Radical Polymerization of Novel *N*-Substituted-*N*-vinylacetamides and Regulated Polymer Structures by Bulky Substituents and Menthol Coordination

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ABSTRACT: *N*-(*p*-Methoxybenzyl)-*N*-vinylacetamide (**1**), *N*-(3,3-diphenylpropyl)-*N*-vinylacetamide (**2**), and *N*-(3-phenylpropyl)-*N*-vinylacetamide (**3**) were synthesized as novel *N*-substituted-*N*-vinylacetamides to investigate polymerizabilities and stereochemistries on polymer main chains by introducing bulky substituents. Polymer was not obtained from **1** with a radical method; however, **2** and **3** gave rise to hexane-insoluble polymers during bulk polymerization with 14% and 84% yields, respectively, implying that alkyl spacers were necessary between amide and phenyl groups. When **3** was polymerized with menthol at 0 °C, both ^{1}H NMR and ^{13}C NMR spectroscopies demonstrated sharper spectral patterns than those of poly(**3**) obtained at 60 °C. Since menthol coordinates with **3** at room temperature as shown by ^{1}H NMR spectroscopy, combinations of additive coordination and substituent bulkiness would be effective approaches to produce regulated polymer structures. Glass transition temperatures of poly(**3**)s also varied from 54 to 67 °C, depending on polymerization conditions and polymer structures.

Introduction

N-Vinylacetamide (NVA) is a functional monomer that provides amphiphilic and non-protonic polymer. After convenient polymerization processes were developed,[1,2] poly(*N*-vinylacetamide)s (PNVAs) were used in functional materials, such as patches,[3,4] water-retaining hydrogels,[5] thickeners,[6] and so on. By introducing alkyl groups to side groups, it is possible to change hydrophilic and hydrophobic balances of PNVAs. For example, poly(*N*-vinyl-*N*-isobutylamide) possesses lower than critical solution temperature (LCST) at around 39 °C,[7] where carbonyl and nitrogen positions are reversed with poly(*N*-isopropylacrylamide) (PNIPAAm). When copolymerized with vinyl acetate, NVA also produces thermosensitive polymers.[8] Besides, *N*-vinylformamide is employed for easier deprotection of amino groups as precursors of poly(vinylamine).[9] More recently, we sought to improve physical and chemical characteristics of PNVA hydrogels by interpenetrating polymer networks, resulting in slightly improved mechanical strengths[10] and cellular affinities.[11] Taking advantage of different radical polymerizability between NVA and styrene, *N*-vinyl parts were used as cross-linkers after polymerization.[12] Those aforementioned functional materials were achieved by the use of originally featured chemical structure of *N*-vinylamides.

On the other hand, controlling the stereoregularity of polymers is important because its physical and chemical characteristics are influenced by tacticity. Many investigators have controlled vinyl polymer tacticities using single-site catalysts[13] and template polymerization approaches.[14] On the contrary, the introduction of bulkiness on monomer substituents provides significant tactics to control stereoregularities. It is famous that triphenylmethyl groups to methyl methacrylate produced one-handed helices,[15] and this approach is widely applied. For example, radical polymerization of methacrylamide derivatives,[16] acrylamide derivatives,[17] anionic polymerization of methacrylate,[18] flexible polystyrene derivatives,[19] cationic polymerization of alkyl vinyl ethers,[20,21] and phenylacetylene to produce helix sense selective polymers[22,23] and others are being developed at the present time. However, little data is available for *N*-vinylalkylamide.[2,24] The reported methods need special polymerization conditions, such as the use of γ-ray irradiation or quite low temperatures to achieve stereoregularity control. Therefore, alternative approaches to control *N*-vinylalkylamides stereoregularities are desired to create varied physical and chemical properties.

In this study, we designed monomer structures for *N*-vinylalkylamides by introducing bulky alkyl groups at *N*-positions proximal to vinyl polymer backbones in order to control tacticity via steric repulsion. At the same time, suitable additives for coordination to carbonyl groups were investigated.

Experimental Section

Materials. NVA (Showa Denko K. K., Japan) was recrystallized from cyclohexane/toluene (3/1, v/v) and dried in vacuum at room temperature. Toluene (Tokyo Chemical Industry Co. Ltd., Japan) was distillated from CaH_2. 4-Methoxybenzyl chloride (Tokyo Chemical Industry Co. Ltd., Japan), (3-bromopropyl)benzene (Tokyo Chemical Industry Co. Ltd., Japan), 3-bromo-1,1-diphenylpropane (Tokyo Chemical Industry Co. Ltd., Japan), sodium hydride (Tokyo Chemical Industry, Japan), anhydrous DMF (Aldrich Co., NJ.), ytterbium(III) trifluoromethanesulfonate hydrate (Tokyo Chemical Industry Co. Ltd., Japan), 2,2′-azobis(isobutyronitrile) (AIBN) (Tokyo Chemical Industry Co. Ltd., Japan), urea (Wako, Japan), (−)-menthol (Aldrich Chemical Co., NJ), (+)-menthol (Tokyo Chemical Industry Co. Ltd., Japan), and (±)-menthol (Tokyo Chemical Industry Co. Ltd., Japan) were used without further purification.

***N*-(*p*-Methoxybenzyl)-*N*-vinylacetamide (1).** In a glass flask, sodium hydride was placed and washed with anhydrous THF (3 mL) twice under nitrogen. NVA (0.6 g, 7.05 mmol) in anhydrous DMF (3 mL) was slowly added at 0 °C. After stirring for 30 min at 0 °C, 4-methoxybenzyl chloride (0.96 mL, 7.05 mmol) was introduced slowly. The reactor was warmed up to room temperature to stir more 3 h. The mixture in 15 mL of ethyl acetate and 10 mL of water, washing the organic layer successively with brine solution, drying it with anhydrous $MgSO_4$, and then further purifying with a silica gel column using 2:1 of hexane:ethyl acetate as eluent, the

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desired pure product **1** was obtained as a liquid (1.23 g, 85% yield). ^{1}H NMR (CD_3CN, 400 MHz) δ: 2.29 (s, 3H, O=C−CH_3), 3.79 (s, 3H, Ar−OCH_3), 4.29 (d, J = 4.8 Hz, 1H × 0.7, CH_2=CH−N, cis), 4.37 (d, J = 5.8 Hz, 1H × 0.3, CH_2=CH−N, trans), 4.44 (d, J = 7.2 Hz, 1H × 0.3, CH_2=CH−N, trans), 4.42 (d, J = 8.2 Hz, 1H × 0.7, CH_2=CH−N, cis), 4.78 (s, 2H × 0.3, N−CH_2−Ar, trans), 4.81 (s, 2H × 0.7, N−CH_2−Ar, cis), 6.89−7.12 (m, 5H, CH_2=CH−N, Ar), 7.54 (dd, J = 8.8 Hz and 16 Hz, 1H × 0.3, CH_2=CH−N, trans). FT-IR (cm^{-1}): 1669, 1619, 1511, 1244, 1030, 842, 590. Anal. Calcd for $C_{12}H_{15}O_2N$: C, 70.22; H, 7.37; N, 6.82. Found: C, 69.79; H, 7.32, N, 6.89. FAB-MS: $[M + 1]^+ = 206.20$.

***N*-(3,3-Diphenylpropyl)-*N*-vinylacetamide (2).** In glass flask, sodium hydride was placed and washed with anhydrous THF (3 mL) twice under nitrogen. NVA (0.6 g, 7.05 mmol) in anhydrous DMF (3 mL) was slowly added at 0 °C. After stirring for 30 min at 0 °C, 3-bromo-1,1-diphenylpropane (1.94 g, 7.05 mmol) was introduced slowly. The reactor was warmed up to room temperature to stir more 3 h. The mixture in 15 mL of ethyl acetate and 10 mL of water, washing the organic layer successively with brine solution, drying it with anhydrous $MgSO_4$, and then further purifying with a silica gel column using 2:1 of hexane:ethyl acetate as eluent, the desired pure product **2** was obtained as a liquid (1.45 g, 74% yield). ^{1}H NMR (C_6D_6, 400 MHz) δ: 1.63 (s, 3H, O=C−CH_3), 1.99 (m, 1H × 0.3, CH_2−CH_2−CH, trans), 2.28 (m, 1H × 0.7, CH_2−CH_2−CH, cis), 2.91 (t, J = 7.6 Hz, 2H × 0.3, N−CH_2, trans), 3.48 (t, J = 7.2 Hz, 1H × 0.3, CH_2−CH(Ph)$_2$, trans), 3.57 (t, J = 7.6 Hz, 2H × 0.7, N−CH_2, cis), 3.80 (t, J = 7.2 Hz, 1H × 0.7, CH_2−CH(Ph)$_2$, cis), 3.93 (d, J = 8.8 Hz, 1H, CH_2=CH−N), 4.00 (d, J = 15.6 Hz, 1H × 0.7, CH_2=CH−N, cis), 4.12 (d, J = 9.6 Hz, 1H × 0.3, CH_2=CH−N, trans), 6.18 (dd, J = 9.2 Hz and 15.6 Hz, 1H × 0.7, CH_2=CH, cis), 6.96−7.15 (m, 10H, Ar), 7.83 (dd, J = 16 Hz and 9.4 Hz, 1H × 0.3, CH_2=CH, trans). FT-IR (cm^{-1}): 1668, 1619, 1387, 1346, 1182, 697. Anal. Calcd for $C_{19}H_{21}ON$: C, 81.68; H, 7.58; N, 5.01. Found: C, 80.67; H, 7.55, N, 4.93. FAB-MS: $[M + 1]^+ = 280.2$.

***N*-(3-Phenylpropyl)-*N*-vinylacetamide (3).** In glass flask, sodium hydride was placed and washed with anhydrous THF (3 mL) twice under nitrogen. NVA (0.6 g, 7.05 mmol) in anhydrous DMF (3 mL) was slowly added at 0 °C. After stirring for 30 min at 0 °C, 3-bromopropylbenzene (1.4 mL, 7.05 mmol) was introduced slowly. The reactor was warmed up to room temperature to stir an additional 3 h. The mixture in 15 mL of ethyl acetate and 10 mL of water, washing the organic layer successively with brine solution, drying it with anhydrous $MgSO_4$, and then further purifying with a silica gel column using 2:1 of hexane:ethyl acetate as eluent, the desired pure product **3** was obtained as a liquid (1.41 g, 98% yield). ^{1}H NMR (C_6D_6, 400 MHz) δ: 1.49 (m, 2H × 0.3, CH_2−CH_2−CH_2, trans), 1.64 (s, 3H, O=C−CH_3), 1.79 (m, 2H × 0.7, CH_2−CH_2−CH_2, cis), 2.17 (t, J = 7.6 Hz, 2H × 0.3, CH_2−Ph, trans), 2.43 (t, J = 8.4 Hz, 2H × 0.7, CH_2−Ph, cis), 2.87 (t, J = 7.6 Hz, 2H × 0.3, N−CH_2, trans), 3.56 (t, J = 8.0 Hz, 2H × 0.7, N−CH_2, cis), 3.94 (d, J = 8.8 Hz, 1H × 0.7, CH_2=CH, cis), 4.03 (d, J = 15.2 Hz, 1H × 0.7, CH_2=CH, cis m, 1H × 0.3, CH_2=CH, trans), 4.19 (d, J = 10 Hz, 1H × 0.3, CH_2=CH, trans), 6.20 (dd, J = 9.2 Hz and 15.2 Hz, 1H × 0.7, CH_2=CH, cis), 6.87−7.15 (m, 5H, Ar), 7.80 (dd, J = 15.6 Hz and 10.2 Hz, 1H × 0.3, CH_2=CH, trans). FT-IR (cm^{-1}): 1668, 1618, 1386, 1346, 1176, 698, 591. Anal. Calcd for $C_{13}H_{17}ON$: C, 76.81; H, 8.43; N, 6.89. Found: C, 76.13; H, 8.32, N, 6.78. FAB-MS: $[M + 1]^+ = 204.2$.

Polymerization of NVA. A typical experimental procedure of NVA polymerization is described for the polymerization in (−)-menthol (1.0 mol/L) at 50 °C. NVA (0.34 g, 4 mmol), (−)-menthol (0.21 g, 0.4 mmol), and AIBN (6.6 mg, 0.04 mmol) were placed in a glass tube and dried under vacuum for 1 h. After nitrogen was filled in the glass tube, the polymerization was initialized by heating at 60 °C in an oil bath. Reaction products of PNVA were precipitated in a large excess of acetone, and the resulting polymers were washed with 100 mL of acetone three times and isolated with a centrifuge. The obtained polymers were dried under vacuum at room temperature.

Table 1. Radical Polymerization of NVA with Additives[a]

entry	additive	[additive]/[NVA]	solvent	[NVA] (mol/L)	temp (°C)	time (h)	yield[b] (%)	tacticity[c] *mm*:*mr*:*rr*
1		0	water	2.0	37	24	>99	24:44:32
2	Yb(OTf)$_3$	0.05	water	2.0	37	24	44	26:45:29
3	urea	1	MeOH	2.0	60	24	>99	25:51:24
4	(−)-menthol	5		2.0	60	20	>99	28:51:21
5	(−)-menthol	5		1.0	50	20	76	30:50:20
6	(+)-menthol	5		1.0	50	20	82	30:50:20
7	(±)-menthol	5		1.0	50	20	>99	30:51:19

[a] Initiator = 2,2′-azobis(2-methylpropionamidine) dihydrochloride for entries 1−3 and azobis(isobutylonitrile) for entry 4. [Initiator]:[NVA] = 1:50. [b] Acetone-insoluble part. [c] Determined by ^{1}H NMR spectra in D_2O at room temperature.

Polymerization of 1−3. A typical experimental procedure of the polymerization is described for the polymerization **3** (3.0 mol/L) at 0 °C. **3** (0.5 g, 2.45 mmol), (−)-menthol (0.21 g, 1.32 mmol), and AIBN (10.1 mg, 0.0615 mmol) were placed in a glass tube and dried under vacuum for 1 h. After nitrogen was filled in the glass tube, toluene was introduced at 0 °C. The polymerization was initialized by UV irradiation (Riko, UVL-400HA, distance = 10 cm). Reaction products of poly(**2**) and poly(**3**) were precipitated in a large excess of hexane, and the resulting polymers were isolated with centrifuge. The obtained polymers were dried under vacuum at room temperature.

Measurements. ^{1}H NMR and ^{13}C NMR were measured by JEOL JNM-GSX400 system. Attenuated total reflection (ATR) IR spectra were obtained with a Spectrum 100 FT-IR spectrometer (Perkin-Elmer). The interferograms were co-added 64 times and Fourier-transformed at a resolution of 4 cm^{-1}. The number-average molecular weights and their distribution were measured by gel permeation chromatography (Tosoh System HLC-8120GPC) with PMMA standards at 40 °C. Two commercial columns (TSKgel SuperH4000 and TSKgel GMH$_{XL}$) were connected in series, and tetrahydrofuran was used as an eluent. Polymer glass transition points (T_g) were measured by differential scanning calorimetry (DSC) using a Seiko Instruments DSC6100. T_g values were determined by the middle point of the transition. A typical run consisted of heating, under nitrogen, from 0 to 210 °C at a rate of 10 °C/min, followed by cooling to 0 at 10 °C/min, and then heating to 210 at 10 °C/min. The data from the second heating run were processed using the Muse ver.3.5. Mass spectra were taken on a JEOL JSM-700 mass spectrometer.

Results and Discussion

As far as we know, only two examples exist in the literature that control PNVA tacticity. In short, isotacticity increases to 50%, when γ-rays are used during solid-state polymerization, while it usually remains around 25% with a radical method in solution.[2] With additives that increase hydrogen bonding to carboxyl groups on NVA, PNVA tacticities are controlled with a wide range from syndiotactic (rr = 34%) to isotactic (49%), as reported by Hirano et al.[24] However, the aforementioned polymerization methods need γ-ray irradiation or extremely low temperature, so improvements in polymerization conditions are necessary. Therefore, we explored more suitable additives for NVA, which possessed tacticity control at relatively high temperatures with radical methods, before introducing bulky substituents to *N*-positions.

Table 1 lists the results from radical polymerizations of NVA with three kinds of additives. Within a range of 40−60 °C, PNVAs were recovered with good yields as acetone-insoluble parts. Lewis acids, which are effective additives for isotactic selectivity of methyl methacrylates[25] and methacrylamides,[26] did not influence the stereoregularity of PNVA such as Yb(OTf)$_3$. Rather, coordination on carboxyl groups seemed to delay polymerization rates (Table 1, entry 2). Urea was employed with the expectation of good hydrogen bonding to NVA, but almost no effect was observed (Table 1, entry 3). On the other hand, isotacticity increased from 24% to 28% when

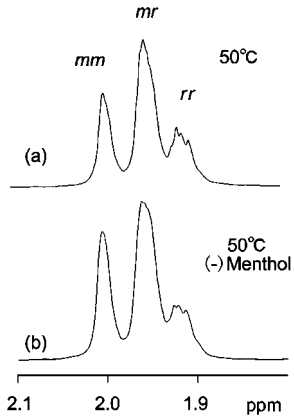
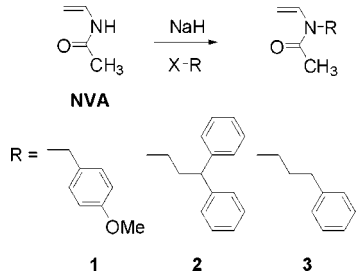


Figure 1. ^{1}H NMR spectra of PNVA obtained in water at 50 °C (a) and in (−)-menthol at 50 °C (b) (in D_2O, 25 °C, 400 MHz).

Scheme 1. Synthesis of *N*-Substituted *N*-vinylacetamides



(−)-menthol was used as a solvent itself (Table 1, entry 4). Alcohols coordinate to carboxyl groups at low temperatures, and alcohol structures influenced PNVA tacticities. It was surprising that isotacticity changed to 30% even at 50 °C with (−)-menthol (Table 1, entry 5), and the same values were obtained from PNVAs with (+)-menthol and (±)-menthol as solvents (Table 1, entries 6 and 7).

^{1}H NMR spectra of PNVAs are shown in Figure 1. Acetyl protons split into three peaks—*mm*, *mr*, and *rr*—due to stereoregularity. Although spectral patterns of PNVA obtained at 0 °C were almost identical to those at 50 °C, slight increases of isotactic peaks around 2.0 ppm were observed when (−)-menthol was used as a solvent, thus suggesting that the bulky alcohol effectively changed PNVA stereostructures.

Next, we designed substituents to introduce at *N*-positions. Although the NVA crystal structure is unknown, several crystal structures of NVA derivatives have been reported in the literature. Among these, 1-acetamido-1-(1-naphthyl)ethylene possesses a linear hydrogen-bonding network with the amide in a packing structure.[27] Aromatic substituents might be effective to arrange regularly. Thus, three kinds of novel NVA derivatives—*N*-(4-methoxybenzyl)-*N*-vinylacetamide (**1**), *N*-(3-phenylpropyl)-*N*-vinylacetamide (**2**), and *N*-(3,3-diphenylpropyl)-*N*-vinylacetamide (**3**)—were designed to investigate polymerizability and polymer structures obtained under various polymerization conditions (Scheme 1).

First, radical polymerizations of **1**−**3** were tested without solvents to examine polymerizabilities, and results are described in Table 2. Bulk polymerization of **1**, which was initially designed for the purpose of removing 4-methoxybenzyl groups after polymerization to protect amide groups, gave no hexane-insoluble parts even at 110 °C during bulk polymerization (Table 2, entry 1). The aforementioned result is reasonable because benzyl groups at *N*-positions in NVA prevent radical polymerization.[12] On the other hand, **2** and **3**, which possess spacers between nitrogen and phenyl groups, were radically polymerized to yield 14% and 84% as hexane-insoluble parts, respectively (Table 2, entries 2 and 3).

Diluted in toluene at 2 mol/L, **3** maintained its radical polymerizability at both 60 and 20 °C to provide hexane-insoluble poly(**3**) with 42% and 14% yields, respectively (Table 2, entries 4 and 5). Since the reactivity of the bulk polymerization of **2** was too low to examine various other polymerization conditions, such as in lower temperatures and using (−)-menthol as an additive, we paid attention to monomer **3** for further screening in this study.

Carbonyl groups in NVA and alcohol form hydrogen bonds at low temperatures, as evidenced by ^{1}H NMR and ^{13}C NMR spectra.[24] In order to find coordination states between (−)-menthol and **3**, ^{1}H NMR spectra of the mixture (1:1) were measured before radical polymerization with an additive. Figure 2 shows ^{1}H NMR spectra of a mixture of **3** and (−)-menthol in benzene-*d* at room temperature. One vinyl proton sifted to a lower magnetic field compared to that of the original **3** (Figure 2a,b). Acetyl protons also moved to lower magnetic fields (Figure 2c,d), suggesting that (−)-menthol exists proximal to **3** and influences magnetic fields. Thus, menthol should influence polymerization processes through hydrogen bonding.

In general, doubly substituted amides generate two *trans*- and *cis*-isomer peaks in ^{1}H NMR spectra. **3** also possesses two isomers peaks at room temperature; however, isomer peaks combine to form one peak in ^{1}H NMR spectra at 60 °C (see Supporting Information, Figure S1). Interestingly, the ratio of *trans*/*cis* of **3** is a constant value (22/78) at 20 and 0 °C (Supporting Information). Therefore, the radical polymerization of **3** below room temperature might permit selective polymerization among isomers. Finally, radical polymerizations of **3** at 20 and 0 °C with (−)-menthol were achieved, including substituent effects, isomer selectivities, and hydrogen bonding with menthol, in order to control the stereoregularity of obtained polymers (Table 2, entries 7−10). UV irradiation with AIBN leads radical polymerization at both 20 and 0 °C; however, *n*-Bu_3B with air did not lead to the polymerization of **3**, although it could radically react with NVA.[24] On the other hand, more concentrated conditions at 3 mol/L gave higher yields (Table 2, entries 8 and 10).

^{1}H NMR spectra of **3** and poly(**3**) in benzene-*d* are shown in Figure 3. Vinyl protons disappeared, and clean polymerizations were confirmed (Figure 3b). However, the broad spectral patterns implied poor regularity in the polymer structures. To investigate the stereoregularity of poly(**3**), around 2 ppm regions of poly(**3**) obtained under various polymerization conditions were compared to one another.

Figure 4 shows ^{1}H NMR spectra of poly(**3**) in benzene-*d* together with that of PNVA in D_2O. When polymerization temperatures decrease from 60 to 0 °C, the spectral pattern of obtained poly(**3**) changed to one whose intensity at lower magnetic fields increases (Figure 4b,c). The aforementioned change suggests that the isotacticity might increase due to *mm* triads of PNVA. The same tendency was observed when menthol was used as an additive (Figure 4d,e). However, spectra around 2 ppm include acetyl protons and methylene protons of polymer main chains and side chains, which make it difficult to determine which hydrogen atoms were mostly influenced by regulated structures.

Figure 5 shows ^{13}C NMR spectra of monomer **3** and poly(**3**)s. Each peak of the poly(**3**) under various conditions slightly differed from one another. Among these, the carbonyl group at around 170 ppm clearly separated into two peaks (171 and 169 ppm) probably due to stereoregularity, such as tacticity and *trans*- or *cis*-isomers. As a result, it revealed that menthol did not influence the polymer structure very much in spite of results from NVA polymerizations (Figure 5b,c). However, apparent

Table 2. Radical Polymerization of 1−3[a]

entry	monomer	solvent	[monomer] (mol/L)	temp (°C)	time (h)	yield[b] (%)	M_n[c] ($\times 10^3$)	PDI[c]
1	**1**		4.9	110	24	0	N.D.	N.D.
2	**2**		3.6	60	24	14	2.0	1.6
3	**3**		5.0	60	24	84	2.6	2.1
4	**3**	toluene	2.0	60	24	42	3.2	1.5
5	**3**	toluene	2.0	20	72	14	1.7	1.7
6	**3**	(−)-menthol	2.0	60	24	36	2.3	1.7
7	**3**	toluene/(−)-menthol(1/3,v/v)	2.0	20	72	19	2.5	1.6
8	**3**	toluene/(−)-menthol (1/3, v/v)	3.0	20	120	73	2.5	2.2
9[d]	**3**	toluene/(−)-menthol (1/1, v/v)	2.0	0	168	0	N.D.	N.D.
10	**3**	toluene/(−)-menthol (1/3, v/v)	3.0	0	72	15	2.2	1.6

[a] Initiator = azobis(isobutylonitrile). UV irradiation for entries 5, 7, 8, and 10. [Monomer]:[initiator] = 40:1. Monomer = 0.3 g. [b] Hexane-insoluble part. [c] Determined by SEC in THF with poly(methyl methacrylate) standard at 40 °C. [d] Initiator = n-Bu_3B with air.

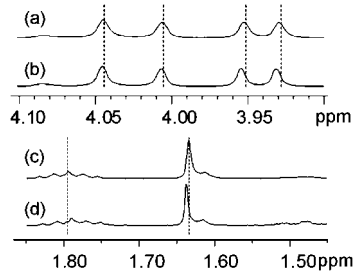


Figure 2. ^{1}H NMR spectra of vinyl protons of **3** (a) and **3** with (−)-menthol (b) and ^{1}H NMR spectra of acetyl protons of **3** (c) and **3** with (−)-menthol (d) (in benzene-d_6, 25 °C, 400 MHz).

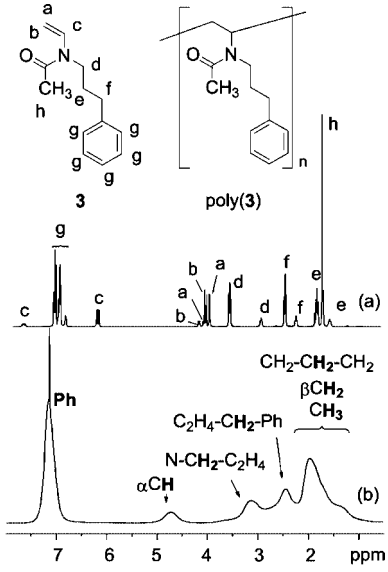


Figure 3. ^{1}H NMR spectra of **3** (a) and poly(**3**) (b) (in benzene-d_6, 25 °C, 400 MHz).

changes were observed in spectra of the poly(**3**) obtained with (−)-menthol at 20 °C, in which the peak at 169 ppm got smaller (Figure 5d). To add to this, peaks at around 22 ppm which split in the same manner behaved in the same way (Figure 5b,d). Surprisingly, the peak at 169 ppm almost disappeared in the spectra of poly(**3**), when (−)-menthol was used at 0 °C with 3 mol/L during radical polymerization (Figure 5e). The poly(**3**) possessed much sharper spectral patterns, suggesting that it possessed a stereochemically regulated structure.

Figure 6 shows results from the DSC measurements. Glass transition temperatures (T_g) were observed in the range of 54 and 67 °C, which indicated that molecular weight differences affected T_g. However, it is noteworthy that higher T_g values were observed when **3** was polymerized with menthol than those of poly(**3**)s without additives. For example, poly(**3**) (M_n = 2600) obtained without solvent (Table 2, entry 3) showed T_g at 60.8

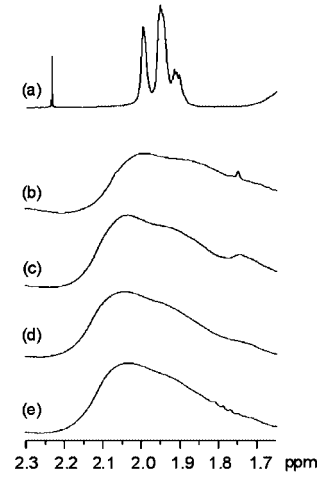


Figure 4. ^{1}H NMR spectra of NVA (a) (in D_2O, 25 °C, 400 MHz) and poly(**3**)s obtained in toluene with 2 mol/L at 60 °C (b), in toluene with 2 mol/L at 20 °C (c), in toluene/(−)-menthol (1/3, v/v) with 3 mol/L at 20 °C (d), and in toluene/(−)-menthol (1/3, v/v) with 3 mol/L at 0 °C (e) (in benzene-d_6, 25 °C, 400 MHz).

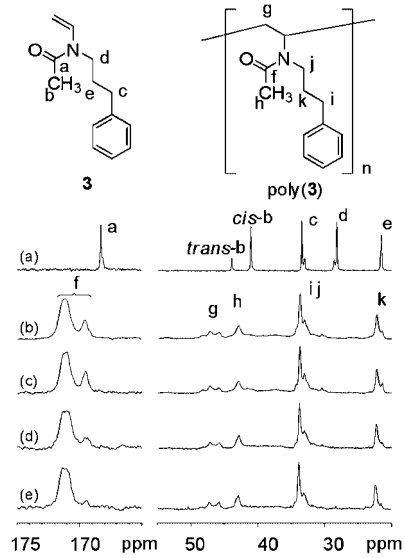


Figure 5. ^{13}C NMR spectra of NVA (a) (in D_2O, 25 °C, 100 MHz) and poly(**3**)s obtained in toluene with 2 mol/L at 60 °C (b), in (−)-menthol with 2 mol/L at 60 °C (c), in toluene/(−)-menthol (1/3, v/v) with 3 mol/L at 20 °C (d), and in toluene/(−)-menthol (1/3, v/v) with 3 mol/L at 0 °C (e) (in benzene-d_6, 25 °C, 100 MHz).

°C, while poly(**3**) (M_n = 2500) with menthol (Table 2, entry 8) showed T_g at 67.1 °C (Figure 6a,b). Similarly, T_g values of poly(**3**)s (M_n = 1700 and 2200) obtained in toluene and toluene/(−)-menthol appeared at 54.3 and 58.0 °C, respectively (Figure 6c,d). This implies that stereoregularities such as *trans/cis-*

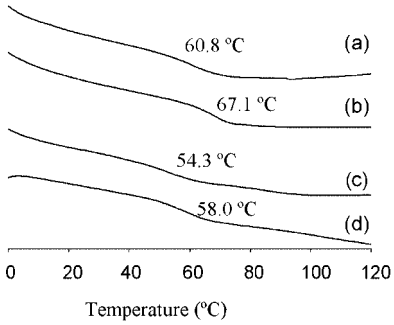
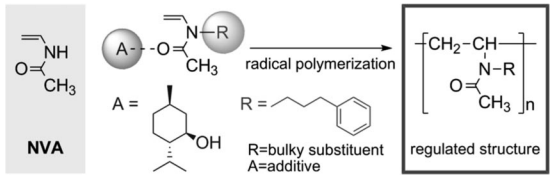


Figure 6. DSC curves of poly(**3**)s obtained by bulk polymerization at 60 °C (a), in toluene/(−)-menthol (1/3, v/v) with 3 mol/L at 20 °C (b), in toluene 2 mol/L at 20 °C (c), and in toluene/(−)-menthol (1/3, v/v) with 3 mol/L at 0 °C (d).

Scheme 2. Radical Polymerization of 3 with (−)-Menthol



isomers and tacticity affected the thermal properties. Therefore, combinations of substituents sizes and coordination alcohol (menthol) are significant approaches to control the stereochemistry of obtained polymers for NVA derivatives.

Conclusions

Radical polymerization of NVA in menthol provided slightly isotactic enriched polymers, showing bulky alcohol was effective in changing PNVA stereoregularity. In order to control stereochemistry on poly(*N*-substituted-*N*-vinylacetamide)s, phenylpropyl groups were introduced to *N*-positions of NVA to synthesize novel monomers **3**. The bulkiness of substituents mildly reduced radical polymerizability; however, **3** polymerized in diluted solutions in toluene at 0 °C. The ^{1}H and ^{13}C NMR spectra of poly(**3**) obtained with menthol at low temperature depicted much sharper spectral patterns than those obtained at 60 °C, suggesting that they possessed more regulated structures. Glass transition temperatures were also influenced by the polymerization conditions. Thus, combinations with bulky substituents and coordination additives would be one of the important approaches to control poly(*N*-substituted-*N*-vinylacetamide) structures, which profoundly affect thermal and mechanical properties.

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Supporting Information Available: Detailed data of ^{1}H NMR and ^{13}C NMR spectra of monomers and polymers, mass spectra of monomers, elemental analysis of monomers, IR spectra of monomers, and GPC charts of polymers. This material is available free of charge via the Internet at http://pubs.acs.org.

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