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Vinyl lactam-based copolymers and terpolymers as high cloud point kinetic hydrate inhibitors in methane-THF-water system

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ABSTRACT

A series of vinyl lactam-based polymers were synthesized and then evaluated as kinetic hydrate inhibitors (KHIs) in methane-tetrahydrofuran (THF)-water system. The inhibition performance of synthesized KHIs was examined and compared with commercially-available KHIs using a high-pressure rocking cell. The VCap/1-vinyl-2-pyrrolidone (VP) copolymer with a molar ratio of 3:1 could reduce hydrate growth rate by 18% greater than poly(*N*-vinylcaprolactam) (PVCap). Moreover, the modification of this copolymer with 3-mercaptopropionic acid (3-MPA) led to producing the novel KHI that more effectively decreased hydrate growth rate than non-modified copolymer. Moreover, the addition of 2-Dimethylaminoethyl methacrylate (DMAEMA) as a third monomer to the polymerization mixture improved the performance of the copolymers by 20%. Cloud point measurements revealed that all the synthesized copolymers, the modified copolymers and the terpolymers had higher cloud point in comparison with PVCap, such that cloud point temperature (T_{cl}) for mercaptoacetic acid (MAA)-modified copolymer and 3-mercaptopropionic acid (3-MPA)-modified copolymer was 43 and 20 °C higher than that of PVCap and these modified copolymers could be developed as novel high cloud point kinetic hydrate inhibitors even in saline solutions.

1. Introduction

Gas hydrate formation is a major concern that can lead to blockage risks in flow lines and hence economic losses [1–4]. However, hydrates may hold some benefits in many fields such as CO_2 sequestration [5]. Gas hydrates can be divided into three structures: structure I hydrate (sI), structure II hydrate (sII), and structure H hydrate (sH). Accordingly, sI hydrate can be formed in the presence of small molecules such as methane and ethane, while propane and tetrahydrofuran (THF) form sII hydrate. As well, sH hydrate is a less common structure of hydrate formed in the presence of both very large and small guest molecules [6–10]. Injection of inhibitors has been used as a reasonably-used method to restrict gas hydrate formation and to avoid the safety accidents caused by hydrate plugging of pipelines in the oil and gas industry [11]. Kinetic hydrate inhibitors (KHIs) are a class of low dosage hydrate inhibitors [12]. KHIs are water-soluble polymeric compounds containing commercially available polyvinylpyrrolidone (PVP) with five-membered lactam rings are attached to its backbone and PVCap is comprised of seven-membered lactam rings [13–15].

Plenty of vinyl lactam copolymers have been previously studied; some copolymers were reported to be superior KHIs to homopolymer of the same monomers. In this respect, Long et al. [16] described the synthesis of VCap/acrylamide copolymer and claimed that it acted better than PVCap. The copolymer of *N*-methyl-*N*-vinylacetamide (VIMA) and VCap with the molar ratio of 3:1 had higher subcooling than PVCap [17]. Moreover, Reyes and Kelland [18] synthesized a series of copolymers of *N*-vinylazacyclooctanone (VACO), consisting of an 8-membered lactam ring, with monomers containing 5 to 7-membered lactam rings. The cloud point of poly *N*-vinylazacyclooctanone (PVACO) was about 15–24 °C, which increased by the addition of the second monomers to the reaction mixture. They correspondingly found that VACO 1:1 copolymers with smaller ring size monomers had shown better performance. In other words, as the ring size of the second monomer was reduced from 7 to 5, the KHI performance of the copolymers improved and VACO/VP copolymer was found to be a superior KHI to PVACO homopolymer. Additionally, Lou et al. [19] synthesized six novel KHIs using free-radical solution copolymerization of VCap and polyethylene oxide (PEO), which were as efficient as Luvicap EG and Gaffix VC-713. Insertion of some effective hydrophilic and hydrophobic functional groups into the given polymers could also enhance KHIs [20]. In this line, Kvamme et al. [21] claimed based on simulation results that hydroxyl group could be placed into PVCap

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structure and result in better solubility and inhibition performance [22]. Chemical modification of KHIs could similarly affect T_{cl} [23–25]. Although PVCap was shown to have better KHI performance than PVP [26], lower solubility of PVCap was observed in high-temperature water than that of PVP. In fact, PVCap is a thermo-responsive polymer and its solubility in water depends on temperature in a way that its T_{cl} is typically around 30–40 °C [27]. It implies that PVCap might precipitate, and it gets unsuitable to be injected into warm fluids at higher temperatures, higher than the T_{cl} of polymer. Also, sodium and chloride ions in water could impact the solubility of polymers, the T_{cl} of a thermo-responsive polymer usually decreases as the salinity increases [28].

To put it in a nutshell, the main purpose of this body of research was to design effective KHIs with high T_{cl} even at high salinities. The synthesized polymers were compared with commercially-available PVP and Luvicap EG. Moreover, the effect of chemical modification was investigated using mercaptoacetic acid (MAA) and 3-mercaptopropionic acid (3-MPA) on performance and T_{cl} of the most efficient copolymer. PVP as a more hydrophilic monomer and 2-dimethylaminoethyl methacrylate (DMAEMA) as a hydrophobic monomer were added to PVCap polymerization solutions with different molar ratios in order to clarify the impact of the second and the third monomers to KHI performance of PVCap. Furthermore, a high-pressure rocking cell was applied to conducting inhibition performance testing of the produced polymers.

2. Experimental section

2.1. Materials

The meticulous data of all the components used in the experiments were illustrated in Table 1. It should be noted that all the chemicals were consumed without any further purification.

2.2. Polymer characterization

The structures of the produced polymers were characterized utilizing Fourier-transform infrared (FTIR) spectroscopy with a wavelength range of 400–4000 cm^{-1}. All the spectra were also recorded on the Thermo Scientific™ Nicolet™ iS50 FTIR. A standard procedure was then applied to measure cloud point temperature (T_{cl}). The visual cloud point method determined the temperature at which the initial signs of turbidity were appeared in polymer solutions. According to the literature [25,29], the method of cloud point measurement had 4 main steps as follow: (1) first, the polymer was dissolved in deionized water (2) a glass tube filled with the polymer solution and placed in a thermo-stable bath. (3) The temperature was increased slowly at the rate of 0.5 °C per minute and the polymer solution in the glass tube was observed carefully. (4) The temperature at which the solution began to show visual sign of haze was recorded as the cloud point temperature. Based on the above method following procedure was used to evaluate the solubility of the produced polymer at high temperature water. The solutions of 0.25 wt% of the produced polymers in deionized water were prepared and heated at a low rate (0.5 °C per minute) in a thermostable bath while being carefully observed. A digital thermometer with an accuracy of ±0.1 K was applied to measuring the temperature inside the bath. The T_{cl} was reported as the temperature at which the first sign of turbidity had been detected. The effects of sodium chloride concentration on T_{cl} were correspondingly evaluated. All the experiments were repeated and the average data were ultimately reported. Moreover, surface tension of aqueous solutions of synthesized polymer at the concentration of 0.25 wt% was determined by a kruss K100 Tensiometer (Kruss GmbH, Germany).

Table 1
Chemicals used for experiments.

Component	Chemical formula	Purity (%)	Supplier
VCap	$C_8H_{13}NO$	97	Merck
1-Vinyl-2-pyrrolidone	C_6H_9NO	≥98	Merck
(2-Dimethylaminoethyl) methacrylate	$C_8H_{15}NO_2$	≥99	Merck
Luvicap EG	$(C_8H_{13}NO)_n$	40 wt% PVCap in ethylene glycol	BASF
PVP (10,000 g/mol)	$(C_6H_9NO)_n$	–	Merck
AIBN	$C_8H_{12}N_4$	97	Fluka
Sodium chloride	NaCl	99.5	Dr. Mojalali
Isopropanol	C_3H_8O	98	Neutron
Diethyl ether	C_4H_8O	99.5	Neutron
n-Hexane	C_6H_{14}	85	Dr. Mojalali
THF	C_4H_8O	99.8	Merck
Nitrogen	N_2	99.99	Technical gas services
Water	H_2O	Deionized	Abtin
Methane	CH_4	99.9	Technical gas services
3-Mercaptopropionic acid	$C_3H_6O_2S$	99	Acros Organics
Mercaptoacetic acid	$C_3H_6O_2S$	97	Merck

2.3. Polymer synthesis

All the homopolymers, copolymers, terpolymers, as well as the modified copolymers were prepared through free-radical solution polymerization using a 50-mL, three-necked, round-bottomed glass flask equipped with a magnetic stirrer, a temperature sensor, and a condenser pipe. Initially, the flask was evacuated and washed using nitrogen three times. Then, a mixture of 26 mg AIBN as an initiator, 18 mmol of monomers (VCap, VP, and DMAEMA) with the certain molar ratio (Table 2), and isopropanol as a solvent was transferred to the glass flask and vacuumed/flushed by nitrogen three times in order to remove oxygen and moisture. Subsequently, the reactor was heated at 75 °C and was stirred for 16 h in a nitrogen atmosphere. The mixture was then cooled to room temperature. Once the solvent was evaporated, the product was dissolved in 10 mL THF and precipitated in 30 mL *n*-hexane and filtered for two time. The solid was then washed in diethyl ether several times. Finally, the product was dried at 40 °C for several days to find its constant weight. The modified copolymers were prepared with the same method, but a specific amount of chain transfer agent (CTA) (0.07 mL) was added to the solution of monomers and initiator in the solvent.

Fig. 1 illustrates the schematic of the polymerization reactions.

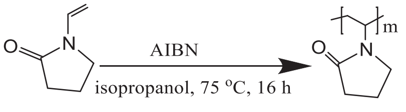
2.4. Apparatus and experimental procedure for KHI testing

The schematic of the equipment for hydrate formation is shown in Fig. 2. The experimental apparatus consisted of 100 mL high-pressure stainless steel cell surrounded by a cooling jacket to adjust the temperature inside the cell. A thermometer with an uncertainty of ±0.1 K and a pressure transmitter with an accuracy of ±0.1 bar were applied to measure the temperature and the pressure of the cell. Also, a data acquisition system was utilized to record the pressure and the temperature of the cell during the process. A speed controller was employed to adjust the rocking rate at 30 rocks per minute. After the cell was evacuated and washed by deionized water 4 times, a solution of THF and water with the molar ratio of 1:17 containing the above-mentioned polymers at the specific concentration was charged into the cell. Afterwards, the rocking rate was held constant. As soon as the temperature reached 277.15 K, the rocking movement of the cell was stopped to pressurize the cell to 3 bar. Afterwards, the system was cooled to 274.15 °C and the temperature remained constant until the end of hydrate formation process and then the rocking movement was started again and the experiment began.

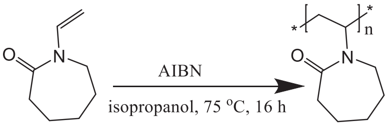
Table. 2
Data of newly-synthesized polymers.

Sample	Monomers	VCap mol%	VP mol%	DMAEMA mol%	Conversion %
Synthesized PVCap	VCap	100	0	0	76
Synthesized PVP	VP	0	100	0	71
P(VP:VCap)I	VCap/VP (1:1)	50	50	0	79
P(VP:VCap)II	VCap/VP (3:1)	75	25	0	72
P(VP:VCap)III	VCap/VP (1:3)	25	75	0	80
Terpolymer I	VCap/VP/DMAEMA (24:71:5)	24	71	5	69
Terpolymer II	VCap/VP/DMAEMA (74:25:1)	74	25	1	75
Terpolymer III	VCap/VP/DMAEMA (71:24:5)	71	24	5	40
mI-P(VP:VCap)II	VCap/VP (3:1) modified with MAA	75	25	0	70
mII-P(VP:VCap)II	VCap/VP (3:1) modified with 3-MPA	75	25	0	77

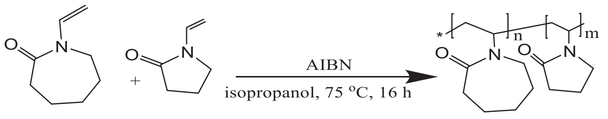
The time at which the rapid decrease in the pressure was observed, reported as the nucleation time. Then, the number of moles of gas consumed during the hydrate formation process was subsequently calculated. In fact, gas consumption was measured from the pressure drop profile after the nucleation time in the reactor. The moles of consumed gas up to time t_i were calculated based on Eq. (1).



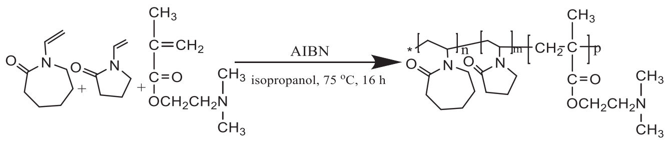
(a) Synthesis of PVP



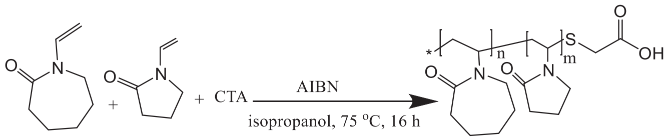
(b) Synthesis of PVCap



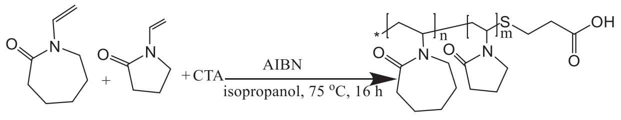
(c) Synthesis of VP/VCap copolymer



(d) Synthesis of VP/VCap/DMAEMA terpolymer



(e) Synthesis of MAA-modified copolymer



(f) Synthesis of 3-MPA-modified copolymer

Fig. 1. Synthesized vinyl lactam-based polymers.

$$n_{ci} = n_0 - n_i = \left(\frac{PV}{ZRT}\right)_0 - \left(\frac{PV}{ZRT}\right)_i \tag{1}$$

where n_{ci}, n_o, and n_i, are moles of gas consumed up to time t_i, initial moles of gas, and moles of gas at time t_i. Note P is the pressure, T is the temperature, V is the volume of gas in the cell, Z is the compressibility factor calculated using Peng-Robinson equation [30], and R is the universal gas constant.

In addition, hydrate growth rate (mmol/min) is indicated as the slope of the curve of gas consumption versus time and it could be calculated applying Eq. (2). In other words, the average growth rate was measured from the gas consumption change during the specific time (Δt_i).

$$r = \frac{n_0 - n_i}{t_i - t_0} \tag{2}$$

It should be noted that a constant cooling method was used to measure maximum subcooling. The following steps were conducted to measure the subcooling. Initially, the reactor pressurized up to 20 bar. Then the reactor was constantly cooled from 26 °C to 1 °C. The hydrate onset temperature (T_{onset}) was obtained at the temperature that a rapid decrease in pressure was appeared. The differences between three phase equilibrium temperature at the initial pressure and the hydrate onset temperature were reported as maximum subcooling [4]. These experiments were repeated at least 3 times and the average maximum subcooling was reported.

2.5. FTIR

The FTIR spectra for the terpolymers and the copolymers compared with the homopolymers are presented in Fig. 3. In the FTIR spectrum of PVCap, the position of a carbonyl (C=O) peak was at 1637 cm^{-1} while in the spectrum of PVP, carbonyl peak was at 1668 cm^{-1}. Two different peaks with the same width located at 1677 and 1634 cm^{-1} were assigned to C=O stretching of VP and VCap respectively in P(VP:VCap)I. The peak at 1677 cm^{-1} corresponding to VP carbonyl was broader compared with 1632 cm^{-1} belonging to VCap carbonyl, demonstrating the higher percentage of VCap in the spectrum of P(VP:VCap)II. However, the peak corresponding to VP carbonyl was broader in spectrum of P(VP:VCap)III owing to the highest percentage of VP. The peaks at 1724, 1670, 1629 cm^{-1} in the FTIR spectrum of terpolymer I corresponded to different carbonyl of DMAEMA, VP, and VCap monomers respectively. However, for terpolymer II the DMAEMA carbonyl peak overlapped VP carbonyl peak due to the higher percentage of VP. Likewise, it disappeared in FTIR spectrum of terpolymer III because of the low percentage of DMAEMA. In the FTIR spectra of the modified copolymers, the peaks belonging to S—H stretching vibration at about 2500 cm^{-1} disappeared thanks to successful chemical modification.

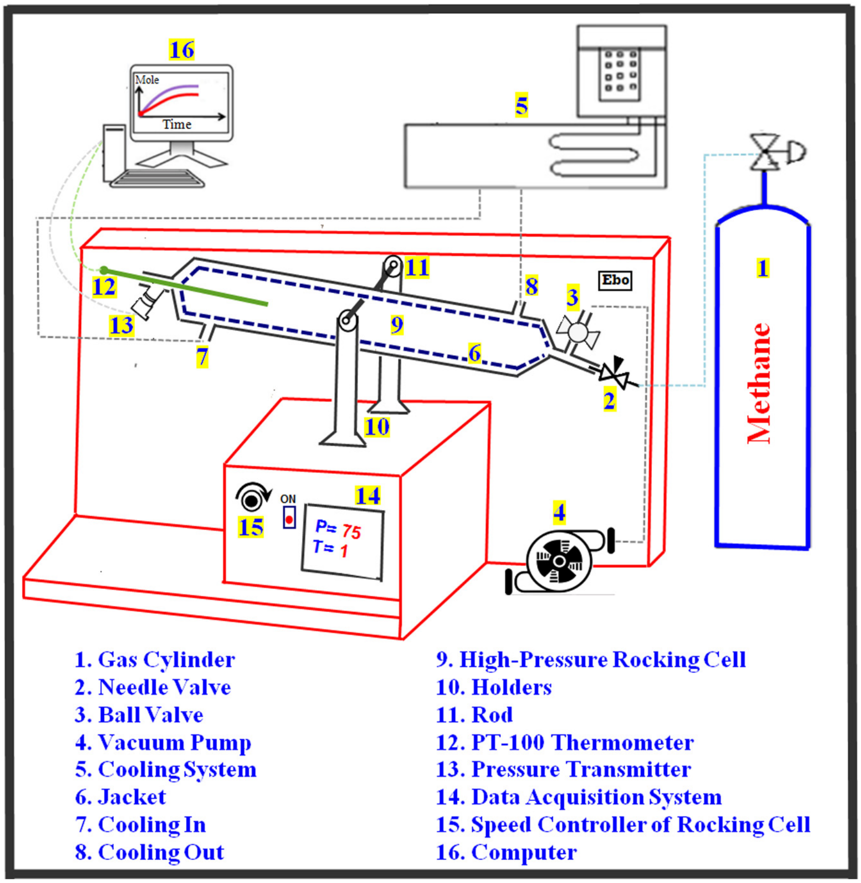


Fig. 2. Schematic of rocking cell apparatus.

3. Results and discussion

3.1. The inhibition potential of synthesized homopolymers compared with commercially-available KHIs

Homopolymers of VCap and VP were synthesized and their KHI performance was compared with commercial PVP and Luvicap EG in methane-THF-water system. THF is perfectly miscible in water and easily forms hydrate at the atmospheric pressure and a molar ratio of 1:17 (THF/water), also it has been extensively applied to evaluate natural gas inhibitors for the reason that natural gas and THF both form the same structure of hydrate (sII hydrate) [6]. Methane hydrate (sI hydrate) and THF hydrate (sII hydrate) have the similar mechanical and thermal properties which could be another reason to use THF for hydrate inhibition studies [31]. It should be noted that methane hydrate forms at high pressure especially in the presence of potent kinetic

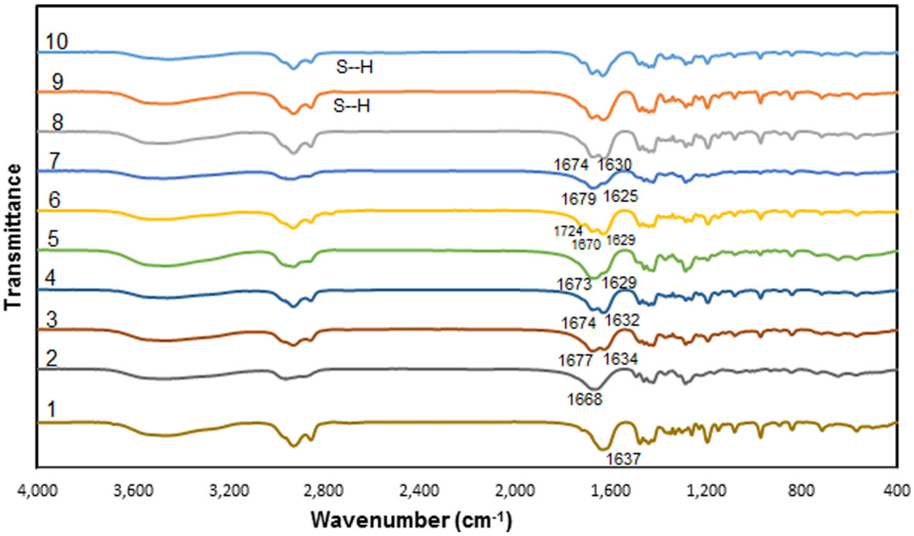


Fig. 3. FTIR spectra of (1) PVCap, (2) PVP, (3) P(VP:VCap)I, (4) P(VP:VCap)II, (5) P(VP:VCap)III, (6) terpolymer III, (7) terpolymer I, (8) terpolymer II, (9) mII-P(VP:VCap)II, (10) mI-P(VP:VCap)II.

hydrate inhibitors, whereas high pressure is not required when the THF is added to form binary methane-THF hydrate [32,33]. Fig. 4 illustrates the effect of homopolymers on methane-THF hydrate formation. The impact of both synthesized and commercial PVP on preventing hydrate formation in terms of both maximum subcooling and growth rate was such poor that the maximum subcooling for commercial PVP was even lower than pure water and the growth rate was similar to that with pure water. The maximum subcooling for synthesized PVP was identical to pure water and it decreases the growth rate in the initial moments of hydrate formation; nevertheless, it could not reduce the growth rate during the rest of hydrate formation experiment. To sum up, in terms of nucleation, commercial PVP performed as promoter while synthesized PVP did not shift the onset temperature of hydrate formation to higher temperature, and in terms of reducing the growth rate, both PVP were not effective. Besides, the synthesized PVCap outperformed all the homopolymers including commercial and synthesized KHIs. Fig. 4 confirms that synthesized PVCap has the greatest maximum subcooling and the lowest growth rate among the homopolymers.

3.2. The KHI performance of the synthesized homopolymers and copolymers of N-vinyl caprolactam and N-vinylpyrrolidone on structure II hydrate

In the present study, the impacts of homopolymers and copolymers of *N*-vinylcaprolactam and *N*-vinylpyrrolidone on structure II hydrate in the methane-THF-water system were evaluated. VP/VCap copolymers with monomer molar ratios of VP to VCap 1:1, 1:3, and 3:1 were named P(VP:VCap)I, P(VP:VCap)II, and P(VP:VCap)III respectively. Initially, the influence of these copolymers at the concentration of 0.25 wt% on hydrate growth rate was assessed. Fig. 5 demonstrates the KHI performance of the copolymers compared with synthesized PVCap and PVP. The results confirm that the copolymers of *N*-vinylcaprolactam and *N*-vinylpyrrolidone exhibited better hydrate inhibition than synthesized PVP and pure water. The performance of VCap/VP-based KHIs was not identical due to their different monomer ratios. Fig. 5(a) confirms that at the first 500 s of hydrate formation process, P(VP:VCap)I and P(VP:VCap)II were superior to PVCap regarding the reduction in hydrate growth rate. As time passed, the KHI performance of P(VP:VCap)I decreased while P(VP:VCap)II performed similarly to PVCap with the passage of times. P(VP:VCap)III also performed well at the initial moments of hydrate formation but as time passed, the effects were weaker even worse than pure water. Although its results was not as poor as that of synthesized PVP.

The values of average hydrate growth rate up to 500, 1000, and 1500 s after the onset of hydrate formation were listed in Table 3. The results reconfirm that PVP during the above-mentioned periods increased the hydrate growth rate compared with pure water while PVCap performed remarkably well. The average growth rates during the initial 500 s in the presence of P(VP:VCap)I and P(VP:VCap)II were 0.073 and 0.061 mmol/min respectively, which were lower than growth rate with PVCap (0.074 mmol/min). However, in the same time duration, average hydrate growth rate with a solution containing P(VP:VCap)III was 0.134 mmol/min which was higher than average growth rate with PVCap. It can be concluded that the molar ratio of monomers

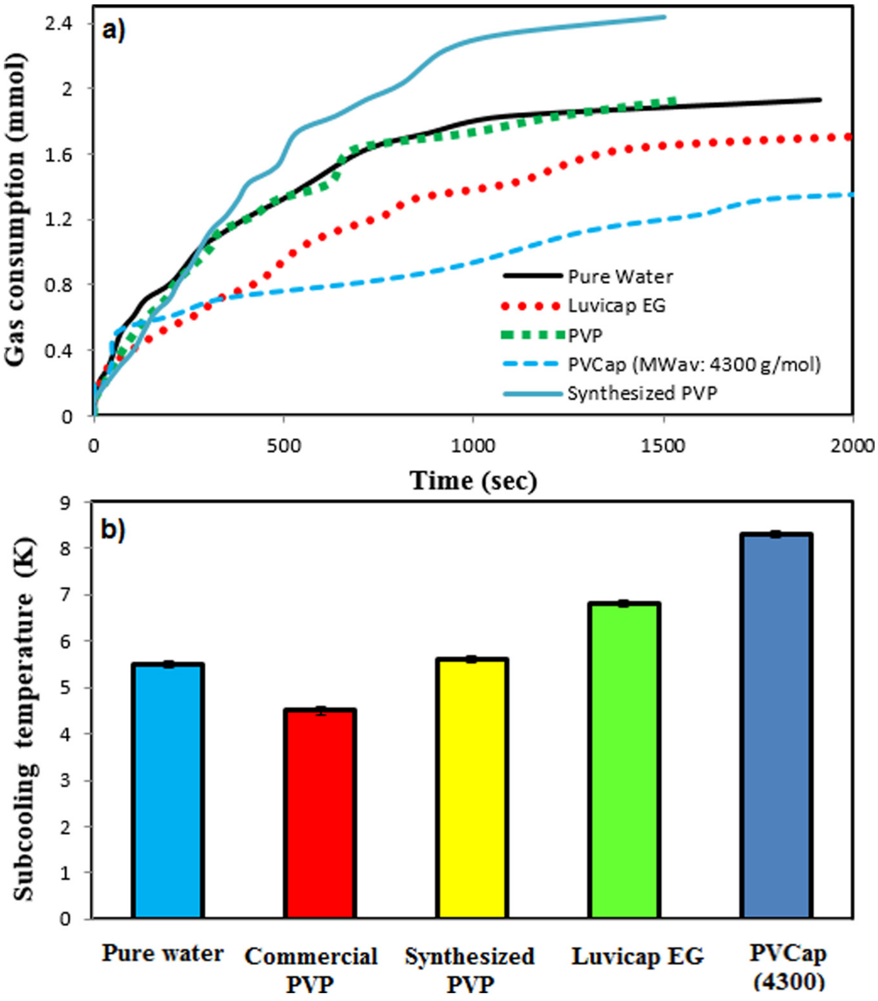


Fig. 4. (a) Inhibition potential of synthesized PVCap compared with commercial KHIs. (b) Maximum subcooling for PVCap and commercial KHIs.

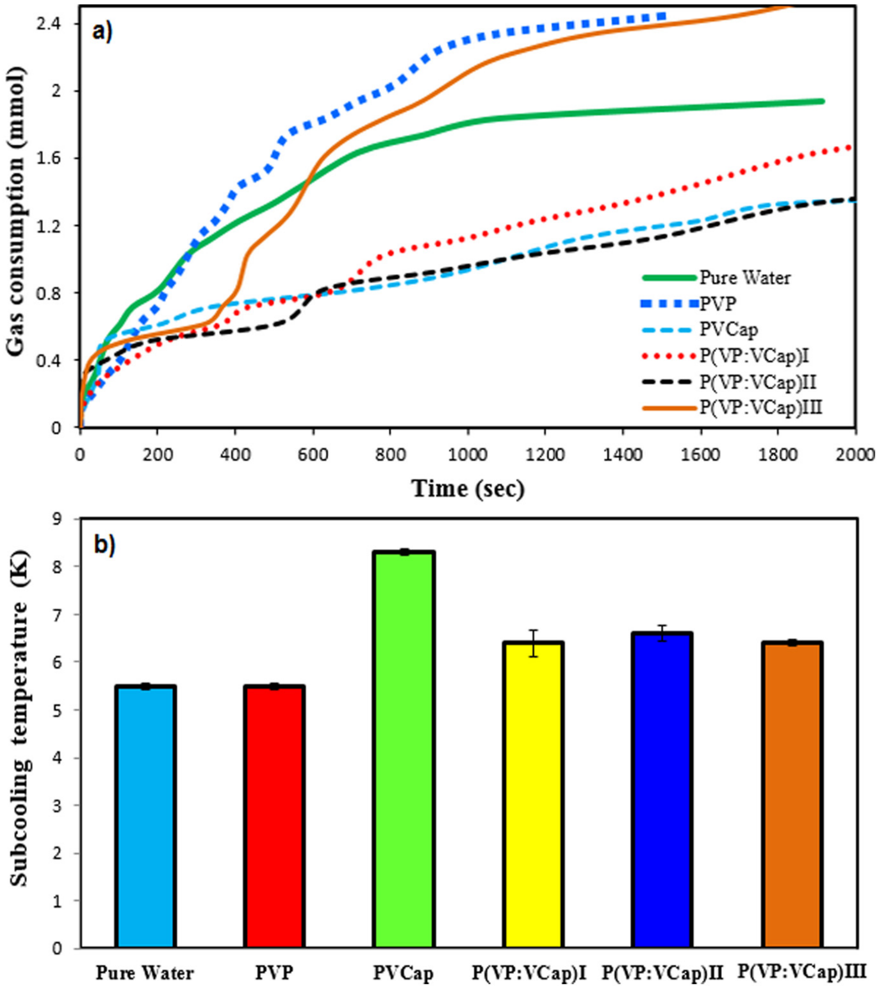


Fig. 5. (a) Inhibition effect of VP/VCap copolymers on structure II hydrate growth rate compared with PVP and PVCap. (b) Values of maximum subcooling for the synthesized copolymers compared with pure water and produced PVP and PVCap.

in copolymers plays a pivotal role in the inhibition of hydrate. In this regard, the more the mole fraction of VCap in copolymer increased, the better performance was obtained. P(VP:VCap)II contains more VCap than P(VP:VCap)I and P(VP:VCap)III; therefore, it showed the best KHI performance. Table 3 illustrates that during the hydrate formation process and in all the time periods, its growth rate was even lower than that with PVCap. To conclude, the VP/VCap copolymers with the monomer molar ratio of 1:1 and 3:1 performed weaker as a KHI than PVCap and P(VP:VCap)II. PVP did not have inhibition effects on structure II hydrate and at higher VP mole fractions, the KHI performance of VP/VCap copolymers decreased. Previous literature has shown that PVP can alter the morphology of hydrate. In other words, the formed hydrate in the presence of PVP is more porous which has large gas/liquid interfacial area; therefore, it may have weak effect on hydrate growth rate and it may act as a promoter when high driving force is provided [34–36]. Also, it seems that VP/VCap copolymers with high percentage *N*-vinylpyrrolidone monomer show relatively similar KHI performance to PVP, meaning that the KHI performance significantly depends on the monomer ratio of VP:VCap in the copolymer.

The effect of synthesized KHIs on maximum subcooling was also investigated. Fig. 5(b) shows the effect of P(VP:VCap)I, P(VP:VCap)II, and P(VP:VCap)III at the concentration of 0.25 wt% on maximum subcooling compared with pure water and the synthesized PVCap and PVP. The results show that the maximum subcooling of the copolymers was greater than that of pure water due to their ability to hinder the nucleation of structure II hydrate. Furthermore, the results demonstrate that the maximum subcooling values for all the copolymers were greater than that of PVP, while they were less than that of PVCap. In other words, there was

Table 3
Values of hydrate growth rate in the presence of the produced polymers.

Aqueous solution	Average growth rate to = 500 s (mmol/min)	Average growth rate to = 1000 s (mmol/min)	Average growth rate to = 1500 s (mmol/min)
Water	0.147	0.104	0.069
PVP	0.171	0.122	0.094
PVCap	0.074	0.049	0.045
P(VP:VCap)I	0.073	0.061	0.053
P(VP:VCap)II	0.061	0.049	0.041
P(VP:VCap)III	0.135	0.116	0.094

a positive correlation between the values of maximum subcooling and molar ratio of the VCap monomer in copolymer, showing that as the molar ratio of VCap decreased, the KHI performance of the copolymers got weaker. Thus, P(VP:VCap)II that has the greatest percentage of VCap among copolymers induced more inhibition than other copolymers with different molar ratios.

Based on comparing the results of inhibition effect of the copolymers on growth rate and maximum subcooling, the lowest molar ratio of VP to VCap exhibited the best performance as a crystal growth inhibitor for structure II hydrate. However, in terms of subcooling, this copolymer did not work as efficiently as PVCap.

Furthermore, Synthesizing VP/VCap copolymers would be beneficial for raising the cloud point of PVCap with the aim of producing suitable KHI to apply where polymer injection occurs into hot or saline fluids. Fig. 6 shows the cloud point temperature of 0.25 wt% solutions of synthesized polymers at varying NaCl salinity. The cloud point temperatures of all the copolymers were greater than PVCap. In this regard, the solubility of P(VP:VCap)III that has the greatest percentage of VP among the copolymers (75%) did not depend on solution temperature even at high concentrations of sodium chloride. Furthermore, P(VP:VCap)I which has the molar ratio of 1:1, has much higher cloud point temperature than PVCap and at NaCl salinity of 0, 0.5, 1, 2, 5, 10 wt% in deionized water the cloud point temperature of this copolymer was 46.2, 45.2, 43.3, 45, 42.7, and 29.1 °C respectively greater than that of PVCap. Also, P(VP:VCap)II which has the greatest influence on reducing hydrate growth rate, could increase the cloud point temperature by 22.2, 21.9, 19.9, 18.3, 17.7, and 11.5 °C higher than PVCap respectively at the concentrations of 0.5, 1, 2, 5, 10 wt% sodium chloride. In fact, although the copolymers with a high percentage of VP did not give good KHI performance, they have much higher cloud point temperature than PVCap and the copolymers with higher percentage of VCap. It is important to consider the properties and KHI performance of polymers for selection of suitable hydrate inhibitors based on their applications; for instance in some industries the injection temperature may be higher than cloud point temperature; in such a case, KHI with greater cloud point would be more appropriate. It should be mentioned that PVP and the VP/VCap copolymer with the highest percentage of VP do not have cloud point temperature. In this regard, P(VP:VCap)II is more acceptable because not only it performed better than PVCap but also its cloud point was higher than that of PVCap. However, when the high cloud point is required, the P(VP:VCap)I can be a reasonable choice, but when the operation temperature is not much high P(VP:VCap)II can be suggested. It should be demonstrated that due to the more solubility of PVP compared with PCVap, the copolymers with higher percentage of VP were more water soluble; therefore, their cloud point was higher. In addition, the more the concentration of NaCl increased, the lower T_{cl} was obtained.

3.3. The inhibition effects of synthesized vinyl lactam-based terpolymers on the kinetics of methane-THF hydrate formation

The results confirmed that the produced copolymers show appropriate KHI performance and at higher mole fraction of VP, as the monomer molar ratio of VP to VCap was increased the weaker performance of copolymer was obtained compared with PVCap. To examine the possibility of boosting the VP/VCap copolymers inhibition potential, synthesis of a terpolymer of *N*-vinylpyrrolidone and *N*-vinylcaprolactam (with the molar ratio of 3:1) containing 5 mol% dimethylaminoethyl methacrylate (DMAEMA) monomer was conducted. Fig. 7(a) presents the inhibition potential of this terpolymer (terpolymer I) compared with P(VP:VCap)III. The molar ratio of VCap monomer to VP in both produced polymers was 1:3. According to these findings, terpolymer I was more powerful hydrate inhibitor than P(VP:VCap)III. Although in the initial moments after the onset of hydrate formation, P(VP:VCap)III decreased the hydrate growth rate, as the time went by and when more crystals were formed, it showed weaker performance in comparison to pure water. In fact, the addition of a third monomer, DMAEMA, to solution of polymerization reaction could strengthen the KHI performance of P(VP:VCap)III, with the monomer VP to VCap molar ratio of 3:1. A reason for the better performance of terpolymer I may lie with the DMAEMA functional group which can perturb water molecules and inhibit hydrate formation. The functional groups of DMAEMA play a significant role in restricting hydrate formation; therefore, the KHI performance of terpolymer I was greater than the copolymer with identical VCap/VP molar ratio.

The findings proved that not only cloud point (T_{cl}) of VP/VCap copolymer with the monomer molar ratio of 1:3 was higher but also it acted more efficiently to decrease structure II hydrate compared with PVCap. Thus, to produce more potent KHI, terpolymers containing 1 and 5 mol% DMAEMA and VP/VCap with the molar ratio of 1:3 were synthesized and their performance was evaluated and compared. Fig. 7(b) illustrates the inhibition performance of P(VP:VCap)II compared with two different terpolymers to inhibit sII hydrate formation; the VP/VCap monomer molar ratio of both terpolymers and the copolymer was 1:3, also terpolymer II and terpolymer III containing respectively 1 and 5 mol% of DMAEMA. The results revealed that both terpolymers

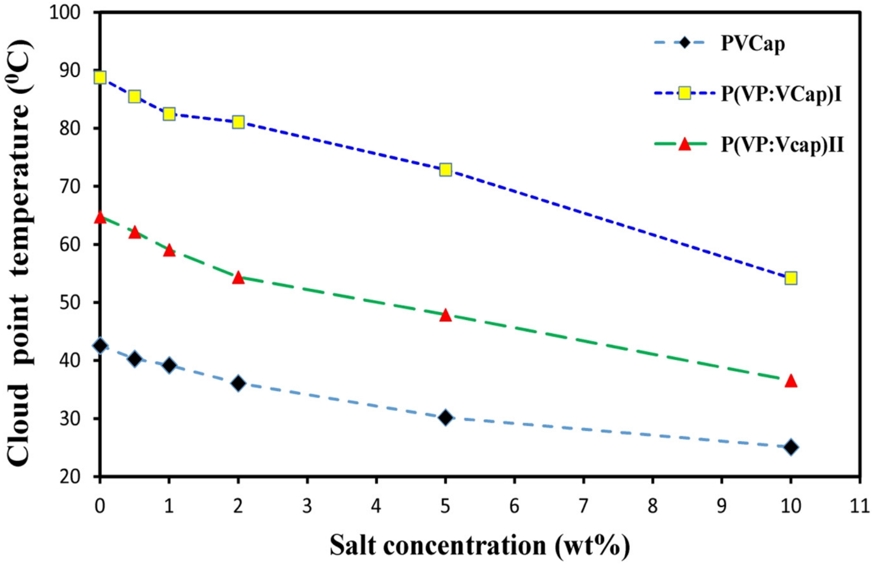


Fig. 6. The temperature of cloud points for the synthesized copolymers at the concentration of 0.25 wt% at varying NaCl salinity.

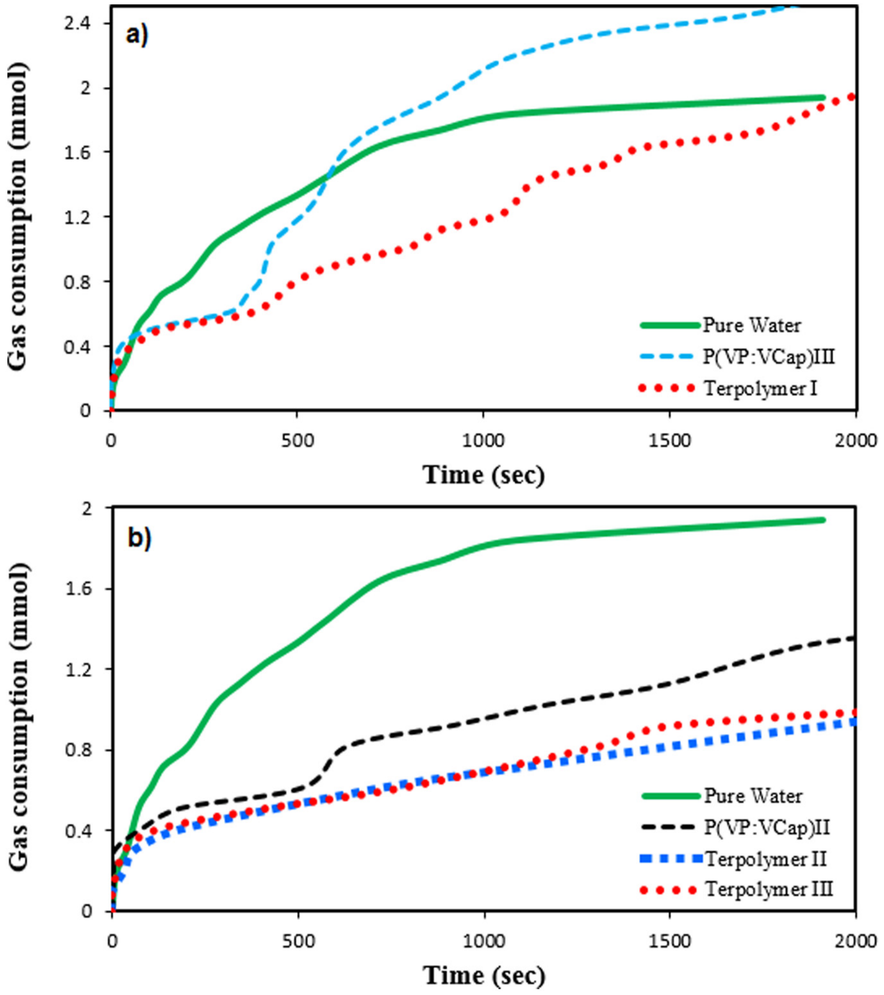


Fig. 7. (a) Inhibition effect of P(VP:VCap)II and terpolymer I (VCap/VP with the molar ratio of 3:1) on structure II hydrate formation. (b) KHI performance of terpolymer II and terpolymer III compared with P(VP:VCap)II.

were superior to the copolymer (P(VP:VCap)II) in terms of reducing the sII hydrate growth rate and hence terpolymer I and terpolymer II outperformed PVCap. The remarkable performance of these terpolymers might be related to the presence of DMAEMA.

Table 4 presents the values of average hydrate growth rate in the presence of the terpolymers. As can be observed, KHI effect of terpolymer II and terpolymer III was stronger than that of terpolymer I because it contains higher percentage of VP. Based on the results of Tables 4 and 3, it can be conclude that in the first 500 s after onset of hydrate formation, terpolymer II and terpolymer III decreased the average growth rate by 34% compared with PVCap and by 20% lower than that of P(VP:VCap) II. Also, this trend was observed during the whole experiments which implies the better performance of the terpolymers compared with PVCap and P(VP:VCap)II that was the most potent copolymer among the synthesized copolymers.

The effect of the terpolymers on maximum subcooling was shown in Fig. 8 According to the results, the terpolymers could shift the sII hydrate onset temperature to lower temperatures. In this regard, the maximum subcooling for terpolymer II and terpolymer III that contain more VCap than terpolymer I was greater than terpolymer I. In other words, the terpolymers with higher molar ratio of VCap to VP can affect the nucleation more effectively. In addition, the maximum subcooling for terpolymer III was a bit higher than that of terpolymer II, and it may be associated to the higher percentage of DMAEMA in terpolymer III. However, in terms of maximum subcooling, these terpolymers gave weaker performance than PVCap but it should be pointed out they were superior to all the synthesized copolymers. The results show that terpolymer II and terpolymer III could be put forward as appropriate KHIs to inhibit sII hydrate formation due to the fact that they indicate the most remarkable KHI effect on structure II hydrate growth rate among all the produced KHIs and also they exhibited stronger effect on nucleation compared with the copolymers.

The cloud point temperature in the presence of the terpolymers was also measured to determine if there is any application limit at high temperatures. Fig. 9 depicts the cloud point temperature of the solution of 0.25 wt% of the terpolymers in deionized water at varying

Table 4
Values of average hydrate growth rate in the presence of the terpolymers.

Aqueous solution	Average growth rate to = 500 s (mmol/min)	Average growth rate to = 1000 s (mmol/min)	Average growth rate to = 1500 s (mmol/min)
Terpolymer I	0.073	0.067	0.061
Terpolymer II	0.049	0.037	0.028
Terpolymer III	0.049	0.037	0.032

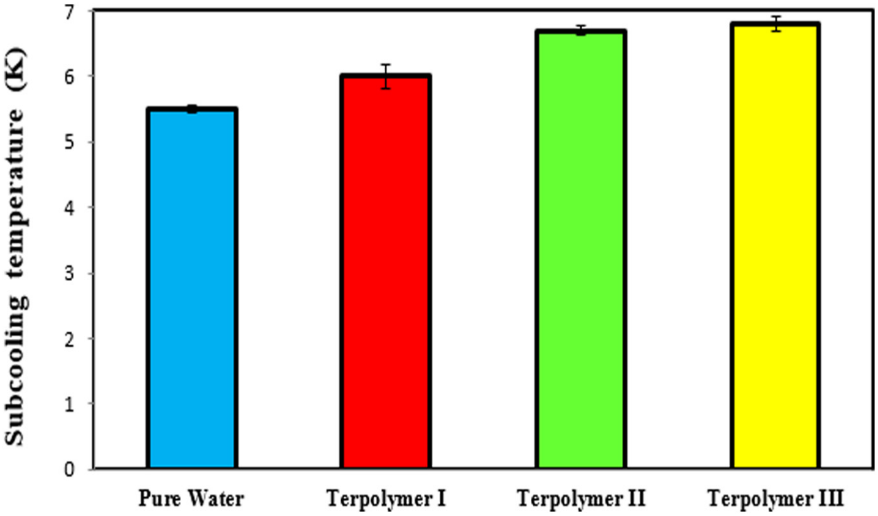


Fig. 8. Maximum subcooling for the terpolymers compared with pure water.

concentrations of NaCl, compared with that of PVCap. All the synthesized terpolymers gave higher cloud point temperature than PVCap, implying that these terpolymers not only showed better inhibition performance to reduce hydrate growth rate than PVCap but also they were more water soluble and did not precipitate at higher temperatures. This trend was also observed at different concentrations of NaCl, and hence the application range of the terpolymers was broader than PVCap. The cloud point temperature of the terpolymers in a solution containing 5 wt% NaCl was even higher than that of PVCap with no NaCl added. Thus, the terpolymers can be powerful KHI to use when the injection is conducted into hot and saline produced fluids. Terpolymer I has the highest cloud point temperature among all the terpolymers since it contains higher percentage of VP than VCap and DMAEMA. Terpolymer III gave a little lower cloud point than terpolymer II. The likely reason for greater cloud point of terpolymer II than that of terpolymer III is the percentage of DMAEMA which is higher in terpolymer III and causes less water solubility.

3.4. The inhibition effect of modified copolymers with MAA and 3-MPA on kinetics of methane-THF hydrate formation

Based on the previous sections, P(VP:VCap)II performed more effectively than other copolymers. The addition of chain transfer agents (CTAs) to reaction mixture may lead to producing more potent copolymers as modified polymers. MAA and 3-MPA were applied to modify P(VP:VCap)II and the modified copolymers were respectively named mI-P(VP:VCap)II and mII-P(VP:VCap)II. In the beginning, the influence of these modified copolymers on hydrate growth rate compared with P(VP:VCap)II was shown in Fig. 10(a). Based on the results, both modified copolymers showed the inhibition effect and were able to reduce the growth rate compared with pure water. In this regard, mII-P(VP:VCap)II acts more efficiently during the whole experiments compared with P(VP:VCap)II. It means that the chemical modification of P(VP:VCap)II using 3-MPA improves the KHI performance of the copolymers. The possible reason is that functional groups of 3-MPA, which were added to the end of modified copolymer chains probably form hydrogen bonds with water, and hence the stronger interaction between the modified copolymer and formed hydrate crystals may provide better adsorption and surface coverage. Therefore, it may conduce to the positive impact of 3-MPA functional groups on decreasing hydrate growth rate. However, MAA-modified copolymer showed less impact on hydrate growth rate. According to the results, only in the initial moments after the onset of hydrate formation, mI-P(VP:VCap)II was superior to P(VP:VCap)II. Table 5 also confirms that in the first 500 s after onset of hydrate formation the average growth rate in the presence of MAA-

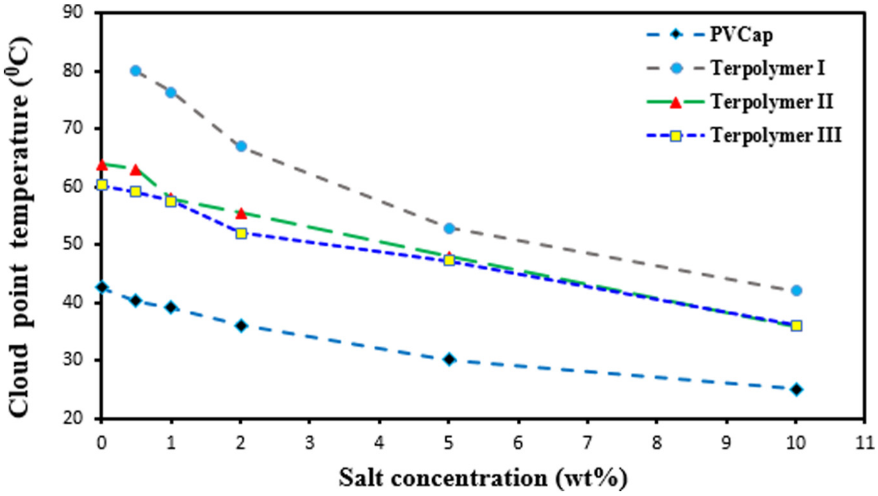


Fig. 9. Cloud points of the terpolymers compared with PVCap in solutions containing NaCl at varying concentrations.

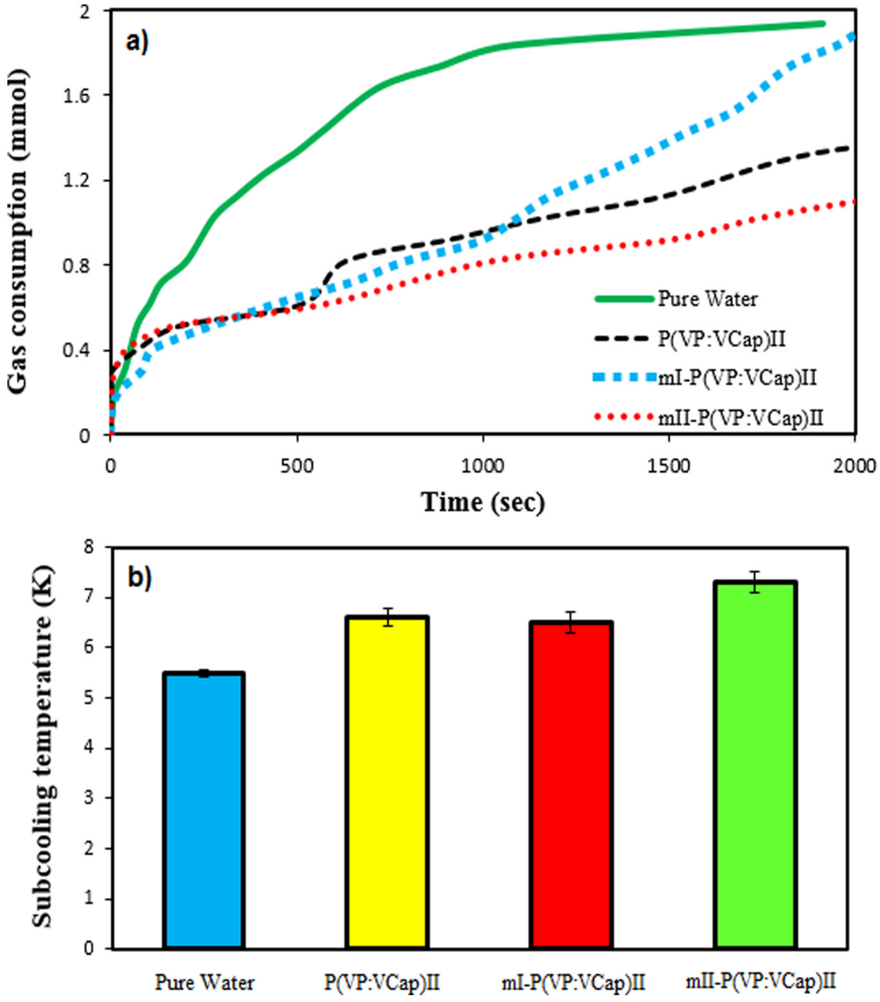


Fig. 10. (a) Inhibition performance of modified copolymers on hydrate growth compared with P(VP:VCap)II. (b) Values of maximum subcooling for modified copolymers.

modified copolymer was less than that of mII-P(VP:VCap)II and P(VP:VCap)II, but its performance got weak with time.

The influence of modified copolymers on maximum subcooling was shown in Fig. 10(b). Based on the findings, mI-P(VP:VCap)II and mII-P(VP:VCap)II have the greater maximum subcooling compared with pure water that implies the inhibition effect on hydrate nucleation. Maximum subcooling in the presence of mII-P(VP:VCap)II was more elevated in comparison with P(VP:VCap)II. In other words, chemical modification applying 3-MAA leads to increasing maximum subcooling and hence enhancing the inhibition potential. However, MAA had negligible effect on maximum subcooling. All in all, modification of P(VP:VCap)II using 3-MPA improved its inhibition performance in terms of both nucleation and reduction of the growth rate.

The effect of the modified copolymers on the cloud point was also examined. Fig. 11 indicates that the cloud point of 3-MPA modified copolymer (mII-P(VP:VCap)II) has an identical cloud point temperature to P(VP:VCap)II, besides this modified copolymer was the most potent inhibitor among all the copolymers. However, the cloud point temperature of MAA-modified copolymer (mI-P(VP:VCap)II) was much greater than P(VP:VCap)II. Chemical modification of copolymer using MAA raised the cloud point temperature to about 21 °C higher than non-modified copolymer, the same trend was found in the varying concentrations of NaCl. Although MAA did not improve the KHI performance of copolymer, the solubility of MAA-modified copolymer was significant. Due to the significant inhibition potential of mII-P(VP:VCap)II and remarkable hydrophilicity of mI-P(VP:VCap)II, these two modified copolymers could be introduced as new KHIs.

3.5. The inhibition effect of the KHIs on nucleation time

The potential of the synthesized polymers to delay the nucleation time was also measured and compared with commercial KHIs and pure water using an isothermal method of hydrate formation. Fig. 12 indicates the relative nucleation time which is the ratio of induction time

Table 5
Average growth rate in the presence of modified copolymers compared with P(VP:VCap)II.

Aqueous solution	Average growth rate to = 500 s (mmol/min)	Average growth rate to = 1000 s (mmol/min)	Average growth rate to = 1500 s (mmol/min)
Water	0.147	0.104	0.069
P(VP:VCap)II	0.061	0.049	0.041
mI-P(VP:VCap)II	0.049	0.055	0.049
mII-P(VP:VCap)II	0.061	0.037	0.024

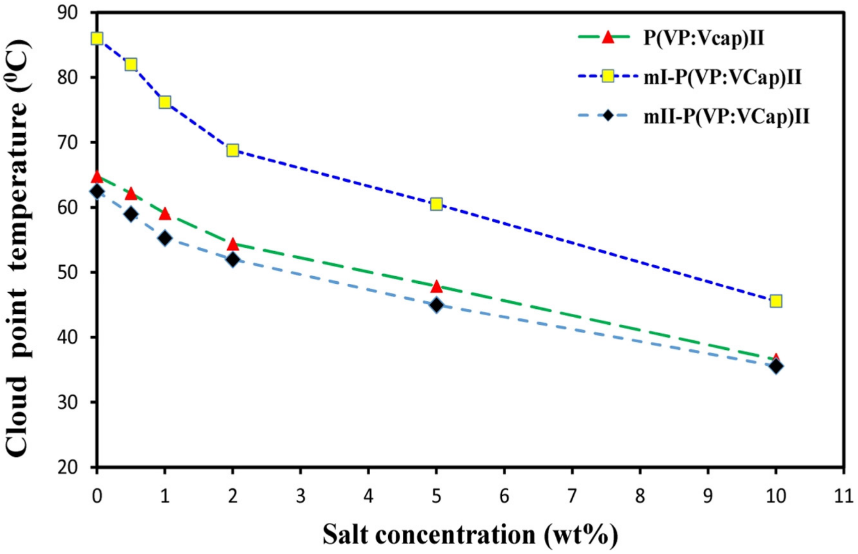


Fig. 11. Cloud point temperature of the aqueous solution of the modified copolymers at varying NaCl concentrations.

in the presence of produced KHI to the induction time of the pure water. Therefore, the higher relative induction time indicates that the KHI was more potent to prolong the nucleation time. Fig. 12(a) presents the relative nucleation time of the synthesized homopolymers and the commercial KHIs. Based on the results, the nucleation time of synthesized PVP and the commercial KHIs were low while synthesized PVCap could prolong the nucleation time efficiently. PVCap could prolong the nucleation time more than 12 times longer than the pure water while the nucleation time in the presence of PVP was almost similar to the nucleation time of the pure water. The relative nucleation time of the produced VP/VCap copolymers was illustrated in Fig. 12(b). The copolymer with the highest percentage of VCap in the copolymer had the greatest nucleation time (12.6 times longer than the nucleation time of the pure water). As the percentage of VCap decreased the shorter nucleation times were obtained. Fig. 12(c) compares the nucleation time of the synthesized terpolymers. The terpolymer with the highest percentage of VP in the copolymer had the lowest nucleation time. In terms of retarding the nucleation time, when the percentage of VCap increased, the terpolymers exactly exhibited the same trend of the copolymers. Furthermore, decreasing the percentage of DMAEMA from 5% to 1% could enhance the performance of KHI to retard the nucleation time. Fig. 13(d) illustrates the nucleation time of the modified VP/VCap copolymer compared with non-modified copolymer with the same molar ratio of VP to VCap. As it shown the 3MPA-modified copolymer could retard the nucleation time more effectively, whereas MAA-modified copolymer did not act as efficiently as the non-modified copolymer.

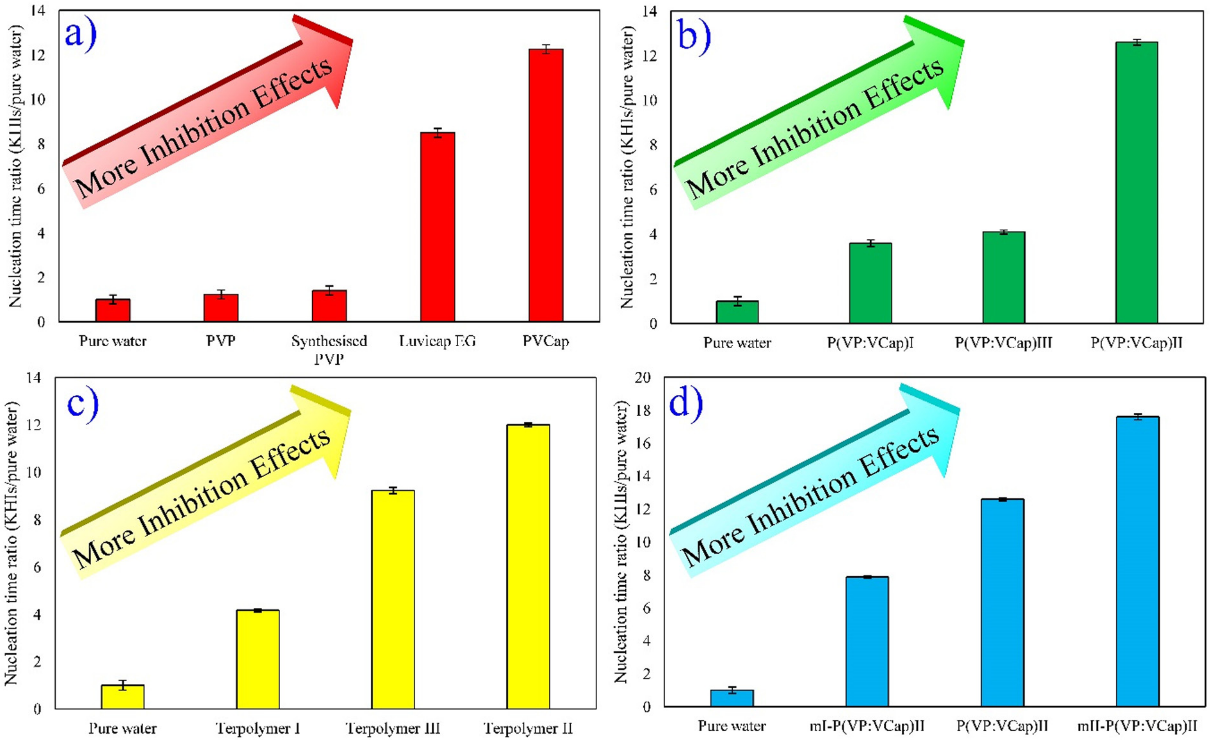


Fig. 12. The nucleation time ratio in the presence of the KHIs compared with pure water.

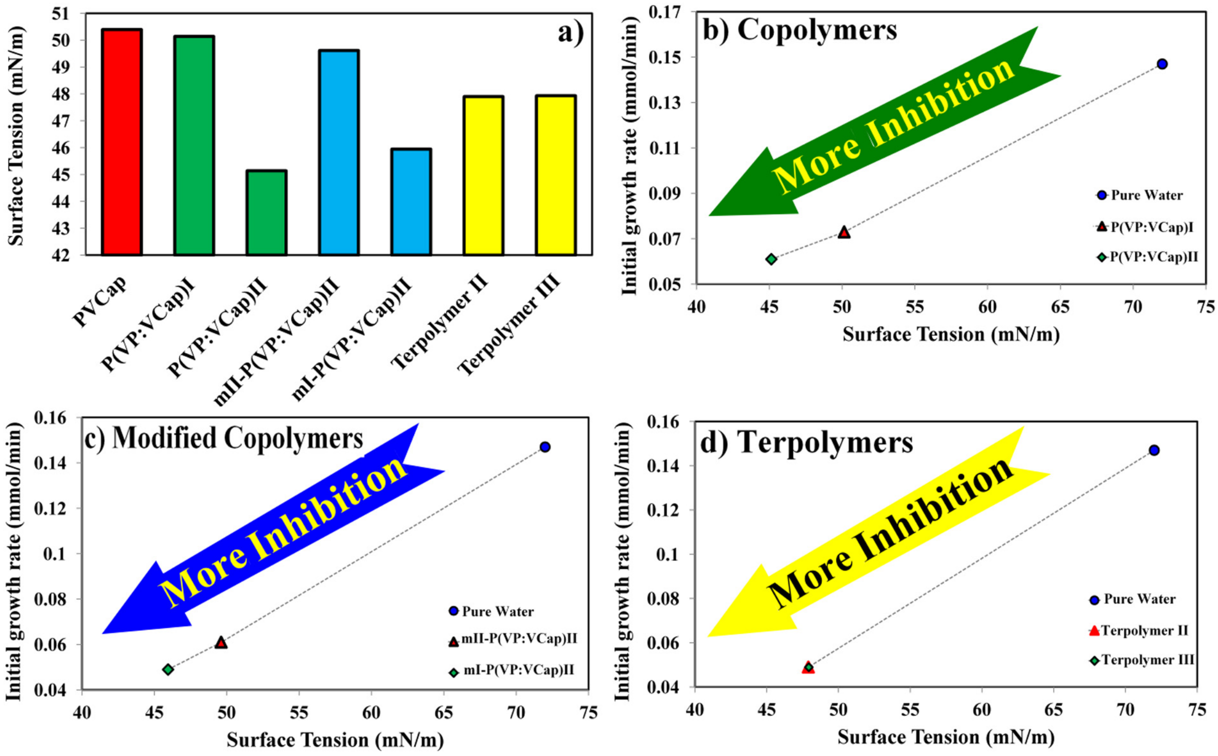


Fig. 13. Surface tension and its relation with hydrate growth in the presence of the copolymers, the modified copolymers, and the terpolymers.

3.6. Effective synthesized KHIs and their possible inhibition mechanisms

The experimental results demonstrated that the synthesized PVCap performed better than both Luvicap EG and the synthesized PVP. In this work, a series of VCap-based copolymers, modified copolymers, and terpolymers were also synthesized and it was found that some of these synthesized KHIs outperformed PVCap to inhibit sII hydrate formation. Among the synthesized KHIs, P(VP:VCap)I, P(VP:VCap)II, mI-P(VP:VCap)II, mII-P(VP:VCap)II, and all the synthesized terpolymers were superior to PVCap in the initial moments of hydrate growth. From the results of the experimental measurements, the surface tension of the solution of the all the above-mentioned KHIs, which were superior to PVCap, was less than that of PVCap (Fig. 13(a)). It therefore seems that the lower surface tension corresponds to better KHI performance. As shown in Fig. 13(b–d), there is a positive correlation between the initial growth rate and the surface tension among the copolymers, the modified copolymers, and the terpolymers. In other words, lower surface tensions corresponded to the polymers with the lower hydrate growth rate among each group of the copolymers, the terpolymers, and the modified copolymers. In fact, lower surface tension resulted in stronger adsorption on hydrate surface and hence the inhibition effect was enhanced [37]. Besides of the surface tension, there are other factors that can affect the KHI performance. For instance, hydrophobic functional groups of KHI molecules also lead to better inhibition effect. Correspondingly, when KHIs adsorb on hydrate surface and cover it, the hydrophobic functional groups may provide a strong barrier on hydrate surface to more effectively restrict the diffusion of water as well as hinder the hydrate formation. Accordingly, mI-P(VP:VCap)II due to its lower surface tension showed better inhibition performance than mII-P(VP:VCap)II in the initial moments of hydrate formation, but as time passed after adsorption on hydrate surface, hydrophobic functional group efficiently acted to produce a barrier and hence mII-P(VP:VCap)II became superior to mI-P(VP:VCap)II during the rest of hydrate formation process.

4. Conclusions

In this study, homopolymers, copolymers, and terpolymers with different molar ratios of VP, VCap, and DMAEMA were successfully synthesized. A high-pressure rocking cell was applied to conduct the KHI test. All the synthesized KHIs showed excellent inhibition performance to prevent sII hydrate. The synthesized PVCap reduced hydrate growth rate by 37% greater than a powerful commercially-available KHI (Luvicap EG). In terms of reduction of the growth rate, copolymers with the higher percentage of VP than VCap (75% and 50%) performed weaker than PVCap, whereas the copolymer with the VP/VCap molar ratio of 1:3 exceeded the PVCap. With regard to maximum subcooling, the PVCap outperformed all the copolymers. However, the cloud point temperature of the copolymers was more than 20 °C greater than that of the PVCap. The addition of DMAEMA as a third monomer to the reaction mixture led to the production of terpolymers, increasing the KHI performance by 20% greater than copolymers with identical VP:VCap molar ratios. Furthermore, as the percentage of DMAEMA in the terpolymer increased, the T_{cl} decreased. The copolymer with the VP to VCap molar ratio of 1:3 was modified applying MAA and 3-MPA. Despite the fact that the MAA-modified copolymer did not exhibit more inhibition effect than the non-modified one, it significantly led to an increase in T_{cl} by 21 °C. In terms of nucleation and reduction of the growth rate, the 3-MPA-modified copolymer showed better inhibition effect than non-modified type with the same monomer molar ratio. Furthermore, a possible mechanism was proposed to explain the inhibition performance of synthesized KHIs based on surface tension measurements and hydrophobic functional groups. According to the mechanism lower surface tension and increase in number of hydrophobic functional groups lead to better KHI performance.

CRediT authorship contribution statement

Hanie Mohsenzade: Conceptualization, Methodology, Software, Validation, Formal analysis, Investigation, Writing - original draft, Writing - review & editing. **Shima Foroutan:** Software, Validation, Investigation. **Ali Dashti:** Supervision, Conceptualization, Methodology, Resources, Data curation, Writing - review & editing, Project administration. **Navid Ramezanian:** Supervision, Methodology. **Hadi Roosta:** Conceptualization, Methodology, Supervision.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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