



# Effects of chemical modification of PVA by acrylamide, methacrylamide and acrylonitrile on the growth rate of gas hydrate in methane-propane-water system

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## ABSTRACT

In this work, two different series of modified polyvinyl alcohols (PVAs) were synthesized for evaluation of their performance as novel inhibitors of hydrate growth. In the first series, three monomers including acrylamide (AM), methacrylamide (MAM), and acrylonitrile (AN) were grafted onto PVA to produce graft copolymers. This series of modified PVAs which contains PVA-g-AM, PVA-g-MAM, and PVA-g-AN, decreased the growth rate of methane-propane hydrate, although their performance was weak in comparison with a well-known kinetic hydrate inhibitor such as polyvinylpyrrolidone (PVP). Among the graft copolymers, PVA-g-AM had the best performance. The second series of modified PVAs including PVA-AM, PVA-MAM, and PVA-AN were synthesized by functionalization of PVA with three demonstrated monomers. Some of these modified PVAs decreased significantly the hydrate formation rate and had superior performance, such that PVA-AM showed even better performance in comparison with PVP and decreased the hydrate growth rate to 75%. Also, the inhibition effects of some other functionalized PVAs were significant. The adsorption of synthesized polymers on hydrate surface was also evaluated by zeta potential measurement for better understanding of the modified PVAs performance as inhibitor of hydrate growth. In addition, surface tension measurement of modified PVAs solutions, investigation of molecular structures, and analysis of some probable mechanisms for inhibitory effects of modified PVAs showed that functionalized PVAs have high potential for application as novel inhibitors of hydrate growth.

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## 1. Introduction

Natural gas hydrates are non-stoichiometric crystalline compounds, which are formed when water and small gas molecules (such as methane, ethane, propane, and carbon dioxide) are contacted under high pressures and low temperatures. The water molecules by hydrogen bond formation can form three different types of cage-like structures (structures I, II and H) depending on the size and shape of the gas molecules [1]. Technological applications of gas hydrates such as storage of natural gas, CO<sub>2</sub> and hydrogen [2–4], gas transportation [5], separation of different gases [6,7], concentration of aqueous solution and liquid foods [8,9], cooling application [10], and seawater desalination [11,12] are potentially useful aspects of hydrate formation. Nevertheless, hydrate formation is more known as a practical problem in oil and gas pipelines. The hydrate crystal particles can agglomerate in the pipelines and subsequently lead to large pressure drops, and even can cause an impermeable plug in transmission lines [13]. Therefore, prevention of hydrate formation is of importance in oil and gas industry.

Dehydration of natural gas [13], electrical heating [14], line burial, and chemical injection [1] are the recommended preventive methods to decrease the risk of hydrate formation in the pipelines. However, the chemical injection is the currently most effective method for prevention of hydrate formation [15]. Thermodynamic hydrate inhibitors (THIs) such as methanol and ethylene glycol (MEG) were the first group of chemical inhibitors. However, the usage of these inhibitors is associated with some problems such as high operating and capital costs, the required large volumes and high recovery costs [16]. These problems led to the development of low dosage hydrate inhibitors (LDHIs). Kinetic hydrate inhibitors (KHIs) and anti-agglomerants (AAs) are two main groups of LDHIs. KHIs retard nucleation and slow down the hydrate growth rate, while AAs reduce the particle adhesion and subsequently prevent the agglomeration of hydrate particles and the plugging of pipelines [17–19].

KHIs are mainly water soluble polymers containing amide groups in their molecular structures. PVP, PVCap, Gaffix VC-713 and polyalkylacrylamides are the most common soluble polymers, which are known as kinetic inhibitors [20]. However, the poor biodegradability of these polymers has led to the research and development of inhibitors with good biodegradability properties [17]. Amino acids [21, 22],

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antifreeze proteins (AFPs) [23], polyaspartamides [24], starches [25], cellulose derivatives [26], chitosan [27], and pectin [28] have been introduced as biodegradable inhibitors in literatures. However, some of these chemicals (such as starches, cellulose derivatives, chitosan, and pectin) have usually low solubility in water and poor performance for prevention of hydrate formation. In this regard, chemical modification of these polymers may improve their solubility and inhibition properties. For example, Talaghat [29] applied a modified starch for prevention of hydrate formation. Their results showed that the efficiency of oxidized starch (as a water-soluble starch) is higher than the PVP. Also, Lee et al. [30] examine the effects of cationic starches as inhibitor and concluded that tapioca starch has a better performance in comparison with other modified starches. In addition, Roosta et al. [31] investigated the effects of a series of modified starches and modified hydroxyethyl celluloses (HECs). They concluded that some modified structures could act as inhibitor and decreased the growth rate of methane-propane hydrate. Unfortunately, the modification of biodegradable polymers for KHIs application has been limited to the aforementioned studies. Therefore, chemical modification of biodegradable polymers can help the development of new biodegradable inhibitors. Among biodegradable polymers, the effect of polyvinyl alcohol (PVA) on the kinetics of hydrate formation is almost unknown; while this structure may be suitable to prevent hydrate growth through the hydrogen bonding ability of its hydroxyl group. In addition, its performance may even be improved when suitable functional groups (especially amide groups) is applied for its chemical modification. However, no investigation has been dedicated to determining the effects modified PVA (as KHIs) on hydrate formation.

In this work, first, the effect of PVA on the kinetics of hydrate formation is investigated. Then, a series of modified PVAs are produced by graft copolymerization of acrylamide, methacrylamide and acrylonitrile onto PVA and their effects on the hydrate growth rate are tested. Also, the kinetic effects of functionalized PVAs on methane-propane hydrate formation are examined and compared with graft copolymers. In addition, the adsorption of synthesized polymers on hydrate surface is experimentally checked for evaluation of performance of modified structures as inhibitors of hydrate growth.

## 2. Experimental

### 2.1. Materials

High-purity nitrogen (99.999%), methane (99.99%), and propane (99.995%) were purchased from Technical Gas Services. PVA, acrylamide (AM), methacrylamide (MAM), acrylonitrile (AN), ammonium persulfate (APS), sodium bisulfite (SB), sodium hydroxide, and tetrahydrofuran (THF) were prepared from Merck, Germany. Also, methanol, isopropanol, acetic acid, and acetone were supplied from Neutron Co. Chemical formula, purity, and the supplier of the components are also listed in Table 1.

### 2.2. Experimental setup for synthesis of modified PVAs

Fig. 1 shows a schematic of the experimental setup used for the preparation of modified PVAs. It consists of a three-necked flask, which was under a nitrogen atmosphere and immersed in a constant-temperature water bath. Also, a water-cooled reflux condenser and a glass valve were installed on the openings of the flask. The other opening of the three necked flask was also capped and sealed by a rubber stopper. For heating and stirring of the water solutions a heat-stir plate and a magnetic stir bar were used. The temperature of water bath was controlled by a thermometer. Also, a vacuum pump was applied to evacuate the reaction flask. The nitrogen atmosphere was maintained throughout the reaction process with the help of nitrogen gas cylinder, regulator and nitrogen lines. In addition, a pH meter (with 0.01 pH units precision) was applied to control of pH during reaction.

**Table 1**

The materials used for synthesis and hydrate formation tests.

Component	Chemical formula	Purity	Supplier
Methane	CH <sub>4</sub>	99.99%	Technical Gas Services
Propane	C <sub>3</sub> H <sub>8</sub>	99.995%	Technical Gas Services
Nitrogen	N <sub>2</sub>	99.999%	Technical Gas Services
Polyvinyl alcohol (PVA)	[–CH <sub>2</sub> CHOH–] <sub>n</sub>	–	Sigma-Aldrich
Polyvinylpyrrolidone (PVP)	(C <sub>6</sub> H <sub>9</sub> NO) <sub>n</sub>	–	Sigma-Aldrich
Acrylamide (AM)	CH <sub>2</sub> CHCONH <sub>2</sub>	≥99%	Merck
Methacrylamide (MAM)	CH <sub>2</sub> C(CH <sub>3</sub> )CONH <sub>2</sub>	≥99%	Merck
Acrylonitrile (AN)	CH <sub>2</sub> CHCN	≥99%	Merck
Ammonium persulfate (APS)	(NH <sub>4</sub> ) <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	≥98%	Merck
Sodium bisulfite (SB)	NaHSO <sub>3</sub>	≥98%	Merck
Sodium hydroxide	NaOH	≥98%	Merck
Tetrahydrofuran (THF)	C <sub>4</sub> H <sub>8</sub> O	≥99.8%	Merck
Acetic acid	CH <sub>3</sub> CO <sub>2</sub> H	≥99.8%	Neutron
Methanol	CH <sub>3</sub> OH	99.9%	Neutron
Isopropanol	(CH <sub>3</sub> ) <sub>2</sub> CHOH	99.5%	Neutron
Acetone	CH <sub>3</sub> COCH <sub>3</sub>	99.0%	Neutron
Water	H <sub>2</sub> O		
Deionized-distilled	Abtin		

### 2.3. Experimental apparatus for hydrate formation tests

The equipments for hydrate formation were according to the schematic shown in Fig. 2. The apparatus mainly consists of a jacketed cell, circulating water bath (Lauda Alpha RA 8, Germany), gas flowing system, speed controller, vacuum pump, and a data acquisition system. The jacketed cell was a high-pressure stainless steel cell with a total volume of 650 mL, which operates with a maximum working pressure of 60 bar. It was also equipped with a mechanical stirrer. The speed of stirrer was variable from 0 to 1500 rpm by the speed controller. Also, the temperature within the jacketed cell could be adjusted in the temperature range of 248.15 to 358.15 K by an external cooling bath (Lauda Alpha RA 8). A Pt100 (platinum sensor) with a precision of ±0.1 K and a pressure transmitter with an uncertainty of ±0.1 bar were applied to measure the temperature and pressure, respectively. The experimental data (temperatures and pressures) were acquired and digitized by a data acquisition system and then was monitored and recorded with the help of a computer. Also, the zeta potential measurements were performed using zeta potential analyzer (Zeta Compact CAD, France) to characterize the adsorption of the inhibitors on hydrate surface. In addition, surface tensions of aqueous solutions were measured at 275 K with a Kruss K100 tensiometer (Kruss GmbH, Germany), which was equipped with a Wilhelmy plate.

### 2.4. Experimental procedure for hydrate formation

First, the high-pressure cell was washed three times with de-ionized water and evacuated by a vacuum pump. Then, 300 mL of aqueous solution of inhibitors was injected into the cell. The temperature was set at 275 K by the circulation of coolant through the jacket of the cell. When the temperature was stabilized at 275 K, the high-pressure cell was pressurized to reach the desired pressure and the stirrer was turned on and set at 400 rpm by speed controller. Also, the data acquisition system and the computer were turned on to record the data. When the solution was saturated with gas mixtures, the temperature was suddenly increased, and the cell pressure was decreased due to hydrate formation. For investigation of the effects of synthesized polymers on the hydrate growth, the moles of gas consumed during hydrate formation were measured and subsequently the average growth rate of hydrate

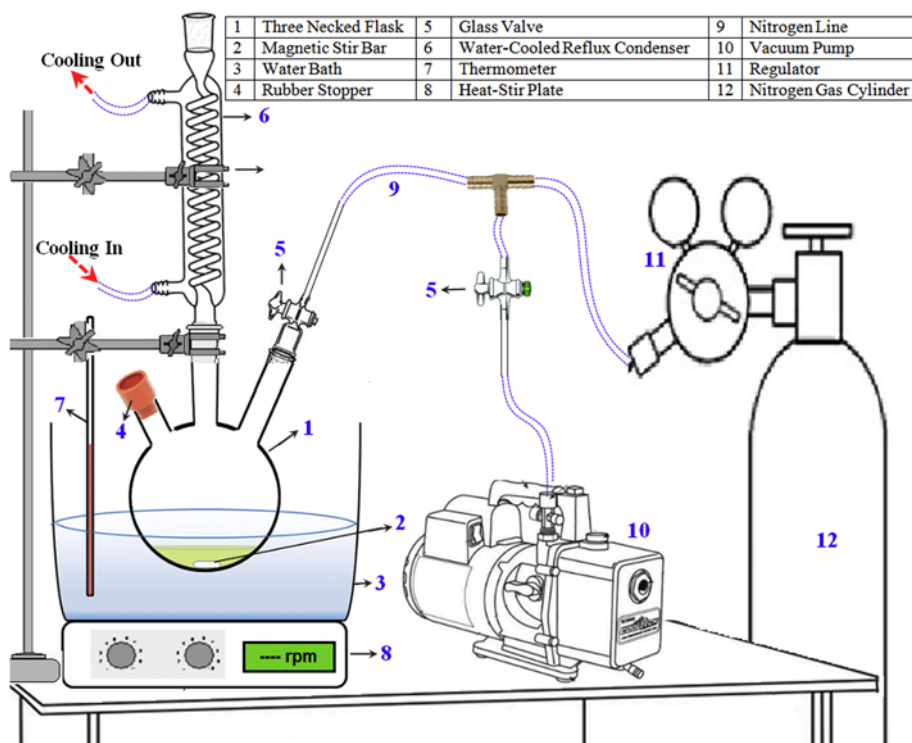


Fig. 1. The schematic of the experimental setup used for the preparation of modified PVAs.

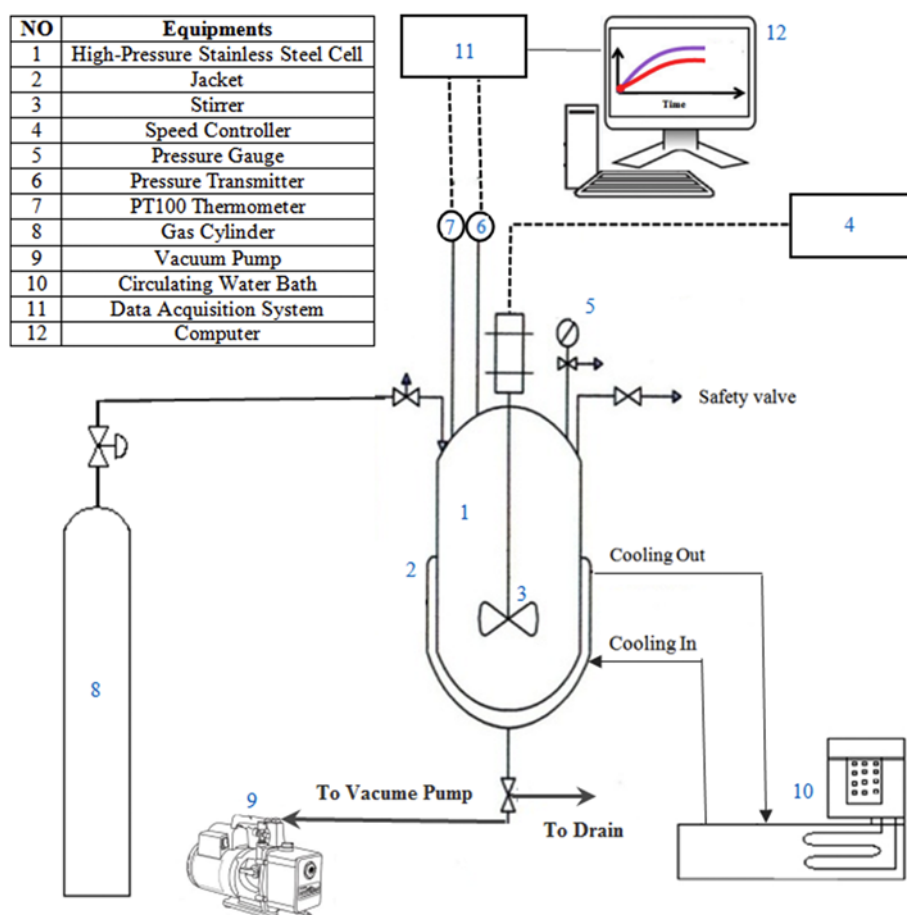


Fig. 2. Schematic of the experimental setup for hydrate formation.

and kinetic parameter of the chemical affinity model ( $-A_i/RT$ ) were calculated. It should be demonstrated that the values of  $-A_i/RT$  were obtained based on our previous work [32] and the following equations.

$$\frac{A_i}{RT} = - \ln \frac{n_{ci}}{n_{cf}} \quad (1)$$

$$\frac{A_i}{RT} = - \frac{A_r}{RT} \left[ - \ln \left( \frac{t_i}{t_k} \exp \left( 1 - \frac{t_i}{t_k} \right) \right) \right] \quad (2)$$

$$\frac{n_{ci}}{n_{cf}} = \left[ \left( \frac{t_i}{t_k} \exp \left( 1 - \frac{t_i}{t_k} \right) \right) \right]^{-\frac{A_r}{RT}} \quad (3)$$

where  $R$ ,  $T$ ,  $A_i$ ,  $A_r$ ,  $n_{ci}$ ,  $n_{cf}$ ,  $t_i$ , and  $t_k$  are universal gas constant, temperature, the chemical affinity at state  $i$ , kinetic parameter of the chemical affinity model, the moles of gas consumed up to time  $t_i$ , total moles of consumed gas, the time required to reach state  $i$ , and the time required to reach equilibrium conditions, respectively.

### 2.5. Synthesis of modified PVAs

The first series of modified structures were produced by graft copolymerization technique. In this respect, three different monomers including acrylamide, methacrylamide, and acrylonitrile were grafted onto PVA to produce modified PVAs (PVA-g-AM, PVA-g-MAM, and PVA-g-AN). The reactions for synthesis of these structures were conducted in a three-necked flask and initiated with a mixture of ammonium persulfate (APS) and sodium bisulfite (SB) as initiator. For this, the flask was evacuated and then backfilled with nitrogen three times and finally was exposed to a continuous flow of nitrogen. After this, 1.0 g of PVA was added to the flask including 20 mL de-ionized water. Then the flask was immersed in a water bath and the heat-stir plate was turned on. When the temperature was adjusted at 70 °C and a homogeneous solution of PVA was achieved, 1.0 g monomer (acrylamide, methacrylamide or acrylonitrile) was added to the solution. The reactions were initiated by adding of initiator to the flask and continued with stirring for 120 min. After this time, the reaction products were first cooled to room temperature and then precipitated with 120 mL of acetone. The obtained graft copolymers were washed 10 times with acetone-water mixture (70:30, v/v) to remove homopolymer. Finally, the pure graft copolymers as modified PVAs were washed with pure acetone and dried at 60 °C in an oven.

In this work, PVA was also functionalized with acrylamide, methacrylamide, and acrylonitrile for production of another series of modified PVAs including acrylamide-functionalized PVA (PVA-AM), methacrylamide-functionalized PVA (PVA-MAM), and acrylonitrile-functionalized PVA (PVA-AN). For synthesis of these modified structures, 1.0 g PVA was dissolved in 20 mL water and heated to 75 °C. When a clear solution of PVA was obtained, an aqueous solution of sodium hydroxide and 2.0 g monomer (acrylamide, methacrylamide or acrylonitrile) were also added to the flask. The reaction was continued under stirring for 120 min. After this time, the flask solution was neutralized by diluted alcoholic acetic acid solution, while the pH was controlled by a pH meter. The final product was obtained by precipitation of the flask solution with acetone, and then was dried in an oven at 50 °C.

## 3. Results and discussion

### 3.1. Characterization of modified PVAs

The polymer tacticity on the molecular structure of PVA for production of the modified PVAs are exhibited in Fig. 3. As is shown, in a series of modified PVAs (graft copolymers), acrylamide, methacrylamide, and acrylonitrile monomers are polymerized onto PVA, while in the other series of modified structures, the PVA is only functionalized by these monomers. The modified PVAs were characterized by Fourier

Transform Infrared (FTIR) spectroscopy in the wavelength range of 4000 to 400  $\text{cm}^{-1}$ . Fig. 4(a–d) reveals the spectral analysis of PVA, PVA-g-AM, PVA-g-MAM, PVA-g-AN, respectively. The results show that the original PVA has a strong absorption between 3000 and 3800  $\text{cm}^{-1}$  due to hydroxyl stretching vibration, while the PVA-g-AM, PVA-g-MAM have a absorption band about 3200  $\text{cm}^{-1}$  (a new peak in the range 3000 and 3800  $\text{cm}^{-1}$ ) that corresponds to association of hydroxyl groups of PVA and amide groups of polyacrylamide, polymethacrylamide. In addition, two other new peaks are observed at 1660 and 1600  $\text{cm}^{-1}$ . The new peak at 1660 corresponds to the carbonyl ( $\text{C}=\text{O}$ ) of amide group (in the structures of PVA-g-AM and PVA-g-MAM). Also, the new peak at 1600 can be attributed to bending vibration of NH group which belongs to the amide group of polyacrylamide, polymethacrylamide. On the other hand, the results of FTIR for PVA-g-AN reveal a remarkable difference of this structure in comparison with the structures of original PVA, PVA-g-AM, and PVA-g-MAM. According to Fig. 4(d), a new peak at 2243  $\text{cm}^{-1}$  is observed which correspond to  $\text{C}\equiv\text{N}$  of acrylonitrile group. In fact, this peak confirmed the presence of acrylonitrile in the structure of PVA-g-AN. Similarly, the results of FTIR for functionalized PVAs showed new peaks at 1660 and 2243  $\text{cm}^{-1}$  which confirmed the participation of amide and acrylonitrile groups in the modified structures.

### 3.2. The effects of PVA on growth rate of gas hydrate in methane-propane-water system

First, the effect of PVA as a biodegradable polymer was investigated on the growth rate of gas hydrate. In this regard, a gas mixture containing 85 mol% methane and 15 mol% propane was used for hydrate formation. Also, the experiments were performed in the presences of 0.25, 0.50, and 0.75 wt% of PVA. The hydrate formation rate was evaluated based on moles of gas consumed during hydrate formation [33] (due to the enclathration of gas molecules into the hydrate lattices). Also, the growth rate of gas hydrate was quantitatively determined by calculation of kinetic parameter of the chemical affinity model ( $-A_i/RT$ ) and the average rate of hydrate growth. Fig. 5 shows moles of gas consumed during hydrate formation with aqueous solutions of PVA and pure water. As is shown, the hydrate growth rate in the presences of PVA is decreased in comparison with pure water. Also, the growth rate decreases with the increase of PVA concentration from 0.25 to 0.75 wt%. In this respect, the calculated values for kinetic parameter of the chemical affinity model ( $-A_i/RT$ ) and the average rate of hydrate growth confirmed the decrease of hydrate formation rate. According to Table 2, when the concentration of PVA solutions is increased from 0.25 to 0.75 wt%, the value of  $-A_i/RT$  is reduced from 0.661 to 0.637 and the average rate of hydrate growth is decreased from 0.54 to 0.42 (mmol/min). These results demonstrate that PVA as a biodegradable polymer can be also considered as an inhibitor of the hydrate growth, although its performance should be evaluated in comparison with a common kinetic hydrate inhibitor such as PVP. Therefore, the inhibition effect of PVP on the hydrate growth was also examined and then compared with PVA. Fig. 6 reveals that the inhibitory effect of PVP on the hydrate growth was significantly stronger than that of PVA. The values of Table 2 also indicate that the hydrate growth rate in the presence of PVP is decreased to 73% in comparison with hydrate formation with pure water; while it is only reduced to 28% in the presence of PVA. In fact, although PVA is known as a biodegradable polymer but its weak inhibition effect on the hydrate growth hinders its application as inhibitor. In this regard, the chemical modification of PVA and polymer tacticity can be considered as a good idea to increase the inhibition effect. It should be demonstrated that the molecular structures of most inhibitors (such as PVP and PVCap) consist of amide groups, while PVA has only hydroxyl groups in its structure, which have insignificant effects on the kinetics of hydrate formation. Therefore, the modification of PVA with the molecules including amide groups (other effective functional groups) may improve the inhibition effect of PVA.



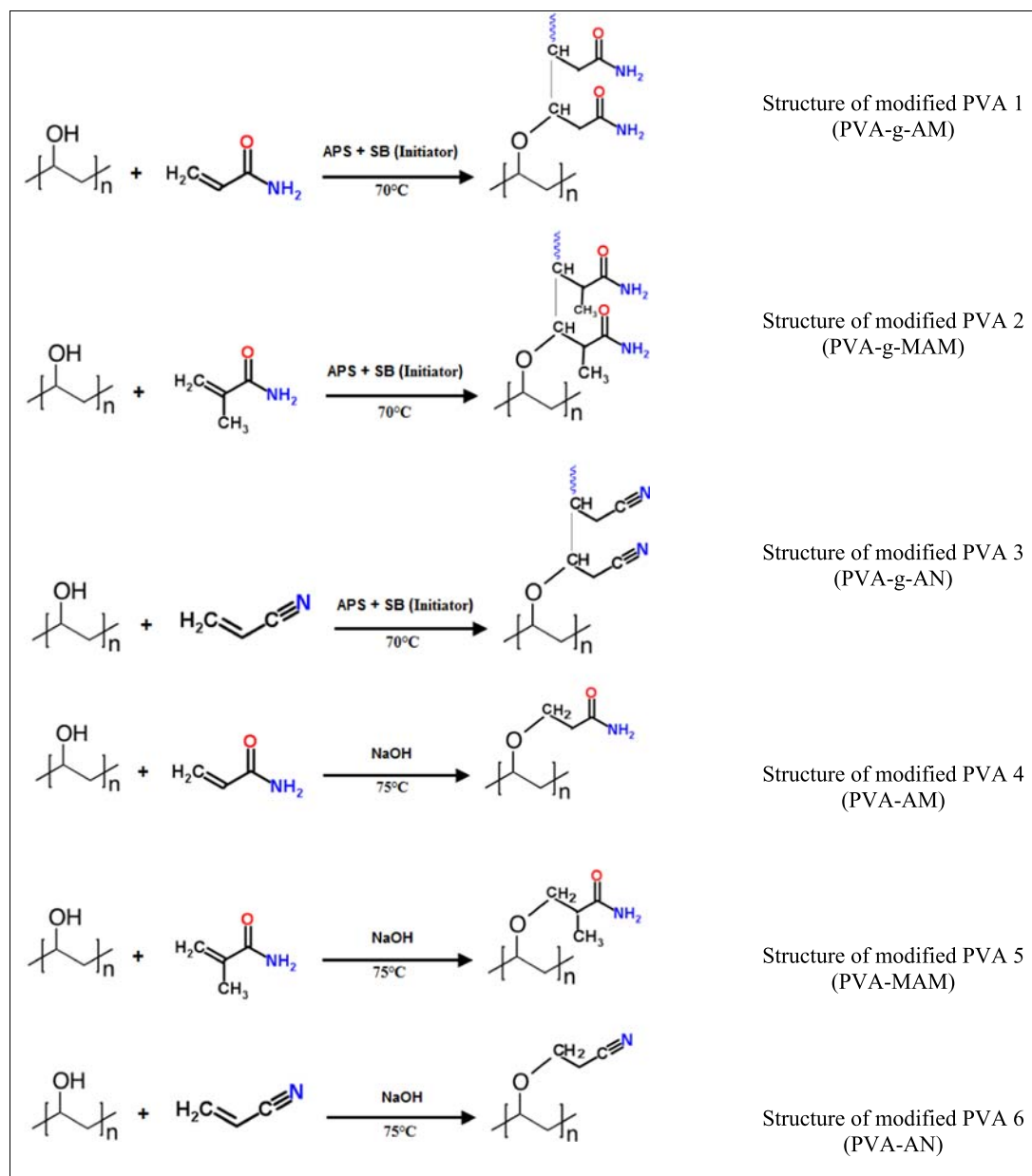


Fig. 3. Polymer tacticity on the molecular structure of PVA for production of modified PVAs.

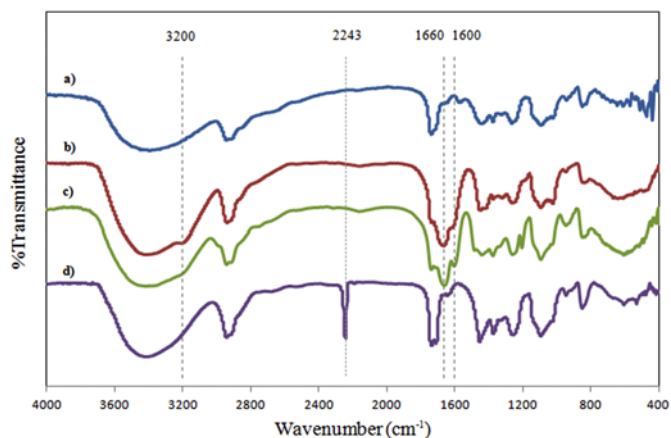


Fig. 4. (a) FTIR spectra of original PVA, (b) PVA-g-AM, (c) PVA-g-MAM, (d) PVA-g-AN.

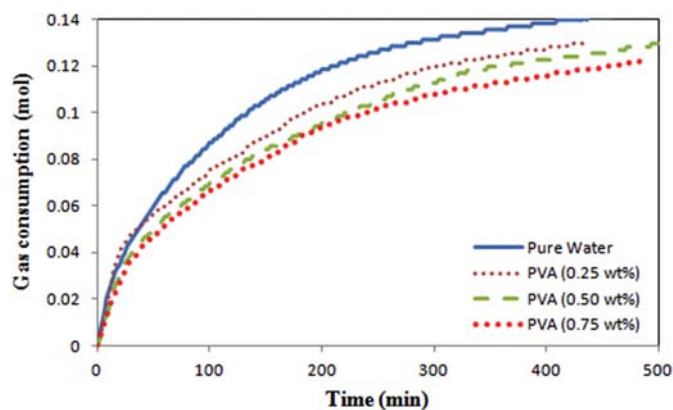


Fig. 5. The effect of PVA at different concentrations on the gas consumption during hydrate formation.

**Table 2**

The kinetic parameters of hydrate growth in the presences of PVA and PVP.

Inhibitors	Concentration (wt%)	Average growth rate (mmol/min) $-A_r/RT$	
Pure	–	0.75	0.697
PVA	0.25	0.54	0.661
PVA	0.50	0.45	0.641
PVA	0.75	0.42	0.637
PVP	0.25	0.20	0.531

### 3.3. The effects of graft copolymers (modified PVAs) on growth rate of gas hydrate in methane-propane-water system

As was demonstrated previously in this work, a series of modified PVAs were produced by graft copolymerization of acrylamide, methacrylamide, and acrylonitrile monomers onto PVA. For investigation of the potential of these copolymers as inhibitors of hydrate growth, their inhibition effects were examined at different concentration. Fig. 7 shows the influences of PVA-g-AM, PVA-g-MAM, and PVA-g-AN copolymers at the concentration of 0.25 wt% on the gas consumption during hydrate formation. The results indicate that PVA-g-AM decreases the hydrate formation rate. Also, it is seen that its inhibitory effect is higher than that of PVA. Among the synthesized copolymers, PVA-g-MAM also shows inhibition effect on the hydrate growth (at the concentration of 0.25 wt%), although its effect was less than that of PVA-g-AM. The obtained values in Table 3 also show that at this concentration, PVA-g-AM decreases the average rate of hydrate growth to 37% (in comparison with hydrate formation in pure water), while in the presence of PVA-g-MAM, it is reduced to about 34%. The obtained values for  $-A_r/RT$  also confirmed that the inhibition effect of PVA-g-AM is more than that of PVA-g-MAM. The results at the concentration of 0.50 wt% also demonstrate that PVA-g-AM is stronger for decreasing the growth rate of hydrate in comparison with PVA-g-MAM. Also, Table 3 indicates that PVA-g-AM decreases hydrate formation rate at the concentration of 0.75 wt% and its effect is higher than that of PVA. It should be demonstrated that the effect of PVA-g-MAM was not tested due to its low solubility at this concentration. Due to this reason, the inhibition effect of PVA-g-AN was only tested at the concentration of 0.25 wt%. Fig. 7 shows that PVA-g-AN can decrease hydrate formation rate and its effect is more than that of PVA, and even exhibits higher inhibition effect in comparison with two other graft copolymer (PVA-g-AM and PVA-g-MAM). However, although PVA-g-AN shows the best performance among graft copolymers, but its low solubility may limit its application. In this regard, it considers that PVA-g-AM would be more useful due to high solubility.

Based on the experimental results, it can be concluded that the chemical modification (by graft copolymerization) improves the

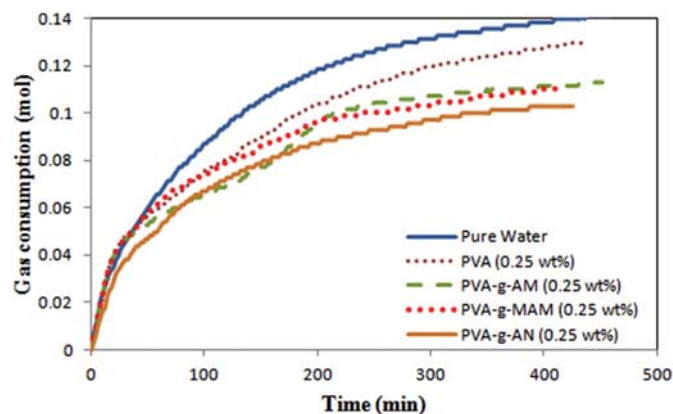


Fig. 7. The effects of PVA, PVA-g-AM, PVA-g-MAM, PVA-g-AN at the concentration of 0.25 wt% on the gas consumption during hydrate formation.

inhibitory effects of PVA. But however, it seems that the inhibitory effects are not remarkable. In this respect, the performance of graft copolymers can be compared to PVP. The obtained values in Table 3 show that PVA-g-AM, PVA-g-MAM, and PVA-g-AN decrease  $-A_r/RT$  to 0.644, 0.647, and 0.607, respectively, while PVP decreases it to 0.531. Therefore, although the performance of PVA is improved by chemical modification, but the inhibition effect of modified PVAs (modified by graft copolymerization) is not significant in comparison with PVP.

According to experimental results it is found that the molecular structure and the type of functional groups present in the modified PVAs are effective on the inhibitory performance. In this regard, Fig. 8 shows that PVA-g-AN (which contains a nitrile functional group in its backbone) has more inhibitory effects in comparison with two other graft copolymers (which have amide functional group in their backbone). Also, the grafting of acrylamide onto PVA leads to better inhibitor in comparison with when methacrylamide is polymerized onto PVA. However, before investigation of the possible reasons for these results, the performance of other modified PVAs should be also examined.

### 3.4. The effects of functionalized PVAs on growth rate of gas hydrate in methane-propane-water system

The other series of modified PVAs were produced by functionalization of PVA with the monomers (acrylamide, methacrylamide, and acrylonitrile). The effects of these modified PVAs were also examined on the kinetics of hydrate formation. Fig. 9 shows the effects of acrylamide-functionalized PVA (PVA-AM) on the gas consumption during hydrate formation. The experimental results indicate that PVA-AM significantly decreases the hydrate formation rate at the concentration of 0.25 wt%. As is shown in Fig. 9, the inhibitory effect of PVA-AM is very significant, even in comparison with PVA at the concentration of 0.75 wt%. The kinetic parameter of chemical affinity and the average rate of hydrate growth in the presence of PVA-AM are significantly decreased in comparison with original PVA (Table 4), such that PVA-AM decreases the growth rate to about 75% at this concentration. The inhibitory effects of PVA-AM were also tested at the concentration

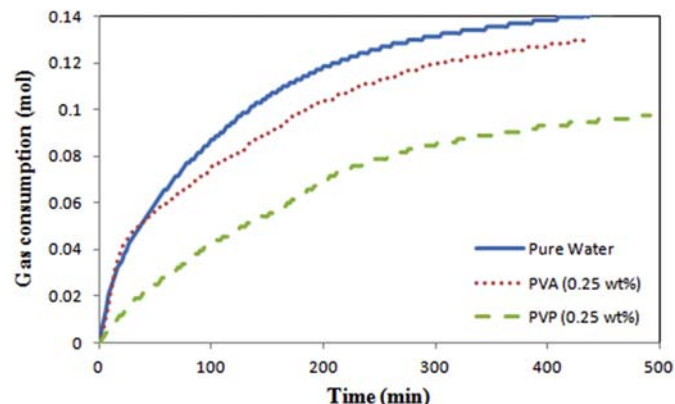


Fig. 6. Comparison between the inhibition effect of PVA and PVP on the growth of hydrate.

**Table 3**

The kinetic parameters of hydrate growth in the presences of graft copolymers.

Inhibitors	Concentration (wt%)	Average growth rate (mmol/min) $-A_r/RT$	
PVA-g-AM	0.25	0.47	0.644
PVA-g-AM	0.50	0.40	0.625
PVA-g-AM	0.75	0.38	0.614
PVA-g-MAM	0.25	0.49	0.647
PVA-g-MAM	0.50	0.44	0.639
PVA-g-AN	0.25	0.37	0.607

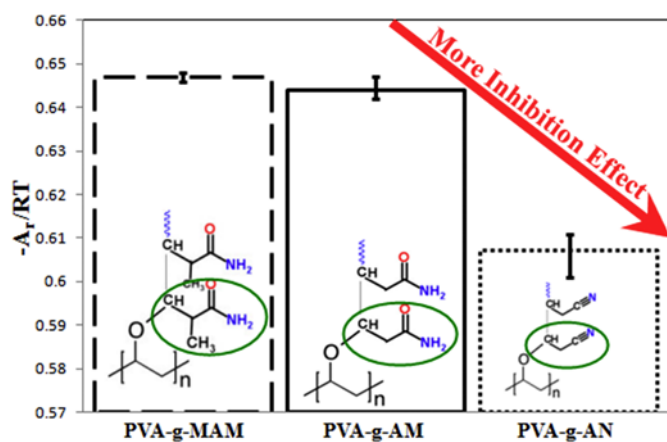


Fig. 8. Comparison between the inhibitory effects of different structures of graft copolymers on the hydrate growth based on the obtained values for  $-A_T/RT$ .

of 0.50 and 0.75 wt%, and the obtained results evidence that PVA-AM has also high potential as inhibitor of hydrate growth at these concentrations. In fact, the results indicate that functionalization of PVA with acrylamide, is an effective method for development of new inhibitors. Therefore, methacrylamide (which its structure is similar to acrylamide) was also applied for functionalization of PVA. According to Fig. 10 (a), methacrylamide-functionalized PVA (PVA-MAM) at the concentration of 0.25 wt% has also decreased the growth rate of hydrate, and its inhibition effect is stronger in comparison with original PVA. With the increase of concentration of PVA-MAM from 0.25 to 0.50 wt%, the inhibitory effect is also increased. On the other hand, the high potential of PVA-MAM at the concentration of 0.75 wt% shows that it can be also introduced as an inhibitor of hydrate growth. The interesting results were also obtained by functionalization of PVA with acrylonitrile. Fig. 10(b) shows that acrylonitrile-functionalized PVA (PVA-AN) has significant effect on the decrease of hydrate formation rate at the concentration of 0.25 wt%. In fact, PVA-AN can be also introduced as a new structure to decrease the growth rate of gas hydrate. The inhibitory effects of this structure could not be tested at the concentrations of 0.50 and 0.75 wt% due to its low solubility. Therefore, although PVA-AN has high potential as inhibitor of hydrate growth, but its low solubility may overshadow its high effectiveness. Based on these results, it can be concluded that by the functionalization of PVA with effective functional groups, new good inhibitors can be produced. In fact, it seems that the performance of the functionalized PVAs depends on the molecular structure of the applied monomers. Fig. 11 exhibits that PVA-AM has the best performance as inhibitor of hydrate growth among the modified PVAs. According to the experimental results, the ranking of PVA and functionalized PVAs to decrease the hydrate growth rate is as

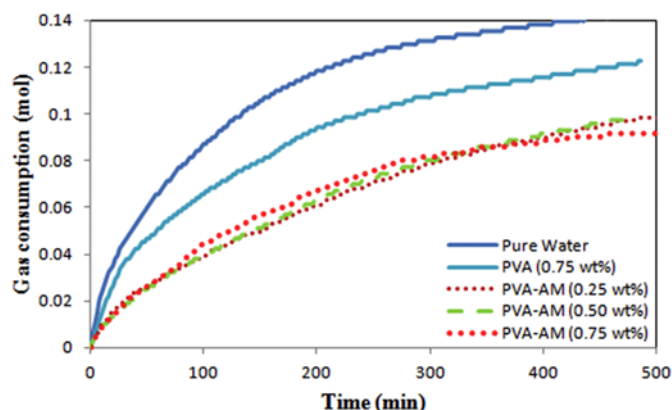


Fig. 9. The inhibition effect of PVA-AM in comparison with original PVA.

Table 4

The kinetic parameters of hydrate growth in the presences of functionalized PVAs.

Inhibitors	Concentration (wt%)	Average growth rate (mmol/min) $-A_T/RT$	
Functionalized PVA-AM	0.25	0.19	0.519
Functionalized PVA-AM	0.50	0.21	0.535
Functionalized PVA-AM	0.75	0.21	0.538
Functionalized PVA-MAM	0.25	0.45	0.634
Functionalized PVA-MAM	0.50	0.34	0.612
Functionalized PVA-MAM	0.75	0.29	0.590
Functionalized PVA-AN	0.25	0.24	0.555

follows: PVA-AM > PVA-AN > PVA-MAM > PVA. For better evaluation of functionalized PVAs, the performance of PVA-AM (as the best synthesized inhibitor) was compared with PVP. Fig. 11 shows that the inhibition effect of PVA-AM is higher in comparison with PVP, although the difference is rather small. The obtained values in Table 4 also indicate that PVA-AM can decrease the hydrate growth rate to 75% (in comparison with hydrate formation in pure water), while in the presence of PVP, it is decreased to 73%. Also, although based on the results of Table 4 the performance of other functionalized PVAs (PVA-MAM and PVA-AN) is not competitive with PVP but have significant effect on hydrate formation rate. In fact, functionalization of PVA as a biodegradable polymer with effective functional groups can be applied for the development of new inhibitors.

### 3.5. Investigation, analysis and comparison of obtained results

Comparison of calculated values for kinetic parameter of the chemical affinity model ( $-A_T/RT$ ) and the average rate of hydrate growth (Tables 3 and 4) exhibits the decrease in growth rate of hydrate by

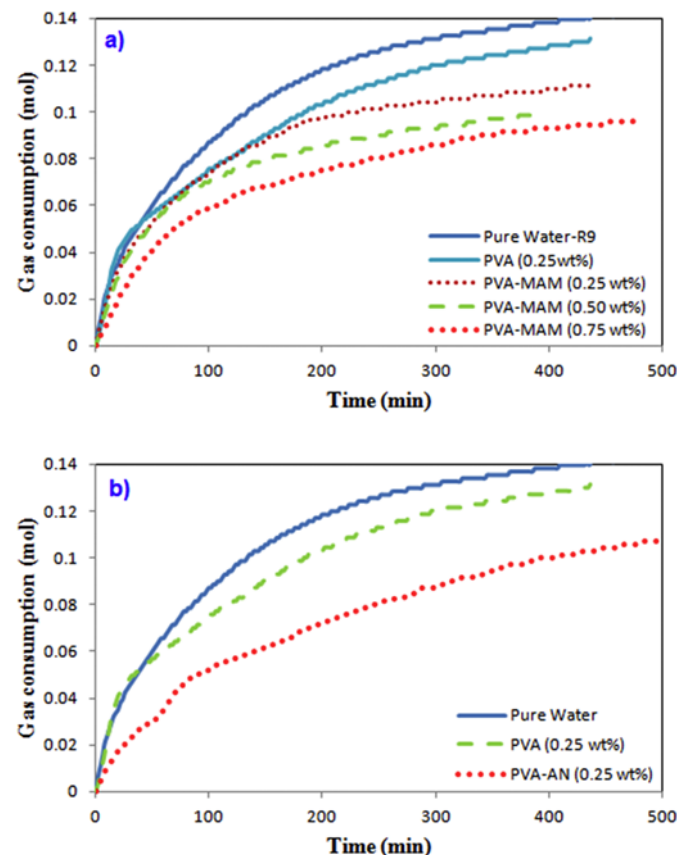


Fig. 10. The inhibition effects of functionalized PVAs (PVA-MAM and PVA-AN) in comparison with original PVA.

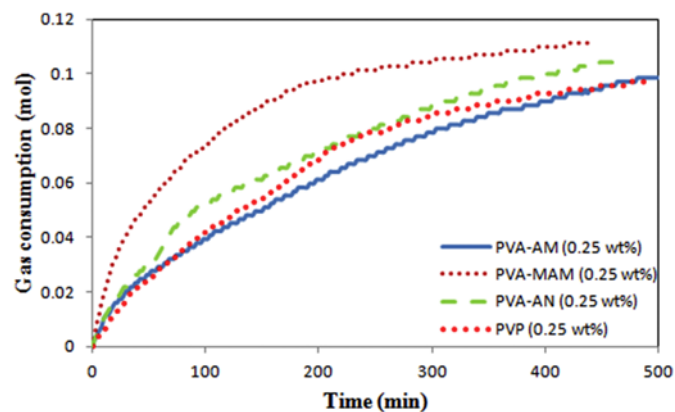


Fig. 11. Comparison between the inhibitory effects of functionalized PVAs and PVP on the growth of hydrate.

functionalized PVAs (PVA-AM, PVA-MAM, and PVA-AN) is very remarkable in comparison with graft copolymers (PVA-g-AM, PVA-g-MAM, and PVA-g-AN). In fact, functionalization of PVA with acrylamide, methacrylamide, and acrylonitrile leads to produce better inhibitors in comparison with when these monomers are polymerized (as a grafted chain) onto PVA. In this regard, a possible reason may be very high molecular weight of the graft copolymers. Some literatures have demonstrated that the graft copolymerization of some monomers (such as acrylamide) onto backbone polymers can lead to produce a very high molecular weight structure [34, 35]. On the other hand, the literatures have reported that the high molecular weight can decrease the inhibition effects [36, 37]. According the presented structures for modified PVAs (Fig. 3), it can be seen that in the molecular structure of functionalized PVAs, the monomers are not polymerized onto backbone polymer and only a low molecular weight monomer is attached to the hydrogen atom of PVA. Therefore, the very high molecular weight of graft copolymers may be the reason of their weak inhibition effects in comparison with functionalized PVAs which are highly effective inhibitors of hydrate growth. In addition, in previous work it was found that the performance of additives (inhibitors or promoters) is also depend on their adsorption on hydrate surface [31]. Therefore, the adsorption of modified PVAs on hydrate surface was also evaluated by the zeta potential measurements in this work. In this respect, first, the structure II hydrate was formed by THF (it should be demonstrated that THF can form the structure II hydrate [38]) and then the zeta potential for different aqueous solutions of modified PVAs was measured at the THF hydrate-liquid interface. The results show that in the presences of PVA and modified PVAs, the zeta potential values can be varied from  $-1.22$  to  $-16.64$  (mV). According to Fig. 12, the absolute values of zeta

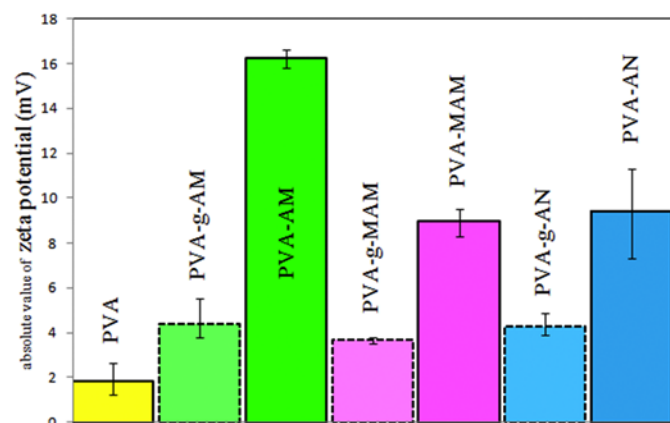


Fig. 12. Zeta potential measurements at the THF hydrate-liquid interface in the presences of modified PVAs.

potential for all modified PVAs are higher in comparison to original PVA. This shows that the effective functional groups (such as amide and nitrile groups) which are added to the structure of PVA increase the adsorption of modified PVAs on hydrate surface and subsequently decrease the hydrate formation rate. In fact, the amide and nitrile functional groups can form more and stronger hydrogen bonds with water molecules of crystal surface and lead to better adsorption of synthesized polymers on hydrate surface. These values also indicate that the adsorption of functionalized PVAs on hydrate surface is higher than that of graft copolymers. Therefore, the high inhibitory effect of functionalized PVAs may be due to their higher adsorption on hydrate crystals, such that PVA-AM with the highest value of absorption among modified PVAs has also the best performance as inhibitor of hydrate growth.

The performance of modified PVAs also depends to their molecular structure. According to Fig. 3 (which was previously presented for molecular structure of the modified PVAs), the molecular structure of PVA-AM and PVA-MAM are very similar together. In fact, their difference is only in the extra  $-\text{CH}_3$  group, which is related to the methacrylamide group of the PVA-MAM. However, there is a significant difference in their performance as inhibitors of hydrate growth. As is seen in Fig. 13, PVA-AM has a significant effect (in the concentration range from 0.25 to 0.75 wt%) to decrease the hydrate formation rate, in comparison with PVA-MAM. For better understanding of these interesting results, the possible mechanisms of inhibitory action of modified PVAs should be investigated. It considers that the amide groups (in the modified PVAs by acrylamide and methacrylamide) play a crucial role for prevention of hydrate growth. According to some literatures [17, 39], the carbonyl group of amide can form strong hydrogen bonds with water molecules of hydrate surface and subsequently the modified PVAs can be adsorbed on the hydrate surface. The adsorbed molecules block the uncompleted cavities of hydrate (as active growth sites) and the entering of the guest gas molecules (such as methane and propane) to these cavities becomes harder. Therefore, the growth of hydrate crystals occurs around and between the polymer (PVA and modified PVAs) strands and subsequently, these limitations of hydrate growth lead to the decrease of hydrate formation rate. On the other hand, these limitations become more remarkable with the increase of adsorption of synthesized polymers on hydrate surface, such that the results also confirmed that the modified PVAs with more adsorption on hydrate surface are also stronger inhibitors of hydrate growth. Also, based on the work of Peng et al. [39], another main reason for the performance mechanism of modified PVAs (including amide derivatives) can be presented. In this respect, the amide groups in the modified PVAs have also significant role. In fact, the high density of hydrophilic amide groups in modified PVAs leads to the concentration of water molecules at the gas-water (hydrate-water) interface be drastically reduced and therefore

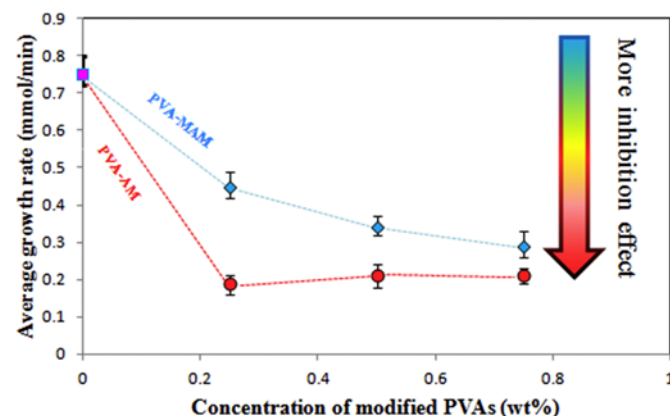
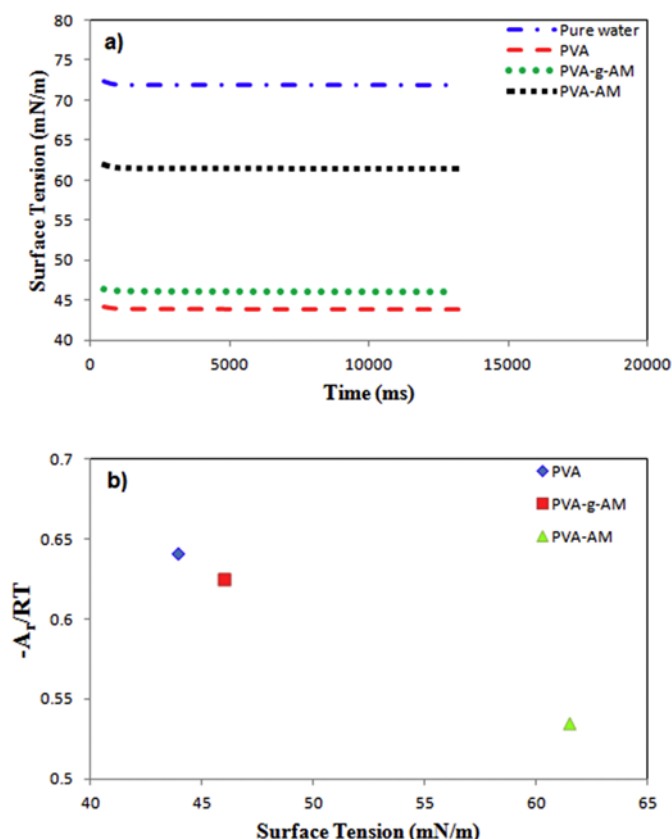
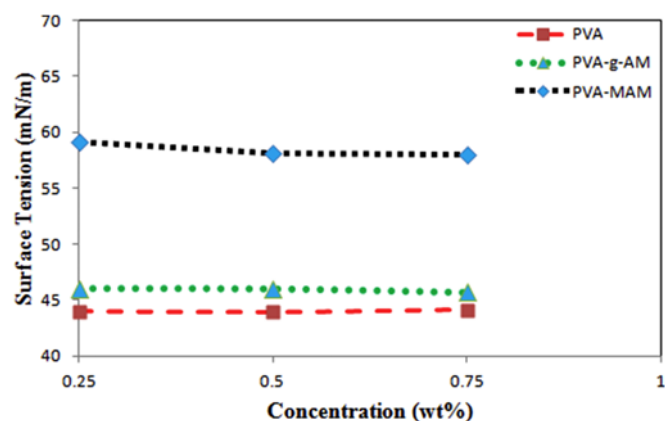


Fig. 13. Comparison between the effects of PVA-AM and PVA-MAM on the growth rate of hydrate at different concentrations.





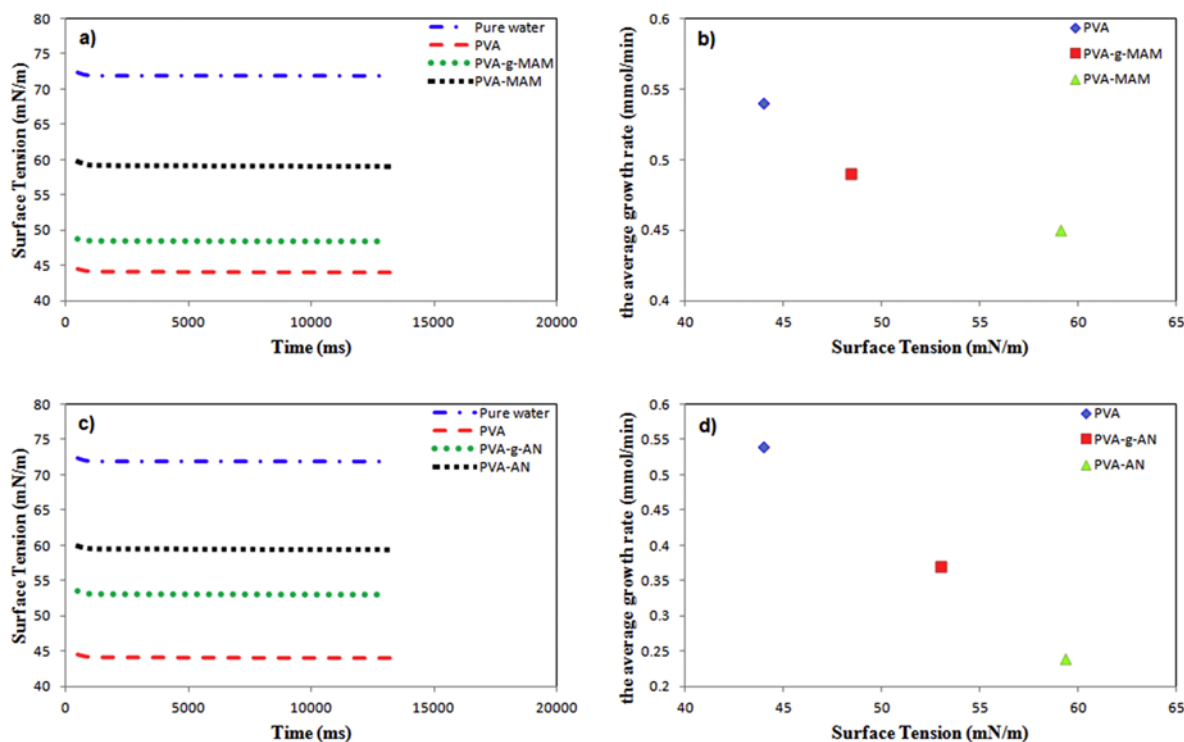
**Fig. 14.** (a) The surface tensions of pure water and aqueous solutions of PVA, PVA-g-AM, and PVA-AM at the concentration of 0.50 wt% (b) the effect of surface tension of PVA and acrylamide-modified PVAs on the value of  $-A_p/RT$ .



**Fig. 16.** The surface tensions of aqueous solutions of PVA, PVA-g-AM, and PVA-MAM at different concentrations.

results to the reduction of hydrate formation rate. According to these descriptions, it considers that the less adsorption of PVA-MAM on hydrate surface (in comparison with PVA-AM) and also the presence of an extra  $-\text{CH}_3$  group in the molecular structure of PVA-MAM (which can decrease the density of hydrophilic groups at water-hydrate interface) may be the possible reasons for the difference of the performance of PVA-AM (as a strong inhibitor) and PVA-MAM (as a weaker inhibitor).

Although some possible mechanisms for inhibition performance of modified PVAs were investigated but some physical properties such as surface tension may overshadow the performance of these modified structures. In fact, the decrease of surface tension is a favorable factor for promoters (due to the decrease of mass transfer resistance in gas-liquid interface, and subsequently the increase of gas-uptake rate in



**Fig. 15.** (a) The surface tensions of pure water and aqueous solutions of PVA, PVA-g-MAM, and PVA-MAM at the concentration of 0.25 wt% (b) the effect of surface tension of PVA and methacrylamide-modified PVAs on the hydrate growth rate (c) The surface tensions of pure water and aqueous solutions of PVA, PVA-g-AN, and PVA-AN at the concentration of 0.25 wt% (d) the effect of surface tension of PVA and acrylonitrile-modified PVAs on the hydrate growth rate.

liquid bulk, and finally the increase of hydrate formation rate [40]) and an unfavorable factor for inhibitors. For investigation of this factor, the surface tension of aqueous solutions of modified PVAs was measured. Fig. 14 shows the surface tension of pure water in comparison with aqueous solutions of PVA, PVA-g-AM, and PVA-AM. As is shown, the surface tension of PVA solution is less than that of pure water, while it has inhibitory effects on hydrate formation. Therefore, it can be presumed that if the surface tension of PVA solution could be increased (closer to the surface tension of pure water) the inhibition effects could even be more increased. This possibility is confirmed based on the experimental results in this regard. Fig. 14(a) shows that with modification of PVA by acrylamide, the surface tensions of modified PVAs solutions are increased in comparison with aqueous solution of original PVA. On the other hand, Fig. 14(b) confirms that the values of  $-A_r/RT$  (which reflect hydrate formation rate) for acrylamide-modified PVAs are decreased with the increase of surface tension. In fact, these results evidence that by modification of PVA, the surface tension becomes closer to the value of water surface tension and subsequently the inhibitory performance becomes better. Also, in Fig. 15 it is determined that the modification of PVA with methacrylamide and acrylonitrile has increased the surface tension and subsequently has led to the decrease of hydrate growth rate. Therefore, it can be concluded that although PVA has inhibition effect, but its low surface tension has decreased its ability to more inhibition effects. However, the chemical modification of PVA can increase its surface tension and potential as inhibitor. On the other hand, the experimental results show that the surface tension of PVA and modified PVAs solutions is almost constant in the applied concentration range. For example, as shown in Fig. 16, the surface tension of PVA, PVA-g-AM and PVA-MAM solutions is almost constant in the concentration range from 0.25 to 0.75 wt%, while, according to previous results, their inhibitory effects was enhanced with the increase of concentration in the demonstrated range. This means that the probable reason of the increase of inhibitory effect at higher concentrations is due to more adsorption of these inhibitors on hydrate surface.

#### 4. Conclusions

In this study, PVA was modified with three monomers including acrylamide, methacrylamide and acrylonitrile by graft copolymerization and functionalization techniques. The graft copolymers including PVA-g-AM, PVA-g-MAM, and PVA-g-AN decreased the growth rate of hydrate to 0.38, 0.44, and 0.37 (mmol/min), respectively, although their performance was weaker than that of PVP which could decrease the growth rate to 0.20 (mmol/min). Interestingly the inhibitory effects of functionalized PVAs were competitive with PVP, such that PVA-AM had even better performance in comparison with PVP and decreased the growth rate to 0.19 (mmol/min). The experimental results indicated that the ranking of PVA and modified PVAs (to decrease the hydrate growth rate of hydrate) is as follows: PVA-AM > PVA-AN > PVA-MAM > PVA-g-AN > PVA-g-AM > PVA-g-MAM > PVA. Also, the investigation and analysis of probable mechanisms for inhibitory effects of modified PVAs showed that adsorption of modified PVAs on hydrate surface, the molecular structure, and surface tension of modified PVAs can influence on the inhibition performance.

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