Full Length Article

Kinetic inhibition of structure I and II hydrate using novel modified poly (N-vinylcaprolactam)s in methane-water and methane-THF-water systems

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ABSTRACT

In the present study, poly(N-vinylcaprolactam)s (PVCaps) as potent kinetic hydrate inhibitors (KHIs) were synthesized to unveil their effect on the structure I (sI) and structure II (sII) hydrate nucleation and growth rate. With the aim of enhancing the KHI performance of PVCap, 3-mercaptopropionic acid, mercaptoacetic acid, and L-cysteine as chain transfer agents (CTAs) were applied to produce polymers with different end groups. The synthesized polymers were evaluated in methane-water system and methane-THF-water system. All of the modified PVCaps outperformed the non-modified PVCap in terms of cloud point temperature (T_{cl}) and decreasing both sI and sII hydrate growth rate. The most effective PVCap to reduce the sI growth rate was mercaptoacetic acid-modified PVCap, while mercaptopropionic acid-modified PVCap was the strongest to slow down the sII growth rate. Furthermore, the synthesized polymers acted better than commercial Luvicap EG and PVP to retard the induction time in a way that the relative inhibition power (RIP) value for PVCap was 1.5 times greater than the RIP when Luvicap EG was used, also the maximum subcooling that synthesized PVCap could tolerated, was 2.7 and 1.5 K greater than that of PVP and Luvicap EG, respectively. Besides, it was found that a blend of PVCap (MWav = 4308 g/mol) with a higher molecular weight PVCap (6900 g/mol) had the best performance to increase the RIP values to 4.07 and 22.87 on sI and sII hydrate, respectively.

1. Introduction

Gas hydrates are crystalline structures in which the lattice of water molecules encage small guest molecules through van der Waals forces at high pressure and low-temperature conditions [1]. According to the type and size of guest molecules, gas hydrates are classified into the following three types of structure: structure I, structure II and structure H. Gas hydrates have the potential as a fuel source for the future needs, in a way that large amount of energy is locked in hydrate reserves which is much more than the energy of fossil fuel resources. Also, they would be beneficial in other fields [2], including transportation of natural gas [3], preventing the emission of carbon dioxide [4,5], cooling systems, separation processes, and optimizing enzyme activity [6], etc. However, despite these advantages, pipeline blockage by gas hydrates may cause a considerable economic loss in the oil and gas industry. To solve this problem, changing the operating conditions, injection of thermodynamic inhibitors (THIs) and low dosage hydrate inhibitors (LDHIs) have been proposed. Reducing the pressure, heating up and burying the flow

line to prevent hydrate formation may not be economic methods. THIs such as alcohols, glycols and some kinds of inorganic salt are used at the high dosages to shift the hydrate thermodynamic equilibrium conditions to lower temperature or higher pressure. Due to economic losses and environmental damage possibly cause by THIs, LDHIs are used to relieve these problems. Kinetic hydrate inhibitors (KHIs) and anti-agglomerants (AAs) are classes of LDHIs. KHIs are water-soluble polymers such as poly(N-vinylcaprolactam) and poly(N-vinylpyrrolidone) (PVP) which delay gas hydrate nucleation and slow down hydrate growth rate [7,8].

KHI studies in the literature found that short polymer chains with a high ratio of surface to volume can perturb water structure better than long polymer chains. However, VCap monomers show little inhibition effect [9–11]. Besides, chemical modification is also a significant way to improve the inhibition performance of the KHIs such that Zhang et al. synthesized carboxyl-terminated PVCap by the addition of mercaptoacetic acid to the polymerization mixture, which caused high hydrophilicity and better inhibition performance of KHIs [12,13]. Also it was shown that polymerization with the addition of mercaptoethanol can

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boost the inhibition performance and increase the biodegradability of PVCap [14]. Furthermore, it was reported that a blend of low and high molecular weight polymers which contains 5–20 mass% low molecular weight polymer and 80–95 mass% high molecular weight polymer, exhibits better KHI performance than unimodal molecular weight distribution polymers [15].

Although PVCap is a powerful KHI, but further research endeavors are needed to develop an easier synthetic route to produce more potent KHIs with high cloud point temperature. The effect of the combination of two different molecular weighs KHIs was studied previously, but for PVCap especially in two different systems (comparison of its KHIs performance in sI and sII hydrate), based on the hydrate growth rate is not studied so far and more research is required to unveil its performance. Some modified versions of some polymers improve KHI performance [16–18]. However, employing mercaptopropionic acid and L-cysteine as chain transfer agents (CTAs) in homopolymerization system and comparing the KHI performance of the produced polymers with other modified and non-modified PVCap, especially their effect on both sI and sII hydrate growth rate need to be investigated. According to some studies, amino acids have been shown to increase the potential for prevention of hydrate formation, although it was not much considerable [19–21]; therefore, the idea for developing commercial KHIs such as PVCap with an amino acid would be useful. For example, L-cysteine-modified PVCap is expected to be more efficient than normal PVCap.

In this paper, a series of KHIs were synthesized in isopropanol medium. Mercaptoacetic acid, 3-mercaptopropionic acid, and L-cysteine were used as chain transfer agents (CTAs) to modify the end group of PVCaps. A high-pressure stainless steel rocking cell was used to investigate the effects of the synthesized polymers on the growth rate, induction time and maximum subcooling of hydrate formation compared with commercial KHIs. Also, the KHI performance of bimodal blend of PVCap was assessed. The KHI potential of all the KHIs in two different systems (sI and sII hydrate) was compared and ranked based on relative inhibition power (RIP) values.

## 2. Experimental section

2.1. Materials

N-vinylcaprolactam monomer (VCap, 97%) was provided from Merck. α,α-azobis (isobutyronitrile) (AIBN, 99%) was obtained from Fluka. 3-mercaptopropionic acid (99%) purchased from Acros Organics. Isopropanol (iPrOH, 98%) was prepared by Arman Sina. L-cysteine (99%), mercaptoacetic acid (97%), tetrahydrofuran (THF, 99.8%), and PVP were purchased from Merck. Luvicap EG was purchased from BASF. Diethyl ether (EE, 99.5%) was obtained from Neutron. Also, *n*-hexane (85%) was obtained from Dr. Mojalali. Deionized water was prepared from Abtin. Nitrogen (99.99%) and methane (99.9%) were purchased from technical gas services. All chemicals are summarized in Table 1.

2.2. Producing of kinetic hydrate inhibitors

The reactions were conducted in a 50 mL three-neck round bottom flask under light nitrogen atmosphere. A mixture of *N*-vinylcaprolactam (NVCap) monomer (1.5 g) and AIBN (20 mg) as an initiator in isopropanol (10 mL) was prepared (Fig. 1). After the polymerization, solvent evaporated and the product of the reaction was dissolved in THF, and then it was precipitated in *n*-hexane twice, and the precipitate was separated from *n*-hexane. Then the produced polymer was also precipitated into diethyl ether. After purification the synthesized polymer were dried at 40 °C for several days until they found their constant weights. The modified PVCaps were prepared in an identical way and with the same amount of component but by adding 0.052 mL of a chain transfer agent (Fig. 2 and Table 2). Also, H-PVCap was synthesized in 5 mL isopropanol. Different functional groups of produced polymers and monomer were determined using Fourier Transform Infrared Resonance

Table 1
The chemicals used for experiments.

Component	Chemical formula	Purity (%)	Supplier
VCap	$C_8H_{13}NO$	97	Merck
AIBN	$C_8H_{12}N_4$	97	Fluka
Isopropanol	C_3H_8O	98	Arman Sina
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
Water	H_2O	Deionized	Abtin
Methane	CH_4	99.9	Technical gas services
Sodium chloride	NaCl	99.5	Dr. Mojalali
PVP	$(C_6H_9NO)_n$	–	Merck
Luvicap EG	$(C_8H_{13}NO)_n$	40 wt%PVCap in ethylene glycol	BASF
3-mercaptopropionic acid	$C_3H_6O_2S$	99	Acros Organics
Mercaptoacetic acid	$C_3H_6O_2S$	97	Merck
L-cysteine	$C_3H_7NO_2S$	99	Merck
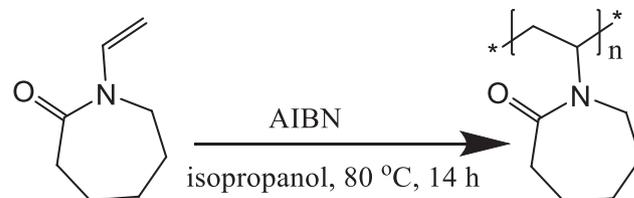
Fig. 1. The synthesis of PVCap.
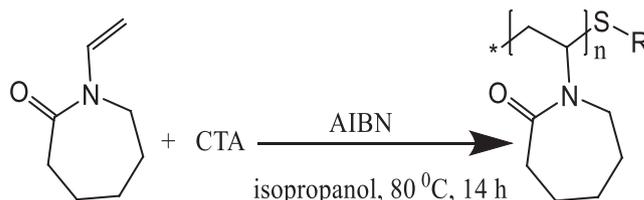
Fig. 2. The synthesis of modified PVCaps in the presence of CTAs.

(FTIR) spectroscopy. Successful polymerization would be confirmed by FTIR results, and the wavelength range is 400–4000 cm^{-1}. Also, molecular weight was measured by gel permeation chromatography (GPC) and THF was used as the mobile phase at 30 °C.
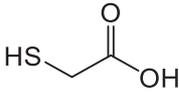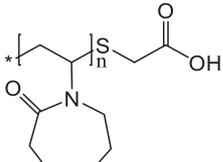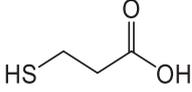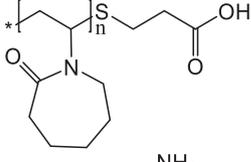
### 2.3. Cloud point measurement of kinetic hydrate inhibitors

Temperature-sensitive polymers such as PVCap precipitate in high-temperature aqueous solution. It is mainly due to breaking the hydrogen bond between water and the PVCap while heating and after that self-aggregation occurs [22]. The temperature of the cloud point was measured by a standard procedure. In a glass tube, 40 mg of produced polymer was dissolved in 16 mL deionized water (0.25 wt%) and then the solution was heated at a slow rate. The temperature at which the first sign of haze appears was recorded as the cloud point temperature (T_{cl}) [13]. Measurement of cloud point was repeated three times, and the average number was reported.

2.4. Apparatus and hydrate experiments

The isothermal method was used to determine the induction time and growth rate of methane hydrate formation. Tests of assessing inhibition performance of synthesized polymers were carried out in a 100 mL high-pressure stainless steel rocking cell [23,24], as shown in Fig. 3.

Table 2

CTAs and synthesized polymers.

Sample	Chain transfer agent (CTA)	Chemical structure	Synthesized polymer
m-PVCapI	Mercaptoacetic acid		
m-PVCapII	3-mercaptopropionic acid		
m-PVCapIII	L-cysteine		
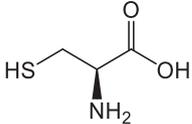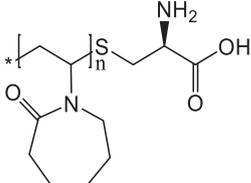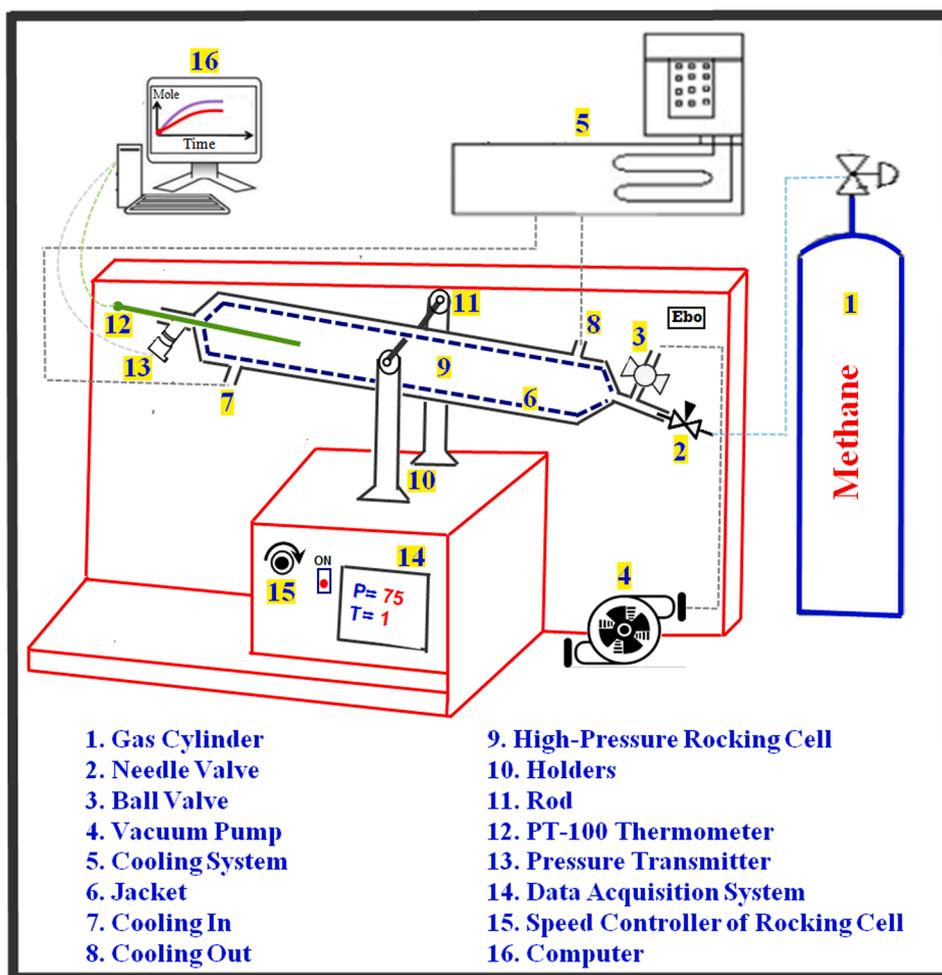
Fig. 3. Schematic of rocking cell apparatus.

A circulator was used to control temperature by a jacket surrounding the cell. An acquisition system was used to record pressure and temperature during the whole time of the experiments. During the test, the reactor rocking rate was 30 rocks per minute. A certain amount of inhibitor was dissolved in 80 mL of deionized water after the cell and lines were evacuated. Then, the solution was injected into the hydrate reactor.

After injection of a solution, rocking started, and the temperature was reduced to 274.15 °C. After that rocking was stopped, the inlet valve of methane was opened, and the pressure was increased to about 75 bar, and then rocking started again. Firstly, small numbers of methane moles were dissolved in the liquid phase. After the induction of nucleation, a sudden pressure drop occurred since gas hydrate was generated. Induction time was determined based on the time period from beginning of the experiments to the onset of hydrate growth. Then the relative inhibition power (RIP) values were calculated based on Eq. (1). It should be mentioned that, all the experiments were repeated, and the average values were reported.

$$RIP = \frac{(Induction\,time\,with\,inhibitor) - (Induction\,time\,without\,inhibitor)}{Induction\,time\,without\,inhibitor}$$

The number of moles of methane which were consumed during the formation of gas hydrate can be calculated by the Peng-Robinson equation. Also in this paper, with the aim of further evaluating the synthesized KHIs, aK^* values which represent kinetic coefficients, are also calculated using a mass transfer model proposed by Englezos et al. [25]. The model is based on chemical potential as driving force of hydrate formation. According to the model the gas consume rate (-dn/dt) can be expressed by Eq. (2):

$$-\left(\frac{dn}{dt}\right) = aK^*\left(\mu_g - \mu_{eq}\right) = aK^*RT\ln\frac{f_g}{f_{eq}} \quad (2)$$

where μ_g, μ_{eq}, R, T, a and K^* respectively denote the chemical potential of gas molecules in gas phase, the chemical potential of guest molecules of hydrate phase under equilibrium conditions, the gas constant, the temperature, the interfacial area and the overall kinetic constant. The hydrate formation rate (r_f) could be calculated by Eq. (3). Where f_g is the fugacity of guest molecules in gas and f_{eq} is the fugacity of guest molecules under equilibrium conditions and V_g is the volume of the gas phase, Δt and Δn represent the difference in time and moles of gas.

$$r_f = \left(\frac{\Delta n}{\Delta t}\right) = \frac{V_g}{RT}\frac{(f_g - f_{eq})}{\Delta t} \quad (3)$$

The produced polymers also tested in methane-THF system. After the cell had been washed by deionized water, it was evacuated applying a vacuum pump. An aqueous solution of the polymers at the specific concentration was prepared and mixed with THF at a molar ratio of 1:17

(THF to water). Then, the solution charged to the reactor. Subsequently injection of methane was carried out to pressurize the cell. Then the reactor was cooled to 274.15 K. The Peng-Robinson equation was also used to calculate the consumed moles of gas during hydrate formation process. A cooling method was also applied to calculate the maximum subcooling for the synthesized polymers and commercial KHIs. In fact, after the injection of the liquid phase and methane to the rocking cell, the temperature inside the cell was cooled at a constant rate to 1 °C, and onset temperature of hydrate growth (T_{onset}) was recorded at the temperature that the rapid decrease in pressure was observed. The difference between T_{onset} and the equilibrium temperature of the system at the initial condition (T_{eq}) was reported as the maximum subcooling ($T_{m.sub} = T_{eq} - T_{onset}$) [11,26].

3. Results and discussion

3.1. Polymer characteristics

The FTIR spectrums of synthesized polymers are illustrated in Fig. 4. The peak at 1658 and 3109 cm^{-1} located in the spectrum of monomer attribute to the double bond which has wholly disappeared in the spectrum of polymers due to successful polymerization. The absorption at 1624 cm^{-1} belongs to the carbonyl group in the monomer and polymer spectra, and it shifted to 1634–1638 cm^{-1} due to the change of conformation during polymerization. The peak at 3260 cm^{-1} corresponds to the hydrogen bonding and/or O–H stretching which has the greater surface area for modified PVCaps due to the presence of more hydroxyl groups and hydrogen bonding compared with normal PVCap. All modified PVCaps show absorption at about 3260 cm^{-1} due to their terminal groups. Disappearing of the peak at 2500 cm^{-1} indicates that CTAs had completely taken part in reaction to produce modified polymers [14,27]. In addition, the results of gel permeation chromatography show that PVCap average molecular weight is 4308 g/mol. The measured value for the molecular weight of H-PVCap was 6900 g/mol. Also, the results of gel permeation chromatography show that the molecular weight of m-PVCapI, m-PVCapII, and m-PVCapIII were 2792, 2584, and 2205 g/mol.

3.2. The cloud point measurements of modified PVCaps

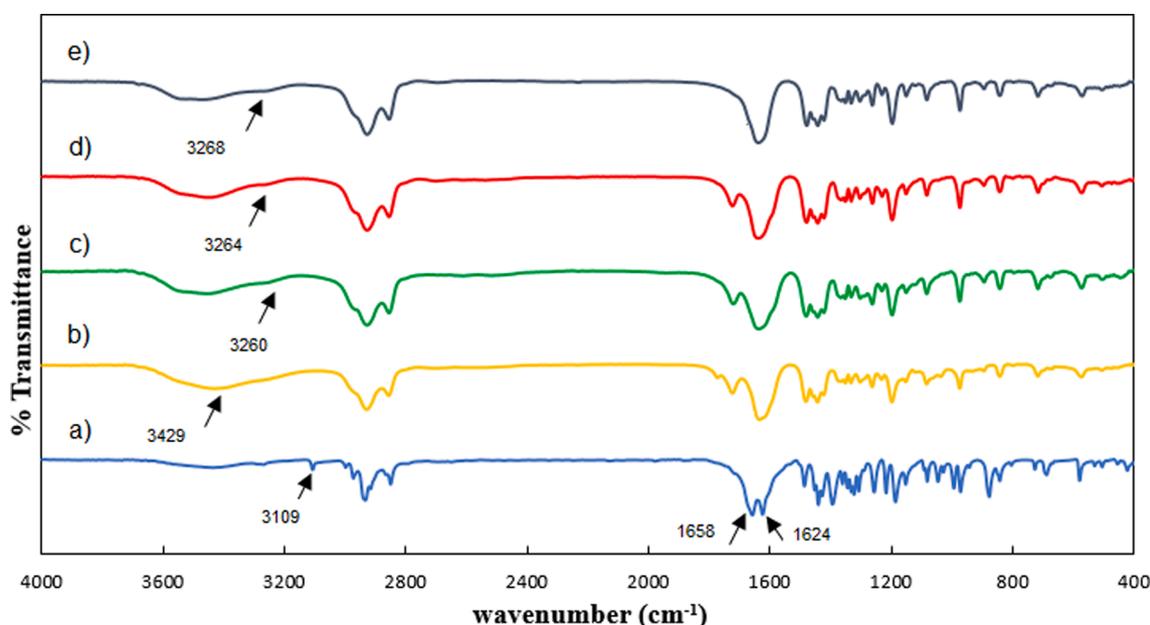The cloud point of KHIs is very important to avoid precipitation in

Fig. 4. (a) FTIR spectra of monomer, (b) PVCap, (c) m-PVCapI, (d) m-PVCapII, (e) m-PVCapIII.

hot or particularly saline fluids. The increase in cloud point temperature can broaden the range of applications of PVCap. In this paper, the cloud point temperature of normal PVCap, H-PVCap, m-PVCapI, m-PVCapII, m-PVCapIII at the concentration of 0.25 wt% was measured. Furthermore, the T_{cl} in the presence of sodium chloride at the concentrations of 0.5, 1, 2, 5, and 10 wt% are also reported in Fig. 5. Based on the results, the T_{cl} of the lower molecular weight PVCap is higher than that of H-PVCap. As the salinity of sodium chloride increased the cloud point temperature was decreased and same trend was observed for all the synthesized polymers. The greater value of T_{cl} of normal PVCap confirms its more hydrophilicity than H-PVCap.

The salinity of water reduces the cloud point temperature, for instance, as the concentration of salt increased the T_{cl} of PVCap decreased from 42.6 °C to 25.1 °C. It implies that at higher concentrations of sodium chloride the application of KHIs is limited. To solve this problem, modification of PVCap using mercaptoacetic acid, 3-mercaptopropionic acid, and L-cysteine are proposed. The modified polymers had a much higher cloud point temperature compared with normal PVCap. The results demonstrate that the T_{cl} of modified PVCap with mercaptoacetic acid (m-PVCapI) decreased from 50.5 °C to 33.3 °C when the salt concentration increased from 0 wt% to 10 wt%, while T_{cl} of modified polymer with 3-mercaptopropionic acid decreased from 50 °C to 31 °C and L-cysteine modified PVCap's T_{cl} reduced from 49.5 °C to 31.5 °C when the concentration of NaCl increased. The functional groups of mentioned above CTAs lead to producing modified PVCaps with the lower molecular weights that are more hydrophilic and hence greater cloud point temperatures were achieved. The chemical structures of mercaptoacetic acid, 3-mercaptopropionic acid, and L-cysteine include hydroxyl, carbonyl and amine groups which cause more hydrophilicity in modified PVCaps.

3.3. Inhibition effect of modified PVCaps on structure I hydrate formation

Firstly, to evaluate the KHI performance of the modified PVCaps, their effect on decreasing the sI hydrate growth rate was investigated. Fig. 6 illustrates the KHI performance of the polymers with different end caps in methane-water system (sI hydrate). All the synthesized polymers gave an immensely better inhibition performance than pure water. Based on the results the m-PVCapI provided a remarkably better KHI performance than all the KHIs and the polymers were ranked depending on their strength to decrease the sI hydrate growth rate as follows: m-PVCapI > m-PVCapII > m-PVCapaIII > PVCap.

The values of $aK*$ which are shown in Table 3 also confirm the previous section results. Based on these values, m-PVCapI has the lowest kinetic coefficient in a way that when it was applied, the kinetic coefficient was 25 times lower than in the presence of normal PVCap. It should be mentioned that when the synthesized polymers were used, the $aK*$ values decreased more than 50% compared with pure water.

The outstanding behavior of modified PVCaps might be affected by their molecular structure as shown in Table 2. It should be mentioned that unlike PVCap, modified PVCaps contain hydroxyl end group structures, therefore they might be able to form stronger hydrogen bonding with water molecules of hydrate surface [28]. According to possible mechanism of KHIs performance, PVCap can adsorb to the surface of the hydrate through the carbonyl group of the repeating units while functional end groups of modified PVCaps can also form hydrogen bonds besides carbonyl groups of their repeating units. Based on this, modified PVCaps, which had hydroxyl groups and lower molecular weights, probably adsorb better than PVCap that might be the reason why they have a better inhibition performance. However, the results demonstrated that m-PVCapI has the most effect on the reduction of growth rate of methane hydrate. In fact, it considers that m-PVCapI end group cause stronger interaction between the polymer and hydrate surface. Therefore, it can lead to a higher inhibition effect.

3.4. Inhibition effect of PVCap, H-PVCap and their blend on methane hydrate formation

In this work, the inhibition performance of two different PVCaps with unequal molecular weight ($MW_{av} = 4308$ g/mol and $MW_{av} = 6900$ g/mol) and a blend of these two polymers were evaluated. The molar ratio of H-PVCap ($MW_{av} = 6900$ g/mol) to PVCap ($MW_{av} = 4308$ g/mol) was 1:4 (H-PVCap: PVCap). In methane-water system (sI hydrate), H-PVCap showed better inhibition performance than the PVCap, also the blend performed similarly to the PVCap as shown in Fig. 7. It should be demonstrated that the inhibition of hydrate crystal growth occurs via the following possible processes: (1) Perturbing the local organization of water; (2) adsorbing to the hydrate surface. Lower molecular PVCaps are believed to perturb the water structure more strongly while higher molecular weight PVCaps may have a more pronounced effect on adsorbing to the hydrate surface with the much longer residence time [29–31]. Although water perturbation has an effect on hydrate nucleation and induction time, polymers adsorption can restrict the hydrate growth rate in a way that higher molecular weight polymer can cover more unoccupied hydrate cavities and hence reduce the diffusion rate of gas in the sI hydrate surface and offer more powerful growth inhibition as it shown in Fig. 7. Besides, very high molecular weight polymers might have less growth inhibition power for the reason that the polymer
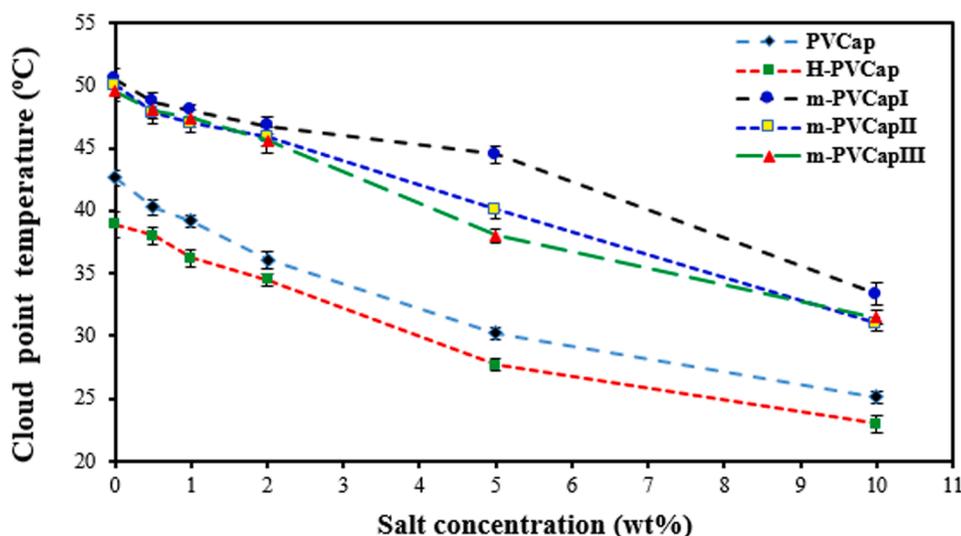

Fig. 5. Cloud point temperature for 0.25 wt% solution of synthesized PVCaps at varying concentration NaCl salinity.
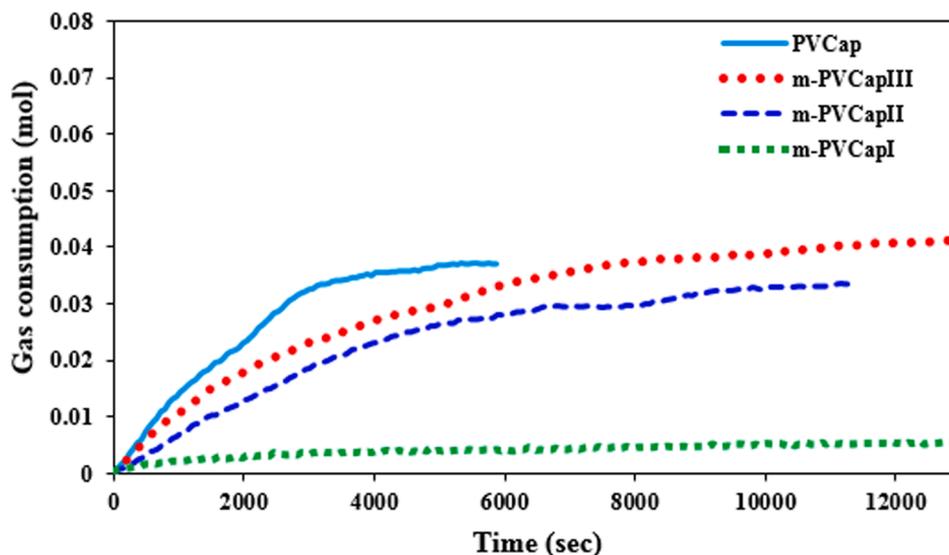
Fig. 6. The effect of modified PVCaps on the gas consumption (sI).

Table 3
Values of *aK** for PVCap and modified PVCap compared with pure water.

Aqueous solution	$aK^* \times 10^7 (mol^2/(s.J))$
Pure water	8.62
PVCap (4308)	3.50
m-PVCapI	0.14
m-PVCapII	0.77
m-PVCapIII	1.15

chains are entangled with each other and cannot cover the cavities potentially [10].

Table 4 represents the *aK** values for PVCap, H-PVCap and the blend of these two compared with pure water during the first moments of hydrate formation. Based on the results, the *aK** values for all samples are lower than that of pure water which implies good inhibition effect of synthesized KHIs. These results also confirm the results of gas consumption curves, the *aK** value of H-PVCap was the lowest which reconfirms its better performance than the lower molecular weight polymer and the blend of the two polymers. H-PVCap reduced the

kinetic coefficient by 81%, whereas PVCap and the blend reduced it by 60% and 66%, respectively.

3.5. The inhibition effect of PVCap on the kinetics of structure II hydrate formation compared with commercial KHIs

To further investigation into synthesized polymers, their influence on growth rate of the methane-THF (sII) hydrate was assessed. The formed hydrate in this system is structure II which is the most common structure in the oil and gas industry [32], therefore the inhibitors were evaluated under more identical conditions to the industry. First, the inhibition potential of the synthesized PVCap (MW$_{av}$ = 4308 g/mol)

Table 4
Values of *aK** for PVCap, H-PVCap and the blend of these two.

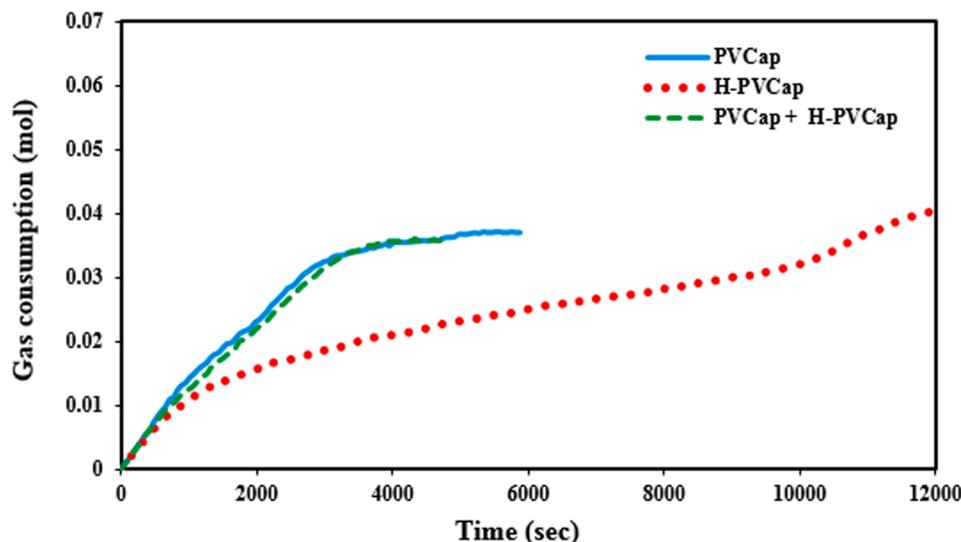| Aqueous solution	$aK^* \times 10^7 (mol^2/(s.J))$
Pure water	8.62
PVCap (4308)	3.50
H-PVCap	1.60
H-PVCap + PVCap	2.88

Fig. 7. The gas consumption during hydrate formation in the presence of synthesized PVCap and H-PVCap and their blend.

compared with commercial PVP and Luvicap EG to decrease the growth rate of hydrate is shown in Fig. 8. Based on the results, PVCap reduced the hydrate growth rate by 55% compared with pure water, while in the presence of Luvicap EG the growth rate decreased only by 25% and PVP did not exhibit inhibition performance. In fact, PVP cannot be counted as an effective inhibitor of structure II. Ke et al. [33] also confirmed that in some occasions, PVP may performed even as promoter.

3.6. The inhibition effect of modified PVCaps on the kinetics of structure II hydrate formation

As mentioned before, with the aim of improving the performance of PVCap, three different chain transfer agent were applied to modify the inhibitors. Mercaptoacetic acid, 3-mercaptopropionic acid, and L-cysteine can be added to the end of PVCaps chains to synthesize m-PVCapI, m-PVCapII, and m-PVCapIII, respectively. The influence of modified PVCap on growth rate of methane-THF hydrate (sII) was evaluated. Fig. 9 shows that the modified PVCaps were superior to normal PVCap. The modified polymer with 3-mercaptopropionic acid presented the best inhibiting results. However, its strength decreased as time passed. In addition, m-PVCapI and m-PVCapIII were also more powerful than PVCap. The reason for better results of m-PVCapI, m-PVCapII, and m-PVCapIII might be due to stronger adsorption of polymer into hydrate surface through hydrogen bonds in the presence of hydroxyl groups of the modified polymers with the lower molecular weights.

3.7. The inhibition effect of PVCap, H-PVCap and their blend on the kinetics of structure II hydrate formation

In this work, the impact of higher molecular weight PVCap (H-PVCap) (MW_{av} = 6900 g/mol) on structure II hydrate was investigated. Fig. 10 shows that H-PVCap outperformed PVCap (MW_{av} = 4300 g/mol) and reduced the sII hydrate growth rate by 57% compared with pure water. In other words, the stronger inhibition of structure II hydrate was observed when the molecular weight PVCap increased to 6900 g/mol. The inhibition performance of a blend with the molar ratio of PVCap/H-PVCap 4:1, was also assessed. Based on the results, a blend of PVCap and H-PVCap (a bimodal KHI) was more potent in comparison with both PVCaps. This blend of PVCaps can decrease the hydrate growth rate by 68% compared with pure water. The blend of low and high molecular weight PVCaps exhibited efficient performance than unimodal molecular weight PVCaps. A probable reason for that is due to the fact that blend of H-PVCap and PVCap can simultaneously inhibit the growth of

large and small particles of hydrate sII. In a way that lower molecular weight polymers can prevent growth of relatively large hydrate particles, whereas larger polymers inhibit tiny hydrate particles [34].

3.8. The effect of the KHIs on the maximum subcooling of sII hydrate formation

Subcooling measurements were performed to further evaluation of inhibition performance of the synthesized polymers. Based on Fig. 11 that illustrates the values of maximum subcooling, PVCap (MW_{av} = 4308 g/mol) can tolerate the maximum subcooling of 8.3 K, whereas the maximum subcooling of Luvicap EG is 6.8 K which reconfirms the better performance of PVCap than Luvicap EG. Moreover, PVP had no effect on the hydrate nucleation in methane-THF-water system, not only it gave lower maximum subcooling but also it could not reduce the growth rate, and hence PVP did not act as a KHI Fig. 11 (a).

The maximum subcooling of modified polymers was also measured. The average values of subcooling for all modified polymers were greater than pure water (Fig. 11 (b)). The modified polymer with mercapto-acetic acid can tolerate the maximum subcooling of 9.5 K which is higher than the subcooling for pure water and normal PVCap. Adding mercaptoacetic acid function groups to PVCap not only decreases the structure II hydrate growth rate but also increases the value of subcooling. Although all the modified polymers were superior to PVCap regarding the decrease in hydrate growth rate, the maximum subcooling range for m-PVCapII and m-PVCapIII is very similar to normal PVCap. Among all the produced polymers the subcooling for m-PVCapI was the greatest, this may due to its higher hydrophilicity that is related to lower molecular weight and hydroxyl end groups. In general, modification of PVCap with such chain transfer agent not only reduce the sI and sII hydrate growth rate and increase the maximum subcooling but also raise the cloud point temperature of KHI even at high concentration of NaCl.

Fig. 11 (c) represents the values of maximum subcooling of PVCap, H-PVCap and the blend of these two high and low molecular weight polymers. All samples gave greater subcooling than pure water. The polymer with higher molecular weight PVCap can tolerate lower maximum subcooling. It seems that the lower molecular weight PVCap was able to perturb the water structure more effectively to retard the nucleation [30]. Sloan et al. [11] reported that at a certain concentration lower molecular weight polymers give greater subcooling. The value of subcooling of blend of polymers was the same as subcooling of the low molecular weight polymer. In general, the blend of high and low molecular weight polymers gave a better KHI performance than both PVCaps to hinder structure II hydrate formation. It can be deduced that
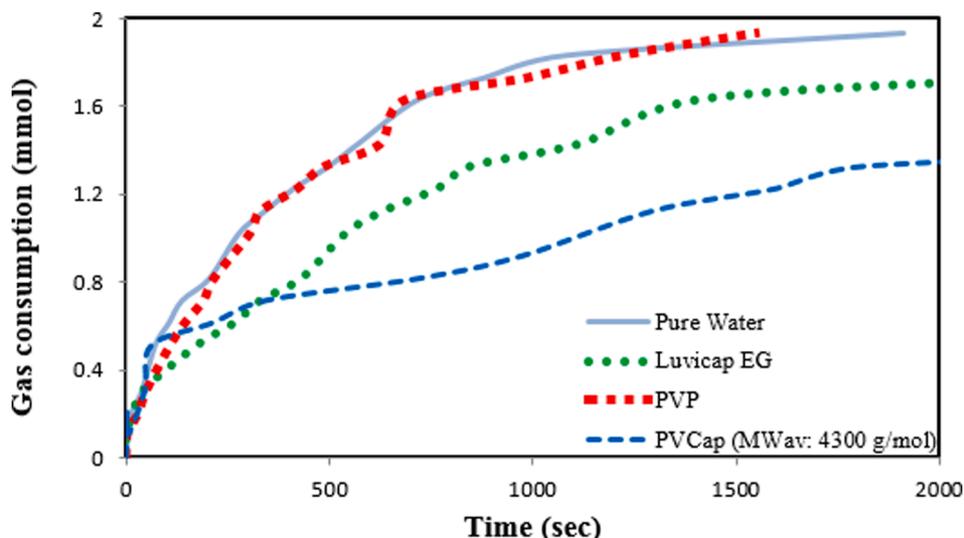

Fig. 8. Inhibition effect of the synthesized PVCap on hydrate growth rate compared with commercial KHIs.
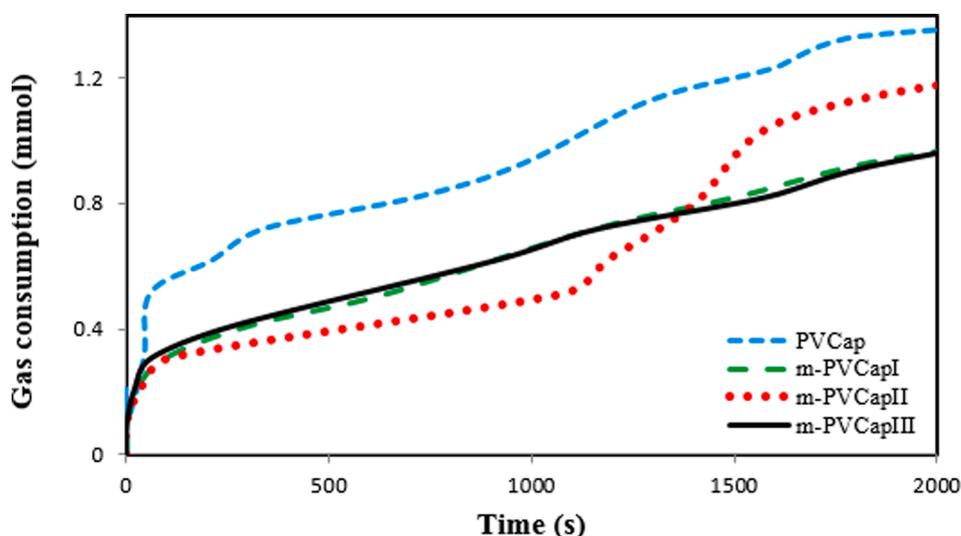
Fig. 9. Effects of the modified PVCaps on the growth rate of structure II hydrate.
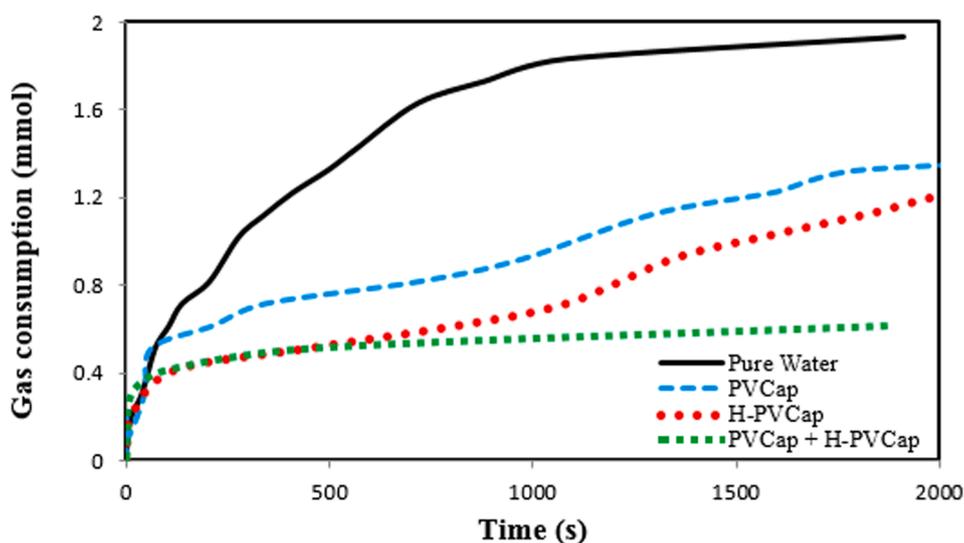

Fig. 10. Inhibition effect of the blend of low and high molecular weight PVCaps compared with unimodal polymers.

more hydrophilicity cause more water perturbation and hence it gives greater maximum subcooling.

The comparison of data of the synthesized PVCaps and commercial Luvicap EG in the present study with the data from literature was also conducted and the results were reported in Table 5. Based on the table, the maximum subcooling is in the range of 3.8 and 8.3 K for THF hydrate formation (sII) when PVCap is applied as inhibitor. The reported results in the table confirm the effect of molecular weight of PVCap on the KHI performance.

3.9. Comparison the inhibition effect of the KHIs to reduce sI and sII hydrate growth rate

Further calculation was provided to compare the effects of the KHIs on sI and sII hydrate. To unveil and evaluate the KHI performance of the polymers, sI and sII hydrate growth rate at specific time during hydrate formation process was calculated. The values of growth rate were calculated based on the mole consumption of methane as soon as the hydrate formation was started, after the induction time. Fig. 12 indicates the hydrate growth rate when 10 percent of the total methane was consumed ($n_{ci}/n_{cf} = 0.1$) where n_{ci} denotes moles of consumed gas up to

the moment of t_i, and n_{cf} is the total consumed moles. Fig. 12 (a) indicates the growth rates of sI hydrate in the presence of m-PVCapI, m-PVCapII, and m-PVCapIII were 84%, 55%, and 26% lower than the hydrate growth rate with PVCap, respectively. Also Fig. 12 (b) show the growth rate for sII hydrate at n_{ci}/n_{cf} of 0.1. All the modified polymers outperformed the PVCap in a way that m-PVCapI, m-PVCapII, and m-PVCapIII decreased the growth rate by 64%, 67%, and 59%. These results mean that polymers which are made using added CTAs improve the KHI performance to inhibit both sI and sII hydrate growth rate. It also indicates that m-PVCapI was more powerful inhibitor to decrease sI hydrate growth rate, while m-PVCapII was the strongest inhibitor to decrease sII hydrate growth rate.

Also the effect of different molecular weighs PVCap and their blend on sI and sII hydrate growth rate was compared. Fig. 13 represents that at $n_{ci}/n_{cf} = 0.1$, higher molecular weight PVCap acted better than the lower molecular weight PVCap to inhibit both sI and sII hydrate. Also, despite the fact that the bimodal blend did not show synergistic effect to reduce sI hydrate growth rate, it performed remarkably to prevent sII hydrate growth rate.
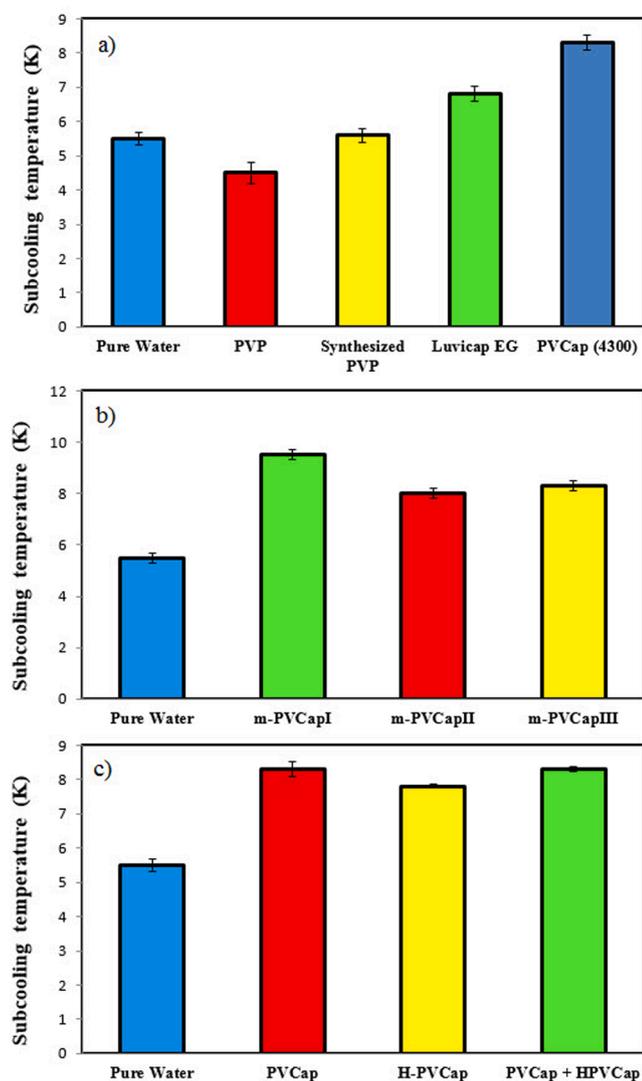
Fig. 11. The values of maximum subcooling of (a) PVCap compared with the commercial KHIs, (b) modified PVCaps, (c) bimodal blend compared with unimodal PVCaps.

Table 5
Comparison of the maximum subcooling temperature in the present study with the results reported in the literature.

Sample	Supplier	Dosage %	ΔT_{sub}	Structure	Reference
PVCap (Mw = 4300)	Synthesized	0.25 wt %	8.3	sII	Present study
PVCap (Mw = 6900)	Synthesized	0.25 wt %	7.8	sII	Present study
Luvicap EG	BASF	0.25 wt %	6.8	sII	Present study
Luvicap EG	BASF	0.45 wt %	3.8	sII	Kelland (2107)[35]
PVCap (Mw = 5900)	Synthesized	0.25 wt %	8.9	sI	Wan (2019) [14]
PVCap (Mw = 4000)	BASF	0.25 wt %	3.8	sII	O'reilly (2015)[10]
PVCap (Mn = 9200)	BASF	0.25 wt %	8	sI	Sloan 1998 [11]
PVCap (Mn = 2100)	BASF	0.25 wt %	10	sI	Sloan 1998 [11]

3.10. Comparison the inhibition effect of the KHIs to retard sI and sII hydrate formation

In this study, the capacity of modified PVCaps to retard sI and sII hydrate formation was also evaluated. Based on the experimental results, all of the produced polymers prolong the induction time compared with pure water and commercial KHIs. The RIP values are presented in Fig. 14 to evaluate the potential of KHIs to prolong the induction time of sI and sII hydrate. The modified PVCaps in terms of extending the induction time of both sI and sII hydrate, were ranked as follows: m-PVCapIII < m-PVCapII < m-PVCapI, and all modified polymers outperformed the non-modified PVCap. The explanation for these may be related to more hyrophilicty of modified PVCaps which can perturb the water more effectively and retard the nucleation.

Based on Fig. 14 (a and b), PVCap (MWav = 4308 g/mol), H-PVCap (MWav = 6900 g/mol) and the blend of these two polymers significantly delayed sI and sII hydrate nucleation and all gave a significantly better performance than pure water. The RIP value of PVCap (MW$_{av}$ = 4308 g/mol) in sI and sII were 0.7466 and 8.94, respectively, whereas the RIP of H-PVCap (MW$_{av}$ = 6900 g/mol) was about 0.48 and 7.51, respectively and for the blend of these two polymers RIP values increased synergistically to 4 and 22.8, respectively. It should be mentioned that based on RIP values, in general, the KHIs have more effect on sII than sI to extend the induction time. As shown in Fig. 5, the cloud point of PVCap (MW$_{av}$ = 4308 g/mol) was higher than H-PVCap (MW$_{av}$ = 6900 g/mol). This implies that lower molecular weight PVCap is more hydrophilic than that with a higher molecular weight, and hence this greater hydrophilicity might cause more water perturbation and perform better than that with a higher molecular weight as a KHI to delay the formation of sI and sII hydrate. The most potent hydrate inhibitor in terms of induction time for both structures was the blend of PVCaps for the reason that the water structure in the presence of two different molecular weight polymers might not be well organized due to the varying interactions of two polymers with water [36].

4. Conclusions

A series of PVCaps and modified PVCaps have been successfully synthesized in isopropanol medium. The results show that the synthesized PVCaps performed stronger than Luvicap EG in terms of increasing the maximum subcooling and decreasing the hydrate growth rate such that the maximum subcooling of synthesized PVCap is 1.5 °C greater than that of Luvicap EG, also PVCap can decrease the sII growth rate by 55% compared with that with pure water, while Luvicap EG decreased it by 25%. Regarding the modified PVCaps, the m-PVCapI were more powerful to inhibit sI hydrate growth compared with other modified PVCaps while m-PVCapII is the strongest inhibitor to decrease sII hydrate, in a way that m-PVCapI reduce sI hydrate growth by 84% and m-PVCapII reduce sII hydrate growth by 67%. The produced polymers were ranked based on their potential to extend the induction time of both sI and sII hydrate as follows: H-PVCap + PVCap blend > m-PVCapI > m-PVCapII > m-PVCapIII > PVCap > H-PVCap. Also, m-PVCapI has the greatest maximum subcooling among the synthesized PVCaps. It could be concluded that adding mercaptoacetic acid, 3-mercaptopropionic acid and L-cysteine to the polymerization systems led to producing PVCaps which gave a slower sI and sII hydrate growth (up to 70%) and about 8 °C higher cloud point than PVCap which can prolong the induction time of both sI and sII hydrate several time greater than that with the normal PVCap. Furthermore, PVCap, H-PVCap and their blend reduced the sII hydrate growth rate by respectively 55%, 57%, and 68% compared with pure water. In other words the blend of low and high molecular weight outperformed the unimodal in terms of reducing sII hydrate growth rate and delaying of the induction time of both sI and sII hydrate.
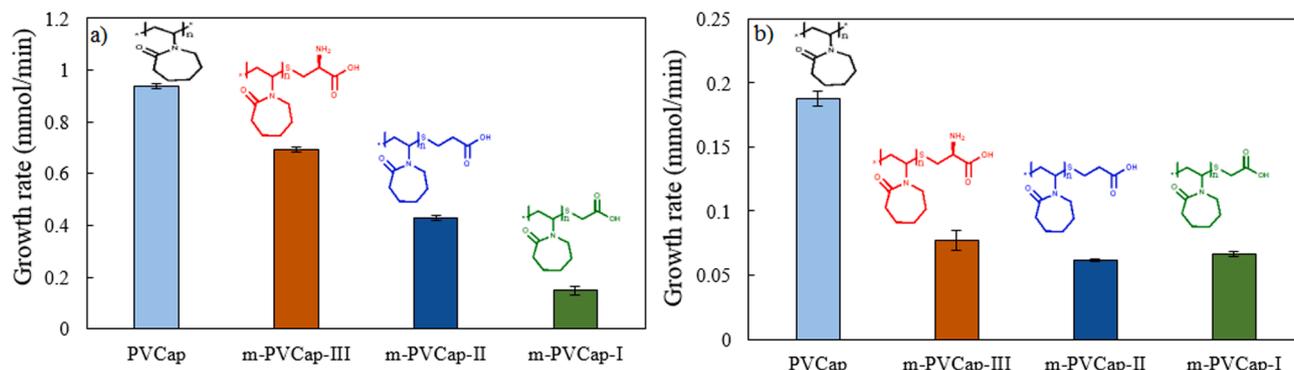
Fig. 12. Comparison of PVCap and modified PVCap at $n_{ci}/n_{cf} = 0.1$ (a) the sI hydrate growth rate (b) the sII hydrate growth rate.
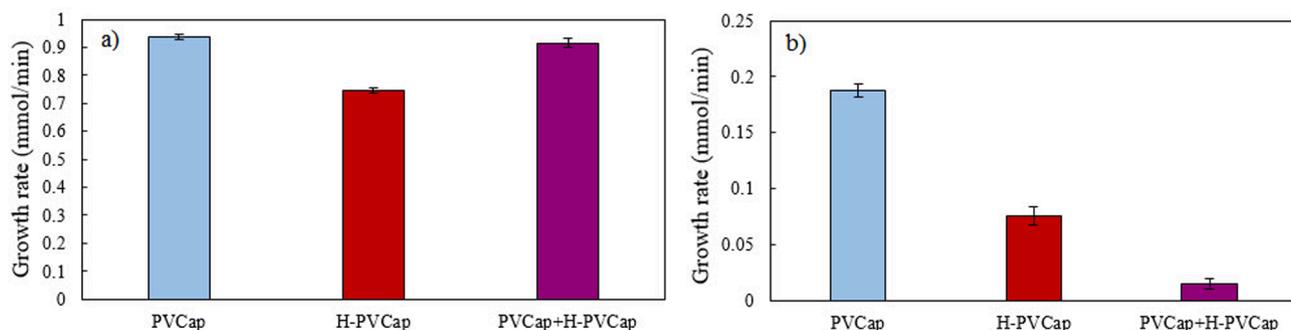

Fig. 13. Comparison of the bimodal blend with PVCap and H-PVCap at $n_{ci}/n_{cf} = 0.1$ (a) the sI hydrate growth rate, (b) the sII hydrate growth rate.
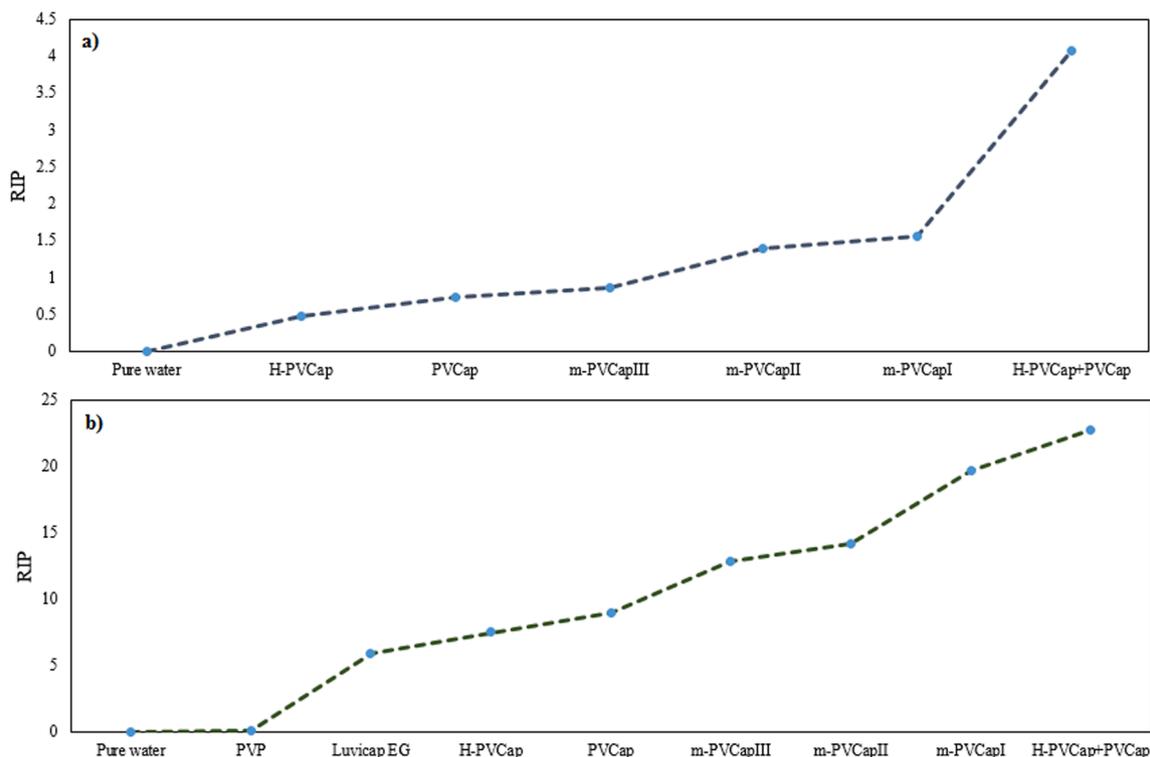

Fig. 14. The RIP values of the KHIs (a) sI hydrate, (b) sII hydrate.

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.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.fuel.2021.120490.

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