

Article

Effect of a Terminated PVCap on Methane Gas Hydrate Formation

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Abstract: Polyvinylcaprolactam (PVCap) is an economic kinetic inhibitor for hydrate formation in pipelines during oil and gas transportation. However, its application is limited because of the low inhibition performance under certain conditions. In this work, a modified PVCap on its chain end is proposed. 2-amino-3-propionic acid mercapto-terminated polyvinyl caprolactam (PVCap-NH₂-COOH) was synthesized and its performance as a KHI for methane hydrate formation was evaluated under different conditions. Results showed that the performance of PVCap-NH₂-COOH as a KHI was better than that of PVCap at the same concentrations. Gas hydrate samples with 1 wt.% PVCap-NH₂-COOH were measured using Raman spectroscopy, XRD, and cryo-SEM. PVCap-NH₂-COOH had a selective action on a specific crystal surface of the hydrates and could prevent methane molecules from entering large cages. Its inhibition ability increased with the decrease in the occupancy rate of large cages. The morphology of the gas hydrate crystal changed from porous in a pure water system to a chaotic but compact structure state in the system with PVCap-NH₂-COOH.

Keywords: natural gas hydrate; formation; inhibition; modification

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1. Introduction

With the recent advancements in oil and gas exploitation that span from the land to the deep sea, the safety of production and transportation has become an important problem. Under certain conditions of temperature and pressure, the natural gas components and water in a pipeline can form gas hydrates during land oil and gas transportation. Moreover, gas hydrates form easily under conditions of temperature and pressure in the deep sea. They are ice-like solids that easily form and block critical regions of pipelines such as valves and throttles as well as corresponding equipment, resulting in serious safety hazards [1]. Depending on the gas species involved, there are three main hydrate structures, sI, sII and sH. Gas hydrates with structures I and II can be found in pipelines. There are two small 5¹² cages and six large 5¹²6² cages per unit cell for Structure I (sI) hydrates, and 16 small 5¹² cages and eight large 5¹²6⁴ cages for Structure II (sII) hydrates.

The occurrence of pipeline accidents owing to hydrate obstruction is a worldwide phenomenon [2]. At present, with the continuous development of offshore oil production and the use of large-diameter high-pressure oil and gas pipelines, the inhibition of gas hydrates formation is of critical importance. There are four main methods to avoid hydrate blockage: water removal, heat preservation, pressure reduction and adding inhibitors. In certain conditions, such as between wellhead and platform, water removal is not feasible. We can also keep gas flow outside the gas hydrate formation zone by heat preservation, but this operation is uneconomical and sometimes difficult to accomplish. Concerning pressure reduction, this reduces the efficiency of pipeline transportation. Therefore, the most common

method is the addition of inhibitors. There are two types of inhibitors: thermodynamic hydrate inhibitors (THIs) and low dosage gas hydrate inhibitors (LDHIs) [3]. THIs change the phase equilibrium condition of a gas hydrate formation. Hydrates cannot form provided that a sufficient amount of inhibitors are added. Conventional thermodynamic hydrate inhibitors such as methanol, glycol or electrolyte have been used. However, owing to the large amount of required THIs, economic considerations are important. Moreover, some of them are harmful to the environment. In some cases, the most commonly used alcohol THIs are restricted. Therefore, LDHIs were proposed and developed. LDHIs can inhibit gas hydrate formation in a limited time with low toxicity, low pollution, a low concentration and low cost [4].

LDHIs include anti-agglomerants (AAs) and kinetic hydrate inhibitors (KHIs), which are used at a low concentration of approximately 1 wt.% [5]. They are environmentally friendly and do not require subsequent separation. As such, they are gaining increasing acceptance as gas hydrate inhibitors. An anti-agglomerant can prevent the aggregation of hydrate particles only when water and oil coexist in the pipeline [5]. Most anti-agglomerants are surfactants and they can disperse hydrate particles in the oil phase. In the w/o flow system, oil as a continuous phase can flow fluently, which indicates that AAs will fail at a high water cut. KHIs prevent gas hydrate nucleation and growth and cannot be used at a high degree of subcooling, which is generally believed to be lower than 8.3 °C [6]. However, the presence of oil or liquid hydrocarbon is not required.

According to the structure of the polymers, KHIs can be divided into four types: polyvinyl-lactam, other polymers containing amide groups, polymers without amide groups, and non-polymers [7–12]. Most KHIs are usually soluble polymers or macromers [13]. The most common and reliable KHIs are polyvinyl lactam compounds, of which polyvinylcaprolactam (PVCap) is a representative example. Some copolymers or trimmers based on N-vinylcaprolactam have also been reported as KHIs [14–24]. In particular, Gaffix VC-713 (a terpolymer, N-vinylpyrrolidone/N-vinylcaprolactam/ N,N-dimethylaminoethylmethacrylate) [16] and inhibex 501 (a copolymer of N-vinylpyrrolidone-co-N-vinylcaprolactam) [17,18] are well known commercial inhibitors.

However, these KHIs are not suitable under certain conditions, and some of them have several limitations. For example, they are difficult to decompose and cannot be used under high subcooling conditions. Moreover, inhibition ability is still a serious problem for these inhibitors under different conditions, which severely limits their use widely. As a result, PVCap-based end chain modification has been investigated to improve inhibition performance and environmental compatibility as well as address the problem of dissolution. Liang et al. synthesized hydroxy-terminated polyvinylcaprolactam (PVCap-OH) [25] and carboxyl-terminated polyvinyl caprolactam (PVCSCOOH) [26]. They found that the cloud point of PVCap-OH was higher and the inhibition performance was better than that of PVCap. PVCSCOOH had a better inhibition performance than PVCap with a similar molecular weight. Liang et al. [27] also tried two end chain modification based on PVCap, and the modified groups improved the inhibition performance of PVCap. Zhang and Kelland [28] reported a series of polymers based on end-group-modified PVCaps with mercaptocarboxylic acid chain transfer agents. Some of them showed better performance than PVCap under certain conditions. Dashti et al. [29] produced end chain modified PVCap with 3-mercaptopropionic acid, mercaptoacetic acid, and L-cysteine as chain transfer agents and reported all of them outperformed PVCap in terms of decreasing both sI and sII hydrate growth rate. Ajiro et al. [30] modified the end caps of PVCap and some of them showed a slight better effect than PVCap.

Here, a terminated-PVCap was synthesized and investigated as a KHI. A group from L-cysteine was added to the chain end of PVCap to synthesize 2-amino-3-propionic acid mercapto-terminated polyvinyl caprolactam (PVCap-NH₂-COOH). The influence of PVCap-NH₂-COOH on methane gas hydrate formation was analyzed, including the inhibition performance, hydrate structure, methane distribution in both large and small

The structures of the synthesized chemicals were characterized using a Bruker TENSOR27 Fourier-transform infrared spectrometer (FTIR) and Bruker AVANCE III nuclear magnetic resonance instrument (^1H NMR).

2.3. Methods and Apparatuses of Hydrate Inhibition Experiments

Two different methods were used: induction time and constant cooling. In the former, the experimental apparatus included four parts: the gas supply system, a reaction cell, data collection system and temperature cooling part, as shown in Figure 2. The main part was a 100 mL stainless steel reactor withstanding a maximum pressure 25 MPa, connected to a buffer tank and placed in a constant temperature cooling bath. The temperature and pressure in the reactor were recorded by a resistance thermometer (PT100) with a maximum precision of ± 0.1 °C and a pressure sensor with an uncertainty of ± 0.025 MPa. The data were logged every 10 s. using an Agilent data collector.

A 20 g experimental solution was loaded into the reactor and methane was used as a hydrate-forming gas. When the temperature was stable at 1.0 °C, the experiment system was vacuumed for about 3 minutes. and then methane was injected into the reactor to 8.0 MPa. Magnetic stirring was then initiated, and the gas hydrate formation experiment began. The start time of the stirring process was recorded as t_0 . The temperature increased and the pressure decreased when gas hydrate formed catastrophically. This time was denoted as the hydrate formation time, t_f . The difference between t_0 and t_f was defined as the induction time (t_i), $t_i = t_f - t_0$. After the gas hydrate formed, the experiment ended if the pressure kept constant for more than 2 h.

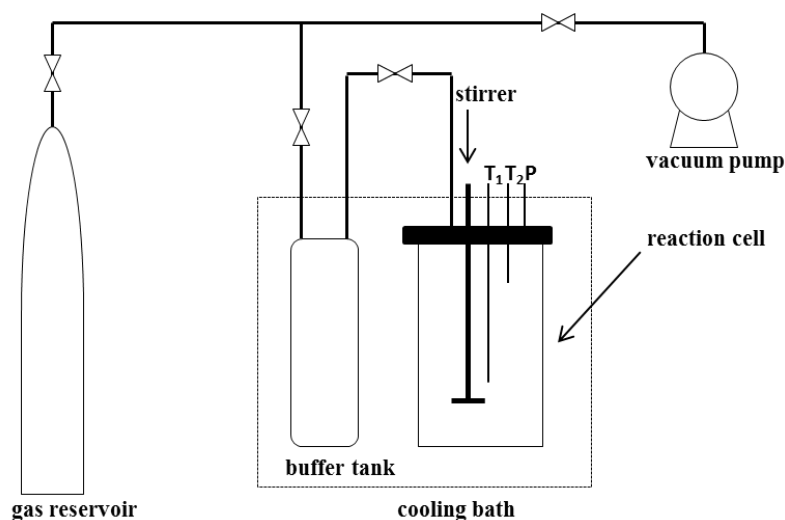


Figure 2. Schematic illustration of the induction time for the gas hydrate formation experiment.

A constant cooling method was used, and the experimental apparatus and operation has been discussed in previous reports [27]. The experimental setup was similar to that shown in Figure 2 and included a 40 mL transparent sapphire autoclave, magnetic stirrer, buffer tank, gas reservoir, and data logging system. The autoclave can withstand a maximum working pressure of 12 MPa, and is equipped with pressure transducers (CYB-20S) with an uncertainty of ± 0.025 MPa and a resistance thermometer (PT100) with a maximum precision of ± 0.1 °C, which was placed in a WGD/J-108 air bath.

The cell was filled with 10 mL of solution; the device was connected and then evacuated. Methane was then injected to achieve a pressure of 9 MPa at room temperature. The gas supply was then shut off and magnetic stirring was initiated. The air bath was set to cool down from 20 °C to -10 °C at a constant cooling rate of 1 °C/h. The onset temperature for hydrate formation (the temperature at which a sharp pressure drop occurred) was recorded as T_o . Here T_e is the corresponding thermodynamic equilibrium temperature of hydrate formation at that pressure when T_o appeared. The maximum subcooling was taken to

be the difference between the equilibrium temperature (T_e) and T_o of the hydrate [25,31], $\Delta T_{sub} = T_e - T_o$.

The experiments were repeated for at least three times and the data closest to the average were chosen as the representatives.

2.4. Characterization of Hydrate Samples Synthesized with and without Kinetic Hydrate Inhibitors

The experimental setup to measure the induction time of gas hydrate formation was also used to prepare methane hydrate samples. The solution (15 mL) was added to a 100 mL cell with a magnetic stirrer. After vacuuming the system, methane (10 MPa) was then introduced into the cell. The cell was kept at 1.0 °C for 8 days while stirring at 1000 r/min. Prior to crystal characterization via PXRD, Raman spectroscopy, and cryo-SEM, hydrate samples were extracted and prepared in a liquid nitrogen atmosphere. A smartlab multifunctional X-ray diffractometer from Rigaku Corporation was used for crystal structural analysis, the experimental temperature was 203.15 K, and the 2θ range was 5°–80°. Low-temperature Raman spectroscopy was performed using a French HORIBA JOBIN YVON LabRAM HR800 laser confocal Raman spectrometer, and the temperature was set to −70 °C. Cryo-scanning electron microscopy was performed using a Hitachi S-4800 cold field emission scanning electron microscope, and the experimental temperature was set to −140 °C.

3. Results and Discussion

3.1. Characteristics of PVCap-NH₂-COOH

The synthesized polymer PVCap-NH₂-COOH was qualitatively analyzed using Fourier-transform infrared (FTIR) spectroscopy and nuclear magnetic resonance (NMR) spectroscopy. The results are shown in Figures 3 and 4.

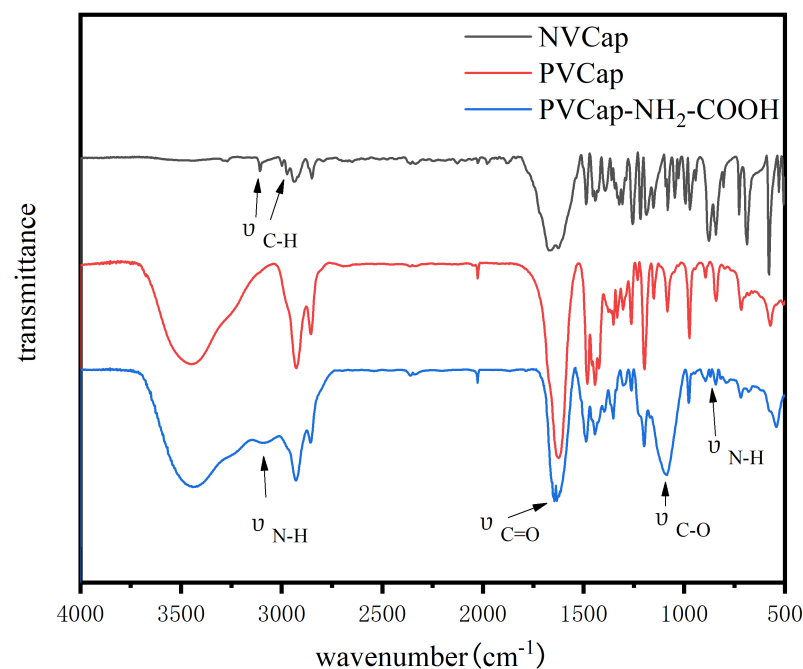


Figure 3. FTIR spectra of NVCap, PVCap and PVCap-NH₂-COOH.

Figure 3 shows the FTIR spectra of NVCap, PVCap and PVCap-NH₂-COOH. In this figure, the absorption peaks at 1635 and 1370 cm^{−1} were assigned to the stretch vibration of C=O and C–N, respectively. The C=C vibration at 1656 cm^{−1} and the C–H vibration at 2973 and 3106 cm^{−1} of the vinyl group in NVCap completely disappeared in PVCap-NH₂-COOH and PVCap, which proved that all the monomers reacted to produce polymers. At the same time, the absorption peaks at 867 and 3089 cm^{−1} were attributed to N–H stretch

vibration from a secondary N-H. The peaks at 1650 and 1085 cm^{-1} were assigned to $\text{C}=\text{O}$ and $\text{C}-\text{O}$ stretch vibration in carbonyl group, respectively. So, the peaks around $-\text{NH}_2$ and $-\text{COOH}$ group both appeared, which indicated that the modified group was added to the compound and the target was synthesized successfully.

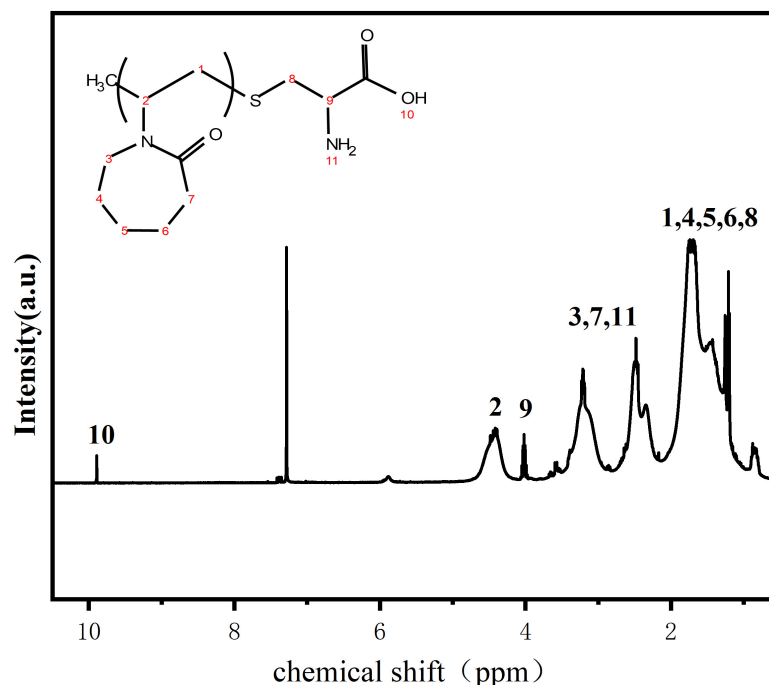


Figure 4. ^1H NMR spectrum of PVCap- $\text{NH}_2\text{-COOH}$.

To determine the position of the functionalized group, the polymer was investigated using ^1H NMR. The results are shown in Figure 4. Typical data for the PVCap- $\text{NH}_2\text{-COOH}$ ^1H NMR (CDCl_3 , [ppm]) spectrum are as follows: PVCap- $\text{NH}_2\text{-COOH}$ ^1H NMR (CDCl_3 , [ppm]): 9.89 (s, 1H, carbonyl OH), 4.40 (s, 1H, main chain CH), 4.00 (s, 1H, terminated group CH), 3.21 (s, 2H, lactam CH_2), 2.48 (s, 2H, NH_2), 1.73–1.21 (m, 10H, main chain CH_2 , lactam CH_2 , terminated group CH_2). Therefore, the ^1H NMR (CDCl_3 , [ppm]) spectrum further confirmed the structure of PVCap- $\text{NH}_2\text{-COOH}$.

3.2. Inhibition Performance of PVCap- $\text{NH}_2\text{-COOH}$

Induction time: at $1.0^\circ\text{C}/8.0\text{ MPa}$, experiments were conducted on the formation of methane gas hydrate with or without PVCap- $\text{NH}_2\text{-COOH}$ to evaluate the inhibitory effect of PVCap- $\text{NH}_2\text{-COOH}$ as a KHI. The experimental results are shown in Figures 5 and 6. In these two figures, gas was injected when the temperature was stable at 1.0°C . After gas intake, the temperature stabilized to approximately 1.0°C . The typical temperature and pressure change during gas hydrate formation was shown in Figure 5. With the addition of 2 wt.% PVCap- $\text{NH}_2\text{-COOH}$, the temperature increased and the pressure decreased simultaneously after 7400 minutes, which suggests that gas hydrate formed. During gas hydrate formation, methane was bound to hydrate cages, which resulted in a pressure drop. Gas hydrate formation is an exothermic reaction that will lead to temperature rise. Therefore, the increase in temperature, accompanied by a decrease in pressure, indicated the formation of hydrates.

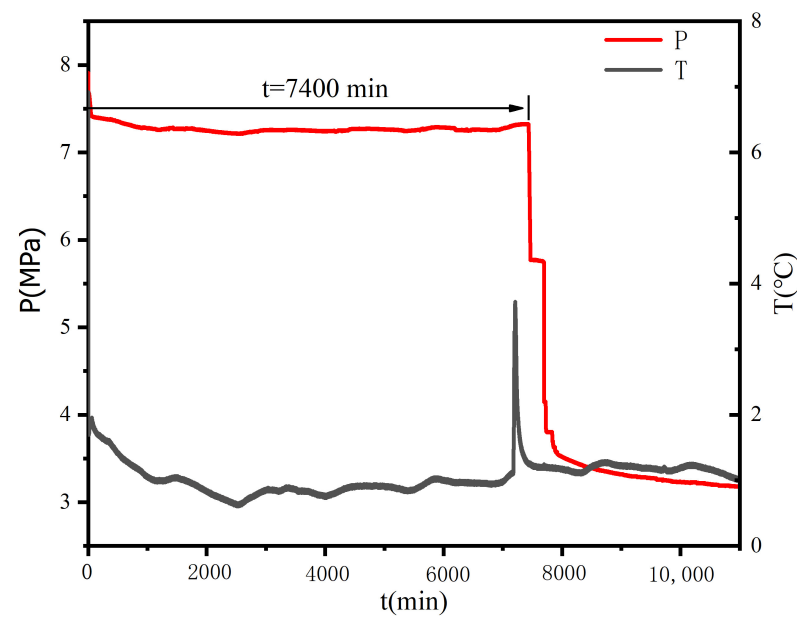


Figure 5. Temporal changes in pressure and temperature during gas hydrate formation with 2 wt.% PVCap-NH₂-COOH.

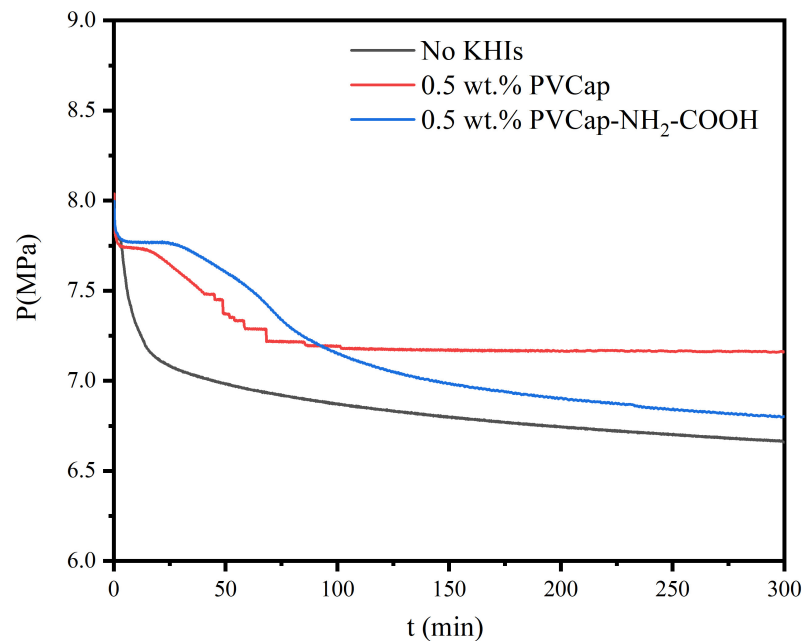


Figure 6. Temporal changes in pressure during gas hydrate formation with different KHIs.

In Figure 6, pressure data were compared among a system of no KHIs, one with 0.5 wt.% PVCap-NH₂-COOH and one with 0.5 wt.% PVCap. For the no KHIs system, the pressure continued to drop after gas injection, so there was approximately zero minutes' induction time. In the pressure curve, there was a plateau for the system with 0.5 wt.% PVCap-NH₂-COOH and 0.5 wt.% PVCap, which meant that gas hydrate formation was inhibited by PVCap-NH₂-COOH and PVCap, and these two showed certain hydrate inhibition ability. However, for the KHIs system before gas hydrate formation, the pressure kept stable for a longer time in the system with PVCap-NH₂-COOH than that with PVCap at 0.5 wt.% concentration. So PVCap-NH₂-COOH showed a better inhibition performance than PVCap.

By comparing the induction time of hydrate formation in the systems with PVCap-NH₂-COOH and PVCap, it can be preliminarily determined that the inhibition ability of the

modified inhibitor PVCap-NH₂-COOH was better than that of PVCap. The advantage of the induction time measurement method to evaluate the effect of a KHI is that it is fast and can quickly obtain a preliminary conclusion. Because kinetic experimental results are easily affected by accidental factors, the data error is relatively large within a limited number of measurements. In this work, especially at the concentration of 0.5 wt.%, the inhibition ability of the modified inhibitor PVCap-NH₂-COOH for methane hydrate formation was only slightly improved compared with PVCap. Therefore, the maximum subcooling degree method was adopted for further detailed analysis of PVCap-NH₂-COOH inhibition performance. Although the data obtained from these two methods are both affected by accidental factors, with the maximum subcooling method the cooling rate is slow, and the error range is relatively small. So, the induction time method was used to obtain preliminary conclusions, and then the maximum subcooling method was used for further study. Combining the data obtained from these two methods, it was convenient to draw more accurate experimental conclusions.

Maximum subcooling: the larger the degree of maximum subcooling, the greater the driving force required for hydrate formation and the better the inhibitor performance. A typical curve of testing maximum subcooling for methane hydrate formation is shown in Figure 7.

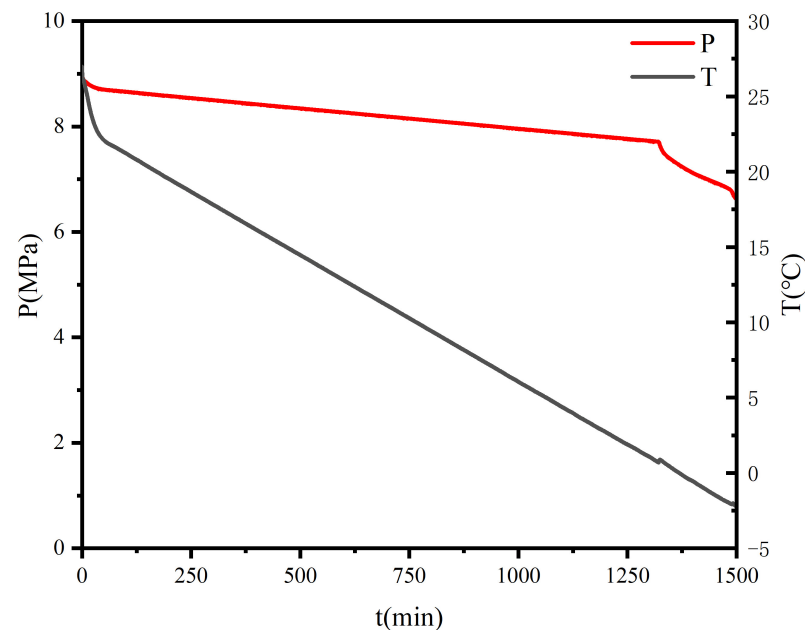


Figure 7. Temporal changes in pressure and temperature during the hydrate inhibition experiment with 0.5 wt.% PVCap-NH₂-COOH.

Figure 7 represents a typical curve used to measure maximum subcooling for hydrate formation. This figure confirms that after adding 0.5 wt.% PVCap-NH₂-COOH, the temperature and pressure in the cell dropped at a constant rate before the hydrate formed. Once the hydrate began to form, gas molecules were trapped in the hydrate cages, which could cause the pressure to drop sharply. This was accompanied by an increase in temperature, which resulted in the fluctuation of the temperature curve. The temperature corresponding to this abrupt fluctuation was considered to be the hydrate formation temperature. According to the calculated equilibrium temperature [1], maximum subcooling is the difference between equilibrium temperature and hydrate formation temperature.

The maximum subcooling of gas hydrate formation for pure water was 4.3 °C. For the systems with different concentrations of PVCap and PVCap-NH₂-COOH, the maximum subcooling increased with increasing concentration, which was shown in Figure 8. Regardless of the concentration, the maximum subcooling of methane hydrate formation with PVCap-NH₂-COOH and PVCap was higher than that of pure water system,

among them that with PVCap-NH₂-COOH was highest. At the same concentration, the methane hydrate formation temperature was lower and the maximum subcooling was higher for the system with PVCap-NH₂-COOH compared to that with PVCap. This indicates that the functionalized polymer of PVCap-NH₂-COOH could inhibit methane gas hydrate formation and increase the inhibition performance compared with PVCap.

The maximum subcooling of PVCap-NH₂-COOH and PVCap was compared at different concentrations. The degree of maximum subcooling of PVCap-NH₂-COOH is much higher than that of PVCap at every concentration mentioned here. The end chain modification is successful and can increase the inhibitory capacity of PVCap. The addition of the hydrophilic group to end chain enhances the hydrophilic properties of the polymer, which improves the interaction capacity between KHI and water molecules.

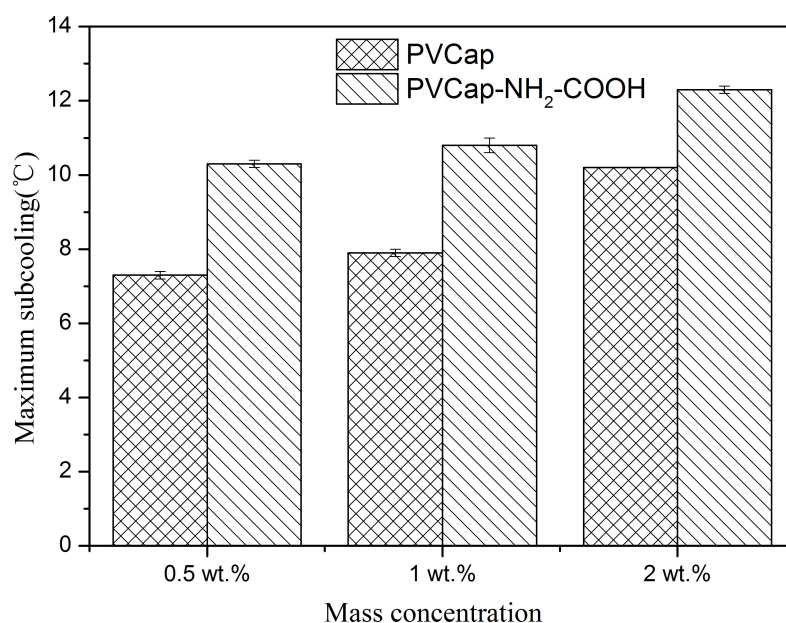


Figure 8. Maximum subcooling of PVCap-NH₂-COOH and PVCap at different concentrations.

The added-NH₂ and -COOH group are hydrophilic groups and can strengthen hydrogen bond interaction between the polymer and water molecules, which makes polymer molecules adsorb to the surface of hydrates easier. The higher the mass concentration in the solution is, the greater the probability adsorbed to the hydrate surface is, so the inhibition performance increases with an increase in concentration KHIs.

3.3. Structural Analysis of Methane Hydrate with PVCap-NH₂-COOH

The crystal structure of methane hydrate with PVCap-NH₂-COOH was characterized using PXRD and Raman spectroscopy.

Under experimental conditions, the crystal structure of the methane hydrate was identified as structure I (sI), and Figure 9 shows the X-ray diffraction profiles of the hydrates with or without polymers. The peaks at 22.5–26.5 were assigned to be the (100), (002), and (101) crystal planes of hexagonal ice. Diffraction peaks at 27–29 were assigned to sI(320) and sI(321), respectively, [32], which can be seen in both systems, and the ice crystal face also appeared.

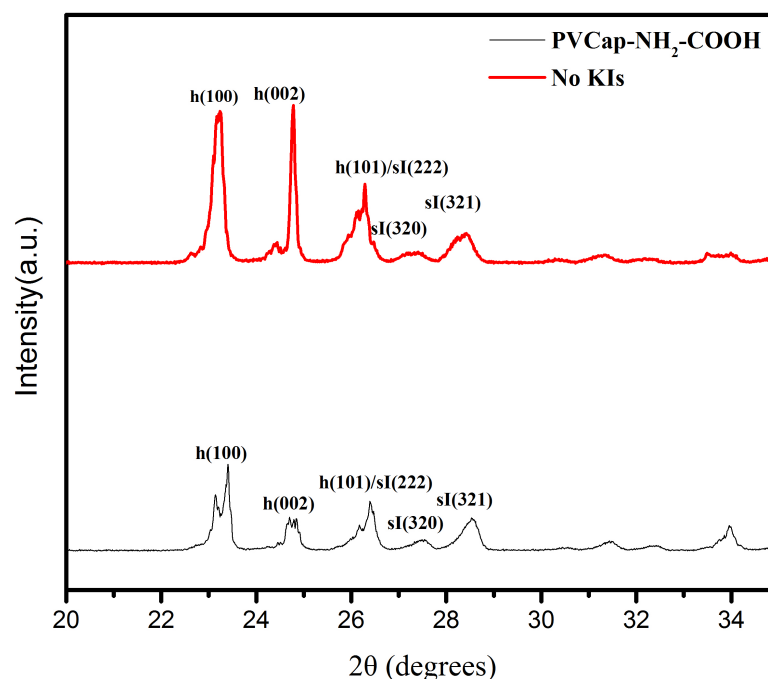


Figure 9. Low-temperature X-ray diffraction image of methane hydrate with 1 wt.% PVCap-NH₂-COOH and pure water.

Comparing the data with or without KHIs, the position and width of the diffraction peaks did not change significantly. Therefore, the addition of 1 wt.% PVCap-NH₂-COOH did not alter the crystal structure, although the relative intensities were different. The intensity ratio (3.2) of sI(321)/sI(320) was much higher at the system with PVCap-NH₂-COOH than that in pure water (2.8), which meant that there was a selective effect of PVCap-NH₂-COOH on specific lattice planes. Amino acids in gas hydrate structures have been investigated and it was discovered that some amino acids could result in lattice distortion and expansion[33]. However, this phenomenon was not observed in this work.

The Raman spectra derived from methane hydrates consist of two strong peaks at 2905 and 2915 cm⁻¹, as shown in Figure 10, which correspond to methane molecules in large cages and small cages, respectively [34,35]. At 1wt.% PVCap-NH₂-COOH and PVCap, the spectral position did not change, which was consistent with other investigations [36]. The data also showed that PVCap-NH₂-COOH and PVCap could not change the gas hydrate structure, indicating that the molecules of these two KHIs did not get into the hydrate cages, as shown in Figure 9. In Figure 10, the relative intensities were different for the ratio of large to small cages (I_l/I_s). According to the peak area in the pure water system, the I_l/I_s was 3.04, but with 1 wt.% PVCap and PVCap-NH₂-COOH, this ratio was 2.75 and 2.61, respectively. In sI methane hydrate, methane molecules were encaged in both large and small cages. However, with the addition of PVCap and PVCap-NH₂-COOH, the relative intensities ratio of large to small cages dropped, and KHIs can change the distribution of gas in large and small cages.

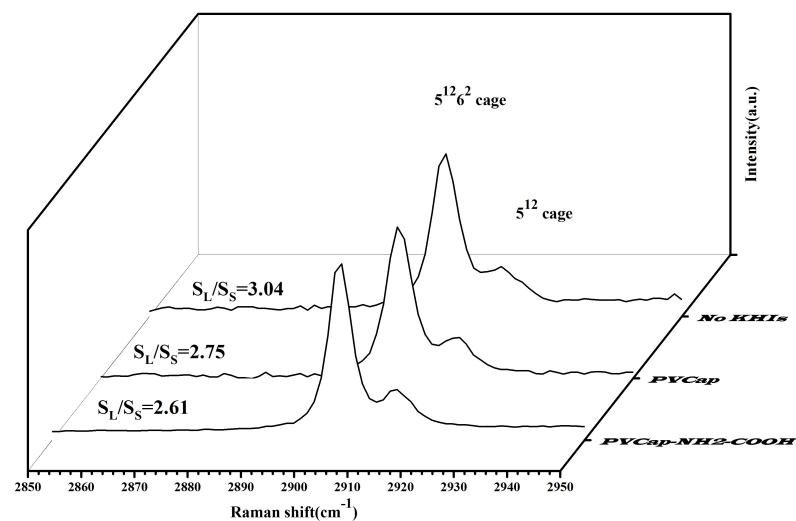


Figure 10. Raman spectrum of methane hydrate with 1 wt.% PVCap-NH₂-COOH, PVCap and pure water.

The data in Table 2 were calculated based on the peak area in Figure 10 and the Gibbs free energy of methane gas hydrate [37]. Theoretically, every cage could trap a gas molecule, but actually, some cages were empty. In Table 2, with 1 wt.% PVCap or PVCap-NH₂-COOH added, the occupancy of large cages dropped significantly, and the ratio of large to small cages (θ_l/θ_s) was reduced. According to Figure 8 the inhibition performance of PVCap-NH₂-COOH was better than that of PVCap, and in Figure 9 and Table 2, large cage occupation with the PVCap-NH₂-COOH system dropped more heavily than that with PVCap. So it can be concluded that these KHIs could affect the distribution of guest molecules in different cages and hinder the entry of methane into the large cages of the hydrate crystals. Furthermore, the stronger the inhibition capacity is, the lower the occupancy of large cages is. The polymer seems to destroy the stability of the cage; it may be that the binding ability of KHIs with a large cage face is much stronger.

Table 2. Occupancy of large/small cages of methane hydrate synthesized with and without KHIs.

Reaction System	Large Cage Occupancy Rate θ_l	Small Cage Occupancy Rate θ_s	Proportion of Large and Small Cages θ_l/θ_s
Pure water	0.966	0.951	1.015
PVCap	0.913	0.997	0.916
PVCap-NH ₂ -COOH	0.871	0.999	0.872

Figure 11 shows the cryo-SEM images for pure water and the system with PVCap-NH₂-COOH. According to Figure 11, the crystal morphology without inhibitors presented dense and regular pores, which is typical of submicron porosity [38]. A uniform and porous overall structure was observed. However, after adding PVCap-NH₂-COOH, the pores of the hydrate structure changed dramatically and tended to be chaotic but compact, and the overall structure was folded and in clusters. It can be seen that after adding PVCap-NH₂-COOH, the crystal morphology of methane hydrate appeared as scale-like and rough. Such morphology can be found in our previous work [36] and is also observed by others [39]. With the addition of PVCap-NH₂-COOH, gas hydrate formation was hindered initially, then the hydrates formed rapidly. This resulted in a compact hydrate morphology, as shown in Figure 11. This morphology is not convenient for transferring gas and heat, which could increase the difficulty of dissociation of the hydrates with PVCap-NH₂-COOH compared to those without a KHI. Inhibitors may prevent further hydrate formation with this dense structure.

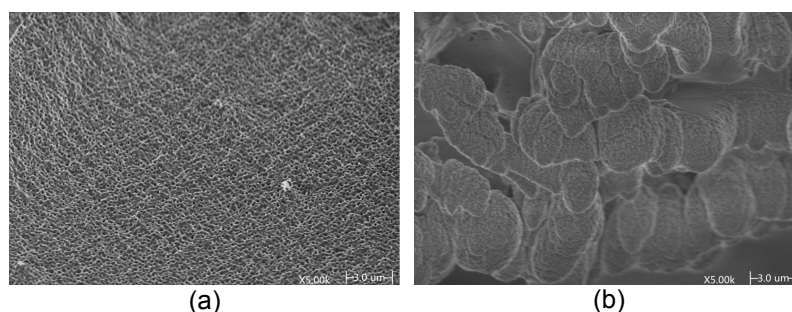


Figure 11. Cryo-SEM image of methane hydrate (a) no additives; (b) with 1 wt.% PVCap-NH₂-COOH.

4. Conclusions

In this work, based on PVCap, a modified KHI, 2-amino-3-propionic acid mercapto-terminated polyvinyl caprolactam (PVCap-NH₂-COOH) was investigated and its performance as a KHI on methane hydrate formation was evaluated. At 1.0 °C/8.0 MPa, PVCap-NH₂-COOH can effectively inhibit methane hydrate formation and prolong the induction time of hydrate formation. With the addition of 2 wt.% PVCap-NH₂-COOH, the induction time of methane hydrate formation was up to 7400 minutes, while there was nearly no induction time for the system without KHIs. With a constant cooling rate of 1 °C/h, the degree of maximum subcooling of methane hydrate formation was measured at different concentrations of PVCap-NH₂-COOH and PVCap. The functionalized polymer of PVCap-NH₂-COOH could inhibit methane gas hydrate formation and increase the inhibition performance compared with PVCap. The degree of maximum subcooling of PVCap-NH₂-COOH is much higher than that of PVCap at every concentration mentioned in this work.

Gas hydrate samples with 1 wt.% PVCap-NH₂-COOH were also measured using PXRD, Raman spectroscopy and cryo-SEM. There was a selective effect of PVCap-NH₂-COOH on some specific lattice planes of the hydrate crystal. With PVCap-NH₂-COOH, the crystal structure of methane hydrate did not change, but it could affect the relative distribution of methane in large and small cages and inhibit gas from entering the large cages of the hydrates. Using cryo-SEM, the crystal morphology of methane hydrate was determined with PVCap-NH₂-COOH. The dense and cluster-like morphology of methane hydrate was observed instead of the porous crystal morphology identified without inhibitors. This increased the difficulty of the gas and heat transfer of the hydrates. Inhibitors may prevent further hydrate formation with this dense structure.

Author Contributions: Z.S., C.T. and D.L.: Conceptualization, Methodology. S.C. and C.T.: perform experiments. C.T., Y.C., D.L. and S.W.: Writing—Reviewing and Editing. All authors have read and agreed to the published version of the manuscript.

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Data Availability Statement: The data that support the findings of this study are available from the corresponding author upon reasonable request.

Conflicts of Interest: The authors declare that they have no conflict of interest.

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