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Design of The Rigid Side Chain for Poly(*N*-vinylamide) Derivatives Bearing The Alkenyl Group and Evaluation of The Inhibition Ability of Tetrahydrofuran Hydrate Crystal Growth

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Key words

Abstract

Kinetic hydrate inhibitors (KHIs) are water-soluble polymers that are used to prevent gas hydrate formation in flow lines during upstream oil and gas production. All commercial polymers have pendant hydrophobic moieties with saturated carbon-carbon bonds. In our previous studies, poly(*N*-vinylamide) derivatives bearing the alkyl groups and the ethylene glycol groups were synthesized and investigated as KHIs. Compared with our previous studies, we have now synthesized poly(*N*-vinylamide) derivatives in which the alkenyl group has been introduced at the *N*-position to improve the rigidity and steric hindrance of the side chain. The KHI performances of synthesized polymers were evaluated by the method of THF hydrate crystal growth. The inhibition ability of THF hydrate crystal growth was dependent on the molecular weight of synthesized polymers. Higher molecular weight polymers, above 4000 g/mol, tend to show higher inhibition efficiencies compared with lower molecular weight polymers, around 1000 g/mol. However, the KHI performance of poly(*N*-vinylamide) derivatives bearing the alkenyl groups was generally lower than the polymers of the previous studies. This indicates that the side chain rigidity and/or steric hindrance do not significantly influence the KHI performance.

Introduction

During upstream production of oil and gas the pressure is high. If the temperature is also low, such as in subseas lines or on land in cold regions, there is the possibility of gas hydrates forming in the flow line. [1] This can lead to loss of production and revenues. Furthermore, sometimes flow lines can become blocked by the gas hydrate crystals, potentially causing accidents during attempts to remove the blockage. [2]

In order to inhibit the generation of gas hydrates in flow lines, several chemical inhibition methods have been developed. [3,4] One of the approaches is the use of the low dosage hydrate inhibitors (LDHIs), which has been used by the oil and gas industry in upstream hydrocarbon transportation operation for about 25 years. [1] Additionally, due to the low dosages required, the deployment of an LDHI can be an economic and an efficient option compared to other gas hydrate inhibition methods. Kinetic hydrate inhibitors (KHIs) is one of the classes of LDHIs. KHIs are water-soluble polymers, sometimes with additional synergists to improve their performance. In general, KHIs kinetically delay the nucleation and hydrate crystal formation processes. Thus the flow of natural gas and water in the gas pipeline becomes unheeded at certain subcooled conditions by the addition of the KHIs. The inhibition mechanisms of gas hydrate by KHI have not yet been revealed, however there are several suggestions submitted, including

sub-critical particle or crystal growth inhibition by the action of the inhibitor on or near

the hydrate surface. [5,6] KHIs are amphiphilic within the monomer units, and the most

effective polymers usually included the hydrophilic amide group close to a small

hydrophobic group. [1,7]

Among the several amphiphilic polymers with the amide groups, well-known KHI

polymers include poly(*N*-vinylcaprolactam)s (PNVC) and poly(*N*-vinylpyrrolidone)

(PNVP)s, poly(*N*-isopropylmethacrylamide) and copolymers thereof. These polyamides

have already been used commercially in KHI formulations but they have a limited

application range, depending in the subcooling, pressure, residence time in the pipeline,

the presence of other production chemicals, the salinity, the hydrocarbon composition and

many other factors. Therefore, there is a need for improved KHI polymers to meet more

extreme conditions. [8-12]

The study of this study was to design poly(*N*-vinylamide) derivatives in order to

develop high performance KHIs. Various chemical structures and amphiphilic properties

with poly(*N*-vinylamide) derivatives have been investigated in our previous researches.

[13-17] These earlier studies have revealed the side chain effect of poly(*N*-substituted-*N*-

vinylamide) derivatives for the KHI performance. The monomers of *N*-substituted-*N*-

vinylamide derivatives were synthesized using two *N*-vinylamide derivatives, *N*-

vinylformamide (NVF) and *N*-vinylacetamide (NVA), which can control the hydrophobicity and the effect of steric hindrance during polymerization. [13,15,18] For example, various alkyl groups were introduced to NVF and NVA, such as *n*-propyl, *i*-propyl, *n*-butyl, *i*-butyl, and others. These polymers showed good KHI performances, as good as commercially available KHIs such as those based on *N*-vinyl caprolactam copolymers. [13,15] We suggested that the performance was influenced by the size of the side chain alkyl groups. One of the proposed KHI mechanisms suggests that the small hydrophobic alkyl groups fit into the holes on the gas hydrate surface. [19].

Other examples of the side-chain effect of poly(*N*-substituted-*N*-vinylamide) derivatives containing oligo ethylene glycol groups have also been reported in previous research. [17] This class was inspired by the knowledge that polyethylene glycols (PEG) are synergists for PNVC as a KHI, although PEGs are poor KHIs by themselves. [20,21] Polymers similar to PEGs, poly(ethylene oxide) (PEO) and polypropylene oxide (PPO), were investigated in blends for KHIs but these polymers were also poor KHIs. [22] The monomers of *N*-vinylamide derivatives bearing ethylene glycol groups containing the methoxy or ethoxy group at the chain end of the side chain were synthesized and polymerized. These polymers showed remarkable behavior that only poly(*N*-vinylamide) derivatives bearing ethoxy groups possess a cloud point. Further, homopolymers showed

good KHI performances compared with copolymers, when evaluated by the method of THF hydrate crystal growth. [17] However, their KHI performances were generally less than poly(*N*-vinylamide) derivatives bearing the alkyl groups. [13,17] These previous studies indicate that the chemical structures of poly(*N*-vinylamide) derivatives at the side chain are important for expressing good KHI performance. Small quaternary ammonium salts, particularly with butyl or pentyl groups, also possess effective inhibition ability of THF hydrate crystal growth. [23] These hydrophobic alkyl groups are probably more expanded in aqueous media compared due to the cation charge. This would lead to local entropy loss when interacting with hydrate particles. This result led us to introduce more rigid unsaturated aliphatic hydrophobic substituents in order to try to improve the inhibition ability of crystal growth.

In this study, we synthesized poly(*N*-vinylamide) derivatives bearing the rigid alkenyl group at the *N*-position in order to investigate the side chain effect on KHI performance. The alkenyl groups which are more rigid hydrocarbyl chains compared with the alkyl groups, cannot rotate like C-C single bonds. Firstly, *N*-vinylamide derivatives bearing the alkenyl groups at the *N*-position were synthesized and polymerized by reversible addition fragmentation chain transfer (RAFT) polymerization using two charge transfer agents (CTAs) to obtain the liner polymer. Following this, the KHI performances

of synthesized poly(*N*-vinylamide) derivatives bearing the alkenyl group were evaluated

by the method of THF hydrate crystal growth. We also discuss the side chain effect of

alkenyl groups at the *N*-position on KHI performance using the results of THF hydrate

crystal growth tests in this study. [13,17]

Experimental

Materials.

N-vinylformamide (NVF), 1-bromo-2-butene, 1-bromo ethyl ether, 3-methyl-2-

butenyl bromide, ethylxanthic acid potassium salt and benzyl bromide,

diethyldithiocarbamic acid benzyl ester were purchased from Tokyo Chemical Industry

Co. Ltd. Methyl-*N*-vinylacetamide (MNVA) was purchased from Sigma-Aldrich Japan.

Sodium hydride (NaH) 60% in oil, magnesium sulfate ($MgSO_4$), dimethyl sulfoxide

(DMSO) and *N,N*-dimethylformamide (DMF) were purchased from Nacalai Tesque Inc.

Azobisisobutyronitrile (AIBN), sodium chloride (NaCl) and ethyl acetate were purchased

from Wako Pure Chemical Industries. Hexane, ethanol, tetrahydrofuran (THF), methanol

and diethyl ether were purchased from AZBIO Corp.

Apparatus

^{1}H and ^{13}C NMR spectra were measured by a JEOL JNM-GMX400 system. The number-average molecular weights and their distribution were measured by size exclusion chromatography (SEC). ChromNAV system (Shimadzu Corporation, Japan) using AS-2055 and RI-2031 was employed with polystyrene standards at room temperature. The column (TSKgel α-M) was used, and DMF (1 mg/mL) was used as an eluent at 0.6 mL/min. Low temperature incubation was performed using FMU-263I (Fukushima Industries Corp. Japan).

Synthesis of S-benzyl-O-ethyl dithiocarbonate (**CTA 1**)

The *S*-Benzyl-*O*-ethyl dithiocarbonate (**CTA 1**) was synthesized according to the literature procedure. [24] Potassium *O*-ethyl dithiocarbonate (1.6 g, 10.0 mmol) was dissolved in ethanol (20 ml) at 50 ℃. Then, benzyl bromide (1.71 g, 10 mmol) was added at this temperature. A colorless precipitate was observed after some minutes then temperature was increased to 70 ℃ and the mixture was stirred at this temperature for 5 hours. Water (80 ml) was added and the product was extracted with ether (100 ml). The combined organic extracts were dried over MgSO$_4$ and filtered. Removal of the solvent afforded a yellow oil (yield 59%, 1.24 g, 5.9 mmol).

Synthesis of 2-butene-N-vinylformamide (*n*BuNVF)

In a glass flask, NaH (10.3 g, 258 mmol) was placed and washed with anhydrous THF (15 mL) twice under nitrogen, and 80 mL of anhydrous DMF was introduced. NVF (18.4 g, 258 mmol) was slowly added at 0ºC. After stirring for 4 h at room temperature, 1-bromo-2-butene (33.2 g, 258 mmol) was slowly added by syringe at 0ºC. The reactor was warmed up to 50°C and stirring continued for 16 hr. Water was introduced into the reaction mixture to terminate the reaction, and the mixture was extracted into 500 mL of hexane/ethyl acetate (v/v=1/4) and 400 mL of water, washing the organic layer successively with water. The organic layer was combined and dried with anhydrous MgSO$_4$, and then further purified on a silicagel chromatography column using hexane/ethyl acetate as eluent and distribution after column chromatography. The pure product of 2-butene-*N*-vinylformamide (*n*BuNVF) was obtained as a liquid (23.9 g, 106.2 mmol 43% yield).

Synthesis of 3-methyl-butene-N-vinylformamide (*i*PeNVF)

In a glass flask, NaH (1.35 g, 33.8 mmol) was placed and washed with anhydrous THF (15 mL) twice under nitrogen, and 80 mL of anhydrous DMF was introduced. NVF (2.40 g, 33.8 mmol) was slowly added at 0ºC. After stirring for 4 hr at room temperature, 1-bromo-3-methyl-2-butene (5.0 g, 33.8 mmol) was slowly added by syringe at 0ºC. The

reactor was warmed up to 50°C and stirring continued for 16 hr. Water was introduced

into the reaction mixture to terminate the reaction, and the mixture was extracted into 500

mL of hexane/ethyl acetate (v/v=1/4) and 400 mL of water, washing the organic layer

successively with water. The organic layer was combined and dried with anhydrous

$MgSO_4$, and then further purified on a silicagel chromatography column using

hexane/ethyl acetate as eluent and distribution after column chromatography. The pure

product of 3-methyl-2-butene-*N*-vinylformamide (*i*PeNVF) was obtained as a liquid (3.16

g, 22.3 mmol 68% yield).

Polymerization

A previous report on RAFT polymerization of cyclic *N*-vinylamide derivatives was

used to determine the best selection for the CTA. [25-27] Thirteen polymers were

synthesized according to the literature procedure. [17,18] The typical procedure is here

illustrated for the radical copolymerization of NVF and *n*BuNVF (Table 1, entry 3). Into

a 20 mL glass tank, NVF (0.53 g, 7 mmol), *n*BuNVF (0.38 g, 3 mmol), **CTA 1** (0.11 g,

0.5 mmol), DMSO (5 ml) and AIBN (0.044 g 0.25 mmol) were combined. The reactor

was capped with septa, then N_2 bubbling was carried out for 2 min. The reaction mixture

was heated up to 60 ℃ to start polymerization. After 7 days, it was cooled down to room

temperature, and the reaction mixture was poured into 10 mL of methanol. The polymer

was washed twice by poor solvent of 500 ml diethyl ether and recovered by centrifugation.

The obtained polymer was dried under vacuum at 30 ℃ over 12 hr. Other syntheses used

the same general method. Variations in monomers and monomer ratios conditions for all

synthesized polymers are given in Table 1.

THF hydrate crystal growth test [17]

NaCl (26.28 g), THF (99.9%, 170 g), and distilled water were mixed to give a final

volume of 900 mL. This ratio is a stoichiometrically correct molar composition for

making structure II THF hydrate, 3THF 17H_2O. The test procedure is as follows: (1) 80

mL of the mixture solution is added in a 100 mL glass beaker. (2) The polymer sample is

dissolved in this solution as each concentration; such as, 0.32 g of polymer in 80 mL of

solution gives a 0.4 wt% (4000 ppm) solution of the polymer. (3) The beaker is placed in

a cooling bath preset to a temperature of -0.5℃. (4) The solution is stirred manually with

a spatula every 5 min, without touching the glass beaker, while being cooled for 20 min.

(5) A hollow glass tube with inner diameter 7 mm was filled at the end with ice crystals

kept at -10℃. The ice crystals are used to initiate THF hydrate formation. (6) The glass

tube was placed almost halfway down in the cooled polymer mixture solution after the

solution had been cooled for 20 min. (7) THF hydrate crystals could be grown at the end

of the glass tube for 60 min. (8) After this time, the tube was picked up, the THF hydrate

crystals weighed, and the crystal growth rate in grams per 1 hour determined. The shape

and morphology of the crystals both in the beaker (if any) and on the end of the glass tube

were visually analyzed.
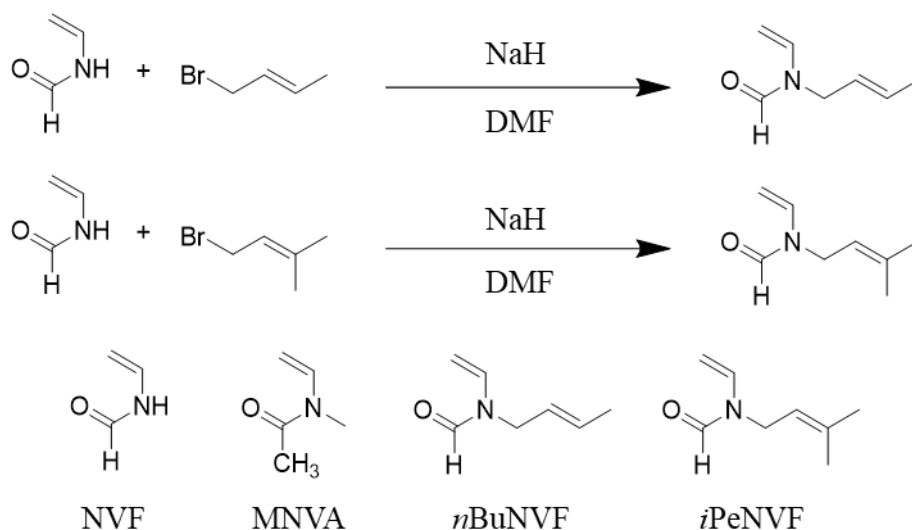
Scheme 1. Synthesis of *N*-vinylamide derivatives bearing the alkenyl groups at the *N*-position and chemical structures of *N*-vinylamide monomers in this study.

Results and discussion

In order to investigate the side chain effect as rigidity of poly(*N*-vinylamide)

derivatives at *N*-position for KHIs, 1-(2-butene)-*N*-vinylformamide (*n*BuNVF) and 1-(3-

methyl-2-butene)-*N*-vinylformamide (*i*PeNVF) were synthesized by the same general

method as our previous research (Scheme 1). [17,18] The side chains of obtained

monomers, *n*BuNVF and *i*PeNVF, are cis-trans mixture. Stereoregularities of the side

chain may have some influence on polymerization reactivity and inhibition ability of THF

hydrate crystal growth. Structural isomers of *n*BuNVF and *i*PeNVF were observed by [1]H

NMR analysis. Peaks are derived not only from the alkenyl groups at the side chain but

also the formamide group; therefore, a lot of peaks appeared in the ^{1}H NMR and ^{13}C NMR

spectra of *n*BuNVF and *i*PeNVF (Figure S1, S2 and Figure 1).
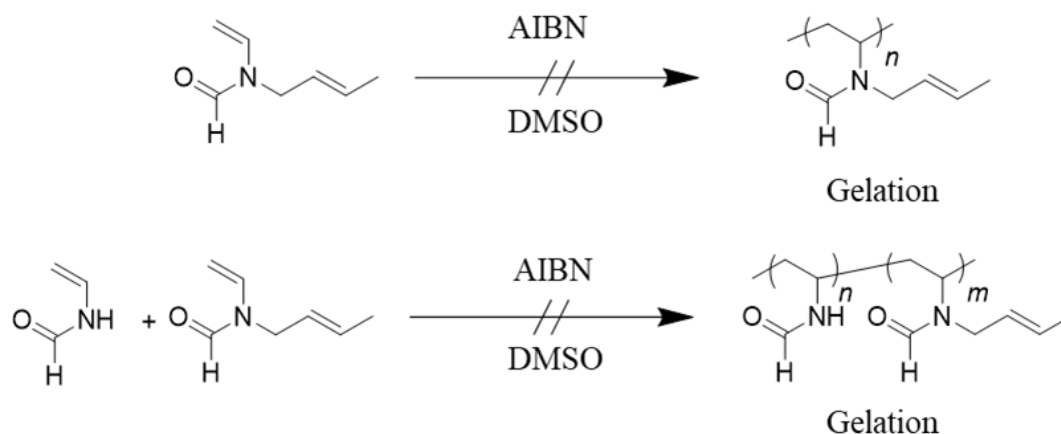
Scheme 2. Synthesis of poly(*N*-vinylamide) derivatives bearing the alkenyl group at the *N*-position by free radical polymerization.

To begin with, we copolymerized *n*BuNVF with NVF by free radical polymerization, because, it is a facile method and easy to make a comparison with previous studies (Scheme 2). However, a gel was formed after the polymerization, which didn't easily dissolve in typically good solvents for poly(*N*-vinylamide) derivatives, such as DMF, DMSO, water, and methanol. Probably, the alkenyl groups at the side chains also reacted via radical species, which could cause cross-linking of the polymer side chains. Therefore, CTAs were used for the polymerization to obtain linear polymers and to avoid gel formation.
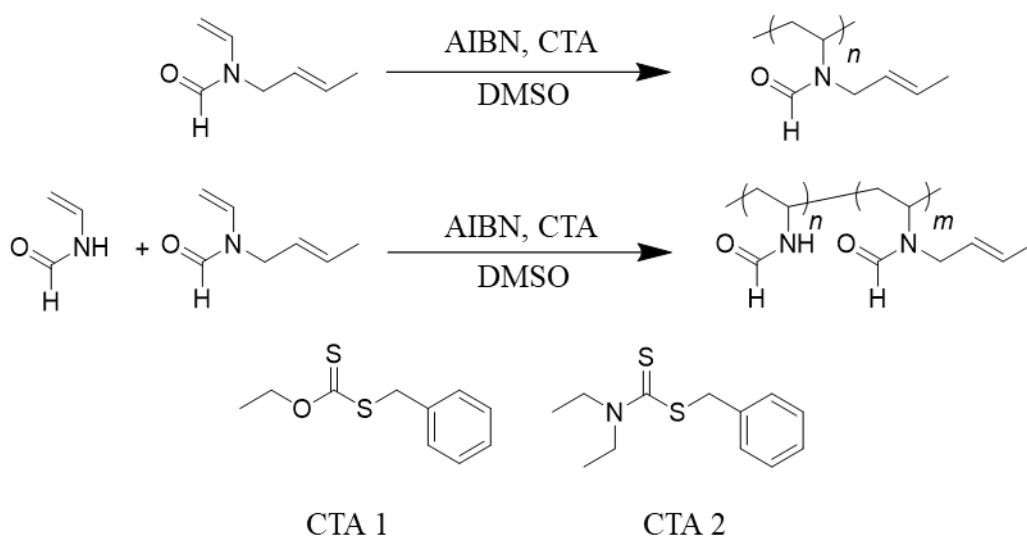
Scheme 3. Synthesis of poly(*N*-vinylamide) derivatives bearing the alkenyl group at the *N*-position by RAFT polymerization and chemical structures of the chain transfer agents in this study.

Scheme 3 shows that syntheses of poly(*N*-vinylamide) derivatives bearing the rigid

alkenyl chain at the *N*-position by RAFT polymerization using two kinds of CTAs. **CTA**

1 and **CTA 2** were selected to conduct the RAFT polymerization because they were

usually used for typically un-conjugated vinyl monomers, vinyl acetate derivatives and

cyclic *N*-vinylamide derivatives, such as a *N*-vinylcarbazole and NVP. Then, the

homopolymers of poly(*N*-vinylamide) derivatives bearing the rigid alkenyl groups were

obtained by RAFT polymerization. These dissolve in methanol and DMSO and they were

purified by re-precipitation by addition of diethyl ether. The obtained polymer was

analyzed by ^{13}C NMR analyses which confirmed that the alkenyl group at the side chain

still remained after polymerization (Figure 1c). The peaks of "a" at around 95 ppm

indicates the vinyl groups of *N*-vinylamide monomers (Figure 1a and 1b), which

disappeared after polymerization (Figure 1c), although the peaks of "b" at around 128

ppm were detected after polymerization (Figure 1c). The peaks of "b" are not only derived

from the vinyl group of *N*-vinylamide monomers but also the alkenyl group at the side

chain. Therefore, it is the alkenyl groups of synthesized polymers that remained after

polymerization. Moreover, the side chains possessed cis-trans isomerism. Thus, the peaks

"b" of *n*BuNVF monomer at around 128 ppm were split (Figure 1b), however, the peaks

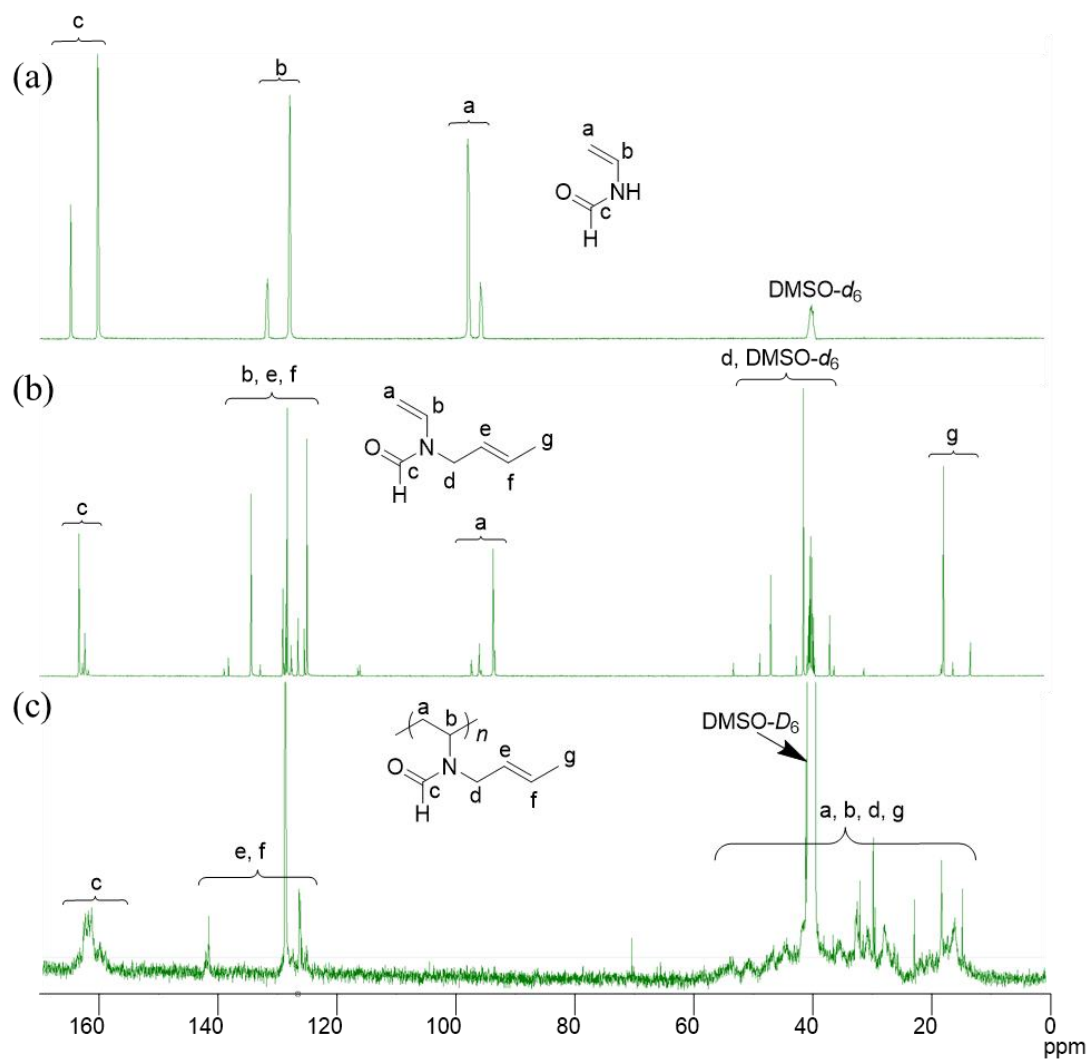"b" of poly(*N*-vinylamide) derivatives bearing the alkenyl group were less split. This

Figure 1. ^{13}C NMR spectrum of NVF (a), nBuNVF (b) and poly(N-vinylamide) derivatives bearing the alkenyl group at the N-position. 400MHz in DMSO-d_6

result may support the hypothesis that the conformation of the side chain of poly(N-vinylamide) derivatives bearing the alkenyl groups are specifically arranged. Following the synthesis of the homopolymers, the copolymers of the poly(N-vinylamide) derivatives were synthesized.

Table 1. Analysis data of poly(*N*-vinylamide) derivatives bearing the alkenyl group at the *N*-position.

Entry	Sample	Monomer 1	Monomer 2	1 : 2	CTA	Yield (%)	$Mn\ (\times 10^3)$	PDI
1			*n*BuNVF	0 : 10	CTA 1	4	1.0	1.3
2			*i*PeNVF	0 : 10	CTA 1	N. D.	N. D.	N. D.
3	Poly(NVF$_7$-*n*BuNVF$_3$)-1.1	NVF	*n*BuNVF	7 : 3	CTA 1	24	1.1	1.8
4	Poly(NVF$_7$-*i*PeNVF$_3$)-1.3	NVF	*i*PeNVF	7 : 3	CTA 1	41	1.3	3.3
5	Poly(NVF$_3$-*n*BuNVF$_7$)-1.1	NVF	*n*BuNVF	3 : 7	CTA 1	33	1.1	1.7
6	Poly(NVF$_5$-*n*BuNVF$_5$)-1.6	NVF	*n*BuNVF	5 : 5	CTA 1	19	1.6	1.5
7	Poly(NVF$_7$-*n*BuNVF$_3$)-2.7	NVF	*n*BuNVF	7 : 3	CTA 1	21	2.7	1.5
8			*n*BuNVF	0 : 10	CTA 2	19	1.0	1.7
9	Poly(NVF$_5$-*n*BuNVF$_5$)-1.3	NVF	*n*BuNVF	5 : 5	CTA 2	56	1.3	2.1
10	Poly(NVF$_7$-*n*BuNVF$_3$)-4.2	NVF	*n*BuNVF	3 : 7	CTA 2	10	4.2	1.4
11	Poly(NVF$_5$-*n*BuNVF$_5$)-5.7	NVF	*n*BuNVF	5 : 5	CTA 2	33	5.7	1.8
12	Poly(NVF$_7$-*n*BuNVF$_3$)-6.3	NVF	*n*BuNVF	7 : 3	CTA 2	70	6.3	2.0
13	Poly(MNVA$_5$-*n*BuNVF$_5$)-1.1	MNVA	*n*BuNVF	5 : 5	CTA 2	38	1.1	1.1

[a]AIBN:CTA:Monomer = 1:2:40; [b]AIBN:CTA:Monomer = 1:2:100; DMSO 60ºC 7days.

Table 1 shows the analytical data of synthesized polymers by RAFT polymerization. The homopolymers of *n*BuNVF were obtained by RAFT polymerization using both CTAs, although their yield and molecular weight were a low value (Table 1, entries 1 and 8). The homopolymer of *i*PeNVF was not obtained and *i*PeNVF possessed the bulky and rigid side chain more than *n*BuNVF (Table 1, entry 2). These results indicate that the effect of steric hindrance at the side chain influences the reactivity of vinyl groups during polymerization. Probably, the bulkiness of the rigid alkenyl groups is more than the alkyl groups. The homopolymer of *n*BuNVF showed poor water solubility due to the high

hydrophobicity. Thus, copolymers of this momomer were synthesized to improve the

solubility in aqueous media. Initially, the molecular weights of copolymers using **CTA 1**

(Table 1, entries 3 to 7) were lower in value compared with copolymers using **CTA 2**

(Table 1, entries 9 to 13). Furthermore, the yields of Poly(NVF$_5$-nBuNVF$_5$)-5.7 and

Poly(NVF$_7$-nBuNVF$_3$)-6.3 were higher in value compared with Poly(NVF$_7$-nBuNVF$_3$)-

4.2, according to the NVF ratio. This implies that **CTA 2** is best applied for N-vinylamide

derivatives compared with **CTA 1**, although it may not be the optimum condition because

PDIs of most copolymers were not close to 1. On the other hand, Poly(MNVA$_5$-

nBuNVF$_5$)-1.1 which shows the low PDI value, 1.1, does not contain NVF units. The

proton of NVF at the amide position was important to make hydrogen bonding and the

polymerization solvent, DMSO, was usually supported to aggregate by the hydrogen

bonding. Therefore, the effect of the proton at the amide position and/or the solvent effect

of DMSO were key points to optimize the choice of CTAs for the achievement of the low

PDI value by RAFT polymerization using N-vinylamide derivatives. In addition, the ratio

of monomer units of copolymers could not be calculated because most of peaks of the ^{1}H

NMR spectra were overlapped. The feed ratios of monomer units are shown in Table 1.

Furthermore, the ratios of NVF or MNVA units of synthesized copolymers were probably

bigger than the feeding monomer ratio because of the effect of steric hindrance at the rigid

side chain. The obtained copolymers were sufficiently hydrophilic and showed good

solubility in aqueous media. Therefore, the inhibition ability of THF hydrate crystal

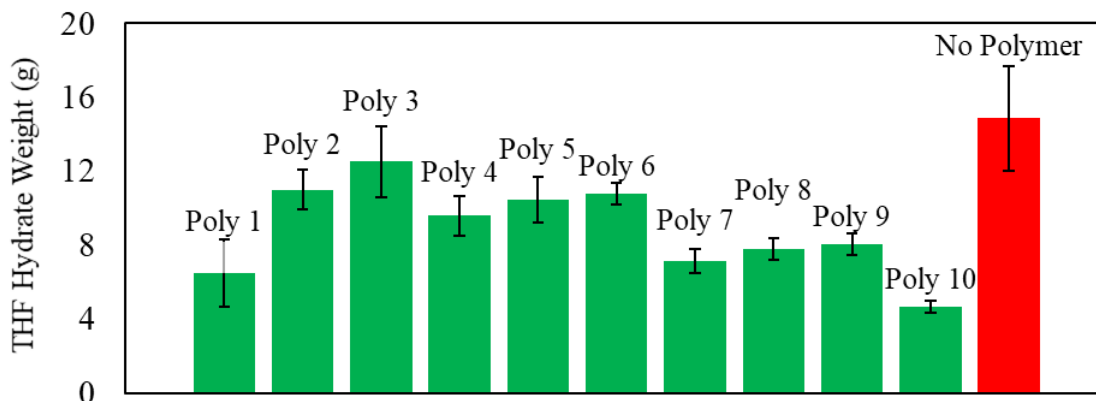growth by these copolymers was able to be evaluated for application as KHI.

Table 2. Inhibition abilities of THF hydrate crystal growth of poly(N-vinylamide) derivatives bearing the alkenyl group at the N-position. (4000 ppm)

Entry	Sample	Abbreviated name for Figure 2	$M_n (\times 10^3)$	PDI	THF hydrate (g)
1	Poly(NVF$_7$-nBuNVF$_3$)-1.1	Poly 1	1.1	1.78	6.47
2	Poly(NVF$_7$-iPeNVF$_3$)-1.3	Poly 2	1.3	3.25	11.01
3	Poly(NVF$_3$-nBuNVF$_7$)-1.1	Poly 3	1.1	1.71	12.51
4	Poly(NVF$_5$-nBuNVF$_5$)-1.6	Poly 4	1.6	1.46	9.59
5	Poly(NVF$_7$-nBuNVF$_3$)-2.7	Poly 5	2.7	1.53	10.47
6	Poly(NVF$_5$-nBuNVF$_5$)-1.3	Poly 6	1.3	2.08	10.79
7	Poly(NVF$_7$-nBuNVF$_3$)-4.2	Poly 7	4.2	1.4	7.15
8	Poly(NVF$_5$-nBuNVF$_5$)-5.7	Poly 8	5.7	1.81	7.77
9	Poly(NVF$_7$-nBuNVF$_3$)-6.3	Poly 9	6.3	1.95	8.05
10	Poly(MNVA$_5$-nBuNVF$_5$)-1.1	Poly 10	1.1	1.07	4.65
11	No Polymer				14.88

Figure 2. Inhibition abilities of THF hydrate crystal growth of poly(*N*-vinylamide) derivatives bearing the alkenyl group at the *N*-position. (4000 ppm)

In this study, we selected the THF hydrate crystal growth approach to evaluate the effect of the new KHI polymers to inhibit the hydrate growth. This method gives a useful parameter of the KHI performance, because, the structure of THF hydrate and typical natural gas hydrate are the same: a structure II clathrate hydrate. [7] This method investigates crystal growth by measurement of THF hydrate weights over a given time period, usually one hour. These experiments were conducted according to previous reports. [19,28-31]

Table 2 and Figure 2 show the inhibition abilities of the THF hydrate crystal growth

of synthesized poly(*N*-vinylamide) derivatives. Homopolymers of poly(*N*-vinylamide) derivatives bearing the alkenyl group showed poor solubility in aqueous media; thus, their inhibition abilities could not be evaluated. Every synthesized copolymer possessed sufficient solubility and some inhibition ability of THF hydrate crystal growth, resulting in the lower weight values of THF hydrate crystal compared to the negative control without polymer.

Compared with those THF hydrate crystal growth inhibition properties of poly(*N*-vinylamide) derivatives bearing the ethylene glycol groups or the alkyl groups, we found generally lower efficiency for the synthesized polymers in this study. For example, one poly(*N*-vinylamide) derivative bearing the alkyl group gives zero growth of THF hydrate crystal under 5000 ppm condition [13], and thus possesses better inhibition ability than synthesized poly(*N*-vinylamide) derivatives bearing the alkenyl group in this study. This indicates the interactions between THF hydrate surfaces and synthesized poly(*N*-vinylamide) derivatives in this study are smaller than for polymers bearing the alkyl group. Poly(*N*-vinylamide) derivatives bearing the alkenyl groups do not show significant cloud point difference to polymers bearing the alkyl group. [17,18] Generally, the hydrophobicity between the alkyl group and the alkenyl group are not so different if chain lengths are the same. This suggests the rigidity and/or the effect of steric hindrance of the

hydrophobic substituents might affect the inhibition of THF hydrate crystal growth.

Poly(NVF$_7$-nBuNVF$_3$)-1.1 showed good THF hydrate crystal growth inhibition ability, with lowest value compared with the initial ratio samples, Poly(NVF$_7$-nBuNVF$_3$)-2.7 and Poly(NVF$_7$-nBuNVF$_3$)-6.3 (Table 1, entries 3, 7 and 11). This may be influenced by the actual composition ratio of copolymers: the ratio of NVF units of copolymers may be higher due to the steric hindrance at the side chain and/or the compatibility between N-vinylamide groups and CTAs during polymerization. This assumption does not conflict with the result of the inhibition ability of Poly(NVF7-iPeNVF3)-1.3 which was lower efficiency compared with above copolymers, such as Poly(NVF7-nBuNVF3)-1.1, Poly(NVF7-nBuNVF3)-2.7 and Poly(NVF7-nBuNVF3)-6.3. (Table 2, entries 1, 2, 5 and 9). The feed ratio of the monomers of Poly(NVF$_7$-nBuNVF$_3$)-1.1 during the polymerization reaction is different from Poly(NVF$_7$-nBuNVF$_3$)-2.7 and Poly(NVF$_7$-nBuNVF$_3$)-6.3 (Table 1, entries 3, 7 and 11). The ratio of the alkenyl units may also be different, which may influence the inhibition abilities of THF hydrate crystal growth. Furthermore, the average weights of THF hydrate formed using Poly(NVF$_7$-nBuNVF$_3$)-4.2, Poly(NVF$_5$-nBuNVF$_5$)-5.7 and Poly(NVF$_7$-nBuNVF$_3$)-6.3 were lower than Poly(NVF$_7$-iPeNVF$_3$)-1.3, Poly(NVF$_3$-nBuNVF$_7$)-1.1, Poly(NVF$_5$-nBuNVF$_5$)-1.6, Poly(NVF$_7$-nBuNVF$_3$)-2.7 and Poly(NVF$_5$-nBuNVF$_5$)-1.3. This suggests that the

polfmer molecular weight effect influenced the inhibition abilities because higher

molecular weight polymers, above 4000 g/mol, tend to show good inhibition abilities

compared with lower molecular weight polymers, around 1000 g/mol.

Above all, Poly(MNVA$_5$-nBuNVF$_5$)-1.1 shows the best performance in this study

and its value is significantly lower than other copolymers (Table 2, entry 10).[16,17]

Monomer units of Poly(MNVA$_5$-nBuNVF$_5$)-1.1 were probably made up of a majority of

MNVA units because the effect of steric hindrance at the rigid side chain was greater than

the methyl group at the side chain and the PDI value was very near 1. This is different

from other copolymers that contained NVF units. Thus, in order to achieve the

development of high efficiency KHIs using the rigid substituents at the *N*-position of

poly(*N*-vinylamide) derivatives, introducing MNVA units as a comonomer was more

effective.

Conclusion

We have designed and synthesized poly(*N*-vinylamide) derivatives, bearing the rigid

alkene groups in order to investigate the side chain effect with regard to KHI properties

on THF hydrate crystal growth. This is the first time small alkenyl groups have been

introduced into KHI polymers. The monomers of *N*-vinylamide derivatives bearing the

alkenyl groups, nBuNVF and iPeNVF, were synthesized and polymerized by RAFT polymerization using two CTAs in order to obtain the linear polymers. The molecular weights of synthesized polymers were low in value compared to previous poly(N-vinylamide) derivatives bearing alkyl modified side chains. Moreover, the PDI value of synthesized polymers were not so low values in spite of using CTA during polymerization. This indicated that the CTAs, **CTA 1** and **CTA 2**, are not applied so much for non-cyclic N-vinylamide monomers probably due to the difference of radical reactivity between cyclic and non-cyclic N-vinylamide derivatives. The synthesized copolymers evaluated for inhibition ability of THF hydrate crystal growth. In comparison with previous poly(N-vinylamide) derivatives bearing the more flexible alkyl groups, poly(N-vinylamide) derivatives bearing the alkenyl group showed lower efficiencies for inhibition ability of THF hydrate crystal growth. Thus, it was surmised that the interactions between hydrate surfaces and poly(N-vinylamide) derivatives bearing the alkenyl group are smaller than those bearing alkyl groups. The rigidity and/or the effect of steric hindrance are probably key factors. Higher molecular weight polymers, Poly(NVF$_7$-nBuNVF$_3$)-4.2, Poly(NVF$_5$-nBuNVF$_5$)-5.7 and Poly(NVF$_7$-nBuNVF$_3$)-6.3, showed better inhibition of THF hydrate crystal growth compared to lower molecular weight polymers, Poly(NVF$_7$-iPeNVF$_3$)-1.3, Poly(NVF$_3$-nBuNVF$_7$)-1.1, Poly(NVF$_5$-nBuNVF$_5$)-1.6, Poly(NVF$_7$-

nBuNVF$_3$)-2.7 and Poly(NVF$_5$-nBuNVF$_5$)-1.3. This is in accord with previous THF hydrate crystal growth studies on other polymer classes.

Acknowledgement

References

(1)   M. A. Kelland, History of the Development of Low Dosage Hydrate Inhibitors. Energy Fuels 20 (2006) 825-847. DOI: 10.1021/ef050427x

(2) M. A. Usman, A. O Olantunde, T. A. Adeosun, L. Egwuenu, Hydrate Management Strategies in Subsea Oil and Gas Flowlines at Shut- in Condition, Petro. Coal 54 (2012) 191-202.

(3) E. D. Sloan A changing hydrate paradigm-from apprehension to avoidance to risk management. Fluid Phase Equilib. 228-229 (2005) 67-74. DOI: doi:10.1016/j.fluid.2004.08.009

(4) J. L. Creek, Efficient Hydrate Plug Prevention. Energy Fuels 26 (2012) 4112-4116. DOI: dx.doi.org/10.1021/ef300280e

(5) B. J. Anderson, J. W. Tester, G. P. Borghi, B. L. Trout Properties of Inhibitors of

Methane Hydrate Formation via Molecular Dynamics Simulations J. Am. Chem. Sci. 127

(2005) 17852-17862. DOI: 10.1021/ja0554965

(6) H. Qin, C. Sun, Z. Sun, B. Liu, G. Chen Relationship between the interfacial tension

and inhibition performance of hydrate inhibitors. Chem. Eng. Sci. 148 (2016) 182-189.

DOI: https://doi.org/10.1016/j.ces.2016.04

(7) W. Ke, M. A. Kelland Kinetic Hydrate Inhibitor Studies for Gas Hydrate Systems: A

Review of Experimental Equipment and Test Methods. Energy Fuels 30 (2016) 10015-

10028. DOI: 10.1021/acs.energyfuels.6b02739

(8) T. Yamasaki, M. Matsumoto, H. Tanaka Adsorption Mechanism of Inhibitor and Guest

Molecules on the Surface of Gas Hydrates J. Am. Chem. Sci. 137 (2015) 12079-12085.

DOI:10.1021/jacs.5b07417

(9) J. Sa, G. Kwak, K. Han, D. Ahn, K. Lee Gas hydrate inhibition by perturbation of

liquid water structure Sci. Rep. 5 (2015) 11526 (9p). DOI: 10.1038/srep11526

(10) F. T. Reyes, M. A. Kelland, N. Kumar, L. Jia First Investigation of the Kinetic

Hydrate Inhibition of a Series of Poly(β-peptoid)s on Structure II Gas Hydrate, Including

the Comparison of Block and Random Copolymers Energy Fuels 29 (2015) 695-701.

DOI: 10.1021/ef502539u

(11) C. D. Magnusson, M. A. Kelland Nonpolymeric Kinetic Hydrate Inhibitors: Alkylated Ethyleneamine Oxides Energy Fuels 29 (2015) 6347-6354. DOI:10.1021/acs.energyfuels.5b01592

(12) H. Qin, Z. Sun, X. Wang, J. Yang, C. Sun, B. Liu, L. Yang, G. Chen Synthesis and Evaluation of Two New Kinetic Hydrate Inhibitors Energy Fuels 29 (2015) 7135-7141. DOI:10.1021/acs.energyfuels.5b01916

(13) H. Ajiro, Y. Takemoto, M. Akashi, P. C. Chua, M. A. Kelland, Study of the Kinetic Hydrate Inhibitor Performance of a Series of Poly(N-alkyl-N-vinylacetamide)s. Energy Fuels 24 (2010) 6400-6410. DOI: 10.1021/ef101107r

(14) P. C. Chua, M. A. Kelland, H. Ajiro, F. Sugihara, M. Akashi, Poly(vinylalkanamide)s as Kinetic Hydrate Inhibitors: Comparison of Poly(N‑vinylisobutyramide) with Poly(N‑isopropylacrylamide). Energy Fuels 27 (2013) 183-188. DOI: dx.doi.org/10.1021/ef301703w

(15) M. A. Kelland, E. Abrahamsen, H. Ajiro, M. Akashi, Kinetic Hydrate Inhibition with N‑Alkyl‑N‑vinylformamide Polymers: Comparison of Polymers to n‑Propyl and Isopropyl Groups. Energy Fuels 29 (2015) 4941-4946. DOI: 10.1021/acs.energyfuels.5b01251

(16) Q. Zhang, R. Kawatani, H. Ajiro, M. A. Kelland, Optimizing the Kinetic Hydrate

Inhibition Performance of N-Alkyl-N-vinylamide Copolymers. Energy Fuels 32 (2018) 4925-4931. DOI: 10.1021/acs.energyfuels.8b00251

(17) R. Kawatani, Y. Kawata, S. Yusa, M. A. Kelland, H. Ajiro, Synthesis of Thermosensitive Poly(*N*-vinylamide) Derivatives Bearing Oligo Ethylene Glycol Chain for Kinetic Hydrate inhibitor. Macromolecules 51 (2018) 7845-7852. DOI: 10.1021/acs.macromol.8b01573

2015, 29 (8), 4941−4946.

(18) R. Kawatani, K. Kan, M. A. Kelland, M. Akashi, H. Ajiro, Remarkable Effect on Thermosensitive Behavior Regarding Alkylation at the Amide Position of Poly(*N*-vinylamide)s. Chem. Lett. 45 (2016) 45 589−591. DOI:10.1246/cl.160145

(19) L. Del Villano, R. Kommedal, R. Hoogenboom, M. W. M. Fijten, M. A. Kelland, A Study of the Kinetic Hydrate Inhibitor Performance and Seawater Biodegradability of a Series of Poly(2- alkyl-2-oxazoline)s. Energy Fuels 23 (2009) 3665-3673. DOI: 10.1021/ef900172f

(20) J. D. Lee, P. Englezos, Enhancement of the performance of gas hydrate kinetic inhibitors with polyethylene oxide. Chem. Eng. Sci. 60 (2005) 5323-5330. DOI: https://doi.org/10.1016/j.ces.2005.05.023

(21) M. A. Kelland, T. M. Svartås, L. D. Andersen, Gas hydrate anti-agglomerant

properties of polypropoxylates and some other demulsifiers. J. Petr. Sci. Eng. 64 (2009) 1-10. DOI: https://doi.org/10.1016/j.petrol.2008.12.001

(22) M. R. Talaghat, Intensification of the performance of kinetic inhibitors in the presence of polyethylene oxide and polypropylene oxide for simple gas hydrate formation in a flow mini-loop apparatus. Fluid Phase Eq. 289 (2010) 129-134. DOI: https://doi.org/10.1016/j.fluid.2009.11.025

(23) A. K. Norland, M. A. Kelland, Crystal Growth Inhibition of Tetrahydrofuran Hydrate with Bis- and Polyquaternary Ammonium Salts. Chem. Eng. Sci. 67 (2012) 483-491. DOI: https://doi.org/10.1016/j.ces.2011.11.003

(24) C. Ladaviere, N. Dorr, J. P. Claverie, Controlled Radical Polymerization of Acrylic Acid in Protic Media Macromolecules 31 (2001) 5370-5372. DOI: 10.1021/ma010358v

(25) H. Mori, H. Ookuma, S. Nakano, T. Endo Xanthate-Mediated Controlled Radical Polymerization of *N*-Vinylcarbazole Macromol. Chem. Phys. 207 (2006) 1005-1017. DOI: 10.1002/macp.200600070

(26) Y. Maki, H. Mori, T. Endo Controlled RAFT Polymerization of *N*-Vinylphthalimide and its Hydrazinolysis to Poly(vinyl amine) Macromol. Chem. Phys. 208 (2007) 2589-2599. DOI: 10.1002/macp.200700330

(27) Y. Maki, H. Mori, T. Endo Synthesis of Amphiphilic and Double-Hydrophilic Block

Copolymers Containing Poly(vinyl amine) Segments by RAFT Polymerization of *N*-Vinylphthalimide Macromol. Chem. Phys. 211 (2010) 45-56. DOI: 10.1002/macp.200900332

(28) T. Y. Makogon, R. Larsen, C. A. Knight, E. D. J. Sloan, Melt growth of tetrahydrofuran clathrate hydrate and its inhibition: method and first results. J. Cryst. Growth 179 (1997) 258-262. DOI: https://doi.org/10.1016/S0022-0248(97)00118-8

(29) R. Larsen, C. A. Knight, E. D. Sloan, Clathrate hydrate growth and inhibition. Fluid Phase Equilib. 150-151 (1998) 353-360. DOI: 10.1016/S0378-3812(98)00335-5

(30) M. A. Kelland, L. Del Villano, Tetrahydrofuran hydrate crystal growth inhibition by hyperbranched poly(ester amide)s. Chem. Eng. Sci. 64 (2009) 3197-3200. DOI: 10.1016/j.ces.2009.03.050

(31) P. C. Chua, M. A. Kelland, Tetra(iso-hexyl)ammonium Bromide-The Most Powerful Quaternary Ammonium-Based Tetrahydrofuran Crystal Growth Inhibitor and Synergist with Polyvinylcaprolactam Kinetic Gas Hydrate Inhibitor. Energy Fuels 26 (2012) 1160-1168. DOI: dx.doi.org/10.1021/ef201849t

THF hydrate was grown

THF, Water, NaCl and **polymer** solution

THF Hydrate
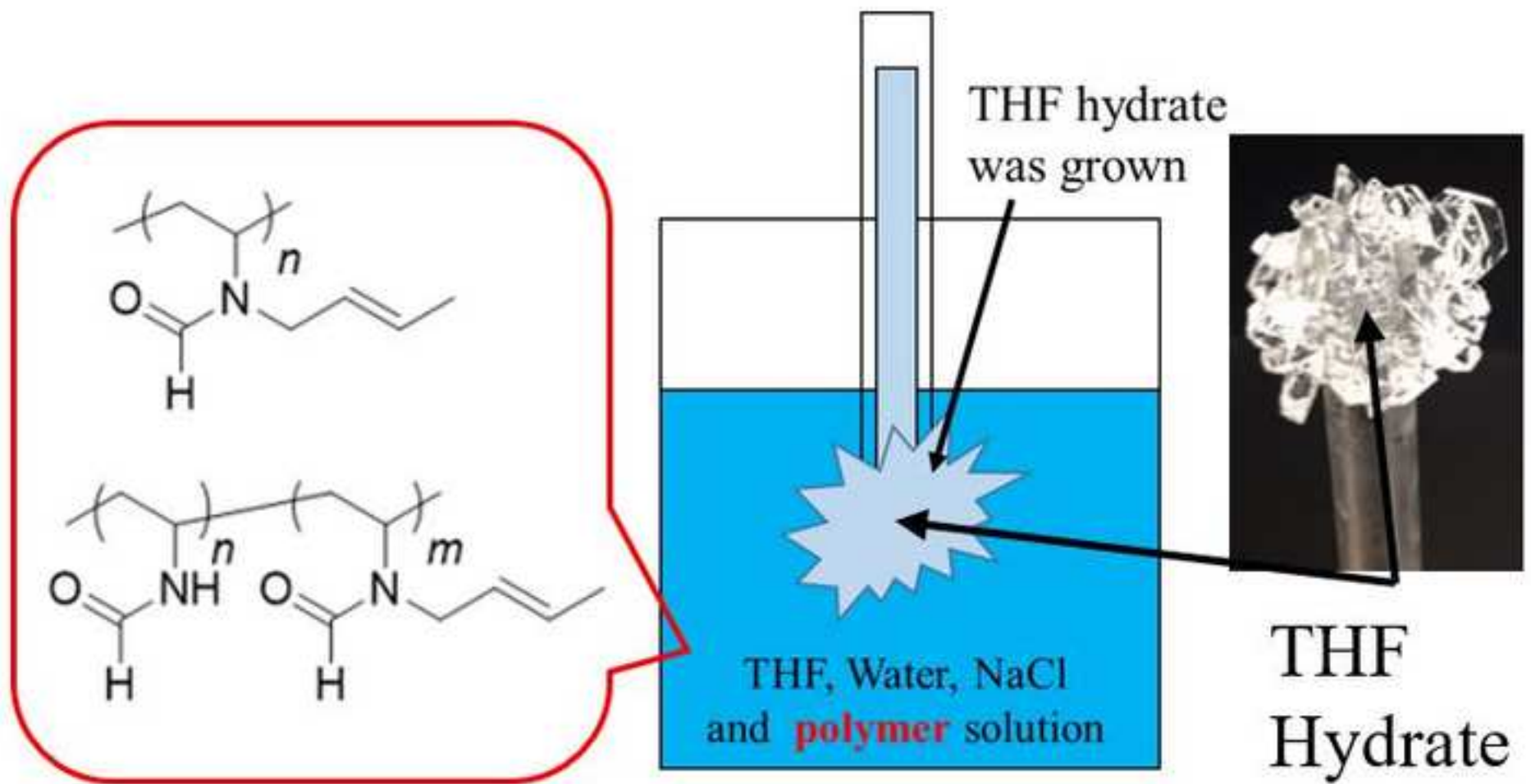
Supporting Information for

Design of the Rigid Side Chain for Poly(*N*-vinylamide) Derivatives Bearing Alkene Group at N-Position and Evaluation of Tetrahydrofuran Hydrate Crystal Growth Inhibition

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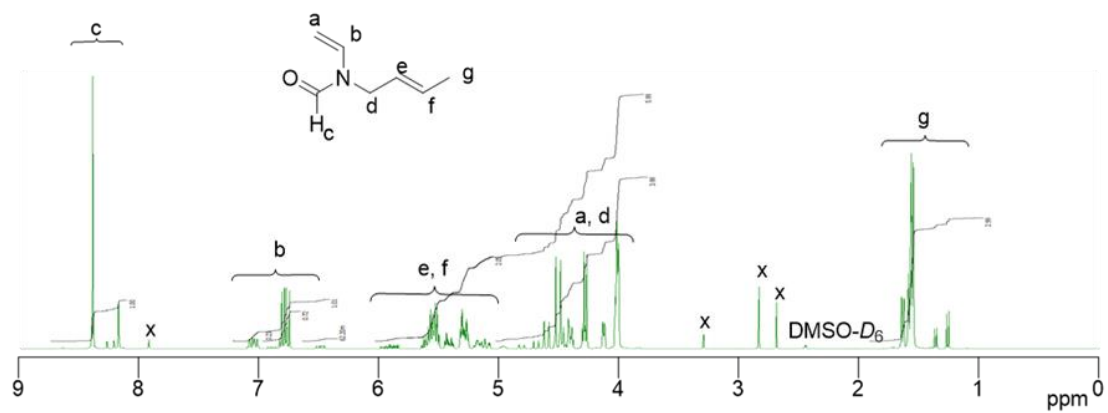
E-mail: ajiro@ms.naist.jp

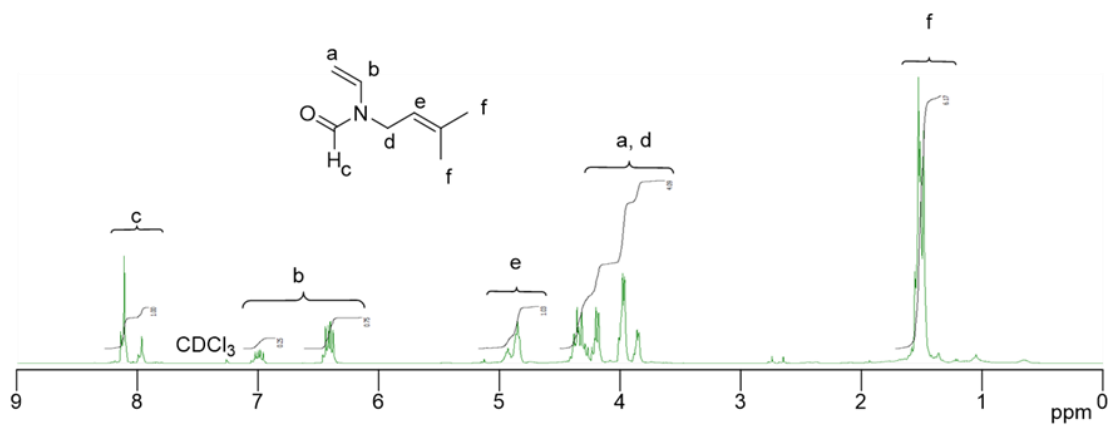Figure S1. ^{1}H NMR spectrum of nBuNVF. 400MHz in DMSO-d_6

Figure S2. ^{1}H NMR spectrum of iPeNVF. 400MHz in CDCl$_3$

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