performance than other vinylic polymers with pendant 5-ring heterocyclic structures and of similar molecular weights. This includes the PVP homopolymer (two commercial PVP samples were used, Entries 8 and 9) as well as two samples of poly(2-isopropenyl-2-oxazoline (PolyiPOx-1) from previous studies (Entries 6 and 7).<sup>21,22</sup> Further, PVMOX, which has a methyl group on the oxazolidinone ring, gave a

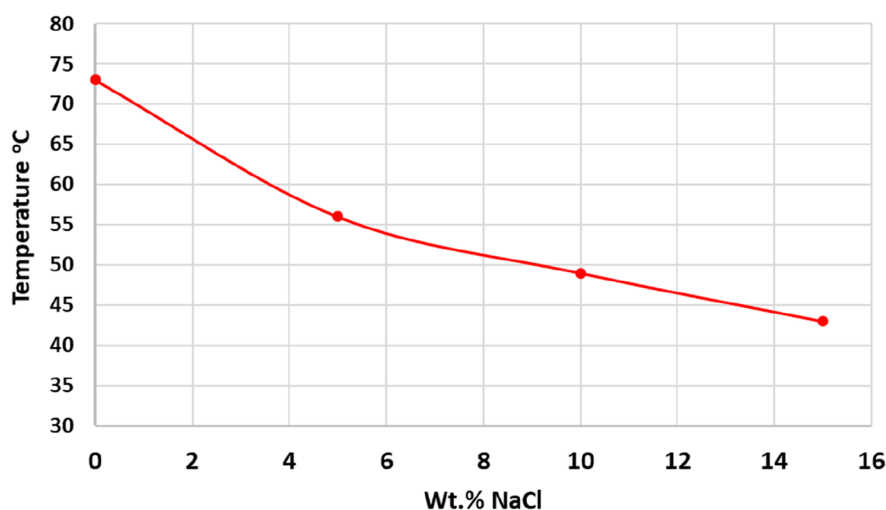


Figure 8. Cloud point ( $T_{cl}$ ) of PVMOX-2.4k at 2500 ppm at varying NaCl salinities.

Table 2. Summary of SCC Rocking Cell Tests with the 2500 ppm Polymer unless Otherwise Indicated<sup>a</sup>

entry	polymer	M <sub>w</sub> (PDI) (g/mol)	cloud pt (°C)	av $T_o$ (°C)	SD for $T_o$ (°C)	av $T_a$ (°C)
1	no additive			17.9	0.7	17.0
2	PVCap	2600 (1.81)	33	10.1	0.3	9.6
3	VP:VCap 1:1	2000–4000	85	8.9	0.2	6.8
4	PNIPMAm (iPrOH) <sup>29</sup>	1600 (3.5)	24	8.7	0.4	7.4
5	PNIPMAm (MEG) <sup>29</sup>	16200 (2.0)	32	10.5	0.3	10.2
6	PolyiPOx-1 <sup>22</sup>	2000 (1.3)	>100	11.1	0.2	10.8
7	PolyiPOx-1 <sup>22</sup>	7100 (1.2)	>100	12.5	0.3	11.8
8	PVP <sup>21</sup>	3400 (1.1)	>100	11.3	0.4	10.5
9	PVP 15k <sup>21</sup>	8000 (n/a)	>100	11.6	0.2	11.0
10	PVP-Me <sup>21</sup>	6900 (1.8)	65	10.4	0.3	9.1
11	PVP-Et <sup>21</sup>	6000 (1.5)	26	9.1	0.5	8.9
12	PVMOX-5.4k	5400 (3.8)	45	11.4	0.2	9.6
13	PVMOX-2.4k			10.7	0.2	9.7
14	PVMOX-2.4k + 5000 ppm iBGE	2400 (2.9)	73	9.7	0.2	7.9
15	VMOX:VCap 1:1 (43.3 wt % in iPrOH)	5300 (6.2)	42	10.4	0.1	8.9

<sup>a</sup>Average of 10 tests for polymers referenced from past studies.

similar or possibly slightly worse performance compared to the methylated PVP homopolymer PVP-Me (Entry 10). A *t* test did not show a clear difference in the performance at the 95% significance level ( $p > 0.95$ ). There is also a molecular weight difference which can make the comparison difficult. However, PVMOX did not perform as well as PVP-Et with the larger ethyl group (Entry 11) although the disadvantage with PVP-Et is the lower cloud point of 26 °C.

Tests were also carried out with PVMOX-2.4k with added iBGE (Entry 14), a known synergist solvent for several polyamides such as PNIPMAm and PVCap.<sup>29–31</sup> Addition of 5000 ppm iBGE to PVMOX-2.4k gave a smaller but statistically significant improvement ( $p < 0.05$  in *t* test) in the KHI performance, dropping the average  $T_o$  value by 1.0 °C.

VMOX is a fairly hydrophilic monomer, so we were also interested in investigating copolymers with the well-known amide-containing monomers, VCap and NIPMAm used in industrial KHI polymers. The reason is that homopolymers of VCap or of NIPMAm have fairly low cloud points making them difficult to use in field operations, and we wanted to see if we could raise the cloud point by copolymerizing them with VMOX but preferably without loss of KHI performance. Copolymerization of VMOX followed the same procedure as for the homopolymerization but with 1 equiv of either VCap or NIPMAm in 2-propanol as the solvent. For KHI studies, the resultant polymers were left in the solvent which has been shown to have very weak synergetic effects with VCap and NIPMAm polymers.<sup>29–31</sup>

For <sup>1</sup>H NMR spectroscopy characterization of the copolymers, the solvent was removed. The spectrum for VMOX:VCap is given in Figure 3 and shows complete polymerization of the monomers with only a small amount of residual 2-propanol. From GPC analysis, VMOX:VCap 1:1 was found to have  $M_n = 5300$  g/mol with a fairly high PDI of 6.2 although we suspect some polymer aggregation in the DMF may have caused this high value. For VMOX:NIPMAm 1:1, the <sup>1</sup>H NMR spectrum showed complete polymerization of the NIPMAm monomer only, to form the PNIPMAm homopolymer with sharp peaks for the unreacted VMOX monomers. The cloud point of the product was 38 °C which was also indicative of the formation of PNIPMAm. We are not sure of the reason for this but will explore this in future studies. The PNIPMAm polymer formed gave a molecular weight of 11000 g/mol by GPC and a PDI of 2.1 suggesting minimal aggregation in the GPC solvent (DMF). Since VMOX was not polymerized in the product polymer, it was not investigated for KHI performance.

At 2500 ppm, VMOX:VCap 1:1 gave an average  $T_o$  value of 10.4 °C (Entry 15), better than the performance of PVMOX-5.4k, which has the most similar molecular weight, and similar to PVMOX-2.4k and PVCap. The VMOX:VCap 1:1 copolymer could probably perform somewhat better at a lower molecular weight. Although the VMOX:VCap 1:1 copolymer does have the advantage of a higher cloud point than PVCap, VMOX:VCap gave no advantage over the VP:VCap 1:1 copolymer (Entry 3) both in terms of KHI performance and cloud point. Thus, VP is probably a better

comonomer for VCap copolymers than VMOX. The *N*-vinyl-*N*-methylacetamide (VIMA) monomer has been shown to perform even better as a comonomer for VCap copolymers but is no longer used in commercial KHI polymers due to reduced manufacturing volumes and the resulting higher unit treatment cost.<sup>32–34</sup>

Generally, for most KHI polymers, the hydrate inhibition performance improves with increasing concentration.<sup>35</sup> Previous work from our group suggests that the performance improvement is best for polymers with strong hydrogen-bonding groups such as amide or amine oxide.<sup>22,29,36</sup> Besides the tests at 2500 ppm discussed above, both PVMOX homopolymer samples were also tested at varying concentrations. The results are summarized in Table 3 showing both

**Table 3. SCC Rocking Cell Tests Results for PVMOX-5.4k, PVMOX-2.4k, and VP:VCap 1:1 at Varying Concentrations**

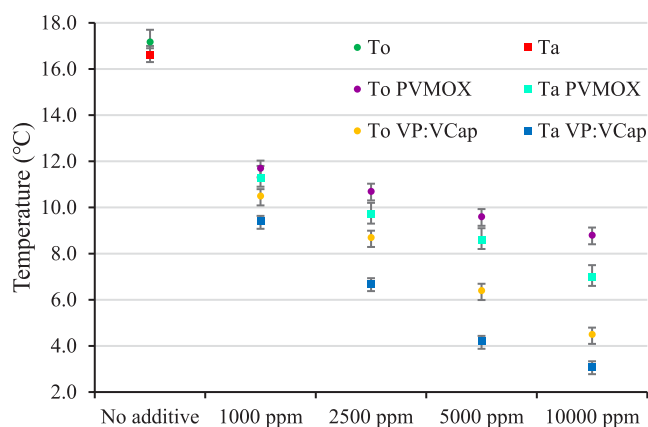
	concn (ppm)	av $T_o$ (°C)	SD for $T_o$ (°C)	av $T_a$ (°C)
no additive		17.2	0.7	16.6
VP:VCap 1:1	1000	10.5	0.5	9.4
	2500	8.7	0.1	6.3
	5000	6.4	0.2	4.2
	10000	4.5	0.4	3.1
PVMOX-2.4k	1000	11.7	0.2	11.3
	2500	10.7	0.2	9.7
	5000	9.6	0.1	8.6
	10000	8.8	0.2	7.0
PVMOX-5.4k	1000	11.2	0.3	10.6
	2500	11.4	0.2	9.6
	5000	10.4	0.2	9.4
	10000	9.0	0.2	6.7

average  $T_o$  (and standard deviation) and  $T_a$  values. The KHI performance for both PVMOX homopolymers generally increased with concentration within the range tested, except for PVMOX-5.4k from 1000 to 2500 ppm. One explanation for this exception is the possibility of aggregation or micelle formation. The general increase in KHI performance was not very large compared to several studies we have reported previously for amide-based polymer KHIs, such as PVCap and PNIPMAm.<sup>29,35</sup> To illustrate this, we carried out tests on the VP:VCap 1:1 copolymer at 1000, 2500, 5000, and 10000 ppm. A graphical depiction of the results and comparison to PVMOX-2.4k of similar molecular weight is shown in Figure 9. The graph shows that the slope for the decrease in  $T_o$  and  $T_a$  values for VP:VCap 1:1 at increasing concentration is steeper than for PVMOX-2.4k. The same trend is seen for PVMOX-5.4k, but the data is not included in Figure 9 to avoid overlap of data and difficulty in seeing the trend clearly.

The results with PVMOX compare well with a general trend that increasing the polymer concentration gives a smaller performance increase for other classes of nonamide KHIs, possibly with the exception of polyamine oxides. We believe the trend is related to the strong hydrogen bonding of the amide and amine oxide functional groups which gives the maximum benefit in arresting hydrate particle growth with increasing aqueous concentration. We are exploring this theory in computer modeling studies.

## CONCLUSION

The kinetic hydrate inhibition performance of homopolymers and copolymers of the 5-ring vinylic monomer 5-methyl-3-



**Figure 9.** SCC rocking cell tests results for PVMOX-2.4k and VP:VCap 1:1 at varying concentrations.

vinyl-2-oxazolidinone (VMOX) has been studied for the first time.

The low molecular weight PVMOX-2.4k homopolymer made using a chain transfer agent gave molecular weight  $M_n = 2400$  g/mol and had a cloud point at 2500 ppm of 73 °C in deionized water. Polymerization of VMOX and VCap gave a 100% yield of the VCap:VMOX 1:1 copolymer, but VMOX did not copolymerize with NIPMAm. The only polymer product was the PNIPMAm homopolymer.

The new VMOX polymers were investigated for KHI performance using slow constant cooling screening tests in rocking cells with a synthetic natural gas blend. At 2500 ppm, PVMOX-2.4k gave a better performance than PVP or PiPOx at a similar molecular weight but not as good as PVCap or VP:VCap 1:1. Isobutyl glycol ether was shown to enhance the KHI performance of PVMOX. PVMOX gave improved performance with increasing concentration but not as steep of an improvement as for VP:VCap 1:1. The results with PVMOX fit with past studies on nonamide-based polymers which showed a similar trend compared to VP:VCap 1:1 and other polyamides such as PNIPMAm. VMOX:VCap 1:1 gave a better KHI performance at 2500 ppm than PVMOX of similar molecular weight.

Further studies on VMOX polymers are in progress using other comonomers, other synergists, high salinity test conditions, and also with methane to form structure I gas hydrate as the thermodynamically preferred phase.

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.energyfuels.1c04417>.

<sup>13</sup>C NMR spectra for PVMOX-2.4k (PDF)

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## Notes

The authors declare no competing financial interest.

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