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3 **Design of The Rigid Side Chain for Poly(*N*-vinylamide) Derivatives Bearing The**
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6 **Alkenyl Group and Evaluation of The Inhibition Ability of Tetrahydrofuran**
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9 **Hydrate Crystal Growth**
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45 **Key words**
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48 Kinetic Hydrate Inhibitor (KHI), Poly(*N*-vinylamide) Derivatives, THF Hydrate Crystal
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1
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3 **Abstract**
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6 Kinetic hydrate inhibitors (KHIs) are water-soluble polymers that are used to
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8 prevent gas hydrate formation in flow lines during upstream oil and gas production. All
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10 commercial polymers have pendant hydrophobic moieties with saturated carbon-carbon
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12 bonds. In our previous studies, poly(*N*-vinylamide) derivatives bearing the alkyl groups
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14 and the ethylene glycol groups were synthesized and investigated as KHIs. Compared
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16 with our previous studies, we have now synthesized poly(*N*-vinylamide) derivatives in
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18 which the alkenyl group has been introduced at the *N*-position to improve the rigidity and
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20 steric hindrance of the side chain. The KHI performances of synthesized polymers were
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22 evaluated by the method of THF hydrate crystal growth. The inhibition ability of THF
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24 hydrate crystal growth was dependent on the molecular weight of synthesized polymers.
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26 Higher molecular weight polymers, above 4000 g/mol, tend to show higher inhibition
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28 efficiencies compared with lower molecular weight polymers, around 1000 g/mol.
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30 However, the KHI performance of poly(*N*-vinylamide) derivatives bearing the alkenyl
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32 groups was generally lower than the polymers of the previous studies. This indicates that
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34 the side chain rigidity and/or steric hindrance do not significantly influence the KHI
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36 performance.
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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

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3 sub-critical particle or crystal growth inhibition by the action of the inhibitor on or near
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6 the hydrate surface. [5,6] KHIs are amphiphilic within the monomer units, and the most
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9 effective polymers usually included the hydrophilic amide group close to a small
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12 hydrophobic group. [1,7]
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16 Among the several amphiphilic polymers with the amide groups, well-known KHI
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19 polymers include poly(*N*-vinylcaprolactam)s (PNVC) and poly(*N*-vinylpyrrolidone)
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22 (PNVP)s, poly(*N*-isopropylmethacrylamide) and copolymers thereof. These polyamides
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25 have already been used commercially in KHI formulations but they have a limited
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28 application range, depending in the subcooling, pressure, residence time in the pipeline,
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31 the presence of other production chemicals, the salinity, the hydrocarbon composition and
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34 many other factors. Therefore, there is a need for improved KHI polymers to meet more
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37 extreme conditions. [8-12]
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42 The study of this study was to design poly(*N*-vinylamide) derivatives in order to
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45 develop high performance KHIs. Various chemical structures and amphiphilic properties
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48 with poly(*N*-vinylamide) derivatives have been investigated in our previous researches.
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51 [13-17] These earlier studies have revealed the side chain effect of poly(*N*-substituted-*N*-
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54 vinylamide) derivatives for the KHI performance. The monomers of *N*-substituted-*N*-
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57 vinylamide derivatives were synthesized using two *N*-vinylamide derivatives, *N*-
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3 vinylformamide (NVF) and *N*-vinylacetamide (NVA), which can control the
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6 hydrophobicity and the effect of steric hindrance during polymerization. [13,15,18] For
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9 example, various alkyl groups were introduced to NVF and NVA, such as *n*-propyl, *i*-
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12 propyl, *n*-butyl, *i*-butyl, and others. These polymers showed good KHI performances, as
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15 good as commercially available KHIs such as those based on *N*-vinyl caprolactam
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18 copolymers. [13,15] We suggested that the performance was influenced by the size of the
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21 side chain alkyl groups. One of the proposed KHI mechanisms suggests that the small
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24 hydrophobic alkyl groups fit into the holes on the gas hydrate surface. [19].
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29 Other examples of the side-chain effect of poly(*N*-substituted-*N*-vinylamide)
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31 derivatives containing oligo ethylene glycol groups have also been reported in previous
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34 research. [17] This class was inspired by the knowledge that polyethylene glycols (PEG)
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37 are synergists for PNVC as a KHI, although PEGs are poor KHIs by themselves. [20,21]
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41 Polymers similar to PEGs, poly(ethylene oxide) (PEO) and polypropylene oxide (PPO),
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44 were investigated in blends for KHIs but these polymers were also poor KHIs. [22] The
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47 monomers of *N*-vinylamide derivatives bearing ethylene glycol groups containing the
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50 methoxy or ethoxy group at the chain end of the side chain were synthesized and
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53 polymerized. These polymers showed remarkable behavior that only poly(*N*-vinylamide)
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56 derivatives bearing ethoxy groups possess a cloud point. Further, homopolymers showed
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3 good KHI performances compared with copolymers, when evaluated by the method of
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6 THF hydrate crystal growth. [17] However, their KHI performances were generally less
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9 than poly(*N*-vinylamide) derivatives bearing the alkyl groups. [13,17] These previous
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12 studies indicate that the chemical structures of poly(*N*-vinylamide) derivatives at the side
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15 chain are important for expressing good KHI performance. Small quaternary ammonium
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18 salts, particularly with butyl or pentyl groups, also possess effective inhibition ability of
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21 THF hydrate crystal growth. [23] These hydrophobic alkyl groups are probably more
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24 expanded in aqueous media compared due to the cation charge. This would lead to local
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27 entropy loss when interacting with hydrate particles. This result led us to introduce more
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30 rigid unsaturated aliphatic hydrophobic substituents in order to try to improve the
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33 inhibition ability of crystal growth.
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38 In this study, we synthesized poly(*N*-vinylamide) derivatives bearing the rigid
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41 alkenyl group at the *N*-position in order to investigate the side chain effect on KHI
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44 performance. The alkenyl groups which are more rigid hydrocarbyl chains compared with
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47 the alkyl groups, cannot rotate like C-C single bonds. Firstly, *N*-vinylamide derivatives
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50 bearing the alkenyl groups at the *N*-position were synthesized and polymerized by
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53 reversible addition fragmentation chain transfer (RAFT) polymerization using two charge
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56 transfer agents (CTAs) to obtain the linear polymer. Following this, the KHI performances
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3 of synthesized poly(*N*-vinylamide) derivatives bearing the alkenyl group were evaluated
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6 by the method of THF hydrate crystal growth. We also discuss the side chain effect of
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9 alkenyl groups at the *N*-position on KHI performance using the results of THF hydrate
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12 crystal growth tests in this study. [13,17]
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19 **Experimental**

20 ***Materials.***

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23 *N*-vinylformamide (NVF), 1-bromo-2-butene, 1-bromo ethyl ether, 3-methyl-2-
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25 butenyl bromide, ethylxanthic acid potassium salt and benzyl bromide,
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27 diethyldithiocarbamic acid benzyl ester were purchased from Tokyo Chemical Industry
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29 Co. Ltd. Methyl-*N*-vinylacetamide (MNVA) was purchased from Sigma-Aldrich Japan.
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32 Sodium hydride (NaH) 60% in oil, magnesium sulfate (MgSO₄), dimethyl sulfoxide
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34 (DMSO) and *N,N*-dimethylformamide (DMF) were purchased from Nacalai Tesque Inc.
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37 Azobisisobutyronitrile (AIBN), sodium chloride (NaCl) and ethyl acetate were purchased
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39 from Wako Pure Chemical Industries. Hexane, ethanol, tetrahydrofuran (THF), methanol
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42 and diethyl ether were purchased from AZBIO Corp.
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57 ***Apparatus***

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3 ¹H and ¹³C NMR spectra were measured by a JEOL JNM-GMX400 system. The
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6 number-average molecular weights and their distribution were measured by size
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9 exclusion chromatography (SEC). ChromNAV system (Shimadzu Corporation, Japan)
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12 using AS-2055 and RI-2031 was employed with polystyrene standards at room
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15 temperature. The column (TSKgel α -M) was used, and DMF (1 mg/mL) was used as an
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18 eluent at 0.6 mL/min. Low temperature incubation was performed using FMU-263I
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22 (Fukushima Industries Corp. Japan).
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25 ***Synthesis of S-benzyl-O-ethyl dithiocarbonate (CTA 1)***

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28 The *S*-Benzyl-*O*-ethyl dithiocarbonate (**CTA 1**) was synthesized according to the
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31 literature procedure. [24] Potassium *O*-ethyl dithiocarbonate (1.6 g, 10.0 mmol) was
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34 dissolved in ethanol (20 ml) at 50 °C. Then, benzyl bromide (1.71 g, 10 mmol) was added
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37 at this temperature. A colorless precipitate was observed after some minutes then
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40 temperature was increased to 70 °C and the mixture was stirred at this temperature for 5
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43 hours. Water (80 ml) was added and the product was extracted with ether (100 ml). The
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46 combined organic extracts were dried over MgSO₄ and filtered. Removal of the solvent
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49 afforded a yellow oil (yield 59%, 1.24 g, 5.9 mmol).
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57 ***Synthesis of 2-butene-N-vinylformamide (nBuNVF)***

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3 In a glass flask, NaH (10.3 g, 258 mmol) was placed and washed with anhydrous
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6 THF (15 mL) twice under nitrogen, and 80 mL of anhydrous DMF was introduced. NVF
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9 (18.4 g, 258 mmol) was slowly added at 0°C. After stirring for 4 h at room temperature,
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12 1-bromo-2-butene (33.2 g, 258 mmol) was slowly added by syringe at 0°C. The reactor
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15 was warmed up to 50°C and stirring continued for 16 hr. Water was introduced into the
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18 reaction mixture to terminate the reaction, and the mixture was extracted into 500 mL of
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21 hexane/ethyl acetate (v/v=1/4) and 400 mL of water, washing the organic layer
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24 successively with water. The organic layer was combined and dried with anhydrous
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27 MgSO₄, and then further purified on a silicagel chromatography column using
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30 hexane/ethyl acetate as eluent and distribution after column chromatography. The pure
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33 product of 2-butene-*N*-vinylformamide (*n*BuNVF) was obtained as a liquid (23.9 g, 106.2
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36 mmol 43% yield).
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44 ***Synthesis of 3-methyl-butene-N-vinylformamide (iPeNVF)***

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47 In a glass flask, NaH (1.35 g, 33.8 mmol) was placed and washed with anhydrous
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50 THF (15 mL) twice under nitrogen, and 80 mL of anhydrous DMF was introduced. NVF
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53 (2.40 g, 33.8 mmol) was slowly added at 0°C. After stirring for 4 hr at room temperature,
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56 1-bromo-3-methyl-2-butene (5.0 g, 33.8 mmol) was slowly added by syringe at 0°C. The
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3 reactor was warmed up to 50°C and stirring continued for 16 hr. Water was introduced
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6 into the reaction mixture to terminate the reaction, and the mixture was extracted into 500
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9 mL of hexane/ethyl acetate (v/v=1/4) and 400 mL of water, washing the organic layer
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12 successively with water. The organic layer was combined and dried with anhydrous
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15 MgSO₄, and then further purified on a silicagel chromatography column using
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18 hexane/ethyl acetate as eluent and distribution after column chromatography. The pure
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21 product of 3-methyl-2-butene-*N*-vinylformamide (*i*PeNVF) was obtained as a liquid (3.16
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24 g, 22.3 mmol 68% yield).
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31 ***Polymerization***

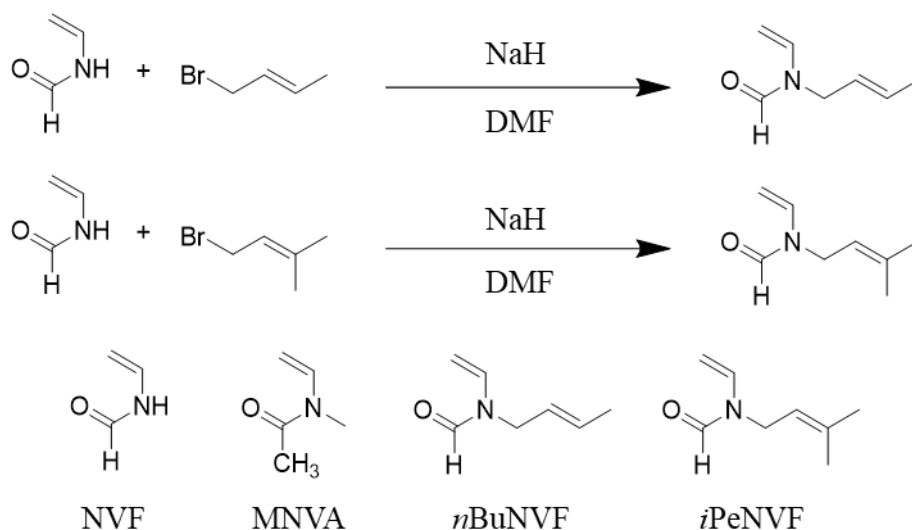
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35 A previous report on RAFT polymerization of cyclic *N*-vinylamide derivatives was
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38 used to determine the best selection for the CTA. [25-27] Thirteen polymers were
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41 synthesized according to the literature procedure. [17,18] The typical procedure is here
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44 illustrated for the radical copolymerization of NVF and *n*BuNVF (Table 1, entry 3). Into
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47 a 20 mL glass tank, NVF (0.53 g, 7 mmol), *n*BuNVF (0.38 g, 3 mmol), **CTA 1** (0.11 g,
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50 0.5 mmol), DMSO (5 ml) and AIBN (0.044 g 0.25 mmol) were combined. The reactor
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53 was capped with septa, then N₂ bubbling was carried out for 2 min. The reaction mixture
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56 was heated up to 60 °C to start polymerization. After 7 days, it was cooled down to room
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3 temperature, and the reaction mixture was poured into 10 mL of methanol. The polymer
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6 was washed twice by poor solvent of 500 ml diethyl ether and recovered by centrifugation.
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9 The obtained polymer was dried under vacuum at 30 °C over 12 hr. Other syntheses used
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12 the same general method. Variations in monomers and monomer ratios conditions for all
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15 synthesized polymers are given in Table 1.
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22 ***THF hydrate crystal growth test*** [17] 23 24

25 NaCl (26.28 g), THF (99.9%, 170 g), and distilled water were mixed to give a final
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28 volume of 900 mL. This ratio is a stoichiometrically correct molar composition for
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31 making structure II THF hydrate, 3THF 17H₂O. The test procedure is as follows: (1) 80
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34 mL of the mixture solution is added in a 100 mL glass beaker. (2) The polymer sample is
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37 dissolved in this solution as each concentration; such as, 0.32 g of polymer in 80 mL of
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40 solution gives a 0.4 wt% (4000 ppm) solution of the polymer. (3) The beaker is placed in
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43 a cooling bath preset to a temperature of -0.5°C. (4) The solution is stirred manually with
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46 a spatula every 5 min, without touching the glass beaker, while being cooled for 20 min.
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51 (5) A hollow glass tube with inner diameter 7 mm was filled at the end with ice crystals
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54 kept at -10°C. The ice crystals are used to initiate THF hydrate formation. (6) The glass
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57 tube was placed almost halfway down in the cooled polymer mixture solution after the
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3 solution had been cooled for 20 min. (7) THF hydrate crystals could be grown at the end
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6 of the glass tube for 60 min. (8) After this time, the tube was picked up, the THF hydrate
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9 crystals weighed, and the crystal growth rate in grams per 1 hour determined. The shape
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12 and morphology of the crystals both in the beaker (if any) and on the end of the glass tube
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16 were visually analyzed.



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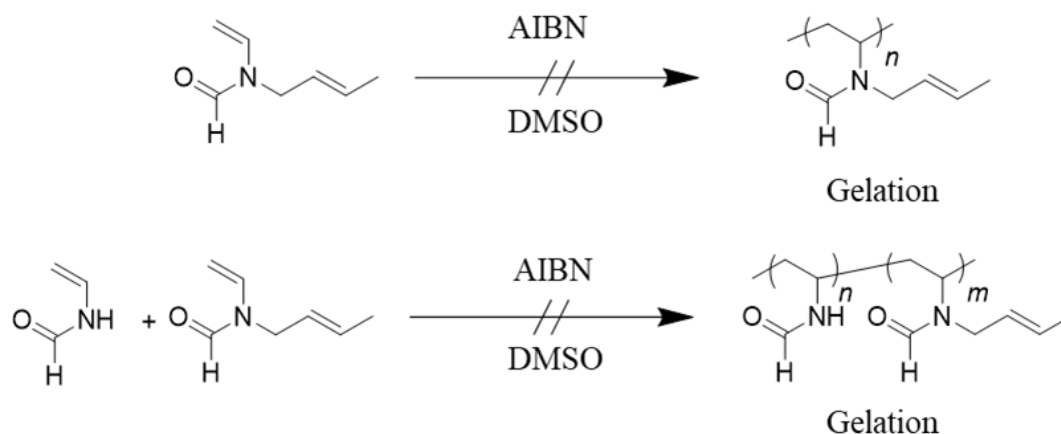
Scheme 1. Synthesis of *N*-vinylamide derivatives bearing the alkenyl groups at the *N*-position and chemical structures of *N*-vinylamide monomers in this study.

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Results and discussion

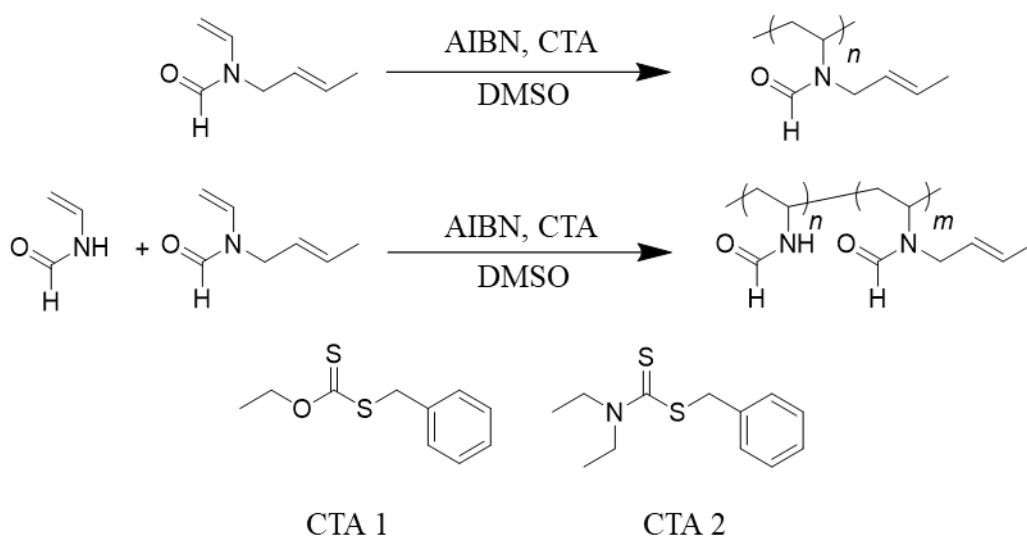
In order to investigate the side chain effect as rigidity of poly(*N*-vinylamide)

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3 derivatives at *N*-position for KHIs, 1-(2-butene)-*N*-vinylformamide (*n*BuNVF) and 1-(3-
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6 methyl-2-butene)-*N*-vinylformamide (*i*PeNVF) were synthesized by the same general
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9 method as our previous research (Scheme 1). [17,18] The side chains of obtained
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12 monomers, *n*BuNVF and *i*PeNVF, are cis-trans mixture. Stereoregularities of the side
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15 chain may have some influence on polymerization reactivity and inhibition ability of THF
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18 hydrate crystal growth. Structural isomers of *n*BuNVF and *i*PeNVF were observed by ¹H
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21 NMR analysis. Peaks are derived not only from the alkenyl groups at the side chain but
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24 also the formamide group; therefore, a lot of peaks appeared in the ¹H NMR and ¹³C NMR
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27 spectra of *n*BuNVF and *i*PeNVF (Figure S1, S2 and Figure 1).
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Scheme 2. Synthesis of poly(*N*-vinylamide) derivatives bearing the alkenyl group at the *N*-position by free radical polymerization.

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3 To begin with, we copolymerized *n*BuNVF with NVF by free radical
4 polymerization, because, it is a facile method and easy to make a comparison with
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6 polymerization, because, it is a facile method and easy to make a comparison with
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8 previous studies (Scheme 2). However, a gel was formed after the polymerization, which
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10 didn't easily dissolve in typically good solvents for poly(*N*-vinylamide) derivatives, such
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12 as DMF, DMSO, water, and methanol. Probably, the alkenyl groups at the side chains also
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14 reacted via radical species, which could cause cross-linking of the polymer side chains.
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19 Therefore, CTAs were used for the polymerization to obtain linear polymers and to avoid
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26 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.

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3 Scheme 3 shows that syntheses of poly(*N*-vinylamide) derivatives bearing the rigid
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6 alkenyl chain at the *N*-position by RAFT polymerization using two kinds of CTAs. **CTA**
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9 **1** and **CTA 2** were selected to conduct the RAFT polymerization because they were
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12 usually used for typically un-conjugated vinyl monomers, vinyl acetate derivatives and
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15 cyclic *N*-vinylamide derivatives, such as a *N*-vinylcarbazole and NVP. Then, the
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18 homopolymers of poly(*N*-vinylamide) derivatives bearing the rigid alkenyl groups were
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21 obtained by RAFT polymerization. These dissolve in methanol and DMSO and they were
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24 purified by re-precipitation by addition of diethyl ether. The obtained polymer was
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27 analyzed by ¹³C NMR analyses which confirmed that the alkenyl group at the side chain
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30 still remained after polymerization (Figure 1c). The peaks of “a” at around 95 ppm
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33 indicates the vinyl groups of *N*-vinylamide monomers (Figure 1a and 1b), which
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36 disappeared after polymerization (Figure 1c), although the peaks of “b” at around 128
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39 ppm were detected after polymerization (Figure 1c). The peaks of “b” are not only derived
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42 from the vinyl group of *N*-vinylamide monomers but also the alkenyl group at the side
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45 chain. Therefore, it is the alkenyl groups of synthesized polymers that remained after
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48 polymerization. Moreover, the side chains possessed cis-trans isomerism. Thus, the peaks
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51 “b” of *n*BuNVF monomer at around 128 ppm were split (Figure 1b), however, the peaks
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54 “b” of poly(*N*-vinylamide) derivatives bearing the alkenyl group were less split. This
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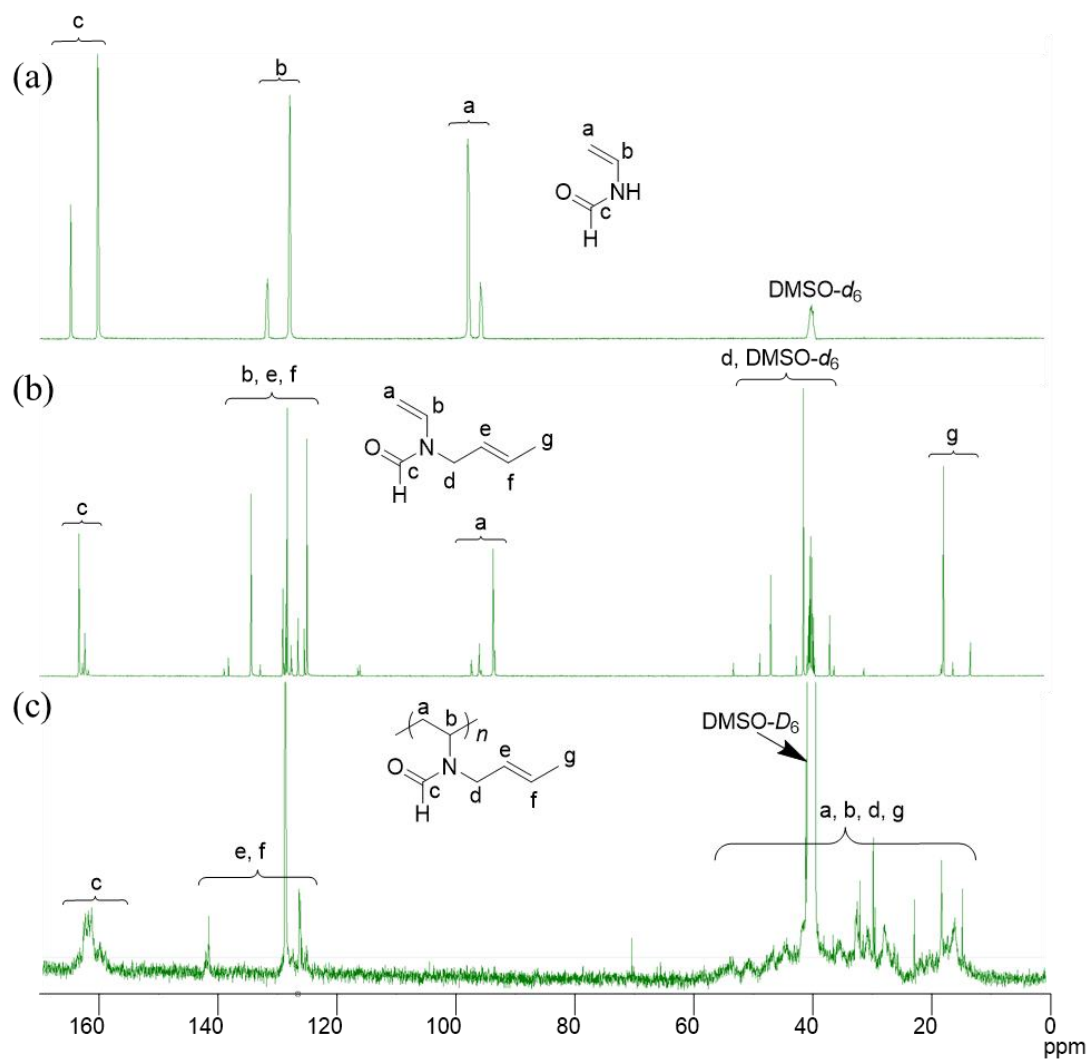


Figure 1. ^{13}C NMR spectrum of NVF (a), $n\text{BuNVF}$ (b) and poly(N -vinylamide) derivatives bearing the alkenyl group at the N -position. 400MHz in $\text{DMSO-}d_6$

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

^aAIBN:CTA:Monomer = 1:2:40; ^bAIBN:CTA:Monomer = 1:2:100; DMSO 60°C 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

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3 hydrophobicity. Thus, copolymers of this monomer were synthesized to improve the
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6 solubility in aqueous media. Initially, the molecular weights of copolymers using **CTA 1**
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9 (Table 1, entries 3 to 7) were lower in value compared with copolymers using **CTA 2**
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12 (Table 1, entries 9 to 13). Furthermore, the yields of Poly(NVF₅-*n*BuNVF₅)-5.7 and
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15 Poly(NVF₇-*n*BuNVF₃)-6.3 were higher in value compared with Poly(NVF₇-*n*BuNVF₃)-
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18 4.2, according to the NVF ratio. This implies that **CTA 2** is best applied for *N*-vinylamide
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21 derivatives compared with **CTA 1**, although it may not be the optimum condition because
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24 PDI of most copolymers were not close to 1. On the other hand, Poly(MNVA₅-
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27 *n*BuNVF₅)-1.1 which shows the low PDI value, 1.1, does not contain NVF units. The
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30 proton of NVF at the amide position was important to make hydrogen bonding and the
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33 polymerization solvent, DMSO, was usually supported to aggregate by the hydrogen
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36 bonding. Therefore, the effect of the proton at the amide position and/or the solvent effect
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39 of DMSO were key points to optimize the choice of CTAs for the achievement of the low
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42 PDI value by RAFT polymerization using *N*-vinylamide derivatives. In addition, the ratio
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45 of monomer units of copolymers could not be calculated because most of peaks of the ¹H
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48 NMR spectra were overlapped. The feed ratios of monomer units are shown in Table 1.
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54 Furthermore, the ratios of NVF or MNVA units of synthesized copolymers were probably
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57 bigger than the feeding monomer ratio because of the effect of steric hindrance at the rigid
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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 - <i>n</i> BuNVF ₃)-1.1	Poly 1	1.1	1.78	6.47
2	Poly(NVF ₇ - <i>i</i> PeNVF ₃)-1.3	Poly 2	1.3	3.25	11.01
3	Poly(NVF ₃ - <i>n</i> BuNVF ₇)-1.1	Poly 3	1.1	1.71	12.51
4	Poly(NVF ₅ - <i>n</i> BuNVF ₅)-1.6	Poly 4	1.6	1.46	9.59
5	Poly(NVF ₇ - <i>n</i> BuNVF ₃)-2.7	Poly 5	2.7	1.53	10.47
6	Poly(NVF ₅ - <i>n</i> BuNVF ₅)-1.3	Poly 6	1.3	2.08	10.79
7	Poly(NVF ₇ - <i>n</i> BuNVF ₃)-4.2	Poly 7	4.2	1.4	7.15
8	Poly(NVF ₅ - <i>n</i> BuNVF ₅)-5.7	Poly 8	5.7	1.81	7.77
9	Poly(NVF ₇ - <i>n</i> BuNVF ₃)-6.3	Poly 9	6.3	1.95	8.05
10	Poly(MNVA ₅ - <i>n</i> BuNVF ₅)-1.1	Poly 10	1.1	1.07	4.65
11	No Polymer				14.88

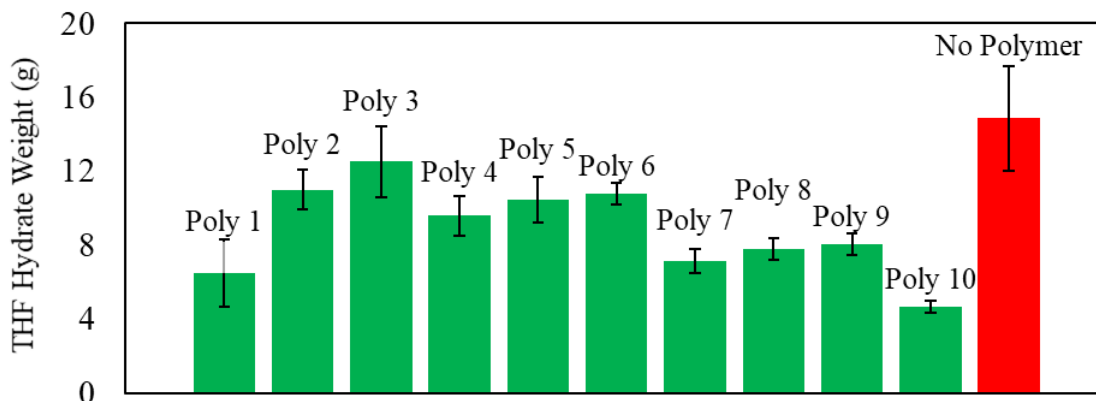


Figure 2. Inhibition abilities of THF hydrate crystal growth of poly(*N*-vinylamide) derivatives bearing the alkenyl group at the *N*-position. (4000 ppm)

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

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3 of synthesized poly(*N*-vinylamide) derivatives. Homopolymers of poly(*N*-vinylamide)
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6 derivatives bearing the alkenyl group showed poor solubility in aqueous media; thus, their
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9 inhibition abilities could not be evaluated. Every synthesized copolymer possessed
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12 sufficient solubility and some inhibition ability of THF hydrate crystal growth, resulting
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15 in the lower weight values of THF hydrate crystal compared to the negative control
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19 without polymer.
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22 Compared with those THF hydrate crystal growth inhibition properties of poly(*N*-
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24 vinylamide) derivatives bearing the ethylene glycol groups or the alkyl groups, we found
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26 generally lower efficiency for the synthesized polymers in this study. For example, one
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28 poly(*N*-vinylamide) derivative bearing the alkyl group gives zero growth of THF hydrate
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30 crystal under 5000 ppm condition [13], and thus possesses better inhibition ability than
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32 synthesized poly(*N*-vinylamide) derivatives bearing the alkenyl group in this study. This
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34 indicates the interactions between THF hydrate surfaces and synthesized poly(*N*-
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36 vinylamide) derivatives in this study are smaller than for polymers bearing the alkyl group.
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38 Poly(*N*-vinylamide) derivatives bearing the alkenyl groups do not show significant cloud
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40 point difference to polymers bearing the alkyl group. [17,18] Generally, the
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42 hydrophobicity between the alkyl group and the alkenyl group are not so different if chain
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44 lengths are the same. This suggests the rigidity and/or the effect of steric hindrance of the
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3 hydrophobic substituents might affect the inhibition of THF hydrate crystal growth.
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6 Poly(NVF₇-*n*BuNVF₃)-1.1 showed good THF hydrate crystal growth inhibition
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9 ability, with lowest value compared with the initial ratio samples, Poly(NVF₇-*n*BuNVF₃)-
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12 2.7 and Poly(NVF₇-*n*BuNVF₃)-6.3 (Table 1, entries 3, 7 and 11). This may be influenced
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15 by the actual composition ratio of copolymers: the ratio of NVF units of copolymers may
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18 be higher due to the steric hindrance at the side chain and/or the compatibility between
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21 *N*-vinylamide groups and CTAs during polymerization. This assumption does not conflict
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24 with the result of the inhibition ability of Poly(NVF₇-*i*PeNVF₃)-1.3 which was lower
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27 efficiency compared with above copolymers, such as Poly(NVF₇-*n*BuNVF₃)-1.1,
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30 Poly(NVF₇-*n*BuNVF₃)-2.7 and Poly(NVF₇-*n*BuNVF₃)-6.3. (Table 2, entries 1, 2, 5 and
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33 9). The feed ratio of the monomers of Poly(NVF₇-*n*BuNVF₃)-1.1 during the
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36 polymerization reaction is different from Poly(NVF₇-*n*BuNVF₃)-2.7 and Poly(NVF₇-
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39 *n*BuNVF₃)-6.3 (Table 1, entries 3, 7 and 11). The ratio of the alkenyl units may also be
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42 different, which may influence the inhibition abilities of THF hydrate crystal growth.
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45 Furthermore, the average weights of THF hydrate formed using Poly(NVF₇-*n*BuNVF₃)-
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48 4.2, Poly(NVF₅-*n*BuNVF₅)-5.7 and Poly(NVF₇-*n*BuNVF₃)-6.3 were lower than
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51 Poly(NVF₇-*i*PeNVF₃)-1.3, Poly(NVF₃-*n*BuNVF₇)-1.1, Poly(NVF₅-*n*BuNVF₅)-1.6,
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54 Poly(NVF₇-*n*BuNVF₃)-2.7 and Poly(NVF₅-*n*BuNVF₅)-1.3. This suggests that the
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3 polymer molecular weight effect influenced the inhibition abilities because higher
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6 molecular weight polymers, above 4000 g/mol, tend to show good inhibition abilities
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9 compared with lower molecular weight polymers, around 1000 g/mol.
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12 Above all, Poly(MNVA₅-*n*BuNVF₅)-1.1 shows the best performance in this study
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14 and its value is significantly lower than other copolymers (Table 2, entry 10).^{16,17}
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17 Monomer units of Poly(MNVA₅-*n*BuNVF₅)-1.1 were probably made up of a majority of
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19 MNVA units because the effect of steric hindrance at the rigid side chain was greater than
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21
22 the methyl group at the side chain and the PDI value was very near 1. This is different
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25 from other copolymers that contained NVF units. Thus, in order to achieve the
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28 development of high efficiency KHIs using the rigid substituents at the *N*-position of
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31 poly(*N*-vinylamide) derivatives, introducing MNVA units as a comonomer was more
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38 effective.
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44 **Conclusion**

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47 We have designed and synthesized poly(*N*-vinylamide) derivatives, bearing the rigid
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3 alkenyl groups, *n*BuNVF and *i*PeNVF, were synthesized and polymerized by RAFT
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6 polymerization using two CTAs in order to obtain the linear polymers. The molecular
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9 weights of synthesized polymers were low in value compared to previous poly(*N*-
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12 vinylamide) derivatives bearing alkyl modified side chains. Moreover, the PDI value of
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15 synthesized polymers were not so low values in spite of using CTA during polymerization.
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18 This indicated that the CTAs, **CTA 1** and **CTA 2**, are not applied so much for non-cyclic
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21 *N*-vinylamide monomers probably due to the difference of radical reactivity between
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24 cyclic and non-cyclic *N*-vinylamide derivatives. The synthesized copolymers evaluated
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27 for inhibition ability of THF hydrate crystal growth. In comparison with previous poly(*N*-
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30 vinylamide) derivatives bearing the more flexible alkyl groups, poly(*N*-vinylamide)
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33 derivatives bearing the alkenyl group showed lower efficiencies for inhibition ability of
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36 THF hydrate crystal growth. Thus, it was surmised that the interactions between hydrate
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39 surfaces and poly(*N*-vinylamide) derivatives bearing the alkenyl group are smaller than
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42 those bearing alkyl groups. The rigidity and/or the effect of steric hindrance are probably
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45 key factors. Higher molecular weight polymers, Poly(NVF₇-*n*BuNVF₃)-4.2, Poly(NVF₅-
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48 *n*BuNVF₅)-5.7 and Poly(NVF₇-*n*BuNVF₃)-6.3, showed better inhibition of THF
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51 hydrate crystal growth compared to lower molecular weight polymers, Poly(NVF₇-
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54 *i*PeNVF₃)-1.3, Poly(NVF₃-*n*BuNVF₇)-1.1, Poly(NVF₅-*n*BuNVF₅)-1.6, Poly(NVF₇-
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3 *n*BuNVF₃)-2.7 and Poly(NVF₅-*n*BuNVF₅)-1.3. This is in accord with previous THF
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6 hydrate crystal growth studies on other polymer classes.
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10 11 12 **Acknowledgement**

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16 We appreciate the help of Mr. Leigh McDowell for English correction.
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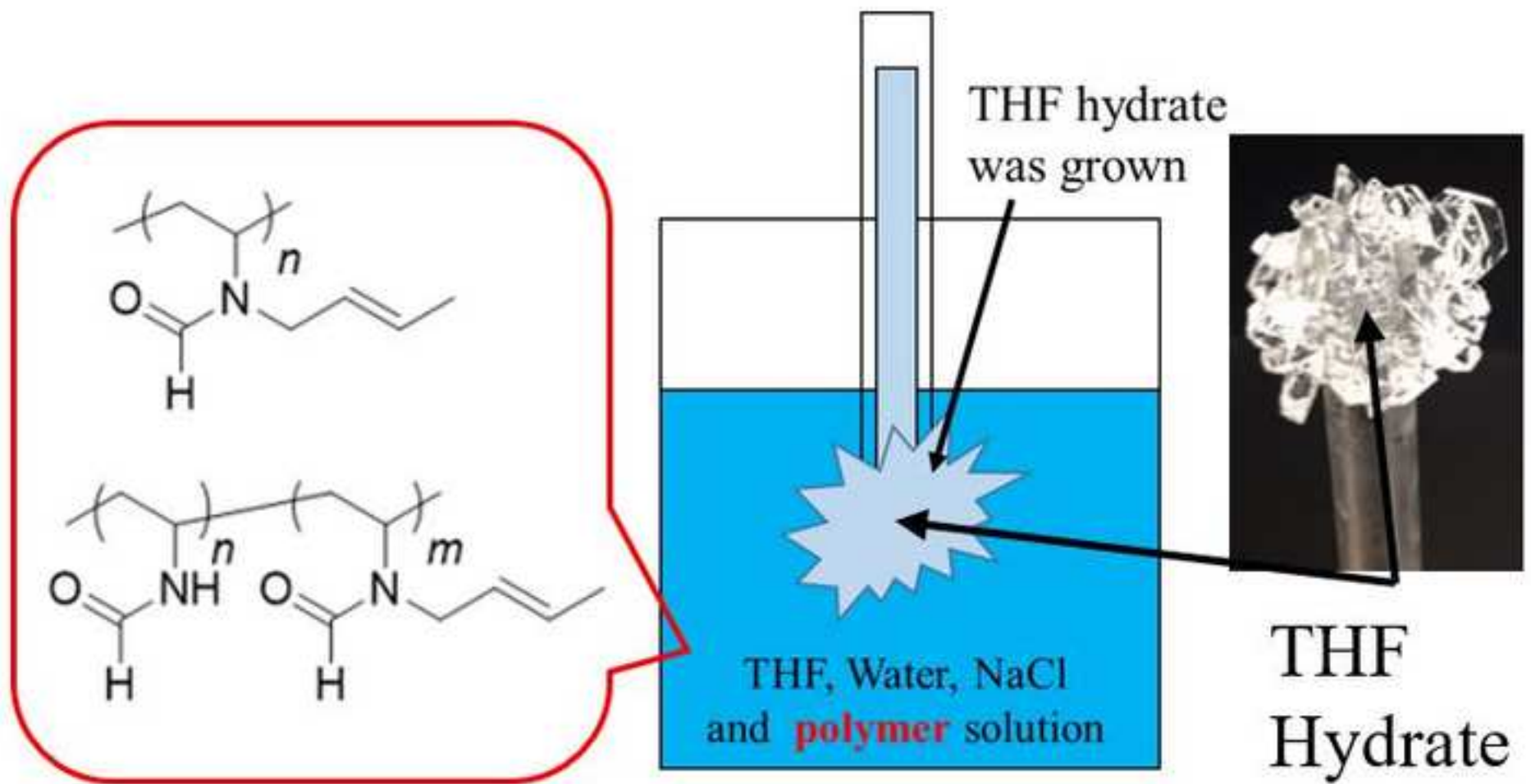
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Supporting Information for

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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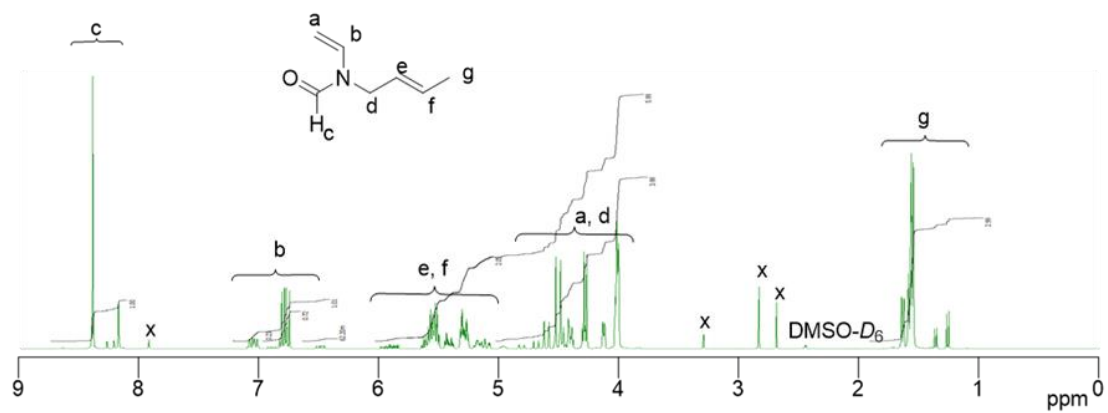


Figure S1. ¹H NMR spectrum of *n*BuNVF. 400MHz in DMSO-*d*₆

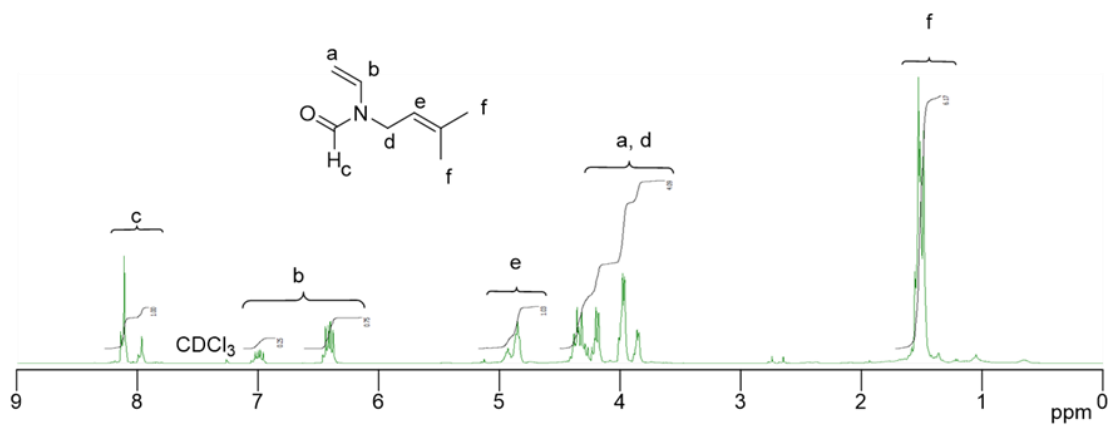


Figure S2. ¹H NMR spectrum of *i*PeNVF. 400MHz in CDCl₃