Amphiphilic Copolymers Containing POSS and SBMA with N-Vinylcaprolactam and N-Vinylpyrrolidone for THF Hydrate Inhibition

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ABSTRACT: Icelike gas deposits deposited in the pipelines under low temperatures and high pressures could remarkably reduce the transport efficiency, and a low dosage of water-soluble polymers could act as kinetic hydrate inhibitors (KHIs) to prevent gas hydrate formation. It was believed that the hydrophobic moiety in the water-soluble polymers played a vital role in enhancing the KHI performance. In this work, amphiphilic copolymers containing hydrophobic polyhedral oligomeric silsesquioxane (POSS) and superhydrophilic sulfobetaine methacrylate (SBMA) as well as N-vinylcaprolactam (VCap) and N-vinylpyrrolidone (VP) were prepared, and an efficient effect of the obtained amphiphilic copolymers on tetrahydrofuran (THF) hydrate inhibition was found. When a certain amount of the amphiphilic copolymers was introduced, the THF hydrate as an analogue of structure II gas hydrates presented a prolonged induction time and gave rise to a looser state rather than a crystalline solid. Analyses of low-field nuclear magnetic resonance and differential scanning calorimetry verified that there were strong interactions between the copolymer and water molecules by incorporating SBMA units, which could enhance the KHI properties of the prepared amphiphilic copolymers. Additionally, the hydrophobic POSS in the amphiphilic copolymers could possibly modulate the hydrophilic/hydrophobic balance, contributing to the synergistical ability of the copolymers for THF hydrate inhibition. It was suggested that the amphiphilic copolymers containing POSS and zwitterionic units with VCap or VP could have potential for the inhibition and antiaggregation of gas hydrates in the transportation pipelines.

INTRODUCTION

Clathrate gas hydrates easily form under low temperatures and high pressures by the molecular interaction of the gas molecules, for example, methane, ethane, propane, and so forth, with water.1−3 The icelike nonstoichiometric compounds of gas hydrates aggregated and deposited in the gas pipelines could result in plugging and then dramatically reduce the transport efficiency.1−3 It was popular to obtain an effective fluidity of gas by adding a high concentration of thermodynamic hydrate inhibitors, such as methanol and ethylene glycol, but this approach may have expensive costs and hazards to the environments.3 Alternatively, a series of low-dosage hydrate inhibitors of kinetic hydrate inhibitors (KHIs) and antiagglomerates (AAs) were developed to inhibit the formation and aggregation of gas hydrates.3

Typically, poly(N-vinylactam)s with cyclic structure and amide groups, such as poly(N-vinylpyrrolidone) (PVP) and poly(N-vinylcaprolactam) (PVCap), could be used as KHIs to delay gas hydrate nucleation and crystal growth.3,4 It was assumed that the KHI molecules may adsorb on the hydrate surface and reduce the hydrate–hydrocarbon interfacial tension.1 The inhibiting properties of PVP and PVCap have been fully examined,3,5 and some kinds of VCap- or VP-involved copolymers were also reported to increase the gas inhibition performance by introducing a functional monomer with ionic or hydrophobic groups.3,4,8,9 For example, a commercial terpolymer of VCap, VP, and dimethylaminoethyl methacrylate called as Gaffix VC-713 had a significant gas inhibition effect with respect to PVP and PVCap homopolymers.3,4 Furthermore, a terpolymer of VCap, VP, and 2-acrylamide-2-methyl-1-propane sulfonate (AMPS) possessed an enhanced salt and temperature tolerance by incorporating the anionic AMPS units.3,7 The copolymer of VCap and 1-vinyl-3-alkylimidazolium bromide also indicated the promising KHI performance to prevent or delay gas hydrate formation especially in highly saline aqueous systems.8

The hydrophobic moiety in the water-soluble polymers plays an essential role in enhancing the KHI performance. It was
and the polydispersity index (PDI) of the prepared copolymers were estimated by gel permeation chromatography (GPC) using a sodium acetate buffer (0.5 M of NaAc and 0.5 M of HAc, pH = 4.5) as the mobile phase in a Viscotek GPC system at 30 °C, with a flow rate of 1.0 mL/min. No adequate results can be obtained for POSS-P(V-co-P-co-S)1 and P(V-co-P). The number-average molecular weight of POSS-P(V-co-P-co-S)3 was apparently higher than expected. The hydrophobicity of the prepared amphiphilic copolymers could be improved when the lactam ring size was increased. The hydrophobic butyl and phenyl groups were ever incorporated to obtain modified PVP that showed good kinetic inhibition performance via lowering gas/liquid interfacial tension.9,10 By introducing the hydrophobic fluoroalkyl group, poly(fluoroalkyl acrylamide)s also showed higher inhibition efficiency than those with alkyl groups.11 Actually, the hydrophobic groups in the structure of AAs similar to those of surfactants could prevent the aggregation of gas hydrates by adjusting and controlling its morphology so that the fluid could flow rather than plugging.12,13 Even though the above-mentioned results have been obtained, there are still much work remaining to be further clarified, especially for the effect of hydrophobicity on the gas hydrate inhibition properties.12

According to the geometries of the gas molecules in the water cages, clathrate gas hydrates can be classified as crystal structure I, structure II, and structure H, which were generated under specific thermodynamic conditions.12 Without the need to elevate pressure, water-soluble tetrahydrofuran (THF) and water nonsoluble cyclopentane hydrates were usually adopted as analogues of structure II gas hydrates to study the KHI performance.13,14 Several methods for the measurement of the induction time and the inhibitor concentration have been attempted to examine the inhibition properties of KHIs and AAs more accurately.15,16 Additionally, the microscopic and macroscopic appearances of the gas hydrates were observed directly to study the hydrate–water droplet interaction that was considered as the dominated factor on hydrate agglomeration.17,18

Zwitterionic polymers have been widely studied for antifouling applications in biomedical engineering because of their strong hydration effect.19 In our previous studies, the amphiphilic copolymers containing hydrophobic polyhedral oligomeric silsesquioxane (POSS) and zwitterionic sulfobetaine methacrylate (SBMA) have been synthesized and demonstrated the anti-icing and antifogging abilities owing to the hydrophilic/hydrophobic balance as well as the hydrogen bond and electrostatic interactions between the copolymer and water molecules.20,21 POSS with low surface energy could endow the copolymers with the hydrophobic properties,22 and the superhydrophilic SBMA units containing zwitterions could increase the water affinity of the copolymer via the strong electrostatic interactions.23 With respect to the similar nature of gas hydrate to ice, in this work, amphiphilic POSS-poly(VCap-co-VP-co-SBMA) copolymers were synthesized via atom transfer radical polymerization (ATRP) for hydrate inhibition. THF hydrate was adopted as structure II model, and the induction time and morphology of the THF hydrate were measured by introducing the prepared amphiphilic copolymers. Low-field nuclear magnetic resonance (NMR) and differential scanning calorimetry (DSC) were used to examine the interaction between the copolymers and water molecules. It was hypothesized that the hydrophilic components of VCap, VP, and zwitterionic SBMA as well as hydrophobic POSS could have a synergetic performance for gas hydrate inhibition. With hydrophilic and hydrophobic counterparts, amphiphilic copolymers themselves are expected with preferred properties of KHIs as well as AAs for gas hydrate inhibition.

### RESULTS AND DISCUSSION

**Chemical Characterization.** As shown in Figure 1, the amphiphilic copolymers consisted of POSS, VCap, VP, and SBMA were prepared via ATRP, and the THF hydrate inhibition performance was examined with the participation of the copolymers. The synthesizing conditions of the prepared copolymers are shown in Table 1. POSS-poly(VCap-co-VP-co-SBMA) copolymers prepared with three different feeding ratios were abbreviated as POSS-P(V-co-P-co-S)1, POSS-P(V-co-P-co-S)2, and POSS-P(V-co-P-co-S)3, respectively. For
comparison, poly(VCap-co-VP-co-SBMA) by using ethyl-2-bromoisobutanoate (EBIB) or ammonium persulfate (APS) as the initiator was synthesized and abbreviated as P(V-co-P-co-S)A and P(V-co-P-co-S)C, respectively, and the binary copolymer poly(VCap-co-VP) designated as P(V-co-P) was also prepared by using azobisisobutyronitrile (AIBN).

The chemical structure of the synthesized copolymers was characterized by 1H nuclear magnetic resonance (1H NMR) and Fourier transform infrared (FTIR) spectroscopy. As shown in Figure 2a, there are representative δH (ppm) at 4.40 (a, j), 3.17 (c, l), 1.95 (h, p), 1.30−1.80 (b, d−f), 0.77−1.22 (i, g, and r), 3.75 (n), 3.53 (k), 2.92 (o), 2.37 (g), and 2.23 (m) in all the 1H NMR spectra, verifying that POSS-P(V-co-P-co-S)3, P(V-co-P-co-S)A, P(V-co-P-co-S)C, and P(V-co-P) have been successfully synthesized.24,25

The FTIR spectra of the synthesized copolymers are shown in Figure 2b. The stretching vibration characteristic peaks at 1112 cm−1 are apparent, which associate with Si−O−Si in POSS.20 The peaks at 2954 and 1323 cm−1 are attributed to the C−H stretching vibration and the C−H bending vibration, respectively. The signals at 1721, 1661, and 1466 cm−1 belong to the characteristic absorption peaks of C=O in ester and amide groups and the C−H stretching vibration in the −N+(CH3)2− groups, respectively. Meanwhile, the characteristic peaks at 1039 and 1183 cm−1 belong to the characteristic absorption peaks of POSS and S=O in the P(V-co-P) spectrum.

Figure 2. 1H NMR spectra (a) of POSS-P(V-co-P-co-S)3, P(V-co-P-co-S)A, P(V-co-P-co-S)C, and P(V-co-P) in D2O and FTIR spectra (b) of the prepared copolymers.

Figure 3. Induction time measurement (a) and the effect of the concentration of POSS-P(V-co-P-co-S)3 (b) and the different copolymers at 0.1 wt % concentration (c) in a 19 wt % THF aqueous solution on the induction time. Statistical significance of Student’s t test: *p < 0.05 and **p < 0.01.
**Induction Time.** The 19 wt % THF aqueous solution was employed as a gas hydrate model of structure II for the measurement of induction time. As shown in Figure 3, four droplets of each sample were examined simultaneously, and the induction time was recorded when transition from transparent into opaque occurred for any of the droplets (indicated with a yellow circle in Figure 3a). The induction time was evaluated for the THF hydrate containing diverse concentrations (0.01, 0.05, 0.1, 0.3, 0.5, and 0.7 wt %) of the amphiphilic copolymer POSS-P(V-co-P-co-S)₃ (Figure 3b) and different copolymers at 0.1 wt % concentration (Figure 3c). As shown in Figure 3b, the inhibiting properties on THF hydrate formation displayed the initial increased trend with the increasing concentration of POSS-P(V-co-P-co-S)₃ from 0.01 to 0.1%, but the induction time dropped when the concentration increased to 0.7 wt %. In addition, in the concentration range of 0.1–0.5 wt %, it showed a relatively better suppression effect on the formation of THF hydrates with a significant difference, and the discrepancy of the performance was not significant among the concentrations of 0.1, 0.3, and 0.5 wt %. The results could be attributed to the hydrogen bond interaction between the copolymers and water molecules, which also resulted in the formation of different kinds of bound water, which was analyzed by DSC in the following section.

The induction time of THF hydrates containing different copolymers at the same concentration of 0.1 wt % was recorded in Figure 3c. It could be seen that the amphiphilic copolymers containing the POSS groups could significantly inhibit the THF hydrate formation than the P(V-co-P-S)₃ and P(V-co-P) copolymers without the POSS groups. Meanwhile, the amphiphilic copolymers with different molecular weights showed almost similar antiaggregation properties of THF hydrates. It could be assumed that the hydrogen bonds between the hydrophilic moiety of the amphiphilic copolymer and water promoted the copolymer adhering to the surface of THF hydrates, inhibiting the formation of THF hydrates.

On the other hand, the POSS groups around the outside of the THF hydrates by rearranging could endow the copolymers with the antiaggregation properties. In addition, the hydrophilic/hydrophobic equilibrium of amphiphilic copolymers could positively influence the antiaggregation of the THF hydrates. Importantly, the copolymer P(V-co-P-co-S)₃ synthesized via ATRP showed superior antiaggregation performance to P(V-co-P-co-S)₃, the copolymer with the same structure synthesized via free-radical polymerization, owing to the lower value of polydispersity. The copolymers with narrow molecular weight distribution favored the formation of a regular and symmetrical void structure when adhering to the hydrate surface. In contrast, the copolymers with broad polydispersity were subjected to form litty and myriad void structure, resulting in inferior antiaggregation of the THF hydrates. To make things even worse, the gas hydrate would grow with a higher speed when copolymers with broad molecular weight distribution were added. Therefore, the induction time may be related to the structure and concentrations of the amphiphilic copolymers.

It is worth to mention that there are differences in the measurement of induction time and the mechanism between the THF hydrate and the gas hydrate because of the solubility of THF in water. For convenience without the need to elevate pressure, we used the THF hydrate in this study. For further investigation, it is suggested to utilize cyclopentane as the structure II guest molecule with reduced water solubility that can limit both nucleation probability and growth rate or a natural gas mixture that can mimic structure II gas hydrate formation at high pressures and low temperatures in cooling rocking cells.

**THF Hydrate Morphology.** We observed the THF hydrate morphology during crystallization by an optical microscope equipped with a high-speed camera and a low-temperature stage at −30 °C. Typical crystal morphologies of THF hydrates containing 0.01, 0.05, 0.1, 0.3, 0.5, and 0.7 wt % of POSS-P(V-co-P-co-S)₃ are shown in Figure 4. The crystals of pristine THF hydrates without the copolymer showed a compact arrangement (Figure 4a), and the similar morphologies of the THF hydrates containing 0.01 and 0.05 wt % of POSS-P(V-co-P-co-S)₃ (Figure 4b,c) indicated that the lower concentrations of the copolymer could not efficiently exhibit THF hydrate inhibition. When the utilized concentration of POSS-P(V-co-P-co-S)₃ reached 0.1 wt % (Figure 4d), the THF hydrate crystal morphology in polygon was observed. As the concentration of POSS-P(V-co-P-co-S)₃ increased to 0.3 wt % (Figure 4e) and 0.5 wt % (Figure 4f), the THF hydrates appeared in a clear outline and regular arrangement, indicating a great inhibiting behavior. However, the THF hydrate crystals became bigger when the concentration increased to 0.7 wt % (Figure 4g). The results are corresponding to the effect on the induction time, similar to the biomimetic ice recrystallization activity of random copolymers reported in ref 27.

The macroscopic crystallization process was also observed by dropping a 20 μL droplet of the 19 wt % THF aqueous solution with/without the amphiphilic copolymer POSS-P(V-
co-P-co-S)₃ on a 2 × 2 cm² metal plate, as shown in Figure 5. Typically, it could be seen that the pristine 19 wt % THF/water droplet presented a compact solid appearance. However, the droplet of the 19 wt % THF aqueous solution containing 0.1 wt % POSS-P(V-co-P-co-S)₃ showed looser crystals, suggesting that a low dose of POSS-P(V-co-P-co-S)₃ displayed the antiaggregation ability of the gas hydrates.

Mobility State of Water Molecules Measured by Low-Field NMR. To probe the mobility states of protons of water in the THF hydrates, low-field ¹H NMR relaxometry was employed to measure the water molecule activity by substituting TDF for THF. Figure 6a shows the relaxation time (T₂) inversion when adding a series of concentrations of POSS-P(V-co-P-co-S)₃ in the 19 wt % TDF/H₂O solution. It can be seen that the mixed solution containing the copolymer displayed diminishing values of T₂, compared to that of the pristine 19 wt % TDF/H₂O. The shorter T₂ indicated a more difficult proton exchange, resulting in the slower reorientational mobility of water molecules. The SO₃⁻ groups from SBMA units in the copolymer enhanced the hydrogen bond network in the 19 wt % TDF/H₂O solution and formed strong hydration layers on the hydrate surfaces. In addition, prompt chemical exchange of protons led to unimodal distribution of T₂ curves. Meanwhile, Figure 6b shows the T₂ inversion for different copolymers with 0.1 wt % concentration in the 19 wt % TDF/H₂O solution. It was assumed that T₂ of POSS-P(V-co-P-co-S)₃ exhibited a lower value compared to POSS-P(V-co-P-co-S)₁ and POSS-P(V-co-P-co-S)₂, indicating that the copolymer molecular weight did not significantly influence the T₂. However, when the molecular weight of the copolymer was beyond a certain range, the acting force would be exerted between the copolymer and water molecules. Additionally, T₂ of P(V-co-P-co-S)₄ was lower than that of P(V-co-P-co-S)₅, inferring that the copolymer with narrow polydispersity had a better interaction with water molecules owing to the arrangement and stretch in the solution. For the T₂ curve of P(V-co-P-co-S)₅, a smaller peak appeared at 616 ms, which can be attributed to the inhomogeneity of the solution and brought about different microenvironment and proton exchange. In the T₂ curve of P(V-co-P-co-S)₆, there was an abnormal increased value of T₂, and it was assumed that the proton exchange between the copolymer and water molecules was hampered because of the broad polydispersity.²⁸,²⁹

Nonfreezable Bound Water Amount in the Copolymers. For further understanding of the antiaggregation properties of the prepared copolymers, the amounts of bound water, nonfreezable bound water, and freezable water in the copolymers were evaluated by the DSC analysis. Figure 7 shows the heating thermograms of the copolymers with the similar water content (W_c ≈ 0.8) at a heating rate of 10 °C/min. It can be seen that most of the melting peaks of the samples could be fitted into two peaks, a smaller one around −20 to −12 °C and a sharp one at −7 to 0 °C close to the melting point of pure deionized water. They could correspond to the melting enthalpies of freezable bound water (W_b) and nonfreezable free water (W_f), respectively, depending on the endothermic states of the copolymers during the melting process. It could be verified that there was nonfreezable bound

Figure 5. Transition of the crystal morphology for THF hydrates with/without the copolymer POSS-P(V-co-P-co-S)₃.

Figure 6. Relaxation time (T₂) inversion spectra of water in the 19 wt % TDF/H₂O solution containing POSS-P(V-co-P-co-S)₃ with diverse copolymer concentrations (a) and the different copolymers with 0.1 wt % concentration (b).

7375
water in most of the copolymers, similar to our previous studies. However, for P(V-co-P), it was difficult to distinguish freezable bound water and freezable free water in the DSC curve.

Water amounts at different states in the copolymer/water binary systems with similar total water contents analyzed by DSC are collected in Table 2. The results revealed that POSS-P(V-co-P-co-S)\textsubscript{1}, POSS-P(V-co-P-co-S)\textsubscript{2}, POSS-P(V-co-P-co-S)\textsubscript{3}, P(V-co-P-co-S)\textsubscript{A}, and P(V-co-P-co-S)\textsubscript{C} attended by water contents ∼0.8 were evaluated with the nonfreezable bound water contents (W\textsubscript{nf}) of 0.20, 0.23, 0.25, 0.25, and 0.17 mg/mg, respectively, indicating similar nonfreezable bound water contents in these copolymers. In addition, the total bound water contents showed similar results about 0.32−0.40 mg/mg, suggesting that all the copolymers containing VCap, VP, and SBMA with or without POSS may have similar situations of polymer−water interactions at a molecular level, which agreed with our previous reports.

**Mechanism of the Amphiphilic Copolymers on THF Hydrate Inhibition.** With water molecule-formed pentagon structure by the hydrogen bond interaction, a supposed structure II THF hydrate is shown in Figure 8, in which the THF molecules as the object are tied up in the crystal void. The hydrophilic moieties of the amphiphilic copolymer could cohere with the THF hydrate through the hydrogen bonds of amide groups in VCap or VP units and electrostatic interaction of SBMA units to inhibit the nucleation and growth of the THF hydrates. On the other hand, hydrophobic POSS groups could adjust the hydrophilic/hydrophobic balance of the copolymer, leading to enhanced inhibition behaviors. Also, the amphiphilic copolymer could display the antiaggregation property for hydrates as AAs because of the performance similar to that of surfactants. Accordingly, the POSS groups surrounded by hydrates and poly(VCap-co-VF-co-SBMA) acted on hydrates for enhancing the dispersion of hydrate particles and antiaggregation of the THF hydrates.

### EXPERIMENTAL SECTION

**Materials.** Aminopropyllsobutyl POSS was purchased from Hybrid Plastics, USA. VCap and VP were supplied by Hangzhou Lookchem Internet Technology Co., Ltd., China. 2-Bromoisobutyryl bromide and EBIB (>99%) were supplied by Beijing J&K Scientific Co., Ltd., China. [2-(Methacryloyloxy)ethyl] dimethyl-(3-sulfopropyl) ammonium hydroxide, i.e., sulfobetaine methacrylate (SBMA), N,N,N′,N″-pentamethyl dipropylenetriamine (PMDETA, >97%), and triethylamine (>99%) were obtained from Tianjin Xi’ensi Aupu

**Table 2. Water Amounts (mg/mg) at Different States in the Copolymers with Similar Total Water Contents Analyzed by DSC**

| sample                  | \(W_\text{f}\) | \(W_\text{f}^\text{a}\) | \(W_\text{b}\) | \(T_{\text{fbm}}\) (°C) | \(W_\text{f}^\text{b}\) | \(T_{\text{ffm}}\) (°C) | \(W_\text{nf}\) | \(W_\text{b}\) |
|-------------------------|----------------|-----------------|----------------|-----------------|----------------|-----------------|----------------|---------|
| POSS-P(V-co-P-co-S)\textsubscript{1} | 0.83           | 0.63            | 0.17           | −12.62          | 0.46            | −0.67           | 0.20            | 0.37    |
| POSS-P(V-co-P-co-S)\textsubscript{2} | 0.80           | 0.60            | 0.17           | −14.02          | 0.43            | −0.96           | 0.23            | 0.40    |
| POSS-P(V-co-P-co-S)\textsubscript{3} | 0.80           | 0.55            | 0.14           | −15.94          | 0.41            | −1.96           | 0.25            | 0.39    |
| P(V-co-P-co-S)\textsubscript{A}       | 0.83           | 0.58            | 0.12           | −19.13          | 0.46            | −2.68           | 0.25            | 0.37    |
| P(V-co-P-co-S)\textsubscript{C}       | 0.82           | 0.65            | 0.15           | −18.52          | 0.50            | −3.65           | 0.17            | 0.32    |
| P(V-co-P)                              | 0.83           | 0.83            | 0.83           | −6.06           | 0.83            | −6.06           | 0.83            | 0.83    |

\textsuperscript{a}Melting temperature of freezable bound water determined as the fitting peak temperature in the heating curve. \textsuperscript{b}Melting temperature of freezable free water estimated from the melting peak.

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Figure 7. DSC thermograms of the copolymers with similar total water content (\(W_\text{c} \approx 0.8 \text{ mg/mg}\)) at a heating rate of 10 °C/min.

Figure 8. Schematic mechanism of the amphiphilic copolymer POSS-poly(VCap-co-VF-co-SBMA) for THF hydrate inhibition.
The antiaggregation performance of the THF hydrates was the crystalline THF hydrate was observed and photographed. From room temperature to dropping a 10 μL droplet on a coverslip and placed on the pump.

The sample was prepared by using POSS-P as the initiator that was prepared according to refs 20 and 30. Typically, POSS-Br (0.02 mmol), VCap (1.2, 2.4, or 3.6 mmol), VP (0.6, 1.2, or 1.8 mmol), SBSMA (0.2, 0.4, or 0.6 mmol), and PMDETA (0.1 mmol) were dissolved in 2 mL mixed solvent of THF/water (1/1, v/v) and were injected into the 10 mL standard Schlenk flask. The reaction mixture was stirred at 35 °C for 40 h. The POSS-poly(VCap-co-VP-co-SBSMA) copolymer was obtained by dialysis against deionized water for 3 days (MWCO 2000) and recovered by lyophilization. For comparison, poly(VCap-co-VP-co-SBSMA) without POSS was also synthesized by using EBIB or APS as the initiator, and the binary copolymer poly(VCap-co-VP) was also prepared by using AIBN under similar conditions.

**Characterization.** The chemical structure of the prepared copolymers was characterized by 1H NMR and FTIR. The 1H NMR spectra were recorded on an Inova 500 MHz spectrometer (USA) using D2O as the solvent, and the FTIR spectra were recorded on a PerkinElmer Spectrum 100 spectrometer (USA) using the KBr pellet technique.

**Induction Time Tests.** A 19 wt % THF aqueous solution was used as a gas hydrate analogue of structure II. The induction time was measured by the crystallization time of the droplets (5 μL) of the THF solution containing a certain amount of the copolymer. The samples on the 2 × 2 cm2 iron plates were placed on a cold plate (Tianjin Jing Yi Industry & Trade Co., Ltd., China) and controlled at −15 °C (25% relative humidity). The induction time was recorded when any of the four droplets changed from transparent to opaque. The results presented are the average of 7–10 measurements of each sample. Statistical analyses were performed using Student’s t test. A p-value less than 0.05 indicated statistical significance.

**Morphology Observation.** The morphology of the 19 wt % THF aqueous solution with and without copolymers was recorded by a high-speed camera (the Cooke Corporation, USA) with a mercury fluorescent lamp in the microscope (BX51, Olympus, Japan). The sample was prepared by dropping a 10 μL droplet on a coverslip and placed on the cold plate (BCS196, Linkam, UK). The sample was cooled from room temperature to −30 °C at a cooling rate of 10 °C/min and maintained for 10 min, and then the morphology of the crystalline THF hydrate was observed and photographed. The antiaggregation performance of the THF hydrates was measured by dropping 20 μL droplets of 19 wt % THF aqueous solution with or without the copolymer POSS-P-(V-co-P-co-S)3 on the iron plate. After being placed on a cold plate predetermined at −15 °C (25% relative humidity) for a certain time, the droplet sample was stirred by a pipette tip and it quickly became solid. The appearance change of the droplet was recorded by a digital camera at once.

**Low-Field NMR Tests.** The low-field 1H NMR measurements were carried out on a Bruker minispec mq20 spectrometer at a 20 MHz proton resonance frequency according to ref 31. Samples at different concentrations in the 19 wt % TDF aqueous solution were placed in the NMR tube with a 10 mm outer diameter. The free induction decay signals were recorded with Carr–Purcell–Meiboom–Gill (CPMG) pulse sequences, where the spin-spin relaxation time (T2) distribution curve was obtained through an inverse Laplace transform-based CONTIN analysis. The minispec has a typical π/2 pulse length of about 3 μs and a receiver dead time of about 13 μs.

**DSC Analysis.** The bound water amount in the copolymers was analyzed by DSC (TA Q2000, USA) according to our previous study.20 Brieﬂy, the samples were prepared by adding a certain amount of deionized water into the copolymers (about 4–5 mg) and stabilized in the aluminum pan for 10 days at room temperature. When no mass changes were detected, the samples were tested at a cooling/heating rate of 10 °C/min by purging nitrogen gas in the range of 20 to −70 °C. The total water content (Wt), the freezable water content (Wf), the nonfreezable bound water content (Wnb), and the bound water content (Wfb) in the samples were calculated according to the following equations:21−35

\[
W_t = \frac{m_w}{m_p}
\]

\[
W_f = A_c/(334m_p)
\]

\[
W_{nb} = W_c - W_f
\]

\[
W_b = W_{nb} + W_{fb}
\]

where \(m_w\) and \(m_p\) represent the masses of water and the copolymer, respectively. \(A_c\) was the integration of the endothermic peak in the heating curves and 334 denoted the enthalpies of free and freezable water (J/g).20 The freezable bound water content (Wfb) was referred to the area of the symmetric peak around −15 °C in the heating runs, and the freezable free water content (Wfb) was the difference between Wf and Wnb according to refs 32 and 33. The bound water content (Wb) was the sum of Wfb and Wnb. The melting temperatures of the freezable bound water (Tfbm) and the freezable free water (Tfb) were designated as the peak temperatures of the fitting symmetric peak and the melting peak, respectively, in the heating curves of the samples.

**CONCLUSIONS**

The amphiphilic copolymers containing POSS, VCap, VP, and SBSMA synthesized via ATRP demonstrated a great performance on THF hydrate inhibition. The induction time of the THF hydrates containing 0.1–0.5 wt % of the resultant copolymer POSS-P-(V-co-P-co-S)3 displayed the ability of inhibiting nucleation and formation. POSS-P-(V-co-P-co-S)3 showed a high value of nonfreezable bound water analyzed by DSC and a lower relaxation time T2 measured by LF NMR. Moreover, the microcosmic crystallization morphology of regular and clear polygonal outline and the macroscopic crystallization process of THF hydrates containing POSS-P-(V-co-P-co-S)3 manifested an important effect on antiaggregation, attributing to the amphiphility and the hydrogen bond interaction between the copolymers and water molecules. It
was assumed that the VCap- and VP-related units in the copolymers could behave as KHIs because of their cyclic structure including the nitrogen element, and zwitterionic SBMA in the amphiphilic copolymers could enhance the KHI properties by its strong electrostatic interaction with water molecules. In addition, the hydrophobic POSS groups could regulate the hydrophilic/hydrophobic balance, endowing the amphiphilic copolymer with the properties of THF hydrate inhibition. The amphiphilic copolymer POSS-poly(VCap-co-VP-co-SBMA) would contribute to novel potential applications for gas hydrate inhibition during transportation in the pipeline.

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**Notes**
The authors declare no competing financial interest.

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**REFERENCES**

(1) Aman, Z. M.; Koh, C. A. Interfacial Phenomena in Gas Hydrate Systems. *Chem. Soc. Rev.* 2016, 45, 1678–1690.

(2) Khurana, M.; Yin, Z.; Linga, P. A Review of Clathrate Hydrate Nucleation. *ACS Sustainable Chem. Eng.* 2017, 5, 11176–11203.

(3) Kamal, M. S.; Hussein, I. A.; Sultan, A. S.; von Solms, N. Application of Various Water Soluble Polymers in Gas Hydrate Inhibition. *Renewable Sustainable Energy Rev.* 2016, 60, 206–225.

(4) Perrin, A.; Mussa, O. M.; Steed, J. W. The Chemistry of Low Dosage Clathrate Hydrate Inhibitors. *Chem. Soc. Rev.* 2013, 42, 1996–2015.

(5) Li, S.; Wang, Y.; Lang, X.; Fan, S. Effects of Cyclic Structure Inhibitors on the Morphology and Growth of Tetrahydrofuran Hydrate Crystals. *J. Cryst. Growth* 2013, 377, 101–106.

(6) Gulbrandsen, A. C.; Svartaas, T. M. Effect of Poly Vinyl Carboxylate Concentration on the Dissociation Temperature for Methane Hydrates. *Energy Fuels* 2017, 31, 8505–8511.

(7) Zhao, X.; Qiu, Z.; Huang, W. Characterization of Kinetics of Hydrate Formation in the Presence of Kinetic Hydrate Inhibitors during Deepwater Drilling. *J. Nat. Gas Sci. Eng.* 2015, 22, 270–278.

(8) Rebolledo-Libreros, M. E.; Reza, J.; Trejo, A.; Guzmán-Lucero, D. J. Evaluation of Copolymers from 1-Vinyl-3-Alkylimidazolium Bromide and N-Vinylcaprolactam as Inhibitors of Clathrate Hydrate Formation. *J. Nat. Gas Sci. Eng.* 2017, 40, 114–125.

(9) Qin, H.-B.; Sun, Z.-F.; Wang, X.-Q.; Yang, J.-L.; Sun, C.-Y.; Liu, B.; Yang, L.-Y.; Chen, G.-J. Synthesis and Evaluation of Two New Kinetic Hydrate Inhibitors. *Energy Fuels* 2015, 29, 7135–7141.

(10) Qin, H.-B.; Sun, C.-Y.; Sun, Z.-F.; Liu, B.; Chen, G.-J. Relationship between the Interfacial Tension and Inhibition Performance of Hydrate Inhibitors. *Chem. Eng. Sci.* 2016, 148, 182–189.

(11) Mady, M. F.; Min Bak, J.; Lee, H.-J.; Kelland, M. A. The First Kinetic Hydrate Inhibition Investigation on Fluorinated Polymers: Poly(fluoroalkylacrylamide)s. *Chem. Eng. Sci.* 2014, 119, 230–235.

(12) Nguyen, N. N.; Nguyen, A. V. Hydrophobic Effect on Gas Hydrate Formation in the Presence of Additives. *Energy Fuels* 2017, 31, 10311–10323.

(13) Ke, W.; Kelland, M. A. Kinetic Hydrate Inhibitor Studies for Gas Hydrate Systems: A Review of Experimental Equipment and Test Methods. *Energy Fuels* 2016, 30, 10015–10028.

(14) Smith, J. D.; Meuler, A. J.; Bradlow, H. L.; Venkatesan, R.; Subramanian, S.; Cohen, R. E.; McKinley, G. H.; Varanasi, K. K. Hydrate-phobic Surfaces: Fundamental Studies in Clathrate Hydrate Adhesion Reduction. *Phys. Chem. Chem. Phys.* 2012, 14, 6013–6020.

(15) Talaghat, M. R. Experimental Investigation of Induction Time for Double Gas Hydrate Formation in the Simultaneous Presence of the PVP and l-Tyrosine as Kinetic Inhibitors in a Mini Flow Loop Apparatus. *J. Nat. Gas Sci. Eng.* 2014, 19, 215–220.

(16) Yang, J.; Tohidi, B. Determination of Hydrate Inhibitor Concentrations by Measuring Electrical Conductivity and Acoustic Velocity. *Energy Fuels* 2013, 27, 736–742.

(17) Liu, C.; Li, M.; Zhang, G.; Koh, C. A. Direct Measurements of the Interactions between Clathrate Hydrate Particles and Water Droplets. *Phys. Chem. Chem. Phys.* 2015, 17, 20021–20029.

(18) Cha, M.; Couzis, A. A.; Lee, J. W. Macroscopic Investigation of Water Volume Effects on Interfacial Dynamic Behaviors between Clathrate Hydrate and Water. *Langmuir* 2013, 29, 5793–5800.

(19) Leng, C.; Sun, S.; Zhang, K.; Jiang, S.; Chen, Z. Molecular Level Studies on Interfacial Hydration of Zwitterionic and Other Antifouling Polymers In Situ. *Acta Biomater.* 2016, 40, 6–15.

(20) Li, C.; Li, X.; Tao, C.; Ren, L.; Zhao, Y.; Bai, S.; Yuan, X. Amphiphilic Antifogging/Anti-icing Coatings Containing POSS-PDMAEMA-PSBMA. *ACS Appl. Mater. Interfaces* 2017, 9, 22959–22969.

(21) Tao, C.; Bai, S.; Li, X.; Li, C.; Ren, L.; Zhao, Y.; Yuan, X. Formation of Zwitterionic Coatings with an Aqueous Lubricating Layer for Antifogging/Anti-icing Applications. *Prog. Org. Coat.* 2018, 115, 56–64.

(22) Liu, B.; Zhang, K.; Tao, C.; Zhao, Y.; Li, X.; Zhu, K.; Yuan, X. Strategies for Anti-icing: Low Surface Energy or Liquid-infused? *RSC Adv.* 2016, 6, 70251–70260.

(23) Leng, C.; Hung, H.-C.; Sieggreen, O. A.; Li, Y.; Jiang, S.; Chen, Z. Probing the Surface Hydration of Nonfouling Zwitterionic and Poly(ethylene glycol) Materials with Isotopic Dilution Spectroscopy. *J. Phys. Chem. C* 2015, 119, 8775–8780.

(24) Yang, B.; Wang, C.; Zhang, Y.; Ye, L.; Qian, Y.; Shu, Y.; Wang, J.; Li, J.; Yao, F. A Thermoresponsive Poly(N-vinylcaprolactam-co-Sulfobetaine Methacrylate) Zwitterionic Hydrogel Exhibiting Switchable Anti-biofouling and Cytocompatibility. *Polym. Chem.* 2015, 6, 3431–3442.

(25) Lu, X.; Gong, S.; Meng, L.; Li, C.; Yang, S.; Zhang, L. Controllable Synthesis of Poly(N-vinylpyrrolidone) and its Block Copolymers by Atom Transfer Radical Polymerization. *Polymer* 2007, 48, 2835–2842.

(26) Sharifi, H.; Englezos, P. Accelerated Hydrate Crystal Growth in the Presence of Low Dosage Additives Known as Kinetic Hydrate Inhibitors. *J. Chem. Eng. Data* 2014, 60, 336–342.

(27) Stubbs, C.; Lipecki, J.; Gibson, M. I. Regioregular Alternating Polyampholytes Have Enhanced Biomimetic Ice Recrystallization Activity Compared to Random Copolymers and the Role of Side Chain versus Main Chain Hydrophobicity. *Biomacromolecules* 2017, 18, 295–302.

(28) Chi, Y.; Xu, S.; Xu, X.; Cao, Y.; Dong, J. Studies of Relationship Between Polymer Structure and Hydration Environment in Amphiphilic Polyampholytes. *J. Polym. Sci., Part B: Polym. Phys.* 2017, 55, 138–145.

(29) Chen, J.; Gong, X.; Zeng, C.; Wang, Y.; Zhang, G. Mechanical Insight into Resistance of Betaine to Urea-Induced Protein Denaturation. *J. Phys. Chem. B* 2016, 120, 12327–12333.

(30) Ma, L.; Geng, H.; Song, J.; Li, J.; Chen, G.; Li, Q. Hierarchical Self-assembly of Polyhedral Oligomeric Silsesquioxane End-capped Stimuli-responsive Polymer: From Single Micelle to Complex Micelle. *J. Phys. Chem. B* 2011, 115, 10586–10591.
(31) Zhang, R.; Yu, S.; Chen, S.; Wu, Q.; Chen, T.; Sun, P.; Li, B.; Ding, D. Reversible Cross-linking, Microdomain Structure, and Heterogeneous Dynamics in Thermally Reversible Cross-linked Polyurethane as Revealed by Solid-state NMR. *J. Phys. Chem. B* 2014, 118, 1126–1137.

(32) Weise, U.; Maloney, T.; Paulapuro, H. Quantification of Water in Different States of Interaction with Wood Pulp Fibres. *Cellulose* 1996, 3, 189–202.

(33) Nwaka, D.; Tahmasebi, A.; Tian, L.; Yu, J. The Effects of Pore Structure on the Behavior of Water in Lignite Coal and Activated Carbon. *J. Colloid Interface Sci.* 2016, 477, 138–147.

(34) Tahmasebi, A.; Yu, J.; Su, H.; Han, Y.; Lucas, J.; Zheng, H.; Wall, T. A Differential Scanning Calorimetric (DSC) Study on the Characteristics and Behavior of Water in Low-Rank Coals. *Fuel* 2014, 135, 243–252.

(35) Nakano, T.; Nakao, T. Coagulation Size of Freezable Water in Poly(vinyl alcohol) Hydrogels Formed by Different Freeze/Thaw Cycle Periods. *Polym. J.* 2011, 43, 875–880.

(36) Ostrowska-Czubenko, J.; Pieróg, M.; Gierszewska-Drużyńska, M. Water State in Chemically and Physically Crosslinked Chitosan Membranes. *J. Appl. Polym. Sci.* 2013, 130, 1707–1715.

(37) Varma-Nair, M.; Costello, C. A.; Colle, K. S.; King, H. E. Thermal analysis of polymer–water interactions and their relation to gas hydrate inhibition. *J. Appl. Polym. Sci.* 2007, 103, 2642–2653.