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N-Oxide Polyethers as Kinetic Hydrate Inhibitors: Side Chain Ring Size Makes the Difference

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ABSTRACT: The formation of gas hydrates in flow lines is one of the most severe problems for flow assurance in the gas and oil industry. Developing effective kinetic hydrate inhibitors (KHIs) to avoid the problem of gas hydrate formation has attracted widespread attention. In this study, a series of poly(glycidyl amine *N*-oxide)s (PGAOs) with 5−7-membered rings as side chains, poly(pyrrolidine glycidyl amine *N*-oxide)s (PPyrGAOs), poly(piperidine glycidyl amine *N*-oxide)s (PPiGAOs), and poly(azepane glycidyl amine *N*-oxide)s (PAzGAOs), with varying molecular weights, have been synthesized. The KHI performance of these glycidyl amine *N*-oxide polyethers has been evaluated in high-pressure rocking cells with the synthetic natural gas (SNG) mixture. The PGAOs with lower molecular weights gave better KHI performance, and at 2500 ppm, the best one gave an average T_o value of 9.8 °C (ΔT = 10.4 °C), which is on a par with polyvinylcaprolactam (PVCap). Even in high concentration of brine solution, none of the PGAOs showed a cloud point up to 95 °C. Employing molecular weights of around 4 kg/mol, the KHI performance of the PGAOs follows the following trend, correlating with the ring size: PPyrGAO < PPiGAO < PAzGAO. However, at higher molecular weight, the ring size of the pendant group did not affect the KHI performance of the PGAOs. PPiGAO with the smaller piperidine ring groups gave better inhibition effect than PAzGAO when the molecular weights were at approximately 8 kg/mol. In addition, the KHI performance of one of the best PAzGAOs was tested in the concentration range from 1000 to 5000 ppm, and an increase of the KHI performance with increasing concentration of polymer was observed. The amine *N*-oxide functional group is critical for the KHI performance of these polymers, as poly(pyrrolidine glycidyl amine)s (PPyrGAs) and poly(azepane glycidyl amine)s (PAzGAs) with amine groups instead of the *N*-oxide gave a negligible inhibitory effect.

INTRODUCTION

Gas hydrates are clathrate crystalline solids consisting of water crystal structures as well as physically trapped gas molecules, such as nitrogen, carbon dioxide, and light hydrocarbons like methane, ethane, and propane.[1−3] Structure I (sI) hydrate, structure II (sII) hydrate, and structure H (sH) hydrate can be formed at conditions of low temperature and high pressure. The temperature−pressure phase boundaries and type of gas hydrates formed will depend on the gas composition.[4]

The formation of gas hydrates is one of the biggest problems of gas and oil flow assurance, especially in offshore development.[5−7] If the temperature is low, such as in the subsea and cold climate operation area, gas hydrates are easy to form. Once gas hydrates form in the flow line or any other place in the production and transportation system, they tend to be difficult to remove. Thus, to avoid the problem of gas hydrate formation in gas and oil industry, the best strategy is to prevent gas hydrates from forming.

Many methods, including hydraulic methods, water removal, thermal methods, and chemical methods, have been proposed to prevent the formation of gas hydrates. Among these mentioned gas hydrate prevention methods, chemical methods, especially the method of injecting low-dosage hydrate inhibitors (LDHIs), are relatively more efficient and cost-saving.[8−10] Kinetic hydrate inhibitors (KHIs) belong to LDHI, as the effective dosage of KHI can be less than 5 wt %. Since the early 1990s, when the very first efficient KHI polyvinylpyrrolidone (PVP) was reported, hundreds of KHIs have been discovered. A few kinds of KHIs have been commercialized, such as *N*-vinylcaprolactam (VCap)-based homopolymers and copolymers, *N-iso*-propylmethacrylamide (NiPMAM) homopolymers and copolymers, and hyperbranched polyesteramides, and polyester pyroglutamates are also available commercially (Figure 1). Most reported KHIs and nearly all the current commercial KHIs are amide group-containing polymers.[11,12]

Recently, several series of nonamide polymers, such as poly(isopropenyloxazoline),[13] poly(vinylphosphonate) diesters,[14] poly(alkyl ethylene phosphonate)s,[15] poly(amine *N*-oxide)s,[16−18] poly(vinylsulfonamide)s,[19] poly(vinylaminal)s,[20] poly(sulfobetaine methacrylate)s,[21] and polysaccharides like starch, chitosan, and pectin,[11] have been reported to be excellent KHIs (Figure 2). Poly(amine *N*-oxide) nonamide KHIs have attracted increasing attention, due to the immense structural variability, their superior hydrophilicity, and, most importantly, the remarkable inhibition performance of amine *N*-oxide polymers. Reports showed that hyperbranched

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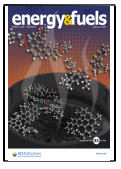

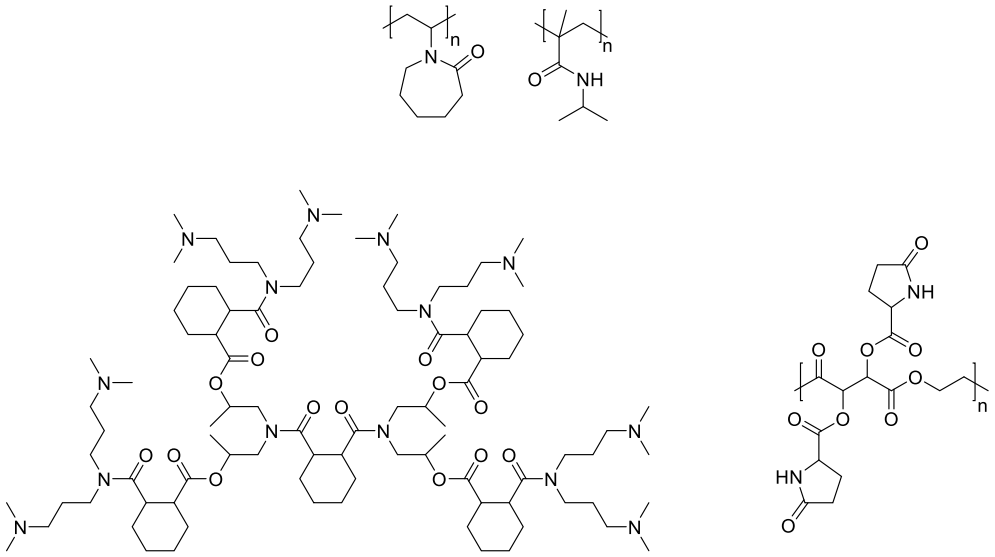

Figure 1. Structures of various commercial KHIs. Poly(*N*-vinylcaprolactam), PVCap (top left); poly(*N*-*iso*-propylmethacrylamide), PNiPMAM (top right); hyperbranched polyesteramide (bottom left); polyester pyroglutamate (bottom right).

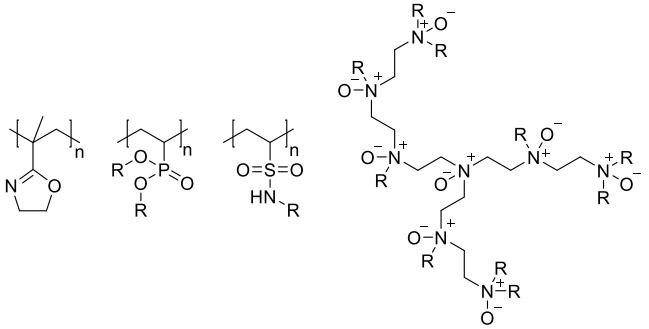

Figure 2. Structures of nonamide KHIs. From left to right: polyisopropenyloxazoline, poly(dialkyl vinylphosphonate)s, poly(vinylsulfonamide)s, and hyperbranched polyethylenimine-alkyl-amine *N*-oxides (HPEI-R-AOs). R = alkyl group.

polyethylenimine-alkyl-amine *N*-oxides (HPEI-R-AOs), especially those with large alkyl groups, can inhibit the formation of both sI and sII hydrates effectively.[17,22] Lately, Zhang et al. reported that poly(piperidine glycidyl amine *N*-oxide) (PIGAO) showed considerable KHI performance on sII hydrate. The best results were on par with the highly established commercial PVCap.[23] In addition, even in high-salinity solution, the PIGAOs gave no cloud point when heated up to 95 °C, while the cloud point of PVCap in aqueous solution is around 35 °C.[10,24,25] For many KHI series, the polymer with lower cloud point gave better inhibition performance.[26] Ring expansion to a 7-membered azepane ring for the pendant group is a key strategy to decrease the cloud point of the KHI polymer.[27,28] Thus, enlarging the six-membered ring of the PIGAOs may improve the inhibition performance of this poly(amine *N*-oxide) KHI series, which motivated this study. We also included polymers with the 5-membered pyrrolidine ring for comparison to the pyrrolidone ring found in several commercial *N*-vinylpyrrolidone-based KHI polymers.

In addition, previous studies showed that a larger size of the pendant cyclic groups of a KHI polymer can lead to better inhibition performance. For example, with the molecular weights (M_n) at around 4 kg/mol, poly(*N*-vinyl lactam)s gave an improved inhibition performance, when the size of the pendant ring groups increased from five to eight members.[28] Also, poly(3-methylene-2-piperidone) (3M2Pip) containing larger cyclic pendant groups was reported to be a better KHI inhibitor than poly(3-methylene-2-pyrrolidone) (3M2P).[27] At a molecular weight of approximately 20 kg/mol the polyvinylaminal with cyclohexyl groups gave better inhibition performance than its analogue with cyclopentyl groups.[20]

In this study we have synthesized a series of poly(glycidyl amine *N*-oxide)s (PGAOs) with varied cyclic imines, namely poly(pyrrolidine glycidyl amine *N*-oxide)s (PPyrGAOs), poly(piperidine glycidyl amine *N*-oxide)s (PPiGAOs), and poly(azepane glycidyl amine *N*-oxide)s (PAzGAOs), respectively (Figure 3). The molecular weights (M_n value) of these

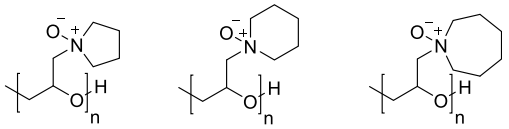

Figure 3. Structures of PPyrGAO (left), PPiGAO (middle), and PAzGAO (right).

PGAOs range from 1.4 to 8.5 kg/mol. The inhibition performance on sII hydrates of these synthesized PGAOs was evaluated by using synthetic natural gas (SNG) mixture in high-pressure rocking cells.

EXPERIMENTAL SECTION

Materials. All chemicals for the syntheses and characterization of monomers and polymers were purchased from Acros Organics, Fisher Scientific, Roth, Sigma-Aldrich, TCI, VWR, or Deutero GmbH. Epichlorohydrine and pyrrolidine were obtained in 99% purity from Acros Organics, and piperidine was obtained in 99% purity from Sigma-Aldrich; azepane was obtained in 98% purity from Alfa Aesar. Benzyloxyethanol and ethylene glycol monobutyl ether with purities of 98 or 99%, respectively, were purchased from TCI.

Instrumentation. ^{1}H NMR (300 MHz) and ^{13}C NMR (75 MHz) spectra were recorded on a Bruker Avance III HD 300 (5 mm BBFO-Probe with *z*-Gradient and ATM). Size exclusion chromatography (SEC) was typically carried out in *N*,*N*-dimethylformamide (DMF) at 50 °C, containing 1 g/mL lithium bromide with a flow rate of 1 mL/

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min on an Agilent 1100 Series, HEMA columns with 300/100/40 Å porosity, and Agilent G1362A RID as refractive index detector. Calibration was performed with poly(ethylene oxide) (PEG) standards by Polymer Standards Service (PSS, Mainz, Germany). SEC of in DMF-insoluble polymers was done at 40 °C in hexafluoroisopropanol containing 3 g/L potassium trifluoroacetate with a flow rate of 0.8 mL/min, using columns packed with modified silica (PFG columns) 100/1000 Å porosity and calibrated with poly(methyl methacrylate) (PMMA) standards by PSS.

Synthesis of Monomers. The syntheses of the glycidyl ether monomers were adapted from the literature synthesis of piperidine glycidyl amine.[29] In the following, the synthesis of azepane glycidyl amine (AzGA) is described exemplarily.

Azepane (15.0 mL, 1 eq, 0.13 mol) was kept at 0 °C by a water/ice bath, while 10.2 mL of epichlorohydrin (1 eq, 0.13 mol) was added dropwise under vigorous stirring. After addition, the mixture was stirred for 90 min at 0 °C. While the mixture was slowly allowed to reach room temperature, a cooled solution of 5.2 g of NaOH (1 eq, 0.13 mol) in 12 mL of water was added. After stirring overnight, the mixture was diluted with 50 mL of water and extracted three times with 50 mL of diethyl ether each time. The combined organic phases were dried over $MgSO_4$, and the solvent was removed under reduced pressure; subsequently, the product was isolated in high purity by distillation under reduced pressure in typical yields of 60−70%. AzGA was identified as a colorless liquid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.01 (dtd, J = 6.5, 3.8, 2.7 Hz, 1H, −C$\underline{H}$−), 2.78−2.54 (m, 1H, −C$\underline{H_2}$−CH−; 1 H, −CH−C$\underline{H_2}$−N−; 4H, −N(−C$\underline{H_2}$−CH_2)$_2$−), 2.48−2.38 (m, 1H, −C$\underline{H_2}$−CH−; 1H, −CH−C$\underline{H_2}$−N−), 1.69−1.43 (m, 8H, (C$\underline{H_2}$)$_4$). ^{13}C NMR (75 MHz, $CDCl_3$): δ 60.66 (−CH−$\underline{C}H_2$−N−), 56.06 (−N−($\underline{C}H_2$−CH_2)$_2$−), 50.99 (−$\underline{C}$H−), 45.13 (−$\underline{C}H_2$−CH−), 27.97 (−N−(CH_2−$\underline{C}H_2$)$_2$−), 26.94 (−N−(CH_2−CH_2−$\underline{C}H_2$)$_2$−).

Pyrrolidine glycidyl amine (PyrGA) and piperidine glycidyl amine (PiGA) were synthesized in a similar manner. However, for PyrGA, 1.5 equiv of epichlorohydrin and NaOH were used in the reaction, and stirring was reduced from overnight to 30 min; petroleum ether was used for the extraction procedure. In the synthesis of PiGA, the mixture was stirred for 2 h at 0 °C, and the NaOH solution was added after the mixture reached room temperature. The characterization data for PiGA was reported previously.[29] PyrGA was identified as a colorless liquid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.05 (dtd, J = 6.7, 4.0, 2.7 Hz, 1H, −C$\underline{H}$−), 2.77−2.68 (m, 1H, −C$\underline{H_2}$−CH−; 1 H, −CH−C$\underline{H_2}$−N−), 2.53 (tdd, J = 6.5, 4.7, 3.3 Hz, 4H, −N(−C$\underline{H_2}$−CH_2)$_2$−), 2.46 (dd, J = 5.0, 2.7 Hz, 1H, −C$\underline{H_2}$−CH−), 2.37 (dd, J = 12.8, 6.5 Hz, 1H, −CHC$\underline{H_2}$−N−), 1.79−1.71 (m, 4H, −N−(CH_2−C$\underline{H_2}$)$_2$−). ^{13}C NMR (75 MHz, $CDCl_3$): δ 58.50 (−CH−C$\underline{H_2}$−N−), 54.50 (−N−($\underline{C}H_2$−CH_2)$_2$−), 50.86 (−$\underline{C}$H−), 45.36 (−$\underline{C}H_2$−CH−), 23.36 (−N−(CH_2−$\underline{C}H_2$)$_2$−).

Polyether Synthesis. The synthesis of the novel polyethers consisted of two steps, adapted from a literature protocol for poly(piperidine glycidyl amine-*N*-oxide).[29] (1) The initiator ethylene glycol monobutyl ether (EGBE) (1 equiv) or benzyloxyethanol (BnO) (1 equiv), respectively, was combined with a solution of KO^{t}Bu (0.5 equiv) and 18-crown-6 (1 equiv) in a benzene/methanol 5:1 mixture in a dried Schlenk flask. After removal of the solvents, monomer was added, and the polymerization was carried out at 40 °C for 48−72 h. After purification by liquid−liquid extraction and removal of the solvents, the polymer poly(glycidyl amine) (PGA) was isolated. (2) The oxidation of PGA (1 equiv) was performed by addition of aqueous H_2O_2 solution (1.2 equiv) and stirring overnight at room temperature. After drying, fully oxidized poly(glycidyl amine *N*-oxide) (PGAO) was obtained in typical yields of 70−90%.

Kinetic Hydrate Inhibitor Performance Tests. The kinetic hydrate inhibitor performance tests of the synthesized glycidyl amine *N*-oxide polyethers were carried out in a high-pressure rocker rig, provided by PSL Systemtechnik, Germany. This high-pressure equipment contains five separate cells, so five parallel experimental results can be obtained from one testing process.[30,31] A synthetic natural gas (SNG) mixture (Table 1), which theoretically forms sII hydrate as the most stable phase, was used to supply the high pressure in the cells.

Table 1. Composition of SNG Mixture

component	mol %
nitrogen	0.11
n-butane	0.72
isobutane	1.65
propane	5
CO_2	1.82
ethane	10.3
methane	80.4

The hydrate onset temperature (T_o) and the rapid hydrate formation temperature (T_a) obtained from the slow constant cooling (SCC) tests were used to evaluate the kinetic hydrate inhibitor performance of the polymers in this study. The brief procedure of the SCC test is as follows: 20 mL of KHI solution was loaded into the five test cells, each of which has a maximum inner volume of 40 mL. Usually, KHI solutions were made at least 24 h before the SCC tests to ensure complete dissolution of the polymers. The five cells were placed sequentially in the water bath of the rocker rig. A procedure of repeated vacuum pumping and filling with SNG mixture was applied to remove air from the cells. Approximately 76 bar of SNG mixture was added to each cell, when the temperature for each cell had stabilized at 20.5 °C. The inlet/outlet value of each cell was then switched off. Subsequently, the temperature of the cooling bath was slowly decreased with the cooling rate set at 1 °C/h. During the constant cooling period, the cells were rocked (20 full swings/min, maximum 40°) for agitation. The temperature and pressure data for each cell were recorded and saved in a local computer. Figure 4 shows an example of the temperature−time and pressure−time curves for all the five cells from one SCC test process.

Figure 5 shows an example of how to analyze the hydrate onset temperature (T_o) and the rapid hydrate formation temperature (T_a) from the pressure and temperature curves. As the temperature constantly decreased, the pressure in the cell also decreased linearly. When the gas molecules in the cell were consumed to form gas hydrates, the pressure curve deviated from the original linear track. The temperature at the point of the first pressure deviation (P_o) was identified as T_o. The temperature at the point of the fastest pressure deviation (P_a) was called T_a.

RESULTS AND DISCUSSION

After we utilize the anionic ring opening polymerization (AROP) of the epoxide monomers pyrrolidine glycidyl amine (PyrGA), piperidine glycidyl amine (PiGA), and azepane glycidyl amine (AzGA) as well as the two different initiators benzyloxyethanol (BnO) and ethylene glycol monobutyl ether (EGBE), a series of poly(glycidyl amine)s were prepared and oxidized to obtain poly(glycidyl amine *N*-oxide)s (PGAOs). The preparation of the monomers was performed in analogy to known literature procedures by the reaction of epichlorohydrin with the corresponding amine.[29] To the best of our knowledge, PyrGA and AzGA were used as intermediates in organic reactions but have never been polymerized to date.[32] Both ^{1}H NMR and ^{13}C NMR spectra of PyrGA and AzGA are given in Figures S1−S3. Via the crown ether-assisted AROP of the monomers, the corresponding polyethers were synthesized in yields of 70−90% with narrow dispersity, typically below 1.23 (Table 2). The molecular weights determined by ^{1}H NMR spectroscopy (spectra before and after oxidation in Figures S5 and S6) show discrepancies to the molecular weights calculated by size exclusion chromatography (SEC), caused by the different elution behavior of the functionalized

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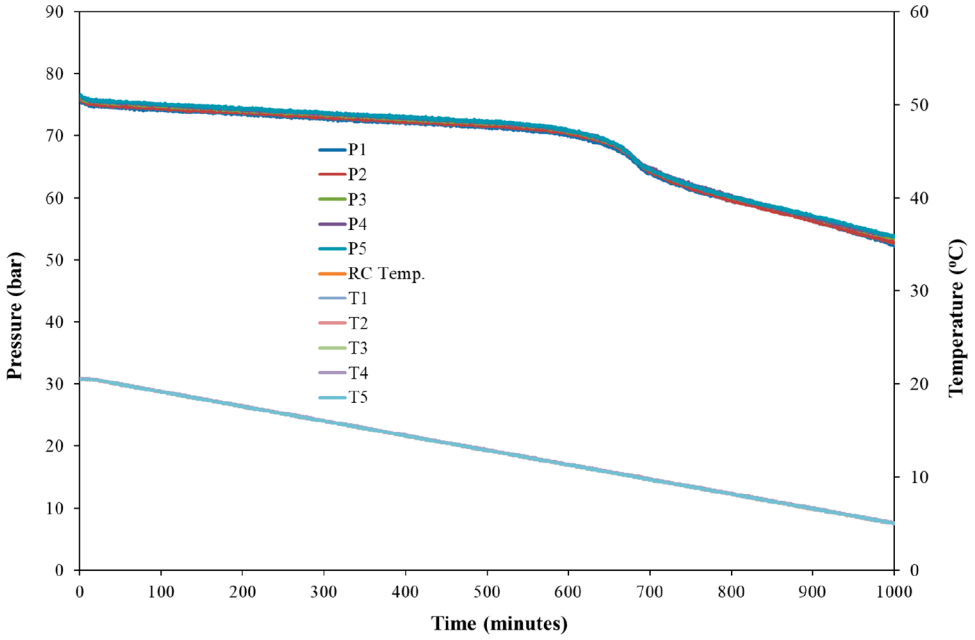

Figure 4. Example of the temperature−time and pressure−time curves for all the five cells from one SCC test process. Each cell contained 20 mL of EGBE-PAzGAO$_{38}$ solution at 2500 ppm. RC temp means the temperature of the cooling bath of RC5.

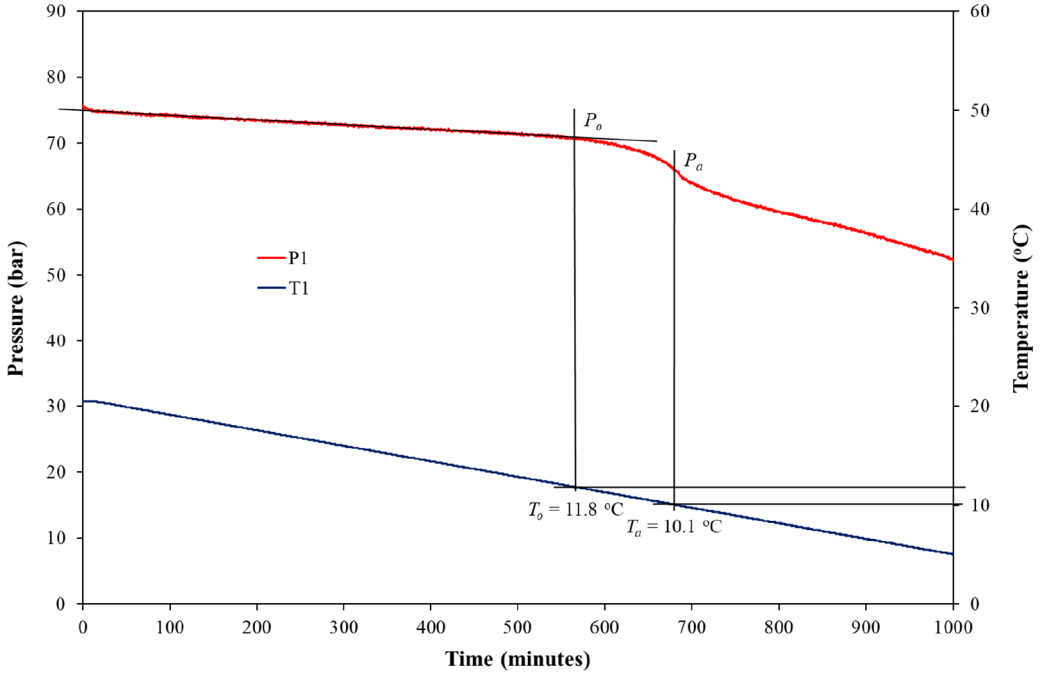

Figure 5. Example of analyzing the hydrate onset temperature (T_o) and the rapid hydrate formation temperature (T_a) for one cell. The cell contained 20 mL of EGBE-PAzGAO$_{38}$ solution at 2500 ppm.

polyethers in comparison to the PEG standards used for calibration (we note that Mn was measured by NMR using two different solvents because of the solubility change due to the oxidation step). This effect was reported previously by different authors.[33,34] While the SEC curves of polymers insoluble in *N,N*-dimethylformamide show a monomodal distribution, the molecular weights and dispersities are not comparable due to the PMMA standard used for these measurements.

Table 3 summarizes the results of the KHI performance for the synthesized PGAOs at the concentration of 2500 ppm. The results of deionized water (DIW) and polyvinylcaprolactam (PVCap) were also listed in this table for comparison. The PVCap (2∼4 kg/mol) solid used in this study was obtained from the commercial Luvicap EG by removing the monoethylene glycol solvent. The average T_o (T_o (av)) and average T_a (T_a (av)) values for each polymer were calculated from at least five repeated tests. Subcooling (ΔT) was calculated by using the equilibrium temperature at the pressure of P_o (see Figure 5) minus the value of T_o. The difference between T_o (av) and T_a (av) indicates the degree of how a KHI polymer stops the rapid hydrate formation once the detectable gas hydrates occurs. As T_o value refers to the first detectable gas

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Table 2. Characterization Data of PGA and PGAO

name	M_n[a] kg/mol	M_n[b] kg/mol	$Đ$[b]	M_n (PGAO)[c] kg/mol
EGBE-PPyrGA$_9$	1.3	0.6	1.17	
EGBE-PPyrGAO$_{18}$	2.4	1.0	1.09	2.7
BnO-PPyrGAO$_{20}$	2.7	1.3	1.04	3.0
EGBE-PPiGAO$_{10}$	1.5	0.8	1.10	1.7
EGBE-PPiGAO$_{24}$	3.5	1.2	1.07	3.9
EGBE-PPiGAO$_{49}$	7.0		1.19[d]	7.8
EGBE-PAzGAO$_{14}$	2.3	0.9	1.06	2.5
EGBE-PAzGAO$_{23}$	3.7	0.8	1.23	4.1
EGBE-PAzGAO$_{38}$	6.0		1.87[d]	6.6
EGBE-PAzGAO$_{49}$	7.7		1.21[d]	8.5

[a]Molecular weights determined by ^{1}H NMR (300 MHz, $CDCl_3$). [b]Determined by SEC (DMF, PEG-calibration). [c]Determined by ^{1}H NMR (300 MHz, D_2O) [d]Determined by SEC (HFIP, PMMA-calibration).

Table 3. Summarised Results of the KHI Performance Obtained from the SCC Tests[a]

name	M_n[b] kg/mol	T_o (av) (°C)	ΔT (av) at T_o (°C)	T_a (av) (°C)	T_o (av) − T_a (av) (°C)
DIW		16.3	4.1	16.2	0.1
PVCap	2−4	10.4	9.8	9.9	0.5
EGBE-PPyrGAO$_{18}$	2.7	13.5	6.8	11.2	2.3
BnO-PPyrGAO$_{20}$	3.0	13.2	7.1	12.0	1.1
EGBE-PPiGAO$_{10}$	1.7	9.8	10.4	8.7	1.0
EGBE-PPiGAO$_{24}$	3.9	11.7	8.5	10.6	1.1
EGBE-PPiGAO$_{49}$	7.8	13.3	7.0	12.2	1.1
EGBE-PAzGAO$_{14}$	2.5	9.8	10.4	9.1	0.6
EGBE-PAzGAO$_{23}$	4.1	10.0	10.2	9.2	0.8
EGBE-PAzGAO$_{38}$	6.6	11.7	8.5	10.1	1.6
EGBE-PAzGAO$_{49}$	8.5	13.6	6.7	12.2	1.4
EGBE-PPyrGA$_9$	1.3	17.0	3.4	16.5	0.5
EGBE-PAzGA$_{14}$	2.3	17.1	3.3	16.7	0.4
EGBE-PAzGA$_{23}$	3.7	16.8	3.6	16.4	0.4

[a]Concentration at 2500 ppm. [b]Determined by ^{1}H NMR (300 MHz, D_2O).

hydrate formation, which is the most important parameter for evaluating the KHI performance of a polymer, we will focus on discussing T_o values. In addition, as seen in Table 3, when comparing the performance of the KHI polymers, their T_a values almost follow the same trend as that of the T_o values. Generally, lower T_o values translate to better KHI performance.

All PGAOs gave better KHI performance than DIW. EGBE-PPyrGAO$_{18}$ and BnO-PPyrGAO$_{20}$ are poly(pyrrolidine glycidyl amine *N*-oxide)s with a similar number of monomer units, and they gave similar KHI performance despite the varying initiators with an aliphatic or aromatic group, respectively. BnO-PPyrGAO$_{20}$, EGBE-PPiGAO$_{24}$, and EGBE-PAzGAO$_{23}$ gave a T_o (av) value of 13.2, 11.7, and 10.0 °C, respectively, indicating that the poly(pyrrolidine glycidyl amine *N*-oxide), poly(piperidine glycidyl amine *N*-oxide), and poly(azepane glycidyl amine *N*-oxide) with a similar number of monomer units at around 20 gave different KHI performances. EGBE-PAzGAO$_{23}$ gave better KHI performance than EGBE-PPiGAO$_{24}$, while EGBE-PPiGAO$_{24}$ was superior to BnO-PPyrGAO$_{20}$. This means that, when M_n (which is around equal to M_w, for the three polymers mentioned here) is around 4 kg/mol, the PGAOs with a larger size of the pendant ring groups gave better KHI performance. Interestingly, in 2012, Chua and Kelland already reported that an increasing ring size leads to improved KHI performance for the poly(*N*-vinyl lactam)s at $M_w \approx 4$ kg/mol, and they presumed that the reason for this tendency may involve polymer tacticity.[28,35,36] They hypothesized that the increasing steric bulk of the *N*-vinyl lactam probably leads to a more syndiotactic structure of the polymer when polymerized, and syndiotactic structures can maximize the polymer surface/volume ratio. It is the pendant amphiphilic groups of the polymer that interfere with the hydrate nucleation and crystal growth processes. Therefore, at a given concentration, maximizing the surface area to volume ratio will make the best use of the polymer. However, this is not the case for polyethers, as there is no evidence for a change of tacticity. However, a large surface/volume ratio may enhance the KHI performance of a polymer. Thus, the polymer with the largest pendant ring groups performed the best. In addition, according to the adsorption mechanism reported by Yagasaki et al.,[37] the azepane ring could have the suitable size for the KHI polymer to stabilize at the hydrate surface, thus providing stronger adsorption affinity for preventing gas hydrates from further growth.

To see how the molecular weight affects the KHI performance of the PGAOs, the performance of a series of EGBE-PPiGAOs and EGBE-PAzGAOs with different degrees of polymerization ranging from 10 to 49 was tested. The results of the PPiGAOs with varying monomer units showed a trend that the larger the molecular weight, the worse KHI performance of the polymer. The same was observed for the PAzGAO series (Table 3 and Figure 6). This trend can be found in many of previously reported KHI series.[18,38,39] The PGAOs with the lowest molecular weight were on par with PVCap regarding inhibition of sII gas hydrate formation.

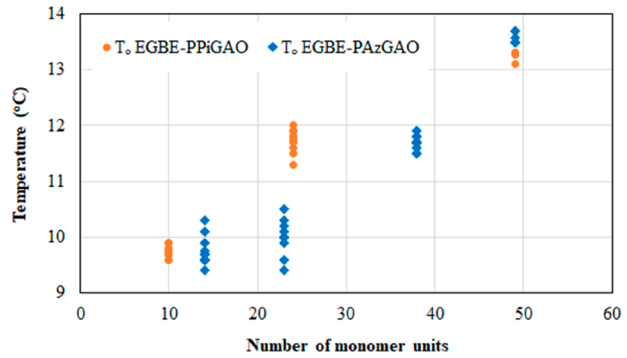

Figure 6. T_o values of EGBE-PPiGAO and EGBE-PAzGA with varying degrees of polymerization.

However, when comparing the PGAOs with a similar degree of polymerization, the KHI performance of the EGBE-PAzGAOs with a larger ring size was not always better than that of the EGBE-PPiGAOs. For example, EGBE-PPiGAO$_{10}$

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and EGBE-PAzGAO$_{14}$ gave the same T_o (av) value of 9.8 °C. To our surprise, EGBE-PPiGAO$_{49}$ and EGBE-PAzGAO$_{49}$ with higher molecular weights gave T_o (av) values of 13.3 and 13.6 °C, respectively. The P value between the average T_o values of PPiGAO$_{49}$ and PAzGAO$_{49}$ is 0.001, calculated from a t-test, which means that the confidence of a significant difference between them is as high as 99.9%; i.e., the KHI performance of PPiGAO$_{49}$ is statistically significantly better than that of PAzGAO$_{49}$.[43] A possible reason why, at high molecular weights, EGBE-PAzGAO$_{49}$ gave worse KHI performance than EGBE-PPiGAO$_{49}$ might be that there is more overlapping area for the larger azepane groups to curve the hydrate surface region, so the coverage area per monomer unit is reduced. Reduced coverage area renders weak adsorption effect, thus causing poor inhibition performance.[40]

At the concentration of 2500 ppm, none of the PGAOs showed a cloud point when heated up to 95 °C. To determine a possible cloud point, each polymer solution was slowly heated to 95 °C, and visual observations were made. No turbidity was observed at any stage of the heating process indicating no cloud point up to this temperature. The test was repeated for assurance of the result. In addition, no cloud point occurred for the two best PGAOs EGBE-PPiGAO$_{10}$ and EGBE-PAzGAO$_{14}$ in 15 wt % (150 000 ppm) sodium chloride solution upon heating to 95 °C. Usually, the polymer with lower cloud point is expected to give better KHI performance,[26] and the amine polyethers without being oxidized are more hydrophobic than the corresponding PGAOs. Therefore, the KHI performance of three amine polyethers EGBE-PPyrGA$_9$, EGBE-PAzGA$_{14}$, and EGBE-PAzGA$_{23}$ were measured. All of them are very poor KHIs, which means that the amine is not a suitable functional group to inhibit gas hydrate formation.

The KHI performance of one of the best PGAOs EGBE-PAzGAO$_{23}$ was determined at varying concentrations. The results are summarized in Table 4 and Figure 7. Similar to many other KHI polymers with hydrogen-bonding functional groups,[27,41,42] the KHI performance of poly(azepane glycidyl amine N-oxide) increased dramatically with increasing concentration.

Table 4. Summary of the KHI Performance Results of EGBE-PAzGAO$_{23}$ at Different Concentrations

name	concentration (conc) (ppm)	T_o (av) (°C)	ΔT (av) at T_o (°C)	T_a (av) (°C)	T_o (av) − T_a (av) (°C)
EGBE-PAzGAO$_{23}$	1000	12.3	8.0	11.7	0.6
	2500	10.0	10.2	9.2	0.8
	5000	7.9	12.3	6.6	1.3

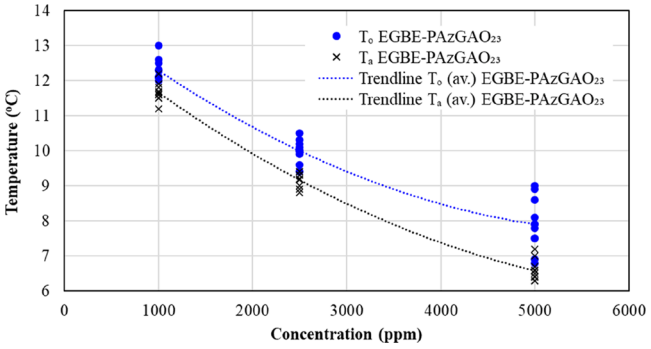

Figure 7. T_o and T_a values of EGBE-PAzGAO$_{23}$ at varying concentrations.

CONCLUSION

In this study we have synthesized and tested the KHI performance of a series of novel polyethers with cyclic amine side chains and oxidized these compounds to the corresponding amine N-oxides. Poly(pyrrolidine glycidyl amine N-oxide)s (PPyrGAOs), poly(piperidine glycidyl amine N-oxide)s (PPiGAOs), and poly(azepane glycidyl amine N-oxide)s (PAzGAOs) with different molecular weights and degrees of polymerization have been introduced. At a molecular weight (M_n value) of approximately 2 kg/mol, translating to degrees of polymerization (P_n) of 10 and 14, respectively, PPiGAO gave the same KHI performance as PAzGAO. When M_n increased to around 4 kg/mol (P_n of 20−24), the trend of the KHI performance of the glycidyl amine N-oxide polyethers can be summarized in this order: PPyrGAO < PPiGAO < PAzGAO. However, at a higher molecular weight $M_n \approx 8$ kg/mol (P_n of 49), PAzGAO with larger azepane ring groups resulted in slightly worse KHI performance in comparison to that of PPiGAO.

Within each poly(glycidyl amine N-oxide) series with the same monomer units, there is a clear trend showing that the polymer with higher molecular weight gave worse KHI performance. With the concentration range from 1000 to 5000 ppm, the KHI performance was better when the concentration of the polyether was increased.

Poly(pyrrolidine glycidyl amine)s (PPyrGAs) and poly(azepane glycidyl amine)s (PAzGAs) gave very poor KHI performance on sII gas hydrate, while their corresponding glycidyl amine N-oxide polyethers showed considerable performance as well as excellent compatibility with 15 wt % NaCl brine solution. Thus, the ring size affects the inhibition effect, and the proper functional groups are also critical for KHI performance.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.energyfuels.0c04333.

^{1}H and ^{13}C{1H} NMR spectra of AzGA and PyrGA monomers and ^{1}H NMR spectra of the polymers PAzGA$_{38}$, PazGAO$_{38}$, PPyrGA$_{18}$, and PPyrGAO$_{18}$ (PDF)

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Notes

The authors declare no competing financial interest.

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