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# Synergy Effect Study of Poly(N-isoacrylamide) with Tetra Butyl Phosphonium Bromide on Methane Hydrate Formation

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**Abstract**

Natural gas hydrate plugging is one of the costly and challenging problems for the oil and gas industry, especially for subsea fields. One way to prevent gas hydrate formation at low cost is the use of low-dosage hydrate inhibitors (LDHI). Poly(N-isopropylmethacrylamide) (PNIPAM) with amide group have previously been shown to be an outstanding low-dosage hydrate inhibitor (LDHI). PNIPAMs are usually polymerized via radical polymerization, which can allow control over the molecular weight. We have synthesized PNIPAMs using control radical polymerization giving a fairly high degree of polymerization control. Additionally various Kinetic Hydrate Inhibitors (KHIs) were tested as $CH_4$ hydrate inhibitors with polymeric hydrate inhibitor, PNIPAM. Furthermore, to check the synergetic effects of tetra butyl phosphonium bromide (TBPB), PNIPAM and their mixture TBPB-PNIPAM were tested as KHIs for methane gas hydrate formation. In this paper we present results on the performance of various polymeric inhibitors in KHI tests on methane gas in stirred autoclaves and on structure I hydrate formation. When PNIPAM alone was used as a single KHI, PNIPAM exhibited worst performance among the KHIs tested in this study. However the mixing of TBPB with PNIPAM further extended the induction time and reduced the $CH_4$ hydrate growth rate. TBPB was an excellent synergist in blends with PNIPAM for kinetic hydrate inhibition of structure I forming $CH_4$ hydrate. In summary, the mixture TBPB-PNIPAM was proven that great synergist for prevent the $CH_4$ hydrate and good potential in achieving the industrial application of Oil & Gas production technology and therefore was a significantly meaningful discovery in the field of energy production.



*Keywords:* Radical polymerization, PNIPAM, TBPB, KHIs, $CH_4$ Hydrate, Synergy

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## 1. Introduction

Natural gas hydrate formation can cause plugging in flow lines of gas and oil production, which can lead to catastrophic economic loss and safety concerns [1]. Consequently, research on the development of new and effective inhibitors has been increased to prevent the gas hydrates during natural gas and oil subsea production and transportation [2-4]. Alcohol and Mono ethylene glycol(MEG), which are hydrogen bond between water, shifting hydrate formation conditions toward the inhibition region, and thus, these chemicals are called thermodynamic hydrate inhibitors(THIs) [5-6]. But large amount of THIs are usually required to prevent hydrate plugging of the flow lines, which increases costs too much for oil and gas production [7]. Hence, another type of hydrate inhibitors suggesting low dosage hydrate inhibitors (LDHIs) was developed and used to reduce the operation cost [6]. LDHIs classified as kinetic hydrate inhibitors (KHIs) and anti-agglomerants (AAs), delay the induction time (nucleation time) and retard the crystal growth rate of gas hydrate at low dosage (0.5 – 2wt%). Generally, the KHIs are polymeric materials that kinetically retard the nucleation and growth of hydrate crystals, while the AAs are surfactants that bind to hydrate particles prevent the hydrate growth/agglomeration. Most classes of KHI polymers contain amide groups. A group of KHIs based on the polymer of alkyl acrylamide was developed. It was also pointed out that poly(N-isopropylacrylamide)s are also recognized for its performance just as KHIs, especially when isopropyl serves as the alkyl group [8]. Furthermore, quaternary ammonium salts have been used as synergists, particularly for N-vinylcaprolactam polymers.
In this study, we report the synthesis of PNIPAM and compared the inhibition performance of synthesized PNIPAM, which is evaluated with commercial inhibitor, TBPB and TBPB-PNIPAM mixture conditions.

## 2. Experiment

### *2.1. Materials*

NIPAAm (Tokyo Kasei Kogyo Co.) was recrystallized from a hexane–benzene mixture solution. Toluene was purified through washing with sulfuric acid, water, and 5% aqueous NaOH; this was followed by fractional distillation. Methanol (MeOH) and ethanol (EtOH) were distilled before use. Tri-nbutylborane (n-Bu3B) as a THF solution (1.0 M), HMPA (Aldrich Chemical Co.), t-BuOH (Aldrich Chemical Co.), isopropyl alcohol (IPA), and 3-methyl-3-pentanol (Aldrich Chemical Co.) were used without further purification for polymerization reactions.

### *2.2. Synthesis of PNIPAM*

Polymerization of PNIPAM: NIPAM (1.062 g, 9.4 mmol) and 3-methyl-3-pentanol (3.835 g, 37.5mmol) were dissolved in toluene to prepare a 20 mL solution. A total of 16 mL of the solution was transferred to a glass ampule and cooled to 0 °C. Polymerization was initiated by adding n-Bu3B solution (5.0 mL) in tetrahydrofuran (THF) (1.0 M) to the monomer solution. The reaction was terminated after 24 h by adding a small amount of a solution of 2,6-di-tbutyl-4-methylphenol in THF at the polymerization temperature. The reaction mixture was poured into a large amount of diethyl ether, and the precipitated polymer collected by filtration then dried *in vacuo*. The polymer yield was determined gravimetrically.

### *2.3. Characterization*

Analysis of $^{1}$H-nuclear magnetic resonance (NMR): The synthesized polymers were dissolved in $D_2O$, and then $^{1}$H NMR spectra of the polymers were obtained using a Varian 400 (Varian, Palo Alto, CA, U.S.A.) spectrometer.
Analysis of fourier transform infrared spectra (FT-IR): Infrared spectra were collected using potassium bromide pellets on a PerkinElmer FRONTIER spectrometer.
Methane gas hydrate Experimental apparatus and procedure: The experimental apparatus, as shown in Figure 1, mainly consists of a stainless-steel reactor (372.5 mL), a supply vessel (566.5 mL), a refrigeration system, a water bath, and a data acquisition system. Prior to each hydrate kinetic experimental run, the reactor was filled 125cm$^{-1}$

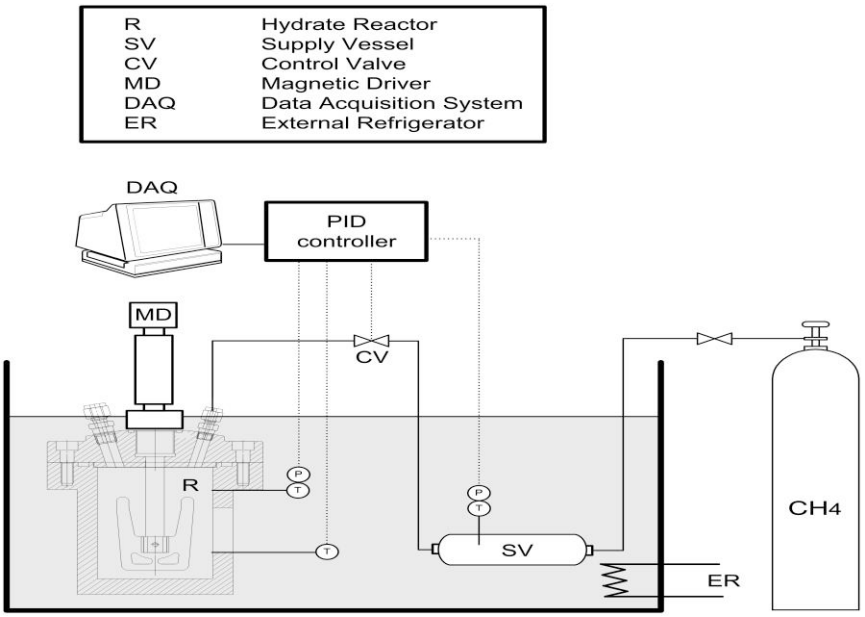


Fig.1. Schematic diagram of the gas hydrate experimental apparatus

of aqueous test sample (pure water or a liquid solution of the inhibitor), and then the reactor was flushed at least 3 times with methane gas to remove any residual air.

Subsequently, the whole system was kept at a desired temperature, and the reactor was filled with methane gas until the experimental pressure was obtained. All experiments were conducted at 7.0 MPa and 276.15 K (4.7 K subcooling). Once the temperature was stabilized, the solution was agitated using a magnetically driven impeller with a rotational speed of 300 rpm, which was determined to be suitable for our experiment and was applied to every experimental run.

In a literature review, there was no significant difference in gas consumption between 0.1, 0.5, and 1 wt % performance of the hydrate inhibitor [9]. On the basis of this study, the inhibitor performance of PVCap was tested at an economic dosage of 0.1 wt %. As methane gas in the reactor is consumed during the hydrate formation, additional gas was automatically supplied from the supply vessel and the moles of gas uptake over time were calculated from the pressure drop profile in the supply vessel (>7.0 MPa) with respect to the initial pressure. A more detailed description of the experimental procedure is available in a previous report [10].

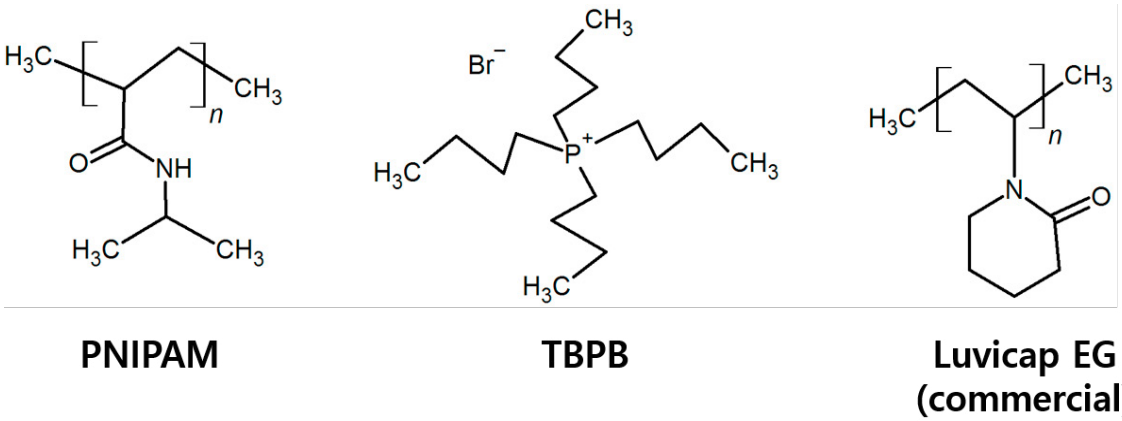


Fig.2. Structure of various KHIs used in this study: PNIPAM, TBPB, Luvicap EG

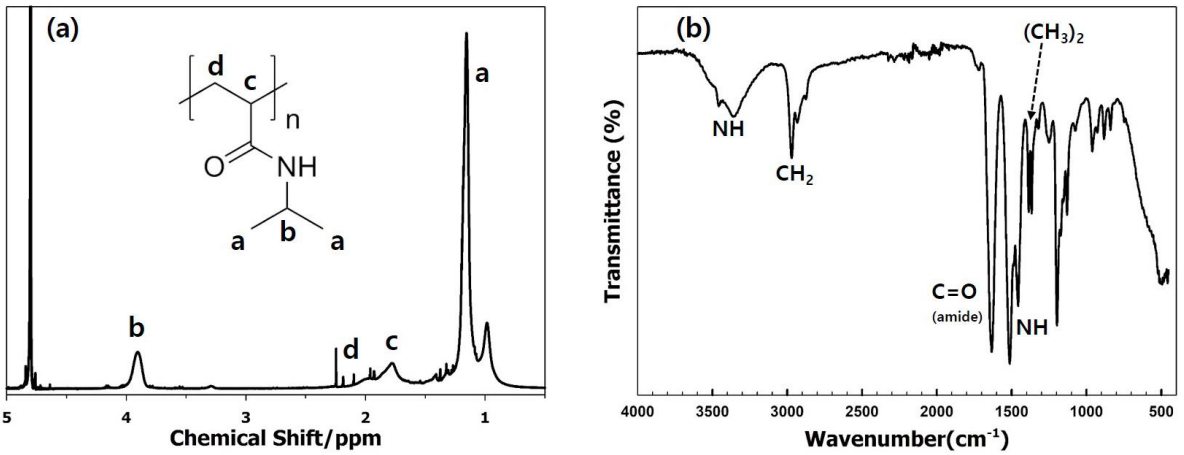


Fig.3. (a) $^{1}$H NMR spectrum of PNIPAM, (b) FT-IR spectrum of PNIPAM,

## 3. Result and Discussion

### *3.1. $^{1}$H NMR spectrum of PNIPAM*

Figure 1 shows the $^{1}$H NMR spectra of PNIPAM prepared via Radical polymerization. In addition, the spectrum of the PNIPAM reveals the resonance of the repeat unit: $CH_2$ backbone, c and d (1.55−2.35ppm), $CH_3$, a (1.15 ppm); NCH2 of isopropyl b (3.9 ppm); respectively. The peak of the solvent $D_2O$ at 4.8 ppm.

### *3.2. FT-IR spectrum of PNIPAM*

In the FT-IR spectrum presented in Fig. 2a, the absorption peaks at 1653, 1554 and 1381 cm$^{-1}$ can be assigned to the amide I band (mainly due to the C=O stretching vibration), amide II band (a combination of the N–H bending and C–N stretching vibration), and $CH_3$ bending vibration, respectively. In addition, the peak shoulder at about 1725 cm$^{-1}$ can be ascribed to the C=O stretching vibration of the monomer unit.

### *3.3. Inhibition effect of PNIPAM alone*

In order to check the inhibition performance, each KHIs (0.1 wt % dissolved in distilled water) was tested at semi-batch reactor under 7 MPa, 276.15K and 300 rpm. As shown in Figure 4(a), the induction time for $CH_4$ hydrate formation at various kinds of KHIs and PNIPAM. All the experiments showed that the induction time was considerably delayed in the presence of the inhibitors. In the absence of any KHIs, recorded induction time was 2 min. On the other hand, when various KHIs or synthesized PNIPAM were present in water, various induction times of 28-385 min were recorded. To obtain accurate results, the experiments were repeated 3 times and were shown in Figure 4.

Luvicap EG with ethylene glycol had the best nucleation inhibition performance compared to the other KHIs and synthesized PNIPAM at the same conditions. Although the induction time of TBPB was less than 20min, growth time was the longest among the tested inhibitors. Luvicap EG and PNIPAM with amide group polymer KHIs inhibit hydrate formation by adsorption on hydrate surface/particles [11]. However, TBPB likewise quaternary salts are composed of small cations and anions which are dispersed in aqueous solutions and interact with water molecules, which could retard $CH_4$ hydrate nucleation and growth [12].

### 3.4. Inhibition effect of PNIPAM with TBPB

Figure 4(b) show positive synergy effect with TBPB-PNIPAM mixtures on the $CH_4$ hydrate formation. The individual performance of TBPB or PNIPAM showed very poor inhibition result (induction time: within 30min.). However, the mixture of TBPB and PNIPAM effectively reduced the hydrate growth rate, which resulted in a low slope of the $CH_4$ consumption trace, compared to individual performance of TBPB or PNIPAM. The most remarkable difference between these results and that of the single inhibitor test is that PNIPAM-TBPB mixture exhibited a dramatical increase in the growth time for hydrate formation by about three times.

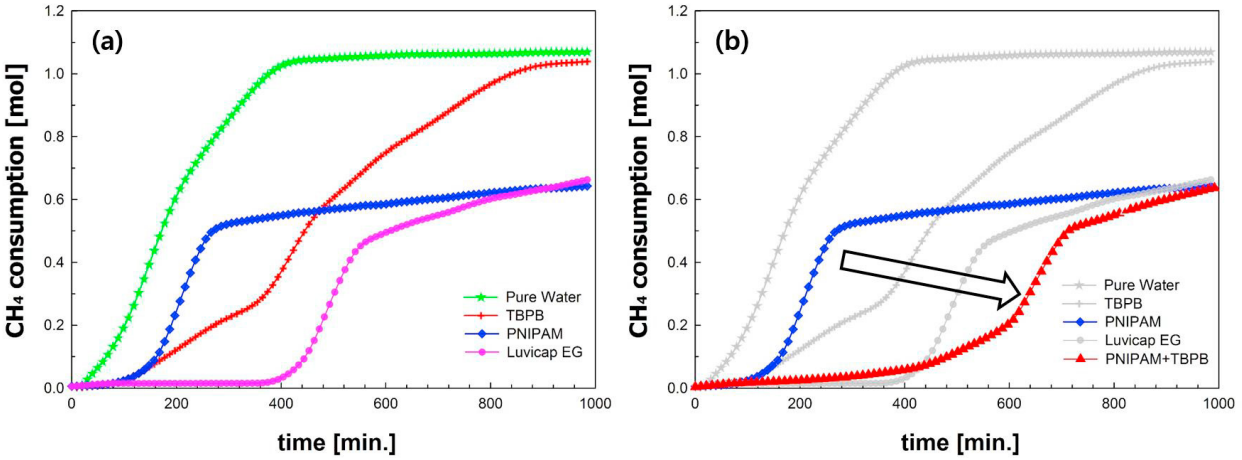


Fig. 4. Consumption comparison of $CH_4$ hydrate (a) in the absence of TBPB-PNIPAM mixture (b) in the presence of TBPB-PNIPAM mixture

## 4. Conclusion

In this study, we have synthesized PNIPAM via free radical polymerization. This polymer was tested for KHI performance of $CH_4$ gas hydrate in a high-pressure autoclave and commercial PVCap-based KHI Luvicap EG and TBPB-mixture was compared. As the results of the hydrate kinetic measurements shows the addition of Luvicap EG (PVCap) as a hydrate inhibitor significantly delayed hydrate nucleation and also prevented further gas hydrate formation. However when PNIPAM was used alone as a single KHI, it exhibited the worst performance among the KHIs tested in this study. The mixing of TBPB with PNIPAM further extended the induction time and reduced the $CH_4$ hydrate growth rate. TBPB was an excellent synergist in blends with PNIPAM for kinetic hydrate inhibition of structure I forming $CH_4$ hydrate. The synergetic inhibition effect might be related to perturbation between water molecule and hydrate particle.

## Acknowledgements

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