

Pushing the Known Performance Envelope of Kinetic Hydrate Inhibitors—Powerful Synergy of Trialkylamine Oxides with Acrylamide-based Polymers

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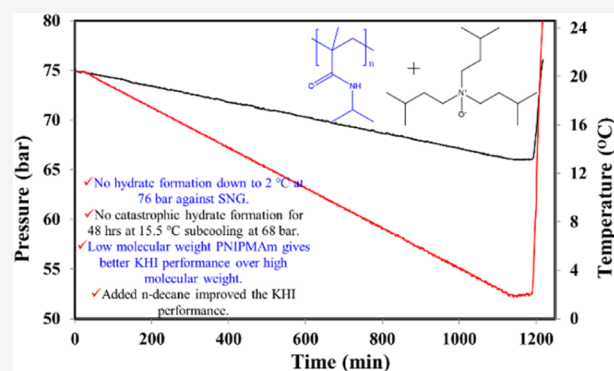
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ABSTRACT: Poly(*N*-isopropyl methacrylamide) (PNIPMAm) and copolymers are a class of commercially used kinetic hydrate inhibitors (KHIs) for deployment in oil and gas field production flow lines. Here, we report improvements of the KHI performance of PNIPMAm in the presence of various alkyl amine oxide (chain lengths C3–C6)-based synergists. A structure II hydrate-forming gas mixture was used to examine the KHI performance of PNIPMAm in slow constant cooling (ca. 1 °C/h) high-pressure (76 bar) rocking cell experiments. Blends of amine oxide as a synergist with PNIPMAm extended the hold time to first-detected gas hydrate formation. The KHI performance of PNIPMAm is improved going from propyl to butyl but is even better for pentyl, isopentyl, and isohexyl substituents on the amine-*N*-oxide. With added isobutyl glycol ether as the solvent, a solution of 1000 ppm low-molecular-weight (4700 g/mol) PNIPMAm (20.1% solution in isobutyl glycol ether) with 1000 ppm triisopentylamine oxide (TiPeAO) gave no detectable hydrate formation down to 2 °C. The same formulation in isothermal tests at 68 bar and 4 °C in the presence of externally added liquid hydrocarbon (*n*-decane) giving 15.5 °C subcooling gave no catastrophic hydrate formation for 48 h. These are the some of the best results we have seen in our steel rocking cells. Good synergy of TiPeAO with polyacryloylpyrrolidine was also observed but not as good as with PNIPMAm. The study also highlights that overdosing the polymer or synergist in the blends can worsen the KHI performance, probably by unwanted interaction between the two chemicals.



1. INTRODUCTION

Light hydrocarbon gases can form crystalline gas hydrate by becoming entrapped inside the cagelike water lattices under elevated pressure and low temperature. These conditions are often met in subsea gas and oil production flow lines. The possibility of restrictions or plugging of these lines by gas hydrates causes potential risk to the flow assurance. Kinetic hydrate inhibitors (KHIs) are a subclass of low-dosage hydrate inhibitors used for preventing gas hydrate plugging of upstream oil and gas production flowlines so that the fluids can be driven out before a catastrophic hydrate formation happens.^{1–6} KHIs are usually dosed at between 0.3 and 3.0 wt % and contain one or more water-soluble polymers as the main active components. KHIs can delay gas hydrate crystal nucleation and disrupt crystal growth depending on the subcooling, residence time, and a whole host of other factors. There is even evidence that KHIs can totally inhibit hydrate crystal growth up to a certain subcooling level.^{7–9}

Amphiphilic water-soluble polymers that contain both hydrophobic and hydrophilic functional groups are the main components for KHI formulations. The KHI performance of

any polymer depends on several factors including the method of synthesis, the molecular weight, the stereochemistry of the pendant groups, and the presence and interaction with other additives.¹⁰ Most current commercially available KHI polymers are polyamides. They include homopolymers and copolymers of *N*-vinylactams, *N*-isopropylmethacrylamide (NIPMAm), and hyperbranched poly(esteramide)s.^{3–6,10,11} These polymers can adsorb onto the surface of the crystal hydrate as a pseudo-guest through the polymeric pendant group and can prevent or delay nucleation of the hydrate crystal. However, polymers with other hydrophilic groups besides amides have also been shown to have good KHI performance, especially polyamine oxides.^{12–14} The exact KHI mechanism is not fully understood, but it may be due to the strong hydrogen bonding afforded by

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both amides and amine oxides with water molecules aiding gas hydrate nucleation inhibition and crystal growth inhibition.⁴

KHI polymers are formulated with solvents that not only reduce the viscosity to a pumpable level but can also enhance the inhibition performance. These solvents are mostly oxygenated solvents and include alcohols, ketones, glycol ethers, and esters.^{15–19} Recently, we found that PNIPMAm synthesized in *n*-butyl glycol ether (*n*BGE) or *iso*-butyl glycol ether (*i*BGE) as the reaction solvent performed better than PNIPMAm synthesized in isopropyl alcohol or monoethylene glycol.²⁰ A range of other additives can also be used.²¹ These include quaternary ammonium and phosphonium salts, ionic liquids, amine oxides, various surfactants, and water-soluble polymers such as polyglycols, polyethyleneoxide, polyamines, and polyetheramines.^{22–31} These enhancers are often called synergists. The definition of synergy is the interaction or cooperation of two or more substances to produce a combined effect *greater* than the sum of their separate effects. Synergists can help delay the hydrate crystal growth but can also act as hydrate antinucleators and thus help to increase the polymers' KHI performance and lower the treatment cost.

Monomeric amine oxides have been reported to be excellent synergists for *N*-vinyl caprolactam polymers with a structure II hydrate-forming gas (the same as used in the present study).³² Trialkylamine oxides with *n*-propyl, *n*-butyl, *iso*-pentyl, or *n*-pentyl showed good synergy, with tri(*n*-pentyl)amine oxide giving the best results. However, as far as we are aware, there are no reports of the synergy of amine oxides with poly(*N*-alkylmethacrylamide)s, such as polymers of NIPMAm. Tetrabutylphosphonium bromide has been shown to exhibit strong synergy with poly(*N*-isopropylacrylamide) on structure I hydrate.^{33,34}

Here in this work, we aimed at an evaluation of the possible synergistic effects of different trialkylamine oxides on the KHI performance of the PNIPMAm homopolymer in high-pressure rocking cells using a synthetic natural gas (SNG) mixture. The amine oxide giving the highest synergistic effect was also tested for synergism with a lower-molecular-weight PNIPMAm as well as with polyacryloylpyrrolidine (PAPYD). In some tests, *i*BGE was added as a solvent synergist since KHI formulations for use in the field will be formulated in the solvent.

2. EXPERIMENTAL SECTION

2.1. Materials. PNIPMAm (Mw 43,100 g/mol, PDI 1.7 and Mw 4700 g/mol, PDI 1.6 by GPC analysis) was synthesized by the literature method.¹⁹ PAPYD (Mw 10,000 g/mol) was kindly donated by Nippon Shokubai Co., Ltd, Japan, synthesized from the acryloylpyrrolidine monomer using a free radical polymerization method as previously reported.³⁵ Tri-*n*-pentylamine, triisopentylamine, and *i*BGE were obtained from TCI, Europe. Tri-*n*-propylamine and tri-*n*-butylamine were obtained from Sigma Aldrich. The synthesis protocol of 4-methyl-*N*-(4-methylpentyl)-*N*-pentylpentan-1-amine and trialkylamine oxides has been described previously.³² In this study, we synthesized tri-*n*-propylamine oxide (TnPrAO), tri-*n*-butylamine oxide (TnBAO), tri-*n*-pentylamine oxide (TnPeAO), triisopentylamine oxide (TiPeAO), and 4-methyl-*N*-(4-methylpentyl)-*N*-pentylpentan-1-amine oxide [nPe(*i*Hex)₂AO]. Low-molecular-weight PNIPMAm was synthesized and kept in *i*BGE without any workup, meaning the polymer was kept in the *i*BGE reaction solvent as a 20.1 wt % solution of polymer in *i*BGE, denoted as PNIPMAm-2 and tested for KHI performance directly assuming 100% conversion of the monomer. For PNIPMAm-1b and PAPYD-1b, we made a 20.1 wt % solution of respective polymers, obtained after work up and purification, by dissolving the polymer powder in *i*BGE. Figure 1 represents the chemical structures of synthesized PNIPMAm and

PAPYD. The general structure of trialkylamine oxides, used as synergists in this study, is given in Figure 2.

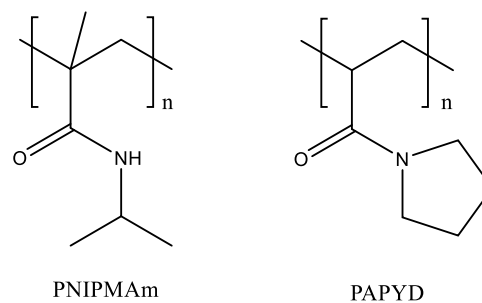


Figure 1. Chemical structure of PNIPMAm and PAPYD.

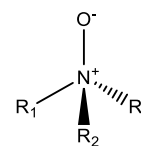


Figure 2. General chemical structure of trialkylamine oxides.

2.2. KHI Performance Tests in High-Pressure Rocking Cells.

To determine the KHI performance ranking of the acrylamide-based polymers, we used a set of five high pressure steel rocking cells, each with a volume of 40 mL, and a steel ball for agitation supplied by PSL Systemtechnik GmbH, Germany (Figure 3). We used a SNG mixture



Figure 3. KHI test equipment showing the steel rocking cells placed in a cooling bath.

as the gas hydrate formation material, whose thermodynamically stable phase is structure II hydrate. This SNG composition is given in Table 1. We used our standard slow constant cooling (SCC) test method which we have used in many previous studies using this equipment.^{22–25} It allows the reader to compare the results to many other classes of additives tested in our laboratories by giving a rough screening of the KHI performance. A study recently showed that slow ramped cooling experiments gave good reproducibility and recommended lowering the temperature by 0.5 °C every 3 h.²⁶ However, KHI experiments at this rate could take several days for good

Table 1. Composition of the SNG Mixture

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

additives. We believe the cooling rate (1 °C/h) in our method is a good enough compromise to screen new additives.

The pressure was approximately 76 bar at the start of each SCC experiment. At this pressure, the average equilibrium temperature (T_{eq}) of 20.2 ± 0.05 °C was obtained from five repeat tests by using the standard laboratory dissociation experiments, which agrees very well with the T_{eq} value of 20.5 °C calculated from Calsep's PVTSim software.^{22,27,28}

The SCC procedure was as follows:

- 1 20.0 mL of KHI in aqueous solution was loaded to each cell
- 2 The system was first vacuumed by a pump and then purged with around 5 bar of SNG to remove the air in the cells. When the pressure of the cells decreased to the atmosphere level, the vacuum procedure was applied once more.
- 3 Approximately 76 bar SNG mixture was loaded to the cells at a temperature of 20.5 °C.
- 4 The cells were cooled down gradually from 20.5 to 2 °C at a rate of 1 °C/h and were rocked to make the solution distributing evenly.
- 5 The temperature and pressure data for each cell were recorded by the temperature and pressure sensors during the cooling procedure.

A typical graph of pressure–time and temperature–time from all five cells in one experiment is shown in Figure 4. We determine the

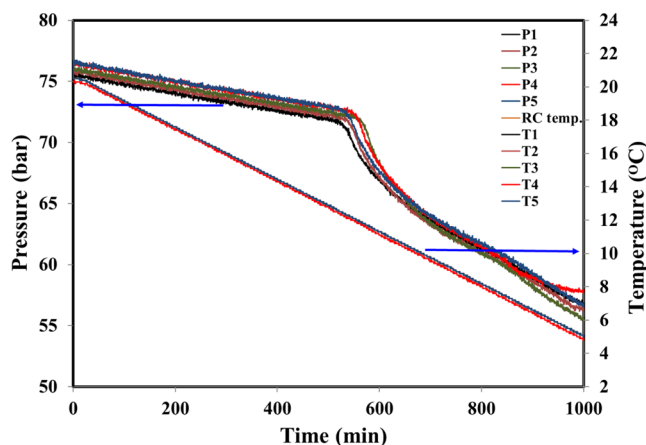


Figure 4. Typical pressure–time and temperature–time graphs of all five cells obtained from a SCC KHI experiment. This example is for 1000 ppm PNIPMAm (Mw 43100 g/mol, powder).

gas hydrate onset temperature (T_o) and the gas hydrate rapid formation temperature (T_a) from the corresponding pressure changes. Figure 5 gives the graphical representation for data from one cell. In Figure 5, there is a slight pressure drop at the very beginning as some of the SNG mixture dissolves in the aqueous phase. With the temperature gradually cooling down, the pressure–time graph should then be a fixed slope line without gas consumption in the cell as it is a closed system. However, the pressure drops at 12.5 °C (T_o), which means some detectable amount of SNG mixture is incorporated into solid gas hydrates at this temperature and time. Then, at 12.2 °C (T_a), the quickest pressure drop rate occurs, and this means that the gas

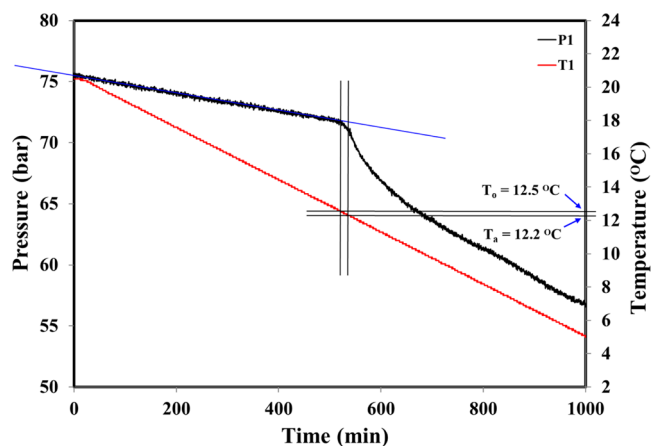


Figure 5. Example of T_o and T_a calculation in a standard constant cooling KHI experiment. 1000 ppm PNIPMAm (Mw 43,100 g/mol, powder).

hydrate forms at its fastest. The degrees of scattering in T_o values ($\leq 20\%$) and T_a values ($\leq 15\%$) are due to the stochastic nature of gas hydrate formation and are as expected from previous studies.^{29,30}

We also used our standard isothermal test method to compare the KHI performance of PNIPMAm in the presence of a synergist against time at a fixed temperature (4 °C). The standard isothermal test procedure follows the same first three steps as the SCC described above. Then, the test method proceeds as follows:

- 1 The cells were cooled down from 20.5 to 4 °C within 2 h, and the rocking was continued for another 48 h at 4 °C. The pressure was approximately 68 bar at this temperature, and the subcooling was approximately 15.8 °C. When 1 mL of decane was also added to the cells, the subcooling was approximately 15.5 °C.³⁶
- 2 The time and pressure data for each cell were recorded during the whole procedure.

A typical graph of pressure–time and temperature–time from all five cells in one isothermal experiment is shown in Figure 6. We determine the gas hydrate onset time (t_o) and the gas hydrate rapid formation time (t_a) from the corresponding pressure changes.

Figure 7 shows the graphical representation for the data of isothermal test from one cell in Figure 6 that showed a fast pressure drop. In Figure 7, there is a pressure drop with a fixed slope line, with

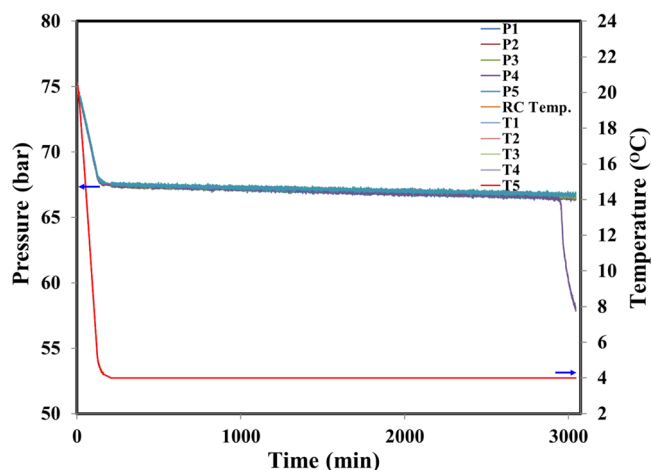


Figure 6. Typical pressure–time and temperature–time graphs of all five cells obtained from an isothermal KHI experiment. This example is for 500 ppm PNIPMAm (Mw 4700 g/mol, 20.1% solution in iBGE) and 1000 ppm TiPeAO with 1 mL of *n*-decane in each cell.

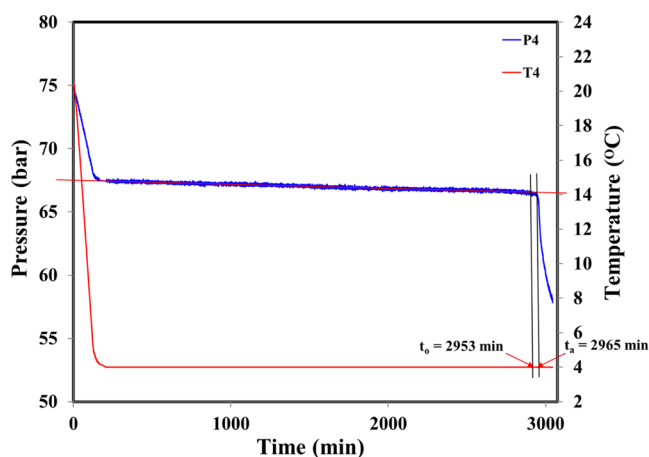


Figure 7. Example of t_o and t_a calculation in an isothermal KHI experiment. This example is for 500 ppm PNIPMAm (Mw 4700 g/mol, 20.1% solution in *i*BGE) and 1000 ppm TiPeAO with 1 mL of *n*-decane in each cell.

the temperature gradually cooling down from 20.5 to 4 °C and becoming constant at 4 °C. Afterward, any pressure drop means some detectable amount of the SNG mixture is incorporated into solid gas hydrates at this time, which is denoted as the gas hydrate onset time (t_o). Then, the quickest pressure drop rate occurs, and that corresponding time is denoted as the gas hydrate rapid formation time (t_a).

3. RESULTS AND DISCUSSION

All SCC KHI test results of PNIPMAm in the presence of different amine oxide synergists plus results with deionized

water (DIW) only and PNIPMAm alone are summarized in Table 2. In some SCC tests, we added *i*BGE as the solvent which is known to boost the performance of PNIPMAm.¹⁹ Pure PNIPMAm or PAPYD without the solvent is denoted with suffix -1a, whereas polymers in the *i*BGE solvent are denoted with suffix -1b. Each average T_o value and average T_a value was calculated from at least five standard constant cooling tests. The T_o value denotes the temperature at which the first macroscopic detectable gas hydrate is formed in a solution. We have equated the KHI performance of polymer solutions mostly based on their T_o values. Thus, the lower the T_o value of any test solution, the better the KHI performance. $T_o - T_a$ values can give some measure of the ability of the KHI to arrest crystal growth, but comparisons must be done with caution if the T_o values differ significantly.

Deionized water gave hydrate formation at an average T_o value of 16.9 °C, and PNIPMAm (Mw 43,100 g/mol, PNIPMAm-1a) alone gave an average $T_o = 7.8$ °C with 5000 ppm, $T_o = 9.9$ °C with 2500 ppm, and 12.2 °C with 1000 ppm concentration. From Table 2, it can be observed that the addition of different amine oxide synergists to PNIPMAm gave a wide range of enhanced KHI performance compared to the individual performance of the polymer. The improvement depends on the polymer molecular weight distribution, the size of the alkyl group in the amine oxides, and the concentrations used. Initially, we attempted to determine the synergistic KHI performance of amine oxides with 5000 ppm PNIPMAm-1a in DIW. We found that the onset temperature was quite low (7.8 °C) using PNIPMAm alone at this concentration. This made it difficult to compare the best amine oxides as they all gave very

Table 2. Summary of SCC KHI Test Results (NH Means No Pressure Drop Due to Hydrate Formation)

polymer	Mw (g/mol)	polymer conc. (ppm)	synergist	synergist conc. (ppm)	T_o (av.) °C	T_a (av.) °C	$T_o - T_a$ (av.) °C
PNIPMAm-1a	43,100 (powder)	1000	TiPeAO + 4000 ppm <i>i</i> BGE	2500	16.9	16.8	0.5
				2500	15.2	13.8	1.4
				2500	12.2	11.8	0.4
				2500	11.3	10.7	0.6
				1000	7.6	7.1	0.5
				2500	4.8	4.4	0.4
				2500	3.3	2.6	0.7
				2500	3.4	3.2	0.2
				2500	3.3	3.0	0.3
				2500	9.9	9.6	0.3
PNIPMAm-1b	43,100 (20.1% in <i>i</i> BGE)	2500	TnBAO	1000	6.5	6.1	0.4
				2500	4.5	3.9	0.4
				5000	2.7	<2.0	
				5000	7.8	7.6	0.3
				2500	5.4	4.9	0.5
				1000	8.6	8.0	0.6
				500	12.0	11.2	0.8
PNIPMAm-2	4700 (20.1% in <i>i</i> BGE)	2500	TiPeAO	2500	4.2	3.7	0.5
				1000	7.3	6.7	0.6
				1000	NH	NH	
				1000	10.2	9.8	0.4
				500	3.5	3.2	0.3
				500	9.6	9.1	0.5
PAPYD-1a	10,000 (powder)	2500	TiPeAO	2500	5.8	5.4	0.4
				1000	4.2	3.1	1.1
PAPYD-1b	10,000 (20.1% in <i>i</i> BGE)	500	TiPeAO	1000	5.3	4.4	0.9
				2500			

low T_o values. So, to compare the synergistic effect of various amine oxides, we had to reduce the polymer concentration.

We halved the polymer concentration to 2500 ppm but soon realized that the onset temperatures with 5000 ppm TnBAO were still too low to allow comparison with other good synergists. This was a good sign of powerful synergy. Table 2 shows that 2500 ppm PNIPMAm-1a has the average T_o value of about 6.5, 4.5, and 2.7 °C with 1000, 2500, and 5000 ppm TnBAO synergist concentration, respectively. Next, we carried out tests with a solution of 1000 ppm PNIPMAm-1a and 1000 ppm TnBAO which gave an average T_o value of about 7.6 °C. Therefore, we continued with testing using 1000 or 500 ppm polymer with 1000 or 2500 ppm synergist for better comparison.

Our previous studies showed that the size and shape of the hydrophobic groups are critical for optimal KHI performance.³⁷ Therefore, we investigated the KHI performance of PNIPMAm in the presence of more hydrophilic and hydrophobic alkyl groups containing amine oxides. We discovered that the tripentylated amine oxides (TnPeAO and TiPeAO) as well as nPe(iHex)₂AO are more powerful synergists than TnBAO, whereas TnPrAO was the worst synergist in this study. For example, we can see in Figure 8 that

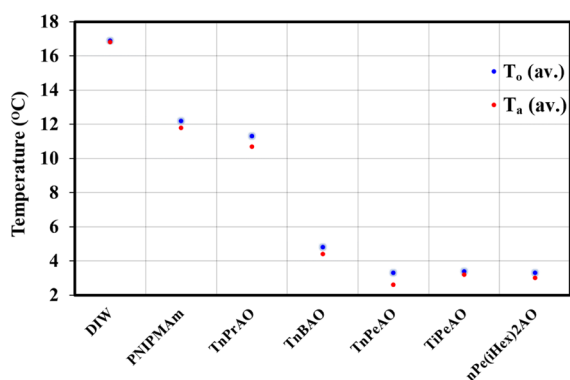


Figure 8. Graphical display of the synergetic effect of 2500 ppm of different amino oxides with 1000 ppm PNIPMAm-1a.

1000 ppm PNIPMAm-1a mixed with 2500 ppm different amine oxides shows the average T_o value at about 11.3 °C for TnPrAO, about 4.8 °C for TnBAO, about 3.4 °C for TiPeAO, about 3.3 °C for TnPeAO, and about 3.3 °C for nPe(iHex)₂AO. The synergistic effect of TnPrAO on the KHI performance of PNIPMAm is poor because here the alkyl substituent group is too short and not sufficiently hydrophobic. A longer alkyl chain than C3 is necessary for a significant synergistic effect of amine oxide with PNIPMAm.

From Figure 8, we can see that the average T_o values for 1000 ppm PNIPMAm-1a with 2500 ppm of the three pentylated synergists were about 1.5 °C lower than for TnBAO (and up to 8.0 °C lower than for TnPrAO), a statistically significant difference from *t*-tests ($p < 0.05$ in all cases), and there is no statistically significant difference between the synergism results of TiPeAO, TnPeAO, and TnPeAO.³⁸ Tri-*n*-hexylamine oxide alone was not tested due to negligible water solubility.³²

Molecular modeling on quaternary ammonium salts has shown that butyl or pentyl groups can occupy incomplete $5^{12}6^4$ cages on the 1,1,1 structure II hydrate surface.² As known for quaternary ammonium salts such as tetra(*n*-butyl)ammonium

bromide (TBAB) and tetra(*n*-pentyl)ammonium bromide, amine oxides such as tributyl amine oxide (TBAO) are also known to form clathrate hydrates.³⁹ Therefore, it was assumed that they also might make good hydrate crystal growth inhibitors. We assume that this inhibition mechanism for amine oxides includes penetration of alkyl groups into hydrate cavities and also includes hydrogen bonding between the amine oxide group and latticed water molecules on the growing hydrate particle surfaces. In addition, the trialkylamine oxides can hinder hydrate nucleation by the hydrophobic alkyl groups perturbing the bulk water phase. The larger alkyl group will have the strongest effect, provided solubility in the aqueous phase is maintained.³²

The same general trend of increasing hydrophobicity of the amine oxides giving increased synergy was also observed with tetraalkyl quaternary ammonium salts with PVCap.⁴⁰ In that study, tetra(*n*-hexylammonium bromide (THexAB) gave KHI synergism with PVCap superior to that of TBAB, even though TBAB was a better THF hydrate crystal growth inhibitor. This was taken as an indication that direct adsorption of KHI additives onto hydrate crystal surfaces may not be the only KHI mechanism operating. It was suggested that the more hydrophobic THexAB is perturbing the nucleation of hydrate more than the less hydrophobic TBAB. In the same way, the extra hydrophobicity and concomitant water perturbation may be at least partly why the three amine oxides [TnPeAO, TiPeAO, or nPe(iHex)₂AO] give greater synergy with PNIPMAm than with TBAO.

From the results of Table 2, we can conclude that amine oxide synergists having substituent chain lengths of C5–C6 give better KHI performance of PNIPMAm than substituent chain lengths of C3–C4. That means as the hydrophobicity of the alkyl substituents of the amine oxides increases, the synergism effect improves, which helps PNIPMAm to give better KHI performance.

Then, we checked the KHI performance of POPYD in the presence of a pentylated amine oxide synergist (we used TiPeAO as an example) to compare its performance with PNIPMAm-1a. 2500 ppm POPYD (Mw 10,000 g/mol, powder, POPYD-1a) alone gives an average T_o value at about 9.6 °C, and it gives an improved performance with an average T_o value of about 5.8 °C in the presence of 2500 ppm TiPeAO, which is 2.4 °C higher than a lower concentration of PNIPMAm-1a (1000 ppm) and TiPeAO (2500 ppm). Hence, PNIPMAm-1a gives better KHI synergy performance with TiPeAO than POPYD. Our previous studies showed that the molecular weight, size, and shape of the hydrophobic groups in a polymer are critical for optimal KHI performance.¹⁹ So, for better comparison of KHI performance between PNIPMAm and POPYD, we chose a comparable molecular weight PNIPMAm (Mw 4700 g/mol, 20.1% solution in iBGE, denoted as PNIPMAm-2 afterward) and tested its KHI performance alone or in the presence of a synergist. Then, we tested 500 ppm POPYD (20.1% in iBGE, denoted as POPYD-1b afterward) + 1000 ppm TiPeAO. (If we used 1000 ppm POPYD, we would run the risk of getting $T_o < 2$ °C and then we cannot compare the two results if both are < 2 °C.) The result with the blend gave an average $T_o = 4.2$ °C indicating it has slightly worse performance than PNIPMAm-2 ($T_o = 3.5$ °C). We presume that the reduced side group flexibility and the lower hydrogen bond formation nature of POPYD (with no N–H proton), compared to PNIPMAm, are possible reasons behind the weaker KHI performance.

PNIPMAm made and kept in *i*BGE has previously been reported to perform better than the corresponding powder polymer when the synergistic effect of *i*BGE had been considered. Our previous study shows that the combined effect of the low molecular weight of PNIPMAm and the presence of *i*BGE can give improved KHI performance.¹⁹ The synergism effect of the *i*BGE may be associated either with stabilizing the PNIPMAm at the gas hydrate–water interface or significantly enhancing the absorption of the polymer on the hydrate growth sites rather than on hydrate nucleation sites. In this study, *i*BGE also plays a significant role in the improvement of KHI performance of high-molecular-weight PNIPMAm (Mw 43,100 g/mol, 20.1% solution in *i*BGE, denoted as PNIPMAm-1b) as it gives around 3.6 and 4.5 °C more subcooling than 1000 and 2500 ppm PNIPMAm-1a alone, respectively. Figure 9 represents a graphical comparison

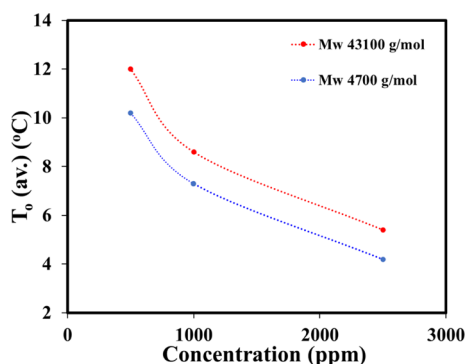


Figure 9. Comparison study of KHI performance at different concentrations of low- and high-molecular-weight PNIPMAm in the same condition (20.1% solution in *i*BGE).

of KHI performance of both high- and low-molecular-weight PNIPMAm in *i*BGE, which confirms that low-molecular-weight PNIPMAm gives average T_o values about 4.2, 7.3, and about 10.2 °C with 2500, 1000, and 500 ppm of polymer concentration, respectively, which is better (around 1.2–1.8 °C more subcooling) than high-molecular-weight PNIPMAm at the same polymer concentration. Likewise, *i*BGE also helps to improve the KHI performance of 2500 ppm PAPYD-1b with 4.3 °C more subcooling than PAPYD powder (denoted as PAPYD-1a) alone.

For a concentration of 2500 ppm PNIPMAm-2 in the presence of 2500 ppm TiPeAO, we did not observe any detectable hydrate formation down to 2 °C. We even got the

same result with 1000 ppm of both polymer and synergist solution. Hence, both this concentration of the polymer and the synergist are enough to prevent gas hydrate formation with the extra synergistic effect of *i*BGE. So, we reduced the polymer concentration further to 500 ppm and found an average T_o value at about 3.5 °C in the presence of 1000 ppm TiPeAO, which is equal to the KHI performance of 1000 ppm PNIPMAm-1a in the presence of 2500 ppm TiPeAO. This result confirms that low-molecular-weight PNIPMAm gives better KHI performance than high-molecular-weight PNIPMAm under the same conditions.

In Table 2, another interesting thing to notice is that despite having a higher molecular weight (43,000 g/mol), PNIPMAm-1b has KHI performance similar to that of PAPYD-1b (10,000 g/mol) at 2500 ppm without any synergist. The similar performance of these two polymers when tested alone with no synergists is down to three factors: (1) the different size and shape of the pendant alkylamide groups, (2) the methyl groups in the backbone of PNIPMAm-1b, and (3) the molecular weight distribution.^{2,4} Previous work suggests that factors 1 and 2 improve the performance of PNIPMAm relative to PAPYD, whereas the higher molecular weight is detrimental. We presume these competing factors cancel each other out to give polymers of similar performance.

Furthermore, to check that there is no significant synergy directly between trialkylamine oxides and *i*BGE, we have tested the KHI performance of a mixture of 2500 ppm TiPeAO and 4000 ppm *i*BGE without any polymer in a standard SCC test at 76 bar. This test gave average T_o at about 15.2 °C indicating poor performance. Our previous study also shows that 5000 ppm tri-*n*-butylamine oxide has the average T_o value of about 14.5 °C, and 5000 ppm tri-*n*-pentylamine oxide has the average T_o value of about 13.9 °C which also verifies that trialkylamine oxides alone cannot act as a good KHI.³²

Due to the very low onset temperatures in the SCC tests, we conducted isothermal tests at 68 bar and 4 °C. All standard isothermal test results of both high- and low-molecular-weight PNIPMAm in the presence of different amine oxide synergists are summarized in Table 3. Isothermal tests can give more scattering in the data than SCC tests (30–40% compared to 15–20%) but are still useful to give a rough gauge of KHI performance if repeated several times to get some statistical significance. Here, each average t_o value and average t_a value were calculated from at least five standard isothermal tests. The t_o value denotes the time duration from the beginning of a test at which the first macroscopic detectable gas hydrate is formed

Table 3. Summary of Isothermal KHI Test Results of PNIPMAm (with Varying Mw) with Synergist

polymer/Mw (g/mol)	conc. ppm	synergist	conc. ppm	solvent	conc. ppm	t_o (av.) min	t_a (av.) min
PNIPMAm-1a/43100	2500					<120	<120
	2500	TnPeAO	5000	<i>n</i> BGE	5000	228	279
	2500	TiPeAO	5000			401	420
	2500	TiPeAO	5000	<i>n</i> BGE	5000	954	979
	2500	nPe(iHex) ₂ AO	5000	<i>n</i> BGE	5000	1247	1482
PNIPMAm-1b/43100 (20.1% in <i>i</i> BGE)	1000	TiPeAO	1000			NH	NH
	500	TiPeAO	1000			270	347
PNIPMAm-2/4700 (20.1% in <i>i</i> BGE)	500	TiPeAO	1000			329	346
	500	TiPeAO	1000	decane	1 mL in each cell	2953	2965
	1000	TiPeAO	1000			2171	2205
	1000	TiPeAO	1000	decane	1 mL in each cell	NH	NH
	2500	TiPeAO	2500			872	886

in a solution at a constant temperature, so we have equated the KHI performance of polymers mostly based on its t_0 values. As like standard cooling experiments, the first sign of pressure drops in a standard isothermal test that is not because of the drop in temperature is taken as the initial evidence of gas hydrate formation. However, exact nucleation of gas hydrate formation may have already started sometime earlier but was undetectable on a macroscopic scale.

The first observation we made was that although in SCC experiments, high-molecular-weight PNIPMAm gave good KHI performance in the presence of TnPeAO, TiPeAO, or nPe(iHex)₂AO synergist, these polymer and synergist combinations show poor or moderate performance in the isothermal test at 4 °C. This was true even in the presence of *n*BGE as a solvent synergist. *n*BGE has been shown to be a good solvent synergist for many KHI polymers, also for PNIPMAm.^{18,19} Therefore, we used *n*BGE as a solvent synergist to improve the KHI performance of high-molecular-weight PNIPMAm and amine oxide solutions. However, the results showed that *n*BGE did not improve the KHI performance significantly. The best performance we got for PNIPMAm-1a with 2500 ppm concentration is 954 min as average t_0 in the presence of 5000 ppm of both TiPeAO as the synergist and *n*BGE as the solvent synergist and 1247 min as average t_0 in the presence of 5000 ppm of both nPe(iHex)₂AO and *n*BGE. Thus, the KHI performance of PNIPMAm was boosted as the branching or hydrophobicity of the substituent groups in amine oxide rose from the *n*-pentyl to isopentyl to isohexyl group.

We also used *i*BGE as a solvent synergist in isothermal tests. It worked considerably better than *n*BGE giving a strong improvement of KHI performance of PNIPMAm and amine oxide solutions. For example, a solution of 1000 ppm PNIPMAm-1b in the presence of 1000 ppm TiPeAO synergist gave excellent KHI performance. In this case, we did not observe the catastrophic hydrate formation over 48 h at 4 °C, but we noticed a very tiny pressure fall during the whole experiment period (<1 bar) and in each cell, indicating that this was not a leak. This suggests that gas hydrate nucleation might have started there, but these optimal concentrations of polymer and synergist were able to disrupt further catastrophic crystal growth.

We also observed good KHI performance with PNIPMAm-2 for the same combination of polymer and synergist concentration with t_0 of 2171 min which is better than 500 ppm polymer and 1000 ppm synergist solution (t_0 of 329 min) and even also surprisingly better than the higher concentration (2500 ppm) of both polymer and synergist solution (t_0 of 872 min). This result indicates 1000 ppm polymer and 1000 ppm TiPeAO are the optimal concentrations to prevent the catastrophic crystal growth in an isothermal test for both high- and low-molecular-weight PNIPMAm. We assume there must be some interaction between the polymer and the synergist at the higher concentrations tested which lowers the KHI efficacy.

We were also interested to check the effect of *n*-decane as an artificial liquid hydrocarbon phase on the KHI performance of PNIPMAm with the amine oxide synergist. We added 1 mL of *n*-decane to each cell of the polymer and amine oxide solution before the isothermal test. Moving from a two-phase (solid and gas) system to a three-phase (solid, liquid, and gas) system can change the polymer as well as the synergist composition, their structure into the aqueous phase, the phase partitioning, and also the system equilibrium.⁴¹ As Table 3 shows, for 500 ppm

PNIPMAm-2 and 1000 ppm TiPeAO solution, addition of decane improved the KHI performance, with the average t_0 value increasing from 329 min without decane to 2953 min. A mixture of 1000 ppm PNIPMAm-2 and 1000 ppm TiPeAO solution also gave an improved KHI performance with the average t_0 value of 2171 min without decane but no detectable hydrate formation up to 48 h with decane.

4. CONCLUSIONS

A series of aliphatic trialkylamine oxides have been investigated as synergists to improve the KHI performance of PNIPMAm and POPYD in high-pressure rocking cells using a SNG mixture. Sufficient hydrophobicity of the amine oxide is required to give reasonable improvement of the KHI performance of the polymer, but the best THF hydrate crystal growth inhibitor (TBAO) is not the best synergist. This is the same trend observed with tetraalkyl quaternary ammonium salts with PVCap.⁴¹ This gives further support to a KHI mechanism which is not solely based on direct crystal growth inhibition by surface adsorption.

Our result shows that a longer alkyl chain than C3 is necessary for a significant synergistic effect of amine oxide with PNIPMAm or POPYD. The best KHI performance of PNIPMAm was observed for the amine oxide synergists which have substituent chain lengths of C5–C6. The synergistic effect of amine oxides improved in the order TnPrAO < TnBAO ~ TiPeAO ~ TnPeAO < nPe(iHex)₂AO. The best SCC test result was 1000 ppm PNIPMAm-2 and 1000 ppm TiPeAO with no detectable hydrate formation down to 2 °C. TiPeAO gave better synergy with PNIPMAm than with POPYD. TiPeAO also gave better synergy with the lower molecular weight of the two PNIPMAm polymers (4700 vs 43,100 g/mol).

The isothermal study gave similar trends as the SCC study plus more information. The isothermal study showed that the solvent synergism of *i*BGE is better than *n*BGE in a solution of PNIPMAm with TiPeAO, which suggests that a branched alkyl group has better synergism effect than a straight alkyl group.

The effect of added *n*-decane as the liquid hydrocarbon phase improved the KHI performance of PNIPMAm in *i*BGE plus TiPeAO. A blend of 1000 ppm PNIPMAm (Mw 4300) in *i*BGE with 1000 ppm TiPeAO gave no fast hydrate formation with added decane for over 48 h at 68 bar and 4 °C (ca. 15.5 °C subcooling). This is one of the best results we have seen in rocking cell experiments. We believe these results are probably pushing the boundaries for known KHI performance to greater subcooling. Interestingly, higher dosages of KHI did not give good results. This suggests that unwanted polymer–synergist interactions may be taking place which lower the activity of the mixture to inhibit hydrate formation.

Further investigation to understand the KHI mechanism at the optimal concentration and structural interaction of the KHI inhibitors with gas hydrate cages at different concentrations of the polymer and the synergist are ongoing. We will also continue to investigate the synergism effect of amine oxides on the KHI performance of both low- and high-molecular-weight PNIPMAm against a structure I gas hydrate-forming system, saline solutions, and higher pressures.

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Notes

The authors declare no competing financial interest.

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